PRINCIPLES OF INORGANIC CHEMISTRY

A TEXT BOOK

for

B.Sc., B.Sc. (Hons.) & M.Sc. Students of Indian Universities as also for Candidates appearing for Various Competitive Examinations

LATE B. R. PURI
M.Sc., Ph.D., F.R.I.C., F.N.A.,
Formerly, Prof. of Physical Chemistry,
Panjab University, Chandigarh

L. R. SHARMA
M.Sc., Ph.D., F.R.I.C. (London),
Formely, Prof. of Physical Chemistry,
Department of
Chemical Engineering &Technology,
Panjab University, Chandigarh

K. C. KALIA
M.Sc., Ph.D., (I.I.T., Kanpur)
Formerly, Prof. of Inorganic Chemistry,
Department of Chemistry,
Punjabi University, Patiala

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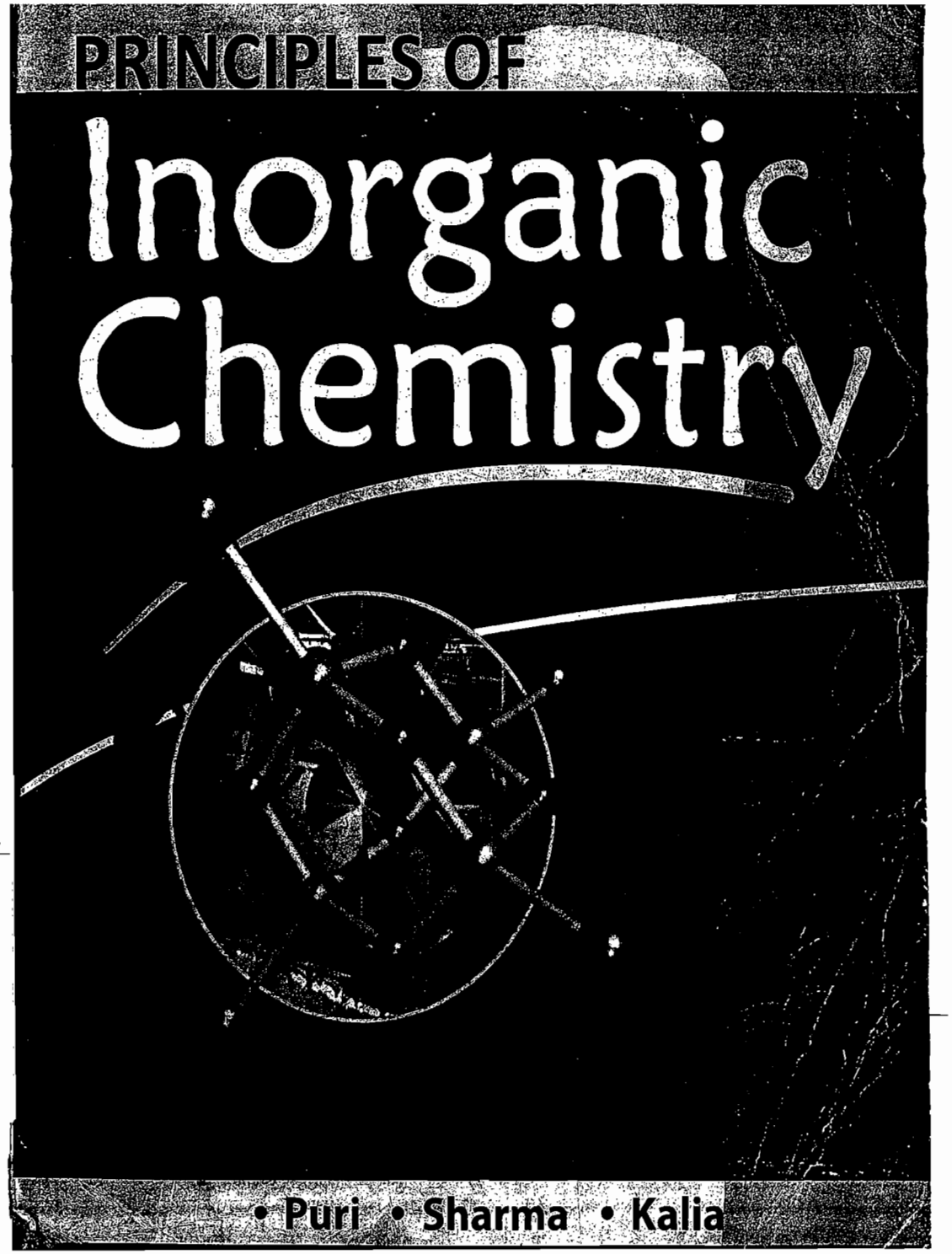

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Preface to the Thirty First Edition

The authors take pleasure in presenting the thirty first edition of their prestigious publication **Principles of Inorganic Chemistry**. The entire text has been thoroughly revised and updated in every respect. While minor but otherwise essential additions have been made in all the chapters dealing with representative elements, transition elements and inner transition elements, some important additions have been made in chapters covering group theory, organometallic compounds and inorganic polymers. The additions to group theory include additional applications of group theory covering relaxation of selection rules for electronic transitions, study of the method of descending symmetry and the study of electron absorption spectra using plane polarised light. Character tables for important symmetry groups have also been given in this chapter. A significant addition to the present edition is a new chapter describing the **quantitative treatment of crystal field theory.** Mathematical expressions have been derived for calculating V_{oct}, $V_{tetragonal}$, V_{tet} and Dq values. The fact that in an octahedral ligand field potential, the energy of e_g orbitals increases by 6 Dq while that of t_{2g} orbitals decreases by 4 Dq, has been established mathematically.

The book now adequately covers almost all the modern topics in inorganic chemistry. The publication, therefore, can be rightly called **modern inorganic chemistry.**

We take this opportunity to express our sincere thanks to all the students and fellow teachers who took pains to send us their valuable suggestions and criticism for further improvement of the text.

The authors sincerely hope that the present revised and improved edition of the book will be warmly received by the students and the teachers alike. Any suggestions for further improvement of the text would be most welcome.

AUTHORS.

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WAVE MECHANICAL CONCEPTS OF ATOMIC STRUCTURE

1

John Dalton (1809) regarded the atom as a hard, dense and *smallest indivisible particle of matter*. However, the emission of negatively and positively charged particles from radioactive elements as well as from gases on the passage of electricity at very low pressures, convinced the scientists that *atom is not indivisible but consists of smaller fundamental particles*. It is now fully established that atom consists of three major fundamental particles called *electrons, protons* and *neutrons*.

Electron is a negatively charged particle having a charge equal to $1{\cdot}60206\times10^{-19}$ C and a mass equal to $9{\cdot}1091\times10^{-31}$ kg. Since the charge on the electron is the *smallest charge of electricity*, it is usual to speak of the charge on an electron as *unit negative charge*. The mass of electron on atomic mass scale is 0·0005487 a.m.u.

Proton is a positively charged particle with charge equal and opposite to that of electron and mass equal to $1{\cdot}6727\times10^{-27}$ kg. Thus, proton carries a *unit positive charge* and on atomic mass scale has a mass equal to 1·00728 a.m.u.

Neutron is a neutral particle having mass equal to $1{\cdot}6748\times10^{-27}$ kg. Thus, neutron carries *no charge* and on atomic mass scale has a mass equal to 1·00866 a.m.u.

Since atom is electrically neutral, it contains an equal number of electrons and protons.

Rutherford's Nuclear Model of the Atom. According to Rutherford's nuclear model :

1. An atom consists of a *minute positively charged body* located at its centre. It is called the **nucleus.** The nucleus, though small, contains all the protons and neutrons. Since the mass of an atom is almost entirely due to the presence of protons and neutrons, it is evident that *almost the entire mass of an atom resides in the nucleus.*

2. The nucleus is surrounded by a suitable number of **electrons** revolving around it to balance the positive charge on the nucleus.

3. Most of the space between the nucleus and the revolving electrons in an atom is empty (the radius of the atom is about 10^5 times as large as the radius of the nucleus).

The centrifugal force arising from the circular motion of electrons balances the force of electrostatic attraction between the nucleus and the electrons. The electrons, therefore, do not fall into the nucleus.

Objection to Rutherford's Model. It was pointed out by Niels Bohr that Rutherford's atom should be highly unstable. J. C. Maxwell had shown a few years earlier that whenever an electric charge is subjected to acceleration, it emits radiation and loses energy. Bohr argued, therefore, that since an electron, a charged particle, moves round the nucleus in an orbit as in Rutherford's model, it is subjected to acceleration. The electron should, therefore, continuously emit radiation and lose energy. As a result of this, its orbit should become smaller and smaller and finally it should drop into the nucleus. This, however, does not happen. Bohr supplied a solution to this problem on the basis of the quantum theory of radiation put forth by Max Planck in 1901. Before discussing Bohr's theory, we may give a brief description of Planck's quantum theory.

Planck's Quantum Theory of Radiation. In order to explain the spectral distribution of energy radiated by a black body, Max Planck put forth his celebrated theory known as the **quantum theory of radiation.** According to this theory :

1. Radiant energy is not emitted or absorbed continuously but *discontinuously* in the form of tiny bundles of energy called *quanta.*

2. Each quantum is associated with a definite amount of energy E which is proportional to the frequency (ν) of radiation, that is, $E \propto \nu$ or $E = h\nu$, where h is a fundamental constant known as ***Planck's constant.*** The numerical value of h is $6{\cdot}626 \times 10^{-34}$ J s.

3. A body can emit or absorb energy only in whole number multiples of quantum, *i.e.*, $E = nh\nu$ where $n = 1, 2, 3$..... This means that a body can emit or absorb energy equal to $1h\nu$, $2h\nu$, $3h\nu$..... Energy in fractions of a quantum, *i.e.*, $0{\cdot}7\ h\nu$, $1{\cdot}2\ h\nu$, $3{\cdot}6\ h\nu$, $4{\cdot}86\ h\nu$, etc., cannot be lost or absorbed. This is known as ***quantisation of energy.***

Photoelectric Effect and Quantum Theory. Sir J. J. Thomson, in some of his famous experiments, observed that when light of a *certain frequency* strikes the surface of a metal, *electrons are ejected from the metal.* The phenomenon of ejection of electrons from the surface of a metal when light of a suitable frequency strikes on it, is known as **photoelectric effect.** The ejected electrons are called *photoelectrons.* It may be noted that only a few metals show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light. Cesium, which amongst the alkali metals, has the lowest ionisation energy, is also the metal from which electrons are ejected most easily. This metal is, therefore, used largely in photoelectric cells.

It is important to note that light of *any* frequency will *not* be able to cause ejection of electrons from a metal surface. Only that light which is associated with a certain minimum frequency, called *threshold frequency,* can cause ejection of electrons.

The photoelectric effect cannot be explained on the basis of the classical wave theory of light according to which energy of light is directly related to the amplitude of electromagnetic wave and hence to the intensity of the radiation irrespective of its frequency. If this view is correct, light of *any frequency,* if made sufficiently intense, can cause ejection of electrons. But this does not happen.

The quantum theory of radiation affords an easy explanation for the photoelectric effect. According to this theory, light consists of bundles of energy called *photons,* the energy of the photon being equal to $h\nu$ where ν is the frequency of the light. When a photon of light of frequency ν_0 (threshold frequency) strikes an electron in a metal, it imparts its entire energy ($= h\nu_0$) to the electron. This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus. Thus, each photon can eject one electron. If the frequency of the light is less than ν_0, there will be no ejection of electron. Now suppose the frequency of the light falling on a metal surface is higher than the threshold frequency. Let it be ν. When photon of this light strikes a metal surface, some of its energy (which is equal to the energy binding the electron with the nucleus), is consumed to separate the electron from the metal and the remaining energy will be imparted to the ejected electron to give it certain velocity, u. The ejected electron would thus be associated with kinetic energy $= 1/2\ mu^2$.

Einstein, applying quantum theory, showed that

$$h\nu = \phi + 1/2\ mu^2 \qquad ...(1)$$

where ϕ is the binding energy of the electron. It is also known as *work function* or *threshold energy.* Expressing ϕ in terms of threshold frequency, we may write, $\phi = h\nu_0$ so that

$$h\nu = h\nu_0 + 1/2\ mu^2 \qquad ...(2)$$

or

$$1/2\ mu^2 = h(\nu - \nu_0) \qquad ...(3)$$

Eq. 3 was tested by Millikan. The kinetic energies of the emitted electrons for various frequencies of light were determined by finding the opposing potential required to stop the photoelectric current. Knowing

kinetic energy corresponding to a given incident light of frequency ν and also knowing ν_0, *i.e.*, the threshold frequency, required just to cause ejection of electrons, the value of h was calculated. It was found to be $6{\cdot}570 \times 10^{-34}$ J s. This was in excellent agreement with the value $6{\cdot}626 \times 10^{-34}$ J s obtained from experiments on black body radiations.

Bohr's Model of the Atom

Niels Bohr, a Danish physicist, put forward his model of the atom in 1913. He retained Rutherford's model of a very-small positively charged nucleus at the centre which contains all the protons and neutrons present in an atom. Bohr also agreed that the negatively charged electrons are revolving round the nucleus in the same way as the planets are revolving round the sun. But he took a bold step forward by applying Planck's quantum theory to the electron revolving round the nucleus. The **important postulates of Bohr's theory** are :

1. *The electrons in an atom revolve around the nucleus only in certain selected circular orbits.* As long as the electron remains in a particular orbit, it neither loses nor gains energy. In other words, *the energy of an electron remains constant in a particular orbit.* This leads to the idea that *each orbit is associated with a definite energy, i.e.,* with *a definite whole number of quanta of energy.* The orbits, therefore, are also known as **energy levels** or **energy shells.** Bohr gave numbers 1, 2, 3, 4, etc., (starting from the nucleus) to these energy levels . These numbers are now termed as principal quantum numbers. The various energy levels are also designated by letters K, L, M, N, etc. The farther the energy level from the nucleus, the greater is the energy associated with it.

2. As long as the electron is associated with a particular amount of energy, it continues to stay in a a particular orbit. These obits are, therefore, also named as **stationary states.**

3. *The energy of an electron cannot change continuously.* It changes only **abruptly** as the electron *jumps* from one energy level to another. The same idea has been expressed by the statement that *for a change of electronic energy, the electron has to jump and not to 'flow' from one energy level to another.*

4. *The angular momentum of an electron moving round the nucleus is* **quantised.** An electron, like any other body moving in a circular orbit, has an angular momentum given by mvr where m is the mass, v is the linear velocity of the electron and r is the radius of the orbit. Bohr postulated that the angular momentum of an electron in an atom can have only *definite* or *discrete values* given by the expression

$$\text{Angular momentum} = mvr = n\,(h/2\pi) \qquad ...(4)$$

where n is any integer (1, 2, 3, etc.) Thus, the angular momentum of an electron may be $h/2\pi$ or a simple whole number multiple of $h/2\pi$ such as $2h/2\pi$, $3h/2\pi$,...$nh/2\pi$. This principle is known as **quantisation of angular momentum.**

Bohr's Equation for the Energy of Electron in Hydrogen or a Hydrogen-like Atom. Working on the above postulates, Bohr was able to calculate the energy of the electron moving in different orbits round the nucleus in a hydrogen or a hydrogen-like atom. He assumed, as had been suggested by Rutherford, that the electron remains in its orbit because the electrostatic force of attraction exerted by the nucleus is exactly balanced by the centrifugal force arising from its circular motion.

A hydrogen atom, having one proton in the nucleus and one electron outside the nucleus, is represented in Fig. 1.

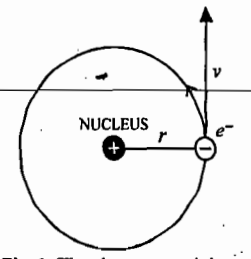


Fig. 1. The electron revolving around the nucleus in a hydrogen atom.

Let the charge on the nucleus be $+Ze$. For hydrogen atom, $Z = 1$ and for hydrogen-like atoms such as He^+ and Li^{2+}, $Z = 2$ and 3, respectively. The electron with charge $-e$ revolves round the nucleus in an orbit of radius r. Let v be the tangential velocity and m be the mass of the electron.

According to the laws of classical mechanics, the centripetal force acting on the electron in a hydrogen-like system, given by $Ze \times e/r^2$, tends to pull the electron towards the nucleus. However, the centrifugal force acting on the electron, given by mv^2/r, tends to take it away from its orbit. Under the influence of these two opposing forces, the electron keeps on revolving in its orbit. When the two forces balance,

$$Ze^2/r^2 = mv^2/r \quad ...(5)$$

Hence,

$$v^2 = Ze^2/mr \quad ...(6)$$

According to Bohr's postulate, the angular momentum, mvr, is an integral multiple of $h/2\pi$, *i.e.*, $mvr = n\,(h/2\pi)$ which leads to the expression

$$v = nh/2\pi mr \quad ...(7)$$

Squaring Eq. 7,

$$v^2 = n^2h^2/4\pi^2m^2r^2 \quad ...(8)$$

Eliminating v^2 from Eqs. 6 and 8, we have

$$Ze^2/mr = n^2h^2/(4\pi^2m^2r^2) \quad ...(9)$$

or

$$Ze^2 = n^2h^2/(4\pi^2mr) \quad ...(10)$$

According to Eq. 10, the radius r of the orbit is given by

$$r \equiv r_n = \frac{n^2h^2}{4\pi^2Zme^2} \quad ...(11)$$

Since, for hydrogen atom, $Z = 1$, hence,

$$r_n = \frac{n^2h^2}{4\pi^2me^2} \quad ...(12)$$

For hydrogen atom in the ground state ($n = 1$), the radius (r_1) is designated as the **Bohr's radius,** a_0. Thus,

$$r_1 \equiv a_0 = \frac{h^2}{4\pi^2me^2} \quad ...(13)$$

The total energy E of electron revolving in the nth orbit is equal to the sum of the kinetic energy ($= 1/2\, mv^2$) and the potential energy ($= -Ze^2/r_n$). Accordingly,

$$E = 1/2\, mv^2 - Ze^2/r_n \quad ...(14)$$

From Eq. 6,

$$mv^2 = Ze^2/r_n \quad ...(15)$$

Substituting the above value of mv^2 in Eq. 14, we have

$$E = \frac{Ze^2}{2r_n} - \frac{Ze^2}{r_n} = -\frac{Ze^2}{2r_n} \quad ...(16)$$

Substituting the value of r_n from Eq. 11 in Eq. 16, we get

$$E = -\frac{Ze^2}{2} \times \frac{4\pi^2Zme^2}{n^2h^2} \quad ...(17)$$

Thus, the **energy of electron in the nth orbit,** which we may designate as E_n, is given by

$$E_n = -\frac{2\pi^2Z^2me^4}{n^2h^2} \quad ...(18)$$

This is the famous **Bohr equation** applicable to hydrogen and hydrogen-like atoms such as He^+, Li^{2+}, Be^{3+}, etc.

In SI system, Eqs. 11 and 18 take the forms :

$$r_n = \frac{(4\pi\varepsilon_0)n^2h^2}{4\pi^2Zme^2} \quad ...(19)$$

$$E_n = -\frac{2\pi^2Z^2me^4}{(4\pi\varepsilon_0)^2n^2h^2} \quad ...(20)$$

The factor $4\pi\varepsilon_0$ is known as the **permittivity factor.** Its numerical value is $1{\cdot}11264 \times 10^{-10}\ C^2\ N^{-1}m^{-2}$.

We may now calculate some important quantities.

Bohr's Radius. According to Eq. 19, Bohr's radius of hydrogen atom (a_0) is given by

$$a_0 \equiv r_1 = \frac{(4\pi\varepsilon_0)h^2}{4\pi^2me^2} = \frac{(1{\cdot}11264\times10^{-10}\ C^2\ N^{-1}\ m^{-2})(6{\cdot}626\times10^{-34}\ J\ s)^2}{4\pi^2(9{\cdot}109\times10^{-31}\ kg)(1{\cdot}602\times10^{-19}C)^2}$$

$$= 0{\cdot}529\times10^{-10}\ m = 0{\cdot}529\ Å$$

Velocity of Electron. According to Eq. 7, the velocity of electron, say, in the first orbit of hydrogen atom, is given by

$$v_1 = \frac{(1)(6{\cdot}626\times10^{-34}\ J\ s)}{2\pi(9{\cdot}109\times10^{-31}\ kg)(0{\cdot}529\times10^{-10}m)} = 2{\cdot}188\times10^{6}\ m\ s^{-1}$$

It may be noted that this velocity is about (1/150)th of the velocity of light.

The velocity of electron in excited states, *i.e.*, when the electron is revolving in higher orbits of the hydrogen atom is obtained by putting $n = 2, 3, 4$, etc., in Eq. 7, provided the radius of the particular orbit is known. The radius can be calculated with the help of Eq. 12.

Energy of Electron. The energy of electron in hydrogen atom in ground state, *i.e.*, when it is revolving in the first orbit ($n = 1$), is easily obtained from Eq. 20. Thus,

$$E_1 = -\frac{(2\pi^2)(1)^2(9{\cdot}109\times10^{-31}kg)(1{\cdot}602\times10^{-19}C)^4}{(1{\cdot}11264\times10^{-10}\ C^2N^{-1}m^{-2})^2(1)^2(6{\cdot}626\times10^{-34}J\ s)^2} = -2{\cdot}179\times10^{-18}\ J\ per\ atom$$

$$= \frac{(-2{\cdot}179\times10^{-18}\ J\ atom^{-1})\,(6{\cdot}022\times10^{23}\ atoms\ mol^{-1})}{1000\ J/kJ} = -1312{\cdot}19\ kJ\ mol^{-1}$$

Since $1eV = 1{\cdot}602 \times 10^{-19}$ J, hence

$$E_1 = \frac{-2{\cdot}179\times10^{-18}\ J\ per\ atom}{1{\cdot}602\times10^{-19}J/eV} = -13{\cdot}6\ eV\ (per\ atom)$$

The energy of electron in excited states can be obtained by putting $n = 2, 3, 4$, etc., in Eq. 20.

Bohr's Theory and the Origin of Hydrogen Spectrum. Hydrogen atom contains only one electron. But its emission spectrum consists of a large number of lines (Table 1). Bohr supplied the reason. A given sample of hydrogen contains a very large number of atoms, of the order of several millions. Suppose energy is supplied to this sample of the gas. Now different atoms will absorb different amounts of energy. The solitary electron in different atoms will, therefore, shift to different energy levels depending upon the energy absorbed by the atoms. Some of the hydrogen atoms, for example, may absorb sufficient energy to shift their electrons to the second energy level only while some others may absorb more energy and may be able to shift their electrons to third or even to one of the higher energy levels. The electrons then tend to fall back, almost immediately, to one or the other of the lower energy levels. The various possibilities by which the electrons fall back from various excited state energy levels to lower energy levels (called

electronic transitions), are depicted in Fig. 2. During each transition, energy is released which appears in the form of radiation of specific frequency and hence of specific wave length.

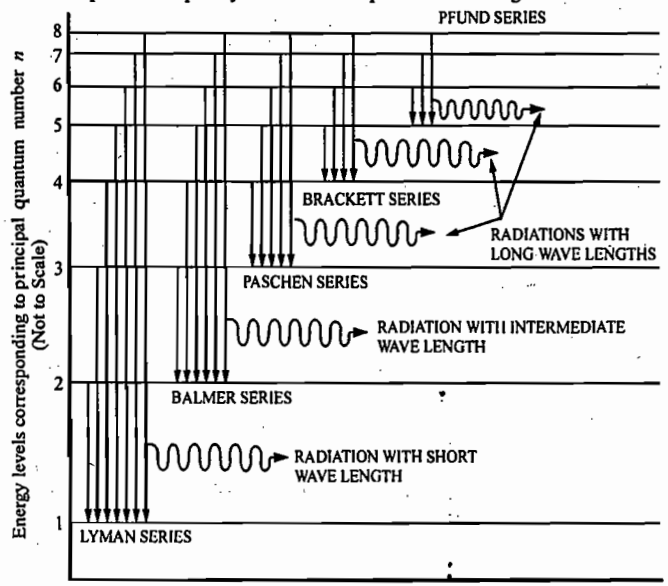


Fig. 2. The origin of hydrogen spectum.

Suppose an electron lying in energy level n_2 where its energy is E_2, jumps to a lower energy level n_1 where its energy is E_1. The energies in these two states, vide Eq. 20, are

$$E_2 = -\frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 n_2^2 h^2} \text{ and } E_1 = -\frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 n_1^2 h^2}$$

The difference in energy $\Delta E = E_2 - E_1$ would be emitted in the form of radiation of a specific frequency and hence of specific wave length. The emission spectrum of hydrogen would thus show a line at the frequency of the emitted radiation. If ν is the frequency of the spectral line, then

$$\Delta E = -\frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 n_2^2 h^2} + \frac{2\pi Z^2 me^4}{(4\pi\varepsilon_0)^2 n_1^2 h^2} \quad ...(21)$$

or

$$\nu = \frac{\Delta E}{h} = \frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad ...(22)$$

or

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad ...(23)$$

where $\bar{\nu}$, called the **wave number**, is the reciprocal of wave length in metres. It may be recalled that in Eq. 23, e is the charge in coulombs, m is the mass of electron in kg, h is Planck's constant in J s and c is the velocity of light in m s^{-1}.

The quantity $\frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 h^3 c}$ is called **Rydberg constant, *R***. Its value for the hydrogen atom is 109677·58 cm^{-1}.

The appearance of various series of spectral lines in the emission spectrum of hydrogen can be easily explained with the help of Eq. 23. The **Lyman series** are produced when the electron jumps from the second, third, fourth or a higher energy level to the first energy level. The frequencies of the various spectral lines of this series can thus be obtained by substituting $n_1 = 1$ and $n_2 = 2, 3, 4$, etc., in Eq. 23. The **Balmer series** result when the electron jumps from third, fourth, fifth, etc., energy levels to the second energy level. The frequencies of the various spectral lines of the Balmer series can, thus, be obtained by substituting $n_1 = 2$ and $n_2 = 3, 4, 5, 6$, etc. In the same way, the **Paschen series** originate from the electronic jumps from the fourth, fifth, sixth, etc., energy levels to the third energy level. The frequencies of these spectral lines can be obtained by substituting $n_1 = 3$ and $n_2 = 4, 5, 6$, etc., in Eq. 23, and so on.

The frequencies (in wave numbers) of the spectral lines of the three series calculated from Eq. 23 and those determined experimentally, are given in Table 1.

TABLE 1

Frequencies in Wave Numbers (m^{-1}) of Various Lines in the Emission Spectrum of Hydrogen

Lyman Series		Balmer Series		Paschen Series	
Experimental values	Calculated values	Experimental values	Calculated values	Experimental values	Calculated values
82·2×10^5	82·2×10^5	15·20×10^5	15·2×10^5	5·32×10^5	5·30×10^5
97·5	97·5	20·60	20·60	7·79	7·80
102·8	102·7	23·00	23·05	9·13	9·12
105·2	105·2	24·30	24·35	9·95	9·95
106·3	106·2	25·20	25·18	10·50	10·45
107·2	107·1	25·70	25·55	108·0	107·9

The agreement between the experimental and the calculated values is excellent. This offered a very strong support to Bohr's theory of the hydrogen atom.

Example 1. The electron in a hydrogen atom revolves in second orbit. Calculate : (1) The energy of the electron in this orbit. (2) The radius of the second orbit. (3) The frequency and wave length of the spectral line when the electron jumps from second orbit to the ground state. Given : mass of electron = 9·109×10^{-31} kg, charge on electron = 1·602×10^{-19} coulomb, velocity of light = 3·0×10^8 m s^{-1}, $4\pi\varepsilon_0$ = 1·11264 × 10^{-10} C^2 N^{-1} m^{-2}.

Solution : 1. Energy of Electron in Second Orbit. Energy of electron in hydrogen atom in the nth orbit is given by the expression

$$E_n = -\frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 n^2 h^2} \quad \text{(Eq. 20)}$$

$$E_2 = -\frac{(2)(3{\cdot}1416)^2 (9{\cdot}109\times10^{-31}\text{kg})\times(1{\cdot}602\times10^{-19}\text{C})^4}{(1{\cdot}11264\times10^{-10}\text{C}^2\text{N}^{-1}\text{m}^{-2})^2\ (4)\ (6{\cdot}626\times10^{-34}\text{J s})^2}$$

$$= -\ 5{\cdot}447\times10^{-19}\ \text{J (per atom)}$$

$$= -\frac{(5{\cdot}447\times10^{-19}\text{J})\ \text{atom}^{-1}\ (6{\cdot}022\times10^{23}\ \text{atoms mol}^{-1})}{1000\ \text{J/kJ}} = -\ 328{\cdot}02\ \text{kJ mol}^{-1}$$

2. Radius of Second Orbit. Radius of nth orbit in hydrogen atom is given by the expression

$$r_n = \frac{(4\pi\varepsilon_0)n^2 h^2}{4\pi^2 me^2} \quad \text{(Eq. 19)}$$

$$\therefore \quad r_2 = \frac{(1{\cdot}11264\times10^{-10}\,C^2N^{-1}m^{-2})\ (4)\ (6{\cdot}626\times10^{-34}\ J\ s)^2}{4\ (3{\cdot}1416)^2\ (9{\cdot}109\times10^{-31}kg)\ (1{\cdot}602\times10^{-19}C)^2}$$

$$= 2{\cdot}115 \times 10^{-10}\,m = 2{\cdot}115\ Å$$

3. (a) Frequency of the Spectral Line. The frequency of spectral line in the case of hydrogen atom when the electron jumps from the second orbit to the ground state is given by

$$\nu = \frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 h^3}\left(\frac{1}{1^2}-\frac{1}{2^2}\right) \qquad \text{(Eq. 22)}$$

$$= \frac{(2)\ (3{\cdot}1416)^2(9{\cdot}109\times10^{-31}kg)\ (1{\cdot}602\times10^{-19}\ C)^4}{(1{\cdot}11264\times10^{-10}\ C^2\cdot N^{-1}\ m^{-2})^2\times(6{\cdot}626\times10^{-34}\ J\ s)^3}\left[\frac{1}{1^2}-\frac{1}{2^2}\right]$$

$$= 2{\cdot}466 \times 10^{15}\ s^{-1}$$

(b) Wave length of the Spectral Line. Wave length of the spectral line would be given by

$$\lambda = \frac{c}{\nu} = \frac{3{\cdot}0\times10^8\ m\,s^{-1}}{2{\cdot}466\times10^{15}\ s^{-1}} = 1{\cdot}2165 \times 10^{-7}\,m = 1216{\cdot}5\ Å$$

Sommerfeld's Extension of Bohr's Theory. Bohr's theory of hydrogen atom enabled calculation of energies associated with various permissible orbits in the hydrogen atom. The calculated values were found to be in good agreement with the experimental values. Bohr's theory could also explain successfully the frequencies of various series of spectral lines in the hydrogen spectrum. The theory was, therefore, largely accepted and Bohr was awarded Nobel Prize in recognition of this work. However, a few years later, the use of spectroscopes of high resolving powers revealed the presence of *fine structures (i.e.,* groups of closely spaced lines in the spectrum of hydrogen. Bohr's theory could not explain the emission of groups of these closely spaced spectral lines. The theory was, therefore, extended by Sommerfeld by putting forward the idea of **elliptical orbits**.

According to Sommerfeld, an electron revolving around a central positively charged nucleus is so influenced by the nuclear charge that it is set into motion in *elliptical orbits* with the nucleus situated at one of the foci (Fig. 3). Thus, while according to Bohr's theory, electrons move in circular orbits, according to Sommerfeld's modification, electrons move in elliptical orbits. In the latter case, there will be a major axis and a minor axis having different lengths. As the orbit broadens, the lengths of the two axes become closer and they become equal when the orbit becomes circular, as shown in Fig. 3. Thus, the circular orbit is only a special case of elliptical orbits.

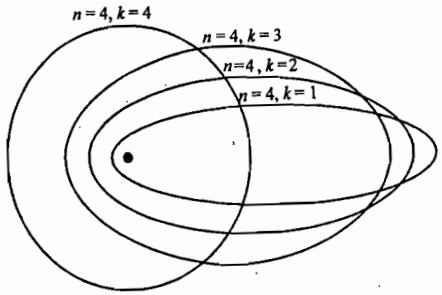


Fig. 3. Sommerfeld's elliptical orbits for $n = 4$.

The electron moving in an elliptical orbit will have its angular momentum. This momentum, according to the quantum theory, must also be quantised and thus can have only a limited number of values given by the factor $kh/2\pi$ where k is an integer known as the ***azimuthal quantum number***. It can be shown that n, the *principal quantum number* used by Bohr and k, the *azimuthal quantum number* ~~used by Sommerfeld, are related to each other as~~

$$\frac{n}{k} = \frac{\text{length of major axis}}{\text{length of minor axis}} \qquad ...(24)$$

Thus, for any given value of n (except 1), k can have more than a single value. When $k = n$, the orbit becomes circular. But, as k becomes smaller, the orbits become elliptical with greater and greater eccentricity. These facts are illustrated in Fig. 3. It may be noted that k cannot be zero because in that case minor axis would be zero which would imply linear motion of the electron passing through the nucleus.

As can be seen on reference to Fig. 3, the number of possible values of k is equal to the principal

quantum number n. Thus, if n is 4, k can have values varying from 4 to 1. It may have values of 4, 3, 2 and 1. When n is 1, k can have only one value.

According to Sommerfeld's extension of Bohr theory, referred to, sometimes, as Bohr-Sommerfeld theory, the energy depends not only on n, the principal quantum number but also, to some extent, on the azimuthal quantum number, k. Hence, the transition of an electron from one energy level n_2 to another energy level n_1 will be slightly different as it would also depend upon the various possible values of k in the two states. This explains the occurrence of groups of closely spaced lines observed in the hydrogen spectrum by using highly refined spectroscopes. The frequencies of these closely spaced lines were found to be in agreement with the values calculated from Bohr-Sommerfeld theory.

Alternative Explanation for the Emission of Multiple-line Spectrum of Hydrogen. The emission of groups of closely spaced spectral lines in the spectrum of hydrogen can be explained more effectively by taking into consideration the role of angular momentum of the electron, as illustrated below.

Electron moving around the nucleus in a particular orbit has a particular angular momentum called the *orbital angular momentum*. A portion of the energy of the electron is associated with its angular momentum which is described by the quantum number l called the **angular momentum quantum number**. This is related to the principal quantum number n as $l = n - 1$, the value of l will be 0, 1, 2, ... according as the value of n is 1, 2, 3, ..., respectively. The sublevels or subshells corresponding to $l = 0, 1, 2, 3,$ ..... are designated as *s, p, d, f,* ..... sublevels, respectively. Thus, if $n = 1$, l will have only one value, *i.e.*, 0 and there will be only one sub-shell, *viz.*, *s* subshell. For $n = 2$, l will have two values, *i.e.*, 0 and 1. There would thus be two subshells, *i.e.*, *s* and *p* subshells. If $l = 0$, the electron will be located in the *s* subshell of second major energy shell and if $l = 1$, the electron will be located in the *p* subshell of the second major energy shell. For $n = 3$, l will have three values, *i.e.*, 0, 1 and 2. There would thus be three subshells, *viz.*, *s, p* and *d* subshells according as the value of l is 0, 1 and 2 respectively, in which the electron can be located and so on.

The existence of various subshells in a given major energy shell, accounts for the appearance of groups of closely spaced lines in the spectrum of hydrogen observed using spectroscopes of high resolving power since the electronic transitions take place not only between the major energy shells but also between the various energy subshells.

According to Heisenberg's uncertainty principle (to be discussed shortly), it is impossible to determine simultaneously the exact position and exact velocity (momentum) of a small moving particle like an electron. The postulate of Bohr's theory that electrons revolve around the nucleus in *well defined orbits with well defined velocities* is thus not tenable. In order to overcome this shortcoming, the use of the term orbit in electronic motion has been dispensed with. In its place, we exclusively make use of the term **energy level** or **energy shell**. This is because the velocity of the electron can be measured with certainty but not its position.

Particle and Wave Character (Dual Character) of Electron. Einstein had suggested in 1905 that light has a *dual character* : as *wave* and also as '*particle*'. de Broglie proposed that *matter also has a dual character* : as wave and also as particle.

In Bohr's theory, electron is treated as a particle. But, according to de Broglie's theory, *electron has a dual character*, both as a material particle and as a wave. He derived (see below) an expression for calculating the wave length λ associated with the motion of a particle of mass m moving with velocity u, according to which $\lambda = h/mu$ where h is Planck's constant.

Derivation of de Broglie's equation. The de Broglie's equation for the wave-particle duality of electron can be easily derived by using Einstein's mass-energy relationship, *viz.*, $E = mc^2$. Equating this energy with the energy of a photon, we have

$$h\nu = mc^2 \qquad ...(25)$$

Since $\nu = c/\lambda$, hence

$$hc/\lambda = mc^2 \qquad ...(26)$$

or

$$\lambda = h/mc \qquad ...(27)$$

Replacing c by the velocity u of the particle, we have

$$\lambda = h/mu = h/p \qquad ...(28)$$

where p is the momentum of the particle. Eq. 28 is known as **de Broglie's equation**.

Distinction between matter waves and electromagnetic waves. It should be carefully noted that matter waves are *distinctly different* from electromagnetic waves. The speed of these waves is not the same as that of light. These waves cannot be radiated in empty space. They are certainly not emitted by the particle under consideration; they are simply associated with its motion. The wave lengths of matter waves are generally very small as compared with the wave lengths of electromagnetic waves.

Experimental Verification of de Broglie's Equation. The verification of de Broglie's equation is possible only by deriving from it certain consequences which may then be tested experimentally.

Let an electron of charge e be accelerated by a potential V. Then its kinetic energy would be Ve. The kinetic energy is also written as $1/2\, mu^2$ where u is the velocity of the electron.

$$1/2\, mu^2 = Ve \qquad ...(29)$$

$\therefore$ Inserting this value of u in de Broglie's equation, we have

$$\lambda = h / (2Vem)^{1/2} \qquad ...(30)$$

Substituting numerical values of various quantities, we have

$$\lambda = \frac{6{\cdot}626\times10^{-34}\,\text{J s}}{[(2)(V)(1{\cdot}602\times10^{-19}\,\text{C})(9{\cdot}109\times10^{-31}\,\text{kg})]^{1/2}} \qquad ...(31)$$

$$= 12{\cdot}26\times10^{-10}\,V^{-1/2}\ \text{metre}$$

where V is the numerical value of potential in volts.

If an electron is accelerated through a potential of 100 volts, its wave length should be $1{\cdot}226\times10^{-10}$ m, *i.e.*, 1·226 Å. If potentials are varied between 10 and 10,000 volts, λ should vary between 3·877 and 0·1266 Å. It is well known that X-rays have wave lengths of this order. It is also well known that crystalline solids can act as diffraction gratings for X-rays having wave lengths of the above order. Therefore, if de Broglie's view regarding wave-particle duality of electron is correct, the crystalline solids should act as diffraction gratings for a beam of electrons as well. This has been found to be so experimentally.

The Davisson and Germer Experiment. The de Broglie's bold hypothesis regarding wave character of electron received first experimental support from Davisson and Germer in 1927. In their experiment, electrons were emitted from a hot filament and were accelerated by a potential ranging between 40 and 68 volts before striking a nickel plate, as shown in Fig. 4.

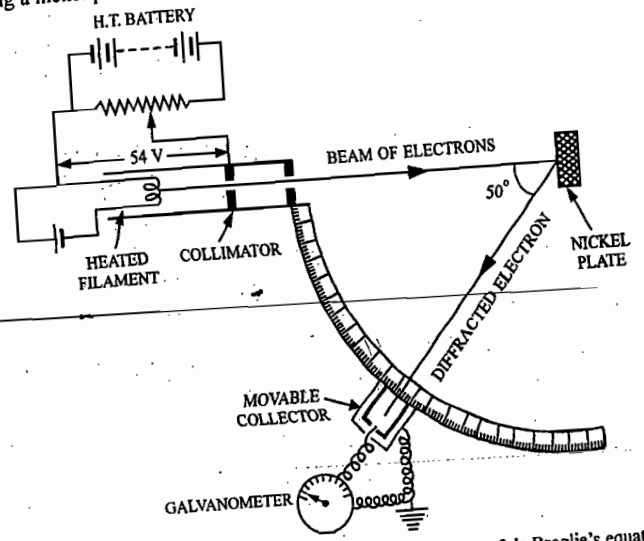


Fig. 4. The Davisson and Germer experiment for verification of de Broglie's equation.

They found that the impact of electrons resulted in the *production of diffraction patterns which were similar to those given by X-rays under similar conditions.* Since X-rays possess wave character, *the electrons must also have wave character associated with them.* Thus, this experiment gave *direct evidence for the wave character of electron.*

The intensities of electron waves scattered by the nickel plate at different angles were measured. It was found that the reflection was most intense and took place at an angle of 50° when electrons were accelerated through 54 volts. Substituting the value of V as 54 volts in Eq. 31, it can be shown that the value of λ, the wave length of the electron wave comes out to be 1·668Å. This wave length also lies in the X-ray range. This is another point of similarity between electron waves and X-rays. It should be possible, therefore, to apply Bragg's equation, derived for X-ray diffraction, to electron diffraction as well. According to this equation

$$2\,d\sin\theta = n\lambda \qquad ...(32)$$

where n is an integral multiple (1, 2, 3, etc.) of wave length λ for a reflection of maximum intensity, d is the distance between successive lattice planes of the crystal (nickel plate in the present case) and θ is the grazing angle of the wave. Davisson and Germer found the value of λ to be very close to that obtained by de Broglie's equation. Davisson and Germer's experiment thus offered full support to de Broglie's views and his equation.

The de Broglie's concept about dual character of matter is significant only for microscopic particles such as electrons, protons, atoms and molecules. It loses its significance when applied to macroscopic bodies. This is because the wave lengths of matter waves associated with macroscopic bodies are too small to be measured by any conceivable technique. Therefore, we can safely comment that "macroscopic bodies have no de Broglie wave lengths."

The wave length associated with an electron of mass $9{\cdot}11\times10^{-31}$ kg moving with a velocity of 10^6 m s^{-1} is 7·27Å, as shown below :

$$\lambda = \frac{h}{mu} = \frac{6{\cdot}626\times10^{-34}\,\text{J s}}{9{\cdot}11\times10^{-31}\,\text{kg}\times10^{6}\,\text{m s}^{-1}} = 0{\cdot}727\times10^{-9}\,\text{m} = 7{\cdot}27\text{Å} \qquad (\text{J} = \text{kg m}^2\,\text{s}^{-2})$$

On the other hand, the wave length associated with a ball weighing 0·01 kg and moving with the same velocity as that of electron (10^6 m s^{-1}) is $6{\cdot}626\times10^{-28}$ Å, as shown below :

$$\lambda = \frac{h}{mu} = \frac{6{\cdot}626\times10^{-34}\,\text{J s}}{0{\cdot}01\,\text{kg}\times10^{6}\,\text{m s}^{-1}} = 6{\cdot}626\times10^{-38}\,\text{m} = 6{\cdot}626\times10^{-28}\,\text{Å}$$

This wave length is far far shorter than the wave length of any electromagnetic radiation.

Example 2. The kinetic energy of an electron has been found to be $5{\cdot}76\times10^{-15}$ J. Calculate the wave length associated with the electron. (Mass of electron = $9{\cdot}1\times10^{-31}$ kg, $h = 6{\cdot}626\times10^{-34}$ J s).

Solution : Kinetic energy of the electron $= 1/2\, mu^2 = 5{\cdot}76\times10^{-15}$ J (given)

$\therefore$ $mu^2 = 5{\cdot}76\times10^{-15}\times2$ J

or $$u^2 = \frac{5{\cdot}76\times10^{-15}\times2\,\text{J}}{9{\cdot}1\times10^{-31}\,\text{kg}} = 1{\cdot}266\times10^{16}\,\text{m}^2\,\text{s}^{-2} \qquad (\text{J} = \text{kg m}^2\,\text{s}^{-2})$$

or $u = 1{\cdot}12\times10^{8}$ m s^{-1}

Using de Broglie equation, $$\lambda = h/mu = \frac{6{\cdot}626\times10^{-34}\,\text{J s}}{(9{\cdot}1\times10^{-31}\,\text{kg})(1{\cdot}12\times10^{8}\,\text{m s}^{-1})} = 6{\cdot}50\times10^{-12}\,\text{m}$$

$$= 0{\cdot}0650\ \text{Å}$$

Wave nature of electron and quantisation of angular momentum. Consider an electron moving in a circular orbit around a nucleus. The associated wave train would be as shown in Fig. 5. Evidently, if the wave is to remain continually in phase (Fig. 5*a*), the circumference of the circle must be an integral multiple of wave length λ, that is,

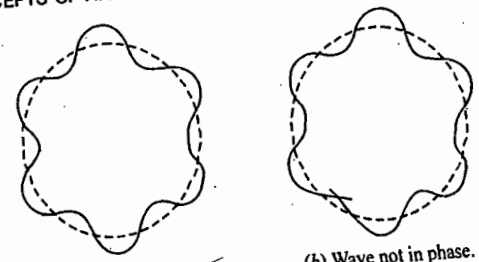
$$\text{circumference} = n\lambda$$

$$2\pi r = n\lambda = nh/mu$$

$$\therefore \quad mur = n\,h/2\pi$$

Evidently, if the circumference is bigger or smaller than the value $nh/2\pi$ given in Eq. 33, the wave will no longer remain in phase (Fig. 5*b*).

Since mur represents the angular momentum of the electron, it follows from Eq. 33 that the electron can move only in those orbits for which the angular momentum is an integral multiple of $h/2\pi$. In other words, *the angular momentum is quantised.* This is nothing but Bohr's postulate which was put forth by him without any theoretical basis.



(*a*) Wave continually in phase. (*b*) Wave not in phase.

Fig. 5. The wave trains associated with an electron moving in a circular path around a nucleus.

Heisenberg's Uncertainty Principle. According to this principle, *it is not possible to determine precisely both the position and the momentum (or velocity) of a moving minute particle.* This principle is mathematically expressed as :

$$(\Delta x) \times (\Delta p) = h/4\pi \qquad ...(34)$$

where Δx is uncertainty with regard to the position and Δp is uncertainty with regard to the momentum of the particle. Evidently, if Δx *is very small, i.e.,* the position of the particle is known more or less exactly, Δp would be *large, i.e.,* uncertainty with regard to momentum will be large. Similarly, if an attempt is made to measure exactly the velocity (momentum) of the particle, the uncertainty with regard to position will become large.

The physical concept of the uncertainty principle may become clear when it is realised that all observations have to be made by the impact of light radiations (photons). If the object is of reasonable size, its position or velocity will not be altered by the impact of light photons. Hence, it will be possible to know precisely both the position and the velocity of the object. In other words, the uncertainty Δx or Δp would be negligible. But this cannot be so when the object is extremely minute, such as an electron moving, say, in a circular path. *It will suffer a change in its velocity and path due to the impact of even a single photon of light used to observe it.*

In view of the uncertainty principle, Bohr's model, in which electrons are considered as particles revolving in *definite orbits with definite velocities* becomes untenable. It is not possible to know exactly the position of an electron moving with *a particular velocity* as is implied in Bohr's model. Instead, *it is possible only to state or predict the* **probability** *of locating an electron moving with a particular velocity in a given region of space around the nucleus at a given time.*

Example 3. An electron has a speed of 300 m s^{-1} accurate upto 0·001%. What is the uncertainty in locating its position ? Mass of an electron = 9·1×10^{-31} kg

Solution : According to uncertainty principle, $(\because p = mu)$

$$\Delta x \times m\,\Delta u = h/4\pi$$

$$\Delta u = \frac{0{\cdot}001}{100} \times 300 \text{ m s}^{-1} = 0{\cdot}003 \text{ m s}^{-1}$$

$$\therefore \quad \Delta x \times 9{\cdot}1\times10^{-31} \text{ kg} \times 0{\cdot}003 \text{ m s}^{-1} = 6{\cdot}626 \times 10^{-34} \text{ J s}/4\pi \qquad (\text{J} = \text{kg m}^2 \text{ s}^{-2})$$

$$\Delta x = 1{\cdot}93 \times 10^{-2} \text{ m}$$

or

Example 4. A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0·1 Å. What is the uncertainty involved in the measurement of its velocity ? Mass of electron = 9·1 × 10^{-31} kg and Planck's constant (h) = 6·626 × 10^{-34} J s.

Solution : According to uncertainty principle,

$$\Delta x \times \Delta p = h/4\pi$$

$$\Delta x \times m\Delta u = h/4\pi$$

or

$$\Delta x = 0{\cdot}1 \times 10^{-10} \text{ m}$$

$$\therefore \quad 0{\cdot}1\times10^{-10} \text{ m} \times 9{\cdot}1\times10^{-31} \text{ kg} \times \Delta u = 6{\cdot}626 \times 10^{-34} \text{ J s}/4\pi$$

$$\Delta u = 5{\cdot}79 \times 10^{6} \text{ m s}^{-1} \qquad (\text{J} = \text{kg m}^2 \text{ s}^{-2})$$

Example 5. A cricket ball weighing 100 g *is to be located within* 0·1Å. What is the uncertainty in its velocity ? Comment on your result.

Solution : According to uncertainty principle,

$$\Delta x \times \Delta p = h/4\pi$$

or

$$\Delta p = h/(4\pi\,\Delta x)$$

$$\Delta x = 0{\cdot}1 \text{ Å} = 1 \times 10^{-11} \text{ m}$$

$$\therefore \quad \Delta u = \Delta p/m = \frac{h}{4\pi\Delta x \times m} = \frac{6{\cdot}626\times10^{-34} \text{ J s}}{4\pi(10^{-11} \text{ m})\ (0{\cdot}1 \text{ kg})}$$

$$= 5{\cdot}27 \times 10^{-23} \text{ m s}^{-1} \qquad (\text{J} = \text{kg m}^2 \text{ s}^{-2})$$

Comparing this value with the usual velocity of a cricket ball, we find that this uncertainty in velocity is negligible. This means that we can disregard the uncertainty principle for the motion of macroscopic bodies. In such cases, both the position and velocity can be simultaneously determined to a reasonable degree of precision.

Example 6. According to Bohr's theory of hydrogen atom, the velocity of electron in the first orbit is 10^6 m s^{-1}. Suppose the electron can be located in the orbit within 0·1Å. What will be the uncertainty in its velocity ? Comment on your result.

Solution : According to uncertainty principle,

$$\Delta p \times \Delta x = h/4\pi$$

or

$$m\,\Delta u \times \Delta x = h/4\pi$$

$$\Delta x = 0{\cdot}1\text{Å} = 1 \times 10^{-11} \text{ m}$$

$$\Delta u = \frac{h}{4\pi m\,\Delta x} = \frac{6{\cdot}626\times10^{-34} \text{ J s}}{4\pi(9{\cdot}1\times10^{-31}\text{kg})(10^{-11}\text{m})} = 5{\cdot}79 \times 10^{6} \text{ m s}^{-1}$$

But $\quad u = 10^6 \text{ ms}^{-1}$ (given)

This means that the uncertainty in velocity is greater than the velocity itself ! This appears to be ridiculous. One can avoid making such a statement by bearing in mind that when the position of the electron is specified with sufficient accuracy, it is meaningless to talk about its velocity at the same time.

The Compton Effect. Compton found that if monochromatic X-rays, *(i.e.,* X-rays having one particular wave length), are allowed to fall on carbon or some other light element, the scattered X-rays have wave lengths longer than the wave length of the incident rays. In other words, the scattered X-rays have lower frequency, *i.e.,* lower energy than the incident X-rays. Since scattering is caused by electrons present in the atoms of the elements, it is evident that some interaction between X-rays and electrons has taken place and this has resulted in decrease in the energy of the former. This decrease in energy or increase in wave length of X-rays after scattering from the surface of an object is known as **Compton effect.**

By applying the law of conservation of energy and the law of conservation of momentum and assuming X-rays to consist of 'particles' (photons), each possessing energy equal to $h\nu$, Compton derived the following equation :

$$\Delta\lambda = (2h/mc)\sin^2\theta/2 \qquad ...(35)$$

where $\Delta\lambda$ is the increase in wave length (termed as **Compton shift**) produced as a result of the collision, m is the rest mass of the electron, c is the velocity of light and θ is the angle between the incident and the scattered X-rays.

According to this equation, Compton shift should be independent of the wave length of the incident X-rays. This has been found to be so experimentally. Further, the values of Compton shift, as obtained

from the above equation by substituting the known values of h, c, m and θ, have been found to be in close agreement with the experimental values.

Compton effect provides a good illustration of the uncertainty principle. Suppose, X-rays are employed to determine the position and momentum of an electron. As a result of mutual interaction of X-rays and the electrons, the wave length of X-rays increases, *i.e.*, the frequency or energy of the X-rays decreases. This energy must have been transferred to the electron and, therefore, the momentum of the electron must have changed during the process. Consequently, the momentum (and hence velocity) of the electron cannot be determined with certainty.

Compton effect also provides evidence for the corpuscular or photon nature of radiation.

The Compton equation (35) can also be written as

$$\Delta\lambda = \lambda' - \lambda = \frac{2h}{mc} \times \frac{1}{2}\left[1 - \cos 2\theta/2\right] = \left(\frac{h}{mc}\right)(1 - \cos\theta) \qquad ...(36)$$

We see that the wave length λ' of scattered X-rays is always greater than the wave length λ of incident X-rays. The quantity $\Delta\lambda$ is also called the **wave length shift.** The wave length shift is independent of the nature of the substance and the wave length of incident X-rays. It depends only on the scattering angle θ. The following three cases may be considered :

Case 1. $\theta = 0°$, *i.e.*, the scattered radiation is parallel to the incident radiation. In this case, $\cos\theta = 1$ so that $\Delta\lambda = 0$, *i.e.*, there is no wave length shift.

Case 2. $\theta = 90°$, *i.e.*, the scattered radiation is perpendicular to the incident radiation. In this case, $\cos\theta = 0$ so that

$$\Delta\lambda = \frac{h}{mc} = \frac{6{\cdot}626 \times 10^{-34}\ \text{J s}}{(9{\cdot}109 \times 10^{-31}\ \text{kg})(3 \times 10^{8}\ \text{m s}^{-1})} \qquad (\text{J} = \text{kg m}^2\,\text{s}^{-2})$$

$$= 0{\cdot}02422 \times 10^{-10}\ \text{m} = 0{\cdot}0242\ \text{Å}$$

Case 3. $\theta = 180°$, *i.e.*, the radiation is scattered in a direction opposite to the incident radiation. In this case, $\cos\theta = -1$ so that

$$\Delta\lambda = 2h/mc = 2 \times 0{\cdot}0242\ \text{Å} = 0{\cdot}0484\ \text{Å}$$

QUANTUM MECHANICS OR WAVE MECHANICS

Classical mechanics, formulated by Isaac Newton, is obeyed by *macroscopic* particles such as planets and rigid bodies. Since the *microscopic* particles such as electrons, protons, atoms and molecules exhibit wave-particle duality, they do not obey Newtonian dynamics. On the other hand, they obey quantum mechanics or wave mechanics, the laws of which were formulated by Born, Heisenberg and Jordan in 1925 and by Schrodinger in 1926. The Schrodinger formulation is more familiar to chemists than the Born-Jordan-Heisenberg formulation. In classical mechanics, the state of a system is defined by specifying the forces acting on the particle and the exact position and velocity acquired by the particle as a result of these forces. It is impossible, however, to specify simultaneously the exact position as well as exact velocity in the case of a microscopic particle (Heisenberg uncertainty principle). Therefore, while classical mechanics allows us to predict the exact paths (or trajectories) taken by the particles of a macroscopic system, quantum mechanics gives the **probabilities** of the location of the particles of a microscopic system at various places in space.

As we shall see shortly, in quantum mechanics, the state of a system is defined by the *state function* or **wave function** ψ, which is a function of the coordinates of the particles of the system and is also a function of time (since the state may change with time). Thus, for a two-particle system, the wave function can be written as

$$\psi = f(x_1, y_1, z_1, x_2, y_2, z_2, t)$$

where x_1, y_1, z_1 are the coordinates of particle 1, etc. For an n-particle system, the equation governing the time-dependence of ψ is given by

$$\sum_{i=1}^{n} -\frac{\hbar^2}{2m_i}\left(\frac{\partial^2\psi}{\partial x_i^2} + \frac{\partial^2\psi}{\partial y_i^2} + \frac{\partial^2\psi}{\partial z_i^2}\right) + V(x_i, y_i, z_i, t)\psi = i\hbar\frac{\partial\psi}{\partial t}$$

where m_i is the mass and V is the potential energy of the particle.

The above equation is the celebrated time-dependent second-order differential equation, known as the Schrodinger wave equation.

It may be noted that if the velocity of a microscopic particle is far less than the velocity of light, then quantum mechanics gives the same results as Newton's classical mechanics. Also when the systems are in highly excited quantum states, classical mechanics and quantum mechanics tend to yield the same results.

The Postulates of Quantum Mechanics or Wave Mechanics. The formulation of quantum mechanics or wave mechanics for the wave mechanical treatment of the structure of atom rests upon a few postulates which, for a system moving in one dimension, say, the x-coordinate, are given below.

First Postulate. The physical state of a system at time t is described by the wave function $\psi(x, t)$.

Second Postulate. The wave function $\psi(x, t)$ and its first and second derivatives $\partial\psi(x, t)/\partial x$ and $\partial^2\psi(x, t)/\partial x^2$ are continuous, finite and single-valued for all values of x. Also, the wave function $\psi(x, t)$ is *normalized, i.e.,*

$$\int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)\,dx = 1 \qquad ...(37)$$

where ψ^* is the *complex conjugate* of ψ formed by replacing i with $-i$ wherever it occurs in the function ψ. $(i = \sqrt{-1})$

Third Postulate. A physically observable quantity can be represented by a *Hermitian operator.* An operator A is said to be Hermitian if it satisfies the following condition :

$$\int \psi_i^* \hat{A}\psi_j\,dx = \int \psi_j (\hat{A}\psi_i)^*\,dx \qquad ...(38)$$

where ψ_i and ψ_j are the wave functions representing the physical states of the quantum system, *i.e.*, a minute particle such as an electron, proton, an atom or a molecule.

Fourth Postulate. The allowed values of an observable A are the eigenvalues, a_i, in the operator equation

$$\hat{A}\psi_i = a_i\psi_i \qquad ....(39)$$

Eq. 39 is known as an *eigenvalue equation.* Here $\hat{A}$ is the operator for the observable (physical quantity) and ψ_i is an eigenfunction of $\hat{A}$ with eigenvalue a_i. In other words, measurement of the observable A yields the eigenvalue a_i.

Fifth Postulate. The average value (or, the expectation value), $\langle A \rangle$, of an observable A, corresponding to the operator $\hat{A}$, is obtained from the relation

$$\langle A \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{A}\,\psi\,dx \qquad ....(40)$$

where the function ψ is assumed to be normalized in accordance with Eq. 37. Thus, the average value of, say, the x-coordinate is given by

$$<x> = \int_{-\infty}^{\infty} \psi^* \hat{x}\, \psi\, dx \qquad ...(41)$$

Sixth Postulate. The quantum mechanical operators corresponding to the observables are constructed by writing the classical expressions in terms of the variables and converting the expressions to the operators, as shown in Table 2.

TABLE 2

Wave Mechanical Operators for Evaluating Various Classical Variables

Classical variable	Quantum mechanical operator	Operator	Operation
x	$\hat{x}$	x	Multiplication by x
p_x	$\hat{p}_x$	$-i\hbar\frac{\partial}{\partial x}$	Taking derivative with respect to x and multiplying by $-i\hbar$
x^2	$\hat{x}^2$	x^2	Multiplication by x^2
p_x^2	$\hat{p}_x^2$	$-\hbar^2\frac{\partial^2}{\partial x^2}$	Taking second derivative with respect to x and multiplying by $-\hbar^2$
t	$\hat{t}$	t	Multiplying by t
E	$\hat{E}$	$i\hbar\frac{\partial}{\partial t}$	Taking derivative with respect to t and multiplying by $i\hbar$

Seventh Postulate. The wave function $\psi(x, t)$ is a solution of the time-dependent equation

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t} \qquad ...(42)$$

where $\hat{H}$ is the *Hamiltonian operator* of the system.

The Schrodinger Wave Equation. It is evident from the earlier discussion that moving electrons behave both as particles and as a wave. If the electrons behave as a wave, there must be a wave equation to describe their behaviour. Erwin Schrodinger, in 1926, gave a wave equation to describe the wave behaviour of electrons in atoms and molecules. In Schrodinger wave model of an atom, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical functions ψ which are related with the probability of finding electrons at various places around the nucleus.

The Schrodinger wave equation for an electron wave propagating in three dimensions in space, is written as follows :

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad ...(43)$$

or

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad ...(44)$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

∇^2 is known as *Laplacian mathematical operator*. A mathematical operator such as $\int$, $\frac{d}{dx}$ or $\sqrt{\ }$ appears alongwith a mathematical quantity or a function upon which it operates. Thus, in $\sqrt{2}$, $\sqrt{\ }$ is a mathematical operator and 2 is the mathematical quantity on which it operates. Similarly, in x^2, the power 2 is a mathematical operator operating upon the quantity x. A mathematical operator without the accompanying quantity or function has no meaning. ∇^2 alone, therefore, has no meaning unless it is accompanied by ψ.

It may be noted that $\nabla^2\psi$ does not mean ∇^2 multiplied by ψ. It means that the mathematical operator ∇^2 operates upon the mathematical function ψ.

The concept of operators is very important in wave mechanics. We have already listed a few operators in the sixth postulate. Here we shall briefly deal with the algebra of operators. If $\hat{A}$ and $\hat{B}$ are two operators and f is a function upon which they operate, then

$$(\hat{A}+\hat{B})f = \hat{A}f + \hat{B}f \qquad ...(45)$$

and

$$(\hat{A}-\hat{B})f = \hat{A}f - \hat{B}f \qquad ...(46)$$

Thus, we can generate new operators $\hat{A}+\hat{B}$ and $\hat{A}-\hat{B}$ by adding and subtracting $\hat{A}$ and $\hat{B}$. Also

$$\hat{A}+\hat{B} = \hat{B}+\hat{A} \qquad ...(47)$$

and

$$\hat{A}-\hat{B} = -\hat{B}+\hat{A} \qquad ...(48)$$

The multiplication of operators can be carried out by doing successive operations with two or more operators on a function. If $\hat{A}$ and $\hat{B}$ are two operators and f is their *operand*, then we can obtain the quantity $\hat{A}\hat{B}f$ as follows :

We first operate on f with $\hat{B}$ to obtain f'.

$$\hat{B}f = f'$$

Then, f' is operated upon by $\hat{A}$ to obtain f''.

$$\hat{A}f' = f''$$

Thus, we have

$$\hat{A}\hat{B}f = f'' \qquad ...(49)$$

It should be remembered that the order of application of operators is always from right to left as they are written. Application of the same operator several times in succession is written with a power. Thus, we have

$$\hat{A}\hat{A}f = \hat{A}^2 f \qquad ...(50)$$

The algebra of operators should be distinguished from the algebra of ordinary numbers. If a and b are two numbers, then we know that

$$a \times b = b \times a \qquad ...(51)$$

However, if $\hat{A}$ and $\hat{B}$ are two operators, then their *product* $\hat{A}\hat{B}$ may or may not be equal to $\hat{B}\hat{A}$. If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then the two operators are said to commute with each other or said to be commutable.

The mathematical function ψ is a function of the space coordinates or variables x, y, z and should be expressed as $\psi(x, y, z)$. For the sake of brevity, however, it is written as ψ only. A *real* mathematical

function of x, y, z can be plotted in Cartesian space (three-dimensional space). The function ψ signifies the *amplitude* of the electron wave and is called the *wave function.*

In Schrodinger wave equation, x, y, z are the three space coordinates, m is the mass of the electron, E is the total energy and V is the electrostatic potential energy associated with the electron. $\frac{\partial^2 \psi}{dx^2}$, $\frac{\partial^2 \psi}{\partial y^2}$ and $\frac{\partial^2 \psi}{\partial z^2}$ are the double differentials of ψ with respect to x only, y only and z only, respectively.

Formulation of Schrodinger Wave Equation. Schrodinger assumed the electron waves to be similar to the stationary waves, *i.e.*, the waves produced by the vibrations of a stretched string. Consider such a wave being propagated in x direction. Let w be the amplitude of the wave at any point whose coordinate is x at time t. The equation for such a wave motion may be expressed as

$$\frac{\partial^2 w}{\partial x^2} = \frac{1}{u^2} \times \frac{\partial^2 w}{\partial t^2} \qquad ...(52)$$

where u is the velocity with which the wave propagates. The amplitude w in differential Eq. 52 depends upon x and t.

Eq. 52. can be solved only if w can be written as a product of two mathematical functions, one of which depends on x only [*i.e.*, the function f (x)] and the other on t only [*i.e.*, the function g (t)], that is, if we can write w as

$$w = f(x)\, g(t) \qquad ...(53)$$

For stationary waves, the function g (t) is represented by the expression

$$g(t) = A \sin(2\pi\nu t) \qquad ...(54)$$

where ν is the frequency of vibration and A is the maximum amplitude of the wave. Double differentiation of Eq. 54 with respect to time gives

$$\frac{\partial^2 g(t)}{\partial t^2} = -4\pi^2\nu^2 A \sin(2\pi\nu t) = -4\pi^2\nu^2 g(t) \qquad ...(55)$$

Similarly, double differentiation of Eq. 53 with respect to time and with respect to coordinate x, yields respectively,

$$\frac{\partial^2 w}{\partial t^2} = f(x)\frac{\partial^2 g(t)}{\partial t^2} = -f(x)\, 4\pi^2\nu^2 g(t) \qquad ...(56)$$

and

$$\frac{\partial^2 w}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2} g(t) \qquad ...(57)$$

Substituting the values of $\frac{\partial^2 w}{\partial t^2}$ and $\frac{\partial^2 w}{\partial x^2}$ in Eq. 52, we get

$$\frac{\partial^2 f(x)}{\partial x^2} g(t) = -\frac{1}{u^2} 4\pi^2\nu^2 g(t) f(x) \qquad ...(58)$$

or

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2\nu^2}{u^2} f(x) \qquad ...(59)$$

But, we know that $u = \nu\lambda$ where λ is the wave length of the stationary wave. Hence,

$$\nu/u = 1/\lambda \qquad ...(60)$$

Replacing ν/u by $1/\lambda$ in Eq. 59, we get

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x) \qquad ...(61)$$

Eq. 61 is the equation for a uni-dimensional stationary wave propagating in one direction (*i.e.*, x direction) only. We may now extend this equation to three dimensions by replacing f(x) [an amplitude function of variable x] by $\psi(x, y, z)$ [an amplitude function of the variables x, y, z]. Similarly, the factor $\frac{\partial^2 f(x)}{\partial x^2}$ of uni-dimensional Eq. 61 will now be replaced by $\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}$ in a three-dimensional equation. The factor $\frac{\partial^2 \psi}{\partial x^2}$ is double differentiation of $\psi(x, y, z)$ with respect to x only keeping y and z constant ; $\frac{\partial^2 \psi}{\partial y^2}$ is double differentiation of $\psi(x, y, z)$ with respect to y only keeping x and z constant and $\frac{\partial^2 \psi}{\partial z^2}$ is double differentiation of $\psi(x, y, z)$ with respect to z only keeping x and y constant). Hence, Eq. 61 in three-dimensional space takes the form

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\psi \qquad ...(62)$$

The above equation is applicable to all minute particles including electrons. Substituting the value of $\lambda = h/mu$ (de Broglie's relation) in Eq. 62, we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 m^2 u^2}{h^2}\psi \qquad ...(63)$$

where m is the mass and u is the velocity of the particle. The total energy E of the particle is the sum of its kinetic energy $(= 1/2\, mu^2)$ and the potential energy, V. Thus,

$$E = 1/2\, mu^2 + V \qquad ...(64)$$

or

$$mu^2 = 2(E - V) \qquad ...(65)$$

or

$$u^2 = 2(E - V)/m \qquad ...(66)$$

Substituting the above value of u^2 in Eq. 63, we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 m^2}{h^2} \times \frac{2}{m}(E - V)\psi \qquad ...(67)$$

or

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad ...(68)$$

Eq. 68 is the well known **Schrodinger wave equation** proposed by him in 1926. It is customarily written in the following form :

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi = E\psi \qquad ...(69)$$

or $$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi \qquad ...(70)$$

where $\hbar$ is $h/2\pi$ and ∇^2 is the Laplacian operator defined as $\nabla^2 = \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$.

The complete mathematical operator of ψ in Eq. 69 is the Hamiltonian operator $\hat{H}$. Thus,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \qquad ...(71)$$

Eq. 70, therefore, becomes $$\hat{H}\psi = E\psi \qquad ...(72)$$

The Hamiltonian operator $\hat{H}$ consists of two parts, *viz.*, the kinetic energy part $\left(-\frac{\hbar^2}{2m}\nabla^2\right)$ and the electrostatic potential energy part (V). The solution of Schrodinger wave equation implies finding out appropriate ψ which satisfies the wave equation.

The Schrodinger wave equation, being a second order differential equation, has innumerable solutions, many of them having no significance at all. Out of these, only those solutions are significant which give certain definite and acceptable values of the total energy E. The acceptable value of total energy E given by a solution is called eigenvalue and the corresponding function ψ which gives eigenvalue of the energy, is called eigenfunction. Thus, every function is not an eigen (or acceptable) function.

Conditions to be satisfied by an eigen (or acceptable) wave function. An acceptable solution of the Schrodinger wave equation, *i.e.*, an eigen wave function, must satisfy the following conditions :

1. The function should be finite.
2. It should be single-valued (*i.e.*, it should not have more than one value at a point in space).
3. It should be continuous (*i.e.*, the function if plotted in space should not show a break).
4. $\partial^2\psi/\partial x^2$, $\partial^2\psi/\partial y^2$, etc., should also be continuous.
5. The function should be normalised, *i.e.*, $\int_{-\infty}^{+\infty}\psi d\tau = 1$

Probability Density and Significance of ψ. According to Heisenberg's uncertainty principle, we can never know the exact position of the electron moving around the nucleus with a particular velocity. Therefore, we talk in terms of the probability of its location in any given region. In other words, we define its position by a probability function. Such a probability function will vary with the position of the region in space in which we want to find the probability of the existence of the electron. If $\rho(x, y, z)$ is such a probability function, then the probability that the electron will be found in the small cubic volume element of dimension $dxdydz$, is given by the product of $\rho(x, y, z)$ and the volume of the small element, *i.e.*, by

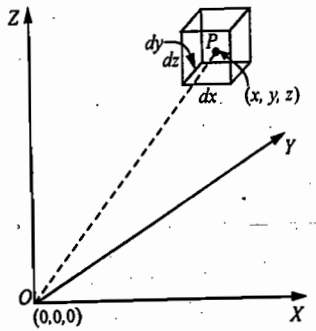


Fig.6. Representation of small volume elements $dxdydz$ (or $d\tau$) surrounding the point $P(x, y, z)$

$\rho(x, y, z)\,dxdydz$. The small volume element, represented by a cube of dimensions dx, dy, dz and surrounding the point $P(x, y, z)$ is shown in Fig. 6. The small volume element $dxdydz$ around the point x, y, z is also written as τ. The function ρ is also known as **probability density**. Imagine that the whole space is divided into a number of such volume elements. The total probability of finding the electron in the whole space will be given by the summation of all the terms of the type $\rho dxdydz$ or $\rho d\tau$. Since the electron has to be somewhere in space, the total probability must be equal to unity. Thus,

$$\int_{-\infty}^{+\infty}\rho\, d\tau = \int_{-\infty}^{+\infty}\rho\, dx\, dy\, dz = 1 \qquad ...(73)$$

The concept of probability accounts for the fundamental law of nature that our knowledge of the position of a small moving particle can never be absolute.

Suppose the solution of the wave equation for a single particle is a function $\psi(x, y, z)$, called the *wave function*. The factor ψ represents the amplitude of the wave, as already mentioned. It has no physical significance as such. In the case of waves, it is the square of the amplitude (*i.e.*, ψ^2) that has any significance rather than the amplitude (*i.e.*, ψ) itself. This is illustrated below :

Consider the dual nature of electromagnetic radiation. According to the wave theory, the intensity of radiation is measured by the square of the amplitude of the wave, a quantity obtained by solving the relevant wave equation. The photon theory relates intensity of radiation with the number of photons in a given volume, *i.e.*, photon density. Since photons are small particles, photon density will be related to the probability of their existence in the given volume, *i.e.*, the probability density. Thus, the probability density, *i.e.*, the probabilityof finding a photon in a given volume, gets related to the square of the amplitude of the associated wave. By analogy, therefore, ψ^2 (*i.e.*, the square of the amplitude) will be a measure of the probability of finding electron in the given volume. Accordingly,

$$\rho(x, y, z) \propto \psi^2(x, y, z) = k\,\psi^2(x, y, z) \qquad ...(74)$$

We choose the proportionality constant k in such a way that the proportionality is replaced by equality. If $\psi(x, y, z)$ is the solution of Schrodinger wave equation for any system, then ψ multiplied by any constant is also the solution of the same wave equation. This means we can take $(1/\sqrt{k})\psi$ instead of ψ in Eq. 74 so that Eq. 74 takes the form

$$\rho(x, y, z) = k \times \frac{1}{k}\psi^2(x, y, z) = \psi^2(x, y, z) \qquad ...(75)$$

$$\therefore \quad \int_{-\infty}^{+\infty}\rho\, d\tau = \int_{-\infty}^{+\infty}\psi^2 d\tau = 1 \qquad \left(\because \int_{-\infty}^{+\infty}\rho\, d\tau = 1, \text{ vide Eq. 73}\right) \qquad ...(76^*)$$

The factor $\psi^2 d\tau$ represents the probability of locating the electron in the small volume element $d\tau$.

*If ψ is a complex wave function, then the integrand ψ^2 in Eq. 76 is replaced by $\psi^*\psi$ (ψ^* is the complex component of ψ). This is so because the right hand side of Eq. 76 is real. Hence the left hand side has also to be real. For example, if ψ is a complex wave function $a + ib$ or $Ae^{im\phi}$, then ψ^2 will also be a complex wave function $(a + ib)^2$ or $A^2e^{2im\phi}$. But $\psi^*\psi$ would be $(a + ib)^*(a + ib)$ or $A^2e^{2im\phi}e^{-im\phi}$, that is, $\psi^*\psi$ would be real, being $(a^2 + b^2)$ or A^2e^0. (The complex component of $(a + ib)$ is $(a - ib)$.

Concept of Electron Charge Cloud. Let us consider hydrogen atom in its ground state. Suppose it is possible to see hydrogen nucleus and its lone electron. Let us assume that the nucleus remains at a fixed place whereas the electron keeps on moving. If it were possible for the electron to register its position by a dot, say, after every 1/1000th of a second for one thousand seconds, the maximum concentration of such dots would be closest to the nucleus and would go on decreasing as the distance of electron from the nucleus increases in all directions. This shows that the maximum probability of locating the electron is closest to the nucleus and goes on decreasing as the distance from the nucleus increases. It may be noted that it is not possible to specify the actual position of the electron. All that we can ever know is a definite region of space within which there is a probability for the existence of the electron. The electron probability distribution in three-dimensional space around the nucleus constitutes what is known as the **electron charge cloud.** The region where such an electron cloud is thickest, *i.e.*, where the number of dots registering the position of electron is maximum, is the region where the probability of locating the electron is maximum.

A model of hydrogen atom showing the electron charge cloud is shown in Fig. 7. Thus, the region within the sphere is a region of high probability. This means that the electron spends most of its time within this spherical region. In contrast to Bohr's concept, this region, according to wave mechanical model, does not have sharp boundaries.

Fig. 7. Electron charge cloud in hydrogen atom.

Solutions of Schrodinger Equation for Some Simple Systems

The Schrodinger equation can be solved exactly for the following simple systems :

1. *Particle in a One-dimensional Box.* 2. *Particle in a Three-dimensional Box.* 3. *Hydrogen atom.*

1. Particle in a One-dimensional Box. Consider a particle of mass m which is confined to move in a one-dimensional box of length a having infinitely high walls (Fig. 8). For the sake of simplicity, it is assumed that the potential energy of the particle is zero everywhere inside the box, that is,

$$V(x) = 0 \qquad ...(77)$$

Thus, inside the box, the Schrodinger equation in x dimension, *viz.*,

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}\right) + V(x)\right]\psi(x) = E\psi(x) \qquad ...(78)$$

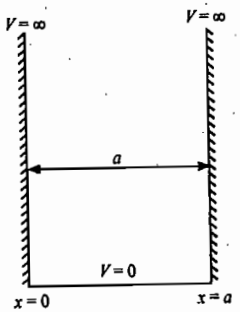


Fig. 8. Particle in a one-dimensional box.

takes the form

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}\right) = E\psi(x) \qquad ...(79)$$

Mathematically, Eq. 79 may be written as

$$\frac{d^2\psi}{dx^2} + \left[\frac{2mE}{\hbar^2}\right]\psi = 0 \qquad ...(80)$$

or as

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad ...(81)$$

where k^2 $(= 2mE/\hbar^2)$ is a constant independent of x.

Eq. 81 is an ordianry second-order differential equation which has solution of the form

$$\psi = A\cos kx + B\sin kx \qquad ...(82)$$

where A and B are constants.

For a particle moving *outside* the box where $V(x) = \infty$, the Schrodinger equation 78, is written as

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}\right) + \infty\right]\psi(x) = E\psi(x) \qquad ...(83)$$

which can be mathematically written as

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(E-\infty)\psi = 0 \qquad ...(84)$$

This equation is satisfied if ψ is zero everywhere *outside* the box which means that the particle cannot be found outside the box, *i.e.*, it is confined *within the box.* This implies that ψ must be zero at the walls of the box, *i.e.*, at $x = 0$ and $x = a$. Since ψ has to be a continuous function of x, it leads to the conclusion that in Eq. 82, A must be zero. Thus, the solution of Eq. 81 is of the form

$$\psi = B\sin kx \qquad ...(85)$$

Since $\psi = 0$ at $x = 0$ and at $x = a$, hence $B\sin ka = 0$ or $\sin ka = 0$ or $ka = n\pi$ so that

$$k = n\pi/a \qquad ...(86)$$

where n (= 1, 2, 3, 4...) is the principal quantum number. Hence, the allowed solutions of Eq. 81 are :

$$\psi = \psi_n = B\sin\left(\frac{n\pi x}{a}\right) \quad \text{where } n = 1, 2, 3..... \qquad ...(87)$$

The probability of finding the particle within the box in the small length segment dx is $\psi^2 dx$. Since the particle must be found within the box, therefore, $\int_0^a \psi^2 dx$ or $\int_0^a B^2\sin^2\frac{n\pi x}{a}dx = 1$. The solution of this equation gives B as $\left(\frac{2}{a}\right)^{1/2}$.

Hence,

$$\psi = \left(\frac{2}{a}\right)^{1/2}\sin\frac{n\pi x}{a}. \qquad ...(88)$$

This is the solution of Schrodinger equation for a particle in a one-dimensional box.

From Eqs. 80 and 86,

$$2mE/\hbar^2 = n^2\pi^2/a^2$$

or

$$E \equiv E_n = \frac{n^2\hbar^2\pi^2}{2ma^2} = \frac{n^2h^2}{8ma^2} \quad \text{where } n = 1, 2, 3... \qquad ...(89)$$

Eq. 89 is the expression for the **energy of the particle** in a one-dimensional box. Since the energy depends upon the quantum number n, which can have any integral value, the energy levels of the particle in the box are quantized.

Example 7. An electron is confined in a one-dimensional box of length 1 Å. Calculate its ground state energy in electron volts (eV).

Solution : *For the ground state, $n = 1$.*

∴ From Eq. 89, the ground state energy of the electron is given by

$$E_1 = \frac{(1)^2\,(6{\cdot}626\times10^{-34}\,\text{J s})^2}{(8)\,(9{\cdot}109\times10^{-31}\,\text{kg})\,(10^{-10}\,\text{m})^2\,(1{\cdot}602\times10^{-19}\,\text{J/eV})} = 37{\cdot}6\ \text{eV}$$

2. Particle in a Three-Dimensional Cubical Box. Let us now consider the motion of a particle of mass m confined to a three-dimensional cubical box with edges of length a and volume equal to a^3. The potential is zero within the box and is infinite outside the box and at its boundaries. The Schrodinger equation for the particle is

$$\left[\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right]\psi(x,\ y,\ z) = E\,\psi(x,\ y, z) \qquad ...(90)$$

Eq. 90 may be rewritten as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\left(\frac{2mE}{\hbar^2}\right)\psi = 0 \qquad ...(91)$$

Assuming that the wave function ψ is a product of three parts $X_{(x)}$, $Y_{(y)}$ and $Z_{(z)}$ which separately depend on x only, y only and z only, respectively, we have

$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z) \qquad ...(92)$$

Hence, $\dfrac{\partial^2\psi}{\partial x^2} = YZ\dfrac{\partial^2 X}{\partial x^2}$; $\dfrac{\partial^2\psi}{\partial y^2} = XZ\dfrac{\partial^2 Y}{\partial y^2}$; $\dfrac{\partial^2\psi}{\partial z^2} = XY\dfrac{\partial^2 Z}{\partial z^2}$

Substituting the above values in Eq. 91 and dividing throughout by $(2m/\hbar^2)\,XYZ$, we have

$$\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial y^2}+\frac{1}{Y}\frac{\partial^2 y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right)+E=0 \qquad ...(93)$$

If engery E is written as the sum of three contributions E_x, E_y and E_z associated with the three coordinates, then Eq. 93 can be separated into the following three equations :

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) = E_x \quad \text{for motion along } x\text{-axis. } (E_x \text{ is independent of } y \text{ and } z) \qquad ...(94)$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right) = E_y \quad \text{for motion along } y\text{-axis. } (E_y \text{ is independent of } x \text{ and } z) \qquad ...(95)$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right) = E_z \quad \text{for motion along } z\text{-axis. } (E_z \text{ is independent of } x \text{ and } y) \qquad ...(96)$$

It can be seen that Eq. 94 (which can be rewritten as $-\dfrac{\hbar^2}{2m}\dfrac{\partial X}{\partial x^2} = E_x X$) is similar to Eq. 79 and, hence leads to a similar solution given by the equation

$$E_x = n_x^2 h^2 / 8ma^2 \qquad ...(97)$$

Similar equations can be written for the solutions of Eqs. 95 and 96.

Thus,
$$E = E_x + E_y + E_z = \frac{(n_x^2+n_y^2+n_z^2)\,h^2}{8ma^2} \qquad ...(98)$$

where $n_x, n_y, n_z = 1, 2, 3, 4$ ..... .

Eq. 98 is the expression for the **energy of a particle in a three-dimensional cubical box.**

Schrodinger Wave Equation for Hydrogen and Hydrogen-like Systems

For a hydrogen-like atom, the nuclear charge is $+Ze$ and charge on the electron is $-e$.

∴ Potential energy of the electron, $V = -Ze^2/r$ ...(99)

For this system, therefore, the Schrodinger wave equation takes the form

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}\left(E - \frac{-Ze^2}{r}\right)\psi = 0 \qquad ...(100)$$

or
$$\left(\frac{\partial}{\partial x^2}+\frac{\partial}{\partial y^2}+\frac{\partial}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \qquad ...(101)$$

It is convenient to solve this equation if we substitute polar coordinates r, θ and ϕ in place of Cartesian coordinates x, y and z. The correlation between the two types of coordinates is illustrated in Fig. 9.

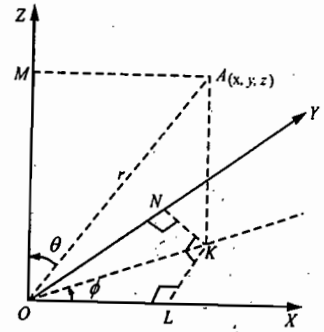


Fig. 9. Correlation between Cartesian coordinates (x, y, z) and polar coordinates $(r, \theta$ and $\phi)$.

The conversion of Cartesian coordinates into polar coordinates is given below.

Consider a point A with coordinates x, y, z, in space.

Let AK be the perpendicular from A on XY plane and KL, KN and AM be perpendiculars on the axes, X, Y and Z, from the points K, K and A, respectively.

Let $OA = r$ and let θ be the angle which the line OA makes with the Z-axis and let ϕ be the angle which the line OK makes with the X-axis (Fig. 9.)

Then,
$$z = OM = r\cos\theta \quad \text{and} \quad OK = AM = r\sin\theta$$
$$y = ON = KL = OK\sin\phi = r\sin\theta\sin\phi$$
$$x = OL = OK\cos\phi = r\sin\theta\cos\phi$$

Eq. 101 in terms of polar coordinates transforms as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{r^2\partial\psi(r,\theta,\phi)}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{\sin\theta\ \partial\psi(r,\theta,\phi)}{\partial\theta}\right)$$

$$+\frac{1}{r^2\sin^2\theta}\times\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)\psi(r,\theta,\phi) = 0 \quad ...(102)$$

Remember that ψ will now be a function of variables r, θ and ϕ instead of x, y and z ; that is why we have written $\psi(r,\theta,\phi)$ instead of $\psi(x,y,z)$ in Eq. 102.

The solution of Eq. 102, *i.e.*, evaluation of $\psi(r,\theta,\phi)$, is possible only if function ψ can be written in the form

$$\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi) \quad ...(103)$$

where $R(r)$ is a function depending on r but is independent of the other two polar coordinates, θ and ϕ ; $\Theta(\theta)$ is a function dependent on θ and is independent of r and ϕ and $\Phi(\phi)$ is a function dependent on ϕ and is independent of r and θ.

The function $R(r)$ is known as the *radial wave function* while the functions $\Theta(\theta)$ and $\Phi(\phi)$ are called *angular wave functions*.

By expressing $\psi(r,\theta,\phi)$ as $R(r)\,\Theta(\theta)\,\Phi(\phi)$ in Eq. 102, we get a complicated equation (not written here) which can, however, be split into the following three simpler equations :

(1) $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) - \frac{\beta}{r^2}R(r) + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)R(r) = 0 \quad ...(104)$$

This equation is a function of r only and, on solution, yields the following expression for $R(r)$:

$$R(r)_{n,l} = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{\lfloor n-l-1}{2n\left(\lfloor n+l\right)^3}}\, e^{-\rho/2}\rho^l\, L_{n+l}^{2l+1}(\rho) \quad ...(105)$$

where $\rho = \left(\frac{2Z}{na_0}\right)r$ and $L_{n+l}^{2l+1}(\rho)$ is the associated Laguere polynomial. The numbers n and l are the two integral quantum numbers required for the solution of $R(r)_{n,l}$ and a_0 is Bohrs radius of H atom. It is obvious from the above expresion that l can, at the maximum, be equal to $(n-1)$ and not any higher value (why ?)

(2) $$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) - \frac{m^2\Theta(\theta)}{\sin^2\theta} + \beta\Theta(\theta) = 0 \quad ...(106)$$

This equation is a function of θ only and, on solution, yields the following expression for $\Theta(\theta)$:

$$\Theta_{l,m}(\theta) = \sqrt{\frac{(2l+1)(l-|m|)}{2\lfloor l+m}}\, P_l^m(\cos\theta) \quad ...(107)$$

where $P_l^m(\cos\theta)$ is the associated Legendre polynomial. It is obvious from the expression for $\Theta(\theta)$ that

the maximum absolute value of the newly introduced quantum number m can be equal to l only and not any higher value (why ?). Hence, m can have values equal to $\pm l, \pm(l-1), \pm(l-2)$..... 0.

(3) $$\frac{\partial^2\Phi(\phi)}{\partial\phi^2} + m^2\Phi(\phi) = 0 \quad ...(108)$$

This equation is a function of ϕ only and, on solution, gives $\Phi(\phi)$:

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{\pm im\phi} \quad ...(109)$$

The total wave function $\psi(r,\theta,\phi)$ is then written as $R(r)\,\Theta(\theta)\,\Phi(\phi)$ (Eq. 103)

The total wave function is normalized so that

$$\int_0^r R_{n,l}^* R_{n,l}\, r^2 dr \int_0^\pi \Theta_{l,m}^*\Theta_{l,m}\sin\theta d\theta \int_0^{2\pi}\Phi_m^*\Phi_m\, d\phi = 1 \quad ...(110)$$

That is, $$\int_0^r R_{n,l}^* R_{n,l}\, r^2 dr = 1\ ;\ \int_0^\pi \Theta_{l,m}^*\Theta_{l,m}\sin\theta d\theta = 1 \text{ and } \int_0^{2\pi}\Phi_m^*\Phi_m\, d\phi = 1 \quad ...(111)$$

The radial wave function $R(r)$ *gives the energy and size of the orbitals* and the angular wave function, which is the product of $\Theta(\theta)$ and $\Phi(\phi)$, *gives the shapes of the orbitals*. These aspects have been discussed below in some details.

1. The Radial Wave Function, $R(r)$

The solution of Eq. 104 for hydrogen and hydrogen-like systems *yields two quantum numbers, n and l*. The quantum number n can have integral values of 1, 2, 3, etc. and is ***analogous to the principal quantum number of Bohr theory.*** The quantum number l can have integral values from $n-l$ to 0 and is ***similar to the azimuthal quantum number of Bohr-Sommerfeld theory.*** The various values of l are given special designations, *viz.*, *s*, *p*, *d* and *f* for $l = 0, 1, 2$ and 3, respectively. The radial wave function is, therefore, generally written as $R_{n,l}(r)$ or simply as $R_{n,l}$ for the sake of simplicity.

The radial wave functions for electron present in different *s* and *p* orbitals are given below :

$R_{1,0}$, *i.e.*, $R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$ [represents radial wave function of electron in 1*s* orbital

$R_{2,0}$, *i.e.*, $R_{2s} = 2^{-3/2}\left(\frac{Z}{a_0}\right)^{3/2}(2-\sigma)\,e^{-\sigma/2}$ [represents radial wave function of electron in 2*s* orbital

$R_{2,1}$, *i.e.*, $R_{2p} = 2^{-1}\left(\frac{Z}{a_0}\right)^{3/2}\sigma\, e^{-\sigma/2}$ [represents radial wave function of electron in 2*p* orbital

In the above functions, a_0 is Bohr's radius, Z is the atomic number and σ is Zr/a_0.

An mentioned above the radical wave function gives the size of the orbitals depending upon the value of $R_{n,l}$.

2. The Angular Wave Function

The angular wave function which is the product of $\Theta(\theta)$ and $\Theta(\phi)$, as already mentioned, is expressed in terms of spherical harmonics of the point A (x, y, z) of Fig. 9. These are defined as

$$Y_n^{m_A} = \Theta_{n,m_A} \Phi_{m_A} \qquad ...(112)$$

where

$$\Theta_{n,m_A} = \sqrt{\frac{(2n+1)}{2}\frac{\lfloor n-|m_A| \rfloor}{\lfloor n+|m_A| \rfloor}}\, P_n^{m_A}(\cos\theta) \qquad ...(113)$$

and

$$\Phi_{m_A} = \frac{1}{\sqrt{2\pi}} e^{i m_A \phi} \qquad ...(114)$$

In the above equations, $P_n^{m_A}$ is the associated Legendre polynomial function and both Θ_{n,m_A} and Φ_{m_A} are normalised.

The general form of associated Legendre polynomial $P_n^{m_A}(x)$ is :

$$P_n^{m_A}(x) = (1-x^2)^{|m_A|/2} \frac{d^{m_a} P_n(x)}{d_x^{m_a}} \qquad ...(115)$$

where $P_n(x)$ is Legendre polynomial which is given by

$$P_n(x) = \frac{1}{2^n \lfloor n} \frac{d^n (x^2-1)^n}{d^n} \qquad ...(116)$$

In the general expression (112) for spherical harmonics we do not assign any specific meaning to n and m_A. These are simply numbers. It is evident from Eq. 113 that the maximum value of $|m_A|$ can be n. In other words, $|m_A|$ can have values $= \pm n, \pm(n-1), \pm(n-2)$ .....0 only.

In order to evaluate the spherical harmonics of point A for different sets of n and $|m_A|$, we need the values of $P(x)$, and $P_n^{m_A}(x)$. The expression (116) for $P(x)$ yields the following results :

$$P_0(x) = 1 \qquad \therefore \quad P_0(\cos\theta) = 1$$

$$P_1(x) = x \qquad \therefore \quad P_1(\cos\theta) = \cos\theta$$

$$P_2(x) = \frac{1}{2}(3x^2-1) \qquad \therefore \quad P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_3(x) = \frac{1}{2}(5x^3-3x) \qquad \therefore \quad P_3(\cos\theta) = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$$

$$P_4(x) = \frac{1}{8}(35x^4-30x^2+3) \qquad \therefore \quad P_4(\cos\theta) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$

Similarly, the expression (115) for $P_n^{|m_A|}(x)$ yields the following results :

$$P_0^0(x) = 1 \qquad \therefore \quad P_0^0(\cos\theta) = 1$$

$$P_1^0(x) = x \qquad \therefore \quad P_1^0(\cos\theta) = \cos\theta$$

$$P_1^{|1|}(x),\ i.e.,\ P_1^{\pm1}(x) = (1-x^2)^{1/2} \qquad \therefore \quad P_1^{\pm1}(\cos\theta) = \sin\theta$$

$$P_2^0(x) = \frac{1}{2}(3x^2-1) \qquad \therefore \quad P_2^0(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^{|1|}(x),\ i.e.,\ P_2^{\pm1}(x) = 3x(1-x^2)^{1/2} \qquad \therefore \quad P_2^{\pm1}(\cos\theta) = 3\cos\theta\sin\theta$$

$$P_2^{|2|}(x),\ i.e.,\ P_2^{\pm2}(x) = 3(1-x^2) \qquad \therefore \quad P_2^{\pm2}(\cos\theta) = 3\sin^2\theta$$

$$P_3^0(x) = \frac{1}{2}(5x^2-3)x \qquad \therefore \quad P_3^0(\cos\theta) = \frac{1}{2}\cos\theta(5\cos^2\theta - 3)$$

$$P_3^{|1|}(x),\ i.e.,\ P_3^{\pm1}(x) = \frac{3}{2}(1-x^2)^{1/2}(5x^2-1) \qquad \therefore \quad P_3^{\pm1}(\cos\theta) = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$$

$$P_3^{|2|}(x),\ i.e.,\ P_3^{\pm2}(x) = 15x(1-x^2) \qquad \therefore \quad P_3^{\pm2}(\cos\theta) = 15\cos\theta\sin^2\theta$$

$$P_3^{|3|}(x),\ i.e.,\ P_3^{\pm3}(x) = 15x(1-x^2)^{3/2} \qquad \therefore \quad P_3^{\pm3}(\cos\theta) = 15\sin^3\theta$$

$$P_4^0(x) = \frac{1}{8}(35x^4-30x^2+3) \qquad \therefore \quad P_4^0(\cos\theta) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$

$$P_4^{|1|}(x),\ i.e.,\ P_4^{\pm1}(x) = (1-x^2)^{1/2}(7x^3-3x)\frac{5}{2} \qquad \therefore \quad P_4^{\pm1}(\cos\theta) = \frac{5}{2}\sin\theta\cos\theta(7\cos^2\theta - 3)$$

$$P_4^{|2|}(x),\ i.e.,\ P_4^{\pm2}(x) = (1-x^2)(7x^2-1)\frac{15}{2} \qquad \therefore \quad P_4^{\pm2}(\cos\theta) = \frac{15}{2}\sin^2\theta(7\cos^2\theta - 1)$$

$$P_4^{|3|}(x),\ i.e.,\ P_4^{\pm3}(x) = 105x(1-x^2)^{3/2} \qquad \therefore \quad P_4^{\pm3}(\cos\theta) = 105\sin^3\theta\cos\theta$$

$$P_4^{|4|}(x),\ i.e.,\ P_4^{\pm4}(x) = (1-x^2)^2 \times 105 \qquad \therefore \quad P_4^{\pm4}(\cos\theta) = 105\sin^4\theta$$

With the help of the results reported above and making use of Eqs. 112—114, we can easily arrive at the following values for spherical harmonics, $Y_n^{m_A}$:

$$\Theta_{0,0} = \frac{1}{\sqrt{2}} \qquad Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

$$\Theta_{1,0} = \sqrt{\frac{3}{2}}\cos\theta \qquad Y_1^0 = \sqrt{\frac{3}{2}}\frac{1}{\sqrt{2\pi}}\cos\theta$$

$$\Theta_{0,\pm1} = \sqrt{\frac{3}{4}}\sin\theta \qquad Y_1^{\pm1} = \sqrt{\frac{3}{4}}\sin\theta\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$$

$$\Theta_{2,0} = \sqrt{\frac{5}{8}}(3\cos^2\theta - 1) \qquad Y_2^0 = \sqrt{\frac{5}{8}}(3\cos^2\theta - 1)\frac{1}{\sqrt{2\pi}}$$

$$\Theta_{2,\pm1} = \sqrt{\frac{15}{4}}\sin\theta\cos\theta \qquad Y_2^{\pm1} = \sqrt{\frac{15}{4}}\sin\theta\cos\theta\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$$

$$\Theta_{2,\pm2} = \sqrt{\frac{15}{16}}\sin^2\theta \qquad Y_2^{\pm2} = \sqrt{\frac{15}{16}}\sin^2\theta\frac{1}{\sqrt{2\pi}}e^{\pm i2\phi}$$

$$\Theta_{3,0} = \sqrt{\frac{7}{8}}\cos\theta(5\cos^2\theta - 3) \qquad Y_3^0 = \sqrt{\frac{7}{8}}\cos\theta(5\cos^2\theta - 3)\frac{1}{\sqrt{2\pi}}$$

$$\Theta_{3,\pm1} = \sqrt{\frac{21}{32}}\sin\theta(5\cos^2\theta - 1) \qquad Y_3^{\pm1} = \sqrt{\frac{21}{32}}\sin\theta(5\cos^2\theta - 1)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$$

$$\Theta_{3,\pm2} = \sqrt{\frac{105}{16}}\sin^2\theta\cos\theta \qquad Y_3^{\pm2} = \sqrt{\frac{105}{16}}\sin^2\theta\cos\theta\frac{1}{\sqrt{2\pi}}e^{\pm i2\phi}$$

$$\Theta_{3,\pm3} = \sqrt{\frac{35}{32}}\sin^3\theta \qquad Y_3^{\pm3} = \sqrt{\frac{35}{32}}\sin^3\theta\frac{1}{\sqrt{2\pi}}e^{\pm i3\phi}$$

$$\Theta_{4,0} = \sqrt{\frac{9}{128}}(35\cos^4\theta - 30\cos^2\theta + 3) \qquad Y_4^0 = \sqrt{\frac{9}{128}}(35\cos^4\theta - 30\cos^2\theta + 3)\frac{1}{\sqrt{2\pi}}$$

$$\Theta_{4,\pm1} = \sqrt{\frac{45}{32}}\sin\theta\cos\theta\,(7\cos^2\theta - 3) \qquad Y_4^{\pm1} = \sqrt{\frac{45}{32}}\sin\theta\cos\theta\,(7\cos^2\theta - 3)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$$

$$\Theta_{4,\pm2} = \sqrt{\frac{45}{64}}\sin^2\theta\,(7\cos^2\theta - 1) \qquad Y_4^{\pm2} = \sqrt{\frac{45}{64}}\sin^2\theta\,(7\cos^2\theta - 1)\frac{1}{\sqrt{2\pi}}e^{\pm i2\phi}$$

$$\Theta_{4,\pm3} = \sqrt{\frac{315}{32}}\sin^3\theta\cos\theta \qquad Y_4^{\pm3} = \sqrt{\frac{315}{32}}\sin^3\theta\cos\theta\,\frac{1}{\sqrt{2\pi}}e^{\pm i3\phi}$$

$$\Theta_{4,\pm4} = \sqrt{\frac{315}{256}}\sin^4\theta \qquad Y_4^{\pm4} = \sqrt{\frac{315}{256}}\sin^4\theta\,\frac{1}{\sqrt{2\pi}}e^{\pm i4\phi}$$

While expressing angular wave functions of hydrogen-like systems in terms of spherical hormonics, we use symbols l and m in place of n and m_A, respectively, in Eqs. 112—114. Accordingly, we write :

$$Y_l^m = \Theta_{l,m}\Phi_m \qquad ...(117)$$

$$\Theta_{l,m} = \sqrt{\frac{(2l+1)}{2}\frac{|l-|m|}{|l+|m|}}\,P_l^m\cos\theta \qquad ...(118)$$

$$\Phi_m = \frac{1}{\sqrt{2\pi}}e^{im\phi} \qquad ...(119)$$

The symbols l and m used in Eqs. 117—119 for hydrogen-like system are referred to as orbital angular momentum quantum number and magnetic quantum number, respectively.

As already mentioned, while the radial wave function $[R(r)]$ gives the size of the orbitals, the angular wave function [the product of $\Theta_{l,m}(\theta)$ and $\Phi_m(\phi)$], now designated as spherical harmonics, gives the shape of the orbitals. $Y_l^m = \Theta_{l,m}(\theta)\,\Phi_m(\phi)$. Therefore, the **complete wave function**, which is obtained by the product of the radial wave function and the angular wave function, *i.e.*, the spherical harmonics, gives both the size and the shape of the orbitals.

Let us write complete wave functions for some of the orbitals and deduce their shapes.

Complete wave function for *s* orbitals and their shapes. For an *s* orbital, $l = 0$, therefore, $m = 0$. The complete wave function is, therefore, written as

$$R_{n,0}(r)\,Y_0^0 = R_{n,0}(r)\frac{1}{\sqrt{2}}\times\frac{1}{\sqrt{2\pi}} = R_{n,0}(r)\frac{1}{2\sqrt{\pi}} \qquad ...(120)$$

Since the complete wave function in this case is independent of the angles θ and ϕ, therefore, the orbital is *symmetrical* along all directions for a particular r, *i.e.*, it has a **spherical shape**. The 1*s* orbital has no radial node whereas 2*s* and 3*s* orbitals have one and two radial nodes, respectively, as shown in Fig. 10.

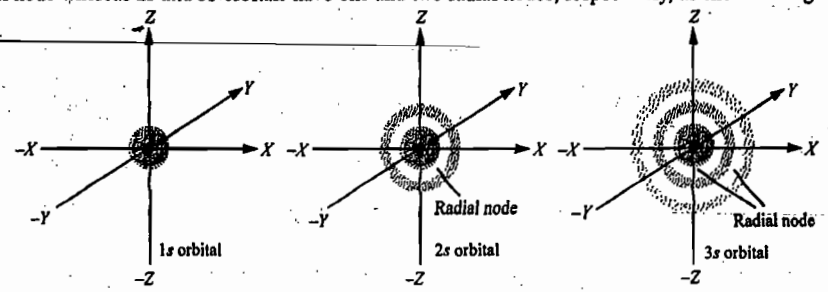


Fig. 10. The shapes of varius *s* orbitals

Complete wave function for *p* orbitals and their sphapes. For *p* orbitals $l = 1$, therefore, $m = 0, +1, -1$. The corresponding complete wave functions are written as (0), (+1) and (–1), respectively. The sets of single electronic wave functions having the same l and the same m but different m_s are written as (m_1), (m_2), etc. Thus,

$$(0) = R_{n,1}(r)\,Y_1^0 = R_{n,1}(r)\sqrt{3/2}\cos\theta\times1/\sqrt{2\pi} = R_{n,1}(r)\sqrt{3/4\pi}\cos\theta \qquad ...(121)$$

$$(+1) = R_{n,1}(r)\,Y_1^{+1} = R_{n,1}(r)\sqrt{3/4}\sin\theta\times1/\sqrt{2\pi}\,e^{+i\phi} \qquad ...(122)$$

$$(-1) = R_{n,1}(r)\,Y_1^{-1} = R_{n,1}(r)\sqrt{3/4}\sin\theta\times1/\sqrt{2\pi}\,e^{-i\phi} \qquad ...(123)$$

While the wave function represented by Eq. 121 is real, the wave functions represented by Eqs. 122 and 123 are not real as they contain the imaginary quantity i and as such cannot be visualised. An acceptable solution of wave equation is that which yields a real wave function. In order to obtain real wave functions for *p* orbitals, two linear combinations of angular wave functions represented by Eqs. 122 and 123 are taken into consideration. The two normalised linear combinations thus obtained are :

$1/\sqrt{2}\,[(+1)+(-1)]$, *i.e.*, $1/\sqrt{2}\,R_{n,1}(r)(\Theta_{1,+1}\Phi_{+1} + \Theta_{1,-1}\Phi_{-1})$ and

$1/\sqrt{2}\,[(+1)-(-1)]$, *i.e.*, $1/\sqrt{2}R_{n,1}(r)\,(\Theta_{1,+1}\Phi_{+1} - \Theta_{1,-1}\Phi_{-1})$

These wave functions yield the following results :

Combination $1/\sqrt{2}\,[(+1)+(-1)]$ for real *p* wave function $= R_{n,1}(r)\sqrt{3/4\pi}\,\sin\theta\,\cos\phi$ ...(124)

Combination $1/\sqrt{2}\,[(+1)-(-1)]$ for real *p* wave function $= R_{n,1}(r)\sqrt{3/4\pi}\,\sin\theta\,\sin\phi$ ...(125)

Thus, Eqs. 121, 124 and 125 now represent a set of *real* wave functions for *p* orbitals.

Let us now investigate the **shapes of the 2*p* orbitals** represented by the real wave functions as given by Eqs. 121, 124 and 125. Expressing these functions in terms of the Cartesian coordinates, the real *p* wave function, as given by Eq. 121 is

$$(0) = R_{2,1}(r)\sqrt{3/4\pi}\cos\theta \qquad ...(126)$$

$$= R_{2,1}(r)\sqrt{3/4\pi}\times z/r \quad [\because z = r\cos\theta \text{ (Fig. 9)}] \qquad ...(127)$$

This is, evidently, a function of z and is, therefore, known as p_z wave function.

The wave function p_z when plotted in three-dimensional space yields a dumb-bell shaped curve along the z-axis, as shown in Fig. 11.

It can be seen from Eq. 127 that the function p_z will be positive when z is positive and negative when z is negative. It may be noted that + and – signs are geometric signs of the plotted wave functions only and should not be confused with positive or negative charges.

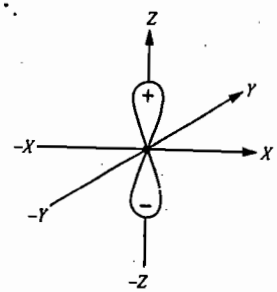


Fig. 11. The shape of p_z orbital

Let us now consider the real wave function given by Eq. 124. Expressing this wave function in terms of Cartesian coordinates, we get

$$1/\sqrt{2}\,[(+1)+(-1)] = R_{2,1}(r)\sqrt{3/4\pi}\,\sin\theta\cos\phi$$

$$= R_{2,1}(r)\,\sqrt{3/4\pi}\times x/r \quad [\because \sin\theta\cos\phi = x/r \text{ (Fig. 9)}] \qquad ...(128)$$

Evidently, the *p* wave function given by Eq. 128 varies with x only. It is, therefore, referred to as p_x wave function. A plot of p_x wave function in three-dimensional space gives a dumb-bell shaped curve along the x-axis, as shown in Fig. 12.

It can be easily seen from Eq. 128 that the function p_x would be positive when x is positive and negative when x is negative.

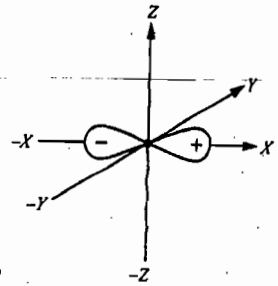


Fig. 12. The shape of p_x orbital

Similarly, the real wave function as given by Eq. 125 when expressed

in terms of Cartesian coordinates yields Eq. 129. Thus,

$$1/\sqrt{2}\,[(+1)-(-1)] = R_{2,1}(r)\ \sqrt{3/4\ \pi}\ \sin\theta\ \sin\phi$$

$$= R_{2,1}(r)\ \sqrt{3/4\pi}\times y/r\ \ [\because \sin\theta\sin\phi = y/r \text{ (Fig. 9)}] \qquad ...(129)$$

Thus, the p wave function in this case varies with y only. It is, therefore, called p_y wave function.

A plot of p_y wave function in three-dimensional space gives a dumb-bell shaped curve along the y-axis, as shown in Fig. 13.

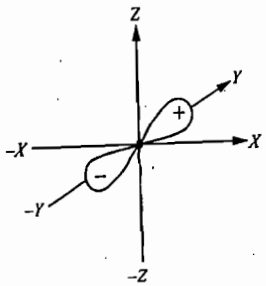


Fig. 13. The shape of p_y orbital

The complete wave functions of $2p$, $3p$, $4p$ orbitals would give rise to dumb-bell shaped curves except for the fact that the $4p$ orbital would occupy more space than $3p$ orbital and $3p$ orbital would occupy more space than $2p$ orbital (Fig. 14).

Also, the $4p$ orbital would have *two radial nodes*, the $3p$ orbital would have *one radial node* and $2p$ orbital would have *no radial node* (the number of radial nodes is given by $n-l-1$).

The shapes of $2p_x$, $3p_x$ and $4p_x$ orbitals with radial nodes are shown in Fig. 14.

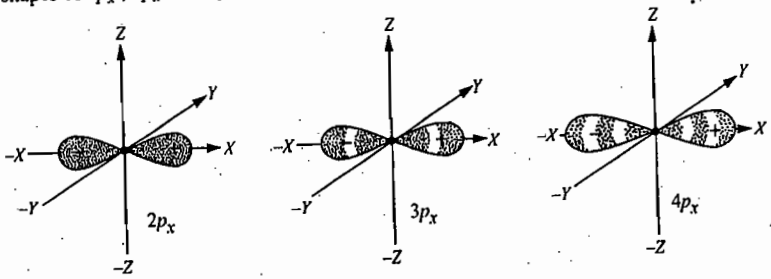


Fig. 14. The shapes of $2p_x$, $3p_x$ and $4p_x$ orbitals.

Complete wave functions for *d* orbitals and their shapes. For d orbitals, $l = 2$ so that $m = 0, +1, +2, -1, -2$. The complete wave functions for the d orbitals may be written as follows :

$$(0) = R_{n,2}(r)\ Y_2^0 = R_{n,2}(r)\sqrt{5/16\pi}\ (3\cos^2\theta - 1) \qquad ...(130)$$

$$(+1) = R_{n,2}(r)\ Y_2^{+1} = R_{n,2}(r)\sqrt{15/8\pi}\ (\sin\theta\ \cos\theta)\,e^{i\phi} \qquad ...(131)$$

$$(+2) = R_{n,2}(r)\ Y_2^{2+} = R_{n,2}(r)\sqrt{15/32\pi}\ (\sin^2\theta)\,e^{i2\phi} \qquad ...(132)$$

$$(-1) = R_{n,2}(r)\ Y_2^{-1} = R_{n,2}(r)\sqrt{15/8\pi}\ (\sin\theta\cos\theta)\,e^{-i\phi} \qquad ...(133)$$

$$(-2) = R_{n,2}(r)\ Y_2^{-2} = R_{n,2}(r)\sqrt{15/32\pi}\ (\sin^2\theta)\,e^{-i2\phi} \qquad ...(134)$$

Of the above five wave functions, only one wave function given by Eq. 130 is real. All other wave functions contain the imaginary quantity i for d orbitals. We obtain real d orbital wave functions by the procedure similar to the one we adopted for obtaining p orbital wave functions. The real d orbital wave functions obtained from linear combination of Eqs. 131 and 133 are : (*i*) $1/\sqrt{2}\,[(+1)+(-1)]$, *i.e.*, $1/\sqrt{2}\,R_{n,2}(r)\,(\Theta_{2,1}\Phi_1 + \Theta_{2,-1}\Phi_{-1})$ and (*ii*) $1/\sqrt{2}\,[(+1)-(-1)]$, *i.e.*, $1/\sqrt{2}\,R_{n,2}(r)(\Theta_{2,1}\Phi_1 - \Theta_{2,-1}\Phi_{-1})$ and the d orbital wave functions obtained from linear combination of Eqs. 132 and 134 are :

(*i*) $1/\sqrt{2}\,[(+2)+(-2)]$, *i.e.*, $1/\sqrt{2}\ R_{n,2}(r)\,(\Theta_{2,2}\,\Phi_2 - \Theta_{2,-2}\Phi_{-2})$ and (*ii*) $1/\sqrt{2}\,[(+2)-(-2)]$, *i.e.*, $1/\sqrt{2}\ R_{n,2}(r)\,(\Theta_{2,2}\,\Phi_2 - \Theta_{2,-2}\Phi_{-2})$.

From these wave functions, the five real d orbital wave functions obtained are as follows :

$$\text{Real } d \text{ wave function } (0) = R_{n,2}(r)\ \sqrt{5/16\pi}\ (3\cos^2\theta - 1) \qquad ...(135)$$

$$\text{Real } d \text{ wave function } 1/\sqrt{2}\,[(+1)+(-1)] = R_{n,2}(r)\ \sqrt{15/4\pi}\ \sin\theta\cos\theta\cos\phi \qquad ...(136)$$

$$\text{Real } d \text{ wave function } 1/\sqrt{2}\,[(+1)-(-1)] = R_{n,2}(r)\ \sqrt{15/4\pi}\ \sin\theta\cos\theta\sin\phi \qquad ...(137)$$

$$\text{Real } d \text{ wave function } 1/\sqrt{2}\,[(+2)+(-2)] = R_{n,2}(r)\ \sqrt{15/16\pi}\ \sin^2\theta\cos 2\phi \qquad ...(138)$$

$$\text{Real } d \text{ wave function } 1/\sqrt{2}\,[(+2)-(-2)] = R_{n,2}(r)\ \sqrt{15/16\pi}\ \sin^2\theta\ \sin 2\phi \qquad ...(139)$$

Expressing the above wave functions in terms of Cartesian co-ordinates with the help of Fig. 9, we get

(*i*)
$$(0) = R_{n,2}(r)\ \sqrt{15/16\pi}\ (3\cos^2\theta - 1)$$

$$= R_{n,2}(r)\ \sqrt{15/16\pi}\ (3z^2 - r^2)\times 1/r^2 \qquad ....(140)$$

As can be seen, the above d wave function *varies as* z^2. Hence, it is called d_z^2 wave function.

(*ii*)
$$1/\sqrt{2}\,[(+1)+(-1)] = R_{n,2}(r)\ \sqrt{15/4\pi}\ \sin\theta\ \cos\theta\ \cos\phi$$

$$= R_{n,2}(r)\ \sqrt{15/4\pi}\ \times xz/r^2 \qquad ...(141)$$

Since the d wave function *varies as* xz, it is called d_{xz} wave function.

(*iii*)
$$1/\sqrt{2}\,[(+1)-(-1)] = R_{n,2}(r)\ \sqrt{15/4\pi}\ \sin\theta\ \cos\theta\ \sin\phi$$

$$= R_{n,2}(r)\ \sqrt{15/4\pi}\times yz/r^2 \qquad ...(142)$$

Since the d wave function *varies as* yz, it is called d_{yz} wave function.

(*iv*)
$$1/\sqrt{2}\,[(+2)+(-2)] = R_{n,2}(r)\sqrt{15/16\pi}\ \sin^2\theta\ \cos 2\phi$$

$$= R_{n,2}(r)\sqrt{15/16\pi}\sin^2\theta(\cos^2\phi - \sin^2\phi)$$

$$= R_{n,2}(r)\sqrt{15/16\pi}\ (\sin^2\theta\ \cos^2\phi - \sin^2\theta\ \sin^2\phi)$$

$$= R_{n,2}(r)\ \sqrt{15/16\pi}\ (x^2 - y^2)/r^2 \qquad ...(143)$$

Since the d wave function *varies as* $x^2 - y^2$, it is called $d_{x^2-y^2}$ wave function.

(*v*)
$$1/\sqrt{2}\,[(+2)-(-2)] = R_{n,2}(r)\ \sqrt{15/16\pi}\ \sin^2\theta\ \sin 2\phi$$

$$= R_{n,2}(r)\ \sqrt{15/16\pi}\sin^2\theta\ 2\sin\phi\ \cos\phi$$

$$= R_{n,2}(r)\sqrt{15/4\pi}\,\sin\theta\sin\phi\sin\theta\cos\phi$$

$$= R_{n,2}(r)\sqrt{15/4\pi}\;xy/r^2 \qquad ...(144)$$

Since the d wave function *varies as xy*, it is called d_{xy} wave function.

Thus, the five real wave functions of d orbitals are d_{z^2}, d_{xz}, d_{yz}, $d_{z^2-y^2}$ and d_{xy}. These wave functions when plotted in three-dimensional space yield curves as shown in Fig. 15. It may be remembered that all these are solid curves, *i.e., these are three-dimensional* because of their dependence on $r\,(=\sqrt{x^2+y^2+z^2})$.

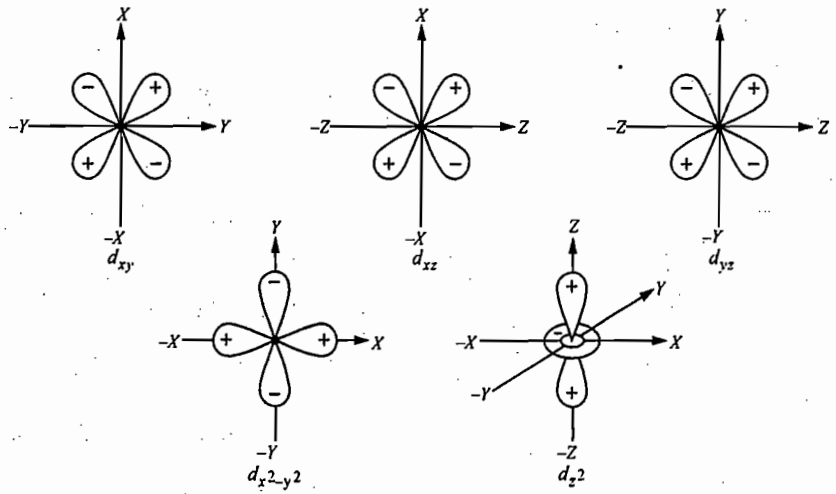


Fig. 15. Shapes of d orbitals

The orbital d_{z^2} has a dumb-bell shaped curve symmetric about the Z-axis, having a ring-like collar in XY plane. The dumb-bell shaped part of the curve has a *positive geometric sign* (because whatever be the sign of z, positive or negative, its square is always positive) whereas the collar in the XY plane has a *negative geometric sign.*

The orbital d_{xy} has a double dumb-bell shape. The quantity xy will be positive when both x and y are positive or when both are negative. However, xy will be negative when either of x or y is negative. Thus, the sign of the curve is positive in first and third quadrants while it is negative in second and fourth quadrants. The shapes of d_{xz}, d_{yz} orbitals can be explained in a similar manner.

The orbital $d_{x^2-y^2}$ is also double dumb-bell shaped but its lobes lie on X and Y axes. The signs of the lobes on X axis will always be positive (because whatever be the sign of x, x^2 will always be positive) whereas the signs of the lobes on Y axis will always be negative (because whatever be the sign of y, $-y^2$ will always be negative). The *exact shapes* of d orbitals are obtained by taking into consideration the total wave function. Accordingly, $3d_{x^2-y^2}$ orbital would be similar in shape to $4d_{x^2-y^2}$ orbital or $5d_{x^2-y^2}$ orbital except for the fact that

1. A $5d$ orbital would have *two*, a $4d$ orbital would have *one* and a $3d$ orbital would have *no* radial node.

2. A $5d$ orbital would occupy more space than a $4d$ orbital and a $4d$ orbital would occupy more space than a $3d$ orbital, as shown in Fig. 16.

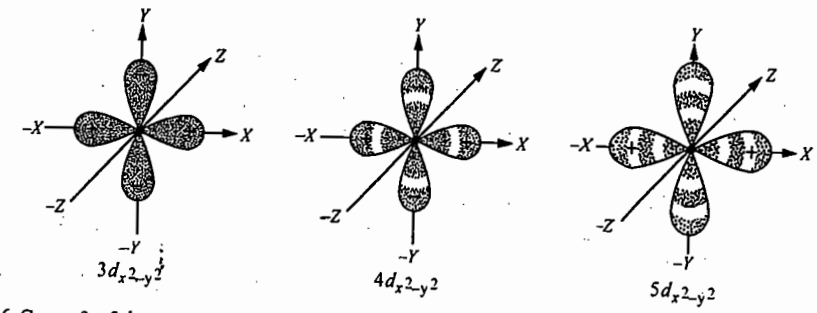


Fig. 16. Curves for $3d_{x^2-y^2}$, $4d_{x^2-y^2}$ and $5d_{x^2-y^2}$ orbitals in three-dimensional space. The curves for the other $3d$, $4d$, $5d$ orbitals can be drawn on similar lines.

In a similar manner, we can determine the shapes of f orbitals

The set of complete wave functions for f orbitals is given below :

$$(0) = R_{n,3}(r)\,Y_3^0$$

$$(\pm1) = R_{n,3}(r)\,Y_3^{\pm1}$$

$$(\pm2) = R_{n,3}(r)\,Y_3^{\pm2}$$

$$(\pm3) = R_{n,3}(r)\,Y_3^{\pm3}$$

The spherical harmonics for the f orbital wave functions have been given earlier. In the set given above, only (0) is real. The rest of the six f orbital wave functions are imaginary. We can derive the real set of f orbital wave functions by following the same procedure as was adopted by obtaining sets of real p and d orbital wave functions. The real f orbital wave functions thus obtained would be desinated as follows :

$f_{z(x^2-y^2)}$, $f_{y(z^2-x^2)}$, $f_{x(y^2-z^2)}$, $f_{z(5z^2-3r^2)}$, $f_{x(5x^2-3r^2)}$, $f_{y(5y^2-3r^2)}$ and $f_{(x,y,z)}$

Energy of Electron in Hydrogen and Hydrogen-like Systems

The solution of Schrodinger wave equation given in standard books in quantum mechanics yields the following expression for the energy of electron in hydrogen or hydrogen-like systems :

$$E_n = \frac{2\pi^2 Z^2 \mu e^4}{(4\pi\varepsilon_0)^2 n^2 h^2} \qquad ...(145)$$

where μ is the reduced mass of the electron and the nucleus defined as $\mu = (m_e \times m_n)/(m_e + m_n)$ where m_e is the mass of electron and m_n is the mass of the nucleus. Since $m_n \gg m_e$, hence $\mu = m_e$. Replacing m by m_e in Eq. 145, we find that Eq. 145 is exactly the same as obtained by Bohr (Eq. 20).

Quantum Numbers (n, l, m). As discussed earlier, the three quantum numbers n, l and m are the direct consequence of the solutions of the Schrodinger wave equation put forth to describe the behaviour of electron as a wave. The principal quantum number n and the angular momentum quantum number l have already been discussed in details. It may be recalled that the principal quantum number n represents the main energy level or energy shell in which the electron is present. It determines to a large extent the energy of an electron moving in a particular energy level. It also determines the average distance of an electron from the nucleus. As the value of n increases, the electron gets farther away from the nucleus and its energy increases. The angular momentum quantum number, l gives a description of the angular

momentum of the electron and the existence of energy subshells which accounts for the appearance of groups of closely spaced lines in the spectrum of hydrogen. The quantum numbers n and l are related as $l = n - 1$.

Magnetic Quantum Number, m. The motion of an electron in an orbit may be likened to the flow of electricity in a coil of wire. Such a flow produces magnetic field (electromagnetic effect). The magnitude of the magnetic field thus generated is proportional to the magnitude of the orbital angular momentum. Since orbital angular momentum is a vector quantity, it can have a number of orientations in space as a result of which the magnetic field and the accompanying magnetic moment can also have a number of orientations in space. The number of these orientations is given by the magnetic quantum number, m. The value of m ranges from $-l$ through zero to $+l$, thus totalling $2l+1$ values. Each value of m represents a particular **orbital** which is defined as the space in which threre is maximum probability of the existence of electron.

Thus, if $l = 0$ (*i.e.*, the subshell is s), m will have only one value, *i.e.*, 0. There will, therefore, be only one orientation of the magnetic moment which means that the s subshell will have only *one orbital*, called the *s orbital*.

If $l = 1$ (*i.e.*, the subshell is p), m will have three values, -1, 0, $+1$. There would thus be three orientations of the magnetic moment. This means that the p subshell will have three orbitals. These are designated as p_x, p_y and p_z orbitals.

If $l = 2$ (*i.e.*, the subshell is d), m will have five values, -2, -1, 0, $+1$, $+2$. Accordingly, magnetic moment will have five orientations in space. This means that d subshell will have five orbitals. These are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2y^2}$ *and* d_{z^2}.

Similarly, it can be shown that the f subshell will have seven orbitals.

Electron Spin and Magnetic Spin Quantum Numbers (s, m_s). In order to explain the nature of atomic spectra, G. Uhlenback and S. Gouldsmit postulated that an electron spins about its own axis and thus generates spin angular momentum which is a vector quantity and is collinear with the axis of spin of the electron. The magnitude of the spin angular momentum of the electron is given by $\sqrt{s(s+1)}\ h/2\pi$ where s is known as the **spin quantum number** of the electron.

The spin angular momentum is quantised in space. That is, it can have only a fixed number of orientations in space about any chosen direction generally referred to as Z direction. The number of orientations in space is given by $2s + 1$. Since for a single electron, s is 1/2, hence only two orientations ($2\times1/2 + 1 = 2$) of spin angular momentum vector are allowed about the Z-axis, one of which has the Z-component equal to $+1/2$ and the other has the Z-component equal to $-1/2$ in units of $h/2\pi$, as shown in Fig 17. The Z-components $+1/2$ and $-1/2$ (excluding the unit $h/2\pi$) are known as **magnetic spin quantum numbers, m_s.**

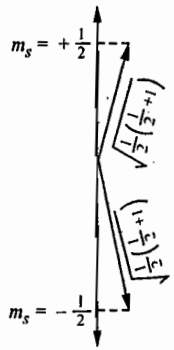


Fig. 17. The space-orientation of spin angular momentum of an electron.

The spin angular momentum of the negatively charged electron also generates magnetic moment which is collinear with the spin angular momentum. Therefore, the allowed orientations of angular momentum and of the magnetic moment, both of which are generated due to the spin of the electron, are the same.

In the case of atoms with single electrons, both the orientations of spin angular momentum (specified by their m_s values) are of equal energy. But in the presence of external magnetic field, their energies become different from each other.

The Zeeman Effect. Zeeman, in 1896, found that when a strong magnetic field is applied to a system whose spectrum is being recorded, *each spectral line gets split up into a number of separate lines.* This

phenomenon is known as the **Zeeman effect.**

As already stated, there are $(2l + 1)$ components of orbital angular momentum vector along any chosen direction, say, the Z-direction. The magnitudes of these components are given by $mh/2\pi$. Since the magnetic field generated due to the motion of electron in an orbital has also $(2l + 1)$ orientations of orbital angular momentum vector and since the magnetic field generated depends upon the magnitude of orbital angular momentum, it will also have $(2l + 1)$ components along the Z-axis whose magnitudes depend on the magnitudes of the Z-components of the orbital angular momentum (*i.e.*, $mh/2\pi$).

In the absence of any external magnetic field, all the orientations of the orbital angular momentum (and hence of the magnetic field generated due to the motion of the electron in the orbital) have equal probability to occur. But, if an external magnetic field is applied along the Z-axis, the orientation with maximum positive value of m will have maximum magnetic field component *parallel* to the direction of the external field applied. Such an orientation of orbital angular momentum will, therefore, be of lowest energy. Similarly, the orientation with maximum negative value of m will have maximum magnetic field component *antiparallel* to the direction of the external magnetic field applied. Such an orientation will, therefore, be of highest energy. Likewise, the energies of all other orientations of orbital angular momenta having different values of m will be different, ranging between the two extremes mentioned above, in the presence of external magnetic field.

Let us consider the example of a d orbital whose orbital angular momentum is $\sqrt{2(2+1)}\,h/2\pi$. It has five orientations of different energies in the presence of external magnetic field. Each orientation has a different Z-component whose value ranges from $+2h/2\pi$ to $-2h/2\pi$, as shown in Fig. 18. Thus, a spectral line obtained in the absence of external magnetic field due to the shift of electron from a higher to a lower d orbital of an atom will be split up into five lines in the presence of the external magnetic field.

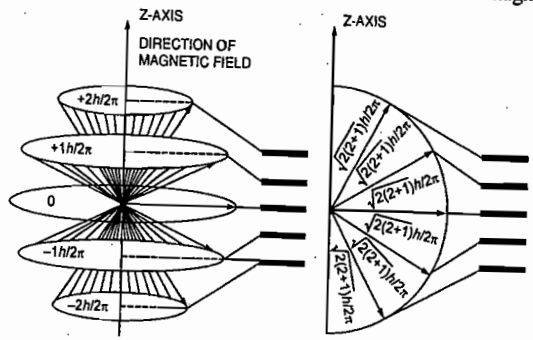


Fig. 18. Five different space orientations corresponding to $l = 2$.

Pauli's Exclusion Principle

This is an important generalisation put forth by Wolfgang Pauli, in 1925, which determines the maximum number of electrons that an energy level can accommodate. Pauli's exclusion principle states that *it is impossible for any two electrons in the same atom to have all the four quantum numbers identical.* Thus, in the same atom, any two electrons may have three quantum numbers identical but not the fourth which must be different. This principle is very useful *in determining the maximum number of electrons that can occur in any quantum group.* For K shell, for instance, since $n=1$, l can have only one value (*viz.*, 0) and m can also have only one value (*viz.*, 0). Hence, m_s can be either $+1/2$ or $-1/2$. Thus, there are **two combinations** of the quantum numbers, as shown :

$$n=1 \quad l=0 \quad m=0 \quad m_s = +1/2$$
$$n=1 \quad l=0 \quad m=0 \quad m_s = -1/2$$

This shows that in the K shell, there is only one subshell $l = 0$ and in this only ***two*** **electrons** of opposite spins can be accommodated.

For L shell, since $n = 2$, l can have two values (0 and 1), m can have only one value for $l = 0$ and three values for $l = 1$, *viz.*, -1, 0 and $+1$ and m_s can have two values, *viz.*, $+1/2$ and $-1/2$, for each value of m. These possibilities would give rise to **eight combinations** of the four quantum numbers, keeping in view the *exclusion principle*. Thus, L shell can accommodate **8 electrons**, 2 in the $l = 0$ subshell (s subshell) and 6 in the $l = 1$ subshell (p subshell).

Similarly, it can be shown that the M shell can have **18 electrons**, 2 in the $l = 0$ subshell (s subshell), 6 in the $l = 1$ subshell (p subshell) and 10 in the $l = 2$ subshell (d subshell) and so on.

The *maximum number* of electrons that can be accommodated in the first four principal energy shells as distributed in the various subshells (l values) are given in Table 3.

TABLE 3

Distribution of Electrons in Various Energy Shells and Subshells

Principal energy shell (n)	Subshells (l)	Orbitals (m)	Number of electrons in : Subshell	Number of electrons in : Principal energy shell
1	0 (1s subshell)	0 (one orbital)	2	2
2	0 (2s subshell)	0 (one orbital)	2	8
	1 (2p subshell)	$-1, 0, +1$ (three orbitals)	6	
3	0 (3s subshell)	0 (one orbital)	2	18
	1 (3p subshell)	$-1, 0, +1$ (three orbitals)	6	
	2 (3d subshell)	$-2, -1, 0, +1, +2$ (five orbitals)	10	
4	0 (4s subshell)	0 (one orbital)	2	32
	1 (4p subshell)	$-1, 0, +1$ (three orbitals)	6	
	2 (4d subshell)	$-2, -1, 0, +1, +2$ (five orbitals)	10	
	3 (4f subshell)	$-3, -2, -1, 0, +1, +2, +3$ (seven orbitals)	14	

Pauli's Exclusion Principle – Wave Mechanical Approach

Consider an orbital ψ_A containing two electrons (1) and (2). Ignoring the interelectronic repulsion betweeen the two electrons, we can write the orbital wave function for the system as :

$$\psi = \psi_{A(1)}\,\psi_{A(2)}$$

In writing ψ, the spins of the two electrons have not been taken into account. The possible electron spin wave functions for the two-electron system are $\alpha_1\alpha_2$, $\beta_1\beta_2$, $\alpha_1\beta_2 + \alpha_2\beta_1$ and $\alpha_1\beta_2 - \alpha_2\beta_1$ where α and β are, respectively, the spin wave functions corresponding to $+\frac{1}{2}$ and $-\frac{1}{2}$ spin states of the electrons. Assuming that there is no spin–orbital interaction, the complete wave functions for the system, comprising

of both the spin and the orbital part, can be written as :

$$\psi_{complete} = \psi_{A(1)}\psi_{A(2)}\alpha_1\alpha_2$$

$$\psi_{complete} = \psi_{A(1)}\psi_{A(2)}\beta_1\beta_2$$

$$\psi_{complete} = \psi_{A(1)}\psi_{A(2)}(\alpha_1\beta_2 + \alpha_2\beta_1)$$

$$\psi_{complete} = \psi_{A(1)}\psi_{A(2)}(\alpha_1\beta_2 - \alpha_2\beta_1)$$

According to the wave mechanical statement of Pauli's exclusion principle, the complete wave function of the system must be **asymmetric**. That is, it must change sign when we exchange the coordinates of electrons (1) and (2).

Let us consider the last complete wave function, *viz.*, $\psi_{complete} = \psi_{A(1)}\psi_{A(2)}(\alpha_1\beta_2 - \alpha_2\beta_1)$. The exchange of positions of electrons leads to $\psi_{A(2)}\psi_{A(1)}(\alpha_2\beta_1 - \alpha_1\beta_2)$ which is, evidently, equal to $-\psi_{complete}$. This complete wave function is thus assymmetric and hence acceptable. The first three complete wave functions, however, retain the same sign on exchanging the positions of electrons and are, therefore, symmetric. These are, therefore, not acceptable.

The acceptable complete wave function can be expanded and written as follows :

$$\psi_{complete} = \psi_{A(1)}\psi_{A(2)}\,\alpha_1\beta_2 - \psi_{A(1)}\psi_{A(2)}\,\alpha_2\beta_1 = \begin{vmatrix} \psi_{A(1)}\beta_1 & \psi_{A(1)}\beta_1 \\ \psi_{A(2)}\beta_2 & \psi_{A(2)}\beta_2 \end{vmatrix}$$

Imagine now that both the electrons in the same orbital ψ_A have the same spin. In that case, the above expression can be written as :

$$\psi_{complete} = \begin{vmatrix} \psi_{A(1)}\alpha_1 & \psi_{A(1)}\alpha_1 \\ \psi_{A(2)}\alpha_2 & \psi_{A(2)}\alpha_2 \end{vmatrix} \text{ or } \begin{vmatrix} \psi_{A(1)}\beta_1 & \psi_{A(1)}\beta_1 \\ \psi_{A(2)}\beta_2 & \psi_{A(2)}\beta_2 \end{vmatrix}$$

Since the two columns of the determinant are identical, it becomes equal to zero. Therefore, even though the quantum numbers n, l and m are the same for the two electrons in the same orbital ψ_A, the spins of the two electrons cannot be the same and have to be opposite in order that $\psi_{complete}$ is non-zero.

Suppose that we add one more electron to the ψ_A orbital which already contains two electrons having opposite spins with spin wave functions α and β. The third electron would have either α spin wave function or β spin wave function. The complete wave function can be written as the following 3×3 determinant :

$$\psi_{complete} = \begin{vmatrix} \psi_{A(1)}\alpha_1 & \psi_{A(1)}\beta_1 & \psi_{A(1)}\alpha_1 \\ \psi_{A(2)}\alpha_2 & \psi_{A(2)}\beta_2 & \psi_{A(2)}\alpha_2 \\ \psi_{A(3)}\alpha_3 & \psi_{A(3)}\beta_3 & \psi_{A(3)}\alpha_3 \end{vmatrix} \text{ if the spin wave function of the third electron is } \alpha.$$

and

$$\psi'_{complete} = \begin{vmatrix} \psi_{A(1)}\alpha_1 & \psi_{A(1)}\beta_1 & \psi_{A(1)}\beta_1 \\ \psi_{A(2)}\alpha_2 & \psi_{A(2)}\beta_2 & \psi_{A(2)}\beta_2 \\ \psi_{A(3)}\alpha_3 & \psi_{A(3)}\beta_3 & \psi_{A(3)}\beta_3 \end{vmatrix} \text{ if the spin wave function of the third electron is } \beta.$$

In each of the abvoe two determinants, the two columns are identical. Therefore, both these determinants would vanish.

We conclude from the above discussion that it is impossible for us to *accommodate more than two electrons in the same orbital and that it is impossible for the two electrons in the same orbital to have the same spin*. This leads to the statement of Pauli's exclusion principle that *no two electrons in an orbital can have all the four quantum numbers identical.*

However, it can be shown from the determinantal forms of $\psi_{complete}$ that if the two electrons having the same n, l and m values are present in different orbitals ψ_A, ψ_B, ψ_C, etc., in a system, the spins of the two electrons may or may not be the same.

Number of Various Atomic Orbitals. We have seen above that for *s* subshell (*i.e.*, when $l = 0$), there is only one possible orientation (*i.e.*, *m* has only one value). This means that there is only **one *s* orbital** whatever be the value of the principal quantum number *n*. For *p* subshell (*i.e.*, when $l = 1$), *m* has *three* values. In other words, a *p* subshell can have *three* possible orientations. Thus, there can be **three *p* orbitals** whatever be the value of the principal quantum number *n*. The three *p* orbitals are designated as p_x, p_y and p_z. For *d* subshell (*i.e.*, when $l = 2$), *m* has *five* values, *i.e.*, there are *five* possible orientations. This means that there can be **five *d* orbitals** whatever be the value of the principal quantum number *n*. The five *d* orbitals are designated as d_{xy}, d_{yz}, d_{xz}, d_{z^2}, $d_{x^2-y^2}$. For *f* subshell (*i.e.*, when $l = 3$), *m* has *seven* values, *i.e.*, there are *seven* possible orientations. This means that there can be **seven *f* orbitals** whatever be the value of the principal quantum number *n*. The *f* orbitals have complicated designations, the discussion of which is beyond the scope of the book.

To sum up : There can be *only one s orbital, three p orbitals, five d orbitals* and *seven f orbitals whatever be the major energy shell.*

Example 8. What subshells are possible in $n = 4$ energy level ? How many orbitals are possible for this level ?

Solution : For $n = 4$, the possible values of l are 0, 1, 2 and 3. The corresponding subshells are *s, p, d* and *f*.

For $n = 4$, there is one *s*, three *p*, five *d* and seven *f* orbitals. Therefore, the total number of orbitals for $n = 4$ is 16.

Example 9. An electron is in 3*d* orbital. What possible values for the quantum numbers *n, l, m* and m_s can it have ?

Solution : For 3*d* orbital, $n = 3$, $l = 2$ so that $m = -2, -1, 0, +1, +2$ and $m_s = +1/2$ and $-1/2$ for each value of *m*.

Example 10. Can we have 5*g* subshell ? How many orbitals are possible for this subshell?

Solution : For $n = 5$, l can have values = 0, 1, 2, 3 and 4. The corresponding subshells are 5*s*, 5*p*, 5*d*, 5*f* and 5*g*. Thus, **we can have 5*g* subshell.**

For 5*g* subshell ($l = 4$), the values of *m* are $-4, -3, -2, -1, 0, +1, +2, +3, +4$. There are thus **nine orbitals** in 5*g* subshell.

Energy Level Diagram of a Multi-electron Atom. The energy values of various orbitals belonging to different principal energy levels in a multi-electron atom are depicted in the energy level diagram shown in Fig. 19.

It is seen that in a multi-electron atom, different types of orbitals even in the same principal energy level have different energy values. This is because the energies of these orbitals depend not only on the value of *n* but also on the values of *l*. Thus, the 2*p* orbital (n=2, l=1) has higher energy than the 2*s* orbital ($n = 2$, $l = 0$). Similarly, the energy of the 3*d* orbital ($n = 3$, $l = 2$) is greater than that of the 3*p* orbital ($n = 3$, $l = 1$) which, in turn, is greater than that of the 3*s* orbital ($n = 3$, $l = 0$).

Further, it is seen that there is also a crossing of energies, particularly in the higher energy shells. For example, the energy of 4*s* orbital is lower than that of 3*d* orbital although the former belongs to the higher principal energy shell. Similarly, the energy of 5*s* orbital is lower than that of 4*d* orbital and that of 6*s* orbital is lower than that of 5*d* orbital. Thus, in multi-electron atoms, the energies are determined not only by principal quantum number *n* but also by subsidiary quantum number *l*.

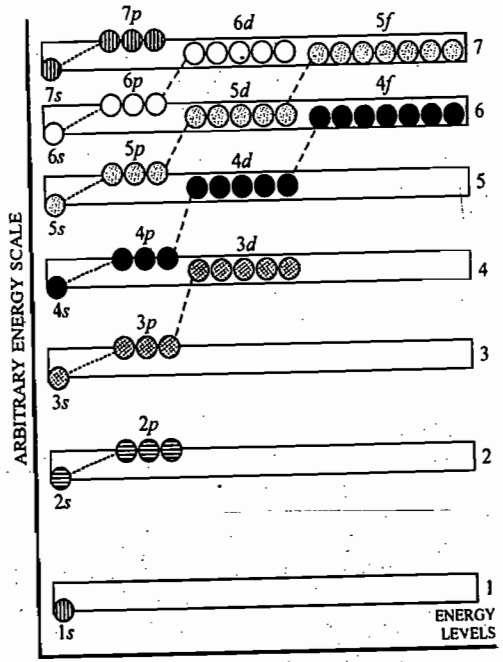


Fig. 19. Energy level diagram of multi-electron atoms.

It may be mentioned, however, that the **energy level diagram of hydrogen or a hydrogen-like atom,** *i.e.*, an atom having only one electron, is *distinctly different* from the energy level diagram of a multi-electron atom. In the former case, *all the orbitals belonging to any particular principal energy level have the same energy.* For example, the 2*s* and the three 2*p* orbitals of second energy level have the same energy. Similarly, the 3*s*, the three 3*p* and the five 3*d* orbitals of the third energy level have the same energy.

The energy of an orbital depends upon (*i*) *nuclear charge* (*ii*) *principal quantum number* and (*iii*) *the presence of other electrons* in the lower energy orbitals having different *l* values. Since in hydrogen or hydrogen-like atoms, there is *only one electron* and the attractive effect of the nuclear charge on the electron remains undisturbed, the energy of any orbital which this solitary electron occupies at any instant is determined by the principal quantum number only. In multi-electron atoms, however, there are a number of electrons. Some of them, occupying lower energy orbitals, *tend to reduce the effect of nuclear charge on the electrons present in higher energy orbitals.* This is due to the fact that these orbitals intervene between the nucleus and the electrons in the higher energy orbitals. This effect is known as **screening effect.** Since the electrons present in *different types of orbitals* (*s, p, d* or *f*) *are screened differently, they are attracted to different extents by the nucleus.* As a result, various orbitals are held at different distances from the nucleus and have different energies. This explains the difference in the energies of *s, p, d* and *f* orbitals even though belonging to the same principal energy shell in a multi-electron atom. The extent of screening of an electron by other electrons in the atom is calculated with the help of some *empirical rules* known as **Slater's rules.**

The Slater's Rules, The Concept of Effective Nuclear Charge

Consider an electron in one of the atomic orbitals of a multi-electron atom. Because of the electrostatic repulsion by other electrons in the same or other orbitals, the nuclear charge felt by this electron will be less than the actual nuclear charge. This electron is said to be screened from the influence of the nuclear charge and *the reduced charge felt by the electron is known as the* **effective nuclear charge.** The intervening electrons screen the electrons present in the peripheral *s, p, d* or *f* orbitals of even the same principal shell to different extents.

The effective nuclear charge for any electron in the configuration of an atom may be calculated with the help of the following correlation :

$$Z_{ef} = Z_{actual} - S \qquad ...(144)$$

where *S* is the **screening constant** or the **shielding constant** whose magnitude determines the extent to which the electron is screened or shielded by other electrons in the atom from the nuclear charge.

The screening constant is evaluated by the following empirical rules known as the **Slater's rules :**

1. The various orbitals are grouped as follows and written in the order given below, starting from the side of the nucleus :

(1*s*) (2*s* 2*p*) (3*s* 3*p*) (3*d*) (4*s* 4*p*) (4*d*) (4*f*) (5*s* 5*p*), etc.

2. For an electron in a group of *s, p* electrons, the value of the screening constant *S* is the sum of the following contributions :

(*i*) No contribution from any electron present in groups of orbitals lying on the right side of the group in which the electron (for which *S* is to be determined) is present.

(*ii*) A contribution of 0·35 from every other electron present in the group of orbitals (say, ns np) under consideration. A contribution of 0·30 from the other electron in 1*s* orbital if the electron for which *S* is to be calculated belongs to 1*s* orbital.

(*iii*) A contribution of 0·85 per electron from all electrons with quantum number $n - 1$, *i.e.*, electrons present in $(n - 1)$th shell.

(*iv*) A contribution of 1·0 per electron from all electrons present in the $(n - 2)$th and the next inner shell.

3. For an electron in a group of *d* or *f* electrons, the rules 2(*i*) and 2(*ii*) apply as such. However, the rules 2(*iii*) and 2(*iv*) are replaced by the rule that the contribution per electron from *all electrons* in the inner shells is 1·0.

We shall now apply these rules to calculate the effective nuclear charges for various electronic systems.

Example 11. What is the effective nuclear charge felt by 1*s* electron of helium atom ?

Solution : The electronic configuration of helium atom is $1s^2$

There is one more 1*s* electron, apart from the electron for which Z_{eff} is to be calculated.

∴ The screening constant, $S = 1 \times 0{\cdot}30 = 0{\cdot}30$

Hence, Z_{eff} felt by 1*s* electron of helium atom $= 2 - 0{\cdot}30 = \mathbf{1{\cdot}70}$

Example 12. What is the effective nuclear charge felt by a 2*p* electron of a nitrogen atom ? What will be the effective nuclear charge felt by its 1*s* electron ?

Solution : Z_{eff} for 2*p* electron :

Electronic configuration of N atom is $1s^2\,2s^2\,2p^3$.

∴ There are four other electrons in (2*s* 2*p*) group.

Screening constant *S* for 2*p* electron $= 4 \times 0{\cdot}35 + 2 \times 0{\cdot}85 = 1{\cdot}40 + 1{\cdot}70 = 3{\cdot}10$

Z_{eff} felt by 2*p* electron $= Z_{actual} - S = 7 - 3{\cdot}10 = \mathbf{3{\cdot}90}$

Z_{eff} for 1*s* electron :

Z_{eff} felt by 1*s* electron $= Z_{actual} - S = 7 - 1 \times 0{\cdot}30 = \mathbf{6{\cdot}70}$

(There will be no contribution from (2*s* 2*p*) electrons in this case as per Slater's rule 2(*i*))

Example 13. Calculate the effective nuclear charge felt by a 3*d* electron of chromium atom (Z = 24).

Solution : The grouping of electrons in Cr atom according to Slater's rules is

$$(1s^2)\,(2s^2\,2p^6)\,(3s^2\,3p^6)\,(3d^5)\,(4s^1)$$

There will be no contribution from 4*s* electron.

There are 4 other 3*d* electrons.

∴ Z_{eff} felt by the 3*d* electron of Cr atom $= 24 - (0{\cdot}35 \times 4 + 1{\cdot}0 \times 18) = \mathbf{4{\cdot}60}$

The Effective Nuclear Charge at the Periphery of An Atom or An Ion. The effective nuclear charge felt at the periphery of an atom or an ion is calculated by considering the screening of the nuclear charge by *all the electrons* present in the electronic configuration of the atom or the ion.

The calculation of the effective nuclear charge at the periphery of an atom or an ion is illustrated below.

Example 14. Calculate the effective nuclear charge at the periphery of nitrogen atom ?

Solution : Imagine an 'extra electron' in the last filled orbital of nitrogen atom.

The screening constant *S* for this extra electron $= 5 \times 0{\cdot}35 + 2 \times 0{\cdot}85 = 3{\cdot}45$

∴ Z_{eff} at the periphery of N atom $= 7 - 3{\cdot}45 = \mathbf{3{\cdot}55}$

Example 15. Calculate the effective nuclear charge at the periphery of chromium atom ?

Solution : Imagine an extra electron in the last filled orbital, *i.e.*, the 4*s* orbital of the Cr atom.

The screening constant *S* for this extra electron $= 1 \times 0{\cdot}35 + (8 + 5) \times 0{\cdot}85 + 1{\cdot}0 \times 10 = 21{\cdot}40$

Z_{eff} at the periphery of Cr atom $= 24 - 21{\cdot}40 = \mathbf{2{\cdot}60}$

Example 16. Calculate Z_{eff} for 3*d* electron, 4*s* electron and at the periphery of a Cu atom.

Solution : Electronic configuration of Cu atom is $(1s^2)\,(2s^2\,2p^6)\,(3s^2\,3p^6)\,(3d^{10})\,(4s^1)$

Z_{eff} felt by 3*d* electron $= 29 - [\,9 \times 0{\cdot}35 + 1{\cdot}0 \times 18\,] = 29 - (3{\cdot}15 + 18) = \mathbf{7{\cdot}85}$

(there is no contribution from 4*s* electron)

Z_{eff} felt by 4*s* electron $= 29 - (0{\cdot}35 \times 0 + 0{\cdot}85 \times 18 + 1{\cdot}0 \times 10)$

$= 29 - 25{\cdot}30 = \mathbf{3{\cdot}70}$

Z_{eff} at the periphery of the atom $= 29 - (\,0{\cdot}35 \times 1 + 0{\cdot}85 \times 18 + 1{\cdot}0 \times 10)$

$= 29 - (\,0{\cdot}35 + 15{\cdot}30 + 10{\cdot}00\,) = \mathbf{3{\cdot}35}$

Other Applications of Slater's Rules. The Slater's rules are also applied to explain the following facts.

1. A 4*s* orbital is filled earlier than a 3*d* orbital. Consider a potassium atom ($Z = 19$). In this case, 18 of 19 electrons occupy orbitals as in argon $(1s^2\,2s^2\,2p^6\,3s^2\,3p^6)$. The 19th electron may enter a 4*s* or a 3*d* orbital.

Let us calculate the Z_{eff} for the 19th electron when it enters the 4*s* orbital.

$$Z_{eff} = 19 - 0 \times 0{\cdot}35 - 8 \times 0{\cdot}85 - 10 \times 1{\cdot}0 = 19 - 16{\cdot}80 = 2{\cdot}20$$

Z_{eff} felt by the 19th electron when it enters the 3*d* orbital

$$= 19 - 0 \times 0{\cdot}35 - 18 \times 1{\cdot}0 = 19 - 18 = 1{\cdot}00$$

Thus, a 4*s* electron would be subjected to a greater electrostatic attraction (due to a higher effective nuclear charge of 2·20) than a 3*d* electron. Consequently, potassium atom with outer electronic configuration $3s^2p^6\,4s^1$ would be associated with lower energy than with outer electronic configuration $3s^2p^6\,3d^1$. As a result, the configuration $3s^2p^6\,4s^1$ would be more stable than the configuration $3s^2p^6\,3d^1$. Thus, a 4*s* orbital is filled earlier than a 3*d* orbital.

2. The transition metal atoms lose n*s* electrons first during Ionization. Consider Mn atom with atomic number 25. It has a configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$ (arranged as per Slater's rules).

Let us calculate Z_{eff} felt by the 3*d* as well as the 4*s* electron.

Z_{eff} felt by the 3*d* electron $= 25 - (0{\cdot}35 \times 4 + 1{\cdot}0 \times 18) = \mathbf{5{\cdot}60}$

Z_{eff} felt by the 4*s* electron $= 25 - (1 \times 0{\cdot}35 + 13 \times 0{\cdot}85 + 1{\cdot}0 \times 10) = \mathbf{3{\cdot}60}$

Evidently, the attraction between the 4*s* electron and the nucleus is less than the attraction between the 3*d* electron and the nucleus of Mn atom. Hence, the removal of the 4*s* electron from an isolated gaseous atom of Mn would be easier than the removal of the 3*d* electron from it.

3. Trends in successive ionization energies. The first ionization energy is always lower than the second ionization energy and second ionization energy is always lower than the third ionization energy and so on. This is because the effective nuclear charge goes on increasing with each removal of electron from an atom. (The student may verify this fact by taking a suitable example and calculating the effective nuclear charge for the unipositive, dipositive and tripositive ions).

4. An anion is always bigger and a cation is always smaller in size than the parent atom. Consider a chlorine atom with electronic configuration $1s^2\,2s^2\,p^6\,3s^2\,3p^5$.

Z_{eff} felt by the last electron of chlorine *atom* $= 17 - (6 \times 0{\cdot}35 + 8 \times 0{\cdot}85 + 2 \times 1{\cdot}0) = \mathbf{6{\cdot}10}$

Z_{eff} felt by the last electron of chloride *ion* $= 17 - (7 \times 0{\cdot}35 + 8 \times 0{\cdot}85 + 2 \times 1{\cdot}0) = \mathbf{5{\cdot}75}$

As can be seen, Z_{eff} in the case of Cl^- ion is less than in the case of Cl atom. Therefore, the electrostatic attraction between the electrons and the nucleus is more in chlorine atom than in chloride ion. As a result, the nucleus would have lesser hold on electrons in the chloride ion than in chlorine atom. Consequently, the size of chloride ion will be larger than the size of chlorine atom.

Now consider a sodium atom with electronic configuration $1s^2\,2s^2\,2p^6\,3s^1$.

Z_{eff} felt by the last electron of Na atom $= 11 - (0{\cdot}35 \times 0 + 8 \times 0{\cdot}85 + 2 \times 1{\cdot}0) = \mathbf{2{\cdot}20}$

Z_{eff} felt by the last electron of Na^+ ion $= 11 - (0{\cdot}35 \times 7 + 2 \times 0{\cdot}85) = \mathbf{6{\cdot}85}$

As can be seen, Z_{eff} in the case of Na atom is less than in the case of the Na^+ ion. Therefore, the hold of the nucleus on the electrons is less in the case of Na atom than in the case of Na^+ ion. Consequently, Na atom is bigger in size than the Na^+ ion.

5. The atomic size within a period goes on decreasing with increase in atomic number. Consider the elements of the First transition series from Sc to Zn. The Z_{eff} goes on increasing with increase in atomic number. Therefore, the hold of the nucleus on the electrons also goes on increasing as we move from Sc to Zn. Hence, the atomic size goes on decreasing with increase in atomic number as we move along the series.

The Slater's rules are also applied for **calculating electronegativities** of atoms by Allred-Rochow method. This aspect would be discussed in the next chapter.

Limitations of Slater's Rules. The Slater's rules have some serious limitations as well.

1. According to Slater's rules, the outer shell electrons do not shield the inner electrons. This may not be true. For example, even the outer *s* electrons penetrate quite close to the nucleus and would thus exercise a shielding effect.

2. We have already discussed that *s* electrons are more penetrating than the *p* electrons of the same shell so that the screening by the *s* electrons will be more than the screening by the *p* electrons. According to Slater's rules, however, the screening by the *s* and *p* electrons of the same shell is the same.

3. According to Slater's rules, the *s*, *p*, *d* and *f* electrons of the same shell screen the higher shell electrons to the same extent. This is, however, not correct. The electrons in *s*, *p*, *d* and *f* orbitals differ so much in their penetrating power. An *ns* electron has greater probability of being present near the nucleus than an n*p* electron. Similarly, an n*p* electron has greater probability of being present near the nucleus than an *nd* electron. The electrons present in these orbitals would not screen the outer shell electrons to the same extent.

Filling of Orbitals in Atoms. *The distribution of electrons in various orbitals in known as* **electronic configuration.** The atom is built up by filling electrons in various orbitals one at a time and by placing each new electron in the next lowest energy orbital. An atom in its lowest energy state is said to be in the normal state or the ground state. This state is the most stable state for the atom.

The filling of orbitals in the ground state is determined by the following rules.

1. Aufbau principle. The aufbau principle states that in the ground state of an atom, the orbital with a lower energy is filled up first before the filling of the orbital with a higher energy commences. In other words, the electrons enter the various orbitals in the order of increasing energy.

The increasing order of energy of various orbitals is :

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*, 6*d*...

The above sequence of energy levels can be easily remembered with the help of the graphical representation shown in Fig. 20.

2. Pauli's exclusion principle. According to this principle, an orbital can contain a maximum of two electrons and these two electrons must be of opposite spin.

3. Hund's rule of maximum multiplicity. This rule states that in the ground state electronic configuration of an atom, electron pairing in orbitals of the same energy will not take place unless all such available orbitals of a given subshell contain one electron each with parallel spin. For example, we know that there are three *p* orbitals (p_x, p_y and p_z) of the *p* subshell in a principal energy level. According to Hund's rule, each of the three *p* orbitals must get one electron each of parallel spin before any one of them gets the second electron of opposite spin.

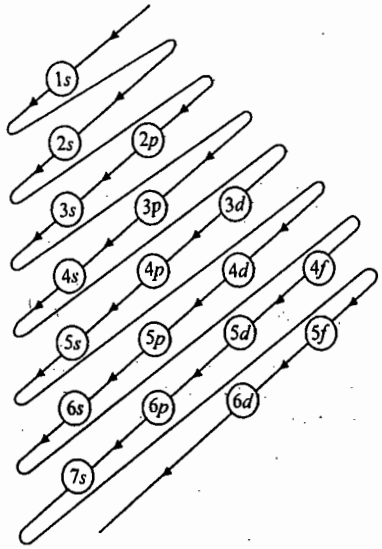


Fig. 20. Sequence of the filling of the various orbitals

Electronic Configurations of Atoms

Based on the sequence given in Fig. 20, the ground state electronic configurations of atoms of various elements of the periodic table are given below. (*Hund's rule is applicable for ground state only*).

Hydrogen has only one electron (Z = 1). This electron will enter the lowest energy orbital which is 1*s*. Thus, the solitary electron of hydrogen atom will occupy 1*s* orbital. The electronic configuration of hydrogen atom is, therefore, represented as $\mathbf{1s^1}$.

The next element, **helium**, has two electrons (Z = 2). One of these electrons occupies the 1*s* orbital as in the case of the hydrogen atom. The second electron can also enter this orbital so as to fill it completely. The electronic configuration of helium is, therefore, represented as $\mathbf{1s^2}$. The two electrons occupying this orbital will have opposite spins.

The next element is **lithium**. It has three electrons (Z = 3). Since there is only one orbital in the first principal energy shell and this has been filled up by the occupancy of two electrons, the third electron in lithium enters the *s* orbital of the second principal energy shell. The electronic configuration of lithium, therefore, is represented as $\mathbf{1s^2\ 2s^1}$.

Arguing in the same way, the electronic configuration of **beryllium** (Z = 4) would be $\mathbf{1s^2\ 2s^2}$.

The next element, **boron** (Z = 5), has five electrons. The 2*s* orbital has already been filled. But, as the principal quantum number is now 2, there are three *p* orbitals still available. The fifth electron, therefore, enters one of these *p* orbitals. The electronic configuration of boron, therefore, is $\mathbf{1s^2\ 2s^2\ 2p^1}$.

The next five elements, namely, carbon (Z = 6), nitrogen (Z = 7), oxygen (Z = 8), fluorine (Z = 9) and neon (Z = 10) of this period get their *p* orbitals successively filled. Their electronic configurations are given in Table 4.

TABLE 4

Electronic Configurations of the First 20 Elements

At. No.	Element	Electronic Configuration			
1	Hydrogen	$1s^2$			
2	Helium	$1s^2$			
3	Lithium	$1s^2$	$2s^1$		
4	Beryllium	$1s^2$	$2s^2$		
5	Boron	$1s^2$	$2s^2\ 2p_x^1$		
6	Carbon	$1s^2$	$2s^2\ 2p_x^1\ 2p_y^1$		
7	Nitrogen	$1s^2$	$2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$		
8	Oxygen	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$		
9	Fluorine	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$		
10	Neon	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$		
11	Sodium	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^1$	
12	Magnesium	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2$	
13	Aluminium	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^1$	
14	Silicon	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^1\ 3p_y^1$	
15	Phosphorus	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$	
16	Sulphur	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$	
17	Chlorine	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$	
18	Argon	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$	
19	Potassium	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$	$4s^1$
20	Calcium	$1s^2$	$2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	$3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$	$4s^2$

It may be noted that in carbon, the arrangement of electrons in p orbitals is $2p_x^1\ 2p_y^1$ and not $2p_x^2$. Similarly, in nitrogen, the arrangement is $2p_x^1\ 2p_y^1\ 2p_z^1$ and not $2p_x^2\ 2p_y^1$. This is in accordance with Hund's rule of maximum multiplicity. According to this rule, electrons occupy all the available orbitals of a given subshell *singly* with parallel spins before they pair up in any orbital.

It will be seen that in neon all the four orbitals of principal energy shell 2 are completely filled, its electronic configuration being $1s^2\ 2s^2\ 2p^6$.

The principal energy shell 3 begins with **sodium** ($Z = 11$). The eleventh electron will, evidently, enter the $3s$ orbital, the configuration being $1s^2\ 2s^2 2p^6\ 3s^1$.

The next seven elements, namely, magnesium (Z = 12), aluminium (Z = 13), silicon (Z = 14), phosphorus (Z = 15), sulphur (Z = 16), chlorine (Z = 17) and argon (Z = 18) follow the sequence described above. Their electronic configurations are also included in Table 4.

Consider now the electronic configuration of the next element which is **potassium** ($Z = 19$). The additional electron (*i.e.*, nineteenth electron) instead of entering $3d$ orbitals, all of which are lying unoccupied so far, goes into the $4s$ orbital. This is because $4s$ orbital is at a lower energy level than $3d$ orbitals (Fig. 20). The electronic configuration of potassium, therefore, may be represented as $1s^2\ 2s^2\ p^6\ 3s^2\ p^6\ 4s^1$. The additional electron in **calcium** ($Z = 20$) follows the same course and goes into the same, *i.e.*, $4s$ orbital, to fill it completely. Therefore, the electronic configuration of calcium is $1s^2\ 2s^2 p^6\ 3s^2 p^6\ 4s^2$.

The next ten elements (Z = 21 to 30) which follow calcium are scandium (Sc), titanium (Ti), vanadium (V), chromium(Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn). In these elements, addition of electrons takes place in the inner $3d$ orbitals while the outer $4s$ orbital remains fully occupied. All these elements are known as the **transition elements.** The electronic configuration of scandium ($Z = 21$), the first transition element, for example, is $1s^2\ 2s^2 p^6\ 3s^2 p^6\ 4s^2\ 3d^1$ while that of zinc ($Z = 30$), the last element of the series, is $1s^2\ 2s^2 p^6\ 4s^2\ 3d^{10}$. Thus, while the filling of $3d$ orbitals begins with scandium, it ends with zinc. The electronic configurations of all the 10 transition elements are represented in Table 5.

TABLE 5

Electronic Configurations of Transition Elements

Scandium ($Z = 21$) to Zinc ($Z = 30$)

Atomic number	Element	Electronic Configuration	Outer Configuration 3d	4s
21	Sc	[Ar] $3d^1\ 4s^2$	↑ ○ ○ ○ ○	↑↓
22	Ti	[Ar] $3d^2\ 4s^2$	↑ ↑ ○ ○ ○	↑↓
23	V	[Ar] $3d^3\ 4s^2$	↑ ↑ ↑ ○ ○	↑↓
24	Cr	[Ar] $3d^5\ 4s^1$	↑ ↑ ↑ ↑ ↑	↑
25	Mn	[Ar] $3d^5\ 4s^2$	↑ ↑ ↑ ↑ ↑	↑↓
26	Fe	[Ar] $3d^6\ 4s^2$	↑↓ ↑ ↑ ↑ ↑	↑↓
27	Co	[Ar] $3d^7\ 4s^2$	↑↓ ↑↓ ↑ ↑ ↑	↑↓
28	Ni	[Ar] $3d^8\ 4s^2$	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓
29	Cu	[Ar] $3d^{10}\ 4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑
30	Zn	[Ar] $3d^{10}\ 4s^2$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓

Anomalous Configurations of Chromium and Copper. It may be noted that the configurations of chromium ($Z = 24$) and copper ($Z = 29$) do not follow the general trend. The electronic configurations of Cr and Cu are expected to be as follows :

$$\text{Cr} : 1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^4\ 4s^2 \quad \text{and} \quad \text{Cu} : 1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^9\ 4s^2$$

But actually their configurations are :

$$\text{Cr} : 1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^5\ 4s^1 \quad \text{and} \quad \text{Cu} : 1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^1$$

These anomalies are attributed to the fact that exactly half-filled and completely filled orbitals, *i.e.*, d^5, d^{10}, f^7 and f^{14} have lower energy and hence possess extra stability. The cause of this extra stability has been discussed in details in a subsequent section. Thus, to acquire increased stability, one of the electrons from $4s$ orbital goes into the nearby $3d$ orbital so that the $3d$ orbitals become exactly half-filled in the case of chromium and completely filled in the case of copper.

For the sake of simplicity, we do not always write the complete electronic configuration. Instead, the configuration of the noble gas preceding the valence shell is not given ; it is represented by its symbol in square bracket. For example, for Na ($Z = 11$), we may write [Ne]$3s^1$ and for Ca ($Z = 20$), we may write [Ar]$4s^2$.

Electronic Configurations of Lanthanides and Actinides. It may be mentioned that the sequence of filling of the various orbitals in the case of lanthanides and actinides, as revealed by spectroscopic analysis, shows a little deviation from the arrangement shown in Fig. 20. After the filling of $6s$ subshell with barium (Z = 56), the next electron in lanthanum (Z = 57), goes to $5d$ subshell and *not to* $4f$ *subshell.* The subsequent electrons in the succeeding elements of the lanthanide series (from Ce to Lu, $Z = 58$ to 71), however, enter the $4f$ subshell as required by the representation in Fig. 20. The filling of $5d$ subshell recommences only after the $4f$ subshell is completely filled with Lu ($Z = 71$). Thus, the configurations of La, Ce, Pr and Gd would be as follows :

La ($Z = 57$) : [Xe] $6s^2 5d^1$

Ce ($Z = 58$) : [Xe] $6s^2 5d^1 4f^1$

Pr ($Z = 59$) : [Xe] $6s^2 5d^1 4f^2$

Gd ($Z = 64$) : [Xe] $6s^2 5d^1 4f^7$

Similarly, after the filling of $7s$ subshell with radium (Z = 88), the next electron in actinium (Z = 89) goes to $6d$ subshell and *not to* $5f$ subshell. The subsequent electrons in the succeeding elements of the actinides (from Th to Lr, $Z = 90$ to 103), however, enter the $5f$ subshell as required by the representation shown in Fig. 20. Thus, the configurations of Ac, Th and Pa would be as follows :

Ac (Z = 89) : [Rn] $7s^2\ 6d^1$

Th (Z = 90) : [Rn] $7s^2\ 6d^1\ 5f^1$

Pa (Z = 91) : [Rn] $7s^2\ 6d^1\ 5f^2$

Electronic configurations of elements upto atomic number 103 are given in Table 6.

Elements Beyond Atomic Number 103

The electrons in elements with atomic numbers 103 to 112 (elements upto atomic number 108 have already been prepared artificially through nuclear reactions) enter the inner $6d$ orbitals continuing the process initiated by actinium. The d subshell gets completely filled with the element with atomic number 112. The common names of elements with atomic numbers 101 to 105 are mendelevium (101), nobelium (102), lawrencium (103), kurchatovium (104) and hahnium (105). However, all the elements with atomic numbers beyond 100 are now named in accordance with IUPAC system as, for example, un-nil-unium (101), un-nil-bium (102), un-nil-trium (103), un-nil-quadium (104), un-nil-pentium (105), un-nil-hexium (106), un-nil-septium (107), un-nil-octium (108), etc. (see Chapter 2 and the periodic table annexed in that chapter).

TABLE 6

Distribution of Electrons in Various Shells and Subshells

Shell		K	L		M			N				O				P				Q	
Subshell		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p
Element	Atomic Number																				
H	1	1																			
He	2	2																			
Li	3	2	1																		
Be	4	2	2																		
B	5	2	2	1																	
C	6	2	2	2																	
N	7	2	2	3																	
O	8	2	2	4																	
F	9	2	2	5																	
Ne	10	2	2	6																	
Na	11	2	2	6	1																
Mg	12	2	2	6	2																
Al	13	2	2	6	2	1															
Si	14	2	2	6	2	2															
P	15	2	2	6	2	3															
S	16	2	2	6	2	4															
Cl	17	2	2	6	2	5															
Ar	18	2	2	6	2	6															
K	19	2	2	6	2	6		1													
Ca	20	2	2	6	2	6		2													
Sc	21	2	2	6	2	6	1	2													
Ti	22	2	2	6	2	6	2	2													
V	23	2	2	6	2	6	3	2													
*Cr	24	2	2	6	2	6	5	1													
Mn	25	2	2	6	2	6	5	2													
Fe	26	2	2	6	2	6	6	2													
Co	27	2	2	6	2	6	7	2													
Ni	28	2	2	6	2	6	8	2													
*Cu	29	2	2	6	2	6	10	1													
Zn	30	2	2	6	2	6	10	2													
Ga	31	2	2	6	2	6	10	2	1												
Ge	32	2	2	6	2	6	10	2	2												
As	33	2	2	6	2	6	10	2	3												
Se	34	2	2	6	2	6	10	2	4												
Br	35	2	2	6	2	6	10	2	5												
Kr	36	2	2	6	2	6	10	2	6												
Rb	37	2	2	6	2	6	10	2	6			1									
Sr	38	2	2	6	2	6	10	2	6			2									
Y	39	2	2	6	2	6	10	2	6	1		2									
Zr	40	2	2	6	2	6	10	2	6	2		2									
** Nb	41	2	2	6	2	6	10	2	6	4		1									
* Mo	42	2	2	6	2	6	10	2	6	5		1									
Tc	43	2	2	6	2	6	10	2	6	5		2									
* Ru	44	2	2	6	2	6	10	2	6	7		1									
* Rh	45	2	2	6	2	6	10	2	6	8		1									
* Pd	46	2	2	6	2	6	10	2	6	10											
* Ag	47	2	2	6	2	6	10	2	6	10		1									
Cd	48	2	2	6	2	6	10	2	6	10		2									
In	49	2	2	6	2	6	10	2	6	10		2	1								
S	50	2	2	6	2	6	10	2	6	10		2	2								
Sb	51	2	2	6	2	6	10	2	6	10		2	3								
Te	52	2	2	6	2	6	10	2	6	10		2	4								

*As a result of inter-electronic repulsions, the electrons differing slightly in their energies have a preference to enter into those subshells which thereby get either completely filled or just half-filled. This explains the anomalous configurations of Cr, Cu, Mo, Ag, Pd, Au, etc.

TABLE 6 (Continued)

Distribution of Electrons in Various Shells and Subshells

Shell		K	L		M			N				O				P				Q	
Subshell		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p
Element	Atomic Number																				
I	53	2	2	6	2	6	10	2	6	10		2	5								
Xe	54	2	2	6	2	6	10	2	6	10		2	6								
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1					
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2					
La	57	2	2	6	2	6	10	2	6	10		2	6	1		2					
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1		2					
Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1		2					
Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1		2					
Pm	61	2	2	6	2	6	10	2	6	10	4	2	6	1		2					
Sm	62	2	2	6	2	6	10	2	6	10	5	2	6	1		2					
*Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	0		2					
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2					
Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1		2					
Dy	66	2	2	6	2	6	10	2	6	10	9	2	6	1		2					
Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1		2					
Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1		2					
Tm	69	2	2	6	2	6	10	2	6	10	12	2	6	1		2					
Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1		2					
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2					
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2					
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2					
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2					
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2					
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2					
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2					
**Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1					
*Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1					
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2					
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1				
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2				
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3				
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4				
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5				
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6				
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			1	
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			2	
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1		2	
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10	1	2	6	1		2	
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1		2	
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1		2	
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1		2	
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1		2	
*Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	0		2	
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1		2	
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1		2	
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	1		2	
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	1		2	
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	1		2	
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	1		2	
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	1		2	
Lr	103	2	2	6	2	6	10	2	6	10	14	1	6	10	14	2	6	1		2	

**Anomalous configurations of Nb, Ru, Rh and Pt, can be explained on the basis of nucleus-electron and electron-electron forces, the discussion of which is beyond the scope of the book.

The electronic configurations of elements with atomic numbers 104 to 112 would be as shown below :

$$Z = 104: \ [Rn]5f^{14}6d^{2}7s^{2}$$

$$Z = 105: \ [Rn]5f^{14}6d^{3}7s^{2}$$

$$Z = 106: \ [Rn]5f^{14}6d^{4}7s^{2}$$

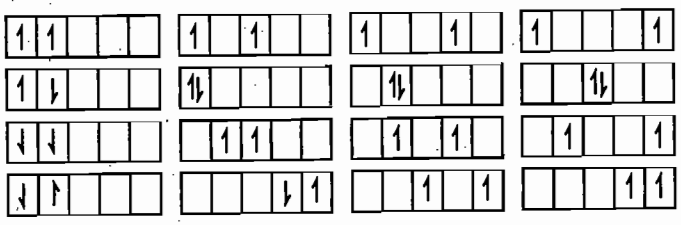
$$Z = 112: \ [Rn]5f^{14}6d^{10}7s^{2}$$

Elements beyond atomic number 112, if discovered, will be normal or representative elements in which $7p$ subshell will be increasingly filled, ending with a noble gas having an atomic number 118. In this way, the seventh period will also have 32 elements.

Extra Stability of Half-filled and Completely-filled Orbitals

Before we discuss the relative stabilities of various electronic configurations, we should clearly understand the ***difference between electronic configuration and electronic arrangement.*** For this, let us consider Ti^{2+} ion. Its outer electronic configuration is $3d^2$. From this we get the information that two electrons are present in a set of five $3d$ orbitals. This configuration gives no information about the manner in which these two electrons are placed in the five $3d$ orbitals.

It can be easily shown through permutations and combinations that there are as many as 45 different ways of placing these two electrons in the five $3d$ orbitals. In other words, *the electronic configuration $3d^2$ can have 45 different electronic arrangements.* Some of these *arrangements* are shown below :



Let us consider two of these arrangements, *viz.*, $(3d_z^2)^1(3d_{x^2-y^2})^1$ and $(3d_{xy})^1(3d_{x^2-y^2})^1$. If we recall the shapes of the d orbitals, we would immediately realise that the *mutual* repulsion of the two electrons would be different in these two arrangements. As a result, *the two electronic arrangements would have different energies.* This is true of many other electronic arrangements of the $3d^2$ configuration. We may thus conclude that any given electronic configuration would give rise to a large number of electronic arrangements which would have *different energies** in spite of the fact that they belong to the same electronic configuration. Therefore, *when we talk of the stability of an electronic configuration, we are ipso facto concerned with the stability of the electronic arrangement of that configuration.* Of all the electronic arrangements permitted by a given configuration, the most stable arrangement can be predicted by Hund's rule of maximum multiplicity, as discussed below.

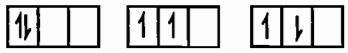
Hund's Rule – Its Basis and Application. We would first discuss the basis of Hund's rule of maximum multiplicity and would see how it can predict the most stable electronic arrangement of a given electronic configuration.

According to Pauli's exclusion principle, if two electrons have the same spin, *i.e.*, the same m_s quantum number, they would occupy different orbitals since they *cannot have* the same values of n, l and m. On the other hand, if the two electrons have opposite spin, they *can occupy* the same orbital, *i.e.*, they *can have* the same values of n, l and m.

*Some of the electronic arrangements may have the same inter-electronic repulsions and hence may have the same energy. Such electronic arrangements are known as degenerate arrangements.

In the case of *degenerate orbitals, i.e.*, orbitals with the same energy, if two electrons are placed in the same orbital, the electrostatic repulsion would be greater than when they are placed in different orbitals. Hence, *for least repulsion, the electrons in degenerate orbitals should be placed* **singly** *until it becomes necessary to place two of them in the same orbital* (*i.e.*, when the number of electrons exceeds the number of degenerate orbitals.) Thus, *the most stable arrangement is one in which there is maximum number of unpaired electrons. This is the first part of* **Hund's rule.**

For illustration, let us find out the most stable electronic arrangement for a p^2 configuration. It can be easily shown that there are 15 ways of arranging two electrons in the three p orbitals. Three of these arrangements are shown below :

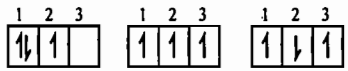


(1) (2) (3)

According to the first part of Hund's rule stated above, the arrangement (1) is *least stable.* Of the remaining two, which one is more stable can be decided by involving the contribution of **exchange energy,** as discussed below.

By advanced mathematical treatment, it can be shown that if *on exchanging the position in space of two electrons with parallel spins, there is no change in the electronic arrangement, it would lead to decrease in energy.* Such a pair of electrons is called the **exchange pair.** The larger the number of exchange pairs of electrons, the greater would be the decrease of energy. *The energy decrease per exchange pair of electrons is termed as* **exchange energy.** It would, evidently, carry a negative sign. As can be seen, there is one exchange pair of electrons in arrangement (2) but none in arrangement (3). Consequently, there would be a loss of energy in the form of exchange energy in arrangement (2) but there would be no such loss in arrangement (3). The arrangement (2) associated with lower energy would thus be more stable than arrangement (3).

Let us now consider the case of a p^3 configuration. This configuration can give rise to 20 electronic arrangements, three of which are shown below :



(4) (5) (6)

According to the first part of Hund's rule, arrangement (4) is *least stable.* Arrangement (5) has *three* exchange pairs of electrons, *viz.*, 1, 2, ; 1, 3 and 2, 3 while arrangement (6) has only *one* such pair, *viz.*, 1, 3. If E is the exchange energy (per exchange pair), then the energy of arrangement (5) would *decrease* by $3E$ and that of arrangement (6) would *decrease* by E. Thus, of the three arrangements shown above, arrangement (5) associated with minimum energy is *most stable.* It follows from the above discussion that *the electronic arrangement with maximum number of parallel electronic spins would be the most stable arrangement of a given configuration since such an arrangement would have maximum number of exchange pairs of electrons and thus would have maximum exchange energy. This is the second part of* **Hund's rule.**

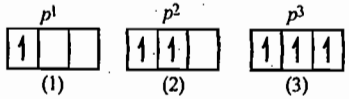
Pairing Energy. As already mentioned, placing of two electrons together in the same orbital results in considerable repulsion. *The energy required for placing two electrons together in the same orbital,* i.e., for pairing of electrons, is called **pairing energy.** Pairing energy, having a positive sign, would tend to increase the energy of the system and hence would tend to destabilise it. Thus, the overall stability of a system would be decided by the aggregate of exchange energy (E) and pairing energy (P).

Referring again to the three electronic arrangements (4), (5) and (6) of p^3 configuration, we notice that the aggregates of exchange energy and pairing energy in the three arrangements are : $-E + P, -3E + 0$

and $-E+0$, respectively. The order of stability of the electronic arrangements would, thus, be (5) > (6) > (4).

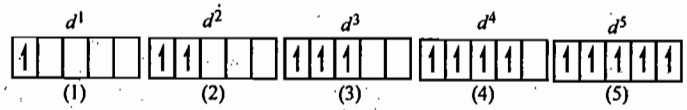
Relative Stabilities of Most Stable Electronic Arrangements of Different Electronic Configurations. So far we have considered the relative stabilities of different electronic arrangements of the same electronic configuration. We shall now take into consideration *the most stable electronic arrangements of different configurations and discuss their relative stabilities.*

The solitary electronic arrangement of p^1 configuration and the most stable electronic arrangements of p^2 and p^3 configurations, in accordance with Hund's rule, are as shown below :



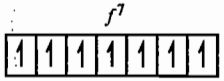
The number of exchange pairs of electrons in (1), (2) and (3) are 0, 1 and 3 (*viz.*, 1, 2, ; 1, 3 ; 2, 3), respectively. Therefore, the exchange energy for (1), (2) and (3) would be 0, $-E$ and $-3E$, respectively. Since no pairing of electrons is required in any of these arrangements, no pairing energy is involved in any of them. Thus, *we see that arrangement* (3) *of p^3 configuration, associated with maximum exchange energy $= -3E$, is the most stable and this is also the arrangement in which all the three degenerate p orbitals are exactly half-filled.*

Similarly, the solitary electronic arrangement of d^1 configuration and the most stable electronic arrangements of d^2, d^3, d^4 and d^5 configurations, are as shown below :



It can be easily shown that the number of exchange pairs of electrons in these arrangements are 0, 1, 3, 6 and 10, respectively. Hence, exchange energy associated with these arrangements would be 0, $-E$, $-3E$, $-6E$ and $-10E$, respectively. Since no pairing of electrons is required in any of these arrangements, hence no pairing energy is involved in any of them. Thus, in this case also, *we see that arrangement* (5) *of d^5 configuration, associated with the maximum exchange energy $= -10E$, is the most stable and this is also the arrangement in which all the five degenerate d orbitals are exactly half-filled.*

In a similar manner it can be shown that of all the electronic arrangements of f^1 to f^7 configurations, the electronic arrangement shown below is the most stable :

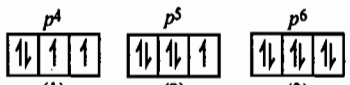


This is also the arrangement in which all the seven degenerate f orbitals are exactly half-filled.

It is evident from the above discussion that *an electronic arrangement containing a set of exactly half-filled degenerate orbitals is more stable than any other arrangement of any configuration.*

Let us now consider the relative stabilities of most stable electronic arrangements of different electronic configurations in which the number of electrons is more than the number of degenerate orbitals, *i.e.*, in which some of the electrons are paired. ~~The configurations p^4 to p^6 and d^6 to d^{10} fall in this category.~~

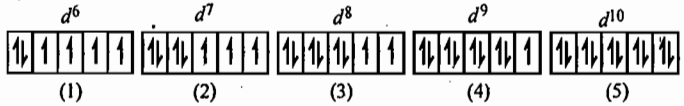
The most stable electronic arrangements of p^4, p^5 and p^6 configurations, in accordance with Hund's rule, are shown below :



The number of electrons with upward spin is 3 in each arrangement giving rise to 3 exchange pairs in each case. The number of electrons with downward spin is 1, 2, and 3, respectively, in arrangements (1), (2) and (3). The corresponding number of exchange pairs would be 0, 1 and 3, respectively. The number of electron pairs occupying the same orbital, as can be seen, is 1, 2, and 3 in arrangements (1), (2) and (3), respectively. It may again be emphasised that while the exchange pairs give rise to exchange energy, the pairing of electrons gives rise to pairing energy.

As a consequence of exchange energy and pairing energy, the net energy change in the case of electronic arrangements (1), (2) and (3) would be $(-3E+P)$, $(-4E+2P)$ and $(-6E+3P)$, respectively. It may be recalled that while exchange energy tends to decrease, the pairing energy tends to increase the energy of the arrangement. This means that the relative stabilities of the three arrangements cannot be predicted on the basis of the aggregates of exchange energy and pairing energy *alone*. Experimentally, the arrangement (3) is found to be more stable than arrangements (1) and (2). This shows that there must be some other stabilising factor in favour of (3).

The most stable electronic arrangements of d^6, d^7, d^8, d^9 and d^{10} configurations, in accordance with Hund's rule, are given below :



Based on the number of exchange pairs and the electron pairs, the aggregates of exchange energy and pairing energy in the above electronic arrangements would be $[-10E+P]$, $[-(10+1)E+2P]$, $[-(10+3)E+3P]$, $[-(10+6)E+4P]$ and $[-(10+10)E+5P]$, as we move from configuration d^6 to d^{10}. On the basis of the same considerations as mentioned above, it can be argued that in this case also, it is not possible to predict as to which of the above arrangements would be most stable. According to experiments, electronic arrangement (5) is more stable than the rest of the arrangements which cannot be accounted for on the basis of exchange energy and pairing energy *alone*.

This shows that *as in the case of arrangement* (3) of p^6 configuration, *there must be some other stabilising factor in favour of arrangement* (5) of d^{10} configuration. This factor is the ***effect of the symmetrical distribution of charge***, as illustrated below.

Symmetrical Distribution of Charge. In order to understand the effect of the symmetrical distribution of charge in orbitals on the stability of electronic arrangements, let us recall the shapes of the various sets of orbitals, one by one. The *s orbital* is *spherical* in shape which implies that the electronic charge would be distributed uniformly in all directions whether there is one or two electrons present in the orbital.

Of the three *p* orbitals, the orbital p_x is symmetrical along the *x*-axis while the orbitals p_y and p_z are symmetrical along the *y*-axis and *z*-axis, respectively. If we place an electron in p_x orbital, *i.e.*, we take into consideration p_x^1 configuration, the electronic charge would be mainly concentrated in the *x*-direction only. Likewise, in p_y configuration, the electronic charge would be mainly concentrated in the *y*-direction. Similarly, in $p_x^2 p_y^1$ configuration, the electronic charge would be mainly concentrated in the *xy* plane. Likewise, the electronic charge would be concentrated more along the *x*-direction in the configuration $p_x^2 p_y^1 p_z^1$ and ~~more in the plane *xy* in the configuration $p_x^2 p_y^1 p_z^1$. It is evident that in~~ all the *p* configurations mentioned above, *the charge is not evenly spread along all the directions.* In other words, *the distribution of charge is non-uniform or unsymmetrical.* On the other hand, *the distribution of charge in the configurations p_x^1 p_y^1 p_z^1* and *p_x^2 p_y^2 p_z^2 would be uniform or symmetrical in all directions.*

Configurations with even or uniform or symmetrical distribution of charge in all directions would evidently be associated with lower energy and hence higher stability than the configurations with unsymmetrical distribution of electronic charge.

To sum up : *A symmetrical distribution of electronic charge leads to a decrease in energy and hence an increase in the stability of the system.*

It follows from the above discussion that of all the d configurations, the configurations d^1_{xy} d^1_{yz} d^1_{zx} $d^1_{x^2-y^2}$ $d^1_{z^2}$ and d^2_{xy} d^2_{yz} d^2_{zx} $d^2_{x^2-y^2}$ $d^2_{z^2}$ would have a *uniform or symmetrical distribution of charge in space*. Therefore, these configurations would be more stable than all other d configurations.

- It can thus be concluded *that electronic arrangements with exactly half-filled or completely filled degenerate orbitals would be more stable than any other electronic arrangement.*

Promotional Energies. Stability of Configurations having Non-degenerate Orbitals

The energy required to promote an electron from a lower energy orbital to a higher energy orbital is known as **promotional energy.** This may be designated as ΔE. Both ΔE and pairing energy (P) are positive.

Let us consider a case in which the lower energy orbital contains two electrons while the higher energy orbital is empty. The energy difference between the two orbitals, *viz.*, ΔE, is the promotional energy, as already stated. This is shown in Fig. 21. In arrangement (a), the two electrons are present in the lower energy orbital. Such an arrangement would be stable if the pairing energy, *i.e.*, the energy required to pair the two electrons in the same orbital is less than the promotional energy, *i.e.*, $P < \Delta E$. If, however, the promotional energy is less than the pairing energy, the two electrons would get unpaired and one of these would get promoted to the higher energy orbital, as shown in arrangements (b) and (c). This shows that if $\Delta E < P$, the arrangements (b) and (c) would be more stable than the arrangement (a).

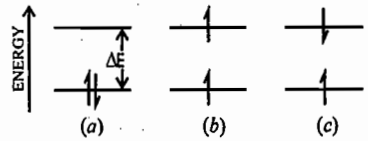
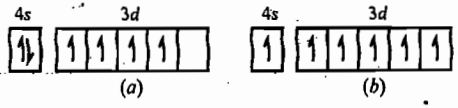


Fig. 21. Possible electron distributions in the two energy levels for a two-electron system :
(a) Both the electrons are present in ground state.
(b) Electrons are evenly distributed with parallel spins
(c) Electrons are evenly distributed but with antiparallel spins.

Out of arrangements (b) and (c), the arrangement (b) would be more stable due to parallel spins of both the electrons. The arrangement (b) has one exchange pair of electrons whereas arrangement (c) has none. The presence of an exchange pair lowers the energy of the arrangement, as already illustrated. Thus, Hund's rule of maximum multiplicity is also applicable to non-degenerate orbitals *provided they have comparable energies, i.e.*, $\Delta E \leq P$. In such cases, the arrangement containing electrons having maximum number of parallel spins and thereby maximum number of exchange pairs would be most stable.

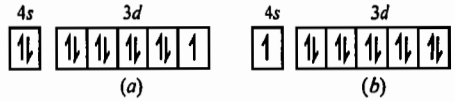
Let us apply the above considerations to some specific cases.

1. Configuration of chromium atom. The two possible outer electronic configurations of Cr atom ($Z = 24$) are (a) $4s^2\,3d^4$ and (b) $4s^1\,3d^5$. The electronic arrangements for these configurations are shown below :



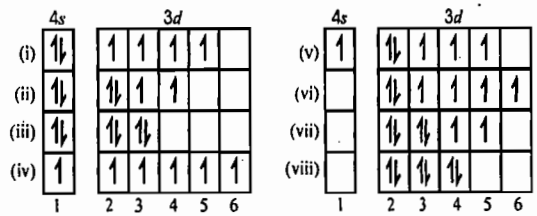
The electronic arrangement (b) is obtained from arrangement (a) by promoting one electron from $4s$ to $3d$ orbital. Since the energy difference between $4s$ and $3d$ orbitals is small, Hund's rule of maximum multiplicity would largely determine the relative stability of the arrangements. The energy of arrangement (a) is $-10E + P$ while that of arrangement (b) is $-15E + \Delta E$. Since ΔE is small, hence arrangement (b) is more stable than arrangement (a). The symmetrical electronic charge distribution in $4s$ and $3d$ orbitals in arrangement (b) further adds to its stability.

2. Configuration of copper atom. The two possible outer electronic configurations for Cu atom ($Z = 29$) are (a) $4s^2\,3d^2$ and (b) $4s^1\,3d^5$. The electronic arrangements for these configurations are shown below :



The electronic arrangement (b) is obtained by promoting electron from $4s$ to $3d$ orbital. Since the energy difference between $4s$ and $3d$ is small, Hund's rule of maximum multiplicity shall largely determine the stability of the arrangement. The energy of arrangement (a) is $-25E + 5P$ while that of arrangement (b) is $-25E + 5P + \Delta E$. On energy considerations, arrangement (b) should be slightly less stable than arrangement (a). But actually arrangement (b) is more stable than (a). Why is it so ? For the answer, we have to take into consideration the type of the electronic charge distribution in arrangements (a) and (b). The electronic charge distribution in the $4s$ orbitals would be *symmetrical* in both the arrangement (a) and (b). In the $3d$ orbitals, however, while the electronic charge distribution is symmetrical in all directions in arrangement (b), it is unsymmetrical in arrangement (a), as has been discussed earlier. The symmetrical charge distribution in arrangement (b) increases the stability of this arrangement to such an extent that it more than overcomes the de-stabilisation due to ΔE. Thus, arrangement (b) is more stable than arrangement (a).

Example 17. Assuming the energy difference between $4s$ and $3d$ orbitals to be small, the following 8 electronic arrangements have been listed for the outer electronic configuration of chromium :



(a) Find out the number of exchange pairs of electrons in each of these arrangements.

(b) Which of these arrangements are not possible according to Aufbau principle.

(c) Which of these arrangements is the most stable ?

Solution : (a) An exchange pair is one which contains electrons *with parallel spins*. The electronic arrangement remains unaltered if the electrons in the said pair exchange their positions. Number of exchange pairs is equal to the number of ways of selecting two electrons out of the electrons having parallel spins in a given arrangement.

In arrangement (i), there are 5 electrons (one $4s$ and four $3d$) with parallel spins. There are **10 exchange pairs**, viz., 1, 2 ; 1, 3 ; 1, 4, ; 1, 5 ; 2, 3 ; 2, 4, 2, 5, ; 3, 4 ; 3, 5 and 4, 5. Mathematically, the number of exchange pairs is given by

$$^5C_2 = \frac{5!}{2!\,3!} = 10$$

In arrangement (ii), there are 6 **exchange pairs** ($= {}^4C_2$) for electrons with upward spins and **1 exchange pair** for electrons with downward spins

The numbers of exchange pairs in the remaining arrangements are as follows :

(iii) **3+3** (iv) **15** (v) **10** (vi) **10** (vii) **6+1** ($viii$) **3+3**

(*b*) According to aufbau principle, the lower energy 4*s* orbital must contain at least one electron before 3*d* orbital starts filling up. Accordingly, **the arrangements (*v*), (*vii*) and (*viii*) are not possible.**

(*c*) **Arrangement (iv) is the most stable** because

(*i*) it has maximum electron exchange energy ($= -15\,E$) and

(*ii*) the electronic charge distribution is *symmetrical in all directions* since the set contains degenerate half-filled orbitals.

Example 18. Some of the possible outer electronic arrangements for sulphur atom are as shown:

Taking into consideration, the exchange energy and pairing energy, work out the most stable electronic arrangement for the sulphur atom.

Solution : The number of exchange pairs for the various arrangements are as follows :

Arrangement (1) : There are 6 exchange pairs for electrons with upward spin and 1 exchange pair for electrons with downward spin.

Arrangement (2) : 3 + 3 Arrangement (3) : 6 + 1

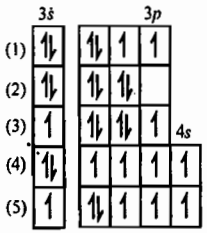
Arrangement (4) : 10 + 0 Arrangement (5) : 10 + 0

Hence, the aggregates of exchange energy, pairing energy and promotional energy in various arrangements are as follows :

Arrangement (1) $-(6+1)\,E+2P$ Arrangement (2) $-(3+3)\,E+3P$

Arrangement (3) $-(6+1)\,E+2P+\Delta E$ Arrangement (4) $-10\,E+P+\Delta E$

Arrangement (5) $-10\,E+P+\Delta E$



E is the magnitude of exchange energy, P is the magnitude of pairing energy and ΔE is the magnitude of promotional energy.

The energy difference, ΔE, between 3*s* and 3*p* and between 3*p* and 4*s* is much greater than the aggregate of exchange energy and pairing energy in any of the arrangements. Hence, electron excitation from 3*s* to 3*p* or from 3*p* to 4*s* is energetically unfavourable.

This rules out the possibility of arrangements (3), (4) and (5).

Exchange energy (stabilising energy) is more and pairing energy (destabilising energy) is less in arrangement (1) as compared to (2). Hence, **arrangement (1) is the most stable.**

QUESTIONS

1. Describe briefly the limitations of Bohr's theory of atomic structure.
2. (*a*) What do you understand by dual character of matter ? Derive de Broglie relation. How was it verified experimentally ?

   (*b*) How are matter waves different from electromagnetic waves ?

   (*c*) Why is the wave nature of matter not apparent in our daily observations ?
3. What do you understand by Heisenberg's uncertainty principle and concept of probability ? Explain that the concept of probability follows from Heisenberg's uncertainty principle.
4. Write down the Schrodinger equation for the wave mechanical model of an atom. Name the three quantum numbers of an electron which are yielded by the solution of this equation. Explain the significance of each quantum number.
5. (*a*) Explain the terms : principal quantum number, angular momentum quantum number, magnetic quantum number and electron spin and magnetic spin quantum number. Explain the significance of each of these numbers.

   (*b*) Discuss in details the Pauli's exclusion principle. Explain how with the help of this principle it is possible to determine the maximum number of electrons that can occur in any energy level.
6. Derive Schrodinger wave equation. Discuss the significance of the wave function ψ in this equation.
7. Write down the equations for the solutions of Schrodinger equation in terms of polar coordinates.
8. What are radial and angular wave functions. What information can we get from these functions ?
9. Derive an expression for the angular wave function in terms of the spherical harmonics.

10. Show from the complete wave function for an *s* orbital that the distribution of electronic charge in an *s* orbital is spherically symmetrical.
11. Write down the complete wave functions for *p* orbitals. From these derive real angular wave functions for these orbitals. Illustrate which real angular wave function corresponds to which *p* orbital.
12. Show from the complete wave function for *p* orbitals that the distribution of charge in *p* orbitals is dumb-bell sphaped.
13. Derive expressions for complete wave functions of *d* orbitals. Explain how these expressions account for the various shapes of the *d* orbitals.
14. Justify + and – signs in various parts of d_{xy}, $d_{x^2-y^2}$, p_x, p_y and p_z orbitals. Do these signs have any relation with charge ?
15. What is meant by screening effect ? Describe Slater's rules. How are these rules useful in determining the effective nuclear charge for any electron in an atom ? What are the limitations of these rules ?
16. Describe in details the Slater's rules. Discuss their important applications.
17. (*a*) What are the main rules for filling of orbitals ? Illustrate your answer with suitable examples.

    (*b*) What values of *n* will permit (*i*) only *s* type of orbital (*ii*) *s*, *p* and *d* types of orbitals ?
18. (*a*) What do you understand by Hund's rule of maximum multiplicity. Apply this rule to show the electronic configurations of oxygen and nitrogen.

    (*b*) Which of the following electronic configurations is correct for the copper atom : $[Ar]3d^{10}4s^1$ or $[Ar]3s^9 4s^2$? Given reason. **[Ans. $[Ar]3d^{10}4s^1$]**

    (*c*) Write the possible values of *l* and *m* for an electron in 3*p* orbital. **[Ans. $l = 1, m = -1, 0, +1$]**
19. (*a*) What is the difference between the energy level diagram of the hydrogen atom and that of a multi-electron atom ? How would you account for this difference ?

    (*b*) Arrange the following orbitals in order of increasing energy for a multi-electron atom :

    1*s*, 3*s*, 5*s*, 2*p*, 4*p*, 5*p*, 3*d*, 4*d*, and 4*f*.
20. Discuss the basis of Hund's rule.
21. Explain the terms : exchange pair, exchange energy, pairing energy and promotional energy.
22. Illustrate the difference between electronic configuration and electronic arrangement.
23. Explain carefully why exactly half-filled and completely filled orbitals are more stable than other orbitals. Illustrate your answer giving suitable examples.
24. Electrons prefer to fill those orbitals which thereby get either exactly half-filled or fully filled. Why is it so. Explain the configurations of Cu and Cr.

2 PERIODIC TABLE AND ATOMIC PROPERTIES

The eighteenth and nineteenth centuries witnessed rapid development of chemistry in all directions. During this period, several new elements were discovered. These elements were found to have numerous properties. It was realised that instead of studying the properties of all these elements *individually*, it would be more convenient to divide them into a few groups or families such that each group contains a number of elements with similar properties.

The first important attempt to divide elements on the basis of their physical and chemical properties was made by Mendeleeff, a Russian chemist, who observed that *when elements are arranged in the order of increasing atomic weights, elements with similar properties appear at regular intervals.* In 1869, he enunciated a law, known as the **periodic law**, which states :

The physical and chemical properties of elements are periodic functions of their atomic weights.

Henry Moseley, a brilliant young British physicist, in 1912, discovered a new property of elements, called **atomic number**, which provided a better basis for the periodic arrangement of the elements. As is well known, atomic number of an element is equal to the number of protons present in the nucleus (or the number of electrons present outside the nucleus) of the atom of the element. The periodic law was, therefore, modified. The **modern periodic law** may thus be stated as :

The properties of elements are periodic functions of their atomic numbers.

Periodic Table. A table in which elements are arranged in the order of increasing atomic number in the manner that the elements with similar properties fall in the same vertical column is known as the **periodic table.** The elements which fall in the same column and resemble one another in their properties are said to belong to the same **group** or **family** of elements. Thus, elements belonging to one particular group or family resemble one another quite closely but differ from the elements belonging to the other groups quite appreciably.

Various forms of periodic table have been put forth from time to time. The fundamental principle in each case, however, has been the same as enunciated in the modern periodic law.

We shall consider only the **modern form,** known as the **long form** of the periodic table.

LONG FORM PERIODIC TABLE

The objective of the periodic table is to *organise and systematise the chemistry of the elements.* The long form periodic table serves this objective very well. It may be recalled that the number of elements known at present is more than 100 including those prepared artificially through nuclear reactions in recent times. A broad study of the characteristics of various groups gives us a fairly good insight into the general behaviour and important properties of most of the elements.

The long form periodic table also helps us to understand the reason why certain elements resemble one another and why they differ from other elements in their properties. The arrangement of elements in this table is also in keeping with their electronic configurations.

Another significant feature of the long form periodic table is that it *helps us to understand the cause of periodicity of properties* and *the reason why similar properties recur at certain regular intervals, i.e.,* after 2, 8, 8, 18, 18 and 32 elements. The numbers, 2, 8, 18 and 32 are, sometimes, referred to as *magic numbers.*

The **long form** periodic table is given at the end of the book. This is constructed by arranging elements in the order of increasing atomic number. The *horizontal rows constitute* **periods** while the *vertical rows constitute* **groups.**

Periods. There are seven periods or horizontal rows in the table. The **first period** is made up of only **2 elements**, namely, *hydrogen* and the noble gas *helium*. The properties of hydrogen are somewhat similar to those of alkali metals (Group 1) and also similar to those of the halogens (Group 17) in some respects. However, it is more reasonable, though not entirely logical, to place it in Group 1. Helium is a typical noble gas and belongs to Group 18.

The second period contains **8 elements.** It starts with *lithium,* an alkali metal of Group 1. The other elements placed in succeeding groups are : *beryllium, boron, carbon, nitrogen, oxygen, fluorine* and lastly, *neon*, a noble gas. Thus, this period also ends with a noble gas placed in Group 18.

The **third period** which begins with *sodium* also contains **8 elements.** These are : *sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine* and the noble gas *argon*. The first seven elements are placed in Groups 1, 2, 13–17 while argon is placed in Group 18. This period, like the first two periods, also ends with a noble gas.

The **fourth period** begins, again, with an alkali metal, potassium. We have to pass now seventeen other elements before we come across a noble gas (krypton). This period, therefore, consists of **18 elements** from potassium ($Z = 19$) to the noble gas, krypton ($Z = 36$). The first two elements, potassium and calcium, show recurrence of properties. Thus, potassium resembles lithium and sodium of Group 1 in which it falls while calcium resembles beryllium and magnesium of Group 2 in which it falls. The difficulty arises after calcium because the next element, scandium, has very little in common with aluminium. We have to pass through 10 elements, from scandium to zinc, before we get an element, gallium, which shows resemblance with aluminium of Group 13. Gallium, therefore, is placed under aluminium in Group 13. The succeeding five elements, namely, germanium, arsenic, selenium, bromine and krypton, are placed, correctly, in Groups 14, 15, 16, 17 and 18, respectively. Of the 18 elements belonging to the fourth period, 8 elements, namely, potassium, calcium, gallium, germanium, arsenic, selenium, bromine and krypton ($Z = 19$, 20 and 31 to 36) are said to be **normal** or **main group** or **representative elements** as they resemble elements of the first two periods under which they are placed. The remaining 10 elements, from scandium to zinc ($Z = 21$ to 30) are called **transition elements.** The difference between the normal and the transition elements lies in the manner of the entrance of electrons. Since chemical properties are determined largely by the number of electrons in the outermost shell, the properties of transition elements, in which the outermost shell (4*s*) continues to have the same number of electrons, do not change radically. In the case of normal elements, on the other hand, the gradation of properties on moving across a period, is well pronounced. The transition elements differ from the normal elements in several other respects also, for example, in showing variable valency, forming coloured ions and being *paramagnetic.* ~~The fourth period is said to be the first long period.~~

The **fifth period**, like the fourth period, also consists of **18 elements** ($Z = 37$ to 54). It begins with rubidium ($Z = 37$) and ends with xenon ($Z = 54$) which, again, is a noble gas. Of the 18 elements, eight ($Z = 37$, 38 and 49 to 54) are normal elements and the remaining ten ($Z = 39$ to 48) are transition elements.

The **sixth period** is also a long period. It consists of **32 elements** ($Z = 55$ to 86). They include 8 normal elements ($Z = 55$, 56 and 81 to 86), 10 transition elements ($Z = 57$ and 72 to 80) and 14 **rare earth elements** ($Z = 58$ to 71). The *rare earth elements* begin with cerium ($Z = 58$) and continue upto lutetium ($Z = 71$). They are so called because they occur very *rarely*. The rare earths are so similar to

one another and also to *lanthanum* that they are called collectively as **lanthanides**. If these elements are placed horizontally in the same group, there will be undue expansion of the table. To avoid this, they are placed as a separate series below the periodic table, as shown.

The **seventh period**, as shown, consists of radioactive elements with atomic numbers 87 and beyond. So far, elements upto atomic number 108 only have been discovered. As mentioned above, elements beyond atomic number 92 have been prepared artificially through nuclear reactions. Just as the elements after lanthanum are called lanthanides, similarly, the elements after **actinium**, *i.e.*, from thorium to lawrencium ($Z = 90$ to 103) are called **actinides**. These elements, too, are placed as a separate series below the periodic table, as shown. The elements beyond uranium which have been prepared artificially by nuclear reactions are called **transuranic elements**. The common names of elements with atomic numbers 93 to 105 are : *neptunium, plutonium, americium, curium, berkeylium, californium, einsteinium, fermium, mendelevium, nobelium, lawrencium, kurchatovium* and *hahnium*. The IUPAC convention of 1977 has suggested new names for elements having atomic numbers beyond 100. These names are un-nil-unium (Unu, 101), un-nil-bium (Unb, 102), un-nil-trium (Unt, 103), un-nil-quadium (Unq, 104), un-nil-pentium (Unp, 105), un-nil-hexium (Unh, 106), un-nil-septium (Uns, 107), un-nil-octium (Uno, 108), un-nil-ennium (Une, 109), un-un-nilium (Uun, 110), un-un-unium (Uuu, 111), un-un-bium (Uub, 112).

Groups. The elements arranged in vertical columns of the periodic table are called **groups**. In the recent long form periodic table, the transition elements are also taken into account while numbering the groups. All the groups are numbered in Arabic numberals. The groups headed by H and He are numbered as Groups 1 and 2, respectively. The groups headed by Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn are numbered as Groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12, resectively. The groups headed by B, C, N, O, F and Ne are numbered as Groups 13, 14, 15, 16, 17 and 18. If the transition elements are taken out, the rest of the elements (the normal elements), excluding hydrogen and helium, arrange themselves in various groups as shown below :

1	2	13	14	15	16	17	18
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
Fr	Ra						

The elements of each group are now analogous to one another. For example, lithium and sodium of Group 1 resemble the elements potassium, rubidium, cesium and francium while beryllium and magnesium of Group 2 resemble the elements calcium, strontium, barium and radium. Likewise, fluorine and chlorine of Group 17 have properties in common with bromine, iodine and astatine, and so on. The elements of Group 18 (noble gases) lie in between the most electronegative halogens and the most electropositive alkali metals.

Cause of Periodicity

We have seen already that elements with similar properties occur at regular intervals in the periodic table. Such elements fall in the same vertical column, *i.e.*, the same group. *The recurrence of similar properties of elements after certain regular intervals when they are arranged in the order of increasing atomic numbers is called* **periodicity**. A question arises : What is the cause of this periodicity ?

To answer this question, we may consider elements of Groups 1, 17 and 18. The electronic configurations of these elements are given in Table 1.

TABLE 1

Electronic Configurations of Elements of Groups 1, 17 and 18

Elements of Group 1	Elements of Group 17	Elements of Group 18
Li : $1s^2\,2s^1$		He : $1s^2$
Na : $1s^2\,2s^2p^6\,3s^1$	F : $1s^2\,2s^2p^5$	Ne : $1s^2\,2s^2p^6$
K : $1s^2\,2s^2\,p^6\,3s^2p^6\,4s^1$	Cl : $1s^2\,2s^2p^6 3s^2p^5$	Ar : $1s^2\,2s^2p^6\,3s^2p^6$
Rb : $1s^2\,2s^2p^6\,3s^2p^6\,d^{10}\,4s^2p^6\,5s^1$	Br : $1s^2\,2s^2p^6\,3s^2\,p^6d^{10}\,4s^2p^5$	Kr : $1s^2\,2s^2p^6\,3s^2p^6d^{10}\,4s^2p^6$
Cs : 2, 8, 18, 18, $5s^2p^6\,6s^1$	I : 2, 8, 18, 18, $5s^2p^5$	Xe : 2, 8, 18, 18, $5s^2p^6$
Fr : 2, 8, 18, 32, 18, $6s^2p^6\,7s^1$	At : 2, 8, 18, 32, 18, $6s^2p^5$	Rn : 2, 8, 18, 32, 18, $6s^2p^6$

The elements belonging to each group have similar properties but they differ from the elements belonging to the other groups. For example, all the alkali metals belonging to Group 1 are *strongly metallic* and *electropositive* as they form cations (*e.g.*, Li^+, Na^+) very readily. The halogens belonging to Group 17 are *strongly non-metallic* and *electronegative* as they form anions (*e.g.*, F^-, Cl^-) very readily. The elements of Group 18 which connect the two extreme types of elements are *chemically least reactive.*

We may now look at their electronic configurations (Table 1). Since electrons in the inner shells do not, ordinarily, take part in any chemical combination, we have to examine only the *outermost electronic configurations* of these elements. We find that *all the elements belonging to a particular family (or group) have similar outer electronic configuration*. Thus,

(*i*) All the elements of Group 1 have *one* electron in the outermost *s* orbitals preceded by the noble gas configuration (ns^2p^6 ; for Li, $1s^2$). Their outer electronic configuration may thus be written as ns^1.

(*ii*) All the elements of Group 17 have *seven* electrons in the outermost level. Two of these electrons are present in the *s* orbitals while the remaining five are present in the *p* orbitals. Their outer electronic configuration is ns^2p^5.

(*iii*) All the elements of Group 18, except helium, have *eight* electrons in the outer level, two of which are accommodated in the *s* orbitals and the remaining six fill the *p* orbitals *completely*. In helium, there are only two electrons both of which are present in 1*s* orbital which is, therefore, completely filled. Thus, all the orbitals are fully occupied in these elements, which, as already mentioned, are chemically inert. Their outer electronic configuration is ns^2p^6 except for helium which is $1s^2$.

The **cause of periodicity** in properties of elements appears to lie, therefore, in the *recurrence of similar outer electronic configurations of their toms at certain regular intervals.*

Cause of Recurrence of Properties at Regular Intervals of Atomic Numbers. We have seen already that elements with similar properties recur at certain regular atomic number intervals in the periodic table. These intervals are : 2, 8, 8, 18, 18, 32 and 32. In other words, we have to pass 2, 8, 18 and 32 elements as the case may be before we come across an element with similar properties. A question arises : Why do we have these particular numbers called *magic numbers* ? The answer is as follows :

As has been discussed in the previous pages and as has been shown clearly in the periodic table affixed at the end of the book, *each period begins with a new major energy level*. The energy level

diagram of various orbitals belonging to different major energy levels is shown in Fig. 1.

As can be seen, for $n = 1$, there is only one orbital (1*s* orbital). We may recall that each orbital can have a maximum of two electrons. We may also recall that one electron is added at a time as we move from one element to the next in the periodic table. It is evident, therefore, that since there is only one orbital associated with $n = 1$, there can be only 2 *elements in the first period.*

When $n = 2$, there are *four* orbitals (one 2*s* and three 2*p* orbitals) as shown in Fig. 1. Hence, *the number of elements in the second period will be* 8.

When $n = 3$, there are *nine* orbitals (one 3*s*, three 3*p* and five 3*d* orbitals). However, the 3*d* orbitals are associated with higher energies than even the 4*s* orbitals. These orbitals, therefore, cannot be occupied before the complete filling of the 4*s* orbitals. The result is that corresponding to $n = 3$, *only four orbitals* (one *s* and three *p* orbitals) *can be occupied.* Hence, *the number of elements in the third period is also* **8.**

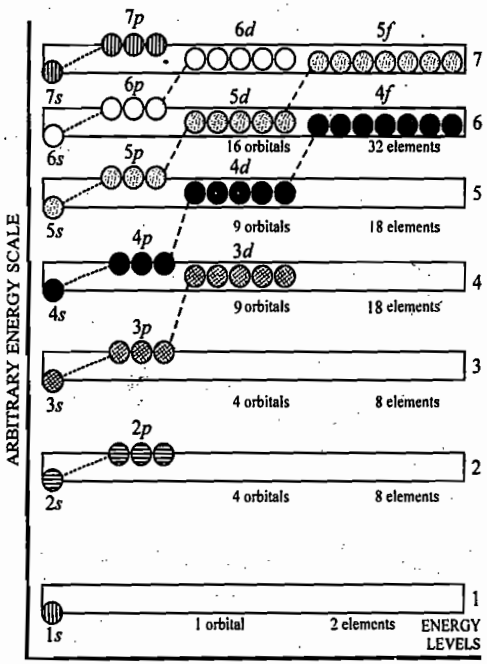


Fig. 1. The energy level diagram depicting energies of various orbitals belonging to different major energy levels.

Following the same line of argument, it can be seen on reference to Fig. 1, that when $n = 4$, there are *nine* orbitals (one 4*s*, five 3*d* and three 4*p* orbitals) to be filled up and hence *the number of elements in the fourth period is* **18.** This is the first long period.

Similarly, when $n = 5$, there are, again, only *nine* orbitals (one 5*s*, five 4*d* and three 5*p* orbitals) to be filled up and hence *the number of elements in the fifth period is also* **18.**

Finally, when $n = 6$ and $n = 7$, there are *sixteen* orbitals to be filled in each case (Fig. 1). Therefore, *there are* **32** *elements in the sixth period and there will also be* **32** *elements in the seventh period* when all of them are discovered. At present, the seventh period is incomplete and contains only 22 elements.

The above discussion clearly explains why the number of elements in the successive periods of the periodic table happens to be 2, 8, 8, 18, 18, 32 and 32. The elements with similar properties, therefore, also appear after intervals of 2, 8, 8, 18, 18, 32 and 32, as we move along the periodic table in the order of increasing atomic numbers.

Division of Elements into *s, p, d* and *f* Blocks

The elements, as arranged in the long form periodic table, can also be divided into **four blocks** known as *s, p, d* and *f* blocks. This classification depends upon the type of the orbitals (*s, p, d* or *f*) into which the last electron of the atoms of the elements enters.

s Block Elements. *The elements whose atoms receive the last electron in the s orbital of their outermost energy shell* are called ***s* block elements.** This block consists of elements of Groups 1 and 2 in which the *s* orbitals are being progressively filled. The elements of Group 1 have the general ground state electronic configuration ns^1. These are called **alkali metals.** The elements of Group 2 have the general ground state electronic configuration ns^2. These are called **alkaline earth metals.**

***p* Block Elements.** *The elements whose atoms receive the last electron in their p orbitals are called* ***p* block elements.** The atoms of elements of Groups 13, 14, 15, 16, 17 and 18 having one, two, three, four, five and six electrons, respectively, in *p* orbitals (while *s* orbitals are already filled) in the outermost shells, constitute *p block.* The general electronic configuration for the atoms of the elements of this block may be written as $ns^2\ np^{1-6}$.

***d* Block Elements.** The atoms of elements of Groups 3 to 12 lying between *s* and *p* blocks have the *s* and *p* orbitals (of their outermost principal energy shell) completely filled. The *d* orbitals in the penultimate (inner to the outermost) shell, however, are still empty (cf. periodic table). The last electron in these elements, therefore, enters the *d* orbitals which, thereby, get progressively filled as we move across a period. Thus, *the elements in which the last electron enters the d orbitals of their last but one (penultimate) energy shells are called* ***d* block elements.** The general electronic configurations of *d* block elements may be written as $(n-1)d^{1-10}\ ns^{1-2}$. These elements are also called **transition elements.** This block consists of three rows called *First, Second* and *Third transition series* which involve the filling of 3*d*, 4*d* and 5*d* orbitals, respectively. The elements from scandium ($Z = 21$) to zinc ($Z = 30$) in the fourth period constitute the *First transition series* ; from yttrium ($Z = 39$) to cadmium ($Z = 48$) in the fifth period constitute the *Second transition series* and from hafnium ($Z = 72$) to mercury ($Z = 80$) in the sixth period constitute the *Third transition series.*

***f* Block Elements.** The elements in which the last electron enters the *f* orbitals of their atoms are called ***f* block elements.** In these elements, the last electron enters the third to the outermost (ante penultimate), *i.e.*, $(n-2)f$ energy shell. It consists of two series of 14 elements each placed at the bottom of the periodic table. The first series follows lanthanum, La ($Z = 57$) and the second series follows actinium, Ac ($Z = 89$) in the order of increasing atomic numbers. These series are called **lanthanides** (from cerium to lutetium) and **actinides** (from thorium to lawrencium), respectively. In lanthanides, 4*f* orbitals and in actinides, 5*f* orbitals are being progressively filled.

These four blocks are distinctly shown in the periodic table.

ATOMIC PROPERTIES

Before we are in a position to understand such topics as chemical bonding between atoms and geometry and shapes of molecules, it is necessary to have adequate knowledge of certain atomic properties. These properties are : (*i*) *Sizes of Atoms and Ions* (*ii*) *Ionisation Energy* (*iii*) *Electron Affinity* and (*iv*) *Electronegativity.*

SIZES OF ATOMS AND IONS

The sizes of atoms and ions are generally reflected in the magnitude of their respective radii. The **radius of an atom** or **an ion** may be taken, in the ordinary sense, as *the distance between the centre of the nucleus and the outermost shell of electrons.* If the atom or the ion is assumed to be spherical, the atomic or ionic radius corresponds to the radius of the sphere. However, the absolute size of an atom is difficult to define because of the following reasons :

(*i*) According to quantum mechanics, *there is no certainty* with regard to the *exact position* occupied by electrons at any time. Theoretically, an electron, at times, may be very close to the nucleus while at other times it may be far away from the nucleus. In other words, it is not possible to define any boundary for an atom or an ion. The electron probability is never zero even at very large distances from the nucleus.

(*ii*) It is not possible to have isolated atoms and the probability distribution of electrons in an atom is appreciably influenced by the presence of other atoms in its environment. As a result, the size of an atom or an ion would change with change in the environment.

Despite these limitations, we need to have some *operational definition* of the radius of an atom or an ion. This is necessary in order to get comparative values for atoms and ions of different elements and also to explain a number of chemical phenomena.

There are three **operational concepts** of these radii. These are :

(1) *Covalent Radius* (2) *Van der Waals Radius* and (3) *Ionic Radius.*

1. Covalent Radius

One half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule, is taken as the **covalent radius** *of the atom of that element.* While defining the covalent radius as above, it is assumed that atoms are hard, incompressible spheres which are touching each other in normal covalent bond formation. However, atoms are neither fully incompressible nor do they touch each other in a covalent molecule. Therefore, the covalent radii calculated on the basis of the above definition cannot be regarded as exact.

The distance between the centres of any two neighbouring atoms (*viz.*, the internuclear distance) can be measured by X-ray diffraction or spectroscopic studies. For instance, we know from spectroscopic data that the distance between the nuclei of two hydrogen atoms in a H_2 molecule is 0·74 Å. Half of this distance, *viz.*, 0·37 Å, gives the covalent radius of the hydrogen atom.

Similarly, the internuclear distances in Cl_2 and Br_2 molecules are 1·98 Å and 2·28 Å, respectively. Accordingly, the covalent radii of chlorine and bromine atoms would be 0·99 Å and 1·14 Å, respectively.

Once we know the covalent radii of some of the elements, we can calculate the covalent radii of other elements from the internuclear distances between the elements whose covalent radii are known and those whose covalent radii are to be determined. For this purpose, the covalent radii are taken to be **additive**. For instance, the covalent radius of carbon is known to be 0·77 Å and the internuclear distance between C and H atoms in CH_4 is found to be 1·14 Å. Therefore, the covalent radius of H atom is 1·14 – 0·77 = 0·37 Å. This value is the same as obtained spectroscopically.

However, the length of a bond between two unlike atoms, *i.e.*, atoms differing appreciably in their electronegativities, is shorter than the sum of their covalent radii. The shortening of bond length is due to the polarity developed in the bond because of difference in electronegativities of the two atoms forming the covalent bond. Consider a covalent bond A – B. If A is more electronegative than B, the electronic charge between A and B which is responsible for bond formation, would be shifted nearer to A resulting in the accumulation of excess negative charge on A and a corresponding excess positive charge on B. *This would result in additional electrostatic attraction between* A and B which would bring A and B further nearer to each other. In other words, the *bond between* A *and* B *gets shortened.* The greater the electronegativity difference between A and B, the shorter would be the bond distance and the smaller would be the covalent radii of A and B as obtained from the bond length, *i.e.*, the internuclear distance.

According to Shoemaker and Stevenson, the actual bond distance between A and B is given by the relation

$$r_{A-B} = r_A + r_B - 0{\cdot}09\,(\chi_A - \chi_B) \qquad ...(1)$$

where r_A is the normal covalent radius of A (equal to half the bond distance A – A), r_B is the normal covalent radius of B (equal to half the bond distance B – B) in Å and χ_A and χ_B are the electronegativities of A and B, respectively. Several modifications of this equation have been suggested to improve upon the evaluation of r_{A-B}. The one suggested by Porterfield is

$$r_{A-B} = r_A + r_B - 0{\cdot}07\,(\chi_A - \chi_B)^2 \qquad ...(2)$$

The covalent radius of an element determined from a double or a triple bond is shorter than the normal covalent radius of the same element determined from a single bond. Thus, the covalent radius of C in ethane is 0·77 Å, in ethylene 0·67 Å and in acetylene it is 0·60 Å. This is due to the fact that in a double or a triple bond, in addition to overlapping of sigma orbitals, there is overlapping of pi orbitals as well. The additional overlapping of pi orbitals results in bringing the two atoms closer thereby reducing the bond length and the covalent radius.

The electron charge cloud around a singly bonded atom is taken as spherically symmetrical. But, this is certainly not so in the case of a multiple bonded atom. The electron charge cloud is so much distorted that it cannot be called *spherical* by any stretch of imagination. In the absence of a symmetrical spherical distribution of charge, it is not proper to call the covalent radius determined for a doubly or a triply bonded atom as 'radius' at all. When there is no sphere, there is no radius, evidently.

Although the covalent radii are not always constant, yet the average covalent radii calculated from non-polar single covalent bonds are quite helpful in determining approximate bond distances in actual or hypothetical compounds.

Most of the metals do not form covalent compounds except for those forming covalent hydrides and organometallic compounds. It is, therefore, not possible to determine the covalent radii of metals. However, *atomic volumes* of metal atoms can be easily determined by dividing their atomic masses by their respective densities. The radii calculated from *atomic volumes* are called **metallic radii**. The covalent radii determined from covalent metal hydrides and organometallic compounds and metallic radii determined from atomic volumes of metal atoms, are found to have almost similar values. It is, therefore, immaterial which term we use for radii of metal atoms.

In many cases, the size of an atom in free state and its size determined from a single, non-polar covalent bond are almost the same. Therefore, the terms covalent radii and atomic radii have been used synonymously in many books.

The covalent radii of elements belonging to various groups of the periodic table are given in Table 2.

TABLE 2

Covalent Radii (Å) of Various Elements

Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	*Group 18
H 0·37							He 0·93
Li 1·34	Be 0·90	B 0·82	C 0·77	N 0·75	O 0·74	F 0·72	Ne 1·31
Na 1·54	Mg 1·36	Al 1·18	Si 1·11	P 1·06	S 1·09	Cl 0·99	Ar 1·74
K 2·03	Ca 1·74	Ga 1·26	Ge 1·22	As 1·19	Se 1·16	Br 1·14	Kr 1·89
Rb 2·16	Sr 1·92	In 1·44	Sn 1·41	Sb 1·38	Te 1·35	I 1·33	Xe 2·09
Cs 2·35	Ba 1·98	Tl 1·48	Pb 1·47	Bi 1·46	Po –	At –	Rn 2·14

*The radii for noble gases are only the van der Waals radii. (see page 66)

It may be emphasised here that the **noble gases** which consist of monoatomic molecules, ordinarily, do not form any covalent bonds. In crystals of noble gases, therefore, no chemical forces are operating between the atoms. The van der Waals forces are the only attractive forces in these cases. Hence, *the atomic radii of noble gas atoms are only the van der Waals radii* which represent the distance of closest approach of the two adjacent atoms of the noble gas concerned in the solid state.

Periodic Trends in Covalent Radii. Generally speaking, *the covalent radii decrease in moving from left to right in any given* **period** and *increase in moving from top to bottom in any given* **group**. Explanation for these variations is given below.

Variation of covalent radii in a period. The variation of covalent radii in a period can be explained easily on the basis of electronic configurations and the effective nuclear charges. Table 3 gives the covalent radii of the elements of the second period. The effective nuclear charges (Z_{eff}) given in the table are calculated with the help of the Slater's rules, as discussed in Chapter 1.

TABLE 3

Covalent Radii of Elements of the Second Period of the Periodic Table

Element	Li	Be	B	C	N	O	F
Atomic number	3	4	5	6	7	8	9
Z_{eff} for K electrons	2·70	3·68	4·71	5·81	6·80	7·79	8·69
Z_{eff} for L electrons	1·30	1·95	2·60	3·25	3·90	4·55	5·20
Electronic configuration	$1s^2 2s^1$	$1s^2 2s^2$	$1s^2 2s^2p^1$	$1s^2 2s^2p^2$	$1s^2 2s^2p^3$	$1s^2 2s^2p^4$	$1s^2 2s^2p^5$
Covalent radius (Å)	1·34	0·90	0·82	0·77	0·75	0·73	0·72

Since the last electron in all these elements is added to L shell, one would expect their sizes (and hence their covalent radii) to be the same. But a glance at Table 3 reveals that the covalent radii are not the same. They go on decreasing with increase in the atomic number within the period. This can be explained as follows :

The greater the effective nuclear charge, the greater would be the force with which the electron is pulled towards the nucleus. It is clear from Table 3 that effective nuclear charge felt by both K and L shell electrons goes on increasing from Li to F. As a consequence, the K as well as L shell electrons tend to lie closer and closer to the nucleus. Thus, there is more and more contraction of both K and L shells and hence there is more and more reduction in the covalent radii in moving from left to right across the period (*i.e.*, from Li to F). The same trend is shown by the elements of the third and subsequent periods as well (Table 2). Since effective nuclear charge felt by K electrons is more than that felt by L electrons, K shell will get contracted to a greater extent than the L shell.

TABLE 4

Atomic Radii of Alkali Metals

Alkali metal	Atomic number	Atomic radius (Å)
Li	3	1·34
Na	11	1·54
K	19	1·96
Rb	37	2·11
Cs	55	2·55

Variation of covalent radii in a group. In order to understand the change in the size of the atoms in the **same group**, the atomic radii for the alkali metals, reproduced in Table 4, may be considered.

It is seen that there is increase in covalent radius on moving from top to bottom. This may be explained as follows : In moving down a group, the number of the principal shell increases and, therefore, the size of the atom increases. This effect, no doubt, is partly annuled by the drawing in of the electron shells on account of the increasing nuclear charge. But the effect of adding a new shell is so large that it overcomes the contractive effect of the increased nuclear charge. Hence, *the radius of the atom increases in moving from top to bottom in* a **group.**

2. Van der Waals Radius

The van der Waals radius is defined *as one half of the distance between the nuclei of two adjacent identical atoms belonging to two neighbouring molecules of an element in the solid state* (Fig. 2). It is essentially the distance between two non-bonded atoms of two adjacent molecules and is related to

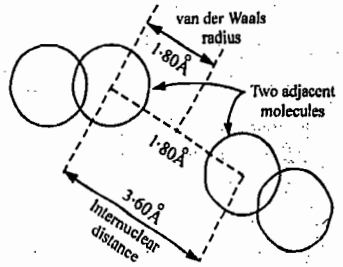


Fig. 2. The van der Waals radius of chlorine.

the effective packing size of the atom when the element is in solid state. The name van der Waals radius is used because the forces existing between the molecules are the van der Waals forces of attraction. The van der Waals radii are obtained from X-ray studies of various elements in the solid state. For example, the internuclear distance between two chlorine atoms of nearest neighbouring molecules is 3·60 Å (Fig. 2). The van der Waals radius of chlorine, therefore, is 1·80 Å.

The van der Waals and covalent radii of some common elements are given in Table 5.

TABLE 5

The van der Waals and Covalent Radii of Some Elements (in Å)

Element	H	N	O	F	Cl	Br	I
Van der Waals radius	1·20	1·50	1·40	1·35	1·80	1·95	2·15
Covalent radius	0·37	0·75	0·73	0·72	0·99	1·14	1·33

As can be seen, covalent radius is *smaller* than van der Waals radius. The reason is that in the formation of a covalent bond, the atoms have to come closer to each other. This also explains why covalent bonds are much stronger than van der Waals forces.

3. Ionic Radius

The ionic radius corresponds to the radius of an ion in an ionic crystal. It may be defined as *the distance from the nucleus of an ion up to which it has influence on its electron charge cloud.* The electron charge cloud, no doubt, may extend theoretically up to a very large distance. However, it is important to characterise each ion by some value. For this purpose, the internuclear distance in any ionic compound is determined from X-ray measurements. *This distance is taken as the sum of the radii of the two ions involved.* Knowing the radius of one, that of the other can be calculated. For example, the distance between the nuclei of Na^+ and F^- ions is determined from X-ray technique. This distance is taken as the sum of the radii of Na^+ and F^- ions. The radius of each of Na^+ and F^- ion is then determined by following the procedure described in Chapter 6 (The Structure of Solids). The radius of Na^+ ion thus obtained may be used to calculate the radii of other anions, such as Cl^-, Br^- and I^- ions, by measuring internuclear distances in NaCl, NaBr and NaI crystals. Similarly, the radius of Cl^- ion may be used to calculate the radii of other cations such as K^+ and Li^+ ions by measuring internuclear distances in KCl and LiCl crystals.

Radii of Cations and Anions. A positive ion, *i.e.*, a **cation**, results from the loss of one or more electrons from the outer shell called the valence shell of an atom. This causes in many cases the removal of the whole of the outer shell of electrons. For example, in lithium there is only one electron in the outer (L) shell. This electron is removed in the change

$$\underset{\substack{1s^2 2s^1 \\ (1{\cdot}34\ \text{Å})}}{Li} \longrightarrow \underset{\substack{1s^2 \\ (0{\cdot}65\ \text{Å})}}{Li^+} + e^-$$

The L shell, therefore, disappears. In magnesium, there are two electrons in the outer (M) shell. Both these electrons are removed in the change

$$\underset{\substack{1s^2 2s^2p^6 3s^2 \\ (1{\cdot}30\text{Å})}}{Mg} \longrightarrow \underset{\substack{1s^2 2s^2p^6 \\ (0{\cdot}65\ \text{Å})}}{Mg^{2+}} + 2e^-$$

The M shell, therefore, disappears in this case also.

Thus, in the formation of a positive ion, the outer shell of electrons is generally removed completely. *The cation*, therefore, *is much smaller than the corresponding atom.* At the same time, with the elimination of one or more *outer* electrons from an atom, the number of electrons decreases while the nuclear charge remains the same. The nuclear charge now acts on a lesser number of electrons. In other words, the effective nuclear charge per electron increases and the electrons are, therefore, pulled in more towards the nucleus than before. This effect also *tends to decrease the radius of the cation.*

The decrease in radius when an atom changes into a cation is shown below in the case of sodium, lead, aluminium, iron and manganese.

Atomic radius of Na = 1·54 Å	Atomic radius Pb = 1·47 Å
Ionic radius of Na^+ = 0·95	Ionic radius of Pb^{2+} = 1·20
Atomic radius of Al = 1·18	Ionic radius of Pb^{4+} = 0·84
Ionic radius of Al^{3+} = 0·50	
Atomic radius of Mn = 1·26	Atomic radius of Fe = 1·26
Ionic radius of Mn^{2+} = 0·80	Ionic radius of Fe^{2+} = 0·76
Ionic radius of Mn^{4+} = 0·46	Ionic radius of Fe^{3+} = 0·64

It is evident that **radius of a cation** is invariably smaller than that of the corresponding atom. The size decreases further with the loss of subsequent electrons when cations of higher valencies are formed.

During the change of an atom into a negative ion, *i.e.*, an **anion**, one or more electrons are added to the valency shell of the atom. As a result, the same nuclear charge acts on a larger number of electrons. In other words, effective nuclear charge per electron is reduced and, therefore, the electrons are held less tightly by the nucleus and the electron charge cloud expands. Thus, the **radius of a negative ion** is invariably larger than that of the corresponding atom. This is shown below in the case of chlorine, bromine, iodine, oxygen, sulphur and nitrogen.

Atomic radius of Cl = 0·99 Å	Atomic radius of O = 0·73 Å
Ionic radius of Cl^- = 1·81	Ionic radius of O^{2-} = 1·45
Atomic radius of Br = 1·14	Atomic radius of S = 1·02
Ionic radius of Br^- = 1·95	Ionic radius of S^{2-} = 1·84
Atomic radius of I = 1·33	Atomic radius of N = 0·75
Ionic radius of I^- = 2·16	Ionic radius of N^{3-} = 1·71

Variation of ionic radii in iso-electronic ions. Iso-electronic ions are those which have the same number of electrons but which differ in the charge on their nuclei (Table 6).

The effect of nuclear charge on ionic size is best illustrated by considering the radii of these iso-electronic species. All of them contain the same number of electrons. They differ only in the charge on the nucleus. It is evident that as the nuclear charge increases, the electrons are held more and more tightly by the nucleus with the result that the ionic radius decreases.

TABLE 6

Radii of Iso-electronic Ions

Ion	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}
Number of electrons	10	10	10	10	10
Charge on the nucleus	+7	+8	+9	+11	+12
Radius (Å)	1·71	1·45	1·33	0·95	0·60

Periodic Trends in Ionic Radii. Generally speaking, the *ionic radii increase in moving from top to bottom in any given group* and *decrease in moving along a period.* The ionic radii of some common ions are given in Table 7.

TABLE 7

Ionic Radii (Å) of Some Common Ions

Group 1	Group 2	Group 13	Group 16	Group 17
Li^+ 0·60	Be^{2+} 0·31	B^{3+} 0·20	O^{2-} 1·45	F^- 1·33
Na^+ 0·98	Mg^{2+} 0·65	Al^{3+} 0·50	S^{2-} 1·84	Cl^- 1·81
K^+ 1·33	Ca^{2+} 0·99	Ga^{3+} 0·61	Se^{2-} 2·02	Br^- 1·96
Rb^+ 1·48	Sr^{2+} 1·10	In^{3+} 0·81	Te^{2-} 2·22	I^- 2·19
Cs^+ 1·67	Ba^{2+} 1·29	Tl^{3+} 0·91		

Variation in a group. It is evident from the data given in Table 7 that ionic radii increase with increase in atomic number within a group. This is easily understandable. Since the atomic size increases as we move down the group, therefore, the ionic radius also increases as we go down the group.

It can also be seen that within a group, there is a rapid increase in ionic radius as we move from one element to another amongst the first few elements but the increase is not so rapid when we do so amongst the last members. For example, the increase in ionic radius is quite rapid as we move from Li^+ to Na^+ and from Na^+ to K^+ but the increase is not that rapid as we move from K^+ to Rb^+ and from Rb^+ to Cs^+. A possible explanation for this behaviour is that between K^+ and Rb^+ ions come the elements of the First transition series. As in these elements the last occupied shell is the same, their increasing nuclear charge with increase in atomic number tends to cause contraction of electron charge clouds of the atoms and the ions. Thus, the radii of ions which follow any of the transition series would be smaller than if only eight elements had separated them from the lighter members of the family.

Variation in a period. Within a period, the radii of cations of normal elements of Groups 1, 2 and 13 decrease with increase in atomic number and so do the radii of anions of elements of Groups 16 and 17. This is again easily understandable. Since the atomic size decreases as we move along a period, the ionic radius also decreases correspondingly.

IONISATION ENERGY (*IE*)

The **ionisation energy**, *IE*, of an element is defined as *the amount of energy required to remove an electron from the outermost shell of an isolated gaseous atom of that element resulting in the formation of a positive ion.* This gives a direct measure of the ease with which an atom can change into a cation, as represented below :

$$M(g) + IE \longrightarrow M^+(g) + e^-$$

The energy required to bring about the above change is called **ionisation energy.** Evidently, *the smaller the ionisation energy, the easier it is for the neutral atom to change into a positive ion.*

Ionisation energies are generally measured by spectroscopic techniques. Another method is to have the vapours of the element in a discharge tube and connect it to a source of current. The voltage applied is gradually increased. At a certain voltage there will be a sudden rise in the current passing through the

tube. The energy corresponding to this voltage is known as the **first ionisation energy** $(IE)_1$. The sudden rise in the current is due to the liberation of an electron from each neutral atom producing an ion, M^+.

If the applied voltage is increased further, there may again be a stage when the current shows a sudden rise. This is due to *the elimination of another electron from each positively charged ion* (M^+) produced earlier. The energy corresponding to this stage is known as the **second ionisation energy,** $(IE)_2$. At this stage, doubly charged ions, M^{2+}, are produced. If the potential is increased even beyond this point, there may again be sudden and sharp rises in the current at certain points. These points correspond to the *loss of three or more electrons* and give the **third** $(IE)_3$ **or higher ionisation energies** of the element. These changes may be represented as follows :

$$M \xrightarrow{(IE)_1} M^+ + e^-$$

$$M^+ \xrightarrow{(IE)_2} M^{2+} + e^-$$

$$M^{2+} \xrightarrow{(IE)_3} M^{3+} + e^-$$

Ionisation energy is measured in electron-volts (eV) as well as in joules or kilojoules. It may be remembered that 1 eV = $1{\cdot}602\times10^{-19}$ joule or $1{\cdot}602\times10^{-22}$ kilojoule.

The values presented in electron-volts give ionisation energy *per atom* while those expressed in kilojoules represent ionisation energy *per mole* (*i.e.*, per Avogadro's number of atoms) of the element. Thus, ionisation energy of hydrogen is 13·595 eV **per atom** of hydrogen and $13{\cdot}595\times1{\cdot}602\times10^{-22}\times6{\cdot}022\times10^{23} = 1312{\cdot}0$ kJ **per mole** of hydrogen.

Let us consider the first and the second ionisation energies for lithium and sodium given below.

$$Li \longrightarrow Li + e^- \;;\; (IE)_1 = 520{\cdot}1 \text{ kJ mol}^{-1}$$
$$Li^+ \longrightarrow Li^{2+} + e^- \;;\; (IE)_2 = 7297{\cdot}2 \text{ kJ mol}^{-1}$$
$$Na \longrightarrow Na^+ + e^- \;;\; (IE)_1 = 495{\cdot}2 \text{ kJ mol}^{-1}$$
$$Na^+ \longrightarrow Na^{2+} + e^- \;;\; (IE)_2 = 4563{\cdot}5 \text{ kJ mol}^{-1}$$

As can be seen, the second ionisation energies are very much higher than the first ionisation energies.

The successive ionisation energies of some common elements are listed in Table 8.

TABLE 8

Successive Ionisation Energies (in kJ per mole) of Some Common Elements

Element	Electronic configuration	$(IE)_1$	$(IE)_2$	$(IE)_3$
Li	$1s^2\,2s^1$	520·1	7297	11810
Be	$1s^2\,2s^2$	899·3	1758	14810
B	$1s^2\,2s^2p^1$	800·1	2428	3660
C	$1s^2\,2s^2p^2$	1086·2	2353	4618
N	$1s^2\,2s^2p^3$	1402·1	2855	4577
O	$1s^2\,2s^2p^4$	1313·7	3388	5297
F	$1s^2\,2s^2p^5$	1680·8	3375	6045
Ne	$1s^2\,2s^2p^6$	2080·4	3963	6130

If one electron has been taken out of an atom, it becomes increasingly difficult to remove the second and subsequent electrons from the resulting positively charged ion on account of electrostatic attraction. This is due to the fact that after the removal of an electron, the number of electrons decreases while the nuclear charge remains the same. Consequently, the remaining electrons are held more tightly by the nucleus and it becomes difficult to remove the second electron. Therefore, the second ionisation energy is greater than the first ionisation energy and, similarly, the third ionisation energy is greater than the second ionisation energy and so on. Thus, $(IE)_3 > (IE)_2 > (IE)_1$.

The first ionization energies obtained spectroscopically for the various elements belonging to different groups are presented in Table 9.

TABLE 9

First Ionisation Energies of Various Elements (kJ mol^{-1})

Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
H 1312·0							He 2372·1
Li 520·1	Be 899·3	B 800·1	C 1086·2	N 1402·1	O 1313·7	F 1680·8	Ne 2080·4
Na 495·2	Mg 737·6	Al 577·4	Si 786·4	P 1011·7	S 999·4	Cl 1255·5	Ar 1520·3
K 418·7	Ca 589·8	Ga 579·0	Ge 760·4	As 944·1	Se 944·9	Br 1140·1	Kr 1350·6
Rb 403·0	Sr 549·3	In 558·2	Sn 708·5	Sb 831·7	Te 869·5	I 1008·1	Xe 1170·2
Cs 375·7	Ba 502·6	Ti 589·2	Pb 715·6	Bi 703·2	Po 813·5	At 916·7	Rn 1037·0

Factors Determining Ionisation Energy. The ionisation energy of an element depends upon the following factors.

1. Atomic size. *The larger the atomic size, the smaller is the ionisation energy.* The reason for this is that as the size of the atom increases, the outer electrons lie farther away from the nucleus. Hence, according to Coulomb's law, the attractive pull of the nucleus on the outer electrons decreases and it becomes easier to knock out an electron from the outermost shell of the atom.

2. Nuclear charge. The force of attraction between the nucleus and the outermost electron increases with increase in nuclear charge. Thus, the greater the nuclear charge, the greater is the energy needed to pull out an electron from the atom. Hence, *ionisation energy increases with increase in nuclear charge.*

3. Number of electrons in the inner shells. *The larger the number of electrons in the inner shells, the smaller is the ionisation energy.* The electrons in the inner shells act as a screen or shield between the nucleus and the electrons in the outermost shell. This is known as **screening effect** or **shielding effect.** The larger the number of electrons in the inner shells, the greater is the screening effect. Consequently, the electrons in the valency shell experience less attraction from the nucleus. Hence, the ionisation energy would be low.

4. Penetration effect or the effect of removal of *s, p, d and f* electrons from the same energy shell. The *s* electrons in their motion around the nucleus have greater probability of coming closer to the nucleus than the *p, d* or *f* electrons of the *same principal energy shell.* In other words, *s* electrons *penetrate more* towards the nucleus than *p* electrons and the penetrating power of the electrons in the

given principal energy shell varies as $s > p > d > f$. Thus, the s electrons experience more attraction from the nucleus than the p, d or f electrons of the same principal energy shell. It follows, therefore, that *the energy required for pulling out an s electron is maximum and it decreases in pulling out a p electron, a d electron or an f electron of the same principal energy shell in the order of their mention.* We may thus say that ionisation energy corresponding to the elimination of an electron from a given energy level varies in the order $s > p > d > f$ electron.

5. Electronic configurations. Certain electronic configurations are more stable than others. For example, *if an atom has fully filled or exactly half-filled orbital* in the valency shell, *its ionisation energy is higher than expected normally from its position in the periodic table.* For example, beryllium and nitrogen in the second period and magnesium and phosphorus in the third period, have slightly higher ionisation energies than would be expected. This is due to the *extra stability of the fully completed s orbitals* in beryllium and magnesium and that of the *exactly half-filled p orbitals* in nitrogen and phosphorus.

Further, it is seen that He, Ne, Ar, Kr, Xe and Rn have highest ionisation energies in their respective periods. This shows that an atom with s^2p^6 configuration (the so-called octet configuration) in its outer shell is highly stable. In this connection it may also be noted that Li^+ and Na^+ ions, which also have s^2p^6 configurations, require very high energies, *viz.*, 7297·2 and 4563·5 kJ per mole, to permit pulling out of an extra electron from them to give Li^{2+} and Na^{2+} ions, respectively.

Variation of Ionisation Energy in the Periodic Table. The following periodic trends in ionisation energy are observed :

a. Variation in a group. *In general, the ionisation energy decreases in going from top to bottom in a* **group.** This is evident from Table 9. On moving down a group

(*i*) the nuclear charge increases

(*ii*) there is gradual increase in atomic size due to increase in the number of the principal energy shell.

(*iii*) there is increase in the number of inner electrons which shield the valence electrons from the nucleus.

The overall effect of increase in atomic size and the shielding effect is much more than the overall effect of increase in nuclear charge. Consequently, the outermost electron is less and less tightly held to the nucleus as we move down the group. Hence, ionisation energy decreases as we go down from top to bottom in any group. There are some exceptions, however. For example, the first ionization energy of indium is less than that of thallium in Group 13 and first ionization energy of Sn is less than that of Pb in Group 14. We shall discuss these exceptions in adequate details while considering the properties of the main group elements in Chapter 12.

b. Variation along a period. *In general, the ionisation energy increases as we move along a period from left to right* (Table 9).

The above variation can be explained as follows. On moving across a period, the atomic size decreases and nuclear charge increases and, therefore, the force of attraction exerted by the nucleus on electron in the outermost shell increases. Consequently, it becomes increasingly difficult to remove an electron from the outer shell of the atom and hence ionisation energy increases. The ionisation energy becomes maximum for the noble gas which has stable electronic configuration, ns^2p^6.

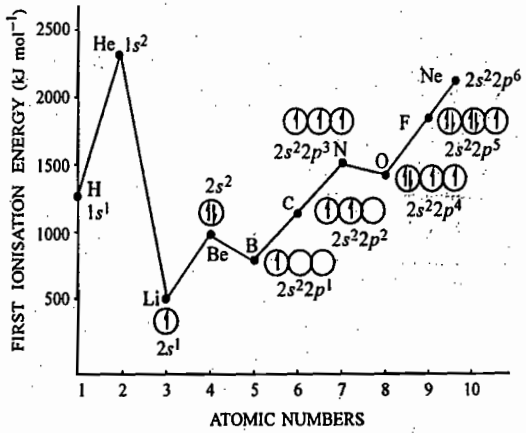


Fig. 4. Variation of ionisation energy with atomic number.

However, the variation in ionization energy along a period is not smooth (Table 9). Some irregularities are distinctly observed. This is due to the fact that atomic size is not the only factor which determines the ionization energy. The variation of ionisation energy with increase in atomic number for the elements of second period is depicted in Fig. 4. The electronic configurations of the elements are also shown in the figure.

It is clear from the figure that ionization energies of boron and oxygen are unexpectedly lower than the ionisation energies of their preceding elements beryllium and nitrogen, respectively. These anomalies are explained as follows : Electronic configuration of boron ($1s^2\,2s^2p^1$) is less stable than that of beryllium ($1s^2\,2s^2$) which has completely filled s orbitals. Moreover, in boron the outermost electron is present in $2p$ orbital which is at a slightly higher energy level than the outermost electron in beryllium. The $2p$ electron of boron is thus less tightly held by the nucleus and hence the ionisation energy of boron is less than that of beryllium. Electronic configuration of nitrogen ($1s^2 2s^2 p_x^1 p_y^1 p_z^1$), in which all the p orbitals are *exactly half-filled*, is more stable than the electronic configuration of oxygen ($1s^2 2s^2 p_x^2 p_y^1 p_z^1$). Therefore, ionisation energy of oxygen is less than that of nitrogen.

ELECTRON AFFINITY (*EA*)

Just as ionisation energy measures the tendency of an atom to change into a cation ($M \longrightarrow M^+ + e^-$), the electron affinity (*EA*) gives a measure of the tendency of an atom to change into an anion ($X + e^- \longrightarrow X^-$). **Electron affinity** is defined as *the amount of energy released when an electron is added to a gaseous isolated atom or ion.*

$$\underset{\text{Atom}}{X(g)} + e^- \longrightarrow \underset{\text{Anion}}{X^-(g)} + \text{Energy } (EA)$$

The greater the energy released in the process of taking up the extra electron, the greater is the electron affinity. The electron affinity of an atom measures *the tightness with which it binds an additional electron to itself.* The electron affinities are expressed in eV per atom or kJ mol^{-1}.

The electron affinities of the various elements belonging to different groups of the periodic table are given in Table 10.

TABLE 10

Electron Affinities of Various Elements (kJ mol^{-1})

Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
Li 59·8	Be ≈ 0	B 26·7	C 122·3	N ≈ 0	O 140·9	F 332·6	Ne 0
Na 53·1	Mg ≈ 0	Al 45·2	Si 133·6	P 72·3	S 200·7	Cl 348·5	Ar 0
K 48·4	Ca ≈ 0	Ga 28·7	Ge 120·0	As 77·2	Se 195·0	Br 324·7	Kr 0
Rb 46·9	Sr ≈ 0	In 29·0	Sn 107·9	Sb 103·0	Te 190·1	I 295·5	Xe 0
Cs 45·5	Ba ≈ 0	Tl 19·2	Pb 35·1	Bi 91·0	Po 180·0	At 270·0	Rn 0

Variation of Electron Affinity in the Periodic Table. In general, *electron affinity decreases in going from top to bottom in a* **group** *and increases in going from left to right across a* **period.** This can be easily explained. On moving down a **group**, the atomic size increases and, therefore, the effective nuclear attraction for the electron decreases. Consequently, the atom will have less tendency to attract additional electron towards itself, *i.e.*, its electron affinity would decrease. On moving across a **period**, on the other hand, the atomic size decreases and hence the force of attraction exerted by the nucleus on the electrons increases. Consequently, the atom has a greater tendency to attract the additional electron, *i.e.*, its electron affinity increases. Thus, as expected, electron affinities of metals are low while those of non-metals are high.

It is seen that halogens have high electron affinities. This is due to their strong tendency to gain an additional electron to acquire the stable s^2p^6 configuration.

The electron affinity decreases from Cl → Br → I, *i.e.*, on moving down the group, as discussed above. However, electron affinity of fluorine is *unexpectedly low*. It cannot be explained by any simple mechanism. It is probably due to small size of the atom. The addition of an extra electron produces high electron charge density in a relatively compact 2*p* subshell resulting in *strong electron-electron repulsion*. The repulsive forces between electrons imply low electron affinity.

Apart from the size of the atom discussed above, the electronic configurations of the elements also influence their electron affinities considerably. This is illustrated below.

Electron affinities of noble gases are zero. This is because their atoms have stable s^2p^6 configurations in their valency shells and there are no chances for the addition of an extra electron.

Electron affinities of beryllium, magnesium, calcium and nitrogen are also practically zero. This is attributed to the extra stability of the fully completed *s* orbitals in Be ($2s^2$), Mg ($3s^2$) and Ca ($4s^2$) and of the exactly half-filled 2*p* orbitals in N($2s^2p_x^1p_y^1p_z^1$). Thus, if an atom has fully filled or exactly half-filled orbitals, its electron affinity would be practically zero.

The trends in electron affinities within a period are also irregular indicating once again that atomic size is not the only criterion for determining electron affinity. Thus, electron affinity of Be is less than that of Li although the atomic size of Be is less than that of Li. Similarly, electron affinity of N is less than that of O although the atomic size of O is less than that of N.

Successive Electron Affinities. Like the second and higher ionisation energies, the second and higher electron affinities are also possible. However, after the addition of one electron, the atom becomes negatively charged and the second electron is to be added to a negatively charged ion. The addition of second electron is opposed by the coulombic force of repulsion and *energy has to be supplied* for the addition of the second electron.

If an atom has a spontaneous tendency, *i.e.*, a *positive tendency*, to gain an electron, then, conventionally, its electron affinity is said to be *positive* and if an atom is reluctant to gain an electron, *i.e.*, it has a *negative tendency* to gain an electron and is forced to accept it, its electron affinity is said to be *negative*. Thus, in the case of oxygen, the first electron affinity $(EA)_1$ is positive since 140·9 kJ of energy is released when a mole of O atoms get converted to O^- ions. In other words, O atom has positive tendency to accept electron. However, the second electron affinity $(EA)_2$ is negative since 770 kJ of energy has to be supplied to convert 1 mole of O^- ions to O^{2-} ions.

Similarly, in the case of sulphur, while the first electron affinity $(EA)_1$ is positive since 200·7 kJ of energy is released when 1 mole of S atoms get converted to S^- ions, the second electron affinity $(EA)_2$ is negative since 333·2 kJ of energy has to be supplied to convert one mole of S^- ions to S^{2-} ions.

Thermodynamically, however, the energy released is given a negative sign and energy absorbed is given a *positive sign*. Accordingly, when a species has a *positive* electron affinity, ΔH, accompanying the addition of an electron to the specie, is *negative* and if it has a *negative* electron affinity, ΔH *is positive*. Thus, for the reaction $Cl + e^- \longrightarrow Cl^-$, while EA (= 348·5 kJ) is positive, ΔH for the process is negative. In various calculations involving ΔH (as, for example, in Born-Haber cycle), the value for electron affinity of chlorine would be taken as $-348{\cdot}5$ kJ mol^{-1} and not $+348{\cdot}5$ kJ mol^{-1}.

ELECTRONEGATIVITY

The term **electronegativity** has been defined differently by different investigators and each of them has suggested a method of his own to calculate electronegativities of different elements. The approaches of some of the investigators are discussed below.

Pauling's Approach. Pauling defined **electronegativity** *as the power of an atom in a molecule to attract electrons to itself*. He calculated electronegativities of different elements from thermodynamic data. He considered that in a reaction of the type

$$1/2\,(A-A) + 1/2\,(B-B) \longrightarrow A-B \qquad ...(2)$$

the bond dissociation energy of $A-B$ is higher than the mean of the bond dissociation energies of A – A and (B – B) bonds and that their difference (Δ) is related to the difference in the electronegativities of A and B according to the following empirical equation :

$$\Delta = E_A - E_B - 1/2(E_{A-A} + E_{B-B}) = 23(\chi_A - \chi_B)^2 \qquad ...(3)$$

where E_{A-B}, E_{A-A} and E_{B-B} represent the bond dissociation energies of A – B, A – A, and B – B bonds, respectively and χ_A and χ_B denote the electronegativities of A and B, respectively. Thus,

$$\Delta = 23(\chi_A - \chi_B)^2 \qquad ...(4)$$

or

$$0{\cdot}208\sqrt{\Delta} = \chi_A - \chi_B \qquad ...(5)$$

Pauling later took the geometric mean instead of the arithmetic mean of E_{A-A} and E_{B-B} and suggested the following empirical correlation :

$$E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2} = \Delta' = 30(\chi_A - \chi_B)^2 \qquad ...(6)$$

or

$$0{\cdot}182\sqrt{\Delta'} = \chi_A - \chi_B \qquad ...(7)$$

In Pauling's equations, the dissociation energies are taken *in kcal* (and not in kJ) per mole.

Assuming arbitrarily the electronegativity of hydrogen to be 2·1, Pauling determined electronegativities of other elements with the help of Eq. 7. These values are given in Table 11.

TABLE 11

Electronegativities of the Main Group Elements

(Pauling's Values)

Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17
H 2·1						
Li 1·0	Be 1·5	B 2·0	C 2·5	N 3·0	O 3·5	F 4·0
Na 0·9	Mg 1·3	Al 1·6	Si 1·9	P 2·2	S 2·6	Cl 3·1
K 0·8	Ca 1·0	Ga 1·8	Ge 2·0	As 2·2	Se 2·5	Br 2·9
Rb 0·8	Sr 1·0	In 1·8	Sn 1·8	Sb 2·0	Te 2·1	I 2·6
Cs 0·7	Ba 0·9	Tl 1·6	Pb 1·8	Bi 2·0	Po 2·0	At 2·2

Example 1. Calculate the electronegativity of fluorine from the following data : E_{H-H} = 104·2 kcal mol^{-1}, E_{F-F} = 36·6 kcal mol^{-1}, E_{H-F} = 134·6 kcal mol^{-1}.

Solution : According to Eq. 6,

$$\Delta = E_{H-F} - (E_{H-H} \times E_{F-F})^{1/2} = 134{\cdot}6 - (104{\cdot}2 \times 36{\cdot}6)^{1/2} = 72{\cdot}85 \text{ kcal}$$

According to Eq. 7,

$$\chi_F - \chi_H = (0{\cdot}182)\,(72{\cdot}85)^{1/2} = 1{\cdot}55$$

$$\chi_F = 1{\cdot}55 + \chi_H = 1{\cdot}55 + 2{\cdot}1 = \mathbf{3{\cdot}65}$$

Example 2. Calculate the electronegativity of carbon from the following data : E_{H-H} = 104·2 kcal mol^{-1}, E_{C-C} = 83·1 kcal mol^{-1}, E_{C-H} = 98·8 kcal mol^{-1}.

Solution : According to Eq. 6,

$$\Delta = E_{C-H} - (E_{H-H} \times E_{C-C})^{1/2} = 98{\cdot}8 - (104{\cdot}2 \times 83{\cdot}1)^{1/2} = 5{\cdot}75 \text{ kcal}$$

According to Eq. 7,

$$\chi_C - \chi_H = 0{\cdot}182\,(5{\cdot}75)^{1/2} = 0{\cdot}44$$

$$\chi_C = 0{\cdot}44 + \chi_H = 0{\cdot}44 + 2{\cdot}1 = \mathbf{2{\cdot}54}$$

Allred and Rochow's Approach. Allred and Rochow defined **electronegativity** *as the electrostatic force of attraction exerted by the nucleus of an atom on the valency electrons.* Making use of the effective nuclear charge at the periphery of the atom, Z_{eff}, as calculated by Slater's rules, they proposed the following empirical relation for calculating the electronegativity :

$$\chi = 0{\cdot}359 \times Z_{eff}/r^2 + 0{\cdot}744 \qquad ...(8)$$

where χ is the electronegativity and r is the covalent radius of the atom in angstrom units. The electronegativities as calculated with the help of Eq. 8 are found to be remarkably close to those reported by Pauling.

Example 3. Calculate the electronegativity of carbon atom following Allred-Rochow's approach. The covalent radius of carbon atom is 0·77 Å.

Solution : According to Slater's rules (Chapter 1),

Z_{eff} at the periphery of C atom $= Z_{actual} - S = 6 - (0{\cdot}35 \times 4 + 0{\cdot}85 \times 2) = 2{\cdot}90$

According to Eq. 8, $\chi_C = 0{\cdot}359 \times 2{\cdot}90\,(0{\cdot}77)^2 + 0{\cdot}744 = \mathbf{2{\cdot}50}$

Example 4. Calculate the electronegativity of silicon following Allred-Rochow approach. Covalent radius of Si = 1·175 Å.

Solution : Electronic configuration of Si is $1s^2 2s^2 p^6 3s^2 p^2$

According to Slater's rules (Chapter 1),

$$Z_{eff} = Z_{actual} - S = 14 - (0{\cdot}35 \times 4 + 0{\cdot}85 \times 8 + 1{\cdot}0 \times 2) = 3{\cdot}80$$

According to Eq. 8, $\chi_{Si} = 0{\cdot}359 \times 3{\cdot}80/(1{\cdot}175)^2 + 0{\cdot}744 = \mathbf{2{\cdot}50}$

Mulliken's Approach. Mulliken suggested that *the average of the ionization energy (IE) and electron affinity (EA) of an atom should be a measure of the* **electronegativity** (χ_M) *of the atom*, that is,

$$\chi_M = 1/2(IE + EA) \qquad ...(9)$$

However, the ionisation energy and the electron affinity of an atom in Mulliken's definition are not the experimentally observed values for the isolated gaseous atom in its ground state. These are instead the calculated values for the atom in its valence state, *i.e.*, when the atom forms a part of a molecule.

For instance, in BeF_2, the ionisation energy of Be atom used in Mulliken's formula is not the one which is experimentally observed for an isolated Be atom having $1s^2 2s^2$ configuration but is the *hypothetical*

energy required to remove an electron from an *sp* hybrid orbital of Be atom. In other words, it is the average of energies *IE(s)* and *IE(p)* required to remove 2*s* and 2*p* electrons from the promoted valence state of Be atom in BeF_2 molecule :

$$\underset{\text{(ground state of Be)}}{1s^2 2s^2} \longrightarrow \underset{\text{(promoted valence state)}}{1s^2 2s^1 2p^1} \xrightarrow{IE\,(s)} 1s^2 2s^0 2p^1$$

$$1s^2 2s^1 2p^1 \xrightarrow{IE\,(p)} 1s^2 2s^1 2p^0$$

The *IE* and *EA* used in Mulliken's formula can be calculated by a complicated mathematical procedure which does not concern us here.

Several empirical equations have been proposed by chemists to bring Mulliken's values at par with the values of χ on Pauling's scale. But no such equation gives satisfactory results for all the elements. One such equation which attempts to give χ_M nearly at par with the value of χ on Pauling's scale is :

$$\chi_M = 0{\cdot}336\left[\frac{IE + EA}{2} - 0{\cdot}615\right] \qquad ...(10)$$

In this equation, *IE* and *EA* are in electron volts.

One advantage of using Mulliken's approach is that the electronegativities of an element, which is present in different oxidation or hybridisation states in different molecules can be calculated. For instance, χ_M of C in sp^3, sp^2, *sp* hybridised states, calculated by Mulliken's approach, are 2·48, 2·66, 2·99, respectively, whereas χ_P (Pauling's values) of C in all its molecules was reported to be 2·55.

Factors influencing Electronegativity. Although the electronegativity of an element is conventionally assigned a definite value, yet it may differ from one molecule to another. The ability of an atom in a molecule to attract electrons towards itself depends upon its environment in the molecule. The electronegativity of an atom would thus depend upon the nature of the other atom with which it is attached in the molecule. The factors which largely determine the electronegativity of an atom are as follows.

Charge on the atom. An atom which acquires a positive charge, either integral or partial, would tend to attract electrons more strongly than a neutral atom. Thus, a cation will be more electronegative than the parent atom which, in turn, would be more electronegative than its anion. Also, the higher the positive oxidation state of an atom in a species, the greater would be its electron-attracting power and hence the greater would be its electronegativity. For example, the oxidation state of central chlorine atom is +1 in HClO and +5 in $HClO_3$. Hence, the chlorine atom will be more electronegative in $HClO_3$ than in HClO. Accordingly, the release of hydrogen as H^+ ion in $HClO_3$ would be much easier than a similar change in HClO. In other words, $HClO_3$ *behaves as a stronger acid than* HClO.

Hybridisation. We know that *s* electrons are more penetrating than the *p* electrons. Therefore, if an atom has hybrid orbitals with a greater *s* character, the electronic charge in such orbitals would remain closer to the nucleus of that atom. This means that *the electronegativity of the atom would increase with increase in s character of its hybrid orbitals.*. For example, in methane, the carbon atom involves sp^3 hybridisation of its orbitals so that the hybrid orbitals have 25% *s* character. In ethylene, the carbon atom involves sp^2 hybridisation of its orbitals and consequently the *s* character of hybrid orbitals increases to 33%. In acetylene, the carbon atom involves *sp* hybridisation of its orbitals and, therefore, the *s* character of hybrid orbitals increases to 50%. Accordingly, the electronegativity of carbon atom increases as we move from CH_4 to C_2H_4 and to C_2H_2. Due to greater electronegativity of carbon atom in ethylene and acetylene, the electron pair of C – H bond is pulled more towards the carbon atom thereby facilitating the release of H atom as H^+ion. Thus, while methane is neutral, ethylene is slightly acidic while acetylene is considerably acidic.

Similarly, the *basicity of amines* also varies with the type of the hybridisation of the orbitals of the nitrogen atom. The higher the *s* character of the hybrid orbitals, the greater would be the electronegativity and the lower would be the electron-donating power of the nitrogen atom and hence the lower would be the basicity of the amine. For example, the molecules RCN, C_5H_5N (pyridine) and $C_6H_5NH_2$, involve, respectively, *sp*, sp^2 and sp^3 hybridisation of the orbitals of the nitrogen atom. Accordingly, the *s* character of the hybrid orbitals of nitrogen atom is 50% in RCN, 33% in pyridine and 25% in aniline. Accordingly, aniline is a stronger base than pyridine which, in turn, is a stronger base than RCN.

Effect of substituents. The electronegativity of an atom depends considerably upon the nature of the substituents attached to that atom. For example, the carbon atom in CF_3I acquires a greater positive charge than in CH_3I. Hence, the carbon atom in CF_3I is more electronegative (*i.e.*, more electron pulling) than in CH_3I. The difference in the electronegativities of an atom caused by the substituents results in different chemical behaviour of that atom. For instance, CF_3I and CH_3I yield different products on hydrolysis :

$$CF_3I + OH^- \longrightarrow CF_3H + IO^-$$

$$CH_3I + OH^- \longrightarrow CH_3OH + I^-$$

Role of ionization energies and electron affinities. According to Mulliken, electronegativity is related to the average of the ionization energy and electron affinity of the atom (Eq. 9). Evidently, the higher the ionization energy and electron affinity, the greater would be the electronegativity of the atom.

Effective nuclear charge. Variation of electronegativity in the periodic table. Allred and Rochow reasoned that the electron attracting power of an atom in a molecule is proportional to the effective nuclear charge, Z_{eff}. Thus, any factor which increases Z_{eff}, should also increase the electronegativity of the atom. For example, Z_{eff} decreases as we go down a group in the periodic table. This is because with increase in atomic number within a group, the atomic size increases. Hence, *electronegativity decreases as we move down a* **group**. Thus, the electronegativity of the halogens *decreases* in the order :

F (4·0) > Cl (3·1) > Br (2·9) > I (2·6).

Z_{eff} increases with decrease in size of the atom and the size of the atom decreases as move along a period from left to right in the periodic table. Accordingly, *electronegativity goes on increasing with increase in atomic number as we move along a* **period**. Thus, electronegativities of the elements of the second period *increase* in the order :

Li (1·0) < Be (1·5) < B (2·0) < C (2·5) < N (3·0) < O (3·5) < F (4·0)

Z_{eff} also depends upon the number of inner electrons which screen the last electron. The larger the number of inner electrons, the greater would be the screening and the lesser would be the effective nuclear charge. Thus, electronegativity would *decrease* with increase in the number of inner electrons in atoms of the elements in the same group. This is an additional reason why the electronegativity of alkali metals *decreases* in the order :

Li (1·0) > Na (0·9) > K (0·8) > Rb (0·8) > Cs (0·7).

Applications of Electronegativities. Electronegativities have very wide range of applications. Some of the important applications are given below.

1. Calculation of partial ionic character of a covalent bond. The development of ionic character in a covalent bond between two atoms, say, *A* and *B*, is due to the difference in the electronegativities of *A* and *B*. The greater the difference in the electronegativities, the greater would be the development of *ionic character and consequently the higher would be the stability of the resulting bond.*

Pauling suggested the following correlation between the electronegativity difference $\chi_A - \chi_B$ and the per cent ionic character of the covalent bond :

$$\text{Per cent ionic character} = [1 - e^{-0.25(\chi_A - \chi_B)}] \times 100 \qquad ...(11)$$

Example 5. The electronegativity difference of the elements in HF is 1·9. Calculate the per cent ionic character of the H–F bond.

Solution : According to Pauling's equation (Eq. 11),

$$\text{Percent ionic character of H–F bond} = [1 - e^{-0.25(1.9)}] \times 100 = 37.77$$

Pauling suggested an alternative empirical equation also for calculating the per cent ionic character, according to which

$$\text{Per cent ionic character} = 18\,(\chi_A - \chi_B)^{1.4} \qquad ...(12)$$

According to this equation, the per cent ionic character of HF comes out to be 44·12. This value is quite close to the one (*viz.*, 44·8) obtained by Pauling from dipole moment of HF (Chapter 4).

2. Calculation of enthalpies of formation of compounds. It is possible to calculate enthalpies of formation of compounds from electronegativities making use of the following empirical equation put forth by Pauling :

$$\Delta H_f = 23 \in (\chi_A - \chi_B)^2 - 55.4\, n_N - 26.0\, n_O \qquad ...(13)$$

where ΔH_f is the enthalpy of formation, n_N and n_O are the numbers of nitrogen and oxygen atoms in the molecule. The value of $\in$ would be 1, 2, 3, etc., depending upon the number of bonds in the molecule. For instance, $\in = 1$ for HCl, $\in = 2$ for $BeCl_2$ and so on. The values of ΔH_f obtained as above are, however, approximate.

Suppose we want to calculate the enthalpy of formation of $BeCl_2$. There are two Be–Cl bonds in this molecule. The values of χ_{Cl} and χ_{Be} are, respectively, 3·1 and 1·5 (Table 11).

$$\therefore \qquad \Delta H_f = 23 \times 2\,[(3.1 - 1.5)^2] - 0 - 0 = \mathbf{117.76\ kcal\ mol^{-1}}$$

(n_N and n_O are zero since there are no nitrogen and oxygen atoms in the molecule)

(The experimental value for ΔH_f is found to 122 kcal mol^{-1})

3. Calculation of bond length. If the two atoms A and B bonded together through a covalent bond differ in their electronegativities, then the covalent bond would acquire some ionic character, as illustrated above. In other words, the bond acquires polarity. The greater the polarity, the shorter would be the length of the bond formed between A and B. Shoemaker and Stevenson proposed the following empirical equation for calculating the bond length in such cases :

$$d_{A-B} = r_A + r_B - 0.09\,(\chi_A - \chi_B) \qquad ...(14)$$

where d_{A-B} is the actual bond distance between A and B ; r_A and r_B are the covalent radii of A and B and $\chi_A - \chi_B$ is the electronegativity difference. The normal length of the covalent bond between A and B would have been equal to $r_A + r_B$. Evidently, the shortening of the bond between A and B due to electronegativity difference is equal to $0.09(\chi_A - \chi_B)$. Due to reduction in length, the bond would be more stable.

Let us calculate the bond distance N–O with the help of Eq. 14. Covalent radii of nitrogen and oxygen atoms are, respectively, 0·75 and 0·74 Å and the electronegativities of N and O are 3·0 and 3·5, respectively. Thus,

$$d_{N-O} = 0.75 + 0.74 - 0.09\,(3.5 - 3.0) = \mathbf{1.445\ Å}$$

The actual N–O bond length is 1·46 Å

Similarly, the length of the C–O bond is given by

$$d_{C-O} = 0.77 + 0.74 - 0.09\,(3.5 - 2.5) = \mathbf{1.42\ Å}$$

The experimental value is exactly the same.

4. Explanation for bond angles. The lesser the electronegativity of the central atom in a polyatomic molecule, the lesser would be the magnitude of the bond angle. This may be explained as follows : If the electronegativity of the central atom is less, it would not be able to hold the bonding electron pairs towards itself. Therefore, the bonding electron pairs would shift more towards the other atoms attached to the central atom. This would result in a decrease in the bond pair–bond pair repulsion and hence a decrease in the bond angle.

For illustration, the bond angles and electronegativities of trifluorides of the Group 15 elements are given below. As expected, the decrease in electronegativity of the central atom results in a decrease of the bond angle.

Compound	Electronegativity of Central Atom	Bond Angle
NF_3	3·0	102°
PF_3	2·2	97°
AsF_3	2·2	96°
SbF_3	2·0	88°

5. Rationalisation of reaction mechanism. It has been observed that when CH_3I reacts with the nucleophile $[Mn(CO)_5]^-$, the following reaction takes place

$$CH_3I + Na^+[Mn(CO)_5]^- \longrightarrow NaI + CH_3Mn(CO)_5$$

The formation of the above reaction products may be explained as follows : Iodine in CH_3I is more electronegative than carbon. This creates a partial positive charge on the carbon atom. The negatively charged nucleophile, thus, attacks the positive site resulting in the formation of $CH_3Mn(CO)_5$.

On the other hand, if we carry out a similar reaction with CF_3I, a totally different product is obtained. Thus,

$$2CF_3I + Na^+[Mn(CO)_5]^- \longrightarrow NaI + Mn(CO)_5I + C_2F_6$$

Because of the presence of highly electronegative F atoms, the electron charge cloud of carbon atom is pulled towards the former. This creates electron charge deficiency at the carbon atom which is made up by the pulling of the electron charge cloud of iodine atom towards the carbon atom (the electron charge cloud of iodine is easily polarisable). This creates a partial positive charge on iodine atom. Therefore, the nucleophile $[Mn(CO)_5]^-$ now attacks the iodine site leading to the formation of $Mn(CO)_5I$.

In a similar way, we can explain the acidic or basic nature of some hydroxy compounds. Consider, for example, HOCl. The chlorine atom in this molecule is in +1 oxidation state. It is, therefore, more electron-attracting than oxygen. The chlorine atom, thus, pulls the electron pair of the O–Cl bond towards itself leaving electronic charge deficiency on the oxygen atom. In order to make up this deficiency, the oxygen atom pulls the electron pair of O–H bond towards itself. This facilitates the release of H atom as H^+ ion by the rupture of the O–H bond. Hence, the hydroxide HO–Cl behaves as an acid.

In $Be(OH)_2$, the electronegativity of Be is less than that of oxygen. Therefore, the electron pair of Be–O bond is pulled more towards oxygen. This facilitates the release of OH^- group with the rupture of the Be–O bond. Hence, $Be(OH)_2$ behaves as a base.

6. Explanation of diagonal relationship. The electronegativity *increases* as we go from Li (1·0) to Be (1·5) (variation of electronegativity in a period) but it *decreases* as we move from Be (1·5) to Mg (1·3) (variation of electronegativity in a group). As a result of these two opposite changes (one along the period and the other down the group), as we move *diagonally*, these two effects partly cancel each other and there is no marked change in electronegativity. This is the reason why Li (1·0) and Mg (1·3) have close values of electronegativities.

Because of similar values of electronegativities and hence of electron-attracting powers, Li and Mg have similar chemical properties.

7. Types of bonds. The type of bond formed between two atoms would, evidently, depend upon the difference in their electronegativities. If this difference is zero or very small, the bond formed would be *covalent* and if the difference exceeds 2·5, the bond formed would be *electrovalent*. If, however, the electronegativity difference is less than 2·5 but otherwise quite appreciable, the bond formed would be *polar covalent*.

QUESTIONS

1. State the modern periodic law. What is the cause of periodicity in the properties of elements ?
   (*a*) "There are only 2 elements in the first period, 8 elements in each of the second and third periods, 18 elements in each of the fourth and fifth periods and 32 elements in the sixth period of the periodic table." Why is it so?
   (*b*) Which of the following elements exhibit similar properties and why ?
   A : $1s^2 2s^2p^6 3s^1$ B : $1s^2 2s^2p^6 3s^2p^6d^{10} 4s^1$ C : $1s^2 2s^1$ [Ans. A and C]
2. (*a*) Explain how the elements are arranged in the long form periodic table. What is meant by a group and a period?
   (*b*) Write the electronic configurations of the elements with atomic numbers 53, 54 and 55. Classify these as a noble gas, an electropositive element and an electronegative element.
   (*c*) Account for the fact that the third period of the periodic table contains 8 and not 18 elements.
3. (*a*) Explain how the elements can be classified into *s*, *p*, *d* and *f* blocks.
   (*b*) To which block do the elements with the following electronic configurations belong :
   (*a*) $1s^2 2s^2p^6 3s^2p^6 4s^1$ (*b*) $1s^2 2s^2p^6 3s^2p^6d^{10} 4s^1$ (*c*) $1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^1$
   (*d*) $1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^{10}f^1 5d^1 6s^2$ (*e*) $1s^2 2s^2$ (*f*) $1s^2 2s^2p^6 3s^2p^6d^{10}4s^2$
   [Ans. (*a*) *s* (*b*) *d* (*c*) *p* (*d*) *f* (*e*) *s* (*f*) *d*]
4. The properties of elements arranged in the order of increasing atomic number recur at atomic number intervals of 2, 8, 8, 18, 18, 32 and 32. How would you account for this ?
5. (*a*) What are main group, transition and inner transition elements ? How are the transition elements distinguished from the main group elements on the basis of electronic configurations ?
   (*b*) Would you call Zn (Z = 30) and Hg (Z = 48) as *s* block or *d* block elements ? Give reasons for your answer.
6. (*a*) What is meant by atomic radius ? How do the atomic radii of elements vary when we move (*i*) down a group (*ii*) across a period ? How would you account for this variation ?
   (*b*) What do you understand by iso-electronic ions ? How does the size vary in the following series : N^{3-}, Na^+, Mg^{2+}, Al^{3+}, O^{2-}, F^- [Ans. $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$]
7. Explain the following :
   (*a*) Van der Waals radius of chlorine is greater than the covalent radius of chlorine.
   (*b*) The atomic radii decrease in moving from left to right in any given period and increase in moving from top to bottom in any given group.
   (*c*) The radius of a cation is invariably smaller and that of an anion invariably larger than that of the corresponding atom.
8. (*a*) Explain the term ionisation energy of an element. On what factors does it depend ?
   (*b*) The ionisation energy of Na^+ is more than that of Ne although both have the same electronic configuration. Explain.
9. (*a*) Explain the term ionisation energy ? How is it measured ? How do the ionisation energies of elements vary as we move (*i*) along a period (*ii*) down a group and why ?
   (*b*) What is meant by the terms : First ionisation energy, second ionisation energy and third ionisation energy ? Why are second ionisation energies so much higher than the first ionisation energies ?

10. (*a*) Explain the term electron affinity. Why are electron affinities of the halogens so high ?

(*b*) Predict which element in each of the following pairs has higher ionisation energy and why :

(*i*) S, P (*ii*) Be, B (*iii*) N, C (*iv*) Ne, F (*v*) I, Br (*vi*) F, Cl (*vii*) Na, K

[Ans. (*i*) P (*ii*) Be (*iii*) N (*iv*) Ne (*v*) Br (*vi*) F (*vii*) Na]

11. (*a*) Define ionisation energy and electron affinity. How do these vary in the periodic table as the atomic number increases ?

(*b*) Account for the following trend in the electron affinities of the halogens ?

F	Cl	Br	I
332·6 kJ mol^{-1}	348·5 kJ mole^{-1}	324·7 kJ mol^{-1}	295·5 kJ mol^{-1}

(*c*) The electron affinities of noble gases are zero. Why ?

12. (*a*) Explain the term electronegativity. How is it related to electron affinity and ionisation energy ?

(*b*) Why is the radius of an atom not defined precisely ?

13. Give reasons for the following :

(*a*) The second ionisation energy of sodium is very high as compared to its first ionisation energy.

(*b*) Electron affinity of fluorine is less than that of chlorine.

(*c*) Ionic radius of K^+ is smaller than that of Cl^-.

(*d*) Electron affinity of N is almost zero while that of F is very high.

(*e*) Size of Cl^- ion is greater than that of Cl atom while that of Na^+ ion is smaller than that of Na atom.

(*f*) Electronegativity increases along a period.

(*g*) Ionisation energies of C, N and O follow the order : C < N > O.

14. Define the following and explain their trends in a period and in a group :

(*a*) Electron affinity (*b*) Electronegativity (*c*) Atomic radius (*d*) Ionisation energy

15. (*a*) "Atomic radius is a measure of the effective size of an atom and it has a different value in different environments." Discuss the statement.

(*b*) Which of the two has higher ionic radius and why ? Al^+ or Al^{3+}.

(*c*) The ionisation energy of Al to form Al^+ is less than that of Mg to form Mg^+ ion. Explain.

16. (*a*) The first and second electron affinities of oxygen are : 141 kJ mol^{-1} and –770 kJ mol^{-1}, respectively. Account for this.

(*b*) The electron affinity of chlorine is 3·7 eV. How much energy in kcal is released when 2 g of chlorine is completely converted to Cl^- ion in the gaseous state ? [Ans. 4·86 kcal]

(*c*) The electronic configurations of some neutral atoms are given below :

A : $1s^2 2s^2 p^6 3s^2$; B : $1s^2 2s^2 p^6 3s^1$; C : $1s^2 2s^2 p^5$; D : $1s^2 2s^2 p^4$

Which of these will have the lowest ionisation energy ? [Ans. B]

17. "The term electronegativity has been defined differently by different investigators." Comment on this statement. Discuss the factors which influence the electronegativity of an atom.

18. How was the term electronegativity defined by Pauling, Allred & Rochow and Mulliken ?

19. Discuss the important applications of electronegativities.

MOLECULAR SYMMETRY AND GROUP THEORY

3

Frequent reference has been made to the applications of symmetry and group theory while discussing molecular orbital theory, electronic energy levels of complexed metal ions, selection rules for electronic absorption spectroscopy, etc., in various chapters. An attempt will now be made to discuss the concepts of symmetry and the group theory in adequate details in a systematic manner using a simple and clear language.

SYMMETRY OPERATIONS AND SYMMETRY ELEMENTS

Symmetry Operations. A **symmetry operation** is the movement of a body with respect to a line, a plane or a point in such a manner that after the movement, every point of the body is coincident with an equivalent (or the same) point lying on the body before movement. That is, the position and the orientation of the body before and after the operation are indistinguishable. *A symmetry operation which brings the body back to its original position is called an* **identity operation.**

Symmetry Elements. A line, a plane or a point with respect to which one or more symmetry operations can be carried out is called a **symmetry element.**

We come across the following types of symmetry elements and symmetry operations.

1. Plane of Symmetry and Reflection Operation. For carrying out a symmetry operation with respect to a plane, the latter may be considered as a two-way mirror. If the reflections of all the atoms through this plane produce an equivalent geometry of the molecule, the plane is known as the **plane of symmetry.** A plane of symmetry must pass through the geometry of the molecule. It is to be noted that atoms of the molecule lying right on the plane of symmetry do not change their positions after the reflection operation. The standard symbol for both the symmetry plane and the reflection through symmetry plane is sigma (σ). In molecules such as NHFCl, NHF_2, CH_2Cl_2. NH_3, BF_3, $[PtCl_4]^{2-}$, CCl_4 and $[CoF_6]^{3-}$, the number of planes of symmetry is 0, 1, 2, 3, 4, 5, 6 and 9, respectively.

If the reflection process is carried out twice or for an *even* number of times through a plane of symmetry, we get back the original or an identical configuration. Thus, σ^2 (or σ^{2n}) is obviously an identity operation. Similarly, the reflection process carried out thrice or for an *odd* number of times through a plane of symmetry gives an equivalent configuration which is the same as obtained from a single reflection operation. Thus, σ^3 (or σ^{2n+1}) operation is the same as σ operation.

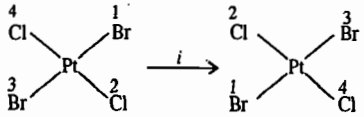
The planes of symmetry can be further subdivided into the following two categories :

a. **Horizontal plane of symmetry** (σ_h) which is perpendicular to the principal axis of symmetry.

b. **Vertical plane of symmetry** (σ_v) which passes through the principal axis of symmetry. There is yet another type of vertical plane of symmetry, *viz.*, the **dihedral plane of symmetry** (σ_d) about which we shall talk a little later in this chapter.

2. Inversion Centre and Inversion Operation. If a molecule can be brought into an equivalent configuration by inverting the coordinates of every atom through the origin (*i.e.*, by changing the coordinates (*x*, *y*, *z*) of every atom to (–*x*, –*y*, –*z*), then the origin which lies within the geometry of the molecule is called the **inversion centre.** Both the inversion centre and the inversion operation are designated by the symbol *i*. Examples of molecules containing an inversion centre are $[PtCl_4]^{2-}$,

trans $[PtCl_2Br_2]^{2-}$ and benzene. The inversion operation carried out on trans $[PtCl_2Br_2]^{2-}$ is illustrated below :

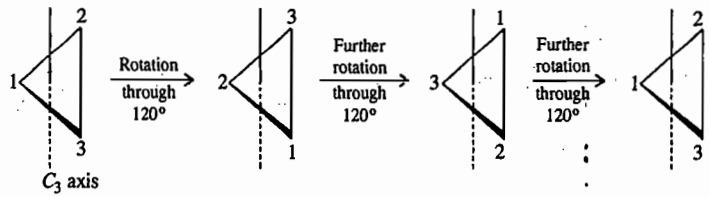


The subscripts 1, 2, 3, 4 are written to indicate which atoms shift and where, as a result of the inversion operation. The operation i^2 is obviously the identity operation.

3. Proper Axis and Proper Rotation. If, on rotation of a molecule with respect to a line, we get an equivalent or an identical configuration, the operation is called **proper rotation** and the line with respect to which such an operation is carried out is called **proper axis of rotation.**

The number of times we get an equivalent or an identical configuration in a complete rotation of 360° about a proper axis is called the **order of the proper axis.** The same symbol C_n is used for designating both the proper axis of rotation and the proper rotation operation where n is the order of the proper axis.

Let us take the example of an equilateral triangle. A line perpendicular to the plane of the triangle and passing through its centre is a proper axis of rotation of the order three since a complete rotation of this triangle through an angle of 360° around this line generates an equivalent (or an identical) configuration three times, as shown below :



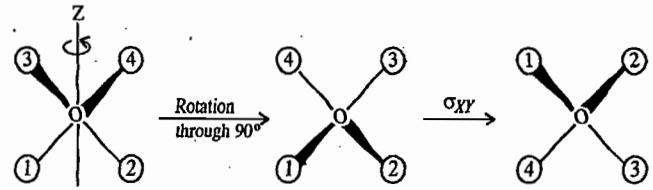
The **order of the proper axis of rotation** can be calculated mathematically by the relation $n = 360°/\theta$ where θ is the minimum angle (in degrees) required for the determination of a single rotation operation. Thus, in the above example, θ is 120° and the order of the proper axis is $360°/120° = 3$. The three symmetry operations carried out in succession as shown above are written as C_3^1, C_3^2 and C_3^3. The last operation which gives the original geometry back is, obviously, an identity operation which is written as E. It is evident that the C_n^n operation always gives back the original geometry and is thus an identity operation invariably. It can be further seen that C_3 rotation operation carried out four times, *i.e.*, C_3^4, is equal to C_3^1 and C_3^5 is equal to C_3^2. In general, $C_n^{n+m} = C_n^m$. There can be present several axes of proper rotation of the same or different order in any geometry. Thus, in the above example, there are three C_2 axes of proper rotation apart from the C_3 axis.

Another point to be emphasised here is that the subscript and superscript numbers of C_n^m can be simplified by dividing these numbers by a common permissible integral factor. Thus, C_4^2 is equal to C_2^1, C_6^2 is equal to C_3^1, C_6^3 is equal to C_2^1 and so on.

4. Improper Rotation Operation and Improper Axis of Rotation. An **improper rotation operation** is one that comprises of *a proper rotation operation around an axis followed by reflection through a plane perpendicular to it* (or vice versa). It is denoted by S_n where n is the order of the rotation axis. It is important to note that, in many cases, neither rotation about an axis nor reflection through a plane perpendicular to this axis may separately be a symmetry operation, but a combination of the two may become a symmetry operation.

Consider the line bisecting angles 3O4 and 1O2 of a regular tetrahedral molecule. If we rotate the tetrahedron through an angle of 90° about this line, we get a different configuration. Similarly, if we reflect all the atoms of the tetrahedral molecule through a plane perpendicular to this line and passing

through the point O, we get a different configuration. However, if we apply the two operations one after the other, they *together* constitute a symmetry operation, as illustrated below :



As can be seen, neither a rotation through 90° around the Z axis nor a reflection through the plane XY is a symmetry operation. But, a combination of the two generates a symmetry operation. There are two other such axes of rotation in the tetrahedron. The student is advised to identify these himself. In the above figure, the numbers are written only to clarify the rotation of the molecule. Otherwise there is no difference in the four bonds originating from the point O. The improper axis of rotation as also the improper rotation operation are indicated by the symbol S_n.

Let us now see how many symmetry operations can be performed around an S_n axis of rotation. The possible rotation operations about an S_4 axis are :

$S_4^1 = \sigma C_4$ which is a genuine improper rotation operation or rotation-reflection operation.

$S_4^2 = \sigma^2 C_4^2 = E C_4^2 = C_4^2 = C_2$; S_4^2 is thus a proper rotation operation.

$S_4^3 = \sigma^3 C_4^3 = \sigma^2 \sigma C_4^3 = E \sigma C_4^3 = \sigma C_4^3$ which is a genuine improper rotation operation.

$S_4^4 = \sigma^4 C_4^4 = E \times E = E$ which is obviously an identity operation.

Thus, an S_4 axis generates four symmetry operations in all, two of which are genuine improper rotation operations, the third is a proper rotation operation and the fourth one is an identity operation. In general, an S_n axis (n is even) generates n symmetry operations some of which are genuine improper rotation operations and some are not.

Let us now see how many symmetry operations can be generated about an S_5 axis. The possible symmetry operations are :

$S_5^1 = \sigma C_5^1$ which is a genuine rotation–reflection operation or improper rotation operation.

$S_5^2 = \sigma^2 C_5^2 = E C_5^2 = C_5^2$ which is a proper rotation operation.

$S_5^3 = \sigma^3 C_5^3 = \sigma^2 \sigma C_5^3 = E \sigma C_5^3 = \sigma C_5^3$ which is a genuine improper rotation operation.

$S_5^4 = \sigma^4 C_5^4 = E C_5^4 = C_5^4$ which is a proper rotation operation.

$S_5^5 = \sigma^5 C_5^5 = \sigma^4 \sigma C_5^5 = E \sigma C_5^5 = E \sigma E = \sigma$ which is a reflection operation.

$S_5^6 = \sigma^6 C_5^6 = E C_5^1 = C_5^1$ which is a proper rotation operation.

$S_5^7 = \sigma^7 C_5^7 = \sigma^6 \sigma C_5^2 = E \sigma C_5^2 = \sigma C_5^2$ which is a genuine improper rotation operation.

$S_5^8 = \sigma^8 C_5^8 = E C_5^3 = C_5^3$ which is a proper rotation operation.

$S_5^9 = \sigma^9 C_5^9 = \sigma^8 \sigma C_5^9 = E \sigma C_5^4 = \sigma C_5^4$ which is a genuine improper rotation operation.

$S_5^{10} = \sigma^{10} C_5^{10} = E C_5^5 = E$ which is an identity operation.

Thus, an S_5 axis generates 10 symmetry operations four of which are genuine improper rotation operations, four are proper rotation operations, one is reflection operation and the tenth is the identity operation. In general, an S_n axis (n is odd) generates $2n$ symmetry operations some of which are

genuine improper rotation operations and some are not.

Equivalent Symmetry Elements and Equivalent Atoms

If a symmetry element A is carried to a symmetry element B by a symmetry operation X, then B can be carried back to A by the reverse of the operation, *i.e.*, X^{-1}. The symmetry elements A and B are then called **equivalent symmetry elements.** Consider, for instance, a square plane. There are four C_2 axes lying in the square plane, as shown in Fig.1.

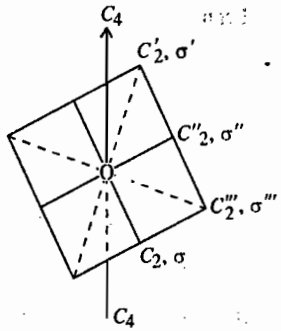
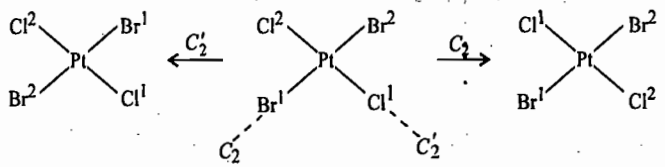


Fig. 1. A square plane

If we carry out C_4 operation around the symmetry axis which is perpendicular to the square plane and passes through O, the C_2 axis is carried to the position of C_2'' and C_2' is carried to the position of C_2'''. But, it is not possible to carry C_2 to C_2' position and C_2'' to C_2''' position by applying any symmetry operation about any symmetry element of the square planar geometry. Thus, C_2 and C_2'' are equivalent as are C_2' and C_2'''. However, C_2 and C_2' are not equivalent. Likewise, C_2'' and C_2''' are not equivalent. Similarly, it can be shown that out of σ, σ', σ'' and σ''' which are perpendicular to the square plane and pass through C_2, C_2', C_2'' and C_2''', respectively, σ and σ'' are equivalent as are σ' and σ'''.

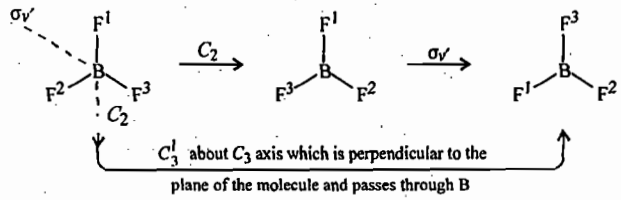
Equivalent atoms in a molecule are those which can all be interchanged by one another by appropriate symmetry operations. Obviously, equivalent atoms must belong to the same chemical species. In trans $[PtCl_2Br_2]^{2-}$ ion molecule, the two Br atoms are equivalent as are the two Cl atoms since an appropriate C_2 operation can interchange the two Cl atoms or the two Br atoms, as shown below :



Product of Symmetry Operations. Suppose we carry out symmetry operation X first and then the symmetry operation Y on a given geometry. The combination of these two operations is always a symmetry operation of that geometry. The combination, called the **'product'**, is written as $YX = Z$. By convention, the order of the symmetry operations carried out on a given geometry is written from right to left. Thus, in the above product, the symmetry operation Z is obtained by carrying out operation X followed by operation Y on the geometry. Similarly, in the product $MLXY = Z$, the symmetry operation Z is obtained by carrying out operations Y, X, L and M in that order on the geometry.

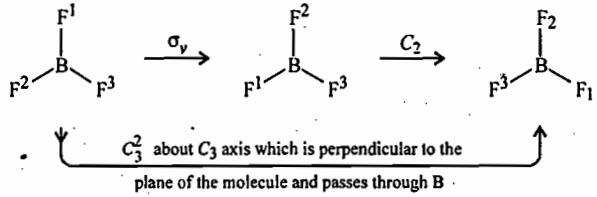
The product YX does not always give the same result as the product XY. In a case where $YX \neq XY$, we say that the operations X and Y *do not commute.* If, however, $YX = XY$, we say that *X and Y commute with each other.*

Let us consider the product $\sigma_v' C_2$, as applied on molecule BF_3. The plane σ_v' is perpendicular to the plane of the molecule and passes through the $B—F^3$ bond (the F atoms are numbered only for better understanding of the symmetry operations). The directions of C_2 and σ_v' are as shown in the figure.



It is evident from the above figure that $\sigma_v' C_2 = C_3^1$.

Let us now find out $C_2\sigma_v'$. This is done by carrying out the two operations as illustrated below :

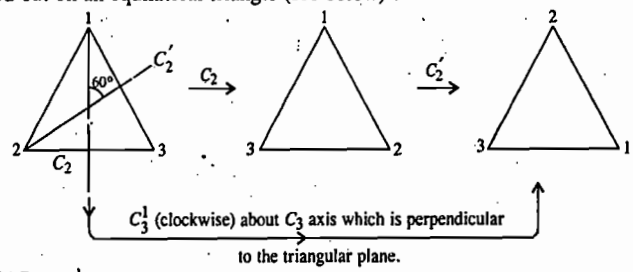


Evidently, $C_2\sigma_v' = C_3^2$. Thus, while the product $\sigma_v' C_2 = C_3^1$, the product $C_2\sigma_v' = C_3^2$, that is, $\sigma_v' C_2 \neq C_2\sigma_v'$. In other words, the operations C_2 and σ_v' do not commute.

It is important to note that the product of an identity operation with any other symmetry operation always yields that symmetry operation. Thus, $C_n^m E = C_n^m$; $\sigma C_2 E = \sigma C_2$; $\sigma_v^3 C_2 = E\sigma C_2 = \sigma C_2$ ($\because \sigma^2 = E$).

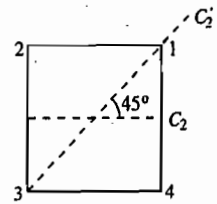
General Relations Amongst Symmetry Elements and Symmetry Operations. The following general relations hold good amongst symmetry elements and symmetry operations.

1. The product of two proper rotations is itself a proper rotation, as is evident from the symmetry operations carried out on an equilateral triangle (see below) :

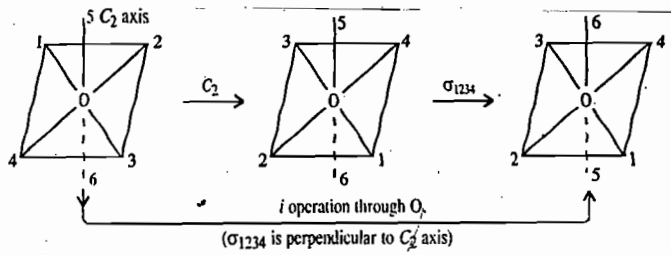


Thus, $C_2' C_2 = C_3^1$

2. The product of two C_2 rotations about axes which intersect at an angle θ, is a rotation by 2θ about an axis which is perpendicular to the plane containing the two C_2 axes. As shown in the example given above, the product of two C_2 rotations about C_2 and C_2' axes which intersect at an angle of 60° is equal to rotation through an angle $2 \times 60°$, *i.e.*, 120° about an axis which is perpendicular to the plane containing the two axes. Similarly, it can be shown that in a square plane, the product $C_2' C_2$ about the two axes which are inclined at an angle of 45° is equal to rotation about the C_4 axis through an angle of 2×45, *i.e.*, 90°. The C_4 axis is perpendicular to the plane containing the two C_2 axes.

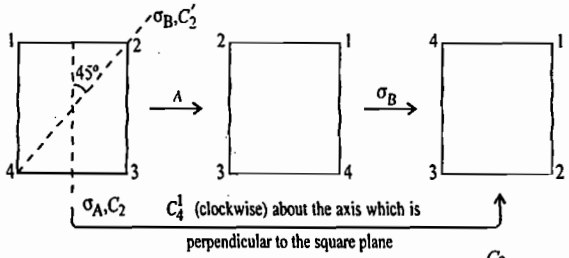


3. A proper axis of even order and a perpendicular reflection plane generate an inversion centre. Consider the example of a regular octahedral molecule which is operated upon as shown below :

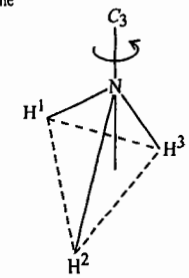


It is clearly evident from the figure that $\sigma_{1234}\, C_2 = i$.

4. The product of two reflections in planes σ_A and σ_B intersecting at an angle θ_{AB} is a rotation through $2\theta_{AB}$ about the axis defined by the line of intersection of the two planes. Consider a square planar geometry in which planes σ_A and σ_B are passing through C_2 and C_2', respectively and are perpendicular to the square plane. The angle between these two planes is 45°. The line of intersection of the two planes σ_A and σ_B is obviously perpendicular to the square plane and is collinear with C_4 symmetry axis. As can be seen from the figure shown, the reflection through σ_A and σ_B is equal to C_4^1 rotation operation about the line of intersection of the two planes.



5. When there is a rotation axis C_n and a plane of symmetry containing it, there must be n-1 more planes like the previous plane. Consider, for example, a pyramidal molecule such as NH_3. It has a three-fold axis of symmetry as shown in the figure. There is a plane of symmetry passing through this C_3 axis and the N—H_1 bond bisecting the angle H^2NH^3. We can easily visualise that there are two more planes of symmetry of this type passing through the C_3 axis.



SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS IN MOLECULES OF SPECIAL SYMMETRY

1. Linear Molecules. Let us consider a CO_2 molecule. The OCO bond axis is the C_∞ axis of symmetry about which infinite number of rotations can be carried out. Similarly, any line perpendicular to OCO bond axis and passing through the middle of the molecule is a two-fold axis of symmetry. One can draw infinite number of such lines. Similarly, one can draw infinite number of planes of symmetry passing through OCO. There is also a plane of symmetry which is perpendicular to OCO bond axis and passes through the centre of the molecule. Apart from this, there is a centre of inversion in the middle of the molecule. Such symmetrical linear molecules are said to belong to $D_{\infty h}$ symmetry point group. Other examples of such molecules are O_2, H_2, N_2, etc.

Let us now consider an unsymmetrical molecule such as NO. There is a C_∞ axis collinear with the bond axis and there are infinite number of σ_vs passing through the C_∞ axis. However, there is no symmetry axis perpendicular to the NO bond and passing through the middle of the NO bond. Such a molecule is said to belong to $C_{\infty v}$ group.

2. Tetrahedral Molecules. A regular tetrahedron can be derived from a cube, as shown in Fig. 2.

Let us consider a regular tetrahedral molecule CH_4 and determine its symmetry elements and symmetry operations :

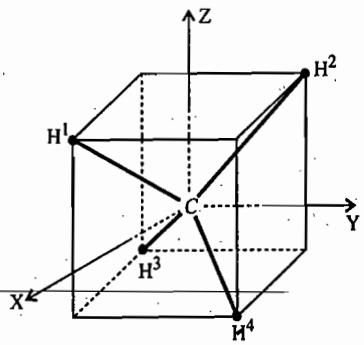


Fig. 2. Derivation of a regular tetrahedron from a cube

(*i*) The molecule has three S_4 axes. If we rotate the tetrahedral molecule shown in the figure through 90° about Z axis and then reflect the resulting geometry through a plane perpendicular to Z axis, *i.e.*, through XY plane, we get an equivalent geometry. Similar operations can be carried out about Y and X axes. Thus, X, Y and Z axes are S_4 axes of improper rotation. Each S_4 axis can generate four symmetry operations, *viz.*, S_4^1, *i.e.*, σC_4^1 ; S_4^2, *i.e.*, $\sigma^2 C_4^2$ which, in fact, is EC_2 or C_2 operation; S_4^3, *i.e.*, $\sigma^3 C_4^3$ or σC_4^3 and S_4^4, *i.e.*, $\sigma^4 C_4^4$ or E operation. Thus, each S_4 axis generates

two genuine rotation-reflection operations or improper rotation operations. Therefore, six S_4 operations are possible on this geometry.

(*ii*) There are three C_2 axes collinear with X, Y and Z axes (each C_2 axis bisects a pair of tetrahedral angles). Each C_2 axis generates one symmetry operation (rotation of the molecule twice about any of the three C_2 axes yields identical geometry). Thus, three C_2 operations are possible in a tetrahedral molecule.

(*iii*) There are four C_3 axes of symmetry, *viz.*, C-H^1, C-H^2, C-H^3 and C-H^4, in this case. Each C_3 axis generates two symmetry operations, *viz.*, C_3^1 and C_3^2 (C_3^3 is an identity operation). Thus, eight genuine C_3 operations are possible in this case.

(*iv*) There are six planes of symmetry each of them passing through two of the six C-H bonds. Each plane of symmetry generates one symmetry operation (each reflection operation carried out twice constitutes an identity operation). Thus, there are six reflection operations.

In all there are twenty four symmetry operations comprising of six S_4 operations, three C_2 operations, eight C_3 operations, six σ operations and one identity operation, which can be carried out on a regular tetrahedral molecule.

3. Octahedral Molecules. Let us now consider an octahedral species ML_6 shown in Fig. 3 and determine its symmetry elements and symmetry operations :

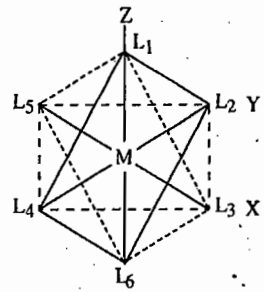


Fig.3. An octahedral species ML_6

(*i*) There are three S_4 axes (along X, Y and Z axes) in this case. Each S_4 axis can generate S_4^1, S_4^2, S_4^3 and S_4^4 operations. But, S_4^2 and S_4^4 are, in fact, C_2 and E operations, respectively. Thus, each S_4 axis generates two improper rotation operations (S_4^1 and S_4^3) and hence three S_4 axes would generate six improper rotation operations.

(*ii*) There are three C_4 axes collinear with S_4 axes (*i.e.*, along X, Y and Z axes). Each C_4 axis generates two genuine C_4 rotation operations, *viz.*, C_4^1 and C_4^3 since C_4^2 is a C_2 operation and C_4^4 is an identity operation. Thus, six C_4 operations are possible on this geometry.

(*iii*) There are three C_2 axes collinear with C_4 axis about which three C_2 operations can be carried out. It may be noted again that $C_2^2 = E$.

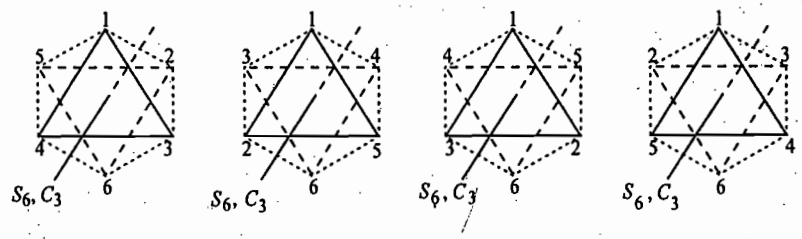
(*iv*) There are six C_2 axes which bisect the angles L_1ML_5, L_1ML_3, L_2ML_3, L_2ML_5, L_1ML_2 and L_1ML_4. These generate six C_2 operations.

(*v*) There are three planes of symmetry marked separately by dotted lines, solid lines and dashed lines in the above figure which pass through the four vertices of the octahedron. These generate three reflection operations.

(*vi*) There are six planes of symmetry, each passing through a C_4 axis and bisecting the angles mentioned in (*iv*) above. These generate six reflection operations.

(*vii*) There is a centre of inversion at M which generates one i operation.

(*viii*) There are four C_3 axes each passing through the centre of opposite triangular face of the octahedron. These can be represented as shown in the following figures :



Each C_3 axis generates two C_3 operations, *viz.*, C_3^1 and C_3^2 (C_3^3 is an identity operation). Thus, the four C_3 axes generate eight C_3 operations.

(*ix*) Collinear with the above mentioned C_3 axis, are the four S_6 axes which means that we rotate the figure through 60° about these axes and then apply the reflection operation through a plane which is in between the two opposite triangular faces. The four pairs of opposite triangular faces and the four S_6 axes are shown in the figure given above. Each such S_6 axis can generate the following six symmetry operations :

S_6^1 which is $\sigma^1 C_6^1$ and is a genuine improper rotation or rotation-reflection operation.

S_6^2 which is $\sigma^2 C_6^2$ or EC_3 or C_3

S_6^3 which is $\sigma^3 C_6^3$ or $E\sigma\, C_2$ or σC_2 or i

S_6^4 which is $\sigma^4 C_6^4$ or $E\, C_3^2$ or C_3^2

S_6^5 which is $\sigma^5 C_6^5$ or $E\sigma C_6^5$ or σC_6^5 which is a genuine improper rotation or rotation-reflection operation.

S_6^6 which is E.

As can be seen, only two of the above mentioned operations are genuine improper rotation operations. Since there are four S_6 axes in the system, these generate eight S_6 symmetry operations.

Thus, in a regular octahedron, forty eight symmetry operations including six S_4, six C_4, nine C_2, nine σ, one i, eight C_3, eight S_6 and one E operations are possible.

SYMMETRY CLASSIFICATION OF MOLECULES

It can be shown that all the axes and the planes of symmetry of any geometry must intersect at least at one common point. Therefore, the collection of symmetry elements of any geometry is known as the **symmetry point group** of that geometry. The symmetry point groups to which the various molecules belong are determined by following the procedure outlined below :

1. Determine whether the molecule belongs to any of the following special symmetry point groups : $C_{\infty v}$, $D_{\infty h}$, T_d, O_h.

2. If the molecule does not belong to any of the above mentioned special groups, search for a proper or an improper rotation axis. If no such axis is present, then look for a plane of symmetry or the centre of symmetry. If only a plane of symmetry is present and there is no other element of symmetry, the molecule belongs to C_s point group. Two symmetry operations, σ and E, can be carried out on such molecules. If only a centre of inversion is present and there is no other element of symmetry, the molecule belongs to C_i symmetry point group. Again two symmetry operations, i and E, can be performed on such molecules. If no symmetry element is present at all, the molecule belongs to C_1 symmetry point group. Only one symmetry operation E can be carried out on such a molecule.

3. If a molecule has an improper axis of rotation of even order and no other element of symmetry (except for a proper axis of rotation collinear with the improper axis of rotation) is present, the molecule belongs to S_4 or S_6 or S_8, etc., symmetry point group. In such a molecule, n symmetry operations about the S_n axis are possible, as already explained.

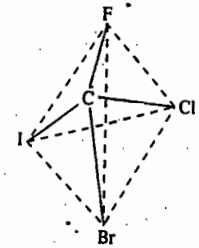
4. If the molecule does not belong to any of the above mentioned groups, look for a highest-order proper axis of rotation C_n, called the principal axis. If there are several proper axes of rotation, choose that axis as principal axis which is of highest order. If there are several proper axes of rotation of highest order, choose that axis as principal axis which is unique in some way. If all proper axes of rotation are alike, the principal axis of rotation is selected at random.

Now look for n C_2 axes perpendicular to the principal axis. If these axes exist, we proceed to step 5. If not, the molecule belongs to C_n or C_{nv} or C_{nh} symmetry point group as the case may be. If there are no symmetry elements other than C_n axis, the molecule belongs to C_n symmetry point group. A total of n

symmetry operations can be carried out around this C_n axis. If there are n σ_vs alongwith a C_n axis, the molecule belongs to C_{nv} symmetry point group. In such molecules, 2n symmetry operations are possible. But, if there is only a horizontal plane of symmetry which is perpendicular to the principal axis of symmetry C_n, the molecule belongs to C_{nh} symmetry point group. Again, 2n symmetry operations are possible in such cases.

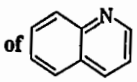
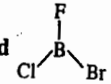
5. If, in addition to C_n, n C_2 axes which are all perpendicular to the C_n axis are also present, the molecule belongs to D_n, D_{nh} or D_{nd} symmetry point group. If no symmetry elements except for C_n and n C_2 axes which are perpendicular to C_n axis, are present, the molecule belongs to D_n symmetry point group. But, if apart from C_n axis and n C_2 axes perpendicular to C_n, a horizontal plane of symmetry is also present, the molecule belongs to D_{nh} symmetry point group. Such molecules would essentially contain n vertical planes of symmetry as well. In molecules with D_{nh} symmetry, 4n symmetry operations are possible. If there is no σ_h but there are n C_2 axes perpendicular to C_n axis and n vertical planes which pass between the C_2 axes, the molecule belongs to D_{nd} point group. In such molecules, 4n symmetry operations are possible. It is to be noted that whereas in molecules with D_{nh} symmetry, there is an S_n improper rotation axis, there exists an S_{2n} improper rotation axis in molecules with D_{nd} symmetry.

The above mentioned notation of symmetry point groups based on the use of C, σ, i symbols for symmetry elements is known as **Schoenfless notation.**

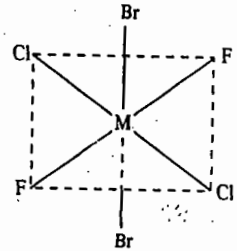


Let us now determine **symmetry point groups of some typical molecules.**

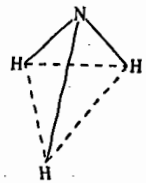
1. Symmetry Point Group of CFClBrI Molecule. It has no element of symmetry and hence it belongs to C_1 **symmetry point group.** The only symmetry operation that can be carried out on the geometry of the molecule is E.

2. Symmetry Point Groups of  **and**  **Molecules.** Each of these molecules contains only a plane of symmetry which is also the plane of the molecule. Thus, both the molecules belong to C_s **symmetry point group.** The symmetry operations that can be performed on these molecules are σ and $\sigma^2 (= E)$.

3. Symmetry Point Group of trans $[MF_2Cl_2Br_2]^{n-}$ Ion. This ion has a C_2 axis (along the Br–M–Br bond) which can be taken as the principal axis and two C_2 axes perpendicular to the principal axis. Apart from this, there is a σ_h axis which is perpendicular to the principal axis. The molecule thus belongs to D_{2h} **symmetry point group.**



Apart from the above mentioned symmetry elements, two σ_vs and a centre of symmetry are also present in the molecule. The eight symmetry operations that can be carried out on this molecule are : three C_2s, two σ_vs, i, σ and E.

4. Symmetry Point Group of NH_3 Molecule, 

. The molecule contains a C_3 axis which is the principal axis of symmetry. Apart from this, there are three σ_vs each of which passes through the C_3 axis and one N—H bond that bisects the angle between the other two N—H bonds. The molecule thus belongs to C_{3v} **symmetry point group.** The six symmetry operations that can be performed on this molecule are C_3^1, C_3^2, C_3^3 $(= E)$ and three σ_vs.

5. Symmetry Point Group of Trans N_2F_2 Molecule, $F{/}N{=}N{/}F$, This molecule contains a C_2 axis passing through the middle of N=N bond and perpendicular to the plane of the molecule which is also a plane of symmetry (σ_h). Apart from this, there is a centre of inversion in the middle of N=N bond. The molecule, thus, belongs to C_{2h} **symmetry point group.** The four symmetry operations possible in this geometry are C_2, σ_h, i and E.

A Complete Set of Symmetry Operations as a Mathematical Group

A complete set of symmetry operations of a geometry behaves like a mathematical group. We shall, first of all, define a mathematical group and then describe the rules which the elements of the group follow. Having done that, we shall show that a complete set of symmetry operations follow these rules and thus constitute a mathematical group.

A **mathematical group** is a collection of elements which are interrelated according to the following rules :

1. The product (or multiplication) of any two elements in the group and the square of each element must be an element in the group. The product or multiplication of elements here means combination of elements of the group. The square of an element means multiplying an element with itself. The product of two elements A and B of the group can be BA or AB. The product AB may not always be equal to BA. Quite often the product AB may give the element C of the group whereas BA may give another element D of the same group. If, for the two elements $AB = BA$, we say that the elements A and B commute with each other. If $AB \neq BA$, we say that the elements A and B do not commute. As a convention, we start multiplying the elements of a combination from right towards left. Thus, in ABC, we multiply C with B to get, say D and then multiply D with A.

2. There is one element in each mathematical group which must commute with all other elements of the group and leave them unchanged. Such an element is known as the **identity element.** Suppose E is an identity element while A is some other element of a group. Then, $EA = AE = A$.

3. The elements of a mathematical group obey the associative law of multiplication, *i.e.*, $AB(CDE) = A(BC)(DE) = (AB)(CD)E$ where A, B, C, D and E are the elements of the same mathematical group.

4. Each element of a mathematical group must have a reciprocal which is also an element of the group. When an element is multiplied by its reciprocal, we get the identity element E of the group, *i.e.*, $AA^{-1} = A^{-1}A = E$. The reciprocal of two or more elements is equal to the product of the reciprocals in the reverse order. Thus, $(ABC)^{-1} = C^{-1}B^{-1}A^{-1}$. The number of elements in a finite group is known as the **order of the group.**

Let us consider the product $X^{-1}AX$ in which X, A and X^{-1} are the elements of a mathematical group. Suppose $X^{-1}AX = B$. Then, B is known as **similarity transform** of A by X and A and B are known as the **conjugate elements.** These conjugate elements have the following properties :

a. Each element is conjugate with itself, *i.e.*, it is possible to find at least one element in the group which would transform A into A. Such an element is the identity element E. Thus, $E^{-1}AE = A$.

b. If element A is conjugate with element B as well as with C, then B and C are conjugate with each other and A, B and C are all conjugate with one another.

c. If element A is conjugate with symmetry element B, then B is conjugate with A, *i.e.*, if $X^{-1}AX = B$, then it is always possible to find another element Y of the group so that $Y^{-1}BY = A$. A complete set of elements which are conjugate with one another is termed as the **class** of the mathematical group. The order of each class, *i.e.*, the number of elements in each class, must be an integral factor of the order of the group.

A simple example of a mathematical group of elements is offered by **all integrals from** $+\infty$ **to** $-\infty$ **including zero.** If we define the product as addition, we see that this mathematical group of the order equal to ∞, obeys all the rules mentioned above. In this example of a mathematical group, zero is the identity element.

We shall now show that a complete set of symmetry operations of a geometry constitute a mathematical group. Let us take the example of planar triangular BF_3 molecule belonging to D_{3h} symmetry group, as shown in Fig. 4.

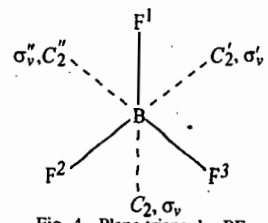
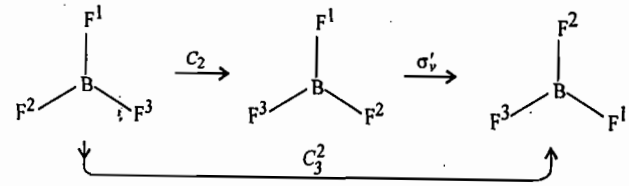


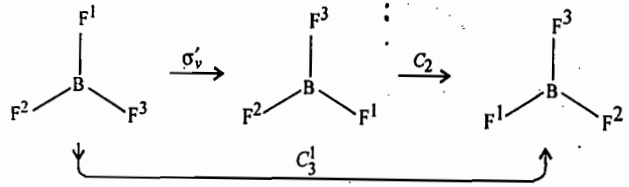
Fig. 4. Plane triangular BF_3 molecule

The complete set of symmetry operations that can be carried out on this molecule are : E, C_3^1, C_3^2, σ_v, σ_v', σ_v'', σ_h, C_2, C_2', C_2'', S_3^1 and S_3^5. Let us determine the product $\sigma_v' C_2$. As already mentioned, we always start multiplying from right to left, Accordingly, the operations carried out on the molecule would be as shown below :



As is obvious from the above figure, the geometry resulting from the operation of $\sigma_v' C_2$ can be obtained by applying a single C_3^2 operation which is also a symmetry operation of D_{3h} group. Similarly, we can take the product of any other two or three symmetry operations. We shall see that the resulting geometry would also be obtained by applying another appropriate single symmetry operation of D_{3h} symmetry group. Thus, the complete set of symmetry operations mentioned above obeys the first rule followed by the elements of a mathematical group.

It is to be noted that in the present case, the product $C_2\sigma_v'$ does not commute with the product $\sigma_v' C_2$ since $C_2\,\sigma_v' = C_3^1$, as shown below :



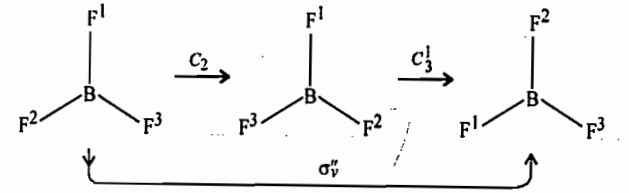
The second rule which the elements of a mathematical group must obey is that there should be at least one element amongst the complete set of elements of the group which when combined with any other element of the group would leave it unchanged. In a complete set of symmetry operations of D_{3h} group, the identity operation E is an operation of this type. Thus, $EC_2 = C_2E = C_2$ and so on.

Let us now consider the product $C_3^1(C_2\sigma_v')$ of three symmetry operations of D_{3h} symmetry point group. The product $(C_2\sigma_v')$ has already been shown to be equal to C_3^1. Hence,

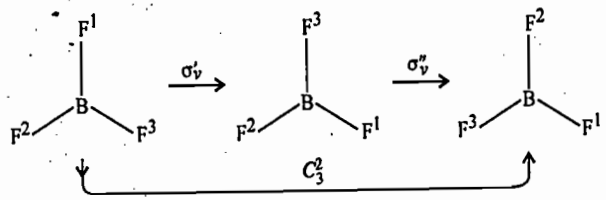
$$C_3^1(C_2\sigma_v') = C_3^1 C_3^1 = C_3^2$$

Let us now evaluate the product $\left(C_3^1 C_2\right)\sigma_v'$.

The product $C_3^1 C_2$ is equal to σ_v'', as shown below :



Hence, $(C_3^1 C_2)\sigma_v' = \sigma_v''\sigma_v'$ which is equal to C_3^2, as shown below :



Thus, $C_3^1(C_2\sigma_v') = (C_3^1 C_2)\sigma_v' = C_3^2$. This shows that the symmetry operations in the present case obey the associative law of multiplication which is the third rule that the elements of a mathematical group must obey.

Consider the product $C_3^2 C_3^1$. This is equal to E. Therefore, the reciprocal of C_3^1 is C_3^2 and of C_3^2 is C_3^1. Similarly, C_2, C_2', C_2'', σ_v', σ_v'', σ_v, σ_h are all their own reciprocals. Thus, like the symmetry elements of a mathematical group, each symmetry operation of D_{3h} point group has a reciprocal which also is a symmetry operation of the point group. Similarly, we can take any other point group and show that *a complete set of symmetry operations of a point group constitutes a mathematical group.*

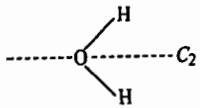
A table which includes the products of the elements of a mathematical group is called **group multiplication table (GMT).**

Each row and each column of such a table is headed by a symmetry element of the group. The product of two symmetry elements AB of the group is the symmetry element at the crossing point of *Bth row and Ath column*. Since the symmetry operations of a point group behave like the symmetry elements of a mathematical group, we can construct a group multiplication table for the products of the symmetry operations. One such group multiplication table of C_{2v} point group, taking H_2O molecule as an example of this point group, is given in Table 1 :

TABLE 1

GMT of C_{2v} Point Group

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E



(σ_v is the plane of the H_2O molecule, σ_v' is perpendicular to the plane of the molecule passing through C_2.)

Suppose we wish to determine $C_2\sigma_v$. It is evident from GMT that the crossing point of σ_vth row and C_2th column is σ_v'. Thus, $C_2\sigma_v = \sigma_v'$. Similarly, the crossing point of C_2th row and σ_vth column is σ_v'. Thus, $\sigma_v C_2$ is also equal to σ_v'.

Classes of Symmetry Operations

Consider the anion $[CoF_5Br]^{3-}$ belonging to point group C_{4v}, whose geometry and symmetry elements are as shown in Fig. 5.

All the vertical planes and dihedral planes of symmetry pass through the C_4 axis. The symmetry operations possible in this case are C_4^1, C_4^3, E, $\sigma_{v(1)}$, $\sigma_{v(2)}$, $\sigma_{d(1)}$, $\sigma_{d(2)}$ and C_2.

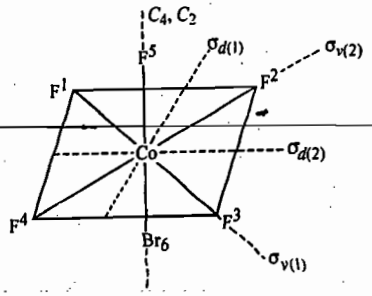


Fig. 5. Geometry and symmetry elements of the anion $[CoF_5Br]^{3-}$

The results of **similarity transformations** of these symmetry elements by C_4^1 and $\sigma_{v(1)}$ are as given below :

$$C_4^{-1} E C_4^1 = E \qquad \sigma_{v(1)}^{-1} E \sigma_{v(1)} = E$$
$$C_4^{-1} C_4^1 C_4^1 = C_4^1 \qquad \sigma_{v(1)}^{-1} C_4^1 \sigma_{v(1)} = C_4^3$$
$$C_4^{-1} C_4^3 C_4^1 = C_4^3 \qquad \sigma_{v(1)}^{-1} C_4^3 \sigma_{v(1)} = C_4^1$$
$$C_4^{-1} C_2 C_4^1 = C_2 \qquad \sigma_{v(1)}^{-1} \sigma_{v(1)} \sigma_{v(1)} = \sigma_{v(1)}$$
$$C_4^{-1} \sigma_{v(1)} C_4^1 = \sigma_{v(2)} \qquad \sigma_{v(1)}^{-1} \sigma_{v(2)} \sigma_{v(1)} = \sigma_{v(2)}$$
$$C_4^{-1} \sigma_{v(2)} C_4^1 = \sigma_{v(1)} \qquad \sigma_{v(1)}^{-1} \sigma_{d(1)} \sigma_{v(1)} = \sigma_{d(2)}$$
$$C_4^{-1} \sigma_{d(1)} C_4^1 = \sigma_{d(2)} \qquad \sigma_{v(1)}^{-1} \sigma_{d(2)} \sigma_{v(1)} = \sigma_{d(1)}$$
$$C_4^{-1} \sigma_{d(2)} C_4^1 = \sigma_{d(1)} \qquad \sigma_{v(1)}^{-1} C_2 \sigma_{v(1)} = C_2$$

As already mentioned, the symmetry operations which are transformed into one another by similarity transformations constitute a **class** of symmetry operations. Thus, there are the following classes of symmetry operations of C_{4v} point group :

$$E\,;\ C_4^1,\ C_4^3;\ \sigma_{v(1)}, \sigma_{v(2)}\,;\ \sigma_{d(1)}, \sigma_{d(2)} \text{ and } C_2$$

The number of symmetry elements in each class is known as its **order**; the order of a class is an integral factor of the order of the group.

Representation of Symmetry Operations by Matrices

Consider a point (x_1, y_1, z_1) in a Cartesian coordinate system. If we reflect this point through XY plane, we get the point (x_2, y_2, z_2), as illustrated in Fig. 6.

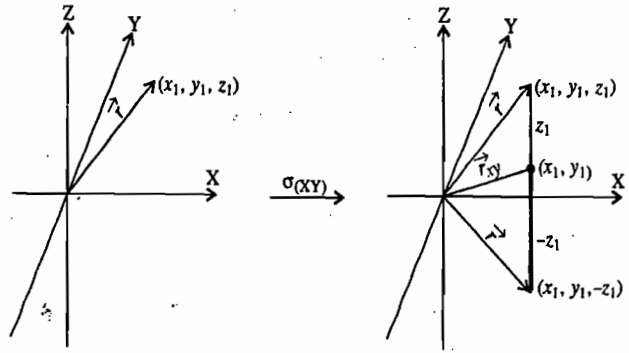


Fig. 6. Reflection of point (x_1, y_1, z_1) in a Cartesian coordinate system through XY plane.

Obviously,

$$x_2 = x_1 = 1x_1 + 0y_1 + 0z_1$$
$$y_2 = y_1 = 0x_1 + 1y_1 + 0z_1$$
$$z_2 = -z_1 = 0x_1 + 0y_1 - 1z_1$$

We can write the above result in the following matrix form :

$$\sigma_{XY}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} x_1 \\ y_1 \\ -z_1 \end{bmatrix} = \begin{bmatrix} 1x_1 + 0y_1 + 0z_1 \\ 0x_1 + 1y_1 + 0z_1 \\ -x_1 + 0y_1 - 1z_1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

Thus, the operation σ_{XY} on the point (x_1, y_1, z_1) can be represented by the matrix $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.

In a similar manner, we can show that the operations σ_{XZ} and σ_{YZ} on the point (x_1, y_1, z_1) can be represented by the matrices $\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ and $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$, respectively.

We shall show that a rotation operation can also be represented by a matrix. Let us consider the rotation of the point (x_1,y_1,z_1) around the Z axis which gives the point (x_4,y_4,z_4). Since the rotation of the point (x_1,y_1,z_1) through any angle around the Z axis, cannot change the z coordinate, z_4 is the same as z_1. In other words, only x and y coordinates of the point will change.

In order to understand the rotation operation better, we shall consider the rotation of the projection of the vector r in the XY plane. Let us call the projection of r in the plane XY as r_{XY}, as shown in Fig. 7. Let the vector r_{XY} in its original position make an angle α with X axis so that

$$x_1 = \vec{r}_{XY} \cos \alpha$$

$$y_1 = \vec{r}_{XY} \sin \alpha$$

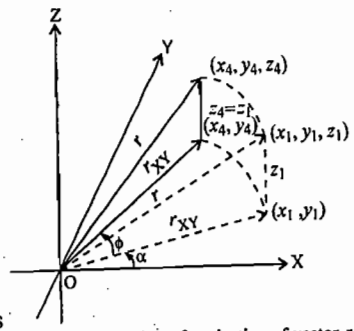


Fig. 7. Rotation of projection of vector r in XY plane

Rotation of vector $\vec{r}_{XY}$ around Z axis by an angle ϕ changes the coordinates of the point from (x_1, y_1) to (x_4, y_4) so that

$$x_4 = \vec{r}_{XY}\cos(\phi+\alpha) = \vec{r}_{XY}\cos\phi\cos\alpha - \vec{r}_{XY}\sin\phi\sin\alpha = x_1\cos\phi - y_1\sin\phi$$

$$y_4 = \vec{r}_{XY}\sin(\phi+\alpha) = \vec{r}_{XY}\sin\phi\cos\alpha + \vec{r}_{XY}\cos\phi\sin\alpha = x_1\sin\phi + y_1\cos\phi$$

$$z_4 = z_1$$

or
$$\begin{bmatrix} x_4 \\ y_4 \\ z_4 \end{bmatrix} = \begin{bmatrix} x_1\cos\phi & -y_1\sin\phi & +0z_1 \\ x_1\sin\phi & +y_1\cos\phi & +0z_1 \\ 0x_1 & +0y_1 & +1z_1 \end{bmatrix}$$

We can write the above result in the following matrix form:

$$C_{Z(\phi)}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_4 \\ y_4 \\ z_4 \end{bmatrix} = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

Thus, $C_{Z(\phi)}$ can be represented by the matrix $\begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$.

The operation i changes the coordinates of the point from (x_1, y_1, z_1) to $(-x_1, -y_1, -z_1)$ so that

$$i\,(x_1, y_1, z_1) = (-x_1, -y_1, -z_1)$$

Writing the result in the matrix form, we have

$$i\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} -x_1 \\ -y_1 \\ -z_1 \end{bmatrix} = \begin{bmatrix} -x_1 & +0y_1 & +0z_1 \\ 0x_1 & -y_1 & +0z_1 \\ 0x_1 & +0y_1 & -z_1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

Thus, i can be represented by the matrix $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.

Lastly we consider improper rotation operation on the point (x_1, y_1, z_1) around the Z axis. This may be represented as follows :

$$S_Z\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \sigma_{XY}\, C_{Z(\phi)}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \sigma_{XY}\begin{bmatrix} x_4 \\ y_4 \\ z_4 \end{bmatrix} = \sigma_{XY}\begin{bmatrix} x_1\cos\phi & -y_1\sin\phi & +0z_1 \\ x_1\sin\phi & +y_1\cos\phi & +0z_1 \\ 0x_1 & +0y_1 & +1z_1 \end{bmatrix}$$

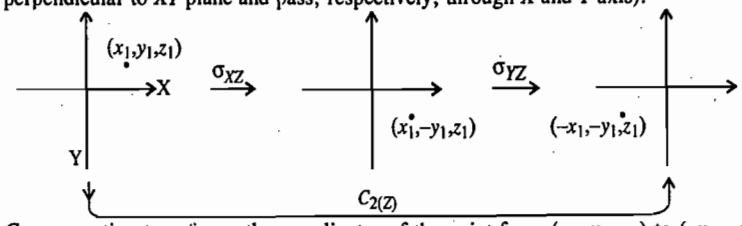
Now
$$\sigma_{XY}\begin{bmatrix} x_4 \\ y_4 \\ z_4 \end{bmatrix} = \begin{bmatrix} x_4 \\ y_4 \\ -z_4 \end{bmatrix} = \begin{bmatrix} x_1\cos\phi & -y_1\sin\phi & +0z_1 \\ x_1\sin\phi & +y_1\cos\phi & +0z_1 \\ 0x_1 & +0y_1 & -1z_1 \end{bmatrix} = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

(σ_{XY} operation leaves x and y coordinates of the point unchanged but changes the sign of z coordinate).

Thus, S_Z can be represented by the matrix $\begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & -1 \end{bmatrix}$.

Similarly, the identity operation on the point (x, y, z) can be written by the matrix, $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$.

The matrix representations of symmetry operations function exactly as do the symmetry operations themselves. For instance, it can be easily shown that $\sigma_{YZ}\,\sigma_{XZ} = C_{2(Z)}$ (see below). (The σ_{XZ} and σ_{YZ} planes are perpendicular to XY plane and pass, respectively, through X and Y axis).



Since $C_{2(Z)}$ operation transforms the coordinates of the point from (x_1, y_1, z_1) to $(-x_1, -y_1, z_1)$, the matrix representing $C_{2(Z)}$ can be shown to be $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$.

Let us now multiply matrices representing $\sigma_{YZ}\,\sigma_{XZ}$. The product is the matrix representing C_{2Z}, as shown below :

$$\underset{\sigma_{YZ}}{\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}\underset{\sigma_{XZ}}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} = \underset{C_{2(Z)}}{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}$$

We have already written matrices representing C_2, σ_{XZ}, σ_{YZ} and E which are the symmetry operations of C_{2v} point group. We did this by taking a point in three-dimensional space. We can also take a set of vectors, atomic orbitals or molecular orbitals, instead of taking a point and obtain sets of matrices which also represent symmetry operations of the point group. Instead of taking H_2O molecule

as the example of C_{2v} point group (as we did before), we can take other molecules such as CH_2Cl_2, cis N_2F_2, cis butadiene ($H_2C{=}CH{-}CH{=}CH_2$), etc., as examples of C_{2v} point group and write different sets of matrices representing the operations of the point group. Thus, a large number of sets of matrices which represent the same set of symmetry operations of the same symmetry point group can be written. A set of matrices representing a complete set of symmetry operations of a point group is known as a **'representation'** of that point group. It is designated by the symbol Γ.

Most of the times, it is very cumbersome to write a 'representation' in terms of a set of full matrices for the symmetry operations. Therefore, instead of writing full matrices, we generally write the **characters** (χ) of the matrices while writing a 'representation'. Thus, the representation corresponding to symmetry operations of C_{2v} point group carried out on point (x_1, y_1, z_1) is given below :

	E	C_2	$\sigma_{v(XZ)}$	$\sigma_{v(YZ)}$
Γ	3	-1	1	1

(Full matrices representing the symmetry operations on the point (x_1, y_1, z_1) have already been given above).

The numerical figures in the above representation give the characters of the matrices representing the symmetry operations whose symbols are written above these numerals.

Let us now, for the sake of practice, write down some more representations of C_{2v} point group taking into consideration the H_2O molecule. Let us associate three mutually perpendicular unit vectors with each atom of H_2O molecule, as shown in Fig. 8 and apply all the symmetry operations of C_{2v} point group on these vectors.

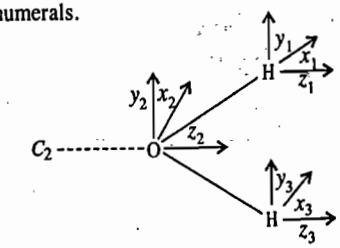


Fig. 8. Association of three mutually perpendicular unit vectors to each atom of H_2O molecule.

It can be shown that

1. All symmetry operations of C_{2v} point group to which H_2O molecule belongs can be represented by matrices of 9×9 dimensions. One such matrice is written below. The student is advised to write other matrices himself.

$$C_2 \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} -1x_3 \\ -1y_3 \\ +1z_3 \\ -1x_2 \\ -1y_2 \\ +1z_2 \\ -1x_1 \\ -1y_1 \\ +1z_1 \end{bmatrix} = \begin{bmatrix} 0x_1+0y_1+0z_1+0x_2+0y_2+0z_2-1x_3+0y_3+0z_3 \\ 0x_1+0y_1+0z_1+0x_2+0y_2+0z_2+0x_3-1y_3+0z_3 \\ 0x_1+0y_1+0z_1+0x_2+0y_2+0z_2+0x_3+0y_3+1z_3 \\ 0x_1+0y_1+0z_1-1x_2+0y_2+0z_2+0x_3+0y_3+0z_3 \\ 0x_1+0y_1+0z_1+0x_2-1y_2+0z_2+0x_3+0y_3+0z_3 \\ 0x_1+0y_1+0z_1+0x_2+0y_2+1z_2+0x_3+0y_3+0z_3 \\ -1x_1+0y_1+0z_1+0x_2+0y_2+0z_2+0x_3+0y_3+0z_3 \\ 0x_1-1y_1+0z_1+0x_2+0y_2+0z_2+0x_3+0y_3+0z_3 \\ 0x_1+0y_1+1z_1+0x_2+0y_2+0z_2+0x_3+0y_3+0z_3 \end{bmatrix} = \begin{bmatrix} 0&0&0&0&0&0&-0&0&0 \\ 0&0&0&0&0&0&0&-0&0 \\ 0&0&0&0&0&0&0&0&1 \\ 0&0&0&-1&0&0&0&0&0 \\ 0&0&0&0&-1&0&0&0&0 \\ 0&0&0&0&0&+1&0&0&0 \\ -1&0&0&0&0&0&0&0&0 \\ 0&-1&0&0&0&0&0&0&0 \\ 0&0&1&0&0&0&0&0&0 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix}$$

The character of the matrix representing C_2 operation on the nine vectors $x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3$ is obviously $(-1 - 1 + 1)$, *i.e.*, -1. The characters of matrices representing E, $\sigma_{v(xz)}$, $\sigma_{v(yz)}$ can be worked out in a similar manner.

2. The vector which shifts its position during a symmetry operation contributes zero to the character of the matrix representing that symmetry operation.

3. The vector which does not change direction and which does not shift its position in space during a symmetry operation contributes $+1$ to the character of the matrix representing that symmetry operation.

4. The vector which reverses its direction during a symmetry operation contributes -1 to the character of the matrix representing that symmetry operation.

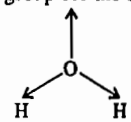
On applying C_2 operation, the vector z_2 remains unaltered whereas vectors x_2 and y_2 reverse their

directions. Therefore, $\chi_{C_2} = -1-1+1 = -1$. Reflecting all the vectors through the plane of the molecule, *viz.*, *YZ*, leaves y_1, y_2, y_3, z_1, z_2 and z_3 unaltered whereas x_1, x_2 and x_3 reverse in direction giving $\chi_{\sigma_{v(YZ)}} = 6-3=3$. Similarly, reflecting all the vectors through *XZ* plane, leaves x_2 and z_2 unaltered whereas y_2 reverses in direction giving $\chi_{\sigma_{v(XZ)}} = 2-1 = 1$. An identity operation will leave all the vectors unchanged in position as well as in direction so that $\chi_E=9$. The representation thus obtained is shown below :

	E	C_2	$\sigma_{v(YZ)}$	$\sigma_{v(XZ)}$
Γ	9	-1	3	1

Proceeding as above, we can write the following representation of C_{2v} point group for the symmetric stretching mode of vibration of H_2O molecule.

	E	C_2	$\sigma_{v(YZ)}$	$\sigma_{v(XZ)}$
Γ	3	1	3	1



(*YZ* is the plane of the molecule as already shown)

However, all the representations written above in terms of characters of matrices corresponding to the various symmetry operations of C_{2v} point group are made up of some finite number of fundamental representations. The representations which are additions of two or more fundamental representations of a symmetry point group are known as **reducible representations** of that point group. The fundamental representations which cannot be reduced (or cannot be broken up) further into simpler representations are called **irreducible representations.**

We shall now discuss the rules with the help of which we can determine the number of fundamental or irreducible representations of any symmetry point group. These rules are :

1. The number of irreducible representations in a group is equal to the number of classes of symmetry operations of the group.

2. The sum of the squares of dimensions of irreducible representations of a point group is equal to the order of the group. Since the square matrix representing the identity operation has all diagonal elements equal to 1, the character under column E of an irreducible representation is obviously equal to the dimension of each matrix of that representation.

3. The sum of the squares of characters of an irreducible representation is equal to the order of the group.

4. In a given representation (reducible or irreducible), the characters of matrices belonging to the symmetry operations in the same class are identical.

5. The two vectors whose components are characters of two different irreducible representations are orthogonal, *i.e.*,

$$\sum_R \chi_{i(R)}\chi_{j(R)} = 0 \qquad ...(1)$$

where R is symmetry operation of the group ; χ_i and χ_j are characters of the same symmetry operation R in ith and jth representations. Alternatively, the sum of the products of characters under each symmetry operation of any two irreducible representations of a group is equal to zero.

Let us find out irreducible representations of some simple symmetry point groups with the help of the above mentioned rules. We shall first of all consider a C_{2v} group. The symmetry operations that are possible in this case are E, C_2, σ_v and σ_v'. It can be seen that each of these operations is a distinct class in itself. Thus, there are four irreducible representations of the symmetry operations in this group. Since $l_1^2 + l_2^2 + l_3^2 + l_4^2 = 4$, hence, $l_1^2 = l_2^2 = l_3^2 = l_4^2 = 1$ (l represents the dimension of matrix of irreducible representation).

Also in each irreducible representation,

$$\chi^2_E + \chi^2_{C_2} + \chi^2_{\sigma_v} + \chi^2_{\sigma_v'} = 4$$

Therefore, χ for each operation in any irreducible representation is ± 1. One of the representations is obviously as given below :

	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1

The other representations should be such that

$$\chi_{1E}\chi_{iE} + \chi_{1C_2}\chi_{iC_2} + \chi_{1\sigma_v}\chi_{i\sigma_v} + \chi_{1\sigma_v'}\chi_{i\sigma_v'} = 0$$

Since χ under E is always positive, therefore, two of the remaining three χ_is (*viz.*, χ_{iC_2}, $\chi_{i\sigma_v}$ and $\chi_{i\sigma_v'}$) should be -1. Accordingly, the other three representations are :

	E	C_2	σ_v	σ_v'
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1

Let us now consider C_{3v} point group. Its symmetry operations are : E, two C_3s and three σ_vs. There are three classes of these symmetry operations. Hence there are three irreducible representations in this group. Since $l_1^2 + l_2^2 + l_3^2 = 6$, therefore, l_1^2, l_2^2 and l_3^2 are, respectively, 1, 1 and 2 ($1^2 + 1^2 + 2^2 = 6$). The two representations of dimensions 1 should have $\chi_E^2 + 2\chi_{C_3}^2 + 3\chi_{\sigma_v}^2 = 6$. Since $\chi^2_E = 1$, hence, χ_E, χ_{C_3} and χ_{σ_v} can each be either $+1$ or -1 and the two representations should be

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1

It can be seen that the two representations are orthogonal to each other since $1\times1 + 2\times1\times1 + 3\times1\times(-1) = 0$. The third representation Γ_3 is of dimension 2. Therefore, χ_E for this representation is 2. Since Γ_3 and Γ_1 are orthogonal to each other as are Γ_2 and Γ_3, therefore,

$$1\times2 + 2\times1\times a + 3\times1\times b = 0$$
$$1\times2 + 2\times1\times a + 3\times(-1)\times b = 0$$

where a and b are, respectively, χ_{C_3} and χ_{σ_v} of the third representation.

$\therefore$ $$2a + 3b = -2$$

and $$2a - 3b = -2$$

From the above two equations, we get $a = -1$ and $b = 0$. Therefore, the third representation is :

	E	$2C_3$	$3\sigma_v$
Γ_3	2	-1	0

so that the complete set of irreducible representations of C_{3v} point group is as follows :

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

As mentioned above, the number of irreducible representations of a point group is fixed but one can write a large number of reducible representations which are, in fact, additions of some irreducible representations.

Suppose ε, A, B, C,..... are matrices which represent symmetry operations of a **reducible** representation. In order to find irreducible representations which add up to give the reducible representation,

we diagonalise each and every matrix of the representation through similarity transformation, by a suitable matrix X, also of the representation, as shown below :

$$X^{-1}\varepsilon X = \varepsilon_1 = \begin{bmatrix} \boxed{\varepsilon'} & & \\ & \boxed{\varepsilon''} & \\ & & \boxed{\varepsilon'''} \end{bmatrix}, \qquad X^{-1}AX = A_1 = \begin{bmatrix} \boxed{A'} & & \\ & \boxed{A''} & \\ & & \boxed{A'''} \end{bmatrix},$$

$$X^{-1}BX = B_1 = \begin{bmatrix} \boxed{B'} & & \\ & \boxed{B''} & \\ & & \boxed{B'''} \end{bmatrix}, \qquad X^{-1}CX = C_1 = \begin{bmatrix} \boxed{C'} & & \\ & \boxed{C''} & \\ & & \boxed{C'''} \end{bmatrix}$$

Then the set of submatrices ε', A', B', C',..... forms an irreducible representation contained in the reducible representation ε, A, B, C,..... . Similarly, (ε'', A'', B'', C'',....), (ε''', A''', B''', C''',....), etc., are irreducible representations contained in the reducible representation ε, A, B, C,..... .

But, in actual practice, we need not follow the above mentioned cumbersome procedure to 'reduce' a reducible representation into irreducible representation. A convenient correlation, *viz.*,

$$a_i = \frac{1}{h}\left[\sum_R \chi_{(R)}\,\chi_{i(R)}\right] \qquad ...(2)$$

can be derived in which a_i is the number of times the ith irreducible representation occurs in the reducible representation. $\chi_{(R)}$ and $\chi_{i(R)}$ are the characters of matrices representing symmetry operation R in the reducible representation and the ith irreducible representation, respectively. The symbol h stands for the order of the group.

We shall illustrate the procedure of reducing a reducible representation into irreducible representations by taking into consideration the reducible representations of C_{2v} point group already given and reproduced below for convenience of reference :

C_{2v}	E	C_2	$\sigma_{v(YZ)}$	$\sigma_{v(XZ)}$
Γ_1	1	1	1	1
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1
Γ_{red_1}	3	1	3	1
Γ_{red_2}	9	-1	3	1

Let us first determine Γ_{red_1}. Using the correlation given above (Eq. 2), we have

$$a_1 = 1/4\,[3\times1 + 1\times1 + 3\times1 + 1\times1] = 2$$
$$a_2 = 1/4\,[3\times1 + 1\times(-1) + 3\times(-1) + 1\times1] = 0$$
$$a_3 = 1/4\,[3\times1 + 1\times(-1) + 3\times1 + 1\times(-1)] = 1$$
$$a_4 = 1/4\,[3\times1 + 1\times1 + 3\times(-1) + 1\times(-1)] = 0$$

Thus, Γ_{red_1} contains Γ_1 two times and Γ_3 one time. Hence, $\Gamma_{red_1} = 2\Gamma_1 + \Gamma_3$.

We can check the correctness of our result by adding characters of Γ_1 twice and of Γ_3 once :

C_{2v}	E	C_2	$\sigma_{v(YZ)}$	$\sigma_{v(ZX)}$
Γ_1	1	1	1	1
Γ_1	1	1	1	1
Γ_3	1	-1	1	-1
Γ_{red_1}	3	1	3	1

Similarly, we can show that $\Gamma_{red_2} = 3\Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + \Gamma_4$

Character Tables

Character tables drawn for various symmetry point groups are widely used for various puposes. These tables are known to have the following characteristics :

1. Each character table is divided into four parts.

2. The **first part** which consists of a single vertical column contains Mulliken's symbols such as A, B, E, T in place of Γ_1, Γ_2, Γ_3, etc., for designating the various irreducible representations. A one-dimensional representation is designated as A or B, a two-dimensional as E and a three-dimensional as T. A one-dimensional representation which is symmetric with respect to the principal axis of symmetry (*i.e.*, $\chi_{C_n} = +1$) is labelled as A while the representation which is antisymmetric with respect to the principal axis of symmetry (*i.e.*, $\chi_{C_n} = -1$) is labelled as B.

If a representation is symmetric with respect to C_2 axis which is perpendicular to the principal axis (*i.e.* $\chi_{C_2} = +1$), then, numeral 1 is put as subscript to the label. If, on the other hand, the representation is antisymmetric with respect to such an axis (*i.e.*, $\chi_{C_2} = -1$), then, 2 is put as subscript to the label. If there is no such C_2 axis, then subscript 1 is put to the label of the representation which is symmetric with respect to σ_v ($\chi_{\sigma_v} = +1$) and subscript 2 is put to the label of that representation which is antisymmetric with respect to σ_v ($\chi_{\sigma_v} = -1$).

Single prime (′) is put to the label of a representation if it is symmetric ($\chi_{\sigma_h} = +1$) and a double prime (″) if it is antisymmetric ($\chi_{\sigma_h} = -1$) with respect to σ_h.

Subscript g is put to the label if the representation is symmetric ($\chi_i = +1$) and u if it is antisymmetric ($\chi_i = -1$) with respect to inversion centre.

The employment of subscripts 1 and 2 for symbols E and T is based on certain rules, the discussion of which is beyond the scope of the book.

3. The **second part** of the table contains characters of the irreducible representations.

4. The **third part** contains symbols x, y, z, R_x, R_y and R_z. These symbols indicate how the vectors x, y, z and the rotations around the X, Y and Z axes, *i.e.*, R_X, R_Y and R_Z, transform.

5. The **fourth part** gives us information about the transformation characteristics of quadratic functions.

A character table for C_{3v} symmetry point group is given below :

Character Table for C_{3v} Symmetry Point Group

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

If the principal axis C_3 is taken to be collinear with Z axis, then σ_v, by definition, passes through Z axis. The z coordinate of the point (x, y, z), therefore, remains unchanged under E, C_3 or σ_v operations.

In other words, $E[z] = [1][z]$, $C_3[z] = [1][z]$ and $\sigma_v[z] = [1][z]$. Hence, z forms the basis of irreducible representation which has $\chi_E = 1$, $\chi_{C_3} = 1$ and $\chi_{\sigma_v} = 1$. Such a representation, as is clear from the table, is A_1. Similarly, it can be shown that x and y *together* form the basis of the irreducible representation E of C_{3v} point group.

It also follows from the table that x^2-y^2 and xy together form the basis of irreducible representation E of C_{3v} point group. Similarly, xz and yz together form the basis of representation E.

WAVE FUNCTIONS AS BASIS OF IRREDUCIBLE REPRESENTATIONS

Consider the wave equation $H\psi_i = E_i\psi_i$ where ψ_i is a non-degenerate eigen wave function of a system, E_i is the energy (eigen value) and H is Hamiltonian operator which is obtained by considering the kinetic and potential energy of the system. Suppose R is the symmetry operation to be applied on the system so that $R\psi_i$ becomes the wave function of the system after applying R on it. Since on applying R, an equivalent configuration which is physically indistinguishable from the original configuration of the system is obtained, therefore, the energy E_i and the energy operator H remain unchanged. The wave equation, after applying R on the system, becomes

$$HR\psi_i = E_iR\psi_i$$

But, $R\psi_i$ must be normalised in order that it is an eigen function. Hence,

$$\int_{-\infty}^{+\infty} R\psi_i^* R\psi_i \, d\tau = 1 \quad \text{or} \quad R^2 \int_{-\infty}^{+\infty} \psi_i^* \psi_i \, d\tau = 1$$

Since ψ_i is already normalised, hence, $R^2 = 1$ or $R = \pm 1$. Thus, we can write $R\psi_i = [+1]\psi_i$ or $[-1]\psi_i$. In other words, R (or, any symmetry operation of the system) can be represented by the matrix $[+1]$ or $[-1]$. Thus, ψ_i forms the basis of (or transforms as) irreducible representation in which R can be represented as $[+1]$ or $[-1]$. Therefore, χ_R can be represented as either $+1$ or -1.

We shall now show that a set of real or complex degenerate wave functions also forms the basis of (or transform as) irreducible representation of a symmetry point group. Let us consider a specific example of a set of degenerate p orbital wave functions which may be represented as

$$p_x = R_{(r)}\sqrt{3/4\pi}\,\sin\theta\cos\phi$$

$$p_y = R_{(r)}\sqrt{3/4\pi}\,\sin\theta\sin\phi$$

$$p_z = R_{(r)}\sqrt{3/4\pi}\,\cos\theta$$

The correlation between polar coordinates (r, θ, ϕ) and Cartesian coordinates (x, y, z) of a point is as shown in Fig. 9.

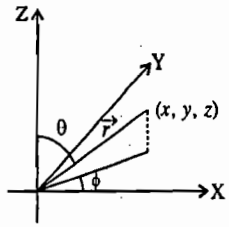


Fig. 9. Correlation between Cartesian coordinates (x, y, z) and polar coordinates (r, θ, ϕ).

Let us apply the symmetry operation of C_{3v} point group on the above set of p orbital wave functions. Accordingly,

$$E(p_x) = p_x; \quad E(p_y) = p_y; \quad E(p_z) = p_z$$

It can be easily visulalised that

$$C_{3(Z)}(p_x) = R_{(r)}\sqrt{3/4\pi}\,\sin\theta\cos(\phi + 120°)$$

$$= -1/2\, R_{(r)}\sqrt{3/4\pi}\,\sin\theta\cos\phi - \sqrt{3/2}\, R_{(r)}\sqrt{3/4\pi}\,\sin\theta\sin\phi = -1/2\, p_x - \sqrt{3/2}\, p_y$$

$$C_{3(Z)}(p_y) = R_{(r)}\sqrt{3/4\pi}\,\sin\theta\sin(\phi + 120°)$$

$$= \sqrt{3/2}\, R_{(r)}\sqrt{3/4\pi}\,\sin\theta\cos\phi - 1/2\, R_{(r)}\sqrt{3/4\pi}\,\sin\theta\sin\phi = \sqrt{3/2}\, p_x - 1/2\, p_y$$

and $C_{3(Z)}(p_z) = p_z$

It may be noted that the $C_{3(Z)}$ operation leaves θ unchanged. It, however, changes ϕ to $(\phi + 120°)$].

Since $\sigma_{v(XZ)}$ operation leaves θ unaltered and changes ϕ to $-\phi$, hence,

$$\sigma_{v(XZ)}\ p_x = R_{(r)}\sqrt{3/4\pi}\ \sin\theta\cos(-\phi) = R_{(r)}\sqrt{3/4\pi}\ \sin\theta\cos\phi = p_x$$

$$\sigma_{v(XZ)}\ p_y = R_{(r)}\sqrt{3/4\pi}\ \sin\theta\sin(-\phi) = -R_{(r)}\sqrt{3/4\pi}\ \sin\theta\ \sin\phi = -p_y$$

$$\sigma_{v(XZ)}\ p_z = R_{(r)}\sqrt{3/4\pi}\ \cos\theta = p_z$$

Thus, we observe that each one of p_x and p_y wave functions transforms into a mixed wave function of p_x and p_y on applying the symmetry operations and they have to be considered together. The wave function p_z, however, transforms into p_z by applying all the symmetry operations of the group. It follows from the above equations, therefore, that

$$E\begin{bmatrix}p_x\\p_y\end{bmatrix} = \begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}\begin{bmatrix}p_x\\p_y\end{bmatrix}; \qquad \therefore\ E = \begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} \text{ and } \chi_E = 2. \text{ Accordingly,}$$

(i) $$C_{3(Z)}\begin{bmatrix}p_x\\p_y\end{bmatrix} = \begin{bmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{bmatrix}\begin{bmatrix}p_x\\p_y\end{bmatrix} \text{ and hence, } C_{3(Z)} = \begin{bmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{bmatrix} \text{ so that } \chi_{C_{3(Z)}} = -1$$

(ii) $$\sigma_{v(XZ)}\begin{bmatrix}p_x\\p_y\end{bmatrix} = \begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}\begin{bmatrix}p_x\\p_y\end{bmatrix} \text{ and hence, } \sigma_{v(XZ)} = \begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} \text{ so that } \chi_{\sigma_{v(XZ)}} = 0$$

In other words, p_x and p_y together form the basis of E representation of C_{3v} point group (or p_x and p_y together transform as E representation of the group).

Also $E[p_z] = [1][p_z]$; $C_{3(Z)}[p_z] = [1][p_z]$; $\chi_{\sigma_{v(XZ)}}[p_z] = [1][p_z]$. Thus, $\chi_E = 1$, $\chi_{C_3(Z)} = 1$ and $\chi_{\sigma_{v(XZ)}} = 1$. Hence, p_z transforms as A_1 representation of C_{3v} symmetry point group. Similarly, by taking sets of real d orbital or f orbital wave functions, it can be shown that they too transform as irreducible representation of the point group to which the system belongs.

We arrive at similar type of result if instead of taking real degenerate wave functions, we take into consideration a set of complex degenerate wave functions. Consider, for instance, the following complex wave functions of p orbitals :

$$p_{+1} = R_{(r)}\,\Theta_1^{+1}\,1/\sqrt{2\pi}\ e^{i\phi}$$

$$p_{-1} = R_{(r)}\,\Theta_1^{-1}\,1/\sqrt{2\pi}\ e^{i\phi}$$

$$p_0 = R_{(r)}\,\Theta_1^{0}\,1/\sqrt{2\pi}\ e^{0}$$

Applying symmetry operations of the group (keeping in mind that Θ_1^{+1} and Θ_1^{-1} are identical), we get the following results :

$$E\begin{bmatrix}p_{+1}\\p_{-1}\end{bmatrix} = \begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}\begin{bmatrix}p_{+1}\\p_{-1}\end{bmatrix} \text{ and}$$

$$\sigma_{v(XZ)}\begin{bmatrix}p_{+1}\\p_{-1}\end{bmatrix} = \begin{bmatrix}R_{(r)}(\Theta)_1^{+1}\,1/\sqrt{2\pi}\,e^{-i\phi}\\R_{(r)}(\Theta)_1^{-1}\,1/\sqrt{2\pi}\,e^{+i\phi}\end{bmatrix} = \begin{bmatrix}p_{-1}\\p_{+1}\end{bmatrix} = \begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\begin{bmatrix}p_{+1}\\p_{-1}\end{bmatrix} \qquad (\because \Theta_1^{+1} = \Theta_1^{-1})$$

($\sigma_{v(XZ)}$ transforms angle ϕ into $-\phi$ but it leaves angle θ unaltered)

Hence, $$E = \begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} \text{ and } \chi_E = 2 \quad ; \quad \sigma_{v(XZ)} = \begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \text{ and } \chi_{\sigma_{v(XZ)}} = 0$$

Since rotation through 120° (or $2\pi/3$ radian), around Z axis changes ϕ to $\phi + 2\pi/3$ and leaves θ

unaltered, hence,

$$C_{3(Z)}\begin{bmatrix}p_{+1}\\p_{-1}\end{bmatrix} = \begin{bmatrix}R_{(r)}(\Theta)_1^{+1}\,1/\sqrt{2\pi}\,e^{+i\phi}e^{i2\pi/3} + 0\,R(\Theta)_1^{-1}\,1/\sqrt{2\pi}\,e^{-i\phi}\\ 0\,R(\Theta)_1^{+1}\,1/\sqrt{2\pi}\,e^{+i\phi} + R(\Theta)_1^{-1}\,1/\sqrt{2\pi}\,e^{-i\phi}e^{-i2\pi/3}\end{bmatrix}$$

$$= \begin{bmatrix}p_{+1}e^{i2\pi/3} + 0\,p_{-1}\\ 0\,p_{+1} + p_{-1}e^{-i2\pi/3}\end{bmatrix} = \begin{bmatrix}e^{i2\pi/3} & 0\\0 & e^{-i2\pi/3}\end{bmatrix}\begin{bmatrix}p_{+1}\\p_{-1}\end{bmatrix}$$

and hence $\chi_{C_3} = e^{i2\pi/3} + e^{-i2\pi/3} = -1$ $\qquad (\because e^{ix} = \cos x + i\sin x)$

Thus, p_{+1} and p_{-1} together transform as E representation of C_{3v} point group.

Also $E[p_0] = [1][p_0]$; $C_{3(Z)}[p_0] = [1][p_0]$ and $\sigma_{v(XZ)}[p_0] = [1][p_0]$, therefore, $\chi_E = 1$; $\chi_{C_3} = 1$ and $\chi_{\sigma_v} = 1$. Thus, p_0 transforms as A_1 representation of the group.

Direct Products of Matrices

The direct product of two square matrices A and B of dimensions 1 and m, respectively, is a square matrix of dimension $1\times m$. The character of the direct product matrix is the product of characters of A and B. *It is to be noted that the direct product of matrices is different from the product of matrices.* Since in a representation we mention the character of matrices representing symmetry operations of the point group, the representation due to direct product of Γ_a and Γ_b is obtained by multiplying characters, under each symmetry operation, of the representations Γ_a and Γ_b. Similarly, the representation due to direct product of Γ_a, Γ_b and Γ_c is obtained by multiplying characters, under each symmetry operation, of the representations Γ_a, Γ_b and Γ_c.

Various representations obtained from the direct products of the irreducible representations of C_{3v} point group are given below :

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$A_1 \times A_2\ (= A_2)$	1×1	1×1	$1\times(-1)$
$A_2 \times A_2\ (= A_1)$	1×1	1×1	$(-1)\times(-1)$
$E \times A_1\ (= E)$	2×1	$(-1)\times 1$	0×1
$E \times E\ (= E + A_1 + A_2)$	2×2	$(-1)(-1)$	0×0
$A_1 \times A_2 \times E\ (= E)$	$1\times 1\times 2$	$1\times 1\times(-1)$	$1\times(-1)\times 0$

The direct products of representations (or, in brief, direct products) are reducible (or irreducible) representations of the group. From the data given in the above table, it can be easily worked out that $A_1\times A_1 = A_1$, $A_1\times A_2 = A_2$, $A_2\times A_2 = A_1$, $E\times A_1 = E$ and $A_1\times A_2\times E = E$. It should be remembered that if f_a and f_b are the functions which form the basis of irreducible representations Γ_a and Γ_b, respectively, of the group, then the function $f_a f_b$ forms the basis of (or transforms as) the direct product representation $\Gamma_a \times \Gamma_b$.

APPLICATIONS OF GROUP THEORY

We shall, briefly, discuss only those applications of group theory which are of interest to inorganic chemistry students. These applications are :

1. Evaluation of Integrals 2. Explanation of Allowed and Forbidden Electronic Transitions 3. Hybridisation of Atomic Orbitals 4. Nature of Bonding in Octahedral and Tetrahedral Complexes 5. Energy Terms in Octahedral Complexes 6. Splitting of Orbitals and Terms in a Chemical Environment 7. Relaxation of Selection Rules for Electronic Transitions 8. Establishing States of Symmetry by the Method of Descending Symmetry and 9. Study of Electron Absorption Spectra using Plane Polarised Light.

1. Evaluation of Integrals

In wave mechanics we frequently come across integrals of the type $\int \psi_a \psi_b \, d\tau$ and $\int \psi_a \psi_b \psi_c \, d\tau$. Most of the times we are only interested in finding out whether these integrals are zero or non-zero. Group theory gives us a quick procedure to find out that. The integral $\int_{-\infty}^{+\infty} f_a f_b \, d\tau$ will be zero unless the integrand $f_a f_b$ is invariant (or a term in it remains invariant) under all the symmetry operations of the point group to which the system belongs. In other words, $f_a f_b$ (or a term in it) should form the basis of a totally symmetric representation in order that $\int_{-\infty}^{+\infty} f_a f_b \, d\tau$ is non-zero. That is, each $R(f_a f_b)$ should be equal to $[+1](f_a f_b)$. In other words, $f_a f_b$ should form the basis of that irreducible representation which contains $\chi_R = +1$ for every symmetry operation of the group. An A_1 representation has a character of $+1$ under all symmetry operations of the group. In other words, A_1 remains invariant under all symmetry operations of the group and hence is a totally symmetric representation.

As already explained, the representation to which $f_a f_b$ forms the basis, can be obtained from the direct product of Γ_a and Γ_b. Thus, the direct product of Γ_a and Γ_b should either be totally symmetric representation A_1 or should contain A_1 irreducible representation of the point group in order that the integral $\int_{-\infty}^{+\infty} f_a f_b \, d\tau$ is non-zero. Similarly, the integral $\int_{-\infty}^{+\infty} f_a f_b f_c \, d\tau$ is non-zero if the direct product of Γ_a, Γ_b and Γ_c is either equal to A_1 or contains A_1 irreducible representation of the point group.

2. Explanation of Allowed and Forbidden Electronic Transitions

As discussed in Chapter 30, the intensity of an electronic transition is directly related to transition moment integral Q which is equal to $\int_{-\infty}^{+\infty} \psi_{1elec} [\vec{M}] \psi_{2elec} \, d\tau$ where M is dipole moment operator and is a vector quantity. It can be resolved into three components $\vec{M}_x, \vec{M}_y$ and $\vec{M}_z$ along X, Y and Z directions. Thus,

$$Q = \int_{-\infty}^{+\infty} \psi_{1elec} \, |\vec{M}| \, \psi_{2elec} \, dt = \int_{-\infty}^{+\infty} \psi_{1elec} \, |\vec{M}_x + \vec{M}_y + \vec{M}_z| \, \psi_{2elec} \, dt$$

$$= \int_{-\infty}^{+\infty} \psi_{1elec} \, |\vec{M}_x| \, \psi_{2elec} \, dt + \int_{-\infty}^{+\infty} \psi_{1elec} \, |\vec{M}_y| \, \psi_{2elec} \, dt + \int_{-\infty}^{+\infty} \psi_{1elec} \, |\vec{M}_z| \, \psi_{2elec} \, dt$$

In order that an electronic transition is allowed, Q should be non-zero. That is, one of the three integrals on the right hand side of the above equation should be non-zero. In other words, the integrand in at least one of the three integrals should be totally symmetric, *i.e.*, the direct product corresponding to the integrands in at least one of the three integrals should be A_1 (or should contain A_1).

Let us consider $e-t_2^*$ transition in a tetrahedral complex (cf. Fig. 20, Chapter 27). The character table drawn for T_d point group is given below :

Character Table for T_d Point Group

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

It can be easily shown that d_{z^2} orbital wave function is, in fact, the function of $2z^2 - x^2 - y^2$. It is thus evident from the table, that $(d_{z^2}, d_{x^2-y^2})$ set of orbitals transforms as E representation and (d_{xy}, d_{xz}, d_{yz}) set transforms as T_2 representation. $\vec{M}_x, \vec{M}_y, \vec{M}_z$ which point towards x, y and z

directions, *together* transform as T_2 representation. Thus, the direct product of the functions in the integrand of Q, *i.e.*, $\psi_e |\vec{M}_x + \vec{M}_y + \vec{M}_z| \psi_{t_2^*}$ is $E \times T_2 \times T_2$ which reduces to $2T_1 + 2T_2 + 2E + A_2 + A_1$ and evidently contains the totally symmetric representation A_1. Thus, Q is non-zero and the electronic transition $e-t_2^*$ is symmetry allowed.

In molecules with a centre of symmetry, the totally symmetric representation, which has $\chi_R = +1$ for each symmetry operation R of the point group is A_{1g}. Therefore, in order that Q is non-zero, the direct product of the functions in the integrand must be either A_{1g} or contain a term A_{1g}. Also, since $g \times u \times g = u$, all $d-d$ transitions (which are, in fact, $g-g$ transitions) are forbidden because the direct product of the functions in the integrand Q must necessarily contain all representations of u type (as explained in Chapter 29).

Let us consider the electronic transition $t_{2g} - t_{1u}^*$ in an octahedral complex which, in effect, is essentially a $d-p$ transition. The integral Q in this case is given by

$$Q = \int_{-\infty}^{+\infty} \psi_{t_{2g}} \, |\vec{M}_x + \vec{M}_y + \vec{M}_z| \, \psi_{t_{1u}} \, d\tau$$

The components $\vec{M}_x$, $\vec{M}_y$, $\vec{M}_z$ of the dipole moment vector are similar to $\vec{x}$, $\vec{y}$ and $\vec{z}$ vectors and they together transform as T_{1u} representation in octahedral symmetry point group, as is evident from the character table for O_h point group given below :

Character Table for O_h Point Group

Oh	E	$8C_3$	$6C_2$	$6C_4$	$3C_2'$*	$i(=iE)$	$6S_4(=iC_4)$	$8S_6(=iC_3)$	$3\sigma_v(=iC_2')$	$6\sigma_d(=iC_2)$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

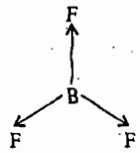
*C_2' is collinear with C_4.

The direct product of the functions in the integrand of Q in octahedral environment is $T_{2g} \times T_{1u} \times T_{1u}$ which reduces to $4T_{2g} + 3T_{1g} + 2E_g + A_{2g} + A_{1g}$. Since the direct product contains the totally symmetric representation A_{1g}, hence Q is non-zero and, therefore, the transition is symmetry-allowed.

3. Hybridistaion

Group theory is of great help in determining the atomic orbitals of the central atom of a species which can form maximum sigma overlap with orbitals of ligands in the given directions. The orbitals of the central atom then mix and give an equal number of equivalent hybrid orbitals. We shall consider examples where the central atoms utilise different types of hybrid orbitals in forming sigma bonds with the ligand orbitals.

a. Hybridisation of Atomic Orbitals of Boron in Boron trifluoride. The geometry of BF_3 molecule is plane triangular. Let us represent the directions in which the central boron atom forms sigma bonds with fluorine atoms by vectors, as shown.



If we apply on these vectors all the symmetry operations of the D_{3h} group to which BF_3 molecule belongs, we obtain the following reducible representation :

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	1	3	0	1

It can be shown that the vector which changes position under a symmetry operation contributes nothing to the character of the matrix representing the symmetry operation. The vector which reverses in direction during a symmetry operation contributes −1 and the vector which neither changes in position nor in direction during a symmetry operation contributes +1 to the character of the matrix representing the symmetry operation.

From the character table of D_{3h} symmetry point group given below, it is clear that $\Gamma_{red} = A_1' + E'$.

Character Table for D_{3h} Point Group

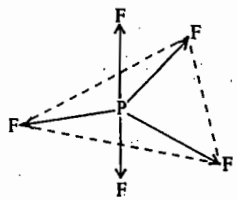
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

The s orbital always transforms as a totally symmetric wave function of the point group which is A_1' in the present case. As is clear from the table given above, d_{z^2} orbital transforms as A_1', and (p_x, p_y) together or $(d_{x^2-y^2}, d_{xy})$ together transform as E'. Hence the following combinations of atomic orbitals are symmetrically most suited for forming sigma bonds in the directions of the arrows in BF_3 molecule :

$$s(a_1')+(p_x,p_y)(e');\ s(a_1')+(d_{x^2-y^2},d_{xy})(e');\ d_{z^2}(a_1')+(p_x,p_y)(e') \text{ and } d_{z^2}(a'_1)+(d_{x^2-y^2},d_{xy})(e').$$

Out of these, the combinations involving d orbitals are of higher energy. Therefore, the most suitable set of atomic orbitals of boron atom which can form sigma bonds in BF_3 molecule is $s(a_1') + (p_x, p_y)(e')$. Thus, (s, p_x, p_y) are the atomic orbitals of boron atom which hybridise to give three equivalent sp^2 hybrid orbitals which permit maximum σ overlap with orbitals of fluorine atoms.

***b.* Hybridisation of Atomic Orbitals of Phosphorus in Phosphorus penta fluoride.** The geometry of PF_5 molecule is trigonal bipyramidal. Once again we represent the directions of sigma bonds which the P atom makes with the ligands as shown in the figure. This molecule also belongs to D_{3h} symmetry point group and the reducible representation obtained in this case is as shown below :



	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	5	2	1	3	0	3

which, with the help of the character table given above for D_{3h} symmetry point group, is reduced to $2A_1'+A_2''+E'$. Thus, the set of atomic orbitals of P atom which is most suited to form sigma bonds in the directions shown in the above figure is : s, d_{z^2} (both a_1')$+p_z(a_2'')+(p_x,p_y)\,e'$. In other words, the atomic orbitals s, d_{z^2}, p_x, p_y and p_z of the central P atom hybridise to give five sp^3d hybrid orbitals which give maximum σ overlap with orbitals of fluorine atoms.

***c.* Hybridistation of Atomic Orbitals of Platinum in the Complex ion $[PtCl_4]^{2-}$.** The geometry of the complex ion is square planar. It belongs to the symmetry point group D_{4h} whose character

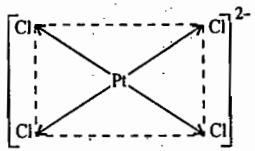


table is given below :

Character Table for D_{4h} Point Group

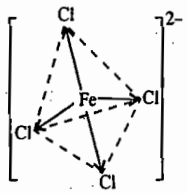
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

Following the same procedure as discussed above, we get

	E	C_4	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{red}	4	0	0	2	0	0	0	4	2	0

Reducing the representation with the help of the above table, we get $\Gamma_{red} = A_{1g} + B_{1g} + E_u$. Thus, the orbitals of platinum atom which are symmetrically most suited for forming sigma bonds in the directions of arrows shown in the figure are either $s(a_{1g}) + d_{x^2-y^2}(b_{1g}) + p_x,p_y(e_u)$ or $d_{z^2}(a_{1g}) + d_{x^2-y^2}(b_{1g}) + (p_x,p_y)(e_u)$. Out of these two combinations, the first one is energetically more favourable. Therefore, s, $d_{x^2-y^2}$ and (p_x, p_y) orbital are most suited energetically as well as symmetrically to form sigma bonds in the required directions. Thus these four orbitals of Pt atom hybridise to give four equivalent dsp^2 or sp^2d hybrid orbitals which give maximum sigma overlap with the orbitals of the ligands.

***d.* Hybridisation of Atomic Orbitals of Fe in $[FeCl_4]^{2-}$.** The complex ion $[FeCl_4]^{2-}$ is known to have a tetrahedral geometry, as shown.

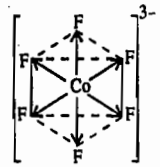


Following the same procedure as mentioned above, it can be easily shown that in a tetrahedral molecule,

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{red}	4	1	0	0	2

From the character table of T_d symmetry point group given earlier, $\Gamma_{red} = A_1 + T_2$. Hence the combinations of atomic orbitals of Fe which are most suited to form sigma bonds in tetrahedral directions are either $s(a_1) + (p_x, p_y, p_z)(t_2)$ or $s(a_1) + (d_{xy}, d_{xz}, d_{yz})(t_2)$. Accordingly, these are the orbitals which hybridise to give four equivalent hybrid orbitals which are tetrahedrally oriented in space. Symmetry considerations predict that both the above mentioned hybridisations, *i.e.*, sp^3 and sd^3 are equally probable. Energetically, sp^3 hybridisation is more favourable, particularly for lighter atoms (such as C) because $2p$ orbitals are of considerably lower energy than $3d$ orbitals. But, in the case of transition metal atoms, the energy difference between p and d orbitals is not very large so that in tetrahedral complexes of transition metals, the sp^3 hybrid orbitals of the metal atom contain a fair amount of d orbital character as well.

***e.* Hybridisation of Atomic Orbitals of Cobalt in $[CoF_6]^{2-}$.** The complex ion $[CoF_6]^{2-}$ has an octahedral structure. By following the same procedure as described above, it can be shown that for an octahedral molecule



	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_v$	$6\sigma_d$
Γ_{red}	6	0	0	2	2	0	0	0	4	2

which when reduced with the help of the character table gives $\Gamma_{red} = A_{1g} + E_g + T_{1u}$. Accordingly, the atomic orbitals of the central metal atom most suited for the formation of sigma bonds with the orbitals of the ligands in the octahedral complex are :

$$s\,(a_{1g})\ ;\ (p_x, p_y, p_z)\,(t_{1u})\ ;\ (d_{z^2}, d_{x^2-y^2})\,(e_g)$$

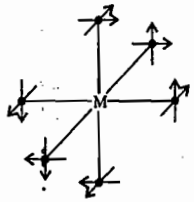
These six orbitals of Co atom thus hybridise to give maximum σ overlap with the orbitals of fluorine atoms. Symmetry considerations, however, do not tell whether the *d* orbitals involved in hybridisation would be inner $(n-1)d$ orbitals or outer *nd* orbitals.

4. Nature of Bonding in Octahedral and Tetrahedral Complexes

Nature of Bonding in Octahedral Complexes

Sigma Bonding. As explained earlier, the most suitable set of orbitals of the metal ion to give sigma overlap with the orbitals of the ligands in an octahedral complex is $s(a_{1g})$, $(p_x, p_y, p_z)\,(t_{1u})$ and $(d_{z^2}, d_{x^2-y^2})\,(e_g)$. Therefore, the six ligand p_σ orbital combinations forming sigma bonds with the orbitals of the metal should also be of the same symmetry, *viz.*, a_{1g}, e_g and t_{1u}.

Pi Bonding. Consider each ligand of the complex having two mutually perpendicular p_π orbitals which are together perpendicular to its p_σ orbital, as, for example, in ligands CO, F^-, Cl^-, etc. Each p_π orbital is shown by an arrow attached to each of the ligand atom positions, as shown in the figure. The head of the arrow indicates + lobe and the tale indicates – lobe of the p_π orbital. The arrows are so placed that the resultant figure retains the octahedral geometry. On applying symmetry operations of O_h symmetry point group, we get the following reducible representation :



	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_v$	$6\sigma_d$
Γ_{red}	12	0	0	0	-4	0	0	0	0	0

which when reduced gives $\Gamma_{red} = T_{1u} + T_{2u} + T_{1g} + T_{2g}$. Thus, the twelve p_π orbitals of ligands will combine to give twelve ligand orbital combinations of $t_{1u} + t_{2u} + t_{1g} + t_{2g}$ symmetry which are most suited for bonding with the metal orbitals of the same symmetry. Since there are no metal orbitals with t_{2u} and t_{1g} symmetry and since t_{1u} metal orbitals are better suited for σ bonding, hence t_{2g} set of metal orbitals combine with t_{2g} ligand orbital combinations to give t_{2g}^{b} and t_{2g}^{a} π molecular orbitals.

Nature of Bonding in Tetrahedral Complexes

igma Bonding. As explained earlier, the metal orbitals which are most suited for sigma bonding in tetrahedral complexes are either $s\,(a_1)$ and $p_x, p_y, p_z(t_2)$ or $s(a_1)$ and $(d_{xy}, d_{yz}, d_{zx})t_2$. The four ligand orbitals, therefore, combine to give combinations of a_1 and t_2 symmetries. The metal and ligand orbital combinations of the same symmetry then overlap to give σ bonding and antibonding molecular orbitals, as illustrated in Chapter 4.

Pi Bonding. Let us assign individual coordinates to each atom in the tetrahedral complex AB_4, as illustrated in Fig. 10. The coordinates of B_1, B_2, B_3 and B_4 atoms are written as (x_1, y_1, z_1), (x_2, y_2, z_2), (x_3, y_3, z_3) and (x_4, y_4, z_4), respectively. Let us assume that p_z orbital of each B atom is utilised in forming A–B sigma bond. All A–B directions (*i.e.*, directions of A–B sigma bonds) are collinear with C_3 axis of symmetry. The p_x and p_y orbitals of each B atom are collinear with its *x* and *y* coordinates. The *x* coordinates of B atoms are drawn in such a manner that x_1, x_2 and the *Z* axis of the figure are in one plane where as x_3, x_4 and *Z* axis of the figure are in another plane, as shown. The p_x and p_y orbitals of each B atom

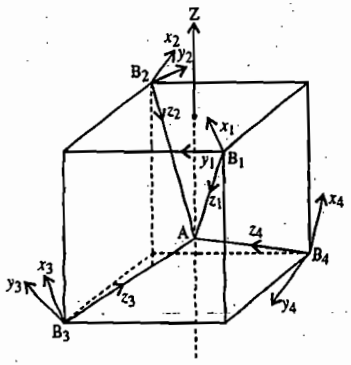


Fig.10. Individual coordinates assigned to each atom in tetrahedral complex AB_4.

are capable of forming pi bonds with the orbitals of atom A of appropriate symmetry. The pi ligand orbital combinations which are most suited to form pi bonds can be determined by following the same procedure as adopted in the case of octahedral complexes. Accordingly, Γ_{red} obtained in a tetrahedral complex is given by

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{red}	8	-1	0	0	0

The characters of Γ_{red} for all symmetry operations except for C_3 operation can be easily determined. The two arrows x_i and y_i which signify p_{x_i} and p_{y_i} orbitals of B_i rotate at an angle of 120° around the AB_i axis (which is a C_3 axis) during a C_3 symmetry operation (B_i is any of the four ligands). It does not change its position during a C_3 operation about the AB_i axis. All the vectors of other three Bs change their positions in this operation). The new vectors x_i' and y_i', also attached to B_i, can be expressed as follows :

$$\begin{bmatrix} x_i' \\ y_i' \end{bmatrix} = C_3 \begin{bmatrix} x_i \\ y_i \end{bmatrix} = \begin{bmatrix} x_i \cos 120^\circ & -y_1 \sin 120^\circ \\ x_i \sin 120^\circ & y_i \cos 120^\circ \end{bmatrix} = \begin{bmatrix} \cos 120^\circ & -\sin 120^\circ \\ \sin 120^\circ & \cos 120^\circ \end{bmatrix} \begin{bmatrix} x_i \\ y_i \end{bmatrix}$$

Therefore, $$C_3 = \begin{bmatrix} \cos 120^\circ & -\sin 120^\circ \\ \sin 120^\circ & \cos 120^\circ \end{bmatrix} \text{ and } \chi_{C_3} = -1$$

The above result can also be obtained easily by putting $\phi = 120°$ in the already derived general relation $C_{Z(\phi)} = \begin{bmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{bmatrix}$.

It is seen from the character table drawn for the T_d symmetry point group that $\Gamma_{red} = E + T_1 + T_2$. Accordingly, the ligand orbital combinations which are most suited for pi bonding are those which have *e*, t_1 and t_2 symmetry. Since there are no metal orbitals of t_1 symmetry and t_2 set of metal orbitals are more suited for σ bonding, hence, it is only the *e* set of metal orbitals which will combine with pi ligand orbital combinations of the same symmetry to give *e* and e^* sets of pi molecular orbitals.

5. Energy Terms of Strong Field Configurations of Octahedral Complexes

In the strong field transition metal octahedral complexes, the electrostatic octahedral crystal field potential, V_{oct} is greater than inter-electronic repulsions amongst *d* electrons. Therefore, in such complexes, the weaker inter-electronic repulsion effect is considered as perturbation over stronger V_{oct} for calculating the energies of the terms. The crystal field potential, V_{oct}, splits the *d* orbitals of complexed metal ions into t_{2g} and e_g subgroups so that the strong field configurations possible for d^2 metal ions are t_{2g}^2, $t_{2g}^1\,e_g^1$ and e_g^2.

Now consider one by one the interaction between two electrons of each of the three configurations:

1. The first strong field configuration t_{2g}^2 can be considered as t_{2g}^1 configuration to which one more electron has been added. It can thus be written as $t_{2g}^1 t_{2g}^1$ and the wave function of this configuration can be written as $\Psi_{t_{2g}}\Psi_{t_{2g}}$. The direct product due to $\Psi_{t_{2g}}\Psi_{t_{2g}}$ is $T_{2g} \times T_{2g}$ which can be shown to be equal to $T_{1g} + T_{2g} + E_g + A_{1g}$ with the help of the character table of O_h point group. Thus, the energy terms which arise due to interaction between two electrons of t_{2g}^2 configuration are T_{1g}, T_{2g}, E_g and A_{1g}. It can be shown (by a complicated procedure) that complete energy terms arising out of t_{2g}^2 configuration, considering the spin multiplicities also, are $^3T_{1g}$, $^1T_{2g}$, $^1A_{1g}$ and ^1E_g. One can see that the sum of total degeneracies of all these terms is 15 (*i.e.*, $3\times3+1\times3+1\times1+1\times2$) which is also the number of electronic arrangements possible for a t_{2g}^2 configuration.

2. Now consider the second strong field configuration $t_{2g}^1\,e_g^1$ of octahedrally complexed metal ion. The wave function for this configuration can be written as $\Psi_{t_{2g}}\Psi_{e_g}$. With the help of the character table for O_h point group, the direct product $T_{2g}\times E_g$ can be shown to be equal to $T_{1g} + T_{2g}$. The complete energy terms arising out of $t_{2g}^1\,e_g^1$ configuration, considering spin multiplicities also, can be shown to be $^1T_{1g}$, $^1T_{2g}$, $^3T_{1g}$ and $^3T_{2g}$. The sum of total degeneracies of the terms of $t_{2g}^1\,e_g^1$ configuration is 12 (*i.e.*, $1\times3 + 1\times3 + 3\times3 + 3\times3$) which is also the number of electronic arrangements possible for $t_{2g}\,e_g^1$ configuration.

3. The third strong field configuration of octahedrally complexed metal ion is e_g^2, the wave function for which can be written as $\psi_{e_g}\psi_{e_g}$. The direct product $E_g \times E_g$ can be, shown to be equal to $A_{1g} + A_{2g} + E_g$. Therefore, the energy terms arising out of interaction of two electrons of e_g^2 configuration are A_{1g}, A_{2g} and E_g. The complete energy terms, considering spin multiplicities also, are $^1A_{1g}$, $^3A_{2g}$ and ^1E_g. The sum of total degeneracies of these terms is 6 (*i.e.* $1\times1 + 1\times2 + 3\times1$) which is also the number of electronic arrangements possible for e_g^2 configuration.

The total number of electronic arrangements of all the strong field configurations of octahedrally complexed metal ions are 45 (*i.e.*, 15 + 6 + 24) which is also the total number of electronic arrangements which arise out of a d^2 configuration of a free metal ion.

6. Splitting of Orbitals and Terms in a Chemical Environment

We know that according to the crystal field theory, a set of five *d* orbitals splits into t_{2g} and e_g sets in an octahedral environment and into t_2 and *e* sets in a tetrahedral environment and that a *p* set of orbitals does not split into any other sets in octahedral or tetrahedral environment. We shall make an attempt to establish the above mentioned facts by applying the group thoery to the splitting of sets of degenerate *d* orbitals into other sets in different chemical environments. We shall also apply the group theory to determine the splitting of terms of many electron systems in different chemical environments.

We start with a single electron in a set of five *d* orbitals of a metal ion under the influence of an octahedral ligand environment. We know that all the *d* orbitals are symmetric with respect to *i* so that the irreducible representations to which the *d* orbital wave functions transform in octahedral environment are only those which have a *g* subscript. It can be seen from the character table for O_h point group given earlier in this chapter that in any irreducible representation of *g* type of O_h point group, whatever is χ_{C_n} is also $\chi_{(iC_n)}$, that is, $\chi_{C_n} \equiv \chi_{iC_n}$

In order to tackle the problem in hand, it is more convenient to make use of the character table for *O* point group (given below) instead of the character table of O_h point group.

Character Table for *O* Point Group

O	E	$6C_4$	$3C_2 (= C_4^2)$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	−1	1	1	−1		
E	2	0	2	−1	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	1	−1	0	−1	(R_x, R_y, R_z) ; (x, y, z)	
T_2	3	−1	−1	0	+1		(xz, yz, xy)

We can write the character table of O_h point group by multiplying each symmetry operation of the point group *O* by the operation *i* of the O_h point group and by writing each irreducible representation of the point group *O* with a *g* as well as with a *u* subscript and by including all $\chi_{(iC_n)}$ in each irreducible representation. It should be kept in mind that, for writing irreducible representation of O_h point group from the irreducible representation of *O* group, $\chi_{(C_n)} = \chi_{(iC_n)}$ in an irreducible representation of *g* type and $\chi_{(C_n)} = -\chi_{(iC_n)}$ in an irreducible representation of *u* type (refer to character table for O_h point group given earlier.)

It can be seen from the character table for point group *O* given above that each operation in point group *O* (except for the identity operation) is a rotation operation. Consider that each rotation operation is carried around the axis from which the angle of rotation θ is measured (say, the *Z*-axis) so that no rotation operation changes the angle θ. This implies that Θ parts of the *d* orbital wave functions remain invariant

under all symmetry operations of the point group *O*. No rotation operation of point group *O* can change the magnitude of *r* so that *R*(*r*) part of the *d* orbital wave functions also remain invariant under all symmetry operations of the point group *O*. The only parts of *d* orbital wave functions which vary with the symmetry operations of point group *O* (which are all rotation operations) are those which depend upon the angle ϕ, *i.e.*, the Φ part of the wave functions. In other words, $A(R(r)\,\Theta_\theta\,\Phi_\phi) = R(r)\,\Theta_\theta\,A(\Phi_\phi)$ where *A* is any symmetry operation of the group. We shall, therefore, take into consideration only those parts of the *d* orbital wave functions which *vary* with the symmetry operations of the point group *O*. These are : $e^{i2\phi}$, $e^{i\phi}$, $e^{i0\phi}$, $e^{-i\phi}$, $e^{-i2\phi}$

(The normalising constants of Φ parts of wave functions also remain invariant under all symmetry operations and hence are not considered.)

Let us first apply the identity operation E on the variable parts of *d* orbital wave functions :

$$E\begin{bmatrix} e^{i2\phi} \\ e^{i\phi} \\ e^{i0\phi} \\ e^{-i\phi} \\ e^{-i2\phi} \end{bmatrix} = \begin{bmatrix} e^{i2\phi} \\ e^{i\phi} \\ e^{i0\phi} \\ e^{-i\phi} \\ e^{-i2\phi} \end{bmatrix} = \begin{bmatrix} 1e^{i2\phi} + 0e^{i\phi} + 0e^{i0\phi} + 0e^{-i\phi} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 1e^{i\phi} + 0e^{i0\phi} + 0e^{-i\phi} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 0e^{i\phi} + 1e^{i0\phi} + 0e^{-i\phi} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 0e^{i\phi} + 0e^{i0\phi} + 1e^{-i\phi} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 0e^{i\phi} + 0e^{i0\phi} + 0e^{-i\phi} + 1e^{-i2\phi} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} e^{i2\phi} \\ e^{i\phi} \\ e^{i0\phi} \\ e^{-i\phi} \\ e^{-i2\phi} \end{bmatrix}$$

so that $\chi_{(E)} = 5$.

The general expression for rotation operation by an angle α on the variable part of the *d* orbital wave functions can be written as :

$$C(\alpha)\begin{bmatrix} e^{i2\phi} \\ e^{i\phi} \\ e^{i0\phi} \\ e^{-i\phi} \\ e^{-i2\phi} \end{bmatrix} = \begin{bmatrix} e^{i2(\phi+\alpha)} \\ e^{i(\phi+\alpha)} \\ e^{i0(\phi+\alpha)} \\ e^{-i(\phi+\alpha)} \\ e^{-i2(\phi+\alpha)} \end{bmatrix} = \begin{bmatrix} 1e^{i2(\phi+\alpha)} + 0e^{i\phi} + 0e^{i0\phi} + 0e^{-i\phi} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 1e^{i(\phi+\alpha)} + 0e^{i0\phi} + 0e^{-i\phi} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 0e^{i\phi} + 1e^{i0(\phi+\alpha)} + 0e^{-i\phi} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 0e^{i\phi} + 0e^{i0\phi} + 1e^{-i(\phi+\alpha)} + 0e^{-i2\phi} \\ 0e^{i2\phi} + 0e^{i\phi} + 0e^{i0\phi} + 0e^{-i\phi} + 1e^{-i2(\phi+\alpha)} \end{bmatrix}$$

$$= \begin{bmatrix} e^{i2\alpha} & 0 & 0 & 0 & 0 \\ 0 & e^{i\alpha} & 0 & 0 & 0 \\ 0 & 0 & e^{i0\alpha} & 0 & 0 \\ 0 & 0 & 0 & e^{-i\alpha} & 0 \\ 0 & 0 & 0 & 0 & e^{-i2\alpha} \end{bmatrix} \begin{bmatrix} e^{i2\phi} \\ e^{i\phi} \\ e^{i0\phi} \\ e^{-i\phi} \\ e^{-i2\phi} \end{bmatrix} \quad \text{or} \quad C(\alpha) = \begin{bmatrix} e^{i2\alpha} & 0 & 0 & 0 & 0 \\ 0 & e^{i\alpha} & 0 & 0 & 0 \\ 0 & 0 & e^{i0\alpha} & 0 & 0 \\ 0 & 0 & 0 & e^{-i\alpha} & 0 \\ 0 & 0 & 0 & 0 & e^{-i2\alpha} \end{bmatrix}$$

The character of such a matrix representing $C(\alpha)$ rotation operation on the variable parts of the *d* orbital wave functions is of the general form :

$$\chi_{C(\alpha)} = \frac{\sin\left(l + \frac{1}{2}\right)\alpha}{\sin(\alpha/2)} \qquad (\alpha \neq 0, 2\pi, 4\pi, \text{etc.})$$

For the d orbital wave functions, $l = 2$. Hence,

$$\chi_{C(\alpha)} = \frac{\sin\frac{5\alpha}{2}}{\sin\frac{\alpha}{2}} \quad \text{and} \quad \chi_{C_2} = \frac{\sin\frac{5\pi}{2}}{\sin\frac{\pi}{2}} = 1 \qquad (\because \alpha = \pi)$$

Similarly,

$$\chi_{C_3} = \frac{\sin\left(\frac{5}{2}\times\frac{2\pi}{3}\right)}{\sin\left(\frac{2\pi}{3}\times\frac{1}{2}\right)} = \frac{\sin\frac{5\pi}{3}}{\sin\frac{\pi}{3}} = -1 \ (\because \alpha = 2\pi/3)$$

$$\text{and } \chi_{C_4} = \frac{\sin\left(\frac{5}{2}\times\frac{\pi}{2}\right)}{\sin\left(\frac{\pi}{2}\times\frac{1}{2}\right)} = \frac{\sin\frac{5\pi}{4}}{\sin\frac{\pi}{4}} = \frac{-1/\sqrt{2}}{1/\sqrt{2}} = -1 \qquad (\because \alpha = \pi/2)$$

Thus, the representation obtained on applying all symmetry operations on variable parts of the d orbital wave functions is written as :

	E	$+\ 6C_4$	$+\ 3C_2 (= C_4^2)$	$8C_3$	$6C_2$
Γ_{red}	5	−1	1	−1	1

On reducing the representation, we find that

$$A_1 \text{ occurs } \frac{5\times1\times1+(-1)\times1\times6+1\times1\times3+(-1)\times1\times8+1\times1\times6}{24} = 0 \text{ time}$$

$$A_2 \text{ occurs } \frac{5\times1\times1+(-1)(-1)\times6+1\times1\times3+(-1)\times1\times8+1\times(-1)\times6}{24} = 0 \text{ time}$$

$$E \text{ occurs } \frac{5\times2\times1+(-1)\times0\times6+1\times2\times3+(-1)(-1)\times8+1\times0\times6}{24} = 1 \text{ time}$$

$$T_1 \text{ occurs } \frac{5\times3\times1+(-1)\times1\times6+1\times(-1)\times3+(-1)\times0\times8+1\times(-)\times6}{24} = 0 \text{ time}$$

$$T_2 \text{ occurs } \frac{5\times3\times1+(-1)(-1)\times6+1\times(-1)\times3+(-1)\times0\times8+1\times1\times6}{24} = 1 \text{ time}$$

Thus, $\Gamma_{red} = E + T_2$ for a single-electron d orbital wave function in point group O. Since all d orbitals have a centre of symmetry, hence $E + T_2$ irreducible representations of point group O refer to $E_g + T_{2g}$ representations of the point group O_h (also having a centre of symmetry). This result clearly establishes that a set of d orbitals containing a single electron splits into e_g and t_{2g} sets of orbitals which, on looking at the chracter tables of point groups O and O_h, can be seen clearly to be d_{z^2}, $d_{x^2-y^2}$ set of orbitals (e_g orbitals) and d_{xy}, d_{xz}, d_{yz} set of orbitals (t_{2g} orbitals).

Alternatively, we may argue that since all d orbitals have a centre of symmetry, the type of irreducible representations to which these will transform under an octahederal ligand environment will have to be g type. All g type of irreducible representations in the point group O_h have $\chi_E = \chi_{(i\,E)}$; $\chi_{C_2} = \chi_{(i\,C_2)}$; $\chi_{C_3} = \chi_{(i\,C_3)}$ and $\chi_{C4} = \chi_{(i\,C_4)}$, as already mentioned above, so that Γ_{red} for the point group O_h can be written as :

	E	$6C_4$	$3C_2 (= C_4^2)$	$8C_3$	$6C_2$	iE	$6i\,C_4$	$3i\,C_2$	$8i\,C_3$	$6i\,C_2$
$\Gamma_{red}(O_h)$	5	−1	1	−1	1	5	−1	1	−1	1

and, on reduction of the above representation of O_h character table,, we observe that

$$A_{2g} \text{ occurs } \frac{(5+6+3-8-6)\times2}{48} = 0 \text{ time}$$

$$A_{1g} \text{ occurs } \frac{(5-6+3-8+6)\times2}{48} = 0 \text{ time}$$

$$E_g \text{ occurs } \frac{(10+0+6+8+0)\times2}{48} = 1 \text{ time}$$

$$\vdots$$

$$T_{1g} \text{ occurs } \frac{(15-6-3-0-6)\times2}{48} = 0 \text{ time}$$

and

$$T_{2g} \text{ occurs } \frac{(15+6-3+0+6)\times2}{48} = 1 \text{ time}$$

(The order of point group O_h is 48 whereas that of point group O is 24).

Thus, we get the same result that a set of d orbitals having a single electron splits into e_g set and t_{2g} set under an octahedral ligand environment. It can be clearly seen from the octahedral character table that while the e_g set comprises of d_{z^2} and $d_{x^2-y^2}$ orbitals, t_{2g} set comprises of d_{xy}, d_{yz}, d_{xy} orbitals.

Let us now investigate the influence of ligand environment on p orbitals of a metal ion containing a single electron. Assuming again that the rotation oprations are carried out about an axis around which the angle θ is measured (say, the Z axis), it is seen that the parts of p orbital wave functions which are influenced by rotations are the Φ parts of the wave functions, *viz.*, $e^{i\phi}$, $e^{i0\phi}$ and $e^{-i\phi}$. The general expression for rotation about an angle α can be written as :

$$C(\alpha)\begin{bmatrix} e^{i\phi} \\ e^{i0\phi} \\ e^{-i\phi} \end{bmatrix} = \begin{bmatrix} e^{i\alpha} & 0 & 0 \\ 0 & e^{i0\alpha} & 0 \\ 0 & 0 & e^{-i\alpha} \end{bmatrix}\begin{bmatrix} e^{i\phi} \\ e^{i0\phi} \\ e^{-i\phi} \end{bmatrix}$$

The character of such a matrix can be written as :

$$\chi_{C(\alpha)} = \frac{\sin\left(l+\frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}} = \frac{\sin\left(\frac{3}{2}\alpha\right)}{\sin\frac{\alpha}{2}} \qquad (\because l = 1)$$

Hence,

$$\chi_{C_2} = \frac{\sin\left(\frac{3}{2}\alpha\right)}{\sin\frac{\alpha}{2}} = \frac{\sin\frac{3}{2}\pi}{\sin\frac{\pi}{2}} = \frac{-1}{1} = -1$$

$$\chi_{C_3} = \frac{\sin\left(\frac{3}{2}\times\frac{2\pi}{3}\right)}{\sin\left(\frac{2\pi}{3}\times\frac{1}{2}\right)} = \frac{\sin\pi}{\sin\frac{\pi}{3}} = 0.$$

$$\chi_{C_4} = \frac{\sin\left(\frac{3}{2}\times\frac{\pi}{2}\right)}{\sin\frac{\pi}{4}} = \frac{\frac{1}{\sqrt{2}}}{\frac{1}{\sqrt{2}}} = 1$$

Further,

$$E\begin{bmatrix} e^{i\phi} \\ e^{i\,0\phi} \\ e^{-i\phi} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} e^{i\phi} \\ e^{i\,0\phi} \\ e^{-i\phi} \end{bmatrix} \quad \text{so that } \chi_E = 3.$$

Therefore, $\Gamma_{\text{reducible}}$ becomes

	E	$6C_4$	$3C_2\,(=C_4^2)$	$8C_3$	$6C_2$
Γ_{red}	3	1	−1	0	−1

which is clearly T_1 representation of the point group O. Remembering that the p orbitals have no centre of symmetry or are asymmetric with respect to the centre of symmetry, these will transform as a u type of irreducible representation or as T_{1u} type of representation of the point group O_h. In other words, the p set of orbitals containing a single electron will remain unsplit and will have the symmetry $t_{1\mu}$ in the octahedral ligand environment.

Alternatively, we may argue that since p orbitals belong to a u type of irreducible representation of the point group O_h, the complete $\Gamma_{\text{reducible}}$ of the point group O_h obtained from the $\Gamma_{\text{reducible}}$ of point group O, can be written as :

	E	$6C_4$	$3C_2\,(=C_4^2)$	$8C_3$	$6C_2$	iE	$6iC_4$	$3iC_2$	$8iC_3$	$6iC_2$
Γ_{red}	3	1	−1	0	−1	−3	−1	+1	0	+1

which is the T_{1u} irreducible representation of point group O_h. (For a u type of representation in O_h point group, $\chi_{C_n} = -\chi_{iC_n}$ as already mentioned)

Thus, p orbitals have the symmetry t_{1u} and remain unsplit (or degenerate) under an octahedral ligand environment.

Similarly, we can show, as illustrated below, that f orbitals containing a single electron split into a_{2u}, t_{1u} and t_{2u} sets of orbitals under an octahedral ligand environment. Based on the assumptions made earlier, it can be shown that $\chi(E) = 7$ and

$$C(\alpha) = \begin{bmatrix} e^{i3\alpha} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & e^{i2\alpha} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & e^{i\alpha} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{i0\alpha} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & e^{-i\alpha} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & e^{-i2\alpha} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & e^{-i3\alpha} \end{bmatrix} \text{ for the point group } O_h.$$

The character of such a matrix representing rotation operation on f orbitals along a particular axis around which θ remains constant is of the form :

$$\chi_{C(\alpha)} = \frac{\sin\left(l+\frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}} = \frac{\sin\left(3+\frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}} = \frac{\sin\frac{7}{2}\alpha}{\sin\frac{\alpha}{2}}$$

Hence,

$$\chi_{C_2} = \frac{\sin\left(\frac{7}{2}\pi\right)}{\sin\frac{\pi}{2}} = \frac{-1}{1} = -1$$

$$\chi_{C_3} = \frac{\sin\left(\frac{7}{2}\times\frac{2\pi}{3}\right)}{\sin\left(\frac{2\pi}{6}\right)} = 1$$

$$\chi_{C_4} = \frac{\sin\left(\frac{7}{2}\times\frac{\pi}{2}\right)}{\sin\frac{\pi}{4}} = \frac{\sin\frac{7\pi}{4}}{\sin\frac{\pi}{4}} = \frac{-\frac{1}{\sqrt{2}}}{\frac{1}{\sqrt{2}}} = -1$$

so that

	E	$6C_4$	$3C_2\,(=C_4^2)$	$8C_3$	$6C_2$
Γ_{red}	7	−1	−1	1	−1

Reducing this representation of point group O into its irreducible representations, we find that

A_2 occurs $\dfrac{7\times1\times1+(-1)(-1)\times6+(-1)\times1\times3+1\times1\times8+(-1)(-1)6}{24} = 1$ time

T_1 occurs $\dfrac{7\times3\times1+(-1)\times1\times6+(-1)(-1)\times3+1\times0\times8+(-1)(-1)\times6}{24} = 1$ time

T_2 occurs $\dfrac{7\times3\times1+(-1)(-1)\times6+(-1)(-1)\times3+1\times0\times8+(-1)\times1\times6}{24} = 1$ time

Thus, $\Gamma_{red} = A_2 + T_1 + T_2$ of the point group O.

Since f orbitals are all of u type, the corresponding terms in the point group O_h are A_{2u}, T_{1u} and T_{2u}. Thus, a set of f orbitals containing a single electron split into a_{2u}, t_{1u} and t_{2u} sets of orbitals.

Alternatively, we can write complete Γ_{red} for point group O_h from Γ_{red} of point group O. Remembering that all $\Gamma_{\text{irreducible}}$ of point group O_h obtained from $\Gamma_{\text{reducible}}$ of point group O_h must be of u type (since all f orbitals are asymmetric with respect to the centre of symmetry), we can calculate the symmetries of subsets of f orbitals as follows :

The complete $\Gamma_{\text{reducible}}$ of point group O_h can be written from $\Gamma_{\text{reducible}}$ of point group O as follows :

	E	$6C_4$	$3C_2$	$8C_3$	$6C_2$	iE	$6iC_4$	$3iC_2$	$8iC_3$	$6iC_2$
$\Gamma_{red}\,(O_h)$	7	−1	−1	1	−1	−7	1	1	−1	1

in which

A_{2u} occurs

$$\frac{7\times1\times1+(-1)(-1)\times6+(-1)\times1\times3+1\times1\times8+(-1)(-1)\times6]+[(-7)(-1)\times1+1\times1\times6+1\times(-1)\times3+(-1)(-1)\times8+1\times1\times6]}{48} = 1 \text{ time}$$

T_{1u} occurs

$$\frac{7\times3\times1+(-1)\times1\times6+(-1)(-1)\times3+1\times0\times8+(-1)(-1)\times6]+[(-7)(-3)\times1+1\times(-1)\times6+1\times1\times3+(-1)\times0\times8+1\times1\times6]}{48} = 1 \text{ time}$$

and T_{2u} occurs

$$\frac{7\times3\times1+(-1)(-1)\times6+(-1)(-1)\times3+1\times0\times8+(-1)\times1\times6]+[(-7)(-3)\times1+1\times1\times6+1\times1\times3+(-1)\times0\times8+1\times(-1)\times6]}{48} = 1 \text{ time}$$

Thus, Γ_{red} of point group O_h yields A_{2u}, T_{1u} and T_{2u} irreducible representations which implies that f orbitals containing a single electron splits into a_{2u}, t_{1u} and t_{2u} subsets under octaheral ligand environment.

The results of splitting of various types of orbitals (containing a single electron) in an octahedral ligand environment are summed up in Table 2.

TABLE 2

Splitting of Various Types of Orbitals in an Octahedral Ligand Environment

Types of orbitals	χ_R				Splittings
	χ_E	χ_{C_2}	χ_{C_3}	χ_{C_4}	
s ($l=0$)	1	1	1	1	a_{1g} (why ?)
p ($l=1$)	3	−1	0	1	t_{1u}
d ($l=2$)	5	1	−1	−1	$e_g + t_{2g}$
f ($l=3$)	7	−1	+1	−1	$a_{2u} + t_{1u} + t_{2u}$
g ($l=4$)	9	1	0	1	$a_{1g} + e_g + t_{1g} + t_{2g}$
h ($l=5$)	11	−1	−1	1	$e_u + 2t_{1u} + t_{2u}$

We can also investigate with the help of the group theory, the influence of tetrahedral, tetragonal and other ligand environments on s, p, d, f, etc., orbitals containing a single electron in each case. The procedure, however, is more complicated and has not been discussed here. Only the results of investigations relating to the splitting of various orbitals in tetrahedral ligand environment are given.

Orbitals	Splittings in Tetrahedral Ligand Environment
s	a_1
p	t_2
d	$e + t_2$
f	$a_2 + t_1 + t_2$
g	$a_1 + e + t_1 + t_2$
h	$e + t_1 + 2t_2$

It is to be noted that since a tetrahedral symmetry point group (T_d) has no centre of symmetry, none of its terms listed in the above table contains g or u subscript. Further, since a T_d point group is different from an O or O_h point group, hence the general formula for $\chi_{C(\alpha)}$ obtained for point group O cannot be applied for the T_d point group. This is the reason why the procedure for calculating $\chi_{(R)}$ for all the symmetry operations of T_d point group for a set of orbitals containing a single electron in tetrahedral ligand environment is different and more complicated than that for a similar set of orbitals in an octahedral ligand environment.

We have given here a few of the important applications of the group theory because our specific aim is to expose the student to the basic concepts of the group theory at appropriate level and to impress upon him that the knowledge of this topic is of primary importance for understanding inorganic chemistry in proper depth.

Splitting of Terms under the Influence of Octahedral Ligand Environment

We shall now consider the behaviour of d^n system ($n > 1$) under the influence of octahedral ligand environment where the magnitude of interelectronic repulsions amongst d electrons are greater than the magnitude of octahedral crystal field potential (V_{oct}) generated by the ligand environment. It is assumed that the stronger interelectronic repulsions give rise to terms which are then influenced and split by the weaker octahedral crystal field potential. Therefore, we are to deal here with the splitting of term of many-electron d^n systems under the influence of octahedral ligand environment. The conclusions arrived at earlier for single-electron systems under the influence of octahedral ligand environment also apply to the splitting

of terms arising for many-electron systems under the influence of identical ligand environment. For instance, just as a single d electron in a free metal atom or ion has a five-fold degenerate wave function corresponding to five values which m may have in Φ part of the wave function, a D term arising from d^n electrons of a metal atom or ion in free state has a five-fold degenerate wave function depending upon the five values which M of the D term may have. The only variable part of the wave function for a D term, under the symmetry opertions of point group O, is $e^{iM\phi}$ (M=+2, +1, 0, −1, −2) in exact analogy with the only variable part orbital $e^{im\phi}$ (m = +2, +1, 0, −1, −2) of the single-electron d orbital wave function under identical ligand environment. Therefore, the splitting of D term wave function in an octahedral ligand environment is analogous to the splitting of single-electron d orbital wave function under the influence of identical ligand environment.

Exactly the same relationship exists between the behaviour of a set of single-electron f orbital wave functions (m = + 3, + 2, + 1, 0, −1, −2, −3) and the F term wave functions (M = + 3, +2, 1, 0, −1,−2, −3) of a d^n system under the influence of octahedral ligand environment. Similarly, the P term wave functions (M = + 1, 0, −1) of a d^n system behaves exactly in the same manner as does a set of single-electron p orbital wave functions (m = + 1, 0, −1) in an octahedral ligand environment.

It may be recalled that while small letters, s, p, d, f, etc., are used to represent the states of a single electron, the capital letters, S, P, D, F, etc., are used to represent the terms arising out of d^n systems. The splittings of the single electron states in a given ligand environment are represented by symmetry symbols such as a_{1g}, e_g, t_{2g}, etc., using small letters whereas the splittings of a term of d^n system in a ligand environment are represented by term such as A_{1g}, T_{1g}, E_g, T_{2g}, etc., using capital letters.

Further, if the point group, to which the ligand environment belongs, has a centre of symmetry, as for example, in an octahedral environment, the subscripts of the splitting terms are determined by the types of the orbitals from which the terms are derived. For instance, all terms of a d^n configuration in an octahedral environment undergo g type of splittings because all d orbitals have a centre of symmetry.

It may be mentioned in passing that under the weak V_{oct} conditions (electronic repulsion > V_{oct}) mentioned earlier, the ligand environment does not interact directly with the electron spins. Hence, the unsplit term as well as its splittings in an octahedral environment will have the same spin multiplicity.

If the point group to which the ligand environment belongs has no centre of symmetry, then no subscripts are used for the split up terms as is the case in the splittings of terms of a d^n system under the influence of a tetraheral ligand environment. Recalling that $V_{tet} = -4/9\ V_{oct}$, that is, $V_{tet} \propto (-V_{oct})$, the splittings of a term of a d^n system under the influence of tetrahedral and octahedral environments are the same. The only difference is that the splittings of the term under tetrahedral environment do not carry the subscripts g or u. However, because of the negative sign in the relationship between V_{tet} and V_{oct}, the order of the energies of split up terms in the two environments are reverse of each other.

The splittings of terms of a d^2 configuration under octahedral and tetrahedral environments are given in Table 3.

TABLE 3

Splittings of Terms of d^2 Configuration in Octahedral and Tetrahedral Environments

Free ion terms	Splittings in octahedral environment	Splittings in tetrahedral environment
^1S	$^1A_{1g}$	$^1A_1$
^1G	$^1A_{1g}$, $^1T_{2g}$, ^1E_g, $^1T_{1g}$	$^1A_1$, $^1T_2$, ^1E, $^1T_1$
^3P	$^3T_{1g}$	$^3T_1$
^1D	^1E_g, $^1T_{2g}$	^1E, $^1T_2$
^3F	$^3A_{2g}$, $^3T_{1g}$, $^3T_{2g}$	$^3A_2$, $^3T_1$, $^3T_2$

7. Relaxation of Selection Rules for Electronic Transitions

As mentioned in Chapter 30, the transition moment integral Q, is given by

$$Q = \int_{-\infty}^{\infty} \psi_{1\,elec} \left| \sum_i e_i \bar{r}_i \right| \psi_{2\,elec} d\tau \qquad ...(3)$$

where $\sum_i e_i \bar{r}_i$ is the electric dipole moment operator of the molecule. This operator is a vector quantity. However, the exact form of the transition moment integral should utilise complete wave function $\psi_{complete}$ of the molecule where $\psi_{complete} = \psi_{elec}\, \psi_{vib}\, \psi_{rot}\, \psi_{trans}$. Thus, in order that an electronic transition becomes allowed, the exact Q should be non zero, *i.e.*,

$$Q = \int \psi_{1elec}\, \psi_{1vib}\, \psi_{1rot}\, \psi_{1trans} \left| \sum_i e_i \bar{r}_i \right| \psi_{2elec}\, \psi_{2vib}\, \psi_{2rot}\, \psi_{2trans}\, d\tau \neq 0 \qquad ...(4)$$

If, as an approximation, it is assumed that ψ_{elec}, ψ_{vib}, ψ_{rot} and ψ_{trans} wave functions of the molecule are all independent of one another and if the electronic absorption spectrum of the sample is recorded in the solid or liquid phase, ψ_{rot} and ψ_{trans} are not likely to change for a molecule during the lifetime of the excited electronic state so that in the above expression for Q, the ψ_{2rot} is the same as ψ_{1rot} and the ψ_{2trans} is the same as ψ_{1trans}. Therefore, Q can be expressed as

$$Q = \int \psi_{1elec} \psi_{1vib} \left| \sum_i e_i \bar{r}_i \right| \psi_{2elec} \psi_{2vib} d\tau \int \psi_{1rot}\, \psi_{2rot}\, d\tau \int \psi_{1trans}\, \psi_{2trans}\, d\tau \qquad ...(5)$$

$$= \int \psi_{1elec}\, \psi_{1vib} \left| \sum_i e_i \bar{r}_i \right| \psi_{2elec}\, \psi_{2vib}\, d\tau \times 1 \times 1 \qquad ...(6)$$

$$= \int \psi_{1elec}\, \psi_{1vib} \left| \sum_i e_i \bar{r}_i \right| \psi_{2elec}\, \psi_{2vib}\, d\tau \qquad ...(7)$$

If we apply the same approximation that ψ_{elec} and ψ_{vib} of the molecule are independent of each other and that during an electronic transition, the vibrational state of the molecule does not change so that $\psi_{1vib} = \psi_{2vib}$, we arrive at the following expression for the transition moment integral :

$$Q = \int \psi_{1elec} \left| \sum_i e_i \bar{r}_i \right| \psi_{2elec}\, d\tau \qquad ...(8)$$

This is the same expression from which Laporte selection rule is derived for the molecules having a centre of symmetry (see Chapter 30).

However, the above expression cannot explain the observation that many Laporte-forbidden absorption bands do appear (though with low energy) in the electronic absorption spectra of such molecules. The occurrence of Laporte-forbidden transitions can be explained if we consider that ψ_{elec} and ψ_{vib} states of the molecule are interdependent on each other and are to be considered together so that

$$Q = \int \psi_{1elec}\, \psi_{1vib} \left| \sum_i e_i \bar{r}_i \right| \psi_{2elec}\, \psi_{2vib}\, d\tau \qquad ...(9)$$

The combined $\psi_{elec}\, \psi_{vib}$ state is called $\psi_{vibronic}$ and the interdependence of the two wave functions is called **vibronic coupling.**

We shall now show that a Laporte-forbidden transition can become partly allowed due to vibronic coupling. Consider an octahedral complex MA_6. There are $3n - 6$, *i.e.*, 15 fundamental modes of vibration of this complex. All these vibrational modes are perfectly symmetric in their ground state and hence belong to A_{1g} irreducible representation. The complete ψ_{vib} of a state is the product of the wave functions of all the vibrational modes, that is,

$$\psi_{vib} = \prod_{i=1}^{3n-6} \psi_{vib_i} \qquad ...(10)$$

where ψ_{vib_i} is the wave function of the *i*th vibrational mode. The representation (rep) to which the ψ_{vib} (ground state) belongs is $A_{1g} \times A_{1g} \times A_{1g} \cdots\cdots\cdots = A_{1g}$.

If, out of the 15 normal vibrational modes, one vibrational mode gets excited to its first excited state while the rest of the normal vibrational modes remain in their ground state, the representation to which ψ_{vib}(excited state) of the molecule belongs is $A_{1g} \times A_{1g} \times A_{1g} \times \cdots\cdots = \Gamma_{excited}$ ($\Gamma_{excited}$ is the irreducible representation to which the excited vibrational mode of the molecule belongs). In other words, ψ_{vib} (excited state) belongs to the same representation to which the excited vibrational mode belongs.

Let us now apply the concept of vibronic coupling to the Laporte-forbidden $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions of the octahedral complex ion $[Co(NH_3)_6]^{3+}$. Only the coordinated nitrogens and Co will be considered for determining the number and the symmetry of the vibrational modes. The irreducible representations to which the first excited state of 15 normal modes of vibration of this octahedral ML_6 species belong are A_{1g}, T_{1g}, E_u, T_{1u} and T_{2u}.

The transition moment integral for the electronic transition $^1A_{1g} \rightarrow {}^1T_{1g}$, considering electronic states to be independent of vibrational states, is given by

$$Q = \int \psi_{A_{1g}} \left| \sum_i e_i \bar{r}_i^{*} \right| \psi_{T_{1g}}\, d\tau \qquad ...(11)$$

Since the direct product of $A_{1g} \times T_{1u} \times T_{1g}$ is $A_{1u} + E_u + T_{1u} + T_{2u}$ which does not contain A_{1g}, this transition moment integral is zero and the transition $^1A_{1g} \rightarrow {}^1T_{1g}$ is Laporte-forbidden. Similarly, Q for the electronic transition $^1A_{1g} \rightarrow {}^1T_{2g}$, is given by

$$Q = \int \psi_{A_{1g}} \left| \sum_i e_i \bar{r}_i \right| \psi_{T_{2g}}\, d\tau \qquad ...(12)$$

Again, the direct product of $A_{1g} \times T_{1u} \times T_{2g}$ is $A_{2u} + E_u + T_{1u} + T_{2u}$ (use octahedral character table to verify the direct product results). It does not contain A_{1g}. Hence this transition is also Laporte-forbidden.

It is observed, however, that the absorption bands due to the two above mentioned transitions do appear in the electronic absorption spectrum of $[Co(NH_3)_6]^{3+}$, though their intensities are low. This clearly indicates that there is some mechanism through which the forbidden transitions become partly allowed. Such a mechanism is vibronic coupling. Suppose, along with an electronic transition, a T_{1u} or T_{2u} vibrational mode also gets simultaneously excited. Using the expression for Q, considering vibronic coupling, we have

$$Q = \int \psi_{1elec}\, \psi_{1vib} \left| \sum_i e_i \bar{r}_i \right| \psi_{2elec}\, \psi_{2vib}\, d\tau \qquad ...(13)$$

where ψ_{1vib} belongs to A_{1g} and ψ_{2vib} belongs to T_{1u} or T_{2u} representation of the O_h group. (The subscript 1 is

The *x*, *y*, *z* components of the electric dipole vector transform as T_{1u} representation of the octahedral group.

used for the ground state wave function and 2 for the excited state wave function). Consider the electronic transition $^1A_{1g} \rightarrow {}^1T_{1g}$ along which the vibrational mode T_{1u} or T_{2u} is also excited simultaneously. The direct product $A_{1g} \times (A_{1g} \times T_{1u} \times T_{1g}) \times T_{1u}$ corresponding to the above Q is $(A_{1u} + E_u + T_{1u} + T_{2u}) \times T_{1u}$ or T_{2u} which contains a term $T_{1u} \times T_{1u}$ or $T_{2u} \times T_{2u}$. Both $T_{1u} \times T_{1u}$ and $T_{2u} \times T_{2u}$, when reduced, contain the term A_{1g}. Hence, the vibronic coupling makes $^1A_{1g} \rightarrow {}^1T_{1g}$ transition partly allowed.

Exactly similar results are obtained for $^1A_{1g} \rightarrow {}^1T_{2g}$ transition along which T_{1u} or T_{2u} vibrational mode of the molecule is also simultaneously excited. The direct product of the integrand Q in such a case will be $A_{1g} \times (A_{1g} \times T_{1u} \times T_{2u}) \times T_{1u}$ or T_{2u} which is $(A_{2u} + E_u + T_{1u} + T_{2u}) \times T_{1u}$ or T_{2u}. This contains the term $T_{1u} \times T_{1u}$ or $T_{2u} \times T_{2u}$ both of which, upon reduction, contain the term A_{1g}. This makes the transition $^1A_{1g} \rightarrow {}^1T_{2g}$ partly allowed because of vibronic coupling.

8. Establishing State of Symmetry by the Method of Descending Symmetry

We have already seen in this chapter that the strong field octahedral configuration e_g^2 can give rise to two sets of states, *viz.*, $^1A_{1g} + {}^3A_{2g} + {}^1E_g$ and $^3A_{1g} + {}^1A_{2g} + {}^1E_g$. The set that actually exists is obtained by using the method of descending symmetry. In this method, the symmetry of the complex is lowered through imagination to such an extent that each orbitally degenerate state of the original symmetry splits up into a set of non-degenerate states of lowered symmetry. The correlation Table 4 gives correlation between the states of various symmetries.

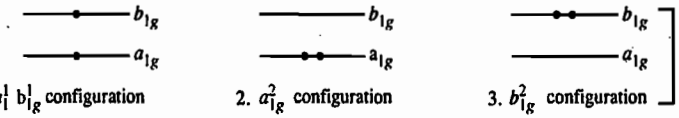
TABLE 4

Correlation between the States of Various Symmetries

O_h	O	T_d	D_{4h}	C_{4v}	C_{2v}	D_{3d}	D_3	C_{2h}
A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_{1g}	A_1	A_g
A_{2g}	A_2	A_2	B_{1g}	B_1	A_2	A_{2g}	A_2	B_g
E_g	E	E	$A_{1g} + B_{1g}$	$A_1 + B_1$	$A_1 + A_2$	E_g	E	$A_g + B_g$
T_{1g}	T_1	T_1	$A_{2g} + E_g$	$A_2 + E$	$A_2 + B_1 + B_2$	$A_{2g} + E_g$	$A_2 + E$	$A_g + B_g + B_g$
T_{2g}	T_2	T_2	$B_{2g} + E_g$	$B_2 + E$	$A_1 + B_1 + B_2$	$A_{1g} + E_g$	$A_1 + E$	$A_g + A_g + B_g$
T_{1u}	T_1	T_2	$A_{2u} + E_u$	$A_1 + E$	$A_1 + B_1 + B_2$	$A_{2u} + E_u$	$A_2 + E$	$A_u + B_u + B_u$
T_{2u}	T_2	T_1	$B_{2u} + E_u$	$B_1 + E$	$A_2 + B_1 + B_2$	$B_{2u} + E_u$	$A_1 + E$	$A_u + A_u + B_u$

It can be seen from Table 4 that if the symmetry of the strong field octahedral complex is lowered to D_{4h} by elongating the trans pairs of the metal–ligand bonds of the octahedron, the only degenerate E_g state of e_g^2 configuration splits up into $A_{1g} + B_{1g}$ states of D_{4h} symmetry. The state A_{1g} remains A_{1g} under both the symmetry environments. The state A_{2g} of O_h symmetry becomes B_{1g} of D_{4h} symmetry.

The one-electron e_g orbitals of the octahedral complex will split up into a_{1g} and b_{1g} non-degenerate levels in the complex of lower D_{4h} symmetry. The two electrons previously present in the e_g orbitals of the octahedral complex will now occupy a_{1g} and b_{1g} non-degenerate levels of the tetragonal complex of lower D_{4h} symmetry. This can occur in the following ways :



1. $a_1^1\ b_{1g}^1$ configuration 2. a_{1g}^2 configuration 3. b_{1g}^2 configuration

Let us now consult the D_{4h} character table and see how many states arise out of each of the configurations given above. The method has already been discussed earlier in this chapter.

1. The $a_{1g}^1\ b_{1g}^1$ configuration of D_{4h} symmetry gives rise to B_{1g} state (the direct product $B_{1g} \times A_{1g} = A_{1g}$). Since there are four ways of arranging one electron in a_{1g} level and one electron in b_{1g} level, the total degeneracy (obtained by multiplying spin multiplicity with the orbital degeneracy) of the B_{1g} state arising out of $a_{1g}^1\ b_{1g}^1$ configuration must be **four** which is possible only if the spin multiplicity of B_{1g} state is 3 as well as 1 (total degeneracy of $^1\mathbf{B}_{1g}$ and $^3\mathbf{B}_{1g}$ states is $1 \times 1 + 3 \times 1 = 4$).
2. The a_{1g}^2 configuration of D_{4h} symmetry gives rise to the term A_{1g} (the direct product of $A_{1g} \times A_{1g} = A_{1g}$). Since there is only one way of placing both the electrons in the same a_{1g} level, the total degeneracy of A_{1g} state must be **one**. Thus, the state arising out of a_{1g}^2 configuration is $^1A_{1g}$ which has a spin multiplicity of 1 (total degeneracy of $^1A_{1g}$ is $1 \times 1 = 1$).
3. The a_{1g}^2 configuration of D_{4h} symmetry gives rise to A_{1g} state ($B_{1g} \times B_{1g} = A_{1g}$). Since there is only one way of arranging both the electrons in the same b_{1g} level, the total degeneracy of the A_{1g} state must be one. Thus, the state arising out of b_{1g}^2 configuration must be $^1\mathbf{A}_{1g}$.

Thus, the six electronic arrangements of two electrons occupying a_{1g} and b_{1g} levels of D_{4h} symmetry give rise to three configurations out of which a total of three states, *viz.*, $^1A_{1g}$, $^1B_{1g}$ and $^3B_{1g}$ arise. It is important to remember that *the spin multiplicity of the parent unsplit state and of its splittings due to lowering of symmetry must remain the same.*

The spin multiplicity of E_g state of octahedral environment cannot be 3 because a ^3E_g state would split into $^3A_{1g}$ and $^3B_{1g}$ states of D_{4h} symmetry. But there is no $^3A_{1g}$ state in the list of the states obtained from D_{4h} symmetry (Table 4). Thus, the spin multiplicity of E_g state for octahedral environment has to be 1. The state ^1E_g splits into $^1A_{1g}$ and $^1B_{1g}$ states of D_{4h} symmetry (Table 4).

There is one more $^1A_{1g}$ state of D_{4h} symmetry left which must correspond to $^1A_{1g}$ state of O_h symmetry. The A_{2g} state of octahedral symmetry, therefore, must correlate with $^3B_{1g}$ state of D_{4h} symmetry.

We may thus summarise the above results in the form of the following table :

O_h Symmetry	D_{4h} Symmetry
$^1A_{1g}$	$^1A_{1g}$
$^3A_{2g}$	$^3B_{1g}$
^1E_g	$^1A_{1g}$ $^1B_{1g}$

Thus, the strong field octahedral configuration e_g^2 splits into $^1A_{1g} + {}^3A_{2g} + {}^1E_g$ states.

Let us now consider the strong field octahedral configuration t_{2g}^2. This configuration gives rise to three *sets* of states, *viz.*, $(^1A_{1g} + {}^1E_g + {}^1T_{1g} + {}^1T_{2g})$, $(^1A_{1g} + {}^1E_g + {}^1T_{1g} + {}^3T_{2g})$ and $(^3A_{1g} + {}^3E_g + {}^1T_{1g} + {}^1T_{2g})$, as discussed earlier. Fifteen electronic arrangements are possible for this configuration, the total degeneracy of each set of the above mentioned states is also 15.

One of the lowered symmetries, in which each of the degenerate states arising out of strong octahedral field splits into the non-degenerate states, is the C_{2h} symmetry. In this C_{2h} symmetry, the degeneracy of one-electron t_{2g} orbitals is lifted to $a_g + a_g + b_g$ non-degenerate levels (see correlation Table 4). It can be seen from this table that A_{1g}, E_g, T_{1g} and T_{2g} states of octahedral symmetry correlate with A_g, $(A_g + B_g)$, $(A_g + B_g + B_g)$ and $(A_g + A_g + B_g)$ states, respectively, of the C_{2h} symmetry.

The t_{2g}^2 configuration of octahedral symmetry gives rise to the following states in the lowered C_{2h} symmetry :

(*i*) The a_g^2 configuration gives rise to A_g state ($A_g \times A_g = A_g$ according to C_{2h} character table). Since the two electrons are present in the same a_g level, their spins must be paired up making only one electronic arrangement possible. This implies that the a_g^2 configuration of C_{2h} symmetry gives rise to only ^1A_g state having a total degeneracy of one ($1 \times 1 = 1$).

(*ii*) The configuration a_g^2 again has both the electrons in the same a_g level. This configuration also gives rise to ^1A_g state as in (*i*).

(*iii*) The b_g^2 configuration gives rise to A_g state ($B_g \times B_g = A_g$ according to C_{2h} character table). Since both the electrons are paired in the same b_g level, the configuration b_g^2 gives rise to ^1A_g state.

(*iv*) The $a_g' a_g'$ configuration in which the two electrons are in two different a_g orbitals gives rise to A_g state ($A_g \times A_g = A_g$ according to C_{2h} character table). Since in this configuration, the spins of the two electrons present in two different a_g orbitals can give rise to four electronic arrangements, the total degeneracy of the states of this configuration must be four. In other words, the $a_g' a_g'$ configuration of C_{2h} symmetry gives rise to ^1A_g and ^3A_g states whose total degeneracy is four ($1 \times 1 + 3 \times 1 = 4$).

(*v*) The $a_g^1 b_g^1$ configuration gives rise to non-degenerate B_g state ($A_g \times B_g = B_g$ according to C_{2h} character table). Since this configuration has one electron in a_g level and one electron in b_g level, the spins of these electrons will generate four electronic arrangements. Therefore, the total degeneracy of the states of this configuration has to be four. Hence, the configuration $a'_g b'_g$ gives rise to ^1B_g and ^3B_g states having a total degeneracy of four ($1 \times 1 + 3 \times 1 = 4$).

(*vi*) The configuration $a^1_g b^1_g$ will also give rise to ^1B_g and ^3B_g states in a similar manner.

We may summarise the result, saying that the t_{2g}^2 configuration of octahedral symmetry gives rise to the following states in the lowered C_{2h} symmetry :

$$4\,^1A_g + {}^3A_g + 2\,^1B_g + 2\,^3B_g$$

From a close study of the correlation Table 4, the following correlations between the states of O_h

symmetry and C_{2h} symmetry can be obtained :

O_h Symmetry	C_{2h} Symmetry
$^1A_{1g}$	$^1A_{1g}$
^1E_g	^1A_g, ^1B_g
$^3T_{1g}$	^3A_g, ^3B_g, ^3B_g
$^3T_{2g}$	^1A_g, ^1A_g, ^1B_g

Remembering that the spin multiplicity of the parent unsplit state of higher symmetry and of its splittings in lower symmetry must remain the same, we conclude that there should be a $^3T_{1g}$ state of octahedral symmetry which splits up into ^3A_g and two ^3B_g states under C_{2h} symmetry. Similarly, there must be a $^1T_{2g}$ state of octahedral symmetry which splits up into two ^1A_g and one ^1B_g state and an ^1E_g state of octahedral symmetry which splits up into $^1A_g + {}^1B_g$ states under C_{2h} symmetry. The $^1A_{1g}$ state of octahedral symmetry correlates with ^1A_g state of C_{2h} symmetry. Thus, the t^2_{2g} configuration of octahedral symmetry splits up into $^1A_{1g} + {}^1E_g + {}^3T_{1g} + {}^1T_{2g}$ states.

9. Study of Electron Absorption Spectra using Plane Polarised Light

The electric dipole vector $\sum_i e_i \vec{r}_i$ of the molecule can be expressed as the vectorial sum $\sum_i e_i \vec{x}_i + \sum_i e_i \vec{y}_i + \sum_i e_i \vec{z}_i$ so that the transition moment integral splits into the following three integrals :

$$Q_x = \int \psi_1 \left| \sum_i e_i \vec{x}_i \right| \psi_2 \, d\tau$$

$$Q_y = \int \psi_1 \left| \sum_i e_i \vec{y}_i \right| \psi_2 \, d\tau$$

$$Q_z = \int \psi_1 \left| \sum_i e_i \vec{z}_i \right| \psi_2 \, d\tau$$

Since e_i, the charge on the ith electron is a scalar quantity, $\sum_i e_i \vec{x}_i$, $\sum_i e_i \vec{y}_i$, $\sum_i e_i \vec{z}_i$ will have the same symmetry properties as $\vec{x}$, $\vec{y}$ and $\vec{z}$, respectively.

In an octahedral complex, the $\vec{x}$, $\vec{y}$ and $\vec{z}$ components of the electric dipole of the molecule are equivalent. Hence, the direction of the oscillating electric vector of light will not alter the extent of interaction with dipole moment operator of the molecule. But, this is not the case in molecules in which one or more of the x, y, z components of the dipole operator belong to *different* representations of the group. For example,

the tetragonal complex, trans $[Co(en)_2Cl_2]^+$, has D_{4h} symmetry. Had the symmetry of the complex been octahedral, two strong crystal field transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ would have been possible. In the tetragonal symmetry (D_{4h}) obtained by elongating the two trans bonds of octahedral symmetry, the A_{1g}, T_{1g} and T_{2g} of O_h symmetry correlate with A_{1g}, $(A_{2g} + E_g)$ and $(B_{2g} + E_g)$ of D_{4h} symmetry, respectively (see correlation Table 5 given below). Thus, in the above mentioned tetragonal trans $[Co(en)_2Cl_2]^+$ complex, the $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ electronic transitions are possible. This is illustrated in Fig. 11.

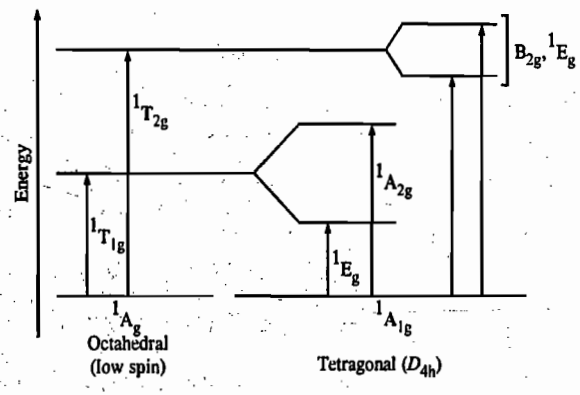


Fig. 11. Electronic energy levels for octahedral (low spin) and tetragonal Co^{3+} complex.

In a tetragonal complex, x and y components of the electric dipole belong to the representation E_u and its z component belongs to the representation A_{2u} of the D_{4h} character table. The transition moment integrals corresponding to the above mentioned electronic transitions in trans $[Co(en)_2Cl_2]^+$ complex, considering electronic wave functions alone, are given in Table 5.

TABLE 5

Correlation between Transition Moment Integral, Q_{elec} and Direct Product Corresponding to its Integrand ΓQ_{elec}

Transition Moment Integral (Q_{elec})	Direct Product Corresponding to its Integrand ΓQ_{elec}
$\int \psi_{A_{1g}} \lvert \sum_i e_i \bar{x}_i + \sum_i e_i \bar{y}_i \rvert \psi_{A_{2u}} d\tau$	$A_{1g} \times E_u \times A_{2g} = E_u$
$\int \psi_{A_{1g}} \lvert \sum_i e_i \bar{x}_i + \sum_i e_i \bar{y}_i \rvert \psi_{B_{2g}} d\tau$	$A_{1g} \times E_u \times B_{2g} = E_u$
$\int \psi_{A_{1g}} \lvert \sum_i e_i \bar{x}_i + \sum_i e_i \bar{y}_i \rvert \psi_{E_g} d\tau$	$A_{1g} \times E_u \times E_u = A_{1u} + A_{2u} + B_{1u} + B_{2u}$
$\int \psi_{A_{1g}} \lvert \sum_i e_i \bar{z}_i \rvert \psi_{A_{2g}} d\tau$	$A_{1g} \times A_{2u} \times A_{2g} = A_{2u}$
$\int \psi_{A_{1g}} \lvert \sum_i e_i \bar{z}_i \rvert \psi_{B_{2g}} d\tau$	$A_{1g} \times A_{2u} \times B_{2g} = B_{1u}$
$\int \psi_{A_{1g}} \lvert \sum_i e_i \bar{z}_i \rvert \psi_{E_g} d\tau$	$A_{1g} \times A_{2u} \times E_u = E_u$

As can be seen, none of the expressions given above, contains A_{1g}. Thus, all the transitions should be Laporte-forbidden. However, the electronic absorption spectrum of this complex does contain low intensity absorption bands. This is due to the interdependence of electronic and vibrational states of the complex species. Therefore, we should use $\psi_{vibronic}$, instead of ψ_{elec} alone, in the transition moment integrals as shown in Table 5.

The transition moment integrals would thus be written as :

$$Q_{vibronic\,(x,y)} = \int \psi_{1elec}\psi_{1vib} \lvert \sum_i e_i \bar{x}_i + \sum_i e_i \bar{y}_i \rvert \psi_{2elec}\psi_{2vib}\, d\tau$$

$$Q_{vibronic\,(z)} = \int \psi_{1elec}\psi_{1vib} \lvert \sum_i e_i \bar{z}_i \rvert \psi_{2elec}\psi_{2vib}\, d\tau$$

We have already observed that the ground vibrational state of this complex belongs to the totally symmetric representation A_{1g} whereas the excited vibrational state belongs to the representation to which the first excited vibrational mode belongs. The symmetries of the first excited vibrational modes of the tetragonal complex are $^2A_{1g}$, B_{1g}, B_{2g}, E_g, $^2A_{1u}$, B_{1u} and $3E_u$. The direct product corresponding to $Q_{vibronic}$ *viz.*, $\Gamma_{vibronic}$, is obtained by multiplying the direct product of Q_{elec} with $\Gamma\psi_{vibronic}$ (ground state) and $\Gamma_{vibronic}$ (excited state). Since $\Gamma_{vibronic}$ (ground state) is A_{1g} and it will not change the result of the direct product, the direct product relating to $Q_{vibronic}$ is obtained simply by multiplying the direct product relating to Q_{elec} with $\Gamma_{vibronic}$ (excited state) which is the same as $\Gamma_{vibronic\ mode}$ (excited state).

Direct product relating to $Q_{vibronic}$ is equal to direct product relating to $Q_{elec} \times \Gamma_{vibronic}$. If this direct product contains a representation multiplied with itself, then it must contain the perfectly symmetric representation A_{1g}. That is, $A_{1u} \times A_{1u}$, $B_{1u} \times B_{1u}$, $E_u \times E_u$, $A_{2u} \times A_{2u}$ etc., must contain A_{1g} representation.

We can easily see that $Q_{vibronic}$ $(^1A_{1g} \rightarrow {}^1A_{2g})$ becomes non zero and the electronic transition $^1A_{1g} \rightarrow {}^1A_{2g}$ becomes allowed if the vibrational mode E_u of the complex also gets simultaneously excited because $\Gamma Q_{vibronic}$ $(^1A_{1g} \rightarrow {}^1A_{2g}) = \Gamma Q_{elec\,(x,y)}$ $(^1A_{1g} \rightarrow {}^1A_{2g}) \times E_u = E_u \times E_u$ and must contain the perfectly symmetric term A_{1g}. Similarly, it can be shown that the electronic transition $^1A_{1g} \rightarrow {}^1B_{2g}$ becomes allowed since $\Gamma Q_{vibronic\,(x,y)}$ $(^1A_{1g} \rightarrow {}^1B_{2g})$ becomes non zero if the vibrational mode E_u is simultaneously excited because

$$\Gamma Q_{vibronic\,(x,y)}\,(^1A_{1g} \rightarrow {}^1B_{2g}) = \Gamma Q_{elec\,(x,y)}\,(^1A_{1g} \rightarrow {}^1B_{2g}) \times E_u = E_u \times E_u$$

Table 6 predicts from $Q_{vibronic\,(x,y)}$ and $Q_{vibronic\,(z)}$ whether the electronic transitions of the tetragonal complex ion, trans $[Co(en)_2Cl_2]^+$, are forbidden or allowed.

TABLE 6

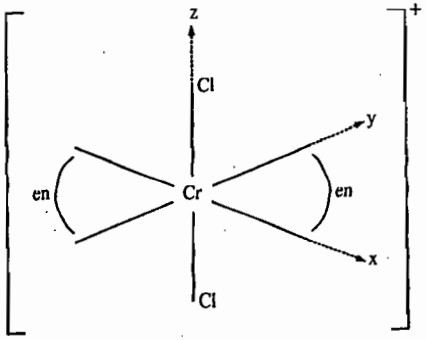
Prediction of Forbidden or Allowed Electronic Transitions in the case of Teragonal Complex Ion trans $[Co(en)_2Cl_2]^+$

Transitions	$A_{1g} \rightarrow A_{2g}$	$A_{1g} \rightarrow B_{2g}$	$A_{1g} \rightarrow E_g$
Direct product corresponding to $\int \psi_{1elec} \lvert \sum_i e_i \bar{z}_i \rvert \psi_{2elec}\, d\tau$	$A_{1g} \times A_{2u} \times A_{2g} = A_{2u}$ (forbidden for all vibrational modes)	$A_{1g} \times A_{2u} \times B_{2g} = B_{1u}$* (allowed by B_{1u} vibrational mode)	$A_{1g} \times A_{2u} \times E_g = E_u$* (allowed by E_u vibrational mode)
Direct product corresponding to $\psi_{1elec} \lvert \sum e_i \bar{x}_i + \sum e_i \bar{y}_i \rvert \psi_{2elec}\, d\tau$	$A_{1g} \times E_u \times A_{2g} = E_u$* (allowed by E_u vibrational mode)	$A_{1g} \times E_u \times B_{2g} = E_u$* (allowed by E_u vibrational mode)	$A_{1g} \times E_u \times E_g = A_{1u} + A_{2u} + B_{1u} + B_{2u}$ (allowed by B_{1u} and A_{1u} vibrational modes)

*$B_{1u} \times B_{1u}$ vibrational mode, $E_u \times E_u$ vibrational mode, $B_{1u} \times B_{1u}$ vibrational mode and $A_{1u} \times A_{1u}$ vibrational mode all contain A_{1g}.

If we grow a *single crystal of the complex* $[Co(en)Cl_2]^+$, with structure as shown, determine its principal axis (called z-axis) by X-ray technique and record the electronic absorption spectra using plane polarized light as source, it is expected that when the z-axis of the complex is mounted parallel to the plane of polarised light, the oscillating electric vector of the polarised light will interact with only the z component of the electric dipole of the complex ion and *not with its x and y components*. The absorption of light will then

depend only on Q_z. If Q_z in such a situation is non zero, the polarised light will be absorbed by the complex ion and the resulting absorption band is called *z* polarised band. If we mount the crystal in such a manner that the principal axis lies perpendicular to the plane of polarized light (*i.e., the plane of the complex ion is parallel to the plane of polarised light*), the oscillating electric vector of plane polarised light will interact only with *x* and *y* components of the electric dipole of the species. If, in such a case, $Q_{x,y}$ is non zero, the complex ion will absorb the polarised light and will thus give rise to *x*, *y* polarised absorption band.



As can be seen from Fig. 11, when octahedral symmetry of the low spin Co^{3+} complex is lowered to D_{4h} symmetry, the $^1T_{1g}$ and $^1T_{2g}$ states split into $A_{2g} + E_g$ and $B_{2g} + E_g$ states so that four transitions in all are possible for a tetragonal Co^{3+} (low spin) complex, as shown in Fig. 11. All the four transitions, being (*x*, *y*) allowed, polarised transitions should appear as (*x*, *y*) polarised absorption bands when the single crystal of the complex is mounted in such a manner that its principal axis (*z*-axis) is perpendicular to the plane of polarised light. On the other hand, if the single crystal of the complex is mounted in such a manner that its principal axis is parallel to the plane of polarised light, only three *z*-polarised absorption bands would appear due to the three *z*-allowed polarised transitions. The transition $A_{1g} \rightarrow A_{2g}$ will not be observed under such conditions as it is *z*-forbidden (see Table 6). The actual (*x*, *y*) polarised electron absorption spectrum of the trans $[Co(en)_2Cl_2]^+$ complex is shown in Fig. 12. As can be seen, three absorption bands are clearly observed. The first two absorption bands are due to $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions and the third broad and higher frequency absorption band is an unresolved composite band due to $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions. (It may be noted that the energy gap between the splittings of T_{2g} octahedral state into E_g and B_{2g} states is much smaller than the energy gap between the splittings of T_{1g} octahedral state into A_{2g} and E_g tetragonal states). In the actual *z*-polarised absorption spectrum, however, the *second absorption band is not observed*. This is due to the fact that the transition $^1A_{1g} \rightarrow {}^1A_{2g}$, which should have given rise to the second absorption band, is a *z-forbidden transition* (Table 6).

The first absorption band which appears under both conditions is, therefore, due to $^1A_{1g} \rightarrow {}^1E_g$ transition. The electronic absorption spectrum of trans $[Co(en)_2Cl_2]^+$ using plane polarised light as the source is given in Fig. 12.

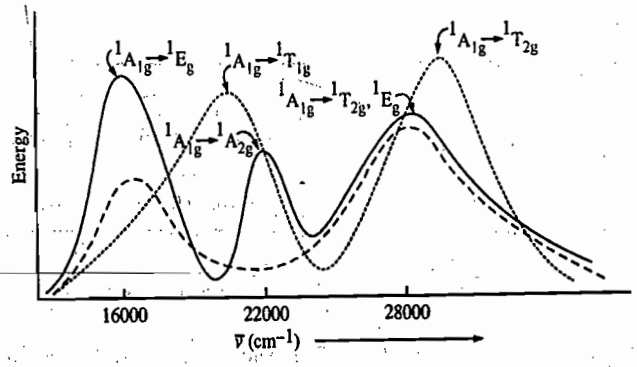
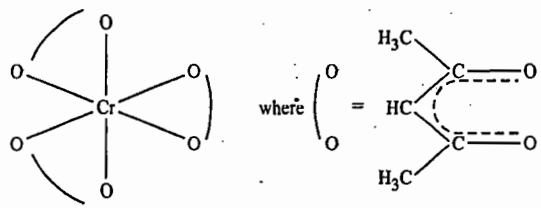


Fig. 12. Electron absorption spectrum of trans $[Co(en)_2Cl_2]^+$ in solid phase. The dotted line (.....) shows the absorption spectrum when the plane of polarised light is ∥ to the principal axis (*i.e.*, *z*-axis). The solid line shows the absorption spectrum when the plane of polarised light is ⊥ to the principal axis. Spectrum of $[Co(en)_3]^{3+}$ shown by dash-dot (-----) line, has been given for the sake of comparison.

Had the complex been perfectly octahedral, it would have shown two absorption bands in its electronic absorption spectrum due to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions (Fig. 11). But, because of the lower symmetry of the trans $[Co(en)_2Cl_2]^+$ complex, the T_{1g} state splits into A_{2g} and E_g states so that the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition absorption band of O_h symmetry splits into $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ absorption bands occurring at 22000 cm^{-1} and 16000 cm^{-1}, respectively. The higher energy T_{2g} state also splits into B_{2g} and E_g states and, therefore, the $^1A_{1g} \rightarrow {}^1T_{2g}$ absorption band should have also split into absorption bands corresponding to $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions. But, due to a very small energy gap between the B_{2g} and E_g splittings of T_{2g} state, only a composite broad band is observed at 28000 cm^{-1} in this case.

It is not always necessary that only a vibronic wave function is required to explain the appearance of electronic absorption spectra in polarized light. Amongst the complexes having lower than octahedral symmetry, for example, the complex tri(acetyl acetonato) Cr(III), can be taken as octahedral if we consider the coordinated oxygen atoms only and neglect the chelate rings altogether. The structure of the complex is shown below :



Under the assumed octahedral symmetry, the three transitions possible are : $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}$(F) and $^4A_{2g} \rightarrow {}^4T_{1g}$(P). However, all these transitions should be Laporte-forbidden and hence no absorption band should appear. But, the actual symmetry of the complex is D_3. The lowering of the symmetry of the complex from O_h to D_3 would transform the A_{2g}, T_{2g} and T_{1g} states of octahedral symmetry to A_2, $(A_2 + E)$ and $(A_1 + E)$ states, respectively, of D_3 symmetry. Also the *x*, *y* components of the electric dipole vector of the complex transform as E and its *z* component transforms as A_2 representation of D_3 group. It is to be remembered that the D_3 symmetry has no centre of symmetry and hence is not governed by Laporte selection rule.

The possible types of transitions with the predictions whether these are allowed or forbidden are given in Table 7.

TABLE 7

Various Transitions with Predictions whether Allowed or Forbidden

Transition	$A_2 \rightarrow A_2$	$A_2 \rightarrow E$	$A_2 \rightarrow A_1$
Direct product relating to $\int \psi_{1elec} \lvert \sum_i e_i \bar{x}_i + \sum_i e_i \bar{y}_i \rvert \psi_{2elec}\, d\tau$	$A_2 \times A_2 \times A_2 = A_2$ (forbidden)	$A_2 \times A_2 \times E = E$ (forbidden)	$A_2 \times A_2 \times A_1 = A_1$ (allowed)
Direct product relating to $\int \psi_{1elec} \lvert \sum_i e_i \bar{x}_i + \sum_i e_i \bar{y}_i \rvert \psi_{2elec}\, d\tau$	$A_2 \times E \times A_2 = E$ (forbidden)	$A_2 \times E \times E = A_1 + A_2 + E$ (allowed)	$A_2 \times E \times A_1 = E$ (forbidden)

As can be seen from Table 7, $A_2 \rightarrow A_2$ transition is a totally forbidden transition whereas the $A_2 \rightarrow E$ transition is *z*-forbidden but (*x*, *y*) allowed. The transition $A_2 \rightarrow E$ will show an absorption band in the electron absorption spectrum of the complex when the principal axis (called *z*-axis) of the single crystal of the complex tri(acetyl acetonato) Cr(III) is mounted perpendicular to the plane of polarised light. The electronic transition $A_2 \rightarrow A_1$ is *z*-allowed and (*x*, *y*) forbidden (Table 7). The absorption band due to $A_2 \rightarrow A_1$ transition will appear in the electron absorption spectrum of the complex only when the principal axis of its single crystal is held parallel to the plane of polarised light incident on the crystal.

CHARACTER TABLES FOR IMPORTANT SYMMETRY GROUPS

Character tables for a few symmetry groups have already been given in this chapter 3. However, for convenience of reference, character tables for all the important symmetry groups have been consolidated at one place here.

1. The C_{nv} Groups

C_{2v}[a]	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

* For a planar molecule, the x-axis is taken perpendicular to the plane.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

C_{4v}[a]	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	(x, y) (R_x, R_y)	(xz, yz)

* If the C_{4v} molecule contains a square array of atoms, the σ_v planes should pass through the larger number of atoms of the square array or should intersect the largest possible number of bonds.

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	R_z	
E_1	2	2cos 72°	2 cos 144°	0	(x, y) (R_x, R_y)	(xz, yz)
E_2	2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1		
B_2	1	−1	1	−1	−1	1		
E_1	2	1	−1	−2	0	0	(x, y) (R_x, R_y)	(xz, yz)
E_2	2	−1	−1	2	0	0		(x^2-y^2, xy)

2. The C_{nh} Groups

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5		$\varepsilon = \exp(2\pi i/3)$
A'	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E'	1	ε	ε^*	1	ε	ε^*	(x, y)	(x^2-y^2, xy)
	1	ε^*	ε	1	ε^*	ε		
A''	1	1	1	−1	−1	−1	z	
E''	1	ε	ε^*	−1	$-\varepsilon$	$-\varepsilon^*$	(R_x, R_y)	(xz, yz)
	1	ε^*	ε	−1	$-\varepsilon^*$	$-\varepsilon$		

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B_g	1	−1	1	−1	1	−1	1	−1		x^2-y^2, xy
E_g	1	i	−1	$-i$	1	i	−1	$-i$	(R_x, R_y)	(xz, yz)
	1	$-i$	−1	i	1	$-i$	−1	i		
A_u	1	1	1	1	−1	−1	−1	−1	z	
B_u	1	−1	1	−1	−1	1	−1	1		
E_u	1	i	−1	$-i$	−1	$-i$	1	i	(x, y)	
	1	$-i$	−1	i	−1	i	1	$-i$		

C_{5h}	E	C_5	C_5^2	C_5^3	C_5^4	σ_h	S_5	S_5^7	S_5^3	S_5^9		$\varepsilon = \exp(2\pi i/5)$
A'	1	1	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E'_1	1	ε	ε^2	ε^{2*}	ε^*	1	ε	ε^2	ε^{2*}	ε^*	(x, y)	
	1	ε^*	ε^{2*}	ε^2	ε	1	ε^*	ε^{2*}	ε^2	ε		
E'_2	1	ε^2	ε^*	ε	ε^{2*}	1	ε^{2*}	ε^*	ε^*	ε^2		(x^2-y^2, xy)
	1	ε^{2*}	ε	ε^*	ε^2	1	ε^{2*}	ε	ε^*	ε^2		
A''	1	1	1	1	1	−1	−1	−1	−1	−1	z	
E''_1	1	ε	ε^2	ε^{2*}	ε^*	−1	$-\varepsilon$	$-\varepsilon^2$	$-\varepsilon^{2*}$	$-\varepsilon^*$	(R_x, R_y)	(xz, yz)
	1	ε^*	ε^{2*}	ε^2	ε	−1	$-\varepsilon^*$	$-\varepsilon^{2*}$	$-\varepsilon^2$	$-\varepsilon$		
E''_2	1	ε^2	ε^*	ε	ε^{2*}	−1	$-\varepsilon^2$	$-\varepsilon^*$	$-\varepsilon$	$-\varepsilon^{2*}$		
	1	ε^{2*}	ε	ε^*	ε^2	−1	$-\varepsilon^{2*}$	$-\varepsilon$	$-\varepsilon^*$	$-\varepsilon^2$		

C_{6h}	E	C_6	C_3	C_2	C_3^2	C_6^5	i	S_3^5	S_6^5	σ_h	S_6	S_3		$\varepsilon = \exp(2\pi i/6)$
A_g	1	1	1	1	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B_g	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
E_{1g}	1	ε	$-\varepsilon^*$	−1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$	−1	$-\varepsilon$	ε	(R_x, R_y)	(xz, yz)
	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε		
E_{2g}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		(x^2-y^2, xy)
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		
A_u	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	z	
B_u	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
E_{1u}	1	ε	$-\varepsilon^*$	−1	$-\varepsilon$	ε^*	−1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$	(x, y)	
	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε	−1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$		
E_{2u}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	−1	ε^*	ε	−1	ε^*	ε		
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-E$	$-\varepsilon^*$	−1	ε	ε^*	−1	ε	ε^*		

3. The D_{nh} Groups

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		(x^2+y^2, z^2)
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}[a]	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	2	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

[a] σ_v passes through the atoms and σ_d bisects the bond angles.

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	1	−1	1	1	1	−1	R_z	
E_1'	2	2 cos 72°	2 cos 144°	0	2	2 cos 72°	2 cos 144°	0	(x, y)	
E_2'	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)
A_1''	1	1	1	1	−1	−1	−1	−1		
A_2''	1	1	1−	−1	−1	−1	−1	1	z	
E_1''	2	2 cos 72°	2 cos 144°	0	−2	−2 cos 72°	− 2 cos 144°	0	(R_x, R_y)	(xz, yz)
E_2''	2	2 cos 144°	2 cos 72°	0	−2	−2 cos 144°	− 2 cos 72°	0		

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

D_{8h}	E	$2C_8$	$2C_8^3$	$2C_4$	C_2	$4C_2'$	$4C_2''$	i	$2S_8$	$2S_8^3$	$2S_4$	σ_h	$4\sigma_d$	$4\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	1	−1	−1	1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	−1	1	1	1	−1	1	−1	−1	1	1	1	−1		
B_{2g}	1	−1	−1	1	1	−1	1	1	−1	−1	1	1	−1	1		
E_{1g}	2	$\sqrt{2}$	$-\sqrt{2}$	0	−2	0	0	2	$\sqrt{2}$	$-\sqrt{2}$	0	−2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	0	0	−2	2	0	0	2	0	0	−2	2	0	0		(x^2-y^2, xy)
E_{3g}	2	$-\sqrt{2}$	$\sqrt{2}$	0	−2	0	0	2	$-\sqrt{2}$	$\sqrt{2}$	0	−2	0	0		
A_{1u}	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	−1	1	1	1	−1	−1	1	1	−1	−1	−1	1		
B_{2u}	1	−1	−1	1	1	−1	1	−1	1	1	−1	−1	1	−1		
E_{1u}	2	$\sqrt{2}$	$-\sqrt{2}$	0	−2	0	0	−2	$-\sqrt{2}$	$\sqrt{2}$	0	2	0	0		(x, y)
E_{2u}	2	0	0	−2	2	0	0	−2	0	0	2	−2	0	0		
E_{3u}	2	$-\sqrt{2}$	$\sqrt{2}$	0	−2	0	0	−2	$\sqrt{2}$	$-\sqrt{2}$	0	2	0	0		

4. The D_{nd} Groups

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1	z	xy
E	1	0	−2	0	0	(x, y)	(xz, yz)
						(R_x, R_y)	

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	−1	1	1	−1	R_z	
E_g	2	−1	0	2	−1	0	(R_x, R_y)	(x^2-y^2, xy)
								(xz, yz)
A_{1u}	1	1	1	−1	−1	−1		
A_{2u}	1	1	−1	−1	−1	1	z	
E_u	2	−1	0	−2	1	0	(x, y)	

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	1	−1		
B_2	1	−1	1	−1	1	−1	1	z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	(x, y)	
E_2	2	0	−2	0	2	0	0		(x^2-y^2, xy)
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	(R_x, R_y)	(xz, yz)

D_{5d}	E	$2C_5$	$2C_5^2$	$5C_2$	i	$2S_{10}^3$	$2S_{10}$	$5\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	1	1	1	−1	R_z	
E_{1g}	2	2 cos 72°	2 cos 144°	0	2	2 cos 72°	2 cos 144°	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	1	z	
E_{1u}	2	2 cos 72°	2 cos 144°	0	−2	−2 cos 72°	− 2 cos 144°	0	(x, y)	
E_{2u}	2	2 cos 144°	2 cos 72°	0	−2	−2 cos 144°	− 2 cos 72°	0		

D_{6d}	E	$2S_{12}$	$2C_6$	$2S_4$	$2C_3$	$2S_{12}^5$	C_2	$6C_2'$	$6\sigma_d$		
A_1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1	1	1	−1		
B_2	1	−1	1	−1	1	−1	1	−1	1	z	
E_1	2	$\sqrt{3}$	1	0	−1	$-\sqrt{3}$	−2	0	0	(x, y)	
E_2	2	1	−1	−2	−1	1	2	0	0		(x^2-y^2, xy)
E_3	2	0	−2	0	2	0	−2	0	0		
E_4	2	−1	−1	2	−1	−1	2	0	0		
E_5	2	$-\sqrt{3}$	1	0	−1	$\sqrt{3}$	−2	0	0	(R_x, R_y)	(xz, yz)

5. The S_n Groups

S_4	E	S_4	C_2	S_4^3		
A	1	1	1	1	R_z	x^2+y^2, z^2
B	1	−1	1	−1	z	(x^2-y^2, xy)
E	$\begin{Bmatrix}1 & i & -1 & -i\\ 1 & -i & -1 & i\end{Bmatrix}$				(x, y); (R_x, R_y)	(xz, yz)

S_6	E	C_3	C_3^2	i	S_6^5	S_6		$\varepsilon = \exp(2\pi i/3)$
A_g	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E_g	$\begin{Bmatrix}1 & \varepsilon & \varepsilon^* & 1 & \varepsilon & \varepsilon^*\\ 1 & \varepsilon^* & \varepsilon & 1 & \varepsilon^* & \varepsilon\end{Bmatrix}$						(R_x, R_y)	(x^2-y^2, xy); (xz, yz)
A_u	1	1	1	−1	−1	−1	z	
E_u	$\begin{Bmatrix}1 & \varepsilon & \varepsilon^* & -1 & -\varepsilon & -\varepsilon^*\\ 1 & \varepsilon^* & \varepsilon & -1 & -\varepsilon^* & -\varepsilon\end{Bmatrix}$						(x, y)	

S_8	E	S_8	C_4	S_8^3	C_2	S_8^5	C_4^3	S_8^7		$\varepsilon = \exp(2\pi i/8)$
A	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B	1	−1	1	−1	1	−1	1	−1	z	
E_1	$\begin{Bmatrix}1 & \varepsilon & i & -\varepsilon^* & -1 & -\varepsilon & -i & \varepsilon^*\\ 1 & \varepsilon^* & -i & -\varepsilon & -1 & -\varepsilon^* & -i & \varepsilon\end{Bmatrix}$								(x, y); (R_x, R_y)	
E_2	$\begin{Bmatrix}1 & i & -1 & -i & 1 & i & -1 & -i\\ 1 & -i & -1 & i & 1 & -i & -1 & i\end{Bmatrix}$									(x^2-y^2, xy)
E_3	$\begin{Bmatrix}1 & -\varepsilon^* & -i & \varepsilon & -1 & \varepsilon^* & i & -\varepsilon\\ 1 & -\varepsilon & i & \varepsilon^* & -1 & \varepsilon & -i & -\varepsilon^*\end{Bmatrix}$									(xz, yz)

6. The Cubic Groups

T	E	$4C_3$	$4C_3^2$	$3C_2$		$\varepsilon = \exp(2\pi i/3)$
A	1	1	1	1		x^2+y^2, z^2
E	$\begin{Bmatrix}1 & \varepsilon & \varepsilon^* & 1\\ 1 & \varepsilon^* & \varepsilon & 1\end{Bmatrix}$					$(2z^2-x^2, -y^2, x^2-y^2)$
T	3	0	0	−1	(R_x, R_y, R_z); (x, y, z);	(xy, xz, yz)

T_h	E	$4C_3$	$4C_3^2$	$3C_2$	i	$4S_6$	$4S_6^5$	$3\sigma_h$		$\varepsilon = \exp(2\pi i/3)$
A_g	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_u	1	1	1	1	−1	−1	−1	−1		
E_g	$\begin{Bmatrix}1 & \varepsilon & \varepsilon^* & 1 & 1 & \varepsilon^* & -\varepsilon^* & 1\\ 1 & \varepsilon^* & \varepsilon & 1 & 1 & \varepsilon^* & \varepsilon & 1\end{Bmatrix}$									$(2z^2-x^2-y^2, x^2-y^2)$
E_u	$\begin{Bmatrix}1 & \varepsilon & \varepsilon^* & 1 & -1 & -\varepsilon & -\varepsilon^* & -1\\ 1 & \varepsilon^* & \varepsilon & 1 & -1 & -\varepsilon^* & -\varepsilon & -1\end{Bmatrix}$									
T_g	3	0	0	−1	1	0	0	−1	(R_x, R_y, R_z)	(xz, yz, xy)
T_u	3	0	0	−1	−1	0	0	1	(x, y, z)	

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z) (x, y, z)	
T_2	3	0	−1	−1	1		(xy, xz, yz)

O	E	$6C_4$	$3C_2(=C_4^2)$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	−1	1	1	−1		
E	2	0	2	−1	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	1	−1	0	−1	(R_x, R_y, R_z); (x, y, z);	
T_2	3	−1	−1	0	1		(xy, xz, yz)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

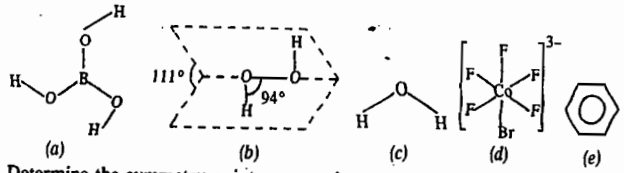
7. The Groups $C_{\infty v}$ and $D_{\infty h}$ For Linear Molecules

$C_{\infty v}$	E	$2C_\infty^\Phi$	...	$\infty\,\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	...	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	...	−1	R_z	
$E_1 \equiv \Pi$	2	$2\cos\Phi$	...	0	(x, y); (R_x, R_y)	(xz, yz)
$E_2 \equiv \Delta$	2	$2\cos 2\Phi$	...	0		(x^2-y^2, xy)
$E_3 \equiv \Phi$	2	$2\cos 3\Phi$	...	0		
...	...	...	...	...		

$D_{\infty h}$	E	$2C_\infty^\Phi$	...	$\infty\,\sigma_v$	i	$2S_\infty^\Phi$	...	∞C_2		
Σ_g^+	1	1	...	1	1	1	...	1		x^2+y^2, z^2
Σ_g^-	1	1	...	−1	1	1	...	−1	R_z	
Π_g	2	$2\cos\Phi$	...	0	2	$-2\cos\Phi$	...	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\Phi$	...	0	2	$2\cos 2\Phi$	...	0		(x^2-y^2, xy)
...	...	...	...	...	...	...	...	...		
Σ_u^+	1	1	...	1	−1	−1	...	−1	z	
Σ_u^-	1	1	...	−1	−1	−1	...	1		
Π_u	2	$2\cos\Phi$	...	0	−2	$2\cos\Phi$	...	0	(x, y)	
Δ_u	2	$2\cos 2\Phi$	...	0	−2	$-2\cos 2\Phi$	...	0		
...	...	...	...	...	...	...	...	...		

QUESTIONS

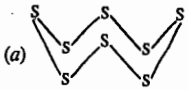
1. Write down the symmetry point groups of the following molecules. How many and which symmetry operations are possible in each case ?



(a) (b) (c) (d) (e)

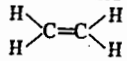
[Ans. (a) C_{3h}, (b) C_2, (c) C_{2v} (d) C_{4v} (e) D_{6h}]

2. Determine the symmetry point groups, the symmetry elements and the symmetry operations that are possible in the following molecules :

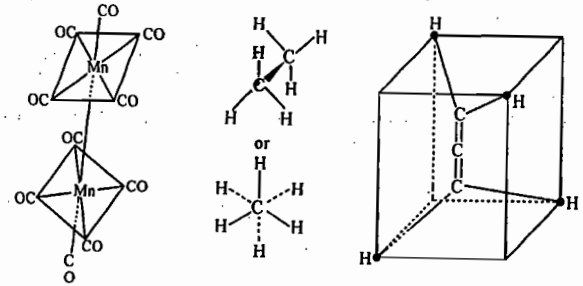


(a) (b) trans $[Co(NH_3)_4ClBr]^+$ (ignore the positions of hydrogens) [Ans. (a) D_{4d} (b) C_{4v}]

3. Determine the symmetry point groups of the molecules given below. Also determine the symmetry operations that can be carried out on the geometry of each molecule.

(a)  (b) PF_5 (c) $PtCl_4^{2-}$ (d) Ferrocene [Ans. (a) D_{2h} (b) D_{3h} (c) D_{4h} (d) D_{5d}]

4. Give the symmetry point groups of the following molecules :



(a) (b) (c)

[Ans. (a) D_{4d} (b) D_{3d} (c) D_{2d}]

5. Determine symmetry point groups of the following :

1. Benzene	2. Ruthacene	3. $Co(NH_3)_4Cl_2$ (trans)	4. *p*-Dichlorobenzene
5. Acetaldehyde	6. Trans N_2F_2	7. Diborane	8. BF_3
9. N_2O_4	10. $[Co(NH_3)_4ClBr]$ (trans)	11. $POCl_3$	12. NO_2^-.

[Ans. 1. D_{6h} 2. D_{5h} 3. D_{4h} 4. D_{2h} 5. C_s 6. C_{2h} 7. D_{2h} 8. D_{3h} 9. D_{2h} 10. C_{4v} 11. C_{3v} 12. C_{2v}]

6. (a) Describe the rules relating to the determination of symmetry point groups of molecules.
   (b) Determine the product of C_2 and σ_v (which is perpendicular to C_2) by taking a point (x_1, y_1, z_1) in space.
7. Construct a Group Multiplication Table for C_{3v} point group by taking NH_3 as an example.
8. Represent NH bonds of ammonia by arrows. Taking these arrows as basis, write down Γ_{red} and show that $\Gamma_{red} = A_1 + E$.
9. What information is conveyed by a Character Table ? Explain by taking a suitable example. List all the rules for writing Mulliken's symbols for irreducible representations.
10. ~~Show that in a tetrahedral molecule, p_x, p_y and p_z *together* transform as T_2 representation of the group.~~
11. What is 'direct product' ? How is it helpful in determining allowed and forbidden electronic transitions ?
12. How is group theory helpful in understanding σ and π bonding in (i) $[M_nO_4]^-$ and (ii) $[Co(CN)_6]^{3-}$?
13. Show that in a strong field octahedral complex, t_{2g}^2 configuration gives rise to $^3T_{1g}$, $^1T_{2g}$, $^1A_{1g}$ and ^1E_g terms whereas e_g^2 configuration gives rise to $^3A_{2g}$, ^1E_g and $^1A_{1g}$ terms.
14. Discuss briefly the various applications of the group theory.

4 CHEMICAL BONDING

Atoms, except those of noble gases, do not have free existence. They readily combine with one another to form molecules. According to the classical view, the phenomenon of combination, called **chemical bonding**, involves *the union of two or more atoms through redistribution of electrons in their outer most shells involving either transference of electrons from one atom to another or sharing of electrons amongst themselves so that all the atoms acquire the stable noble gas configurations of minimum energy.* If the union takes place by the *transference of electrons* from one atom to another, the bonding is said to be **ionic** and if it takes place by the *mutual sharing of electrons* between the atoms concerned, the bonding is said to be **covalent.** There is yet another type of bonding called **coordinate covalent bonding** in which both the electrons shared between the atoms are contributed by one atom only.

In addition to the above, some other types of chemical bonds such as *metallic bond* and *hydrogen bond* are also known.

IONIC BOND

An **ionic bond** results from *complete transference of one or more electrons from the outermost energy shell (valency shell) of one atom to the outermost energy shell of the other atom.* In this way, both the atoms acquire electronic configurations of the nearest noble gases. The atom from which the electrons are transferred, *i.e.,* the atom which *loses the electrons,* acquires a *positive charge* and becomes, what is called, a **positive ion.** The atom which *gains the electrons,* acquires a *negative charge* and becomes, what is called, a **negative ion.** *The electrostatic attraction between the oppositely charged ions results in the formation of a bond between them. This is called an* **ionic bond.** *The number of electrons transferred from or to the atom of an element in order to acquire the stable s^2p^6 configuration in the outer most shell is called the* **electrovalency** *of the element.*

The formation of ionic bond (in fact, of any type of chemical bond) is invariably accompanied by decrease in energy. As an example, we may consider the **decrease in energy in the formation of sodium chloride.** The essential processes which occur in the formation of sodium chloride (*solid*) from sodium (*solid*) and chlorine (*gas*) are as follows :

(i) $$Na\,(s) \xrightarrow[= 108{\cdot}5\ kJ\ mol^{-1}]{\text{Sublimation energy}} Na\,(g)$$

(ii) $$Cl_2\,(g) \xrightarrow[= 243{\cdot}0\ kJ\ mol^{-1}]{\text{Dissociation energy}} 2Cl\,(g)$$

(iii) $$Na\,(g) \xrightarrow[= 495{\cdot}2\ kJ\ mol^{-1}]{\text{Ionization energy}} Na^+\,(g) + e^-$$

(iv) $$Cl\,(g) + e^- \xrightarrow[= -348{\cdot}3\ kJ\ mol^{-1}]{\text{Electron affinity}} Cl^-\,(g)$$

$$(v) \qquad Na^+(g) + Cl^-(g) \xrightarrow[= -758{\cdot}7 \text{ kJ mol}^{-1}]{\text{Lattice energy}} [Na^+][Cl^-](s)$$

The net change of energy involved in all the five steps put together amounts to $108{\cdot}5 + \frac{1}{2}(243{\cdot}0) + 495{\cdot}2 - 348{\cdot}3 - 758{\cdot}7 = -381{\cdot}8$ kJ mol^{-1}. This is the **decrease in energy** in the formation of ionic bond between sodium (*s*) and chlorine (*g*) to form sodium chloride (*s*).

The net energy change obtained by adding all the energy terms, as in the above example, is denoted by ΔH and is referred to as the *enthalpy of formation of the ionic bond*. Evidently, if ΔH is negative, the formation of ionic bond is feasible.

Factors Influencing the Formation of Ionic Bond. The following factors facilitate the formation of an ionic bond between a metal and a non-metal.

1. Ionization Energy. It is defined as *the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom of an element.* The lesser the ionization energy, the greater is the ease of the formation of a cation. Alkali metals and alkaline earth metals have low ionization energies and, therefore, they form metal cations very easily.

2. Electron Affinity. It is defined as *the amount of energy released when an electron is added to an isolated gaseous atom of an element.* The formation of an anion occurs with the addition of one or more electrons to an atom, generally a non-metal atom. The greater the energy released during this process, the easier will be the formation of an anion, evidently. Thus, high electron affinity of a non-metal favours the formation of an anion.

Thus, low ionization energy of an atom (generally a metal atom) and a high electron affinity of another atom (generally a non-metal atom) facilitate the formation of an ionic bond between them.

3. Lattice Energy. It is defined as *the amount of energy released when cations and anions are brought from infinity to their respective equilibrium sites in the crystal lattice to form one mole of the ionic compound.* The higher the magnitude of the lattice energy, the greater is the tendency of the formation of an ionic bond.

For lattice energy to be high, the force of electrostatic attraction between the constituent ions should be high. The force of attraction between two oppositely charged ions in air (vacuum) is given by the well known Coulomb's law as $F = q_1q_2/r^2$ where q_1 and q_2 are the respective charges on the ions and r is the distance between them. This distance is obtained by adding the radii of the positive and negative ions.

The higher the charges on the ions and the smaller the distance between them, the greater is the force of attraction between the ions. Thus, the third factor mentioned above stipulates that *the cation and anion should be small in size and should have high electric charge so that the electrostatic attraction between them is high.*

To take an example, Na^+ ion is smaller than Cs^+ ion. Hence, the force of attraction between Na^+ ion and Cl^- ion in Na^+Cl^- is more than that between Cs^+ and Cl^- ions in Cs^+Cl^-. The lattice energy of Na^+Cl^- is, therefore, more than that of Cs^+Cl^-. The lattice energies of various alkali metal halides are given in Table 1.

TABLE 1

Lattice Energies of Various Alkali Metal Halides (kJ mol^{-1})

Halide ion	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	−994·5	−894·5	−790·2	−756·7	−719·0
Cl^-	−802·6	−758·7	−681·4	−660·6	−618·7
Br^-	−760·8	−714·8	−656·3	−631·3	−593·6
I^-	−710·6	−668·8	−618·7	−597·7	−564·3

It can be easily visualised that *for a given anion, the smaller the radius of the cation, the greater is the strength of the ionic bond.* Similarly, *for a given cation, the smaller the radius of the anion, the greater is the strength of the ionic bond.*

Tendency of Elements to form Ionic Bonds in Relation to their Position in the Periodic Table

As is well known, the elements on the left of the periodic table have *low ionisation energies* while those on the right have *high electron affinities*. Hence, ionic bonds are possible between the elements on the left (metals) and those on the right of the periodic table (non-metals). The elements of Group 1 (alkali metals), for example, react readily with elements of Group 17 (the halogens) to form ionic compounds. The elements of Group 2 (alkaline earth metals) also react with elements of Group 17, but not so readily. The reason is that these metals have two electrons in the valency shells and they have to lose both of them to acquire the stable s^2p^6 configuration in ther outermost shells. The elimination of two electrons from a metal M may be represented as below :

$$M \xrightarrow{(IE)_1} M^+ + e^- \quad ; \quad M^+ \xrightarrow{(IE)_2} M^{2+} + e^-$$

$(IE)_1$ represents the first ionisation energy while $(IE)_2$ represents the second ionisation energy of the metal. When the first electron is taken out of an atom, it becomes increasinlgy difficult to remove the second electron from the resulting positively charged ion. Thus, $(IE)_2$ is very much higher than $(IE)_1$. In order to remove two electrons, evidently, the energy needed is $(IE)_1 + (IE)_2$. Hence, *elements of Group 2 do not have as strong a tendency to form ions as the elements of Group 1 have.*

Amongst the non-metals, elements of Groups 16 and 17 change into negatively charged ions (anions) readily. However, the non-metals of Group 16 (oxygen, sulphur, etc.) do so less readily compared to the non-metals of Group 17. The reason is that their outer configuration is s^2p^4 and thus there are two vacancies in their valency shell. The addition of one electron is accompanied by release of energy giving rise to an ion with a single negative charge but the addition of the second electron takes place with difficulty because of repulsion from its own negative ion. Hence, *energy has to be supplied to add the second electron.* For example, 140·9 kJ mol^{-1} of energy is *released* when oxygen is converted to O^- ion but 769·9 kJ mol^{-1} of energy has to be *supplied* to convert O^- to O^{2-} ion. Thus,

$$O + e^- \longrightarrow O^- ; \qquad \text{Energy released, } \Delta H_1 = -140{\cdot}9 \text{ kJ mol}^{-1}$$

$$O^- + e^- \longrightarrow O^{2-} ; \qquad \text{Energy required, } \Delta H_2 = +769{\cdot}9 \text{ kJ mol}^{-1}$$

Hence, *formation of oxides or sulphides is not so easy as the formation of fluorides or chlorides.*

Tendency to form Cations. *The larger the size of an atom, the greater is the ease with which the valency electrons can be eliminated from it.* Since the atomic volume (atomic mass/density) and hence the atomic radius increases on moving down the group of alkali metals from Li → Na → K → Rb → Cs, the tendency of alkali metals to change into cations increases in the same order. Thus, Na changes into Na^+ ion more easily than Li. Similarly, K changes into K^+ ion more easily than Na and so on. Cesium, the last element of the group which has the largest atomic size, ionises most readily while lithium, the first element which has the smallest atomic size, ionises least readily.

Similarly, amongst the alkaline earth metals (Group 2), Ba, which is the heaviest element with the largest atomic radius, ionises most readily while Be, with the smallest atomic radius in this group, ionises least readily.

Tendency to form Anions. *The smaller the atom, the greater will be its tendency to accept extra electron* (or electrons) *to change into an anion.* For example, amongst the halogens, fluorine, with the smallest atomic size, forms an anion most readily. It is for this reason that *fluorides* of mercury, aluminium and tin are *ionic compounds* while the *chlorides* of these metals are largely *covalent* in character.

Formation of Ions of Higher Charges. As mentioned before, the formation of ions with two positive charges or two negative charges is not so easy as the formation of ions with one positive or one negative charge. The formation of simple ions with three positive or three negative charges is extremely

difficult and, therefore, highly unlikey. Consider, for example, aluminium of Group 13. Its outer electronic configuration is $3s^2p^1$. The successive ionisation energies of aluminium are as follows :

$$Al \xrightarrow{(IE)_1} Al^+ + e^-; \qquad (IE)_1 = 577{\cdot}4 \text{ kJ mol}^{-1}$$

$$Al^+ \xrightarrow{(IE)_2} Al^{2+} + e^-; \qquad (IE)_2 = 1833{\cdot}0 \text{ kJmol}^{-1}$$

$$Al^{2+} \xrightarrow{(IE)_2} Al^{3+} + e^-; \qquad (IE)_3 = 2703{\cdot}5 \text{ kJ mol}^{-1}$$

Thus, a total of 5113·9 kJ mol^{-1} of energy is needed to remove all the three valency electrons to form the trivalent Al^{3+} ion. This is not a feasible proposition since rarely more than 1500 kJ mol^{-1} of energy is available when chemical reactions take place. It is, therefore, easy to understand why the elements of Groups 13 and 14 do not form ionic compounds ordinarily. Instead, they form covalent compounds by the process of sharing of electrons which we shall consider shortly.

Experience shows that simple ions carrying more than two positive charges are rare. However, complex ions carrying more than two positive charges are well known. We shall consider here only one example. Aluminium chloride, $AlCl_3$, is largely a covalent compound. When it is dissolved in water, it undergoes hydration as represented below :

$$AlCl_3 + 6H_2O \longrightarrow AlCl_3.6H_2O \text{ or } [Al(H_2O)_6]^{3+}3Cl^-$$

The hydrated aluminium chloride contains the trivalent complex ion, $[Al(H_2O)_6]^{3+}$. The question arises : How does Al atom now lose three electrons to change into hydrated Al^{3+} ion ? The answer is that the hydration of aluminium chloride is an exothermic process and, therefore, a lot amount of energy is released in the reaction. This energy becomes available to accomplish the release of three electrons from aluminium atom to form hydrated Al^{3+} ion.

Now let us consider why it is not possible, ordinarily, to have anions carrying more than two negative charges. The formation of anions carrying one negative charge, *e.g.*, halides (Group 17) and two negative charges, *e.g.*, sulphides (Group 16) have already been considered. The question arises : Can we have easily anions carrying three negative charges, *e.g.*, nitrides, N^{3-} and phosphides, P^{3-} (Group 15) ? The answer is : No. The reason is that the outer configuration of these atoms is s^2p^3. The addition of three electrons to nitrogen or phosphorus atom requires much more energy than is ordinarily available in chemical reactions. The same is true for other elements of Group 15.

Thus, while formation of simple positive ions is limited, generally, to the atoms of metals of Groups 1 and 2, the formation of simple negative ions is limited, generally, to the atoms of non-metals of Groups 16 and 17. The atoms of elements of middle Groups 13, 14 and 15 do not form ionic compounds ordinarily. As we shall see, they form covalent bonds more readily by sharing their electrons with other atoms.

Variable Valency of Cations. Alkali metals and alkaline earth metals *show only one valency* which is 1 in the case of the former and 2 in the case of the latter. This is because the monovalent cations of alkali metals (such as Na^+, K^+, Rb^+) and divalent cations of alkaline earth metals (such as Mg^{2+}, Ca^{2+}, Ba^{2+}) have most stable noble gas configurations (s^2p^6) in their valency shells.

Several other cations, particularly those of the transition metals, do not have the stable s^2p^6 configuration in their valency shells. In such cases, the outermost shell of the cations is not stable. It further loses one or more electrons giving rise to metal ions of higher valencies. The transition metals thus show variable valency. Iron, cobalt and nickel, for example, form divalent as well as trivalent ions with the loss of 2 or

3 electrons from their valence $3d4s$ orbitals. In fact, most of the transition metals show variable valency by the loss of one or more electrons from their $(n-1)d\ ns$ orbitals.

COVALENT BOND

Lewis Concept of Covalent Bond. G. N. Lewis was the first to suggest, in 1916, that atoms may combine with one another by *sharing of electrons* in their valency shells so that the combining atoms attain the nearest noble gas configurations in their valency shells. The shared electrons contribute towards the stability of both the atoms. This type of linkage is called **covalent linkage** or **covalent bond.** The compounds formed by this mechanism are called **covalent compounds.**

For example, hydrogen and chlorine atoms share one electron each to form HCl.

$$H\cdot + \ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow H:\ddot{\underset{\cdot\cdot}{Cl}}: \quad \text{or} \quad H-Cl$$

In this process, while hydrogen atom acquires electronic configuration of helium, chlorine atom acquires electronic configuration of the nearest noble gas argon.

In the formation of oxygen molecule, each oxygen atom has six electrons in the valence shell and, therefore, they contribute two electrons each for sharing. Thus, two electron pairs are shared and there is a **double bond** between the two oxygen atoms.

$$:\ddot{O}: + :\ddot{O}: \longrightarrow :\ddot{O}::\ddot{O}: \quad \text{or} \quad O=O$$

According to Lewis concept, *the number of electrons which an atom contributes for sharing in a covalent bond* is called its **covalency**. Thus, covalency of hydrogen, chlorine and oxygen is 1, 1 and 2, respectively.

Decrease of Energy in the Formation of Hydrogen Molecule. The formation of a chemical bond of any type is possible only if the approach of the atoms towards one another is accompanied by decrease in energy. When any two atoms approach each other, new forces of attraction and repulsion are set in. The forces of attraction are between the nucleus of one atom and the electrons of the other. The forces of repulsion are between two nuclei amongst themselves as well as between the electrons of the two atoms amongst themselves. The net result of these forces may be attraction or repulsion.

If the net result is **attraction**, *the total energy of the system decreases and a chemical bond results.*

If the net result is **repulsion**, *the total energy of the system increases and no chemical bonding is possible.*

Let us see how the approach of two hydrogen atoms towards each other results in decrease of energy of the system and thus results in the formation of a covalent bond to give hydrogen molecule (H_2).

Consider two hydrogen atoms A and B with nuclei H_A and H_B and corresponding electrons e_A and e_B respectively. When the two atoms approach each other, the following additional attractive and repulsive forces start operating :

a. Attractive forces between electron of atom A (e_A) and nucleus of atom B (H_B) and electron of atom B (e_B) and nucleus of atom A (H_A). These forces decrease the energy of the system.

b. Repulsive forces between two nuclei (H_A and H_B) and two electrons (e_A and e_B) of the two atoms. These forces increase the energy of the system.

The attractive and repulsive forces are pictorially shown in Fig. 1.

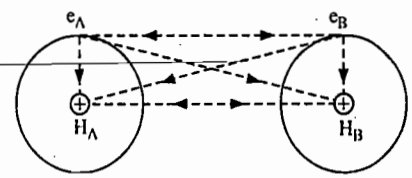


Fig. 1. Attractive and repulsive forces between H atoms in H_2 molecule.

The manner in which the potential energy of the system changes as the hydrogen atoms are brought closer to each other is represented graphically in Fig. 2.

Initially, when the hydrogen atoms lie far away, say, at infinite distance from each other, the electrostatic potential energy of one atom is independent of the presence of the other atom. By convention, this energy is taken arbitrarily as zero. This fact is represented at the far end towards the right of the graph. As the two atoms are brought closer and closer, the electrostatic potential energy goes on decreasing because attractive forces go on becoming more and more dominant. The decrease of potential energy continues till a certain minimum value is attained. If the atoms are brought still closer, the potential energy shows a *sharp rise*. This is due to the fact that the repulsive forces at such small internuclear distances become dominant. Since repulsion always causes increase in energy, the energy of the system increases, as shown in the figure. The formation of a covalent bond between two hydrogen atoms takes place at the point which corresponds to the *minimum* in the potential energy curve.

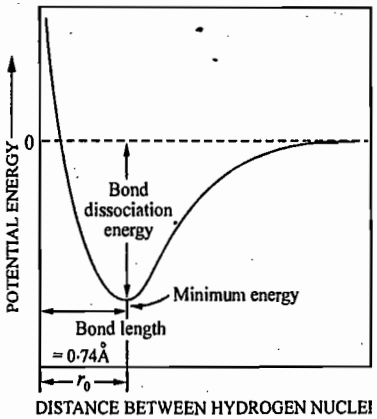


Fig. 2. Variation of potential energy with nuclear distance in the formation of hydrogen molecule.

The position of minimum energy also corresponds to the minimum distance upto which the two nuclei can be brought together before the force of repulsion between them becomes dominant. In other words, this distance corresponds to the bond length. **Bond length** *is, thus, defined as the distance between the nuclei of the two atoms constituting a chemical bond.* In the case of hydrogen molecule, the distance between the two hydrogen atoms coresponding to minimum energy is 0·74 Å. The decrease in potential energy in the formation of H_2 molecule has been found to be 458 kJ mol^{-1}. Evidently, because of decrease of energy, H_2 molecule would be much more stable than H atoms.

*ATOMIC ORBITAL OVERLAP CONCEPT OF COVALENCY

It may be recalled that an orbital can accommodate a maximum of two electrons having opposite spins. *As long as such electron pairs are present in orbitals, they are not available for chemical combination.* If, however, only a single electron is present in an orbital of the outer shell, it will have a tendency to combine with a similar electron present in the orbital of the outer shell of another atom. This results in the formation of a covalent chemical bond between the two atoms. Thus, according to the **orbital overlap concept,** *formation of a covalent bond between two atoms results from the coupling of electrons with opposite spins belonging to orbitals of outermost shells of the two atoms.* The orbitals containing such unpaired electrons are said to *overlap with each other* so that the electron pair now belongs to both the orbitals. This may be illustrated by considering a few examples.

Formation of hydrogen molecule. Hydrogen atom has only one electron in its valency shell. It needs one electron more to complete this shell. In the formation of a stable hydrogen molecule, H_2, the two hydrogen atoms having unpaired electrons approach each other and their 1*s* atomic orbitals overlap when the two approaching atoms reach a point at which the potential energy is minimum. The electrons shared between the two atoms are located in the region of space between the nuclei of the atoms concerned, as represented in Fig. 3. The 1*s* orbitals of

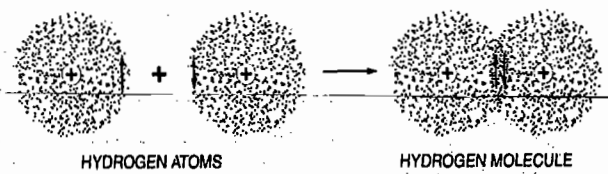


Fig. 3. Formation of hydrogen molecule by overlapping of 1*s* orbitals of both the atoms. The paired electrons have opposite spins.

*The atomic orbital overlap concept of covalency, in fact, forms the basis of the modern theories of covalent bonding (specially the valence bond theory). These theories would be discussed in details a little later in this chapter.

both the atoms, thus, get fully occupied. The bond formed between two hydrogen atoms in this manner is called an ***s – s* bond** since it involves overlapping of *s* orbitals of the two hydrogen atoms. The overlapping of the orbitals takes place along the same axis, as shown. When a bond is formed by overlapping of the orbitals along the same axis, it is known as a **sigma bond.** This type of overlapping takes place to a substantial extent and, therefore, the resulting bond is very strong. The greater the extent of the overlapping of orbitals, the stronger is the covalent bond.

Formation of fluorine molecule. Fluorine atom with electronic configuration $1s^2 2s^2 p_x^2 p_y^2 p_z^1$ has one half-filled *p* orbital. It needs one more electron to fill this orbital. In the formation of fluorine molecule, this half-filled *p* orbital of one atom overlaps with a similar *p* orbital of another atom to form a molecule of fluorine, F_2. This is shown in Fig. 4. In the figure, only *p* orbitals are shown. The completely filled *s* orbitals are omitted for the sake of clarity.

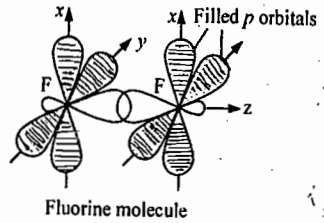


Fig. 4. Formation of fluorine molecule by overlapping of 2*p* orbitals of both the fluorine atoms.

Formation of hydrogen fluoride molecule. As has been shown earlier, the 1*s* orbital of hydrogen can accommodate one electron more. Also one of the 2*p* orbitals of fluorine is only half-filled and, therefore, there is room for one electron more. Hence, 1*s* orbital of hydrogen and the half-filled 2*p* orbital of fluorine overlap and form a covalent bond. This is shown in Fig. 5.

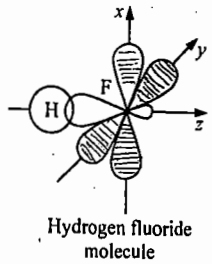


Fig. 5. Formation of hydrogen fluoride molecule by overlapping of 1*s* orbital of hydrogen atom and 2*p* orbital of fluorine atom.

Pi (π) Bonds. As discussed above, the overlapping of atomic orbitals along the same axis results in the formation of sigma bond. There is also another type of bond known as **pi (π) bond.** *This type of bond is formed by the sidewise overlapping (also called lateral overlapping) of the two half-filled orbitals.* The formation of pi bonds may be illustrated by reference to the formation of oxygen and nitrogen molecules.

Formation of oxygen molecule. The electronic configuration of oxygen (Z = 8) is $1s^2 2s^2 2p_x^2 p_y^1 p_z^1$. Oxygen atom has two half-filled 2*p* orbitals. When two oxygen atoms approach each other, one of the two half-filled *p* orbitals of each atom overlaps along the internuclear axis forming a *p – p* sigma bond. The second half-filled *p* orbital of each atom overlaps sidewise to form a pi bond. This is shown in Fig. 6.

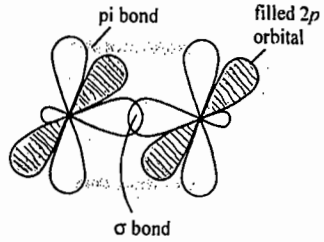


Fig. 6. Formation of oxygen molecule by overlapping of the two half-filled *p* orbitals of each oxygen atom.

Thus, in oxygen molecule, the two oxygen atoms are held together by a *double bond* comprising of one sigma bond and one pi bond.

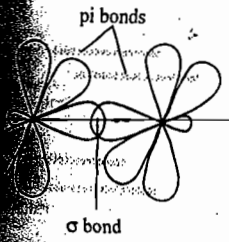


Fig. 7. Formation of nitrogen molecule by overlapping of the two half-filled *p* orbitals of each nitrogen atom.

Formation of nitrogen molecule. The electronic configuration of nitrogen is $1s^2 2s^2 p_x^1 p_y^1 p_z^1$. All the three *p* orbitals are only half-filled in accordance with Hund's rule. Hence, the three half-filled *p* orbitals of one nitrogen atom overlap with the three corresponding half-filled *p* orbitals of another nitrogen atom to form N_2 molecule. This is represented in Fig. 7.

Thus, in nitrogen molecule the two nitrogen atoms are held together by a *triple bond* made up of one sigma bond and two pi bonds.

Relative Strengths of sigma and pi bonds. The strength of a covalent bond depends upon the extent of overlapping of half-filled atomic orbitals. The extent of overlapping between two atoms is always greater when there is end to end overlapping of orbitals than when there is lateral overlapping of orbitals. Hence, a sigma bond is always stronger than a pi bond.

Variable Covalency. Maximum Covalency

Ordinarily, the covalency of an element is equal to the number of unpaired *s* or *p* electrons present in the outermost shell of its atom in the ground state. Thus, hydrogen (electronic configuration : $1s^1$) has its solitary *s* electron unpaired and hence its covalency is one. Fluorine (electronic configuration : $1s^2 2s^2 p_x^2 p_y^2 p_z^1$ has only *one* unpaired *p* electron and its covalency is also 1. Oxygen (electronic configuration : $1s^2 2s^2 p_x^2 p_y^1 p_z^1$ has *two* unpaired *p* electrons and its covalency is 2. Nitrogen (electronic configuration : $1s^2 2s^2 p_x^1 p_y^1 p_z^1$) has *three* unpaired *p* electrons and its covalency is 3. None of these atoms contains *d* orbitals in its electronic configuration.

The outer electronic configuration of sulphur atom in the ground state, *i.e.*, the lowest energy state is $3s^2 p_x^2 p_y^1 p_z^1$. Like oxygen, it has *two* unpaired electrons and exhibits a covalency of 2 (in compounds such as H_2S, SF_2, etc.). Sulphur atom belongs to the third period ($n = 3$). Hence, it has *d* orbitals also which, however, are vacant. When sulphur combines with more electronegative elements such as fluorine, oxygen, chlorine or bromine, sufficient amount of energy is released to cause unpairing of *s* and *p* electrons which get promoted to the vacant *d* orbitals. This unpairing of electrons increases the covalency of sulphur. Thus, if only the *p* electrons are unpaired, the total number of unpaired electrons will be four and if both *p* and *s* electrons get unpaired, the total number of unpaired electrons will be six. The covalency of sulphur in the former case will be 4 and in the latter case 6. This is illustrated in Fig. 8.

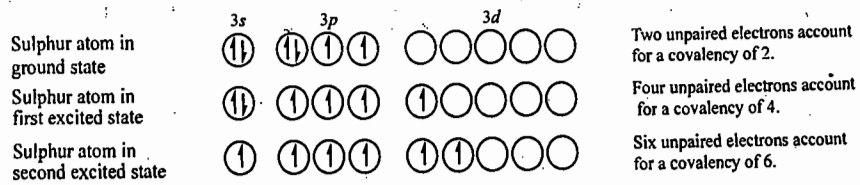


Fig. 8. Variable covalency exhibited by sulphur.

Thus, sulphur exhibits tetracovalency in the formation of compounds like SF_4 and SOF_2 and hexacovalency in the formation of compounds such as SF_6.

The halogens (excepting fluorine) also contain vacant *d* orbitals in their valency shells. These vacant *d* orbitals allow for easy excitation of *p* as well as of *p* and *s* electrons and account for higher covalencies of 3, 5 and 7 in the case of the halogens (other than fluorine). This is illustrated in Fig. 9.

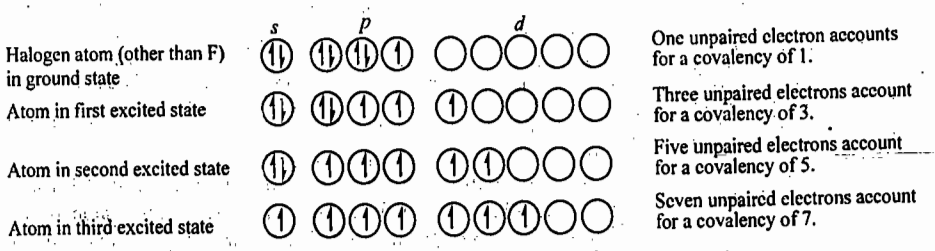


Fig. 9. Variable covalency exhibited by the halogens other than fluorine.

In the ground state, there is only one unpaired electron in the outer electronic configuration of each halogen. Hence, the halogens exhibit covalency of 1, as in the formation of HF, HCl, HBr and HI. In the *first excited state*, of halogens other than fluorine, one pair of *p* electrons gets unpaired providing three

unpaired electrons. This accounts for covalency of 3. Thus, in the interhalogen compounds such as ClF_3, BrF_3 and IF_3, chlorine, bromine and iodine exhibit covalency of 3. In the *second excited state*, both the pairs of *p* electrons get unpaired providing five unpaired electrons which account for covalency of 5. Thus, in $HClO_3$, $HBrO_3$ and HIO_3, all the three halogens exhibit covalency of 5. Similarly, in BrF_5 and IF_5, bromine and iodine exhibit covalency of 5. In the *third excited state*, all the pairs of *p* as well as *s* electrons get unpaired, providing seven unpaired electrons which account for covalency of 7. Thus, in $HClO_4$ and Cl_2O_7, chlorine exhibits covalency of 7.

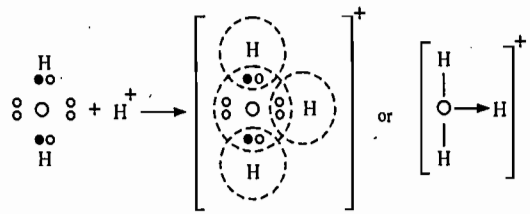
It is evident from the above discussion that elements *whose atoms contain vacant d orbitals* in their valency shells, can, on account of unpairing of *s* and *p* electrons, exhibit variable covalency in forming covalent bonds with more electronegative elements. The **maximum covalency** is generally *equal to the total number of s and p electrons present in the valency shell.* Thus, sulphur having six *s* and *p* electrons (s^2p^4 configuration) exhibits a maximum covalency of 6. The halgoens (Cl, Br, I) having seven *s* and *p* electrons (s^2p^5 configuration) exhibit maximum covalency of 7. Phosphorus having five *s* and *p* electrons (s^2p^3 configuration) exhibits maximum covalency of 5, and so on.

COORDINATE COVALENT BOND OR DATIVE BOND

Lewis proposed that a different type of covalent bond can be formed when both the electrons for sharing between the atoms are contributed by one atom only. This type of bond is known as **coordinate covalent bond or dative bond.**

A coordinate covalent bond is established between two atoms one of which has a complete octet and at the same time possesses at least one pair of unshared electrons while the other is short of the two electrons. The former atom contributes one such pair of electrons for mutual sharing between the two atoms as a result of which the second atom also completes its octet and acquires a stable noble gas configuration. The atom which contributes the pair of electrons is known as the **donor** and the atom which accepts these electrons is called the **acceptor**. The unshared pair of electrons is known as the **lone pair.**

In the formation of hydronium ion, for example, the oxygen atom in water molecule is the donor whereas the hydrogen ion is the acceptor. The coordinate covalent bond is conventionally represened by an arrow pointing from the donor to the acceptor, as shown below in the formation of hydronium ion.



It is important to note that *the coordinate covalent bond once formed is indistinguishable from a covalent bond.*

According to the atomic orbital overlap concept of covalency, a coordinate covalent bond results when an orbital containing a lone pair of electrons in one atom overlaps with an empty orbital present in the other atom. The central atom, oxygen, in water molecule has four orbitals. Two of these orbitals contain bond pairs of electrons while the other two (shaded ones) contain lone pairs of electrons, as shown in Fig. 10. The H^+ ion has an empty *s* orbital which overlaps with one of the orbitals of oxygen atom containing a lone pair of electrons forming hydronium ion, H_3O^+, as illustrated in Fig. 10.

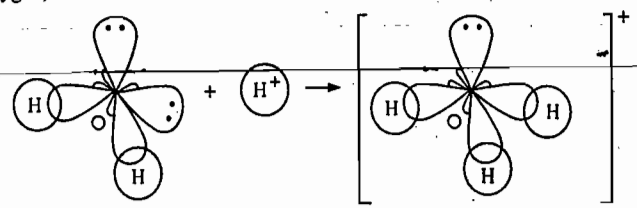


Fig. 10. Formation of hydronium ion.

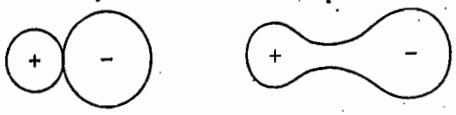
Polarity in Covalent Bonds. A covalent bond formed between two *identical* or *similar atoms* is said to be a **non-polar covalent bond** but if formed between two *dissimilar atoms*, the bond formed is said to be a **polar covalent bond.** The reason is that in the former case the shared electron pair is attracted equally by both atoms and lies exactly midway between them, as in hydrogen molecule, H : H. The molecule formed is said to be a **non-polar molecule.**

In the case of a covalent bond formed between two dissimilar atoms, one of the atoms generally has a greater tendency to attract the electrons towards itself (*i.e.*, it is more electronegative). The electron pair is, therefore, pulled closer to that atom, as in hydrogen fluoride molecule (H :$\ddot{\underset{..}{F}}$:) in which the electron pair shared between hydrogen and fluorine atoms remains closer to the fluorine atom. This unsymmetric distribution of electrons leads to partial charge separation, *i.e.*, development of partial negative charge near fluorine end and partial positive charge near hydrogen end. This is represented in HF and HCl molecules as follows :

$$\overset{+\delta}{H} - \overset{-\delta}{F} \qquad \overset{+\delta}{H} - \overset{-\delta}{Cl}$$

The molecules formed are said to be **polar molecules.** The polar covalent bond, therefore, has *partial ionic character.* The two opposite charges at the ends are called *electrical poles* and the molecules are called ***dipoles.***

Covalent Character of Ionic Bond. Polarisation of Ions. It is a common experience that many times an ionic bond has some covalent character and a covalent bond has some ionic character. The formation of a bond intermediate between an ionic and a covalent bond occurs through a phenomenon known as **polarisation of Ions.** When oppositely charged ions approach each other, the attraction between the positive charge of cation and negative charge of anion and also the simultaneous repulsion between their nuclei and between their electrons results in the *distortion, deformation* or **polarisation** *of the electron charge cloud of the anion.* The electron charge cloud of the anion no longer remains spherical but gets distorted, *i.e.*, polarised towards the cation, as shown in Fig. 11. The electron charge cloud of the cation also gets distorted, *i.e.*, polarised by the anion through a similar process but the polarisation of the cation is far less pronounced because of its small size. The polarisation of ions results in a high electron charge concentration between the two nuclei. This results in the formation of a bond which is intermediate between an ionic and a covalent bond. This type of bond is called **polar covalent bond.** A polar covalent bond is more stable than a pure covalent bond. The higher the degree of polarisation, the greater is the stability of the polar covalent bond. The extent of polarisation depends, evidently, on the polarising power of the cation and the polarisability of the anion.



No polarisation Polarisation of anion

Fig. 11. Polarisation of electron charge cloud of an anion by a cation.

The rules regarding polarisation are known as *Fajan's rules.* These are given below.

Fajan's Rules. 1. The cations with smaller size have higher polarising power, *i.e.*, they cause polarisation of electron charge cloud of an anion to a greater extent. Such cations have positive charge concentrated over a small surface area, *i.e.*, they have a **high charge density** and thus distort the electron charge cloud of the anion highly efficiently. The cations with large size have low polarizing power.

2. The anions with large size have high polarizability, *i.e.*, their electron charge cloud can be deformed easily. The grip of the nucleus on the orbital electrons in large anions will be weak and hence such anions will get polarised by a cation relatively easily.

3. For effective polarisation, there should be a high charge on the cation or the anion or both. The electrostatic forces which cause polarisation, would increase with increase in the charge on the ions.

4. Cations with pseudo inert gas configuration, *viz.*, $ns^2p^6d^{10}$ or with inert pair configuration, *viz.*, $d^{10}(n+1)s^2$, have high polarising power while cations with noble gas configuration, *viz.*, ns^2p^6, have low polarising power. This is due to greater effective nuclear charge in the former cases and smaller effective nuclear charge in the latter cases.

Effects of Polarisation. 1. Bromides and iodides have higher lattice energies (and hence higher stabilities) than expected from theoretical calculations. The extra stability is due to polarisation of the anions resulting in the formation of a polar covalent bond which is more stable than a pure ionic bond.

2. The solubility of ionic compounds in polar solvents decreases with increase in the degree of polarisation, *i.e.*, with increase in the degree of covalent bonding.

3. The hardness of ionic compounds decreases with increase in the degree of polarisation, *i.e.*, with increase in the covalent character.

Per cent Ionic Character of a Polar Covalent Bond. The per cent ionic character of a polar covalent bond depends upon two factors : *1. The Electronegativity Difference of the Bonded Atoms* and *2. Dipole Moment of the Compound Formed.*

1. Electronegativity Difference and Per cent Ionic Character. A pure covalent bond is formed between atoms A and B when the electronegativities of the two atoms are the same. If A and B have different electronegativities, the resulting bond would be a polar covalent bond since the bonding electron pair is pulled more towards the more electronegative atom thereby bringing some excess negative charge on the latter. As a result, some excess positive charge is developed on the less electronegative atom. If A is more electronegative than B, a polar covalent bond $\overset{-\delta}{A} - \overset{+\delta}{B}$ would be formed between A and B. The larger the differece in the electronegativities of A and B, the greater would be the magnitude of δ and the higher would be the polarity of the bond.

Several empirical equations have been proposed to calculate the per cent ionic character of a covalent bond from the electronegativities of the bonding atoms. Two of these equations are the Pauling equation and the Hannay-Smith equation.

The Pauling Equation. Pauling proposed the following empirical equation for determining the per cent ionic character of a covalent bond :

$$\text{Per cent ionic character} = 1 - e^{-\frac{1}{4}(\chi_A - \chi_B)} \qquad ...(1)$$

where χ_A and χ_B are the electronegativities of A and B. He established the following empirical relationship between $\chi_A - \chi_B$ and the per cent ionic character :

$\chi_A - \chi_B$	0·6	1·0	1·4	2·0	2·4	3·0
Per cent ionic character	9	22	39	63	76	89

The Hannay-Smith Equation. Hannay and Smith proposed the following equation for the purpose :

$$\text{Per cent ionic character} = 16\,(\chi_A - \chi_B) + 3{\cdot}5\,(\chi_A - \chi_B)^2 \qquad ...(2)$$

Both the equations, however, give only approximate values.

2. Dipole Moment and Per cent Ionic Character. Consider the bond H – X where X is a halogen atom. If the bond is purely covalent, its dipole moment would be negligibly small. If the bond is ionic, H^+X^-, it implies that complete transfer of an electron has taken place from H to X and the bond would have an appreciable dipole moment which is determined by the product of the electronic charges and the internuclear distance between H and X. For a polar covalent bond which is intermediate between a pure covalent and a pure ionic bond, the dipole moment would be given by the product of the charge (δ) separated due to polarisation and the internuclear distance. The magnitude of δ will depend upon the

extent of the ionic character developed in the bond. Thus,

$$\text{Per cent ionic character} = \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of pure ionic bond}} \times 100$$

For example, in **HF molecule**, the internuclear distance is 0·92 Å and the dipole moment for the ionic structure H^+F^- when an electron is completely transferred from hydrogen atom to fluorine atom is given by $4{\cdot}8\times10^{-10}$ esu $\times$ $0{\cdot}92\times10^{-8}$ cm, *i.e.*, 4·42 D. The actual dipole moment of HF molecule is found to be 1·98 D. (1 Debye = 1×10^{-18} esu cm)

$$\therefore \quad \text{Per cent ionic character} = \frac{1{\cdot}98\,\text{D}\times100}{4{\cdot}42\,\text{D}} = 44{\cdot}8 \approx \mathbf{45}$$

Similarly, **for HCl molecule,** using SI units,

$$\text{Internuclear distance} = 127\,\text{pm} = 127\times10^{-12}\,\text{m}$$

$$\text{Actual dipole moment} = 3{\cdot}44\times10^{-30}\ \text{coulomb metre}$$

$$\left.\begin{array}{l}\text{Dipole moment when an electron is}\\ \text{completely transferred from H to Cl}\end{array}\right\} = 1{\cdot}6\times10^{-19}\,\text{C}\times127\times10^{-12}\,\text{m}$$

$$= 2{\cdot}03\times10^{-29}\,\text{C m}$$

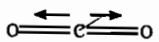
$$\therefore \quad \text{Per cent ionic character} = \frac{3{\cdot}44\times10^{-30}\,\text{C m}}{2{\cdot}03\times10^{-29}\,\text{C m}}\times100 = 16{\cdot}9 \approx 17$$

It may be mentioned, however, that dipole moment calculated from the ionic structure of the compound alone contributes only partly towards the total molecular dipole moment. Other factors such as the differences in the sizes of the two atoms, the hybridisation of orbitals involved and the directions of the lone pairs of electrons with respect to the nucleus also contribute towards the total molecular dipole moment. Hence, the per cent ionic character calculated on the basis of dipole moment obtained from the ionic structure of the compound alone, without considering other factors, is only *approximate*.

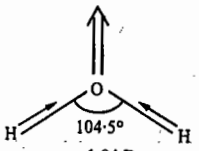
Dipole Moment and Structure of Molecules. A diatomic molecule is polar if the bond formed between the atoms is polar. In such a molecule, the dipole moment of the bond gives the dipole moment of the molecule. For example, the dipole moment of HCl molecule is the same as the dipole moment of HCl bond and is known to be 1·03 D. However, in the case of molecules containing more than two atoms, the dipole moment not only depends upon the individual dipole moments of the bonds but also on the spatial arrangement of various bonds in the molecule. In such cases, the dipole moment of the molecule is the vector sum of the dipole moments of the various bonds. Obviously, the polar or non-polar nature of molecule will depend upon the spatial arrangement of atoms in the molecule. The bonds may be polar yet the molecule may be non-polar.

For example, carbon dioxide (CO_2) and water (H_2O) molecules are both triatomic molecules but the dipole moment of carbon dioxide is zero while that of water is 1·84 D. This can be easily explained on the basis of their structures as illustrated below :

In carbon dioxide molecule, both the carbon–oxygen bonds are polar. But since the molecule is linear, the dipole moment of C = Q bond (2·3 D) on one side of the molecule is cancelled by that on the other side of the molecule giving net zero dipole moment. On the other hand, water molecule is not linear but has a *bent structure* as shown. Therefore, the dipole moment of water molecule is not zero. It is the resultant of the dipole moments of the two O – H bonds inclined at an angle of 104·5° and the contribution of the two lone pairs of electrons on oxygen atom. It has been found to be 1·84 D.

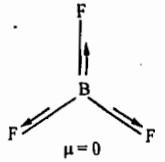


μ = 0

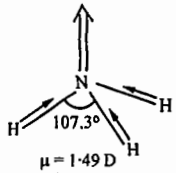


μ = 1·84 D

Likewise, the dipole moment of BF_3 is zero while that of NH_3 is 1·49 D, although both the molecules are tetra-atomic. This is because BF_3 has symmetrical structure in which the three B–F bonds are oriented at an angle of 120° to one another. The three bonds lie in one plane and the dipole moments of these bonds cancel one another giving net dipole moment equal to zero. On the other hand, the ammonia molecule has *pyramidal structure*. The individual dipole moments of three N – H bonds and the contribution of the lone pair of electrons on nitrogen atom to dipole moment give the resultant dipole moment of NH_3 molecule as 1·49 D, as shown.

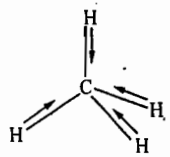


μ = 0

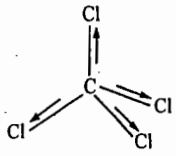


μ = 1·49 D

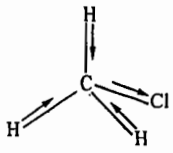
CH_4 and CCl_4 molecules have symmetrical tetrahedral structures and their resultant dipole moments are *zero*. CH_3Cl molecule has also tetrahedral structure but its dipole moment is not *zero* because its structure is not symmetrical and the dipole moments of C – Cl and H– C bonds are not equal. This is illustrated below :



μ = 0



μ = 0



μ ≠ 0

Some Important Characteristics of Covalent Bond. The important characteristics of a covalent bond are its bond length, bond angle and bond energy. These are discussed below.

TABLE 2

Bond Lengths (Å) of Some Common Bonds

Bond	Bond length	Bond	Bond length
H – H	0·74	H – F	0·92
C – H	1·00	H – Cl	1·27
O – H	0·96	H – Br	1·41
F – F	1·42	H – I	1·61
Cl – Cl	1·99	C – C	1·54
Br – Br	2·28	C = C	1·34
I – I	2·67	C ≡ C	1·20

Bond Length. Let us consider a diatomic molecule. The atoms in this molecule are always vibrating with respect to each other. The question of any *fixed* distance between them, therefore, does not arise. We can, however, think of an average distance between the nuclei of the two atoms bonded to each other. This is called bond length or bond distance. Thus, **bond length** is defined as the average distance between the nuclei of two bonded atoms in a molecule. We have already seen that in the formation of hydrogen molecule, when two hydrogen atoms approach each other, a stage is reached when there is maximum electrostatic attraction and minimum repulsion between the two atoms. At this point the potential energy of the system becomes minimum and the atoms get bonded together. The distance between the nuclei of the bonded hydrogen atoms is called the length of the H – H bond. For hydrogen molecule, this length has been found to be 0·74 Å.

The bond lengths have been determined, fairly accurately, in the case of crystals by X-ray diffraction and in the case of gases by spectroscopy. The values obtained for some common diatomic molecules are given in Table 2.

It may be noted that bond length decreases with multiplicity of the bond formed between the two atoms. Thus, C ≡ C bond is shorter than C = C bond which, in turn, is shorter than C – C bond.

Bond Angle. Bond angle may be defined as the angle between two bonds of the atom in a molecule or the internal angle between the orbitals containing bonding electron pairs in the valency shell of the atom in a molecule. For example, the bond angles in H_2O, NH_3 and CH_4 molecules are 104·5°, 107·3° and 109·5°, respectively.

The bond angle gives an idea of the distribution of the orbitals in three-dimensional space around the central atom in the molecule and thus gives an idea of the shape of the molecule.

Bond Strength or Bond Energy. Energy is required invariably to break a chemical bond. For instance, in the breaking of one mole of hydrogen gas into atoms, 458 kJ of energy is required. The bond strength in this case is said to be 458 kJ per mole, *i.e.*, per Avogadro's number of bonds. **Bond strength** or **bond energy** of a particular type of bond is defined as *the energy required to break one mole of bonds of that type in a substance in gaseous state.* The bond energies of some common bonds are given in Table 3.

TABLE 3

Bond Energies of Some Common Bonds

Bond	Bond energy (kJ mol^{-1})	Bond	Bond energy (kJ mol^{-1})
H – H	458·0	O = O	494·6
F – F	154·8	N ≡ N	945·6
Cl – Cl	242·7	C – C	347·0
H – Cl	430·0	C = C	619·0
I – Cl	209·2	C ≡ C	836·8

The strength of the bond indicates the stability of the bond. Thus, N ≡ N bond is more stable than O = O bond. Hence, nitrogen molecule is more stable than oxygen molecule. Consequently, nitrogen is much less reactive than oxygen. The strength of F – F bond is lower than that of Cl – Cl bond. Hence, fluorine is more reactive than chlorine. Similarly, ICl is more reactive than Cl_2.

WAVE MECHANICAL TREATMENT OF COVALENT BOND

The Lewis concept of covalent bond based on sharing of electrons satisfactorily explains the bonding between atoms all of which have a tendency to gain electrons in order to acquire the stable noble gas configurations. It also explains adequately the polarity of molecules. However, the concept remains *purely qualitative* and it cannot answer a number of questions such as

1. Why a covalent bond is formed at all ?
2. How do the electrons distribute themselves in space around the central atom in a molecule ?
3. What are the forces of attractive interaction in a covalent molecule ?
4. What is the concept of bond energy in a covalent bond ?
5. How are the compounds such as PF_5, IF_7, SF_6, BF_3, with central atoms having more than or less than 8 valence shell electrons so stable ?

Wave mechanics has provided satisfactory answers to most of these questions and has led ultimately to the development of more comprehensive theories of covalent bonding. These theories are : 1. *The Valence Bond Theory.* 2. *The Molecular Orbital Theory.*

But, before we discuss the two theories, it would be worthwhile to elucidate the **wave mechanical principles** which are involved in their treatment. These principles are :

1. If ψ_1 is a solution of the wave equation $\hat{H}\psi = E\psi$, then $c_1\psi_1$ is also the solution of the same wave equation where c_1 is a constant known as *coefficient of the wave function.* This means that ψ_1 and $c_1\psi_1$ give the same value of energy E.

2. If ψ_1 and ψ_2 are separately the solutions of the wave equation $\hat{H}\psi = E\psi$, then $c_1\psi_1$, $c_2\psi_2$ and $c_1\psi_1 \pm c_2\psi_2$ are also the solutions of the same wave equation. This means that ψ_1, ψ_2, $c_1\psi_1$, $c_2\psi_2$ and $c_1\psi_1 \pm c_2\psi_2$ would give the same value of energy E. The squares of the coefficients, *viz.*, c_1^2 and c_2^2 give the contributions of ψ_1 and ψ_2, respectively, to the total wave function.

Approximate Solution of Schrodinger Wave Equation. We have already discussed in the first chapter that the Schrodinger wave equation can be solved only for hydrogen and hydrogen-like systems, such as He^+ in which a single electron moves under the influence of a single nucleus. The wave equation cannot be solved for systems containing more than one electron or more than one nucleus. Nevertheless, methods have been devised for finding out approximate ψ closest to the true ψ and the corresponding approximate energy closest to the true energy of multi-electron and multi-nucleus systems. One such method is based on the *variation principle.*

The Variation Principle. Consider the wave equation $\hat{H}\psi = E\psi$. Multiplying each side of the wave equation by ψ and integrating it throughout the space, we get

$$\int_{-\infty}^{+\infty} \psi \hat{H} \psi \, d\tau = \int_{-\infty}^{+\infty} \psi E \psi \, d\tau \qquad ...(3)$$

$$= E \int_{-\infty}^{+\infty} \psi^2 d\tau \qquad (\because E \text{ is constant}) \qquad ...(4)$$

where $d\tau$ is a small space element.

From Eqs. 3 and 4,

$$E = \int_{-\infty}^{+\infty} \psi \hat{H} \psi d\tau \Big/ \int_{-\infty}^{+\infty} \psi^2 d\tau \qquad ...(5)$$

We can, thus, calculate energy E of the system if we know true ψ. If we do not know true ψ, even then we can guess a wave function which is close to the true wave function ψ by using our chemical intuition. If this approximate wave function is ψ_1, then Eq. 5 takes the form

$$\varepsilon = \int_{-\infty}^{+\infty} \psi_1 \hat{H} \psi_1 d\tau \Big/ \int_{-\infty}^{+\infty} \psi_1^2 d\tau \qquad ...(6)$$

where ε, known as **energy function,** will have the dimensions of energy but will *not be equal* to the true energy of the system.

In case ψ and ψ_1 are complex wave functions, then Eq. 3 is written as

$$\int_{-\infty}^{+\infty} \psi^* \hat{H} \psi \, d\tau = \int_{-\infty}^{+\infty} \psi^* E \psi \, d\tau$$

and Eq. 6 is written as

$$\varepsilon = \int_{-\infty}^{+\infty} \psi_1^* \hat{H} \psi_1 d\tau \Big/ \int_{-\infty}^{+\infty} \psi^* \psi_1 d\tau$$

where ψ_1^* is the complex component of ψ_1. In case ψ and ψ_1 are real, then ψ^* is the same as ψ and ψ_1^* is the same as ψ_1. *For the sake of simplicity we have assumed ψ to be real.*

According to the variation principle, if we are able to guess at a number of wave functions ψ_1, ψ_2, ψ_3, etc., which are thought to be close approximations of the true wave function ψ, then we can calculate the energy functions, ε_1, ε_2, ε_3, etc., with the help of Eq. 6. In such a case

1. All the energy functions calculated as above would have *higher values* than the true energy of the system.

2. Out of ε_1, ε_2, ε_3, etc., the energy function with the *minimum value would be closest to the true* energy E.

3. The wave function which gives the minimum value of energy function is the closest approximation of the true wave function ψ.

One may question, why we cannot calculate E directly from the relation

$$E = \hat{H}\psi/\psi \qquad ...(7)$$

The answer is as follows : Eq. 7 can be employed for calculating E only if ψ is a true wave function. If ψ is an approximate wave function (as is usually the case in multi-electron systems), then, $\hat{H}\psi/\psi$ would be a function of x, y, z and would vary from place to place in a three-dimensional space. The value of E would also vary accordingly. In other words, if E is calculated with the help of Eq. 7, it would not be a constant parameter.

The approximate ψ can also be calculated with the help of **Ritz linear combination method** which too is based on the variation principle. Suppose we have reasons to believe that the wave function ψ has some charactristics of a known wave function ψ_1 and some characterisitics of another known wave function ψ_2. The wave function ψ can then be written as a *linear combination of* ψ_1 *and* ψ_2, *i.e.*, as $\psi = c_1\psi_1 + c_2\psi_2$. Accordingly,

$$\text{Energy function,} \quad \varepsilon = \int_{-\infty}^{+\infty} \psi \hat{H} \psi d\tau \Big/ \int_{-\infty}^{+\infty} \psi^2 d\tau \qquad ...(8)$$

$$= \int_{-\infty}^{+\infty} (c_1\psi_1 + c_2\psi_2)\hat{H}(c_1\psi_1 + c_2\psi_2)d\tau \Big/ \int_{-\infty}^{+\infty} (c_1\psi_1 + c_2\psi_2)^2 d\tau \qquad ...(9)$$

The coefficients c_1 and c_2 are so adjusted in the total wave function ψ as to yield a *minimum value* of ε. This is done by differentiating Eq. 9 with respect to c_1 and also with respect to c_2 and then putting $\partial\varepsilon/\partial c_1$ and also $\partial\varepsilon/\partial c_2 = 0$ as these are the conditions for minimization of ε. By doing so we get two equations containing ε, c_1 and c_2. From these equations, we can derive a quadratic equation in ε. The solution of this quadratic equation gives ε, c_1 and c_2. Similarly, if we have reasons to believe that the true wave function ψ has characteristics of known wave functions ψ_1, ψ_2, ψ_3, etc., the actual ψ can then be written as $\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \cdots\cdots$ The coefficients c_1, c_2, c_3, etc., are so adjusted as to yield minimum value of the energy function.

This method has an advantage that if we guess at a wrong wave function (ψ_i), its coefficient (c_i) would automatically come out to be zero.

With the help of the wave mechanical principles elucidated above, it is possible to discuss at length the Valence Bond and the Molecular Orbital theories of covalent bonding.

VALENCE BOND THEORY

The valence bond theory was first put forward by W. Heitler and F. London, in 1927, to explain the stability of a covalently bonded hydrogen molcule. It was extended further by J. C. Slater and L. Pauling. The theory utilises the following wave mechanical principles :

1. If ψ_A and ψ_B are the wave functions for any two completely independent (non-interacting) systems A and B, then the total wave function ψ for these independent systems, taken together, would be given by

$$\psi = \psi_A \psi_B \qquad ...(10)$$

and the total energy E of these non-interacting systems would be equal to the sum of the energies of systems A and B. The total hamiltonian is also equal to the sum of the hamiltonians for the systems A and B, *i.e.*,

$$E = E_A + E_B \text{ and } \hat{H} = \hat{H}_A + \hat{H}_B$$

2. If the wave function for a many-electron system has characteristics of several wave functions $\psi_1, \psi_2, \psi_3 \ldots\ldots \psi_n$, then according to the Ritz principle of linear combination, the wave function ψ closest to the true wave function of the system is given by

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \cdots\cdots c_n\psi_n \qquad ...(11)$$

where $c_1, c_2 \ldots c_n$ are the various coefficients. As already mentioned, the square of the coefficient of a particular wave function gives the contribution of that wave function, generally called the *weightage* of that wave function, to the total wave function. The coefficients c_1, c_2, etc., are so adjusted as to give a *state of lowest energy, i.e., a state of maximum stability*. Further, the wave function ψ should be *normalised* (cf. Chapter 1) so that

$$c_1^2 + c_2^2 + c_3^2 + \ldots\ldots = 1 \qquad ...(12)$$

We will elucidate the Valence Bond theory by taking into consideration the formation of H_2 molecule.

Formation of Hydrogen Molecule. Consider two hydrogen atoms lying far apart from each other so that no interaction between them is possible. Let A and B represent the nuclei and e_1 and e_2 the two electrons. The two atoms of hydrogen may thus be represented as $H_A(e_1)$ and $H_B(e_2)$.

Let the wave functions for the electrons in separated atoms be represented by $\psi_A(1)$ and $\psi_B(2)$. The wave function $\psi_A(1)$ is also called the wave function of the atomic orbital containing electron (1) and the wave function $\psi_B(2)$ is called the wave function of the atomic orbital containing electron (2). According to Eq. 10, the combined wave function ψ for the two separated atoms of hydrogen can be written as

$$\psi = \psi_A(1)\psi_B(2) \qquad ...(13)$$

When the two atoms are brought closer together, their energy changes and, consequently, the energy operator $\hat{H}$ also changes. Assuming that the combined wave function ψ, as represented by Eq. 13, still describes the wave function for H_2 molecule, the energy of the hydrogen molecule, following Eqs. 3 and 4, would be given by

$$E = \int_{-\infty}^{+\infty} \psi_A(1)\,\psi_B(2)\hat{H}\,\psi_A(1)\,\psi_B(2)\,d\tau \Big/ \int_{-\infty}^{+\infty} [\psi_A(1)\psi_B(2)]^2 d\tau \qquad ...(14)$$

The energy changes that take place as the two H atoms are gradually brought closer to each other are shown graphically in Fig. 12.

When the two atoms are far removed from each other, *i.e.*, when the internuclear distance r_{AB} is infinity, the total energy of the system is taken as zero*. As the atoms are brought closer in a region in which the electric field due to one can influence that of the other, the energy of the system starts decreasing till a certain minimum value is reached. This stage corresponds to the formation of H_2 molecule. The internuclear distance at this stage is designated as r_0.

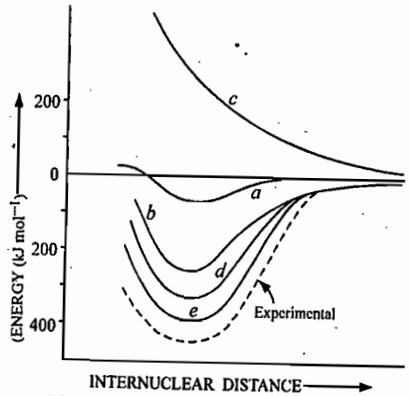


Fig. 12. Variation of energy with internuclear distance in the formation of hydrogen molecule.

When we calculate the enegy of the system of the two hydrogen atoms by using Eq. 14 and plot these energies as a function of internuclear distance, the *curve a* is obtained. The bonding energy given by the minimum in potential energy *curve a* is only 24 kJ mol^{-1}. This is too far below the experimental value of 458 kJ mol^{-1} (represented by the minimum in the *experimental curve*). Moreover, the minimum is found at an internuclear distance of about 0·90 Å (*curve a*) whereas the experimental bond distance in hydrogen molecule is 0·74 Å. Evidently, the wave function $\psi_A(1)\psi_B(2)$, as applied to H_2 system, is not a good approximation. Apparently, some other interactions between the two hydrogen atoms are required to be

*Since we are interested in finding out only the *change in energy* when the two atoms A and B come close to each other from infinite distance to form a bond, the sum of energies of the *two isolated* atoms A and B, when they are at infinite distance from each other, is taken as zero.

taken into consideration to arrive at the correct wave function for the combined H_2 system. Some of these interactions are as follows.

1. Exchange of Electrons. In arriving at Eq. 14, we had assumed that the electrons of the two hydrogen atoms could be distinguished from each other and, therefore, the electron around nucleus A was labelled as e_1 and that around nucleus B was labelled as e_2. This assumption, however, is not correct because when a bond is formed, *the two atomic orbitals overlap* and the two electrons become *indistinguishable* from each other. We can no longer be sure that electron 1 will always be near the nucleus A and electron 2 will always be near the nucleus B. The system of two hydrogen atoms may then be represented by two different states, I and II, as shown below :

$$H_A(e_1)\,H_B(e_2) \qquad\qquad H_A(e_2)\,H_B(e_1)$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

In state I, nucleus A is associated with electron 1 and nucleus B is associated with electron 2. In state II, nucleus A is associated with electron 2 and nucleus B is associated with electron 1. Both the states I and II are equally probable.

If ψ_I and ψ_{II} are the wave functions representing states I and II, respectively, then, according to Eq. 10, we can write

$$\psi_I = \psi_A(1)\,\psi_B(2) \quad \text{and} \quad \psi_{II} = \psi_A(2)\psi_B(1)$$

A linear combination of ψ_I and ψ_{II} (and not ψ_I or ψ_{II} alone) should be employed for calculating the energy of H_2 molecule. There are evidently two possible modes of linear combination, *viz.*, additive and subtractive according to which there are two wave functions, *viz.*, ψ_+ and ψ_-, given by

$$\psi_+ = \psi_I + \psi_{II} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \qquad ...(15)$$

and

$$\psi_- = \psi_I - \psi_{II} = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1) \qquad ...(16)$$

The actual normalised ψ_+ and ψ_- are $1/\sqrt{2}(\psi_I + \psi_{II})$ and $1/\sqrt{2}(\psi_I - \psi_{II})$, resectively. However, since the normalising constant $1/\sqrt{2}$ does not enter into the calculation of energy, it is not written in the expression for ψ_+ and ψ_-.

The energy of the system, calculated by using ψ_+ in the wave equation is shown by the *curve b* while that calculated from ψ_- is shown by the *curve c* in Fig. 12**. It is evident that ψ_- leads to *increase of energy*. Thus, *bonding is not possible in* ψ_-. We may, therefore, regard ψ_- as a **repulsive state.** The wave function ψ_+, however, leads to *fall of energy*. Thus, *bonding is possible in this state.* We may, therefore, regard ψ_+ as a **bonding state.**

The wave function ψ_+ (Eq. 15) which represents the *bonding state* is also referred to as **covalent wave function.** Therefore, it may be written as $\psi_{covalent}$. The reason for this terminology is that in state I as well as in state II, there is equal distribution of charge on both the nuclei A and B.

As mentioned above, the bonding energy calculated from Eq. 14 is only 24 kJ mol^{-1}. The bonding energy corresponding to ψ_+ (Eq. 15) is 303 kJ mol^{-1} and the internuclear distance is 0·80 Å. *The additional energy resulting from the exchange of electrons between the two hydrogen atoms is called* the **exchange energy.** Thus, 303 − 24 = 279 kJ mol^{-1} is the exchange energy for H_2 molecule.

2. Screening Effect of Electrons. The wave function given by Eq. 15 is further improved by considering the screening effect of the electrons. When the two atoms come close to each other, the electron of one atom shields the electron of the other atom from the nucleus so that the electrons do not feel the full charge of the nucleus. The actual charge felt by an electron is termed as its *effective nuclear charge*. This will be, evidently, less than the actual nuclear charge. If we use the effective nuclear charge

**Since both the states I and II are equally probable, a linear combination having equal contributions from ψ_I and ψ_{II} is employed to calculate the energy of H_2 molecule.

and improve the wave function given by Eq. 15, bonding energy of 365 kJ mol^{-1} is obtained. This is depicted by the minimum in the *curve d.*

3. Ionic Character of H – H Bond. The bond energy of 365 kJ mol^{-1} is still appreciably smaller than the experimental value of 458 kJ mol^{-1}. This shows that ψ_+ still does not give the *true wave function* for H_2 molecule. Evidently, further improvement of wave function is needed. Since the calculated value of bond energy is smaller than the experimental value, it is necessary to provide in our model of H_2 molecule an additional factor which will tend to enhance the binding force between the two hydrogen atoms because increase in such a force will lead to increase in the bond energy. The additional factor that has been suggested is the possibility that *momentarily both the electrons may simultaneously be present close to one nucleus or the other. This gives rise to ionic configurations* represented by states III and IV :

$$(e_2\,e_1)\,H_AH_B \qquad\qquad H_AH_B(e_1\,e_2)$$
$$\text{(III)} \qquad\qquad\qquad \text{(IV)}$$

These two ionic structures may be represented as $H_A^-\,H_B^+$ and $H_A^+\,H_B^-$, respectively. However, the coulombic repulsion between the two electrons present so close to each other would far exceed the coulombic attraction between H_A^- and H_B^+ or between H_A^+ and H_B^-. This reduces the probability of the existence of these additional structures to a bare minimum. Nevertheless, the incorporation of these structures as resonance structures does increase the stability of the hydrogen molecule and hence its bond energy.

The states III and IV are, amongst themselves, equally probable and the wave functions corresponding to state III (ψ_{III}) and state IV (ψ_{IV}) may be expressed as

$$\psi_{III} = \psi_A(1)\psi_A(2) \quad \text{and} \qquad ...(17)$$

$$\psi_{IV} = \psi_B(1)\psi_B(2) \qquad ...(18)$$

The total ionic wave function ψ_{ionic} may be expressed as a linear combination of ψ_{III} and ψ_{IV}, as

$$\psi_{ionic} = \psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2) \qquad ...(19)$$

Since both the states III and IV are equally probable, hence there is equal contribution from ψ_{III} and ψ_{IV}, towards ψ_{ionic}.

However, states III and IV are less probable than states I and II as the two electrons present on the same H atom would repel each other and make states III and IV less likely compared to states I and II.

Considering the possibilities of covalent as well as ionic structures, the combined wave function for H_2 molecule is written as

$$\psi = \psi_{covalent} + \lambda\psi_{ionic}$$
$$= [\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] + \lambda\,[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)] \qquad ...(20)^*$$

where λ gives the extent to which the ionic structures contribute to the bonding. For H_2, λ is calculated to be 0·17. Knowing λ, we can find out *the extent of the contribution of the ionic structures.* The fraction λ is called the **mixing coefficient.**

With all these modifications, the calculated bond energy comes out to be about 388 kJ mol^{-1} which can be considered as reasonably close to the experimental value of 458 kJ mol^{-1}. The internuclear

*The actual normalised wave function is $\frac{1}{\sqrt{(1+\lambda^2)}}[(\psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}) + \lambda(\psi_{A(1)}\psi_{A(2)} + \psi_{B(1)}\psi_{B(2)})]$. However, $\left(\frac{1}{\sqrt{1+\lambda^2}}\right)$ is omitted since it does not enter into the calculation of energy.

distance between hydrogen atoms now comes out to be 0·75 Å which is quite close to the experimental value of 0·74 Å. The differences which still persist are considered to be due to some complicated electronic interactions, the discussion of which is beyond the scope of this book.

Bond energies and bond lengths for H_2 molecule corresponding to various wave functions are summed up in Table 4.

Table 4

Bond Energies and Bond Lengths for H_2 Molecule Corresponding to Various Wave Functions

Wave Function	Bond Energy (kJ mol^{-1})	Bond Length (Å)
$\psi = \psi_A(1)\psi_B(2)$	24	0·90
$\psi_{covalent} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$	303	0·80
$\psi_{covalent}$ with screening effect	365	0·76
$\psi = \psi_{covalent} + \lambda\psi_{ionic} = [\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] + \lambda[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)]$	388	0·75
Experimental values	**458**	**0·74**

Singlet and Triplet Wave Functions. In the valence bond treatment of H_2 molecule, the linear combination of the two approriate wave functions yields the following two space covalent wave functions :

$$\psi_+ = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \quad \text{...(Eq. 15)}$$

$$\psi_- = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1) \quad \text{...(Eq. 16)}$$

where ψ_+ is the wave function for the bonding state and ψ_- is the wave function for the repulsive state.

If we exchange the coordinates of electron (1) with those of electron (2) in ψ_+ and ψ_-, the sign of ψ_+ does not change whereas the sign of ψ_- changes from plus to minus so that the wave function changes from ψ_- to $-\psi_-$. Therefore, while ψ_+ is designated as $\psi_{symmetric}$, ψ_- is designated as $\psi_{asymmetric}$.

The complete wave function for the system which includes both the space as well as the spin part of the wave function is written by assuming that these two parts of the wave function do not influence each other, that is, there is no 'spin-orbit' interaction. Accordingly, the complete wave functions for the two states are written as

$$\psi_{+(complete)} = \psi_+ \times \psi_{spin} = \psi_+\alpha_1\alpha_2,\ \psi_+\beta_1\beta_2,\ \psi_+(\alpha_1\beta_2 + \alpha_2\beta_1),\ \psi_+(\alpha_1\beta_2 - \alpha_2\beta_1)$$

$$\psi_{-(complete)} = \psi_- \times \psi_{spin} = \psi_-\alpha_1\alpha_2,\ \psi_-\beta_1\beta_2,\ \psi_-(\alpha_1\beta_2 + \alpha_2\beta_1),\ \psi_-(\alpha_1\beta_2 - \alpha_2\beta_1)$$

where α_1, α_2 are the spin wave functions representing $+\frac{1}{2}$ spin states of electrons 1 and 2, respectively and β_1, β_2 are the spin wave functions representing $-\frac{1}{2}$ spin states of electrons 1 and 2, respectively. As discussed in Chapter 1, the complete wave function of a system is acceptable if it is asymmetric with respect to the exchange of the coordinates of electrons, that is, if the sign of the complete wave function changes on changing the coordinates of electrons.

As can be seen, of the four expressions which can be written for $\psi_{+(complete)}$, there is only a **single** expression for $\psi_{+(complete)}$ which is asymmetric and hence acceptable. Therefore, $\psi_{+(complete)}$ is called a **singlet state.**

Thus, the single asymmetric and hence acceptable $\psi_{+(complete)}$ is $(\psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)})(\alpha_1\beta_2 - \alpha_2\beta_1)$.

However, there are **three** asymmetric and hence acceptable wave functions for $\psi_{-(complete)}$, namely, $(\psi_{A(1)}\psi_{B(2)} - \psi_{A(2)}\psi_{B(1)})\alpha_1\alpha_2$, $(\psi_{A(1)}\psi_{B(2)} - \psi_{A(2)}\psi_{B(1)})\beta_1\beta_2$ and $\psi_{A(1)}\psi_{B(2)} - \psi_{A(2)}\psi_{B(1)})(\alpha_1\beta_2 + \alpha_2\beta_1)$ in which the exchange of coordinates of electrons yields a change of sign of ψ_-. Hence, $\psi_{-(complete)}$ is called a **triplet state.**

Consider again, the singlet state, *viz.*, $\psi_{+(complete)} = (\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1))(\alpha_1\beta_2 - \alpha_2\beta_1)$ which is responsible in forming a chemical bond according to VB theory. The spin part of the wave function is the contribution of the product $\alpha\beta$ of opposite spins of electrons 1 and 2. It does not have any contribution from the parallel spin functions $\alpha\alpha$ and $\beta\beta$ of electrons 1 and 2. It follows from the above that in a chemical bond, the two participating electrons must be of opposite spins.

CONCEPT OF RESONANCE

The physical interpretation of Eq. 20 is that H_2 molecule can neither be represented adequately by the pure covalent bond H – H nor by the ionic structures $H_A^+H_B^-$ and $H_A^-H_B^+$. The true structure lies somewhere in between these three structures.

When a molecule cannot be completely represented by a single structure but its characteristic properties can be described by two or more different structures, then the true structure is said to be a **resonance hybrid** *of these structures.* In such a case we say that there is **resonance** between the various possible structures. The possible structures are called **resonating structures.** As a result of resonance, the energy of the molecule becomes lower than the energy of any of the resonating structures. The molecule with a *lower energy* has *higher stability* and also *higher bond energy.* Thus, *resonance imparts extra stability to the molecule.*

The resonance between two or more structures is represented by drawing double-headed arrows between the various structures, as shown below in the case of hydrogen :

$$\overset{+}{H}_A\overset{-}{H}_B \leftrightarrow H_A - H_B \leftrightarrow \overset{-}{H}_A\overset{+}{H}_B$$

The molecule is said to *resonate* between the three resonance structures.

It may be emphasised here that the various postulated resonating structures of a molecule have *no real existence.* Also, it does not mean that the actual molecule exists for a certain fraction of time in one form and for another fraction of time in another form. In fact, *the actual structure has no pictorial representation.* The resonating structures are only a covenient way of picturing a molecule to account for all the properties of a molecule.

Resonance Energy. As mentioned above, the resonance hybrid is more stable than any of the contributing structures. The extra stability of the resonance hybrid over and above the stability of the most stable of the various resonating structures is reflected through an extra decrease in the energy of the molecule. This extra decrease in energy which results from the extra stabilisation of the molecule because of resonance, is called resonance energy. **Resonance energy** *is thus the difference between the actual energy of the molecule and that of the most stable of the resonating structures.* For example, the resonance energy of carbon dioxide is 138 kJ mol^{-1}. This means that the molecule of CO_2 is about 138 kJ more stable than the most stable contributing structure of the molecule.

Let us assume that E_1, E_2 and E_3 are the energies of the three resonating structures for a molecule and among these E_3 is the lowest energy corresponding to the most stable contributing structure. If E_0 is the actual energy of the molecule (determined experimentally), then, resonance energy is $E_3 - E_0$.

There are certain **rules** which permit the **selection of the structures** which contribute towards resonance. These are given below.

1. The contributing structures should have the same atomic positions. They should differ only in the positions of electrons.

2. The contributing structures should have the same number of unpaired electrons.

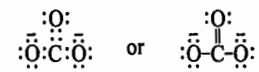
3. The contributing structures should not differ much in energy.

4. Contributing structures should be such that negative charge resides on an electronegative element and positive charge resides on an electropositive element.

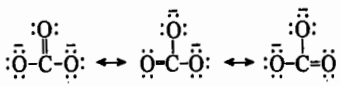
5. In contributing structures, like charges should not reside on atoms close to each other and unlike charges should not be widely separated.

As an illustration, we may consider resonance structures of CO_3^{2-} ion and CO molecule.

Carbonate ion (CO_3^{2-}). According to the octet rule, the electronic structure of carbonate ion (CO_3^{2-}) carrying two negative charges (*i.e.*, with two additional electrons) may be represented as follows :

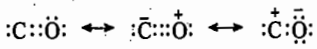


In this structure, there are three carbon-to-oxygen bonds, two of which are single bonds while the third is a double bond. Evidently, a carbon-to-oxygen double bond should be shorter than a carbon-to-oxygen single bond. But it is known from X-ray studies that all the three carbon-to-oxygen bonds in carbonate ion are of equal length which lies in between the usual single and double bond lengths. Pauling explained this observation on the basis of resonance between the three possible structures, as shown below :



This implies that the double bond resulting from the sharing of four electrons is *not localised* between carbon and any one particular oxygen atom. It is spread over all the three oxygen atoms.

Carbon monoxide molecule, CO. Carbon monoxide is a resonance hybrid of the following three resonating structures :



(I) (II) (III)

The carbon – oxygen bond length determined by X-ray diffraction is 1·13 Å which is close to the calculated C ≡ O bond length. This suggests that the bond between carbon and oxygen atoms in CO molecule is *closer to a triple bond*. Hence, structure II predominates.

Structures II and III have dipole moments in the opposite direction. Therefore, as expected, carbon monoxide has very low dipole moment (0·12 D).

LINNET'S DOUBLE QUARTET APPROACH

The valence bond theory, however, could not explain the unexpected paramagnetic behaviour of certain molecules such as O_2. In order to explain this behaviour, Linnet introduced the **concept of double quartet** according to which the 8 electrons (completed octet) around an atom, instead of constituting four pairs of 2 electrons each, constitute *two groups of four electrons each* (hence the name double quartet). The *spins of all the electrons in a quartet are the same*. But the spins of electrons in one quartet is opposite to the spin of electrons in the other quartet. Because of the effects of like charge (*charge correlation*) and same spin (*spin correlation*) of the four electrons in each quartet, each set of four electrons in a quartet has a high probability of occurring in a regular tetrahedral arrangement around the nucleus of the atom.

The charge correlation effect which tends to keep all the electrons of the two quartets apart and Pauli exclusion principle (*i.e.*, spin correlation), which tends to keep electrons of opposite spins together, oppose each other and roughly cancel each other so that the two tetrahedra *are spacially uncorrelated to each other*. This results in a spherical symmetry of electronic charge in free atoms and ions as in Ne, Na^+, F^-, O^{2-}, etc. *The most probable positions* for the electrons of a double quartet of a free ion or atom, which will result in spherical symmetry of electronic charge, are shown in Fig. 13*a*. These tetrahedra become strongly correlated to one another because of the localisation of electron pairs which form the covalent bonds. Since the two electrons in a bond pair have to be of opposite spin, each bond pair shall bind one

corner of one tetrahedron of electrons *having one type of spin* with one corner of the other tetrahedron of electrons *having opposite type of spin*. This is shown below in the case of H_2O, NH_3 and CH_4 molecules (Figs. 13*b*, *c* and *d*).

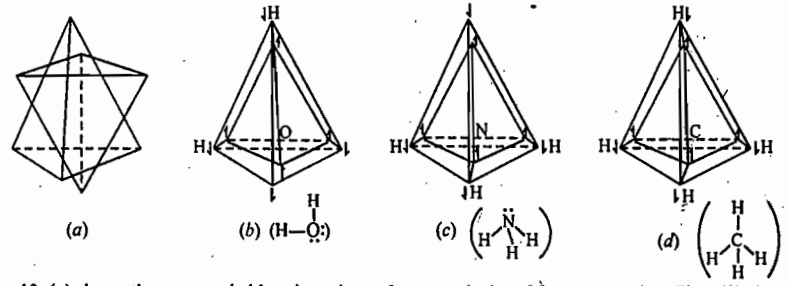
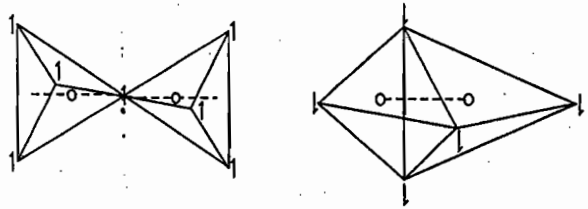


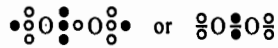
Fig. 13. (*a*) shows the most probable orientations of two tetrahedra of free atom or ion. Figs. (*b*), (*c*) and (*d*) indicate the fixation of tetrahedra around O, N and C nuclei in H_2O, NH_3 and CH_4 molecules respectively.

As is clear from the above figures, the bond pairs of electrons (as in H_2O, NH_3 and CH_4 molecules) fix the spacial orientation of the two tetrahedra of electrons with respect to each other.

In order to **explain the paramagnetic behaviour of O_2**, seven electrons are assigned one type of spin and five electrons are assigned the opposite spin. Each set of electrons is arranged in two tetrahedra around the oxygen nuclei in the following manner :

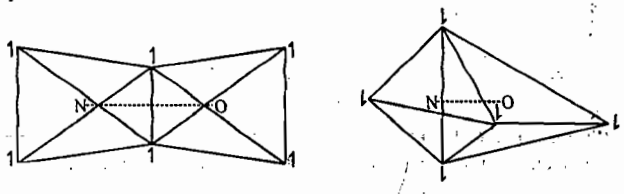


If the two figures are superimposed on each other in such a way that the O-nuclei of two figures coincide, then each O nucleus will be surrounded by eight electrons arranged in two tetrahedra. The resulting situation can be represented as :

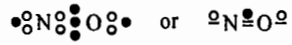


The circles represent electrons with one type of spin and dots represent electrons with the other type of spin. The short line represents an electron pair. The molecule is obviously paramagnetic with a resultant spin equivalent to *two unpaired electrons*. (Four unpaired electrons are having *one type of spin* and the other two unpaired electrons are having the *opposite type of spin*).

The structure of NO molecule can also be explained by the double quartet approach. The IR, X-ray and thermodynamic studies of this molecule reveal that its bond order is intermediate between those of N_2 and O_2 (which contain 6 and 4 electrons, respectively, in the internuclear region). The double quartet approach explains it by means of the following two structures, each consisting of two tetrahedra of electrons one of which contains 6 electrons of one type of spin and the other contains 5 electrons of the other type of spin.



If the two figures are superimposed in such a way that N and O nuclei of the figures coincide and that each nucleus is surrounded by 8 electrons arranged in two tetrahedra, the structure obtained can be written as :



The molecule apparently contains a bond order of $2\frac{1}{2}$ (*i.e.*, it has 5 electrons in the internuclear region). The molecule is paramagnetic because of the resultant one electron unpaired spin, as is experimentally observed.

However, the quartet approach, being entirely empirical, failed to receive any recognition.

MOLECULAR ORBITAL THEORY (MOT)

The wave mechanical treatment of a covalent bond based on the valence bond theory has been discussed above. The second approach to the problem is through another theory known as the **molecular orbital theory**. The two theories reflect distinctly different conceptual approaches to the basic structural model of a molecule. For instance, according to VBT, the two atoms in a diatomic molecule lie close to each other with their completely filled atomic orbitals remaining intact. *Only the half-filled orbital of one atom overlaps with the half-filled orbital of the same symmetry of the other atom* resulting in the formation of a covalent bond. According to MOT, on the other hand, the nuclei of the two atoms lie at appropriate distance and *all the atomic orbitals of one atom overlap with all the atomic orbitals of the other atom provided the overlapping orbitals are of the same symmetry and of similar energy*. The resulting polynuclear molecular orbitals contain all the electrons of the molecule.

The molecular orbital theory was put forth by F. Hund and R.S. Mulliken in 1930s and later further developed by I.E. Lennard-Jones and Charles Coulson.

The **basic principles of molecular orbital theory** are as follows :

1. When nuclei of two atoms come close to each other, *their atomic orbitals interact leading to the formation of* **molecular orbitals.** The atomic orbitals of the atoms in a molecule completely lose their identity after the formation of molecular orbitals.

2. Each molecular orbital is described by a wave function ψ, known as molecular orbital wave function.

3. The molecular orbital wave function ψ is such that ψ^2 represents the probability density or electron charge density.

4. Each molecular orbital wave function (ψ) is associated with a set of quantum numbers which determine the energy and the shape of the molecular orbital.

5. Each ψ is associated with a definite energy value and the total energy of the molecule is the sum of the energies of occupied molecular orbitals.

6. Electrons fill the molecular orbitals in the same way as they fill the atomic orbitals following the aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

7. Each electron in a molecular orbital belongs to all the nuclei present in the molecule.

8. Each electron moving in a molecular orbital has a spin of $+\frac{1}{2}$ or $-\frac{1}{2}$.

The **basic difference** *between an atomic orbital and a molecular orbital* is that while an electron in an atomic orbital is influenced by *one positive nucleus* only, an electron in a molecular orbital is influenced *by all the nuclei* of atoms contained in a molecule.

If we have a simple molecular system comprising of two electrons described by two *one-electron molecular orbital wave functions* ψ_1 and ψ_2, then the *combined configurational wave function for the system, i.e., the molecule*, would be given by

$$\psi = \psi_1\psi_2 \qquad ...(21)$$

If, in general, there are n electrons, then the configurational wave function for the system would be given by

$$\psi = \psi_1\psi_2\psi_3...\psi_n \qquad ...(22)$$

where ψ_1, ψ_2, ψ_3, etc., are one-electron molecular orbital wave functions*.

The individual one-electron molecular orbital wave functions such as ψ_1, ψ_2, ψ_3,.....can be determined with the application of the wave mechanical principles, especially the Ritz method of linear combination of atomic orbitals.

Linear Combination of Atomic Orbitals (LCAO). Molecular Orbital Treatment of Hydrogen Molecule Ion, H_2^+. Linear combination of atomic orbitals which has been described earlier in this chapter, is also employed in the treatment of molecular orbital theory. We shall apply this principle in the molecular orbital treatment of a simple species, *viz.*, H_2^+ **ion**, containing only one electron and then extend the treatment to more complicated systems.

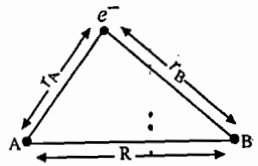


Fig. 14. Representation of H_2^+ ion.

Consider a H_2^+ ion consisting of two H nuclei designated as A and B (Fig. 14). The single electron is supposed to be moving in a molecular orbital formed by the interaction of atomic orbitals of the two hydrogen atoms, H_A and H_B. The potential energy of the H_2^+ system would evidently, be given by

$$V = -\frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \qquad ...(23)$$

where r_A, r_B and R are the appropriate distances, as shown in Fig. 14.

As shown in Chapter 1, the energy operator (*i.e.*, the Hamiltonian operator) $\hat{H}$ for H_2^+ ion is represented as

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V \qquad ...(24)$$

$$= -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \qquad ...(25)$$

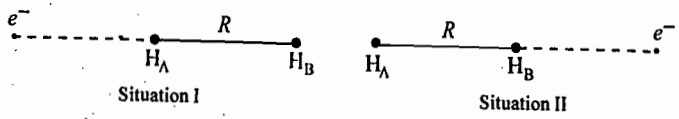
*Strictly speaking, expressions (21) and (22) are true only if we assume ψ_1, ψ_2, and ψ_3, etc., to be totally independent of one another. This is not exactly true since the electrons in the molecular orbitals of a multi-electron system repel one another and, therefore, ψ_1, ψ_2, ψ_3, etc., are dependent on one another to some extent. Hence, the expressions (21) and (22) are only approximations.

Accordingly, the wave equation $\hat{H}\psi = E\psi$ becomes

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R}\right)\psi = E\psi \qquad ...(26)$$

If we know ψ, we can find the energy E of the molecular orbital with the help of Eq. 26. But, it is not possible to ascertain the true ψ for such a system due to reasons already discussed in Chapter 1. However, we can find a wave function which is close to the true ψ, as discussed below.

The electron in H_2^+ ion is moving in molecular orbital under the influence of both the nuclei A and B. When, at some instant, it comes nearer to nucleus A (situation I), the electron would behave as if it was moving in the atomic orbital of H_A. The motion of the electron would then be described by ψ_A (the unmixed atomic orbital of H_A). Similarly, when the electron is nearer to nucleus B (situation II), its motion would be described by ψ_B (the unmixed atomic orbital of H_B).



In between these two situations, the electron would be under the influence of both the nuclei and its motion would be described by a wave function *which is a linear combination of* ψ_A and ψ_B. Thus,

$$\psi = c_A\psi_A + c_B\psi_B \qquad ...(27)$$

where c_A and c_B are the coefficients of the atomic orbital wave functions ψ_A and ψ_B, respectively. The squares of the coefficients, *viz.*, c_A^2 and c_B^2, give, respectively, the contributions of ψ_A and ψ_B to the wave function ψ.

The energy function ε corresponding to this wave function is given by

$$\varepsilon = \int_{-\infty}^{+\infty}\psi\hat{H}\psi\,d\tau \Big/ \int_{-\infty}^{+\infty}\psi^2 d\tau \qquad \text{(cf. Eq. 8.)} \qquad ...(28)$$

$$= \int_{-\infty}^{+\infty}(c_A\psi_A + c_B\psi_B)\hat{H}(c_A\psi_A + c_B\psi_B)d\tau \Big/ \int_{-\infty}^{+\infty}(c_A\psi_A + c_B\psi_B)^2 d\tau \qquad ...(29)$$

Differentiating Eq. 29 with respect to c_A only and then with respect to c_B only and applying the conditions of minimisation of energy, *viz.*, $\partial\varepsilon/\partial c_A = 0$, and $\partial\varepsilon/\partial c_B = 0$, we get a quadratic equation in ε whose solution gives two values of energy function ε. Since these energy functions being of minimum energy, are closest approximations of energy E, we may designate these two values of ε as E_+ and E_-.

Since the probability of occurrence of situation I and situation II, described above, is the same, therefore, the weightages of ψ_A and ψ_B in overall ψ would be the same. Thus, $c_A^2 = c_B^2$.

In order that ψ is an acceptable wave function, it must be normalised, *i.e.*, it must satisfy the condition that $\int_{-\infty}^{+\infty}\psi^2 d\tau = 1$. The atomic orbital wave functions taken for the combination are already normalised, *i.e.*,

$$\int_{-\infty}^{+\infty}\psi_A^2 d\tau = 1 \quad \text{and} \quad \int_{-\infty}^{+\infty}\psi_B^2 d\tau = 1$$

The above conditions give the relation

$$c_A^2 + c_B^2 = 1$$

But, as shown above, $c_A^2 = c_B^2$

$$c_A = \pm c_B = \pm(1/\sqrt{2}) \qquad ...(30)$$

Thus, we get two sets of values for c_A and c_B, *viz.*, $(+1/\sqrt{2}, +1/\sqrt{2})$ and $(+1/\sqrt{2}, -1/\sqrt{2})$ and hence two linear combinations of ψ_A and ψ_B corresponding to each set of the values of c_A and c_B. Accordingly, we have

$$\psi_+ = +(1/\sqrt{2})\psi_A + (1/\sqrt{2})\psi_B = (1/\sqrt{2})(\psi_A + \psi_B) \qquad ...(31)$$

$$\psi_- = +(1/\sqrt{2})\psi_A - (1/\sqrt{2})\psi_B = (1/\sqrt{2})(\psi_A - \psi_B) \qquad ...(32)$$

In the above equations, ψ_+ corresponds to energy E_+ and ψ_- corresponds to energy E_-. The lower value of energy E_+ is lower than either of E_A and E_B (*viz.*, the energies of isolated H_A and H_B). The higher value of energy E_- is higher than either of E_A and E_B. Thus, we see that in the case of H_2^+ ion :

1. A linear combination of two atomic orbitals ψ_A and ψ_B leads to the formation of two molecular orbitals ψ_+ and ψ_-.

2. The energy E_+ of molecular orbital ψ_+ is *lower* than either of E_A and E_B. It is, therefore, designated as **bonding molecular orbital** (BMO).

3. The energy E_- of molecular orbital ψ_- is higher than either of E_A and E_B. It is, therefore, designated as **antibonding molecular orbital** (ABMO).

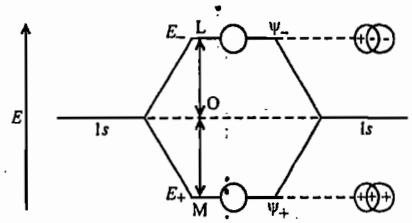


Fig. 15. Energies of bonding and antibonding molecular orbitals.

4. The extent of lowering of energy of the bonding molecular orbital is equal to the extent of increase of energy of the antibonding molecular orbital, as shown in Fig. 15.

5. Detailed LCAO calculations show that the greater the overlap of the two combining atomic orbitals ψ_A and ψ_B, the lower would be the energy of the bonding molecular orbital (ψ_+) formed.

6. The combining atomic orbitals ψ_A and ψ_B are completely used up during the formation of the molecular orbitals ψ_+ and ψ_-. The electron occupying originally the 1*s* atomic orbital of H_A or H_B, now occupies the lower level molecular orbital ψ_+, losing energy = OM and thus gaining in stability.

The molecular orbital treatment for H_2^+ ion, discussed above, can be extended to other homonuclear and heteronuclear systems. In general, whenever atomic orbitals ψ_A and ψ_B, of the same symmetry and of similar energies, of two atoms A and B, overlap, two molecular orbitals ψ_+ and ψ_- would be formed by the linear combination of these atomic orbitals so that the equations for molecular orbitals would be

$$\psi_+ = N_+(\psi_A + \lambda\psi_B) \qquad ...(33)$$

$$\psi_- = N_-(\lambda\psi_A - \psi_B) \qquad ...(34)$$

where λ is called the **mixing coefficient** and N_+ and N_- are called **normalising constants**. The values of these constants are adjusted in such a way that the normalising conditions, *viz.*, $\int_{-\infty}^{+\infty}\psi_+^2 d\tau = 1$ and $\int_{-\infty}^{+\infty}\psi_-^2 d\tau = 1$ are satisfied.

If the molecule AB is homonuclear, the weightages of ψ_A and ψ_B in both ψ_+ and ψ_- would be the same, *i.e.*, $N_+^2 = \lambda^2 N_+^2$ and $N_-^2\lambda^2 = N_-^2$ (weightage or contribution of a wave function is related to square of its coefficient). It readily follows from above that $\lambda^2 = 1$ so that $\lambda = \pm 1$. In such a case, Eqs. 33 and 34 for molecular orbitals would reduce to Eqs. 31 and 32, respectively because $N_+ = N_- = 1/\sqrt{2}$ and $\lambda = \pm 1$.

If, however, the molecule AB is heteronuclear, the weightages of ψ_A and ψ_B would not be the same, *i.e.*, $N_-^2\ \lambda^2 \neq N_-^2$ and $N_+^2 \neq \lambda^2 N_+^2$ so that $\lambda^2 \neq 1$ and the equations for molecular orbitals would remain as Eqs. 33 and 34.

Construction of Molecular Orbital Wave Functions and Valence Bond Wave Functions

In the preceding pages, the wave mechanical treatment of covalent bond has been discussed on the basis of valence bond and molecular orbital theories. The following **typical solved examples** illustrate how the above theories can be made use of for constructing molecular orbital wave functions and valence bond wave functions.

Example 1. Construct a molecular orbital wave function for the bond between H and Cl in HCl assuming that the bond is formed from the 1s electron of H atom and a 3p electron of Cl atom.

Solution : Let H atom be designated by A and Cl atom by B. Let the 1*s* electron of H atom be labelled as electron 1 and 3*p* electron of Cl atom be labelled as electron 2.

According to Eq. 21, $\psi_{MO} = \psi_1\psi_2$ where

$$\psi_1 = c_1\psi_A(1) + c_2\psi_B(1)$$

and

$$\psi_2 = c_1\psi_A(2) + c_2\psi_B(2)$$

$$\therefore \quad \psi_{MO} = [c_1\psi_A(1) + c_2\psi_B(1)][c_1\psi_A(2) + c_2\psi_B(2)]$$

$$= c_1^2[\psi_A(1)\psi_A(2)] + c_1c_2[\psi_A(1)\psi_B(2) + \psi_A(2)\ \psi_B(1)] + c_2^2\ [\psi_B(1)\psi_B(2)]$$

As can be seen, the first and the last terms are *ionic* whereas the middle terms are *covalent*. Also, the covalent terms have *equal weightage* but the ionic terms have *different weightage* from the covalent terms and also from each other.

Example 2. Write down the molecular orbital wave function for H_2^- molecule anion.

Solution : H_2^- molecule anion contains three electrons which may be labelled as 1, 2 and 3. It contains two nuclei which may be designated as A and B. According to Eq. 22,

$$\psi_{MO} = \psi_1\psi_2\psi_3$$

where

$$\psi_1 = c_1\psi_A(1) + c_2\psi_B(1)$$

$$\psi_2 = c_3\psi_A(2) + c_4\psi_B(2)$$

$$\psi_3 = c_5\psi_A(3) + c_6\psi_B(3)$$

Example 3. Using the principle of LCAO for the wave function for H_2^+ ion, obtain the normalised wave functions for the BMO and the ABMO.

Solution : Using the principle of LCAO, the wave function for H_2^+ ion is written as

$$\psi = N(c_1\psi_A + c_2\psi_B) \qquad ...(i)$$

where N is the normalisation constant.

According to the normalization condition, for real ψ

$$\int_{-\infty}^{+\infty} \psi^2 d\tau \equiv <\psi\,|\,\psi>^{**} = 1 \qquad ...(ii)$$

Incorporating the value of ψ from Eq. (*i*) in Eq. (*ii*), we have

$$N^2 <(c_1\psi_A + c_2\psi_B)\,|\,(c_1\psi_A + c_2\psi_B)> = 1$$

or

$$c_1^2[<\psi_A\,|\,\psi_A>] + c_2^2[<\psi_B\,|\,\psi_B>] + 2c_1c_2[<\psi_A\,|\,\psi_B>] = 1/N^2 \qquad ...(iii)$$

It can be shown that $<\psi_A\,|\,\psi_B> = <\psi_B\,|\,\psi_A>$

Assuming that ψ_A and ψ_B are normalised, *i.e.*,

$$<\psi_A\,|\,\psi_A> \equiv \int \psi_A^2 d\tau \quad \text{and} \quad <\psi_B\,|\,\psi_B> \equiv \int \psi_B^2\ d\tau = 1, \text{ we have}$$

$$c_1^2 + c_2^2 + 2c_1c_2S = 1/N^2 \qquad ...(iv)$$

where S is the *overlap integral* defined as

$$S = <\psi_A\,|\,\psi_B> \equiv \int \psi_A\psi_B d\tau \qquad ...(v)$$

From Eq. (*iv*),

$$N = (c_1^2 + c_2^2 + 2c_1c_2S)^{-1/2} \qquad ...(vi)$$

Hence, from Eq. (*i*),

$$\psi = (c_1^2 + c_2^2 + 2c_1c_2S)^{-1/2}(c_1\psi_A + c_2\psi_B) \qquad ...(vii)$$

We know that for BMO of H_2^+ ion, $c_1 = c_2$ and for ABMO, $c_1 = -c_2$.

Hence, from Eq. (*vii*),

$$\psi_{BMO} = (1/\sqrt{2(1+S)})\ (\psi_A + \psi_B)$$

and

$$\psi_{ABMO} = (1/\sqrt{2(1-S)})\,(\psi_A - \psi_B)$$

Example 4. Write down the normalised VB wave functions and normalised MO wave functions for H_2 molecule and comment on the expressions obtained.

Solution : H_2 molecule contains two electrons (labelled 1 and 2) and two hydrogen nuclei (labelled A and B). The pairing of electrons leads to the formation of a covalent bond. In the VB approach, if electron 1 is on nucleus A, then electron 2 would be on nucleus B and vice-versa. Since, however, the two electrons are indistinguishable, therefore, the VB wave function for H_2 molecule can be written as

$$\psi_{VB} = (1/\sqrt{2})\,[\psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}] \qquad ...(i)$$

where $1/\sqrt{2}$ is the *normalization constant* obtained by normalizing ψ_{VB}.

In the MO theory, the MO wave function for H_2 molecule is given by

$$\psi_{MO} = \psi_1\psi_2 \qquad ...(ii)$$

where ψ_1 and ψ_2 are the *normalised* wave functions for MOs of H_2 given by

$$\psi_1 = (1/\sqrt{2})\,[\psi_A(1) + \psi_B(1)] \qquad ...(iii)$$

and

$$\psi_2 = (1/\sqrt{2})\,[\psi_A(2) + \psi_B(2)] \qquad ...(iv)$$

Multiplying ψ_1 and ψ_2, we get the ψ_{MO} as

$$\psi_{MO} = (1/2)[\psi_A(1) + \psi_B(1)][\psi_A(2) + \psi_B(2)] \qquad ...(v)$$

$$= (1/2)[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)] + 1/2[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] \qquad ...(vi)$$

**This type of notation is known as 'bra' and 'ket' notation. In this notation, $\int_{-\infty}^{+\infty} \psi_1\psi_2 d\tau$ and $\int_{-\infty}^{+\infty} \psi_1\hat{H}\psi_2 d\tau$ are written as $<\psi_1\,|\,\psi_2>$ and $<\psi_1\,|\,\hat{H}\,|\,\psi_2>$, respectively.

In Eq. (*vi*), the first two terms represent the probability of finding *both the electrons on the same atom at the same time*. In other words, these terms represent the *ionic structures* of H_2 molecule which may be written as $\overset{-}{H}_A\overset{+}{H}_B$ and $\overset{+}{H}_A\overset{-}{H}_B$.

The last two terms in Eq. (*vi*) represent the *covalent structure* of the H_2 molecule.

Comparing ψ_{VB} and ψ_{MO}, we observe that while the wave function in VBT does not give any weightage to ionic structures, the MOT gives equal weightage to covalent and ionic structures.

Example 5. Write down the wave function for the BMO for a hetero-nuclear diatomic molecule AB assuming that the electron on an average spends 90% of its time on nucleus A and 10% of its time on nulceus B.

Solution : In the LCAO – MO scheme, $\psi_{MO} = c_A\psi_A + c_B\psi_B$

where the coefficients c_A and c_B are such that $[c_A]^2$ and $[c_B]^2$ determine the probability of finding the electron in atomic orbitals ψ_A and ψ_B, respectively. Then, clearly,

$$[c_A]^2 = 90\% = 0{\cdot}9 \text{ and}$$

$$[c_B]^2 = 10\% = 0{\cdot}1$$

Hence,

$$c_A = \pm\sqrt{0{\cdot}9} = \pm\, 0{\cdot}95$$

and

$$c_B = \pm\sqrt{0{\cdot}1} = \pm\, 0{\cdot}32$$

Thus,

$$\psi_{MO} = 0{\cdot}95\,\psi_A + 0{\cdot}32\,\psi_B$$

Example 6. Write down the valence bond wave function for the HF molecule (assuming that it is formed from 1*s* orbital of H and 2p_z orbital of F) in the following three cases : (*a*) HF is purely covalent (*b*) HF is purely ionic and (*c*) HF is 80% covalent and 20% ionic.

Solution : Let the H atom be represented by A and F atom by B. Let the electron numbered 1 be the 1*s* electron of H atom and the electron numbered 2 be the 2p_z electron of F atom.

(*a*) For purely covalent structure of HF, the wave function is written as

$$\psi_{covalent} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_A(1)$$

(*b*) For the purely ionic structure H^+F^-, both the electrons are on the F atom so that

$$\psi_{ionic} = \psi_B(1)\psi_B(2)$$

(*c*) HF is a resonance hybrid shown as

$$H - F \longleftrightarrow H^+F^-$$

$\therefore$

$$\psi_{VB} = c_1\psi_{covalent} + c_2\psi_{ionic} \text{ with } c_1^2 + c_2^2 = 1$$

Since

$$c_1^2 = 0{\cdot}80 \text{ and } c_2^2 = 0{\cdot}20 \text{ (given), hence,}$$

$$c_1 = \sqrt{0{\cdot}80} = 0{\cdot}89$$

and

$$c_2 = \sqrt{0{\cdot}20} = 0{\cdot}45$$

$\therefore$

$$\psi_{VB} = 0{\cdot}89\,[\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)] + 0{\cdot}45\,[\psi_B(1)\psi_B(2)]$$

Electron Charge Densities in Molecular Orbitals of H_2^+ ion

Consider once again a H_2^+ ion. The square of the wave function, *viz.*, ψ^2, *is a measure of the probability density, i.e.*, the probability of finding an electron *in a given volume* of space. Since probability density is directly related to **electron charge density**, hence, ψ_+^2 and ψ_-^2 give electron charge densities in the two molecular orbitals ψ_+ and ψ_- of H_2^+ ion formed in accordance with Eqs. 31 and 32. According to these equations

$$\psi_+^2 = [1/\sqrt{2}\,(\psi_A + \psi_B)]^2 = 1/2\,(\psi_A^2 + \psi_B^2 + 2\psi_A\psi_B) \quad ...(35)$$

and

$$\psi_-^2 = [1/\sqrt{2}\,(\psi_A - \psi_B)]^2 = 1/2\,(\psi_A^2 + \psi_B^2 - 2\psi_A\psi_B) \quad ...(36)$$

If the atomic orbitals ψ_A and ψ_B had not combined, there would have been no overlap between ψ_A and ψ_B. In that case, the overlap density, given by $\psi_A\psi_B$, would have been zero and ψ_+^2 would have been equal to $1/2(\psi_A^2 + \psi_B^2)$. This means that $1/2(\psi_A^2 + \psi_B^2)$ gives the electron charge density in between the nuclei *A* and *B* in the *uncombined atomic orbitals* ψ_A and ψ_B. When the two atomic orbitals *combine to form the molecular orbital* ψ_+, the overlap density $\psi_A\psi_B$ between the two atomic orbitals is non-zero and the electron charge density ψ_+^2 in between the two nuclei is given by $1/2\psi_A^2 + 1/2\psi_B^2 + \psi_A\psi_B$ (Eq. 35). This means that the electron charge density in between the nuclei A and B in the molecular orbital ψ_+ *increases by* $\psi_A\psi_B$.

The increased electron charge density shields the two similarly charged nuclei very effectively and decreases the energy of the molecular orbital in the event of its being occupied by electrons. In other words, the molecular orbital ψ_+ has *lower energy* than the energy of either of the uncombined atomic orbitals ψ_A and ψ_B. This orbital, therefore, leads to the formation of a stable chemical bond and is called **bonding molecular orbital.**

The electron charge density in between the nuclei A and B in molecular orbital ψ_- is given by $1/2\psi_A^2 + 1/2\psi_B^2 - \psi_A\psi_B$ (Eq.36). Evidently, the electron charge density in between the two nuclei in the molecular orbital ψ_- now *decreases by* $\psi_A\psi_B$. Because of the decrease in the electron charge density, the two similarly charged nuclei in this molecular orbital would be screened to a much smaller extent. As a result, the two nuclei would repel each other to a greater extent. This would lead to an increase of energy of the molecular orbital in the event of its being occupied by electrons. In other words, the molecular orbital ψ_- has *higher energy* than the energy of either of the uncombined atomic orbitals ψ_A and ψ_B. Such an orbital, evidently, opposes the formation of a chemical bond and is called **antibonding molecular orbital.**

It is evident that a filled BMO has high electron charge density in the overlap region whereas a filled ABMO has no electron charge density in between the nuclei. This may be illustrated by plotting ψ^2 for the bonding as well as the antibonding molecular orbitals against the internuclear distance of H_2^+ ion. When the electron probability density $(\psi_+)^2$ of the BMO, *i.e.*, $1/2(\psi_A + \psi_B)^2$, is plotted against the internuclear distance, a curve represented by the *solid line* in Fig. 16. is obtained. The plots for the electron charge densities in between the two nuclei in the uncombined atomic orbitals of H atoms for the same internuclear distance are also shown in the figure *by dotted lines*. As mentioned above, the electron charge density in between the nuclei in the uncombined atomic orbitals ψ_A and ψ_B is $1/2\psi_A^2 + 1/2\psi_B^2$. It is clear from the figure that there is greater probability of finding electron between the two nuclei in BMO than in the uncombined AOs.

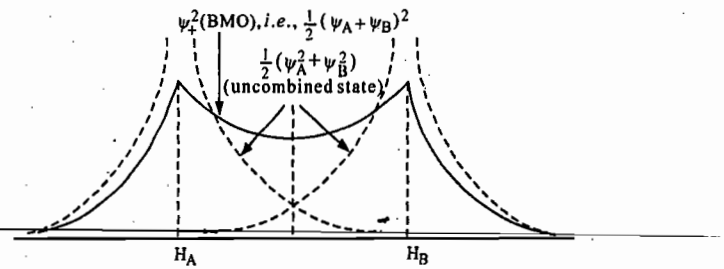


Fig. 16. The plot of electron probability density *vs* internuclear distnace for a BMO shown by a solid line and for the separate uncombined atomic orbitals of hydrogen atoms shown by the dotted lines.

For an ABMO, the picture is quite different. When the electron probability density (ψ_-^2) of an ABMO, *i.e.*, $1/2(\psi_A - \psi_B)^2$, is plotted against the internuclear distance, a curve represented by the *solid line* in Fig. 17 is obtained. This curve indicates that the electron charge density in the middle of

internuclear distance becomes almost zero. As a result, the two nuclei repel each other more effectively than the nuclei of the uncombined atoms A and B at that internuclear distance.

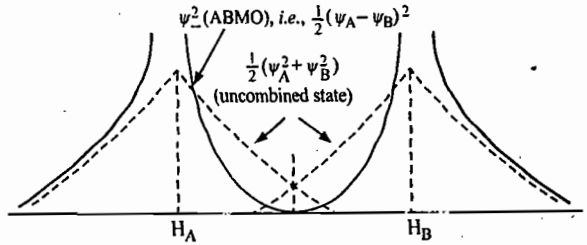
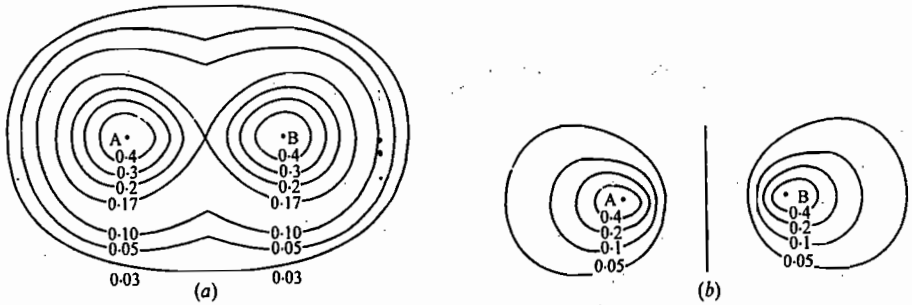


Fig. 17. The plot of electron probability density *vs* internuclear distance for an ABMO shown by solid line and for separate uncombined atomic orbitals of hydrogen atoms shown by dotted lines.

The distinction between bonding and antibonding molecular orbitals can be made more clear by showing the **contours** of electron charge densities or probability densities around the two nuclei A and B for these orbitals, as illustrated in Figs. 18 (*a*) and (*b*).

In a **bonding MO**, the high probability density contours are localised on the two nuclei but tend to polarise *towards the space* located in between the two nuclei. The low probability density contours are, however, *spread over both the nuclei*. This implies enhancement of electronic charge in the space in between the two nuclei.



(*a*) σ(1*s*) Bonding Molecular Orbital (*b*) σ*(1*s*) Antibonding Molecular Orbital

Fig.18. Contours of electron charge densities in bonding and antibonding molecular orbitals.

In an **antibonding MO**, the high as well as low probability density contours are *localised on two nuclei* and tend to polarise away from the space falling in between the two nuclei. This implies depletion of electronic charge from the space in between the two nuclei.

Pictorial Representation of Combination of Atomic Orbitals to form Molecular Orbitals

1. Combination of *s* atomic orbitals. To begin with, we consider a simple case of combination of 1*s* atomic orbital of one hydrogen atom with 1*s* atomic orbital of another hydrogen atom to give *two* MOs. As discussed earlier, there are two ways of linearly combining AOs. One is by the *additive combination* while the second is by the *subtractive combination* of atomic orbitals. The overlapping of two 1*s* atomic orbitals by linear additive combination to form a bonding molecular orbital is shown in Fig. 19. In such a combination, the region between the two nuclei has a (+) × (+), *i.e.*, algebraic + sign. This implies that *the electron charge density in the region between the two nuclei would get intensified.*

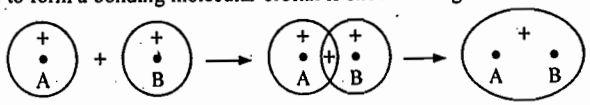


Fig. 19. Formation of a bonding molecular orbital by overlapping of two 1*s* atomic orbitals by linear additive combination.

The high electron charge density in between the two positive nuclei shields them from mutual repulsion and holds them together at the observed distance from each other. Such a linear additive combination gives a BMO. It is designated as σ(1*s*) orbital. The sign σ signifies that the molecular orbital is symmetrical about the molecular axis and the script (1*s*) indicates that it is formed by the combination of 1*s* atomic orbitals.

The overlapping of two 1*s* atomic orbitals by linear subtractive combination is shown in Fig. 20. The region of overlap between the two nuclei has (+) × (–), *i.e.*, algebraic – sign. This implies that *the electron charge density would get removed from the middle of the two nuclei.* It may be noted that a negative overlap means removal of electron charge from the region in between the nuclei. Thus, there will be *no shielding of the nuclei.* The repulsion between the two nuclei would, therefore, increase thereby increasing the energy of the molecular orbital formed (Fig. 20). Such a molecular orbital is termed as ABMO and is designated as σ*(1*s*).

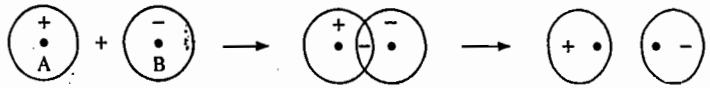


Fig. 20. Formation of antibonding molecular orbital by overlapping of two 1*s* atomic orbitals by linear subtractive combination. The thick dots represent the nuclei.

It may be noted that the positive and negative signs shown above in atomic and molecular orbitals are only algebraic signs of wave functions and *should not be confused with charges.*

Just like the combination of 1*s* atomic orbitals, 2*s* atomic orbitals also combine to form bonding and antibonding molecular orbitals. These are designated as σ(2s) and σ*(2*s*), respectively. They differ from σ(1*s*) and σ*(1*s*) MOs with regard to their size only.

2. Combination of p_z atomic orbitals. There are three *p* atomic orbitals designated as p_x, p_y and p_z. As a convention, the Z-axis is taken as the internuclear axis. The *X* and *Y* axes would then be perpendicular to the nuclear line. The combination of two p_z atomic orbitals belonging to different nuclei would, evidently, give a sigma BMO represented as σ($2p_z$) and a sigma ABMO represented as σ*($2p_z$).

The formation of a σ($2p_z$) BMO by the linear additive combination of two p_z atomic orbitals is represented in Fig. 21. The thick dots represent the nuclei. In this combination, the positive lobes of the two AOs overlap so that *the electron charge density between the two nuclei is enhanced.* The nuclei are thus well shielded from each other. Since the repulsion between the nuclei in such a case is minimum, the energy of this MO is lower than the energy of the atomic orbitals which have gone into its formation.

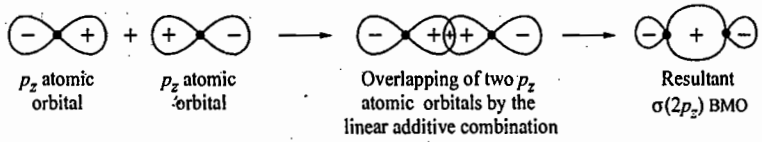


Fig. 21. Formation of a σ($2p_z$) BMO by the linear additive combinatioin of two p_z atomic orbitals.

The corresponding ABMO is obtained by the linear subtractive combination of two p_z atomic orbitals, as represented in Fig. 22.

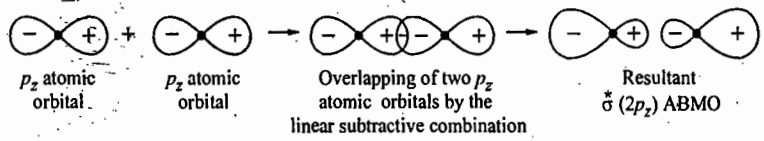


Fig. 22. Formation of a σ* ($2p_z$) ABMO by the linear subtractive combination of two p_z atomic orbitals.

The positive lobe of one p_z AO overlaps with the negative lobe of the other p_z AO resulting in the negative overlapping region. *The electron charge density between the nuclei, therefore, gets depleted.* The similarly charged nuclei are, thus, exposed to each other and hence tend to repel each other. This orbital, being antibonding, is designated as $\overset{*}{\sigma}$ $(2p_z)$. The energy of this ABMO is *higher* than the energy of either of the AOs which have gone into its formation.

3. Combination of p_x and p_y atomic orbitals. Suppose a p_x orbital of an atom overlaps with a p_x orbital of another atom. The overlap would be positive but it would be *side to side* and not end to end as in the case of p_z orbitals. The resulting molecular orbitals will, thus, be called **pi molecular orbitals.** The formation of the BMO, designated as π $(2p_x)$, is shown in Fig. 23.

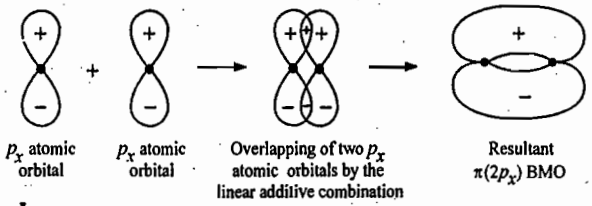


Fig. 23. Overlapping of two p_x atomic orbitals by linear additive combination to give π $(2p_x)$ BMO orbital.

The corresponding ABMO formed by linear subtractive combination of p_x AOs, designated as $\overset{*}{\pi}(2p_x)$, is shown in Fig. 24.

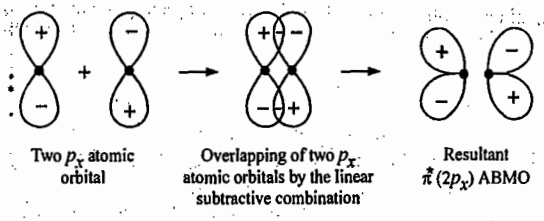


Fig. 24. Overlapping of two p_x atomic orbitals by the linear subtractive combination to form $\overset{*}{\pi}(2p_x)$ ABMO.

The energy of the antibonding molecular orbital would be high because the similarly charged nuclei are not effectively screened by the electronic charge and, therefore, repel each other considerably.

The formation of $\pi(2p_y)$ and $\overset{*}{\pi}(2p_y)$ MOs is similar to the formation of π $(2p_x)$ and $\overset{*}{\pi}(2p_x)$ MOs discussed above. The only difference is that the AOs which combine and MOs which are formed now lie perpendicular to the plane of the paper.

Difference Between Bonding and Antibonding Molecular Orbitals. The difference between bonding and antibonding molecular orbitals has been summed up in Table 5.

TABLE 5
Difference Between Bonding and Antibonding Molecular Orbitals

BMO	ABMO
1. A BMO is formed *by the addition overlap of atomic orbitals.*	An ABMO is formed *by the subtraction overlap of atomic orbitals.*
2. It has *lower energy* than the AOs from which it is formed.	It has *higher energy* than the AOs from which it is formed.
3. The electron charge density in between the nuclei is *high* and hence the repulsion between the nuclei is very low. This results in stabilisation of the BMO. In other words, the electrons in the BMO favour stable bond formation.	The electron charge density in between the nuclei is *low* and hence the repulsion between the nuclei is high. This results in de-stabilisation of the ABMO. In other words,, the electrons in the ABMO oppose bond formation.

Conditions for the Combination of Atomic Orbitals. It should be noted that *any two* atomic orbitals will not essentially combine to form molecular orbitals. There are, in fact, **certain limitations** to the combination of atomic orbitals. These are discussed below :

1. *The energy of the AOs involved should not differ much from one another.* Thus, in the formation of a *homonuclear* diatomic molecule of the type A_2, 1*s* orbital of one atom does not combine with 2*s* orbital of another atom of the *same* element as the energy difference between them is quite high. Likewise, 2*s* orbital of one atom does not combine with 2*p* orbital of another atom of the same element as the energy difference between them is very high.

In the case of *heteronuclear* diatomic molecules of the type AB, however, such combinations may be possible.

2. *The AOs combine only if they overlap to a considerable extent.* This overlap increases the electron charge density in between the two nuclei thereby minimising their mutual repulsion.

3. *The AOs should have the same symmetry about the molecular axis.* Thus, a p_x (or p_y) orbital of one atom *does not* combine with an *s* orbital of another atom. This is illustrated in Fig. 25. The *s* orbital of an atom A is shown to overlap with the p_x orbital of another atom B. But, since the molecular axis is in the *Z*-direction and the p_x orbital is oriented at right angles to this axis, no combination is possible. Thus, no molecular orbital can result in spite of the overlap. In fact, the + overlap is cancelled by the – overlap, as shown in the figure.

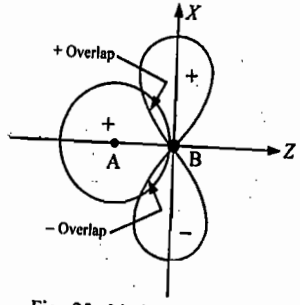


Fig. 25. Limitation of a p_x atomic orbital to combine with an *s* atomic orbital due to lack of symmetry about the molecular axis.

Similarly, a p_y orbital does not combine with an *s* orbital as they have different symmetry.

A p_z orbital, however, is able to combine with an *s* orbital since they have the same symmetry, as shown in Fig. 26.

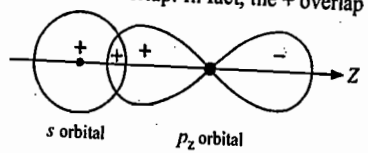


Fig. 26. Freedom of p_z atomic orbital to combine with an *s* orbital because of the same symmetry about the axial line.

The s and *p* atomic orbitals which can combine with each other to form molecular orbitals (assuming *Z*-axis as the internuclear axis) are as shown below :

First orbital	*Second orbital*	*Type of molecular orbital formed*
s	*s*, p_z	σ
p_z	*s*, p_z	σ
p_x	p_x	π
p_y	p_y	π

Energy Level Diagram for Molecular Orbitals. We have seen that 1*s* atomic orbitals of two atoms give two MOs designated as $\sigma(1s)$ and $\overset{*}{\sigma}(1s)$. The 2*s* and 2*p* atomic orbitals (eight AOs on two atoms) give rise to the following eight MOs :

Bonding MOs : $\sigma(2s)$ $\sigma(2p_z)$ $\pi(2p_x)$ $\pi(2p_y)$

Antibonding MOs : $\overset{*}{\sigma}(2s)$ $\overset{*}{\sigma}(2p_z)$ $\overset{*}{\pi}(2p_x)$ $\overset{*}{\pi}(2p_y)$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data. The energy generally increases as we move from left to right in the following list :

$$\sigma(1s),\ \overset{*}{\sigma}(1s),\ \sigma(2s),\ \overset{*}{\sigma}(2s),\ \sigma(2p_z),\ \pi(2p_x) = \pi(2p_y),\ \overset{*}{\pi}(2p_x) = \overset{*}{\pi}(2p_y),\ \overset{*}{\sigma}(2p_z)$$

— Energy increases ⟶

The energy levels of different molecular orbitals are shown diagrammatically in Fig. 27*. In this diagram, the molecular orbitals are shown in the centre and the atomic orbitals which combine are shown on the two extremes. The atomic orbitals of same energy are shown at the same level while the BMOs are shown lower and the ABMOs are shown higher than the corresponding atomic orbitals. This indicates that while the BMOs are more stable, the ABMOs are less stable than the AOs from which they are formed. It is clear from the figure that the extent of stabilization for a BMO is always equal to the extent of destabilization of the corresponding ABMO.

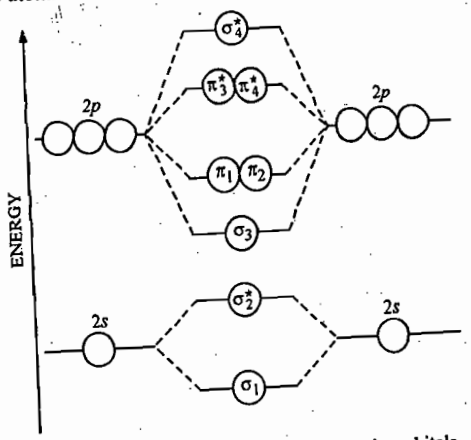


Fig. 27*. Energy levels of different molecular orbitals.

According to a **recent convention**, the molecular orbitals $\sigma(2s)$, $\overset{*}{\sigma}(2s)$, $\sigma(2p_z)$, $\overset{*}{\sigma}(2p_z)$, etc., are written as σ_1, $\overset{*}{\sigma}_2$, σ_3, $\overset{*}{\sigma}_4$, etc., and molecular orbitals $\pi(2p_x)$, $\pi(2p_y)$, $\overset{*}{\pi}(2p_x)$, $\overset{*}{\pi}(2p_y)$, etc., are written as π_1, π_2, $\overset{*}{\pi}_3$, $\overset{*}{\pi}_4$, etc., as shown in Fig. 27. This new nomenclature, which is quite convenient, is particularly useful for heteronuclear molecules.

Spectroscopic studies have revealed that the above sequence of energy levels of MOs is not correct for all molecules. It has been observed that in the case of homonuclear diatomic molecules of Second row elements of the periodic table upto N_2 (*viz.*, Li_2, Be_2, B_2, C_2, N_2), the $\sigma(2p_z)$ MO *is higher in energy than the* $\pi(2p_x)$ *and* $\pi(2p_y)$ MOs. The reversal in the sequence of energy levels of MOs is due to the *mixing of 2s and $2p_z$ orbitals*, as discussed below.

Mixing of Orbitals. We have seen that $\sigma(2s)$ and $\overset{*}{\sigma}(2s)$ MOs are formed by the combination of 2s atomic orbitals of two atoms while $\sigma(2p_z)$ and $\overset{*}{\sigma}(2p_z)$ MOs are formed by the combination of $2p_z$ atomic orbitals of the two atoms. However, if the energy differences between 2s and 2p atomic orbitals are small, there is a possibility of **mixing** of molecular orbitals $\sigma(2s)$ with $\sigma(2p_z)$ as they are of the same symmetry and $\overset{*}{\sigma}(2s)$ with $\overset{*}{\sigma}(2p_z)$ as they are also of the same symmetry with the result that the $\sigma(2s)$ and $\overset{*}{\sigma}(2s)$ MOs do not retain the pure *s* character and the $\sigma(2p_z)$ and $\overset{*}{\sigma}(2p_z)$ MOs do not retain the pure *p* character. In fact, *all the four MOs acquire a mixed sp character*. Due to this *s–p* mixing,

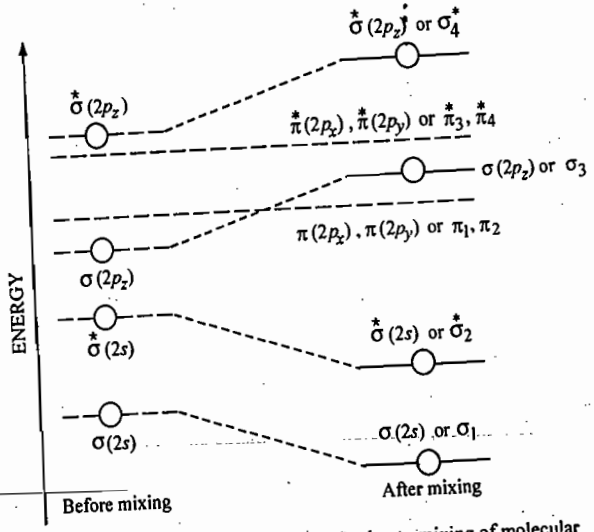


Fig. 28. The change in energies of MOs due to mixing of molecular orbitals of the same symmetry.

*The *d* orbitals are not included in the present discussion since the purpose is to consider the formation of simple diatomic molecules only.

the energies of all the four orbitals change in such a way that the resulting MOs $\sigma(2s)$ and $\overset{*}{\sigma}(2s)$, which also contain some *p* character, become more stable and are thus lowered in energy whereas the MOs $\sigma(2p_z)$ and $\overset{*}{\sigma}(2p_z)$ which contain some *s* character also now become less stable and are thus raised in energy, as illustrated in Fig. 28.

Since $\pi(2p)$ orbitals are not involved in mixing, the energies of $\pi(2p_x)$ and $\pi(2p_y)$ MOs remain unchanged, as shown in the figure.

As can be seen from Fig. 28, *$\sigma(2p_z)$ MO is raised to such an extent that it becomes higher in energy than $\pi(2p_x)$ and $\pi(2p_y)$* MOs. The new sequence of energy of MOs, therefore, becomes

$$\sigma(1s),\ \overset{*}{\sigma}(1s),\ \sigma(2s),\ \overset{*}{\sigma}(2s),\ \pi(2p_x) = \pi(2p_y),\ \sigma(2p_z),\ \overset{*}{\pi}(2p_x) = \overset{*}{\pi}(2p_y),\ \overset{*}{\sigma}(2p_z)$$

—— Energy increases ⟶

or

$$\sigma_1,\ \overset{*}{\sigma}_2,\ \sigma_3,\ \pi_1 = \pi_2,\ \overset{*}{\pi}_3 = \overset{*}{\pi}_4,\ \overset{*}{\sigma}_4$$

—— Energy increases ⟶

Now, a question arises : How is it that the mixing of $\sigma(2s)$ with $\sigma(2p_z)$ and of $\overset{*}{\sigma}(2s)$ with $\overset{*}{\sigma}(2p_z)$ occurs in the case of second row elements upto nitrogen only and not in the case of oxygen and fluorine. The answer lies in the differences in energies of 2s and 2p atomic orbitals of atoms of second row elements, as shown in Table 9.

TABLE 9

Differences in the Energies of 2s and $2p_z$ AOs of Atoms of Second Row Elements

Atoms	Li	Be	B	C	N	O	F
Difference in energies of 2s and $2p_z$ AOs (kJ mol^{-1})	178	262	449	510	570	1430	1970

It is clear from the above table that the differences in energies of 2s and $2p_z$ atomic orbitals of atoms up to nitrogen are small. Therefore, the energy differences between BMOs $\sigma(2s)$ and $\sigma(2p_z)$ [and between ABMOs $\overset{*}{\sigma}(2s)$ and $\overset{*}{\sigma}(2p_z)$] is also small upto N_2. Since $\sigma(2s)$ and $\sigma(2p_z)$ are of the same symmetry, these would mix effectively with each other and energies of the resulting *mixed molecular orbitals* would be considerably different from the energies of pure $\sigma(2s)$ and pure $\sigma(2p_z)$ molecular orbitals. A similar situation occurs in the case of molecular orbitals obtained by mixing of $\overset{*}{\sigma}(2s)$ with $\overset{*}{\sigma}(2p_z)$ molecular orbitals of molecules upto N_2.

In the case of O_2 and F_2, however, the energy differences between 2s and 2p atomic orbitals are quite large. Consequently, the energy differences between $\sigma(2s)$ and $\sigma(2p_z)$ or between $\overset{*}{\sigma}(2s)$ and $\overset{*}{\sigma}(2p_z)$ molecular orbitals in case of O_2 and F_2 are also quite large with the result that neither $\sigma(2s)$ and $\sigma(2p_z)$ nor $\overset{*}{\sigma}(2s)$ and $\overset{*}{\sigma}(2p_z)$ can mix to any significant extent in these molecules. Hence the energies of $\sigma(2s)$, $\sigma(2p_z)$, $\overset{*}{\sigma}(2s)$ and $\overset{*}{\sigma}(2p_z)$ molecular orbitals practically remain unaltered so that the energy of $\sigma(2p_z)$ molecular orbital continues to remain lower than the energies of $\pi(2p_x)$ and $\pi(2p_z)$ molecular orbitals.

Mixing of Orbitals. An Alternative Explanation. The 2s and $2p_z$ atomic orbitals of each atom are of the same symmetry and if the energy difference between the 2s and 2p orbitals of each atom is small, there is a possibility of mixing of these atomic orbitals to produce two mixed sp_z atomic orbitals on *each atom*. The two mixed orbitals, *viz.*, $\psi_{sp_z} = \frac{1}{\sqrt{1+\lambda^2}}\left(\psi_{2s} + \lambda\psi_{2p_z}\right)$ and $\frac{1}{\sqrt{1+\lambda^2}}\left(\lambda\psi_{2s} - \psi_{2p_z}\right)\left(\lambda^2 \neq 1\right)$, on each atom will be of unequal energy. Since the 2s atomic orbital was of lower

energy than the $2p_z$ atomic orbital of the atom, the lower energy mixed sp_z atomic orbital thus formed on each atom will have more contribution from $2s$ atomic orbital and less contribution from the $2p_z$ atomic orbital. Similarly, the higher energy mixed sp_z atomic orbital will have more contribution from the $2p_z$ atomic orbital and less contribution from the $2s$ atomic orbital of the atom. Since all the four mixed sp_z atomic orbitals of both the atoms are of the same symmetry, they linearly combine with one another to give four σ MOs. (The number of molecular orbitals obtained is always equal to the number of atomic orbitals combined). Each such σ MO contains contributions from all the four sp_z atomic orbitals. But, the greater the contribution of an sp_z atomic orbital, the closer to it will be the resulting molecular orbital. Because of the formation of molecular orbitals (σ type) having contributions from s as well as p_z orbitals, it has been calculated that the energy of σ_1 is lower than the energy of $\sigma(2s)$ orbital of Fig. 27 and the energy of σ_3 orbital is higher than the energy of pure $\sigma(2p_z)$ orbital of Fig. 27. While drawing Fig. 27, it was assumed that $\sigma(2s)$ and $\sigma^*(2s)$ molecular orbitals are formed from $2s$ atomic orbitals of the atoms whereas $\sigma(2p_z)$ and $\sigma^*(2p_z)$ molecular orbitals are formed from $2p_z$ atomic orbitals of the atoms.

The modified molecular orbital energy levels for homonuclear diatomic molecules, where $2s$ and $2p$ atomic orbitals are comparable in energy, are shown in Fig. 29. This order of energy levels has been confirmed spectroscopically.

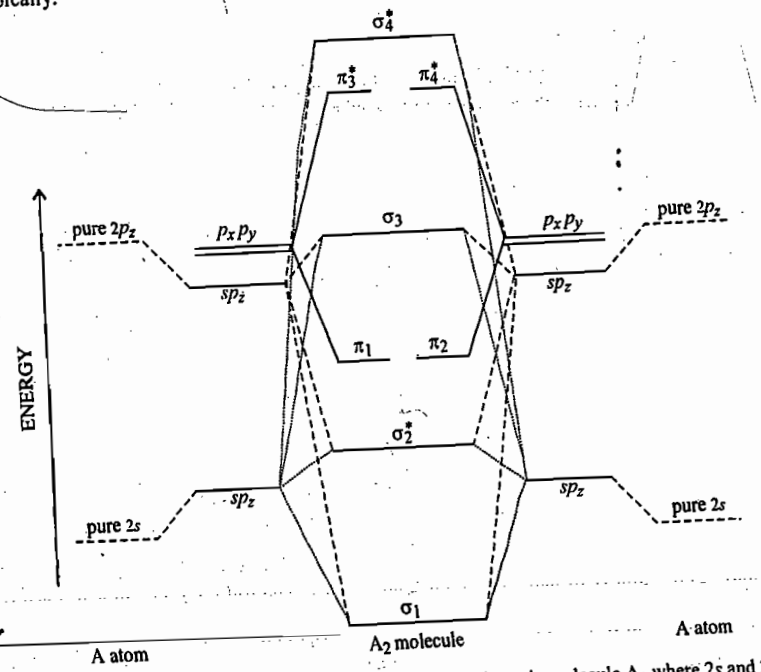


Fig. 29. Modified molecular orbital energy levels of homonuclear diatomic molecule A_2 where $2s$ and $2p$ orbitals are of comparable energy.

In the atoms where the energy difference between $2s$ and $2p$ atomic orbitals is very high, the mixing of $2s$ and $2p_z$ atomic orbitals of an atom is insignificant, even though they are of the same symmetry. Therefore, the atomic orbitals of such atoms as O and F remain almost pure $2s$ and pure $2p_z$ orbitals so that the order of energies of the resulting molecular orbitals of O_2 and F_2 remains the same as shown in Fig. 27. This order has also been confirmed from spectroscopic techniques for O_2 and F_2.

Rules for Adding Electrons to MOs. The molecules are built up by adding electrons to molecular orbitals in the same way as the atoms are built up by adding electrons to atomic orbitals. The principles involved are the same in both cases. These may be summed up as follows :

1. The molecular orbital with lowest energy is filled first.

2. The maximum number of electrons in a molecular orbital cannot exceed two and the two electrons must be of opposite spin.

3. If there are two or more molecular orbitals at the same energy level, pairing of electrons will occur only after each orbital of the same energy has one electron.

Electronic Configurations of Molecules. While discussing the electronic configurations of molecules, we shall frequently make use of a term called **bond order.** This is calculated from the number of electrons in bonding and antibonding molecular orbitals as follows :

$$\textit{Bond order} = \tfrac{1}{2}[\text{ Number of electrons in BMOs} - \text{Number of electrons in ABMOs}]$$

If the number of electrons in bonding and antibonding MOs is the same, the bond order is zero, *i.e.*, no bond is formed. The bond order of 1, 2 or 3 corresponds to single, double or triple bond.

The bond order of a molecule is directly proportional to its bond dissociation energy and inversely proportional to its bond length. This means that the higher the bond order, the larger is the bond dissociation energy of the molecule and the smaller is the bond length.

As would be discussed at appropriate places, the electronic configuration of a molecule helps to predict the magnetic character of the molecule. If all the electrons in a molecule are paired, the substance is *diamagnetic*. On the other hand, if some of the electrons are unpaired, the substance is *paramagnetic*.

Electronic Configurations of Homonuclear Diatomic Molecules. The electronic configurations of some simple diatomic molecules may now be considered.

Hydrogen molecule, H_2. It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in $1s$ orbital and, therefore, there are two electrons to be accommodated in MOs. Both these electrons would be accommodated in the $\sigma(1s)$ BMO. In accordance with Pauli's exclusion principle, these two electrons should have opposite spins. The molecular orbital energy level diagram for H_2 molecule is presented in Fig. 30.

The electronic configuration of H_2 molecule is, thus, $H_2 : \sigma(1s)$ and its **bond order** = 1/2(2 – 0) = 1.

This means that two hydrogen atoms are bonded together by a single bond. The bond dissociation energy of H_2 molecule has been found to be 458 kJ mol^{-1} and bond length equal to 0·74 Å.

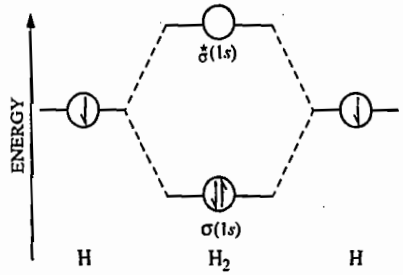


Fig. 30. Molecular orbital energy level diagram of H_2 molecule.

Hydrogen molecule ion, H_2^+. This molecule has been detected spectroscopically when electric discharge is passed through hydrogen gas under reduced pressure. The molecule has only one electron and its electronic configuration is $H_2^+ : \sigma(1s)^2$ and **bond order** = 1/2(1 – 0) = 1/2.

The positive value of bond order indicates that the bond does get formed and the molecule is stable. However, the bond in H_2^+ ion is weaker than that in H_2 molecule. The bond dissociation energy of H_2^+ ion (269 kJ mol^{-1}) is less than that of H_2 molecule (458 kJ mol^{-1}). The bond length in H_2^+ ion (1·04 Å) is larger than that in H_2 molecule (0·74 Å).

Helium molecule, He_2. Each helium atom has two $1s$ electrons and thus there are four electrons to be accommodated in He_2 molecule. Since each molecular orbital, just like atomic orbital, can accommodate only two electrons of opposite spins, only one pair can be accommodated in $\sigma(1s)$ BMO. The other pair will have to be accommodated in $\sigma^*(1s)$ ABMO.

The electronic configuration of He_2 is, thus,

$$He_2 : \sigma(1s)^2\ \overset{*}{\sigma}(1s^2) \text{ and its } \textbf{bond order} = \tfrac{1}{2}(2-2) = 0.$$

The zero bond order indicates that the molecule does not exist. Calculations have shown that the antibonding effect of a filled ABMO is slightly stronger than the bonding effect of a filled BMO. Consequently, there is no possibility whatsoever for the existence of He_2 molecule.

Diatomic Molecules of Second Row Elements. In these elements, the 1*s* orbitals are completely filled. In the formation of molecular orbitals, the electrons in the inner shells (*i.e.*, 1*s* electrons) of each atom remain essentially unperturbed in their respective atomic orbitals and may be kept out of consideration. In the formulation of electronic configurations of these molecules, the letters *KK* are generally used for denoting the fully filled inner shells (*K*-shells) in the two atoms.

Lithium molecule, Li_2. The electronic configuration of lithium (Z = 3) is $1s^2\ 2s^1$. There are six electrons in lithium molecule. The four electrons are present in *K*-shells and there are only two electrons to be accommodated in molecular orbitals. These two electrons go into $\sigma(2s)$ BMO which has lower energy and $\overset{*}{\sigma}(2s)$ ABMO remains empty.

The electronic configuration of Li_2 molecule is thus represented as

$$Li_2 : KK\,\sigma(2s)^2 \quad \text{or} \quad KK\,\sigma_1^2 \text{ and its } \textbf{bond order} = \tfrac{1}{2}(2-0) = 1$$

Thus, there is one Li – Li sigma bond. The bond dissociation energy of the molecule is quite low, being about 105 kJ mol^{-1}. The bond length of the molecule is 2·67 Å.

Beryllium molecule, Be_2. The next element beryllium (Z = 4) has electronic configuration $1s^2\ 2s^2$. In the formation of a diatomic molecule, evidently, two outer electrons of each atom, *i.e.*, four in all, have to be accommodated in molecular orbitals. Two of these (one pair) will go into $\sigma(2s)$ BMO while the other two (the second pair) will have to go into $\overset{*}{\sigma}(2s)$ ABMO.

The electronic configuration of Be_2 molecule is, thus,

$$Be_2 : KK\sigma(2s)^2\overset{*}{\sigma}(2s)^2 \quad \text{or} \quad KK\sigma_1^2\overset{*}{\sigma}{}_2^2 \text{ and its } \textbf{bond order} = \tfrac{1}{2}(2-2) = 0.$$

The zero bond order suggests that the existence of stable Be_2 molecule is not possible.

Boron molecule, B_2. The electronic configuration of boron (Z = 5) is $1s^2\ 2s^2p^1$. The outer shell (*i.e.*, the second shell) of each atom contains 3 electrons. When two boron atoms combine to form the molecule B_2, there are 6 electrons which need to be accommodated in the molecular orbitals of B_2. Two of these will be accommodated in $\sigma(2s)$ molecular orbital (*i.e.*, σ_1 MO) which has the lowest energy and the other two in $\overset{*}{\sigma}_2$ molecular orbital which comes next in the order of increasing energy. Due to the mixing of orbitals as discussed above, the energies of MOs would be as shown in Figs. 28 and 29. Accordingly, the $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbitals (*i.e.*, π_1 and π_2 orbitals) lie at lower energy level than the σ_3 molecular orbital. Since $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbitals (*i.e.*, π_1 and π_2 MOs) have equal energies, therefore, the two electrons distribute themselves between these two orbitals, one going to each orbital according to rule 3 above. As both these π molecular orbitals are bonding molecular orbitals, the B_2 molecule is expected to be stable. Further, since each bonding molecular orbital contains a single, *i.e.*, an unpaired electron, the molecule B_2 is *paramagnetic* as is experimentally observed. (Had there been no mixing of orbitals, the order of energy levels should have been as shown in Fig. 27 and the configuration of B_2 would have been $KK(\sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\sigma 2p_z^2$, *i.e.*, the molecule B_2 should have been diamagnetic which is contrary to experimental observation). The electronic configuration of B_2 molecule is, thus,

$$B_2 : KK\sigma(2s)^2\overset{*}{\sigma}(2s)^2\pi(2p_x)^1\pi(2p_y)^1 \quad \text{or} \quad KK\sigma_1^2\overset{*}{\sigma}{}_2^2\,\pi_1\pi_2$$

and its **bond order** $= \tfrac{1}{2}(4-2) = 1$

The molecule has only one bond. The bond dissociation energy of B_2 molecule has been found to be 289 kJ mol^{-1} and bond length equal to 1·59 Å.

Carbon molecule, C_2. The next element is carbon (Z = 6). Its electronic configuration is $1s^2\,2s^2 2p^2$. The outer shell of each atom contains 4 electrons. In the formation of C_2 molecule, there will be, evidently, 8 electrons to be accommodated in the molecular orbitals of C_2 in accordance with Figs. 28 and 29. The electronic configuration of C_2 molecule is

$$C_2 : KK(2s)^2\overset{*}{\sigma}(2s)^2\pi(2p_x)^2\pi(2p_y)^2 \quad \text{or} \quad KK\sigma_1^2\overset{*}{\sigma}{}_2^2\,\pi_1^2\pi_2^2$$

and its **bond order** = 1/2(6 – 2) = 2

Since, C_2 molecule does not have any unpaired electron, it is *diamagnetic*, as observed experimentally.

The bond dissociation energy of C_2 molecule has been found to be 627·9 kJ mol^{-1} and bond length equal to 1·31 Å.

It may be noted that in this case also, the $\sigma(2p_z)$ or σ_3 molecular orbital is left vacant indicating that it is at a higher energy level than the π_1 and π_2 molecular orbitals. If, in accordance with the energy level diagram shown in Fig. 27, six electrons had gone into $\sigma(2s)$, $\overset{*}{\sigma}(2s)$ and $\sigma(2p_z)$ molecular orbitals, the remaining two electrons would have distributed themselves equally between the two $\pi(2p)$ molecular orbitals which are of equal energy. In that case, the molecule C_2, having two unpaired electrons, would have been paramagnetic. But actually the molecule is diamagnetic. This can be explained only on the basis of the reversal of energies of $\sigma(2p_z)$, *i.e.*, σ_3 and $\pi(2p_x)$, and $\pi(2p_y)$, *i.e.*, π_1 and π_2, molecular orbitals as a result of mixing of molecular orbitals, as discused earlier.

Nitrogen molecule, N_2. Consider, next, the formation of N_2 molecule. The electronic configuration of nitrogen (Z = 7) is $1s^2\ 2s^2\ p^3$. The outer shell in this case contains 5 electrons. Thus, there are 10 electrons to be accommodated in the molecular orbitals of N_2. The electronic configuration of nitrogen molecule is, thus,

$$N_2 : KK\,\sigma(2s)^2\,\overset{*}{\sigma}(2s)^2\pi(2p_x)^2\,\pi(2p_y)^2\,\sigma(2p_z)^2 \text{ or } KK\,\sigma_1^2\,\overset{*}{\sigma}{}_2^2\,\pi_1^2\,\pi_2^2\,\sigma_3^2$$

and its **Bond order** $= \tfrac{1}{2}(8-2) = 3$

Thus, nitrogen molecule contains a **triple bond.**

It is evident that in the formation of N_2 molecule, only one antibonding molecular orbital is involved (the remaining four being all bonding molecular orbitals). Hence, the nitrogen molecule is highly stable. This is confirmed by its high bond dissociation energy, *viz.*, 945·6 kJ mol^{-1} and small bond length equal to 1·10 Å. Also, since there are no unpaired electrons in any orbital, N_2 molecule is *diamagnetic.*

Oxygen molecule, O_2. As already explained, there is negligible mixing of 2*s* and 2*p* atomic orbitals on each O atom. Therefore, the order of energy levels in O_2 is as given in Fig. 27. The electronic configuration of oxygen (Z = 8) is $1s^2\,2s^2p^4$. In the formation of O_2 molecule, 12 outer electrons are to be accommodated in MOs. Four of these electrons fill the $\sigma(2s)$ and $\overset{*}{\sigma}(2s)$ molecular orbitals. Six of them (*i.e.*, 3 pairs) go into the three bonding MOs, *viz.*, $\sigma(2p_z)$, $\pi(2p_x)$ and $\pi(2p_y)$ and the remaining two electrons go into the antibonding MOs. The lowest ones are $\overset{*}{\pi}(2p_x)$ and $\overset{*}{\pi}(2p_y)$. Since both these orbitals are of equal energy, the electrons will distribute themselves one in each orbital. Since there are now two unpaired electrons, the oxygen molecule is *paramagnetic.*

The electronic configuration of oxygen molecule is, thus

$$O_2 : KK\sigma(2s)^2\overset{*}{\sigma}(2s)^2\sigma(2p_z)^2\pi(2p_x)^2\pi(2p_y)^2\overset{*}{\pi}(2p_x)^1\overset{*}{\pi}(2p_y)^1 \text{ or } KK\,\sigma_1^2\,\overset{*}{\sigma}{}_2^2\,\sigma_3^2\,\pi_1^2\,\pi_2^2\,\overset{*}{\pi}{}_3^1\,\overset{*}{\pi}{}_4^1$$

Bond order in this case is $= \tfrac{1}{2}(8-4) = 2$. Oxygen molecule, thus, contains a double bond.

Because of the presence of 4 electrons in ABMOs, oxygen molecule is less stable than nitrogen molecule. Its bond dissociation energy is much less, being 494·6 kJ mol^{-1} and bond length is larger being 1·21 Å.

Fluorine molecule, F_2. Because of large energy difference in 2*s* and 2*p*, orbitals on each F atom, the mixing of these orbitals is negligible and the order of MO energy levels will be as shown in Fig. 27. The electronic configuration of fluorine (Z = 9) is $1s^2 2s^2 p^5$. In the formation of F_2 molecule by the combination of two fluorine atoms, there would be 14 outer electrons to be accommodated in molecular orbitals.

The electronic configuration of fluorine molecule is, thus,

$$F_2 : KK\sigma(2s)^2\, \overset{*}{\sigma}(2s)^2\, \sigma(2p_z)^2\, \pi(2p_x)^2\, \pi(2p_y)^2\, \overset{*}{\pi}(2p_x)^2\, \overset{*}{\pi}(2p_y)^2 \quad \text{or} \quad KK\ \sigma_1^2\ \sigma_2^{*2}\ \sigma_3^2\ \pi_1^2\ \pi_2^2\ \pi_3^{*2}\ \pi_4^{*2}$$

Bond order in this case is $= \frac{1}{2}(8-6) = 1$. The F_2 molecule, thus, contains a single bond. Because of the presence of as many as 6 electrons in ABMOs, the bonding in F_2 is weaker than that in O_2. Therefore, bond dissociation energy of F_2 is very low being 155 kJ mol^{-1} and bond length is 1·42 Å.

Since there are no unpaired electrons, the molecule is *diamagnetic*.

Neon molecule, Ne_2. The order of energy levels in hypothetical Ne_2 should be as given in Fig. 27 because the energy gap between 2*s* and 2*p* orbitals on Ne is very high and the extent of their mixing will be negligible. The electronic configuration of neon (Z = 10), is $1s^2 2s^2 p^6$. In the formation of Ne_2, if possible, 16 outer electrons have to be accommodated in molecular orbitals.

The electronic configuration of *hypothetical* neon molecule is

$$Ne_2 : \quad KK\ \sigma(2s)^2\, \overset{*}{\sigma}(2s)^2\, \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2\, \overset{*}{\pi}(2p_x)^2\, \overset{*}{\pi}(2p_y)^2\, \overset{*}{\sigma}(2p_z)^2$$

or

$$KK\ \sigma_1^2\ \sigma_2^{*2}\ \sigma_3^2\ \pi_1^2\ \pi_2^2\ \pi_3^{*2}\ \pi_4^{*2}\ \sigma_4^{*2}$$

Bond order in this case is equal to $= \frac{1}{2}(8-8) = 0$. Since antibonding MOs slightly dominate over the bonding MOs, Ne_2 molecule would be incapable of existence.

Problem 1. Write the electronic configurations of H_2, H_2^+ and the H_2^- in terms of molecular orbital theory.

Answer. H_2, H_2^+ and H_2^- have 2, 1 and 3 electrons, respectively. Hence, their electronic configurations would be as follows :

H_2 : $\sigma(1s)^2$

H_2^+ : $\sigma(1s)^1$

H_2^- : $\sigma(1s)^2\, \overset{*}{\sigma}(1s)^1$

Problem 2. Why does He_2^+ exist whereas He_2 does not ?

Answer : Electronic configuration of He_2 is : $\sigma(1s)^2\, \overset{*}{\sigma}(1s)^1$

$\therefore$ **Bond order** $= 1/2\,(2-2) = 0$

Electronic configuration of He_2^+ is : $\sigma(1s)^2\, \overset{*}{\sigma}(1s)^1$

$\therefore$ **Bond order** $= 1/2\,(2-1) = 1/2$

Thus, while the bond order of He_2 is zero, that of He_2^+ is 1/2. Hence, He_2^+ exists while He_2 does not.

Problem 3. Of the species O_2, O_2^+ O_2^-, O_2^{2-}, which would have the maximum bond strength ?

Answer : Higher bond orders are associated with shorter bond lengths and higher bond strengths. We will first calculate the bond orders for the various species from their electronic configurations :

$$O_2 : KK\ \sigma(2s)^2\, \overset{*}{\sigma}(2s^2)\, \sigma(2p_z)^2\, \pi(2p_x)^2\, \pi(2p_y)^2\, \overset{*}{\pi}(2p_x)^1\, \overset{*}{\pi}(2p_y)^1$$

$\therefore$ **Bond order** $= 1/2\,(8-4) = 2$

O_2^+ : One electron is removed from $\overset{*}{\pi}(2p_y)$ ABMO.

$\therefore$ **Bond order** $= 1/2\,(8-3) = 2\frac{1}{2}$

O_2^- : One electron is added to $\overset{*}{\pi}(2p_x)$ ABMO.

$\therefore$ **Bond order** $= 1/2\,(8-5) = 1\frac{1}{2}$

O_2^{2-} : Two electrons are added to the outermost ABMO.

$\therefore$ **Bond order** $= 1/2\,(8-6) = 1$

Since O_2^+ has the highest bond order, it has the shortest bond length and hence the maximum bond strength.

Electronic Configurations of Heteronuclear Diatomic Molecules

The cases of heteronuclear diatomic molecules, in which the two atoms constituting a molecule are different, may now be considered. The principles involved in the distribution of electrons are the same as discussed before.

However, the molecular orbital diagrams will not be symmetrical as in the case of homonuclear diatomic molecules. Due to the difference in the electronegativities of the atoms, the electrons in a bonding molecular orbital spend more time near the more electronegative atom. On the other hand, electrons in an antibonding molecular orbital are closer to the less electronegative atom.

While discussing the molecular orbital energy level diagrams of heteronuclear diatomic molecules, it should be kept in mind that all the atomic orbitals of same symmetry will contribute in the formation of an equal number of molecular orbitals. Any molecular orbital thus formed will have greatest contribution from that combining atomic orbital which is nearest to it in energy and least contribution from that combining atomic orbital which is farthest to it in energy.

Let us discuss the electronic configurations and molecular orbital diagrams for some common heteronuclear diatomic molecules.

Carbon Monoxide Molecule, CO. The electronic configurations of C and O atoms are $1s^2 2s^2 p^2$ and $1s^2 2s^2 p^4$, respectively. There are 4 electrons in the outer shell of carbon and 6 electrons in the outer shell of oxygen. Thus, a total of 10 outer electrons are to be accommodated in the molecular orbitals of CO molecule. Because of higher electronegativity of oxygen, its atomic orbitals would be of lower energy than the corresponding atomic orbitals of carbon. Due to this energy difference, the bonding and antibonding molecular orbitals receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals receive more contribution from atomic orbitals of lower energy, *i.e.*, the atomic orbitals of oxygen and would be closer to it in energy than the antibonding molecular orbitals which would be closer to the atomic orbitals of carbon in energy, as shown in Fig. 31. The bonding molecular orbitals would have more characteristics of atomic orbitals of oxygen and antibonding molecular orbitals would have more characteristics of atomic orbitals of carbon.

The $2s$ and $2p_z$ atomic orbitals of C atom mix to produce two atomic orbitals of mixed sp_z character. The higher energy mixed sp_z orbital of C atom is closer in energy to its pure $2p_z$ orbital and has major contribution from it whereas the lower energy mixed sp_z orbital of C is closer in energy to its pure $2s$ orbital and has major contribution from it. Similarly, $2s$ and $2p_z$ atomic orbitals of oxygen atom also mix with each other (though not to the same extent to which the orbitals of C atom mix because the energy difference between $2s$ and $2p_z$ atomic orbitals of oxygen atom is higher than that between the similar atomic orbitals of C atom) to form two atomic orbitals of mixed sp_z character. The higher energy mixed sp_z orbital of O is very close in energy to its pure $2p_z$ orbital and has contribution mostly from $2p_z$ orbital whereas the lower energy mixed sp_z orbital, being very close in energy to pure $2s$ orbital of oxygen atom, has contribution mostly from $2s$ orbital of oxygen atom.

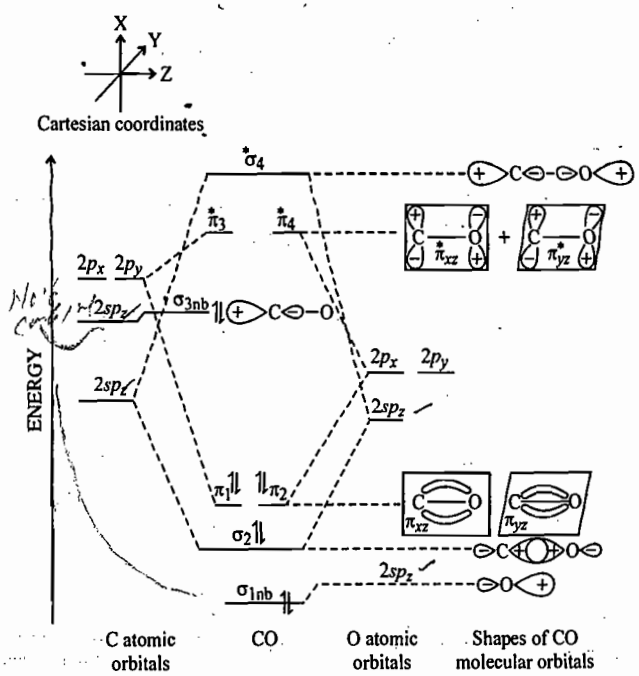


Fig. 31. Molecular orbital energy level diagram (with shapes of molecular orbitals) of CO molecule. Positions of pure $2s$ and $2p_z$ orbitals of C and O are not shown.

Since the orbital energies are lower for more electronegative O atom compared to the energies of similar orbitals of C atom, the lower energy mixed sp_z orbital of C atom is comparable in energy to the higher energy sp_z orbital of O atom, as shown in MOEL diagram of CO (Fig. 31). These two atomic orbitals of comparable energy and of same symmetry combine to give σ bonding and antibonding molecular orbitals. The lower energy sp_z orbital on O and the higher energy sp_z orbital on C atom are so far apart in energy that they *hardly* influence each other with the result that their energies remain almost unchanged. In other words, these orbitals remain *almost* non bonding. As already discussed above, the non bonding sp_z orbital on C (shown as σ_{3nb} in the figure) will have more characteristics of $2p_z$ orbital of C atom and the non bonding sp_z orbital on O atom (σ_{1nb} in the figure) will have more characteristics of $2s$ orbital of O atom. The degenerate set of $2p_x$, $2p_y$ orbitals of C and the similar degenerate set of $2p_x$, $2p_y$ orbitals of oxygen are of π symmetry to form a set of degenerate π_1, π_2 bonding molecular orbitals and another set of degenerate antibonding molecular orbitals. The electronic configuration of CO molecule is, therefore,

$$KK'\ \sigma_{1nb}^2\ \sigma_2^2\ \pi_1^2\ \pi_2^2\ \sigma_{3nb}^2$$

and the **bond order** of CO molecule is obviously 3 (due to two σ bonding and four π bonding electrons. The electrons in the non bonding orbitals do not contribute towards bonding.

Since σ_{3nb} is the highest placed occupied non bonding orbital localised on C atom, its electron pair can easily be donated for forming dative (or coordinate) bond.

Nitric Oxide Molecule, NO. The electronic configurations of N and O atoms are $1s^2 2s^2 p^3$ and $1s^2 2s^2 p^4$, respectively. There are 5 electrons in the outer shell of nitrogen and 6 electrons in the outer shell of oxygen. Thus, a total of 11 outer electrons are to be accommodated in the molecular orbitals of NO molecule.

The spectroscopic data reveal that the order of energy levels in NO molecule is similar to the order of energy levels in O_2 and F_2 molecules meaning that due to considerable energy difference between $2s$ and $2p_z$ atomic orbitals, the mixing of orbitals on each atom is insignificant.

The electronic configuration of NO molecule is, thus,

$$NO : KK\ \sigma(2s)^2\ \sigma^*(2s)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \pi^*(2p_x)^1 \quad \text{or} \quad KK'\ \sigma_1^2\ \sigma_2^{*2}\ \sigma_3^2\ \pi_1^2\ \pi_2^2\ \pi_3^{*1}$$

The **bond order** in this case is $1/2(8-3) = 2\frac{1}{2}$. This represents one σ bond and two π bonds less the antibonding effect of one unpaired electron in the π_3^* molecular orbital. The presence of this antibonding electron makes the NO molecule less stable than the N_2 molecule. This is confirmed by the fact that the bond dissociation energy of nitric oxide, *viz.*, 667·8 kJ mol^{-1}, is less than that of nitrogen which is 945·6 kJ mol^{-1}. Since NO contains an unpaired electron, it is *paramagnetic*.

As in the case of CO molecule, the bonding molecular orbitals would have greater characteristics of atomic orbitals of oxygen and the antibonding molecular orbitals would have greater characteristics of atomic orbitals of nitrogen.

Hydrogen Flouride Molecule, HF. The valence shell atomic orbitals of the same symmetry are $1s$ atomic orbital of H and $2s$ and $2p_z$ atomic orbitals of F (the z-axis is assumed to be the internuclear axis). The two $2s$ and $2p_z$ of F, being of the same symmetry, can mix with each other. However, the extent of mixing of $2s$ and $2p_z$ orbitals will be *small* because the energy gap between these two orbitals is *high*. (For effective mixing of orbitals of same symmetry, the energy gap between them should be low).

The higher energy mixed orbital of F has predominantly p_z character with very little s character and will lie only a *little lower* in energy than the pure p_z orbital. Similarly, the lower energy mixed orbital has predominantly $2s$ character with only a little $2p_z$ character and lies *slightly higher* in energy than the pure $2s$ orbital. The $1s$ orbital of hydrogen atom is more comparable in energy to the higher energy mixed sp_z orbital (which is practically $2p_z$ orbital) of F. The two combine to give σ_1 bonding and σ_3^* antibonding molecular orbitals. The lower energy mixed sp_z orbital of F *cannot effectively combine* with $1s$ orbital of H atom due to large energy difference between this mixed orbital and $1s$ orbital of H atom and, therefore, remain *almost* non bonding (σ_{2nb}) orbital. The molecular orbital energy level diagram of HF is shown in Fig. 32.

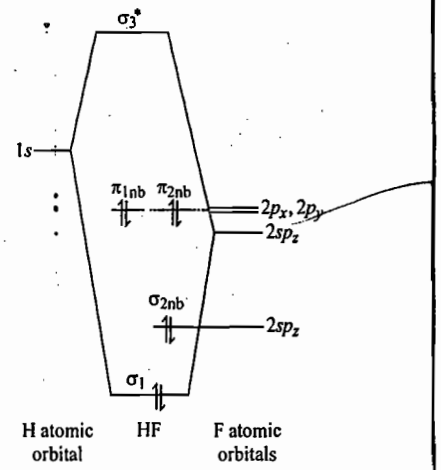


Fig. 32. Molecular orbital energy level diagram of HF molecule. The positions of pure $2p_z$ and $2s$ orbitals of F atom are not shown.

The $2p_x$ and $2p_y$ orbitals of F are suitable for forming only π bonding and antibonding molecular orbitals. Since there are no orbitals of the same symmetry as that of H atom, these remain non bonding and are designated in the figure as π_{1nb} and π_{2nb}. It is clear from the above discussion that σ_1 will have more contribution from $2p_z$ atomic orbital of F and less contribution from $1s$ atomic orbital of F atom whereas σ_3^* will have more contribution from $1s$ orbital of H atom and less contribution from $2p_z$ orbital of H atom. The electronic configuration of HF molecule is thus,

$$K\ \sigma_1^2\ \sigma_{2nb}^2\ \pi_{1nb}^2\ \pi_{2nb}^2$$

and the **bond order** is obviously 1 since only two electrons occupy the bonding molecular orbital σ_1 (the rest of the valence electrons are in non bonding orbitals).

As can be visualised, all the occupied orbitals are either pure F orbitals or have predominantly F orbital characteristics. Therefore, most of the electronic charge will be localised on F atom. This fact is corroborated by a considerably high dipole moment (1·9 D) observed for HF molecule.

Hydrogen Chloride Molecule, HCl. The treatment in this case is exactly similar to the one discussed for HF molecule except for the fact that the valence shell atomic orbitals of the same symmetry that are considered for the formation of molecular orbitals, are 1*s* atomic orbital of H atom and 3*s* and $3p_z$ orbitals of Cl atom. The electronic configuration of HCl molecule is :

$$KL\ \sigma_1^2\ \sigma_{2nb}^2\ \pi_{1nb}^2\ \pi_{2nb}^2$$

and the **bond order** is 1 due to two electrons in bonding molecular orbital. In the case of HCl molecule also, all the occupied orbitals are either pure Cl orbitals or have predominantly Cl orbital character. Therefore, most of the electronic charge gets accumulated on Cl atom of HCl making it considerably polar.

Term Symbols for Diatomic Molecules

Term symbols are used to designate electronic energy levels which arise out of an electronic configuration because of electrostatic repulsions amongst the electrons of a molecule. These terms are very helpful in understanding electronic spectra of molecules.

The term symbols employed for diatomic molecules are written in the following manner :

1. The symbols Σ, π and Δ are used to represent values 0, 1 and 2, respectively for $|M_L|$ or Σm_l of electrons in the diatomic molecules where m_l is the component of orbital angular momentum of a single electron along the nuclear axis and $|M_L|$ is the absolute value of similar overall component for all the electrons in the diatomic molecule. The m_l is 0, ±1 and ± 2 for an electron in σ, π and δ molecular orbitals, respectively.

2. Since all homonuclear diatomic molecules have a centre of symmetry in the middle of their nuclear axis, the overall symmetry to inversion is indicated by u or g and is written as a right subscript of Σ, π, Δ.

3. The electron spin multiplicity is indicated by 2*S* + 1 as the left superscript of Σ, π and Δ (*S* is the total spin of electrons in the system).

4. The term symbol is written as $^{2S+1}|M_L|_{g \text{ or } u}$.

For example, consider a H_2 molecule whose ground state electronic configuration is $\sigma^2(1s)$.

In this case, *S* (*i.e.*, $s_1 + s_2$) is 0 and $|M_L|$, *i.e.*, $(m_{l_1} + m_{l_2})$ is also 0. The σ_{1s} molecular orbital is symmetric with respect to the centre of inversion located in the middle of the nuclear axis, Therefore, the term symbol for σ_{1s}^2 should be $g \times g = g$ type. Hence, the term symbol $^{2S+1}M_{L_{g \text{ or } u}}$ for H_2 molecule in its ground state, is $^1\Sigma_g$.

Consider now hydrogen ion, H_2^+. Its ground state electronic configuration is σ_{1s}^1 so that $S = \frac{1}{2}$ and $2S + 1 = 2$. Since $|M_L| = 0$, hence the term symbol for its ground state. is $^2\Sigma_g$.

Let us now work out the term symbols for O_2 molecule. The ground state electronic configuration of O_2 is $\sigma_1^2\ \sigma_2^2\ \sigma_3^2\ \pi_1^2\ \pi_2^2\ \overset{*}{\pi}_3^1\ \overset{*}{\pi}_4^1$. The electrons in the filled sigma molecular orbitals and the completely filled degenerate set of pi orbitals contribute nothing to the overall component of angular momentum M_L along the nuclear axis. Since both the $\overset{*}{\pi}$ molecular orbitals are symmetric with respect to the centre of symmetry of the oxygen molecule, the term symbol will be $g \times g = g$ type.

Let us first consider the case when both the unpaired electrons in $\overset{*}{\pi}$ molecular orbitals have opposite spins. The m_l for each electron in $\overset{*}{\pi}$ molecular orbital will be +1 or −1 so that $|M_L| = 0$ or 2 and $2S + 1 = 1$ (because *S* is $\frac{1}{2} - \frac{1}{2} = 0$). The term symbols which arise from this situation are $^1\Sigma_g$ and $^1\Delta_g$.

Now consider the case when the spins of both the electrons are in the same direction so that $S = \frac{1}{2} + \frac{1}{2} = 1$ and the spin multiplicity is 3. Since spins of both the electrons in $\overset{*}{\pi}$ orbitals are in the same

direction, their m_l values *have* to be different (Paulis' exclusion principle). That is, m_l for one electron is +1 and for the other electron it is −1 (The + and − signs indicate whether the component of angular momentum m_l is parallel or antiparallel to the nuclear axis). Therefore, $|M_L|$ can only be 0 so that the term is $^3\Sigma_g$.

Out of $^3\Sigma_g$, $^1\Sigma_g$ and $^1\Delta_g$, the first term, *i.e.*, $^3\Sigma_g$, having maximum multiplicity will evidently represent the ground state term of the molecule.

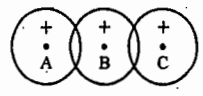
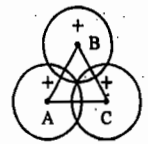
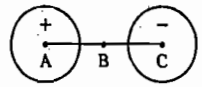
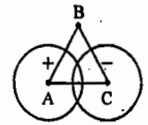
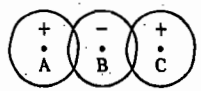
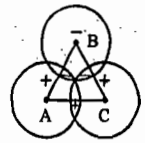
The student is advised to work out the terms for Li_2, Be_2, N_2, F_2, F_2^+ molecules himself.

The term symbols for heteronuclear diatomic molecules are derived in a similar manner. Since a heteronuclear diatomic molecule has no centre of symmetry, we do not write the subscript *g* or *u* in the term symbols of such molecules.

The Σ terms are sometimes further codified by writting + or − as a right superscript depending upon whether the system is symmetric or asymmetric with respect to a plane of symmetry passing through the nuclear axis.

Molecular Orbitals of Polyatomic Species

H_3^+ Ion. The three 1*s* orbitals of H_A, H_B and H_C atoms can overlap with one another to produce an equal number of molecular orbitals. The H_3^+ ion thus formed can either have a linear geometry or a triangular planar geometry leading to two different sets of sigma overlaps. But, in both cases the linear combinations of three 1*s* atomic orbitals can be represented by the same three ψ_{MOs} in the following manner :

Various Combinations of AOs of H_A, H_B and H_C	Diagrammatic Representation for	
	Linear Geometry	Triangular Geometry
$\sigma_1 = \psi_{1MO} = \frac{1}{\sqrt{3}}\left[(\psi_{1s(A)} + \psi_{1s(B)} + \psi_{1s(C)})\right]$		
$\sigma_2 = \psi_{2MO} = \frac{1}{\sqrt{2}}\left[(\psi_{1s(A)} - \psi_{1s(C)})\right]$		
$\sigma_3 = \psi_{3MO} = \frac{1}{\sqrt{6}}\left[(\psi_{1s(A)} - 2\psi_{1s(B)} + \psi_{1s(C)})\right]$		

It is to be noted that each of the σ_1, σ_{2sp} and σ_3 is a normalised function and that each ψ_{1s} is completely utilised while writting σ_1, σ_2 and σ_3. The sum of the squares of the coefficients of each of ψ_{1s} in σ_1, σ_2 and σ_3 is 1.

For H_3^+ ion having linear geometry, σ_1, which has positive overlaps between the three 1*s* orbitals, is obviously a bonding molecular orbital. The molecular orbital σ_2 in a linear geometry cannot have any

overlap and is, therefore, nonbonding while σ_3, having a negative overlap in this geometry is obviously antibonding. The two electrons of H_3^+ will occupy the bonding molecular orbital σ_1 if its geometry is linear.

For H_3^+ ion having triangular geometry, σ_1 is bonding molecular orbital having positive overlaps as is obvious from the figure but σ_2, in which H_A and H_C orbitals form a negative overlap, is antibonding and is thus of higher energy than σ_2 of linear geometry. The molecular orbital σ_3 of triangular geometry is bonding between H_A and H_C involving positive overlaps but is antibonding between H_A and H_B as also between H_B and H_C involving negative overlaps. Therefore, σ_3 of triangular geometry, though antibonding, is of lower energy than σ_3 of linear geometry (why ?). Further it can be shown with the application of group theory that σ_2 and σ_3 of triangular geometry are of equal energy. It can be easily visualised that the triangular planar geometry can be obtained from linear geometry by bending ∠ABC from 180° to 60°. The energies of σ_1, σ_2, σ_3 as a function of ∠ABC can be *calculated*. If a correlation diagram is drawn in the case of H_3^+, it would clearly indicate that a triangular geometry of H_3^+ is more stable than the linear geometry. This is because σ_1 bonding molecular orbital which contains both the bonding electrons is of lower energy in the triangular geometry of H_3^+ because of greater overlaps amongst H_A, H_B and H_c than in its linear geometry, as shown in Fig. 33.

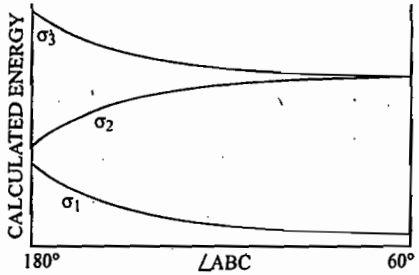
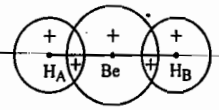


Fig. 33. Plot of calculated energies of molecular orbitals as a function of bond angle.

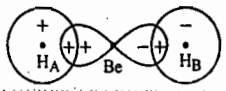
Walsh Diagrams. Normally, we explain the experimentally observed geometries of molecules by certain devised theories and concepts such as VSEPR theory, hybridisation, etc. But Walsh actually calculated the energies of molecular orbitals of a reference geometry and its several distortions for simple triatomic molecules. He correctly predicted the actual geometries of a number of simple triatomic molecules like H_3^+, H_2O, BeH_2, etc., by plotting a graph between the calculated energies of molecular orbitals of the reference geometry and those of the distorted geometries of a molecule *vs* the distortion parameter, *i.e.*, bond angle. The position of minimum energy of the filled molecular orbitals in the graph indicates the most stable geometry of the molecule. Such graphs are known as **Walsh diagrams.** Fig.33 discussed above, in one such diagram.

Beryllium Hydride Molecule, BeH_2. The BeH_2 molecule in gaseous state is linear. It has $D_{\infty h}$ symmetry and contains σ bonds only. From symmetry considerations, the atomic orbitals of Be capable of forming σ bonds in BeH_2 molecule are 2*s* and $2p_z$ orbitals. The p_x and p_y orbitals of Be are not suited for forming σ bonds. The orbitals of the two H atoms which are capable of forming σ bonds are 1*s* atomic orbitals. The two linear combinations of 1*s* atomic orbitals of H which are capable of forming σ bonds with 2*s* and $2p_z$ orbitals of Be are $(\psi_{1s(H_A)} + \psi_{1s(H_B)})$ and $(\psi_{1s(H_A)} - \psi_{1s(H_B)})$. The bonding and antibonding linear combinations of these orbitals are shown below. The bonding combinations have a net positive overlap of orbitals whereas antibonding combinations have a net negative overlap.

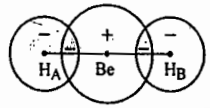
$$\sigma_1 \text{ (bonding)} = a\psi_{2s}(\text{Be}) + b[(\psi_{1s}(H_A) + (\psi_{1s}(H_B)] \quad \ldots$$



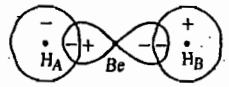
$$\sigma_2 \text{ (bonding)} = c\psi_{2p_z}(\text{Be}) + d[\psi_{1s}(H_A) - (\psi_{1s}(H_B)] \quad \ldots$$



$$\sigma_3 \text{ (antibonding)} = b\psi_{2s}(\text{Be}) - a[\psi_{1s}(H_A) + (\psi_{1s}(H_B)] \quad \ldots$$



$$\sigma_4 \text{ (antibonding)} = d\psi_{2p_z}(\text{Be}) - c[(\psi_{1s}(H_A) - (\psi_{1s}(H_B)] \quad \ldots$$



The molecular orbital energy level diagram of BeH_2 is shown in Fig. 34.

The four valence electrons occupy σ_1 and σ_2 bonding molecular orbitals.

The above simple molecular orbital treatment does not explain the equivalence of the two Be → H bonds which is experimentally established. For explaining this, the concept of hybridisation has to be introduced which is discussed in detail in the next chapter.

Although we began the discussion on BeH_2 by considering the actually observed linear geometry of the molecule, it will be shown with the help of Walsh diagram for AH_2 type of molecules (A belongs to the second period) that any nonlinear or bent geometry of the molecule AH_2 which has *only* 4 valence electrons to be accommodated in its molecular orbitals, will be of higher energy compared to the energy of linear geometry.

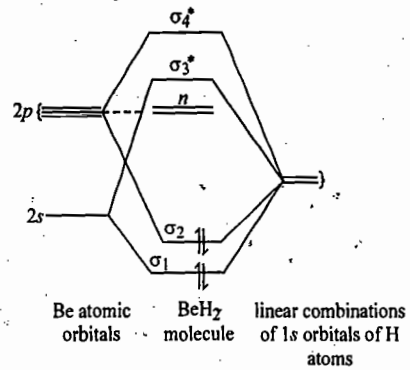
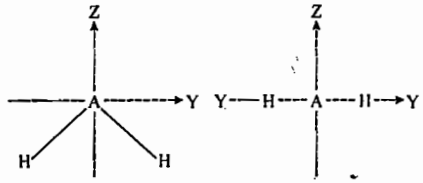


Fig. 34. Molecular orbital energy level diagram of BeH_2 molecule.

Walsh Diagrams for AH_2 Molecules

Consider a molecule AH_2 where the element A belongs to the second period of the periodic table. The molecule AH_2 can either have an angular geometry with c_{2v} symmetry or a linear geometry with $D_{\infty h}$ symmetry. The only orbital available with H atom for bonding is 1*s* orbital and the symmetry-adapted linear combinations of the two 1*s* orbitals of hydrogen atoms which are capable of forming bonds with orbitals of atom A in both the angular and the linear geometry are $\psi_{1s(H_A)} + \psi_{1s(H_B)}$ and $\psi_{1s(H_A)} - \psi_{1s(H_B)}$. These combinations are of a_1 and b_2 symmetry, respectively, in the angular AH_2 molecule and of a_{1g} and a_{1u} symmetry, respectively, in the linear AH_2 molecule.

In the angular AH_2 molecule, the two atomic orbitals of A of a_1 symmetry are 2*s* and $2p_z$ orbitals and the one with b_2 symmetry is the p_y orbital. In the linear AH_2 molecule, the atomic orbital of A which is of a_{1g} symmetry is 2*s* and the atomic orbital of A which is of a_{1u} symmetry is $2p_y$. Consider the axes Y and Z which pass through A and lie in the plane of paper as shown :



We shall first consider bonding in angular AH_2. The combination $(\psi_{1s(H_A)} + \psi_{1s(H_B)})$, which is of a_1 symmetry, combines with two mixed $2sp_z$ orbitals of *A* also of a_1 symmetry, to give three molecular orbitals $1a_1$, $2a_1$ and $3a_1$. The bonding $1a_1$ molecular orbital utilises the mixed sp_z orbital of A having predominant $2p_z$ character and the bonding $2a_1$ molecular orbital utilises the mixed sp_z orbital of A having predominant 2*s* character in the angular AH_2 molecule with ∠HAH of 90°. As the bond angle increases, the participation of $2p_z$ orbital in the mixed sp_z orbital in $1a_1$ decreases and that of 2*s* orbital increases with the result that in the linear geometry of AH_2, it is only the 2*s* orbital (of a_{1g} symmetry) which combines with the combination $\psi_{1s(H_A)} + \psi_{1s(H_B)}$ (also of a_{1g} symmetry) to give the bonding molecular orbital $1a_{1g}$. Since the $2p_z$ orbital of A is of higher energy than the 2*s* orbital, the lesser and lesser participating of $2p_z$ in molecular orbital $1a_1$, will cause a greater and greater decrease in the energy of the molecular orbital in going from the angular AH_2 molecule (∠HAH of 90°) to the linear AH_2 molecule (∠HAH of 180°).

Similarly, in the $2a_1$ molecular orbital in the angular AH_2 molecule, the contribution of $2s$ orbital goes on decreasing with increase in ∠HAH with the result that in the linear AH_2 molecule with ∠HAH = 180°, there is zero contribution of $2s$ orbital. The contribution of the $2p_z$ orbital, on the other hand, goes on increasing with increase in ∠HAH from 90° to 180°. However, $2p_z$ orbital in linear molecule is non-bonding because in the linear molecule ψ_{2pz} and the combination $(\psi_{1s(H_A)} + \psi_{1s(H_B)})$ are of different symmetry. (The decrease in the contribution of $2s$ orbital of A with increase in ∠HAH in $2a_1$ molecular orbital is understandably due to the increasing contribution of this orbital to the lowest energy bonding molecular orbital $1a_1$). In the angular AH_2 molecule, the $2a_1$ molecular orbital is of lower energy than in the linear AH_2 molecule because as can be seen from the Walsh diagram (Fig. 35), this molecular orbital has a positive overlap with the $1s$ orbitals of hydrogen whereas it has no overlap in the case of linear AH_2 molecule. The $3a_1$ molecular orbital is antibonding and this has not been shown in the figure.

The symmetry-adapted combination $(\psi_{1s(H_A)} - \psi_{1s(H_B)})$ of b_2 symmetry combines with p_y orbital of the same symmetry in the angular AH_2 molecule to give bonding and antibonding molecular orbitals of the same symmetry. Only the b_2 bonding orbital is shown in the Walsh diagram. It can be easily visualised that if we go on increasing ∠HOH in the angular AH_2 molecule, the overlap between $(\psi_{1s(H_A)} - \psi_{1s(H_B)})$ and p_y orbital in the bonding b_2 molecular orbital will go on increasing and hence the energy of this molecular orbital will go on decreasing with the result that the b_2 molecular orbital has lowest energy in the linear AH_2 molecule (∠HOH of 180°).

The p_x orbital of A in both the angular and the linear AH_2 molecules is non-bonding. In fact, in the linear geometry of AH_2 molecule, both the p_x and p_y orbitals are degenerate, non-bonding and are of e_{1u} symmetry.

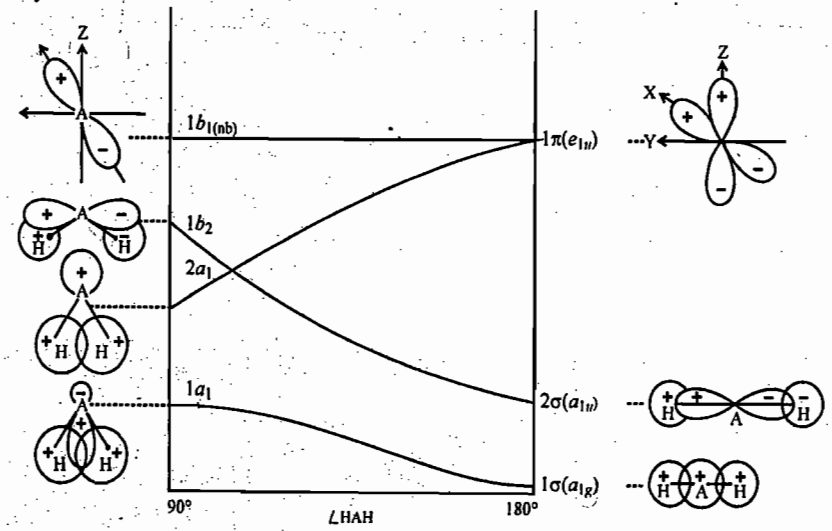


Fig. 35. Walsh diagram showing correlation between molecular orbital energy levels of angular and linear geometries of AH_2 molecule.

The various orbitals which take part in molecular orbital formation of AH_2 molecule are $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals of A and two $1s$ orbitals of hydrogen atoms. Thus, six molecular orbitals are formed out of which the four lower energy molecular orbitals are shown in Fig. 35. The four molecular orbitals can accommodate eight valence electrons which is the maximum number of electrons that are present in AH_2 molecule (A belongs to the second period).

It follows from the Walsh diagram of AH_2 molecules that a linear geometry of BeH_2 would be more favourable than the angular geometry. This is because the two filled lower energy molecular orbitals of linear geometry of BeH_2 are of lesser energy than the two lower energy molecular orbitals of angular geometry of BeH_2.

To sum up, if there are only 4 electrons to be accommdated in the molecular orbitals of the molecule AH_2 (as *e.g.*, BeH_2), the molecule would have a lower energy **linear geometry.**

If however, the number of electrons to be accommodated in molecular orbitals is more than four, as, for example, in H_2O, the third molecular orbital has to be occupied which is of much lower energy in angular AH_2 molecule than in linear AH_2 molecule. The filling of the fourth non-bonding molecular orbital is of no consequence in determining the geometry of AH_2 molecule since this non-bonding molecular orbital is of the same energy in linear as well as in angular geometry of AH_2 molecule. In such a case, the molecule will have an **angular geometry.**

Carbon Dioxide Molecule, CO_2. This molecule belongs to $D_{\infty h}$ symmetry. The orbitals of carbon and oxygen atoms which can form σ bonds in the direction of bond axis (taken as Z-axis) are $2s$ and $2p_z$ orbitals. The $2s$ orbital of carbon is of a_{1g} symmetry whereas its $2p_z$ orbital is of a_{1u} symmetry. The $2s$ orbital of carbon and $2s$ orbitals of oxygen atoms are of the same symmetry. However, they differ too much in energy. Hence, the $2s$ orbitals of oxygen atoms hardly take part in σ bonding. Therefore, the $2s$ orbitals of oxygen atoms are essentially non-bonding.

The two symmetry-adapted combinations of $2p_z$ orbitals of oxygen which can form σ bonds with atomic orbitals of carbon in the Z direction are $(\psi_{2p_z(O_1)} + \psi_{2p_z(O_2)})$ of a_{1g} symmetry and $(\psi_{2p_z(O_1)} - \psi_{2p_z(O_2)})$ of a_{1u} symmetry. The +Z coordinate of each oxygen atom is taken as pointing towards the carbon atom, as shown.

The various molecular orbitals formed from the combination of atomic orbitals of C and O atoms are shown in Fig. 37 on the next page and the molecular orbital energy level diagram of CO_2 molecule is shown in Fig. 36.

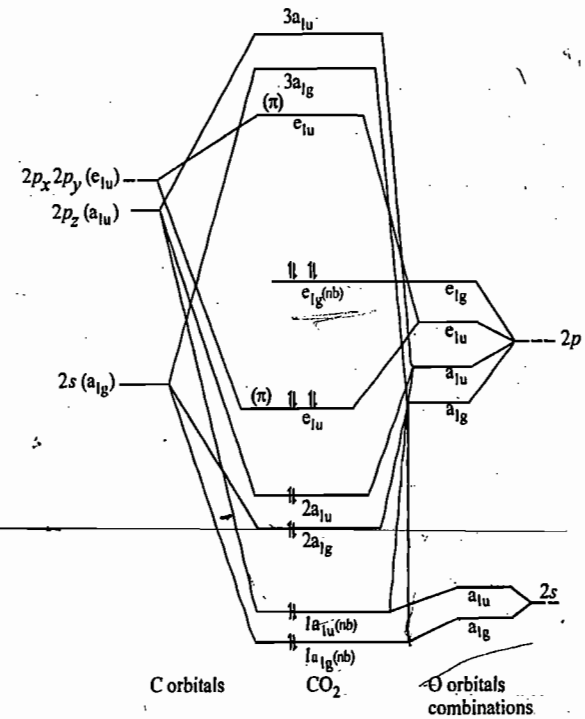


Fig. 36. Molecular orbital energy level diagram of CO_2 molecule.

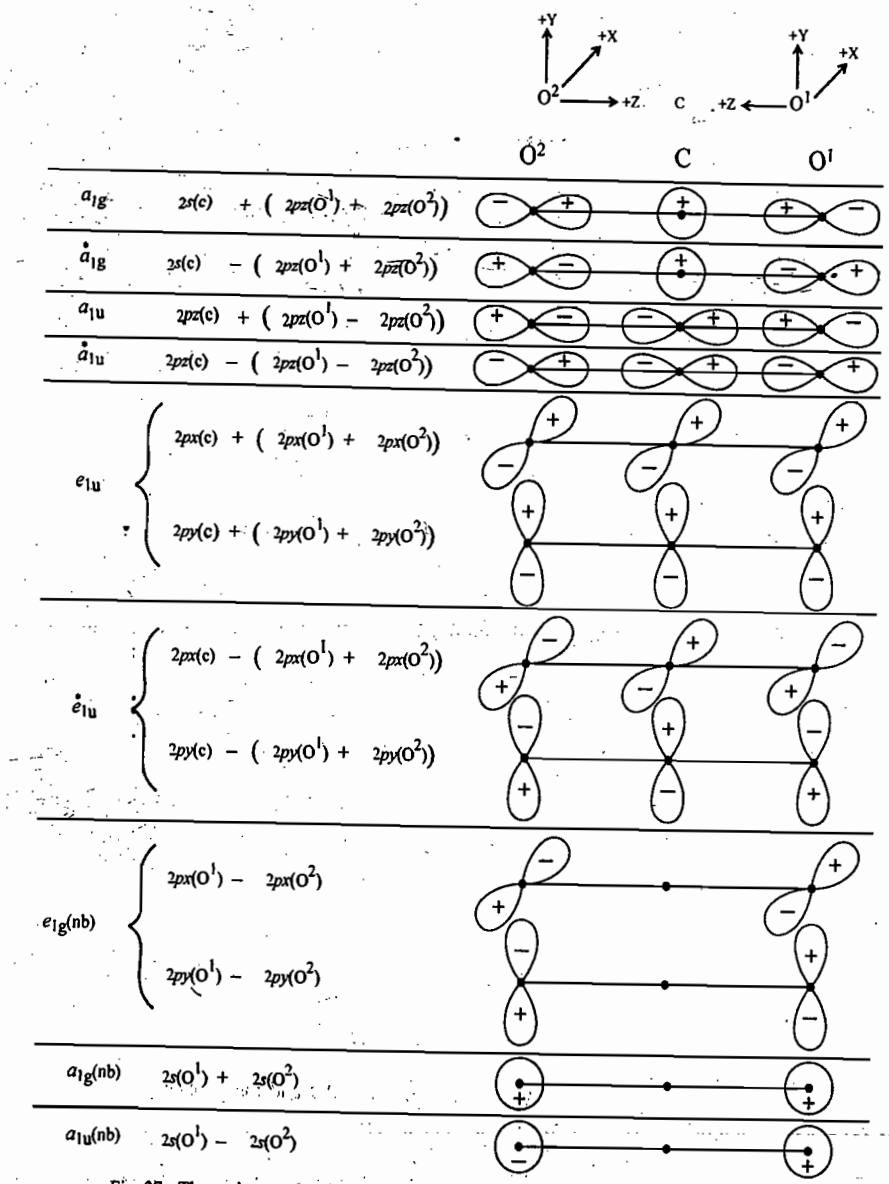


Fig. 37. The various molecular orbitals formed from the combination of atomic orbitals of C and O atom to form CO_2 molecule.

It is evident that CO_2 molecule has 16 valence electrons to be accommodated in its molecular orbitals so that its electronic configuration is written as :

$$CO_2 : 1a_{1g}^2(nb)\ 1a_{1u}^2(nb)\ 2a_{1g}^2\ 2a_{1u}^2\ e_{1u}^4(\pi)\ e_{1g}^4(nb)$$

Ammonia Molecule, NH_3. Each of the 2*s* and $2p_z$ orbitals of N is of the symmetry *a* in C_{3v} point group to which the molecule belongs. The $2p_x$ and $2p_y$ orbitals, *taken together*, are of the symmetry *e*. The three 1*s* orbitals of three H atoms can linearly combine with one another to give three combinations one of which is of the symmetry *a* and the rest of the two combinations, taken together, are of the symmetry *e*. The linear combination *a* of 1*s* atomic orbitals of H combine with 2*s*, $2p_z$ orbitals of N (each one having the symmetry *a*) to give an *equal number* of molecular orbitals (*i.e.*, three molecular orbitals). In the same way, the two linear combinations *e* of 1*s* atomic orbitals combine with p_x, p_y orbitals (also of the symmetry *e*) to give two sets of doubly degenerate molecular orbitals. It is possible to write the wave functions and draw the diagrams of all the seven molecular orbitals of NH_3 as was done in the above mentioned examples of H_3^+ ion and BeH_2. The molecular orbital energy level diagram of NH_3 is shown in Fig. 38.

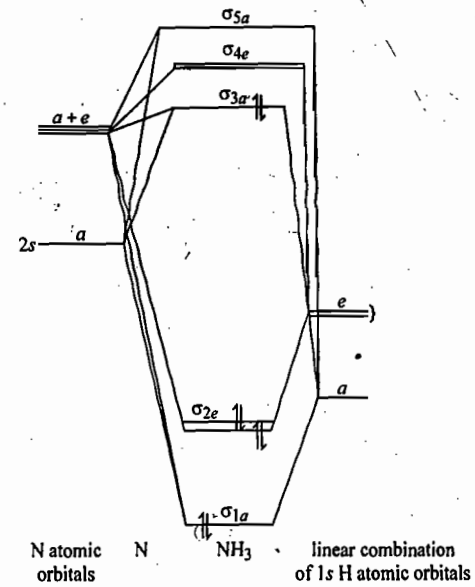


Fig.38. Molecular orbital energy level diagram of NH_3 molecule.

The electronic configuration of NH_3 is $\sigma_{1a}^2\ \sigma_{2e}^4\ \sigma_{3a}^2$. The two electrons in the highest occupied molecular orbital (HOMO), which is *almost non-bonding*, are practically localised on N atom. The remaining occupied molecular orbitals are of bonding type. This simple molecular orbital description of NH_3 tallies with the conventional picture of NH_3 having a lone pair of electrons on N atom and three N – H σ bonds. But it does not explain the equivalence of the three N – H bonds and the observed ∠ NHN. These are explained on the basis of the VSEPR theory and/or the concept of hybridisation as discussed in the next chapter on Hybridisation and Shapes of Molecules.

Problem 4. Of the following species, which has the shortest bond length : NO, NO^+, NO^{2+}, NO^-?

Answer : We shall first calculate the bond orders for the given species from their electronic configurations.

$$NO : KK\ \sigma(2s)^2\sigma(2s)^2\sigma(2p_z)^2\pi(2p_x)^2\pi(2p_y)^2\ \pi^*(2p_x)^1$$

$$\text{or} \quad KK'\sigma_1^2\sigma_2^{*2}\sigma_3^2\pi_1^2\pi_2^2\pi_3^{*1}$$

∴ **Bond order** $= 1/2\,(8-3) = 2\frac{1}{2}$

NO^+ : One electron is removed from the antibonding π_3^* MO.

Bond order $= 1/2(8-2) = 3$

NO^{2+} : One electron is removed from the antibonding π_3^* MO and the other electron is removed from the bonding π_1 (or π_2) MO.

Bond order $= 1/2\,(7-2) = 2\frac{1}{2}$

NO^-: One electron is added to the antibonding π_3^* MO.

Bond order $= 1/2\,(8-4) = 2$

Evidently, the species NO^+ has the highest bond order and thus has the shortest bond length.

Problem 5. Write the electronic configuration of CN^-. What is its bond order ?

Answer : The order of molecular orbitals is the same as in CO. Only the extent of mixing of 2*s* and $2p_z$ orbitals of N occurs to a greater extent in CN^- compared to a similar mixing of the orbitals of O in

CO. The electronic configuration is similar to CO. Thus,

$$CN^- : KK' \sigma^2_{1nb} \sigma^2_2 \pi^2_1 \pi^2 \sigma^2_{3nb}$$

and the **bond order** is 3 due to the presence of six electrons in the bonding orbitals and the rest in nonbonding orbitals. The nonbonding σ_{1nb} is localised on N atom and has predominantly s character whereas σ_{3nb} is localised on C atom and has predominantly p_z character.

Comparison Between Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT)

Common Features. Valence bond and Molecular orbital theories have the following features in common :-

1. The basic principles involved in the distribution of electrons are similar. Thus, an orbital, whether atomic or molecular, cannot have more than two electrons. They are filled in the order of increasing energy. If there are more than one vacant orbitals having the same energy, they would first be filled *singly*.

2. In normal covalent bond formation, the essential interaction, according to both the theories, is the sharing of the bonding electron charge density by both nuclei and concentration of electron charge density between the nuclei.

3. In bond formation, the orbitals of the bonding atoms must overlap according to both the theories.

4. The energies of the overlapping orbitals, according to both the theories, must be comparable and their symmetries should be the same.

Differences

1. While VBT *starts with individual atoms* and considers the interaction between them, MOT *starts with the nuclei* of the constituent atoms.

2. In the valence bond theory, only the half-filled orbitals of the valence shell take part in bonding and the remaining orbitals retain their identity. In molecular orbital theory, however, all the atomic orbitals, whether filled or unfilled, would overlap to form molecular orbitals, provided they have proper symmetry and comparable energy.

3. The wave function in original VBT does not give any weightage to ionic structures (the concept of ionic contribution was incorporated later on as a modification to the original theory). The MOT inherently gives equal weightage to covalent and ionic structures. For example, ψ_{BMO} for H_2 molecule is given by

$$\psi_{BMO} = (\psi_A + \psi_B)_1(\psi_A + \psi_B)_2$$
$$= (\psi_A)_1(\psi_B)_2 + (\psi_A)_2(\psi_B)_1 + (\psi_A)_1(\psi_A)_2 + (\psi_B)_1(\psi_B)_2$$

In this equation, the first two expressions refer to covalent structures and the last two refer to ionic structures.

4. While VBT fails to account for the paramagnetic character of oxygen, MOT offers a satisfactory explanation.

5. While resonance plays an important role in VBT, this concept has no place in MOT.

6. MOT is more exact than the VBT. However, the calculations involved in MOT are much more tedious than those involved in VBT.

METALLIC BOND

Metals are characterised by high electrical and thermal conductivity, bright lustre, malleability, ductility and high tenstile strength. It has been observed that metals, generally, have low ionisation energies because the valency electrons can be taken out relatively easily.

The following three models have been proposed to account for the nature of bonding in metals :

1. *The Free Electron Model. The 'Electron Sea' Model.*
2. *The Valence Bond Model.*
3. *The Band Model : Molecular Orbital Approach.*

1. The Free Electron Model. The 'Electron Sea' Model

According to this model, a metal behaves as if *it is an assemblage of positive ions (kernels) immersed in a 'sea' of mobile electrons* (Fig. 38). *Thus, each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons.*

The force of attraction which binds a metal atom kernel to a number of electrons within its sphere of influence is known as a **metallic bond.**

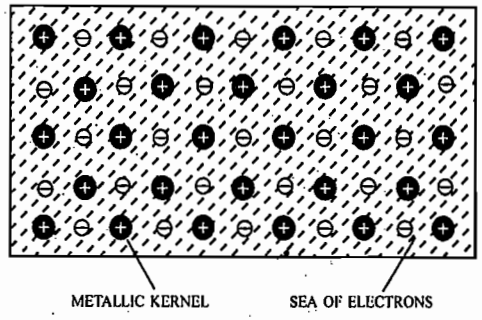


Fig. 38. The electron sea model for metals.

Explanation of Metallic Properties. All the metallic properties such as electrical and thermal conductivity, bright lustre, malleability, ductility, elasticity, etc., can be explained satisfactorily on the basis of the metallic structure described above.

1. The **high electrical conductivity** of metals, for example, is due to the presence of the mobile valency electrons. They move readily in an electric field and thus conduct electricity throughout the metal from one end to the other.

2. The **high thermal conductivity** is also due to the presence of these mobile electrons. If one part of a metal is heated, the electrons in that part acquire a large amount of kinetic energy. Being free, these electrons move rapidly through the crystal and convey heat (*i.e.*, conduct heat) to other parts of the metal.

3. The **bright metallic lustre** can also be explained as due to the presence of the highly mobile electrons. As a beam of light comprising of electromagnetic waves falls on the surface of a metal, the electric field associated with light waves sets the electrons present on the surface of the metal into to and fro oscillations. Now, a moving charge always emits electromagnetic energy. Hence, oscillating electrons emit electromagnetic energy in the form of light. Thus, when light falls on a metal surface, it appears as if light is being reflected. The surface, therefore, emits the typical metallic lustre.

4. The model of free valency electrons can also explain the **softness, malleability** and **ductility** associated with metals. The metallic bond holding the positive ions (say, M^+) and the valency electrons is *non-directional*. In other words, the force of attraction between the M^+ ions and the valency electrons is uniform in all directions. Also the bonds holding the crystal lattice in metals are not rigid unlike those in covalent solids, such as ice which are rigid. The result is that M^+ ions can be easily moved from one lattice site to another. In terms of the crystal, nothing has been changed. The environment of each metal ion remains the same as before since delocalized electrons are available everywhere.

The nearest neighbours can thus be changed easily and new metal bonds can be formed readily. This explains why metals are malleable, *i.e.*, they can be flattened out into thin sheets when hammered. A crystal of ice, on the other hand, is hard. It is neither malleable nor ductile. It is brittle, *i.e.*, it breaks into small pieces when hammered. This is obviously due to the fact that atoms in water (oxygen and hydrogen) are covalently bonded to each other. Covalent bond is thus *rigid* and *highly directional.*

The ease with which the metal ions can be moved from one lattice site to another is also responsible for the fact that the metals are *ductile*, *i.e.*, they can be drawn into wires by very little expenditure of energy. This also explains why metals like sodium and potassium are *soft* and can easily be cut with a knife.

5. Metals have **high tensile strength,** *i.e., they can resist stretching without breaking.* This is due to

the existence of strong electrostatic attraction between the positively charged metal ions and the 'sea' of negative electrons surrounding them. Substances which have covalent bonds, do not possess high tensile strength. This is due to the absence of electrostatic forces of attraction in the crystal, there being no oppositely charged units in the lattice.

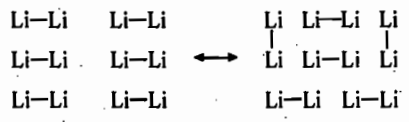
6. Metals possess **elasticity.** *Elasticity is a property by virtue of which a substance can resist a deforming force* or a property by virtue of which *a substance can recover its original form soon after the removal of the deforming force.* The elasticity of metals is also due to the ease with which metal ions can move from one lattice site to another.

7. The delocalized electron model can also explain the well known observation that *only a small force is needed to* **bend** *a straight copper wire sharply.* However, straightening of a bent wire is not so easy. It requires much more force to do so. Not only that ; a small kink always remains. The reason is that the formation of a sharp bend amounts to separation of some of the metal ions from their adjacent electrons and also from their nearest ion neighbours. The previous pattern of ions and electrons is disturbed and a new pattern is set up in the crystal giving rise to new planes and new edges. It is not so easy to restore the previous pattern because the new planes and edges formed during the bending do not ordinarily fit together to restore the original pattern once again.

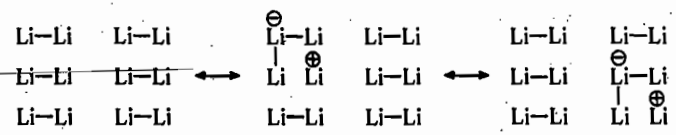
Limitations of the model. The free electron model, however, cannot explain vast variations in properties of certain metals. For example, while mercury melts at such a low temperature as – 39°C, tungsten melts at such a high temperature as 3300°C. While metals, in general, are good conductors of electricity, copper is more than 50 times better conductor than bismuth. Similarly, while metals like sodium and potassium are so soft that they can be cut easily with a knife, osmium is so hard that it can scratch even glass.

2. The Valence Bond Model

An examination of the crystal lattice of lithium atom reveals that each Li atom in this lattice is surrounded by eight nearest Li atoms and six next to nearest Li atoms. Because of the presence of only one valence electron, each Li atom is capable of forming only one normal covalent bond with one of its nearest Li atoms. This Li–Li covalent bond is assumed to resonate **mainly** between all the eight neighbours and **to some extent** between the six next to the nearest neighbours. In this way, each Li atom would bind all its neighbours. The resonance of the Li – Li bonds, which is similar to the resonance of the double bonds in benzene, stabilizes the metallic bond. The resonance of Li – Li bonds between a few Li atoms is shown below :



More stabilisation results from resonance of the following type :



Although the valence bond model does meet some success in explaining some of the characteristics of metals, yet it is only qualitative in nature. The cause of metallic bonding is best explained on the basis of the Band Model involving the concept of molecular orbitals.

As already discussed in this chapter, atomic orbitals overlap to produce molecular orbitals. For example, 1*s* atomic orbital of one H atom overlaps with the 1*s* atomic orbital of the other H atom to form two molecular orbitals of H_2 molecule. The energy of one of the resulting molecular orbitals is higher and of the other is lower than the energy of either of the combining atomic orbitals. The energies of the two molecular orbitals are represented in the form of two energy levels whose magnitudes vary with the internuclear distance between the two atoms, as shown in Fig. 39.

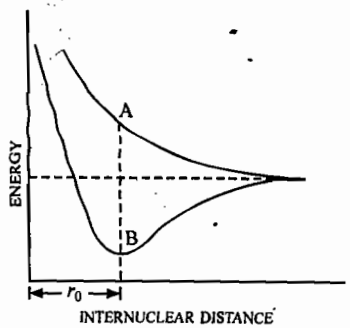


Fig. 39. Variation of the two molecular orbital energy levels with internuclear distance in the case of H_2 molecule. r_0 is the equilibrium internuclear distance.

The energy separation between the two molecular orbital energy levels at equilibrium internuclear distance r_0 is presented by AB.

In general, if there are *n* atomic orbitals, one on each atom, in a metallic crystal, they may overlap to give *n* molecular orbitals corresponding to *n* energy levels. It is essential, however, that the atomic orbitals have the same symmetry and are associated with the same or similar amount of energy. Thus, the larger the number of atomic orbitals satisfying the above conditions, the larger would be the number of molecular orbitals each of which can be represented by a separate energy level. The energy separation between any two adjacent energy levels would go on decreasing with increase in the number of overlapping orbitals. Consequently, if we have an exceedingly large number of overlapping orbitals, the energy separation between any two adjacent energy levels would be exceedingly small so that we get an almost *continuous energy band*, as shown in Fig. 40.

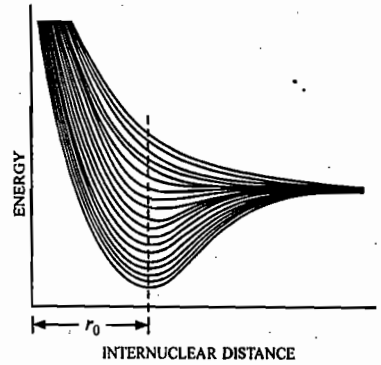


Fig. 40. An almost continuous energy band of energy levels of molecular orbitals obtained by overlapping of an exceedingly large number of atomic orbitals.

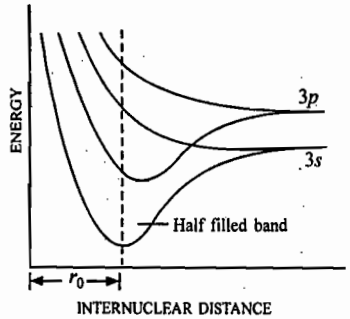


Fig. 41. The valence band of sodium metal. The dotted line indicates equilibrium internuclear distance.

A similar situation exists in case of metals. A metal lattice has an extremely large number of atoms. The atomic orbitals on these atoms with same symmetry and same energy overlap resulting in an almost continuous energy band of extremely large number of energy levels of molecular orbitals. Each energy level in this band is capable of holding two electrons. The overlaping of 3*s* and 3*p* orbitals (valence orbitals) in the crystal lattice of **sodium metal** is shown in Fig. 41.

The overlapping of inner orbitals of same symmetry and same energy produces molecular orbitals which are completely occupied by inner electrons. Also, there is considerable energy gap between the valence orbital energy bands and the inner orbital energy bands so that the electrons from the completely filled inner orbital energy band cannot be excited to the valence orbital energy bands. The fully filled inner orbital energy bands are not shown in the figure. Since the molecular orbitals are common to all

bands of atoms in the lattice, the electrons in the energy levels of these energy bands are common and belong to the whole lattice. In other words, they are completely delocalised.

Since sodium atom has only a single electron in the 3*s* orbital, therefore, in the case of sodium metal, only half of the 3*s* energy level band is occupied by electrons and even on slightest excitation, these electrons can move to the higher energy levels in this band. The mobility of these electrons makes the sodium metal a good conductor of electricity. A similar situation occurs in all the other alkali metals in which the valence energy level band is always half-filled.

The situation in the case of alkaline earth metals is, however, different. In these cases, the outermost valence orbital is fully filled with two electrons so that no vacant energy level of the energy band is available for the electrons to jump to. However, at the equilibrium internuclear distance, the 3*s* energy band and the 3*p* energy band overlap so that some of the vacant energy levels of 3*p* band and the filled energy levels of 3*s* band fall in the same energy range. Consequently, the 3*s* electrons can be easily excited to the 3*p* energy levels in this range. The resulting mobility of electrons makes the alkaline earth metals also good conductors of electricity.

In an **insulator,** there is a large energy gap between the lowest vacant energy band and the highest fully filled energy band even at the equilibrium internuclear distance (Fig. 41). As a result, the electrons cannot be easily excited from the fully filled energy band to the vacant energy band. This makes the material non-conducting.

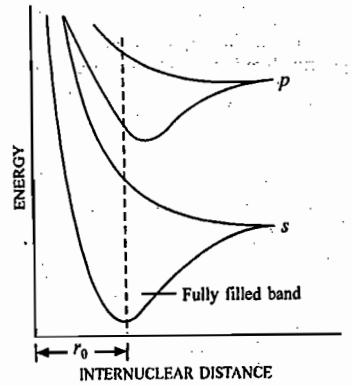


Fig. 42. The valence bands of an insulator.

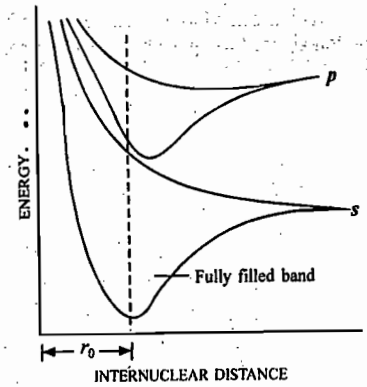


Fig. 43. The valence bands of a semi- conductor.

In a **semi-conductor,** there is a lesser energy gap between the two energy bands (Fig. 43). Although the electrons are not very easily excited from the filled to the vacant energy bands yet these can be excited if an appropriate amount of energy is made available.

HYDROGEN BOND

In compounds of hydrogen with *strongly electronegative* elements, such as fluorine, oxygen and nitrogen, the electron pair shared between the two atoms lies far away from the hydrogen atom. As a result, the hydrogen atom becomes *electropositive* with respect to the other atom. This phenomenon of charge separation in the case of hydrogen fluoride is represented as $\overset{+\delta}{H}-\overset{-\delta}{F}$. Such a molecule is said to be **polar,** as already discussed. The molecule behaves as a **dipole** because one end carries a positive charge and the other end a negative charge. The electrostatic force of attraction between such molecules should be very strong. This is because the *positive end of one molecule* attracts and is attracted by the *negative end of the other molecule.* Thus, *two or more molecules may associate together to form large clusters of*

molecules. This is illustrated below for the association of several molecules of hydrogen fluoride :

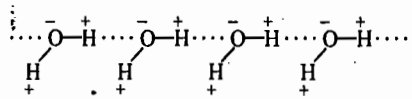
$$\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots$$

The cluster of HF molecules may be described as $(HF)_n$.

The attractive force which binds hydrogen atom of one molecule with electronegative atom (such as fluorine) of another molecule, generally of the same substance, is known as **hydrogen bond.**

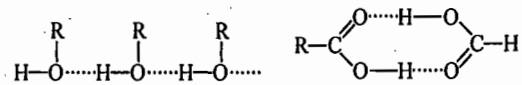
In this case, while the length of the covalent bond between F and H atoms is found to 1·00 Å, the length of the hydrogen bond between F and H atoms of neighbouring molecules has been found to be 1·55 Å.

Water molecule, because of its bent structure, is also a dipole, oxygen end carrying a negative charge and hydrogen end carrying a positive charge, as shown. Hydrogen bonding takes place in this case as well, as shown below :



The cluster of water molecules may be described as $(H_2O)_n$.

Alcohols and carboxylic acids also form associated molecules for the same reason, as illustrated below.



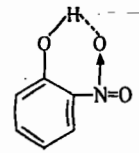
Alcohols Carboxylic acid

It is seen that in water and alcohols, the hydrogen bonding (or the association of molecules) may extend to several molecules as indicated above but in carboxylic acids, the hydrogen bonding is limited to the association of two molecules only.

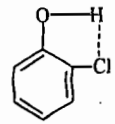
The nature of hydrogen bond. The hydrogen bond *is a class in itself.* It arises from electrostatic forces between the positive end (pole) of one molecule and the negative end (pole) of *another* molecule of the same or some other polar substance. For instance, extensive hydrogen bonding occurs between molecules of water, molecules of ethanol as also between molecules of water and molecules of ethanol. The strength of hydrogen bond has been found to vary between 10 – 40 kJ per mole (*i.e.,* per $6{\cdot}022\times10^{23}$ bonds) while that of a covalent bond has been found to be of the order of 400 kJ per mole. Thus, a hydrogen bond is very much weaker than a covalent bond.

Intramolecular Hydrogen Bonding. In addition to *intermolecular* hydrogen bonding resulting from electrostatic forces of attraction between the positive and negative ends of *different molecules* of the same substance, cases of **intramolecular hydrogen bonding** are also known. *These involve the electrostatic forces of attraction between hydrogen and an electronegative element both present in the* **same molecule.**

Interesting examples are provided by *o*-nitrophenol and *o*-chlorophenol :

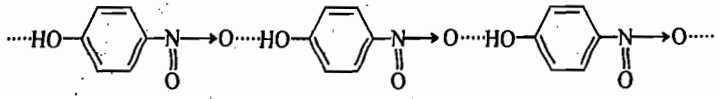


o-Nitrophenol showing intamolecular hydrogen bonding

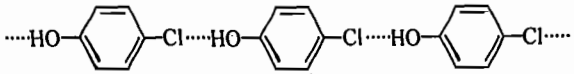


o-Chlorophenol showing intramolecular hydrogen bonding

Para nitrophenol and para chlorophenol, on account of larger distances between the two groups, do not show any intramolecular hydrogen bonding. On the other hand, they show the usual *intermolecular hydrogen bonding*, as illustrated below :



Intermolecular hydrogen bonding in *p*-nitrophenol



Intermolecular hydrogen bonding in *p*-chlorophenol

As a result of intermolecular hydrogen bonding, the para derivatives undergoes association as shown above, resulting in an increase in molar mass and hence an increase in boiling point. In ortho derivative, on account of *intramolecular hydrogen bonding*, no such association is possible. Consequently, the ortho derivatives are more volatile than the para derivatives.

Consequences of Hydrogen Bonding. 1. Boiling Points of Binary Hydrogen Compounds. Let us consider boiling points of binary compounds of hydrogen with various elements of Groups 15, 16 and 17, given in Table 10.

TABLE 10

Boiling Points of Binary Hydrogen Compounds with Elements of Groups 15, 16 and 17

Group 15			Group 16			Group17		
Formula	Molar mass	B.P. (°C)	Formula	Molar mass	B.P. (°C)	Formula	Molar mass	B.P. (°C)
SbH_3	125	– 17·0	H_2Te	130	– 1·8	HI	127·9	– 3·5
AsH_3	78	– 55·1	H_2Se	81	– 42·0	HBr	80·9	– 67·1
PH_3	34	– 84·6	H_2S	33	– 59·6	HCl	36·5	– 85·0
NH_3	17	– 33·0	H_2O	18	+ 100	HF	20·0	+ 19·4

It is seen that although the boiling point in each group *decreases with decrease in molar mass*, there is a sudden *reversal* in the case of ammonia, water and hydrogen fluoride in Groups 15, 16 and 17, respectively. The unusually high boiling point of each compound, evidently, is a consequence of strong intermolecular forces due to hydrogen bonding.

Thus, while H_2S, in which there is no hydrogen bonding, is a *gas*, H_2O, in which there is considerable hydrogen bonding, is a *high boiling liquid*.

Some Unique Properties of Water. Water has some unique properties. Two of these are :

1. *Density in the solid state (ice) is less than that in the liquid state.* This is somewhat unusual because in most substances density in the solid state is more than that in the liquid state.

2. *Water contracts when heated between 0°C and 4°C.* This is again unusual because most substances expand when heated in all temperature ranges.

Both these peculiar features which are due to hydrogen bonding, are discussed below :

1. In ice, the hydrogen bonding between H_2O molecules is more extensive than in liquid water. A substance in solid state has a definite structure and the molecules are more rigidly fixed relative to one another than in liquid state. In ice, the H_2O molecules are *tetrahedrally oriented with respect to one another.* This has been shown in Fig. 44.

At the same time, each oxygen atom is surrounded tetrahedrally by four hydrogen atoms, two of these are bonded covalently and the other two by hydrogen bonds (Fig. 44).

The hydrogen bonds are *weaker* and, therefore, *longer* than the covalent bonds. This arrangement gives rise to an *open cage-like structure*, as shown in the figure. There are evidently a number of 'holes' or open spaces in this structure. These 'holes' are formed because the hydrogen bonds holding the H_2O molecules in ice *are directed at certain definite angles.* In liquid water such hydrogen bonds are fewer in number. Therefore, as ice melts, a large number of hydrogen bonds are broken. The molecules, therefore, move into the 'holes' or open spaces and come closer to one another than they were in the solid state. *This results in a sharp increase in the density.* The density of liquid water is, therefore, higher than that of ice.

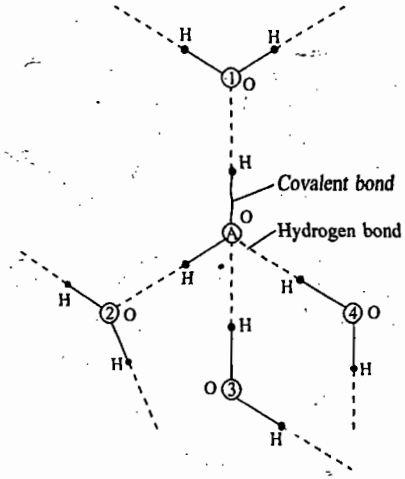


Fig. 44. The tetrahedral open cage-like crystal structure of ice. The central oxygen atom A is surrounded tetrahedrally by the oxygen atoms marked 1, 2, 3 and 4.

2. As liquid water is heated from 0° to 4°C, hydrogen bonds continue to be broken and the molecules come closer and closer together. This leads to *contraction*. However, there is also some expansion of water due to rise in temperature as in other liquids. It appears that upto 4°C, the former effect predominates and hence there is net *contraction in volume.* Above 4°C, however, the normal expansion effect, due to rise in temperature, predominates and hence *the volume increases as the temperature rises.*

Importance of Hydrogen Bonding in Sustaining Life. It can be easily realised that without hydrogen bonding, water would have existed as a gas like hydrogen sulphide. In that case, no life would have been possible on this globe.

Hydrogen bonding also exists in all living organisms whether of animal or of vegetable kingdom. Thus, it exists in various tissues, organs, blood, skin and bones in animal life. It plays an important role in determining structure of proteins which are so essential for life.

Hydrogen bonding plays an important role in making wood fibres more rigid and thus makes it an article of great utility to meet requirements of housing, furniture, etc. The cotton, silk or synthetic fibres owe their rigidity and tensile strength to hydrogen bonding. Thus, hydrogen bonding is of vital importance for our clothing as well. Most of our food materials also consist of hydrogen bonded molecules. Sugars and carbohydrates, for example, have many OH groups. The oxygen of one such group in one molecule is bonded with OH group of another molecule through hydrogen bonding. The stickiness of glue (a protein) or honey (which consists mainly of water and sugar) is also due to hydrogen bonding between the OH or other such groups of different molecules with one another. Hydrogen bonding is thus a phenomenon of great importance in everyday life.

INTERMOLECULAR FORCES

It is now fully established that forces of attraction exist between polar as well as non-polar molecules. These are known as **intermolecular forces** or **cohesive forces** or **van der Waals forces.** These forces originate from two types of interactions, *viz.*, 1. *Dipole-Dipole Interaction* and 2. *Induced dipole–Induced dipole Interaction.*

1. Dipole–Dipole Interaction. In the case of *polar molecules* which have permanent dipoles, the van der Waals' forces are mainly due to electrical interaction between the dipoles known as **dipole-dipole interaction.** For instance, gases such as ammonia, sulphur dioixde, hydrogen fluoride, hydrogen chloride, etc., have permanent dipoles as a result of which there is appreciable dipole–dipole interaction between the molecules of these gases. The magnitude of this type of interaction depends upon the dipole moments of the molecules concerned. The greater the dipole moments, the greater is the dipole–dipole interaction. Because of the attractive interaction, these gases can be easily liquified.

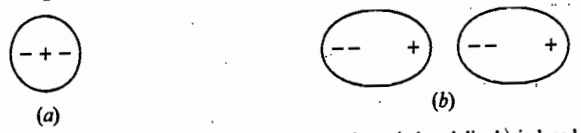
The average interaction energy of the two molecules with permanent dipole moments μ_1 and μ_2 is given by the expression :

$$\text{Interaction energy, } \phi(r) = -2\left(\frac{\mu_1\mu_2}{4\pi\varepsilon_0}\right)^2\left(\frac{1}{r^6}\right)\left(\frac{1}{3kT}\right) \quad ...(37)$$

where r is the distance between the molecules, k is the Boltzmann constant and $4\pi\varepsilon_0$ is the permittivity factor for the medium.

2. Induced dipole-Induced dipole Interaction. London Forces or **Dispersive Forces.** It is now well known that van der Waals forces exist even in non-polar diatomic molecules such as O_2 and N_2 and also in non-polar monoatomic molecules such as He, Ne, Ar, etc. This attraction is evident from the condensation of these gases into liquids at sufficiently high pressures and low temepratures. The existence of van der Waals forces in these molecules could not be understood for several years.

In 1930, F. London provided a satisfactory explanation for the existence of forces of attraction between non-polar molecules according to which electrons of a non-polar molecule keep on oscillating with respect to the nuclei of the atoms. As a result of this, at a given instant, positive charge may be concentrated in one region and negative charge in another region of the same molecule. Thus, a non-polar molecule may become momentarily self-polarised. This polarised molecule may induce a dipole moment in a neighbouring molecule, as shown in Fig. 45.



(*a*) shows average charge distribution in a non-polar molecule.

(*b*) shows induced dipole–induced dipole interaction.

Fig. 45. Origin of cohesive forces in non-polar molecules.

The electrostatic forces of attraction between induced dipoles and the original dipoles (due to oscillation of electrons) are known as **London forces.** These forces are also called **dispersive forces** because the well known phenomenon of dispersion of light is also connected with these dipoles. For a pair of adjacent molecules, London forces vary inversely as the *sixth power* of the distance between them, *i.e.*, $F \propto 1/r^6$.

The approximate interaction energy in this case is given by

$$\phi(r) = -\left(\frac{3E_1E_2}{2(E_1+E_2)}\right)\left(\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2 r^6}\right) \quad ...(38)$$

where E_1 and E_2 are the ionization energies of the two molecules. Other parameters have the same significance as mentioned above.

The van der Waals' attraction in *non-polar molecules* is thus *exclusively* due to London forces. In the case of polar molecules showing permanent dipoles, however, other electrostatic forces due to dipole – dipole interaction also contribute towards the van der Waals attraction, as already discussed.

QUESTIONS

1. (*a*) What is an ionic bond ?
   (*b*) Discuss carefully the formation of an ionic bond in terms of decrease of energy. Derive from it the conditions for the formation of ionic bonds.
   (*c*) Explain giving suitable examples why ions with three positive or three negative charges are rare ?
2. (*a*) Discuss the formation of a covalent bond on the basis of the orbital overlap concept. What is meant by a sigma bond ?
   (*b*) Differentiate between a sigma bond and a pi bond. Explain why a sigma bond is stronger than a pi bond ?
   (*c*) Explain the term covalency. How would you account for variable covalency of an element ? What is the maximum covalency which an element can exhibit ?
   (*d*) Construct a plot of potential energy versus internuclear distance between two hydrogen atoms.
3. (*a*) What do you understand by polar and non-polar molecules ? Is it possible for the non-polar molecules to have polar bonds ? Justify you answer with examples.
   (*b*) Explain why CO_2 and CCl_4 molecules are non-polar while $CHCl_3$ molecule is polar ?
   (*c*) What is meant by dipole moment ? Can its magnitude give an idea about the structure of a molecule ? Explain giving examples.
   (*d*) Which is more polar, H_2S or H_2O and why ?
4. (*a*) What is the difference between coordinate bond and covalent bond ?
   (*b*) Under what circumstances can a fully filled orbital participate in bond formation? Discuss with an example.
   (*c*) PCl_5 exists while NCl_5 does not. Explain.
5. What is Valence Bond theory ? Explain.
   In the potential energy diagram for H_2 molecule, the combined wave function ψ for two hydrogen atoms $\psi = \psi_A(1)\psi_A(2)$ (where $\psi_A(1)$ and $\psi_B(2)$ represent wave functions for two hydrogen atoms H_A and H_B associated with electrons 1 and 2, respectively), results in decrease in energy of the system by 24 kJ mol^{-1}. But the experimental value is 458 kJ mol^{-1}. What improvements in the wave functions of the system are made to account for this difference?
6. (*a*) What is resonance ? Discuss by taking example of CO_3^{2-} ion.
   (*b*) What do you understand by the term resonance energy ? What are the essential rules for writing resonating structures?
7. (*a*) What is Molecular Orbital theory ?
   (*b*) Give the electron charge density diagrams for bonding and antibonding molecular orbitals.
   (*c*) Predict the bond order in C_2 molecule with the help of MO diagram.
8. (*a*) What do you understand by the terms bonding and antibonding molecular orbitals ? Why are they so called ? Illustrate your answer by taking into consideration the structure of hydrogen ion H_2^+.
   (*b*) Is B_2 molecule paramagnetic or diamagnetic ? Discuss.
9. Explain how the atomic orbitals combine to form bonding and antibonding molecular orbitals. What are the limitations to such combinations ? Explain why in a homonuclear molecule, an s orbital of one atom cannot combine with a p_x or a p_y orbital of another atom of the same element.
10. (*a*) Draw molecular orbital diagram for HF molecule.
11. Explain on the basis of MO theory as to why
    (*a*) Oxygen molecule is paramagnetic while nitrogen molecule is diamagnestic.
    (*b*) Hydrogen forms diatomic molecule while helium remains monoatomic.
    (*c*) The bond order in O_2^- is less than that in O_2 which, in turn, is less than that in O_2^+.
12. (*a*) The internuclear distances in some O – O bonds are as follows :

O_2^+	O_2	O_2^-	O_2^{2-}
1·12 Å	1·21 Å	1·30 Å	1·49 Å

    (*i*) Account for the gradation of the internuclear distances in the above series.
    (*ii*) Which of these species are paramagnetic ?
    (*b*) Is it correct to say that bond energy in a diatomic molecule always increases when an electron is lost ?
    (*c*) "While in the case of F_2 molecule, all the orbitals are molecular, in case of HF molecule there is only one orbital which is molecular." Comment on this statement.

(*ii*) Which of these species are paramagnetic ?

(*b*) Is it correct to say that bond energy in a diatomic molecule always increases when an electron is lost ?

(*c*) "While in the case of F_2 molecule, all the orbitals are molecular, in case of HF molecule there is only one orbital which is molecular." Comment on this statement.

13. (*a*) Discuss with the help of the MO theory the formaiton of N_2, O_2 and F_2 molecules. How does the theory explain the difference in the reactivity of N_2, O_2 and F_2 ?

(*b*) Discuss carefully the electronic configurations of NO, CO, HF and HCl molecules.

14. Draw the MO diagrams for the following species :

Be_2, HHe (hypothetical), O_2^-, CO, BN

Explain the magnetic character of these species.

15. Write the electronic configuration of NO molecule.

(*a*) What is the bond order ? (*b*) Will the bond length be shorter or larger than in NO^+ ?

(*c*) How many unpaired electrons will be present ? (*d*) What will be the bond order in NO^- ?

16. With the help of molecular orbital diagrams explain why

(*a*) the bond order in N_2^+ ion is less than that in N_2 molecule whereas the bond order in O_2^+ is greater than that in O_2 molecule.

(*b*) the bond energy of NO^+ is higher than that of NO. (*c*) the bond length of CO^+ is larger than that of CO.

17. (*a*) Write the electronic configuration of a diatomic molecule having bond order three.

(*b*) Compare briefly valence bond and molecular orbital theories.

18. What is meant by metallic bond ? Illustrate the nature of metallic bond on the basis of (*i*) Electron sea model. (*ii*) Valence bond model and (*iii*) The band model (MO approach).

19. Discuss in details the band model of metallic bond. What type of energy bands are obtained in, (*i*) sodium metal (*ii*) an insulator (*iii*) semi-conductor

20. What is meant by hydrogen bonding ? Discuss the nature and consequences of hydrogen bonding. Discuss the importance of hydrogen bonding in sustaining life. Why do H_2O and HF have abnormally high boiling points ?

21. (*a*) What are intermolecular forces ? How do these forces originate ?

(*b*) What are London forces ? What is their origin ?

22. Explain why in the valence bond treatment of H_2, $\psi_{+\ complete}$ is called a singlet state while $\psi_{-\ complete}$ is called a triplet state.

23. What are term symbols ? What is the advantage of using three term symbols ? Wrtie down the term symbols for the following :

H_2^+ molecular ion, O_2 molecule, F_2 molecule, N_2 molecule F_2^+ molecular ion, Be_2, Li_2

24. What are Walsh diagrams ? To what use these diagrams are put ? Explain with the help of a Walsh diagram that[1] the BeH_2 molecule would have a linear geometry and H_2O molecule would have an angular geometry.

25. Discuss the geometry of CO_2 molecule on the basis of Walsh diagram.

5 HYBRIDISATION AND SHAPES OF COVALENT MOLECULES

HYBRIDISATION

Beryllium, boron and carbon (atomic numbers 4, 5 and 6) furnish interesting cases of compound formation. The electronic configurations of these elements are :

Beryllium	(At. No. 4) :	$1s^2\,2s^2$
Boron	(At. No. 5) :	$1s^2 2s^2\,2p_z^1$
Carbon	(At. No. 6) :	$1s^2 2s^2\,2p_z^1 2p_x^1$

According to the atomic orbital overlap concept, beryllium should behave like a *noble gas* since it has no half-filled orbital. Boron, which has only one half-filled orbital, should behave as a *univalent* element and form compounds like BH and BF. Carbon, which has only two half-filled orbitals, should behave as a *bivalent* element and form compounds like CH_2 and CCl_2. But this is not actually the case. Beryllium, unlike noble gases, forms a number of compounds like BeF_2 and BeH_2 in which it is bivalent. Boron forms a number of compounds like BCl_3 and BH_3 in which it is trivalent. Carbon forms millions of compounds in which it is almost invariably tetravalent. The simple examples are CH_4, CCl_4, etc.

In order to explain these anomalies, we make use of a concept called **hybridisation.** This concept, though hypothetical, is extremely helpful.

***sp* Hybridisation of Orbitals of Beryllium.** As mentioned above, the electronic configuration of Be atom in its ground state is $1s^2\,2s^2$. As such, Be should be zero-valent, as already stated. However, the promotion of a $2s$ electron to a $2p$ orbital results in an excited state configuration of Be, *viz.*, $1s^2\,2s^1p^1$ which has *two half-filled orbitals.* Thus, Be atom in its excited state is capable of showing a covalency of 2. The energy required for the promotion of the $2s$ electron comes from the energy that is released when Be and, say, F atoms approach each other to form BeF_2 molecule. It may be pointed out pertinently that all feasible chemical combinations are invariably accompanied by decrease and hence release of energy. Since the energy required by Be atom for the promotion of the electron from $2s$ to $2p$ orbital is less than the energy released due to the formation of the two covalent bonds, the formation of beryllium fluoride is energetically feasible. This offers a plausible explanation for the existence of stable compounds of beryllium such as BeF_2, BeH_2, etc.

Here a difficulty arises. We know that $2s$ and $2p$ orbitals have different energies and hence the two bonds in BeF_2 should have different strengths. This is because one Be–F bond will be formed by the overlapping of $2s$ orbital of beryllium and $2p$ orbital of fluorine while the second Be–F bond will be formed by the overlapping of $2p$ orbital of beryllium and $2p$ orbital of fluorine. But, actually both the bonds are of equal strength. How are we then going to explain equal strengths of both the bonds in beryllium fluoride, F–Be–F ? This is done by *postulating* that *the s and p orbitals of beryllium mix, i.e., hybridise, to give two orbitals of equivalent energy.*

The concept of redistribution of energy in different orbitals of an atom associated with different energies to give new orbitals of equivalent energy (rarely of non-equivalent energy as well) oriented in

space in definite directions is called **hybridisation.** The new orbitals thus formed are called **hybrid orbitals.** The bonds formed by such orbitals are called **hybrid bonds.** The process of mixing of orbitals itself requires some energy. Thus, some additional energy, over and above the energy required for the promotion of the required number of electrons to the higher energy orbitals, is needed for the hybridisation (mixing) of atomic orbitals.

Since in the formation of bivalent compounds of beryllium, *one s* and *one p* orbital is involved in hybridisation, it is called *sp hybridisation* and the two identical orbitals which result from this process are known as *sp hybrid orbitals.*

The amount of energy released $(B.E.)_1$ due to the formation of sigma bonds between Be and X atoms involving *hybrid orbitals* is greater than the energy released $(B.E.)_2$ in case the sigma bonds had involved the *pure s* and *p orbitals.* This is illustrated in Fig. 1 where $(B.E.)_1$ and $(B.E.)_2$ are represented by *AC* and *DF*, respectively

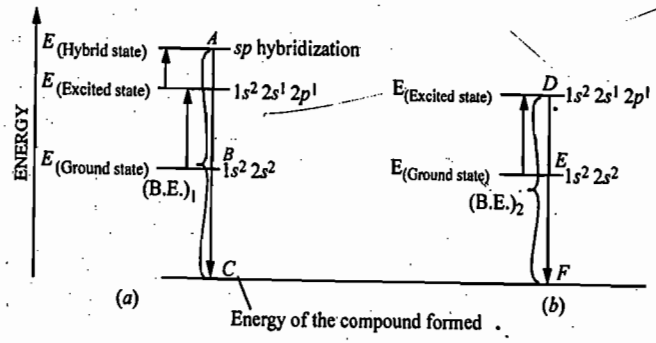


Fig. (1) (*a*) Energy *required* for the promotion of a 2*s* electron to a 2*p* orbital as also for the hybridisation of *s* and *p* orbitals to give *sp* hybrid orbitals in case of Be. $(B.E.)_1$ is the energy *released* when hybrid orbitals are involved in covalent bond formation. $(B.E.)_2$ is the energy *released* in the formation of covalent bonds involving pure *s* and *p* orbitals.

It is evident from the figure that some additional energy is released due to the involvement of the *sp hybrid orbitals* in bond formation. Because of this additional decrease of energy, the sigma bonds formed by *hybrid orbitals* of Be atom are stronger than the bonds formed by *pure s* and *p orbitals.*

The formation of *sp* hybrid orbitals is shown pictorially in Fig. 2.

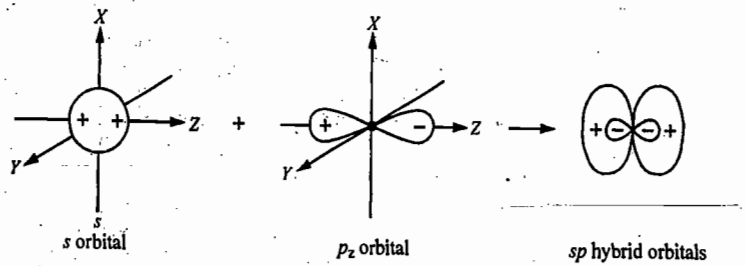


Fig. 2. Formation of two *sp* hybrid orbitals. + and – are geometric signs of the curves.

A pure *s* and a pure *p* orbital (oriented in the Z direction) are shown on the left of the arrow. The two *sp* hybrid orbitals which result from this combination are shown on the right. Each *sp* hybrid orbital consists of one large lobe and one small lobe. The large lobe, it may be noted, is much more spread than the original *p* orbital. This is due to the incorporation of the spherical character of the *s* orbital into

the resulting *sp* hybrid orbitals. The actual shape of an *sp* hybrid orbital is shown in Fig. 3. This clearly depicts the broader size of one of the lobes of the hybrid orbital. Wave mechanically, the shape of the *sp* hybrid orbital is obtained by plotting the hybrid orbital wave function in three-dimensional space. The wave function of the mixed (or hybrid) orbital is obtained by linearly combining the wave functions of pure atomic orbitals as illustrated in a subsequent section. The broader shape enables the hybrid orbital of one atom to bring about *a higher degree of overlapping* with the orbital of the other atom. The resulting bond is very strong since, the greater the degree of overlapping, the stronger is the bond.

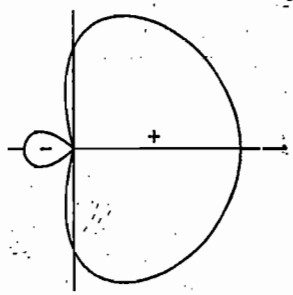


Fig. 3. The actual shape of an *sp* hybrid orbital.

In the formation of BeF_2 molecule, the half-filled p_z orbital of each fluorine atom overlaps with each of the two half-filled *sp* hybrid orbitals of the beryllium atom. In this electron-sharing process, each orbital contains two electrons and beryllium fluoride, BeF_2, results. This is represented in Fig. 4. As is clear from the figure, the overlap which leads to bonding has a + sign always.

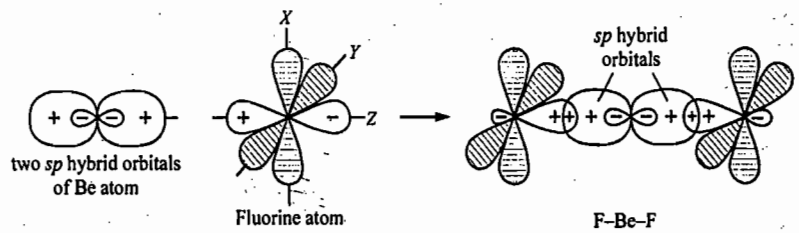


Fig. 4. Formation of beryllium fluoride molecule by overlapping of the half-filled $2p_z$ orbitals of flourine atoms with the two *sp* hybrid orbitals of beryllium atom. The shaded orbitals of fluorine are fully occupied.

sp^2 Hybridisation of Orbitals of Boron. As mentioned earlier, the outer electronic configuration of boron atom in its ground state is $2s^2\ 2p^1$. Promotion of one of the 2*s* electrons into one of the vacant 2*p* orbitals gives rise to an excited state configuration, *viz.*, $2s^1 p_z^1 p_x^1$. There are, thus, three half-filled orbitals which account for tri-covalency of boron. The three orbitals, *viz.*, *one* 2*s* and *two* 2*p* hybridise to give three hybrid orbitals of equivalent energy. The formation of sp^2 hybrid orbitals is shown in Fig. 5.

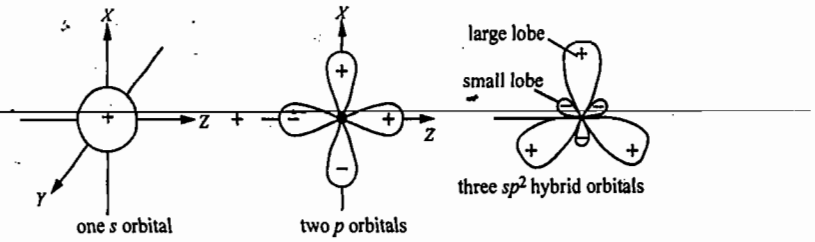


Fig. 5. Formation of three sp^2 hybrid orbitals by overlapping of one *s* and two *p* orbitals.

In the formation of **boron trifluoride molecule**, the half-filled p_z orbital of each fluorine atom

overlaps with each of the three half-filled sp^2 hybrid orbitals of the boron atom, as shown in Fig. 6.

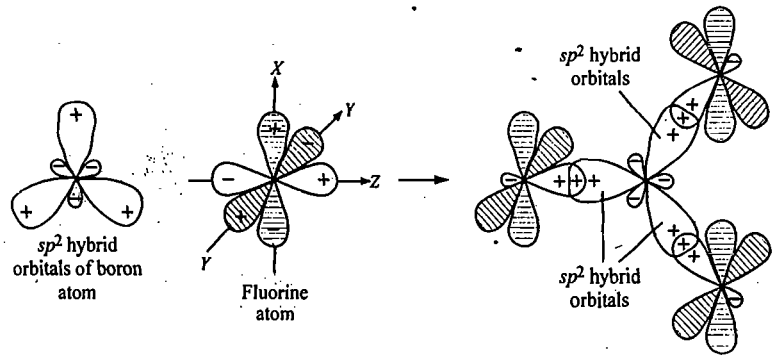


Fig. 6. Formation of boron trifluoride molecule by the overlapping of the half-filled p_z orbitals of three fluorine atoms with the three sp^2 hybrid orbitals of boron atom. The shaded orbitals of fluorine are fully occupied.

A large amount of energy is released during the formation of $sp^2 - p$ sigma bonds in BF_3 molecule. This is illustrated in Fig. 7. The amount of energy thus released is much more than the energy which might have been released if pure s and p orbitals of boron had overlapped with the half-filled p orbitals of fluorine atoms. This accounts for the greater stability of $sp^2 - p$ sigma bonds as compared to the stability of $s - p$ and $p - p$ sigma bonds.

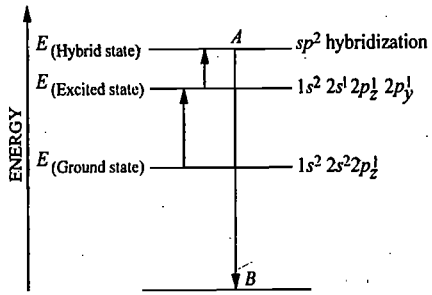


Fig. 7. Energy *required* (*i*) for the promotion of a $2s$ electron to a $2p$ orbital (*ii*) for the hybridisation of s and p orbitals to give sp^2 hybrid orbitals in case of boron atom and (*iii*) energy *released* (represented by *AB*) in the formation of covalent bonds involving sp^2 hybrid orbitals.

sp^3 Hybridisation of Orbitals of Carbon. As mentioned earlier, the outer electronic configuration of carbon atom in ground state is $2s^2 p_z^1 p_x^1$. Promotion of one of the $2s$ electrons into one of the vacant $2p$ orbitals due to the energy released in the formation of CH_4 molecule gives rise to excited state configuration, *viz.*, $2s^1 p_z^1 p_x^1 p_y^1$. There are now four half-filled orbitals which account for tetra-covalency of carbon. The four orbitals, *viz.*, *one s* and *three p*, hybridise to give four sp^3 hybrid orbitals of equivalent energy. The formation of sp^3 hybrid orbitals is shown in Fig. 8.

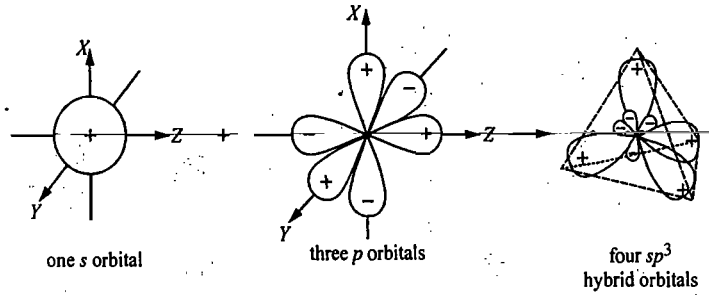


Fig. 8. Formation of four sp^3 hybrid orbitals by overlapping of one s and three p orbitals.

In the formation of **methane molecule,** the half-filled $1s$ orbital of each hydrogen atom overlaps with each of the four half-filled sp^3 hybrid orbitals of carbon atom, as shown in Fig. 9.

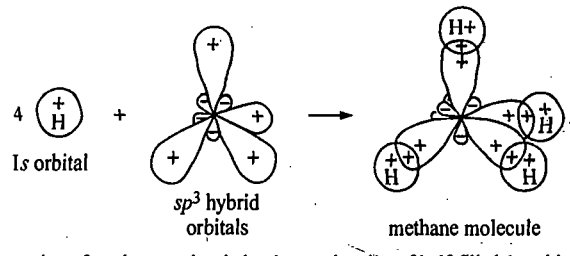


Fig. 9. Formation of methane molecule by the overlapping of half-filled $1s$ orbitals of four hydrogen atoms with the four sp^3 hybrid orbitals of carbon atom.

As before, a large amount of energy is released during the formation of $sp^3 - p$ sigma bonds. This is illustrated in Fig. 10.

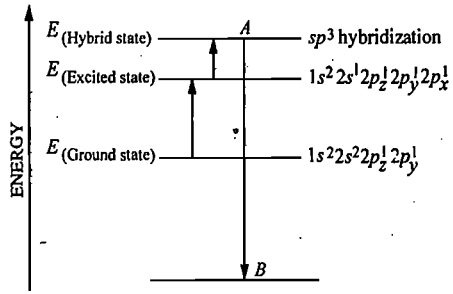


Fig. 10. Energy *required* (*i*) for the promotion of a $2s$ electron to a $2p$ orbital (*ii*) for the hybridisation of s and p orbitals to give sp^3 hybrid orbitals in case of carbon atom and (*iii*) energy *released* (*i.e.*, *AB*) in the formation of covalent bonds involving sp^3 hybrid orbitals.

The salient features of the concept of hybridisation may thus be summed up as follows.

1. One or more electrons from fully filled orbitals of the atom in the ground state, get promoted to the next available orbitals of higher energy (as, for example, from $2s$ to $2p$ orbitals in the case of second row elements and from ns to $(n-1)d$ orbitals in the case of transition elements), resulting in an excited state with appropriate number of half-filled orbitals. This process requires sufficient amount of energy. This energy becomes available as a result of the formation of the compounds from their respective elements. The orbitals in the excited state then undergo hybridisation giving hybrid orbitals of equivalent energy. The process of hybridisation, *i.e.*, mixing of orbitals, further requires some energy. The entire input of energy is, however, more than recovered when the hybrid orbitals combine with the orbitals of other atoms to form covalent bonds.

2. The number of hybrid orbitals formed is equal to the number of pure atomic orbitals which undergo hybridisation.

3. The energy released during covalent bond formation involving the hybrid orbitals is much more than the energy released if covalent bond formation involves the pure atomic orbitals. Therefore, the covalent bonds formed with hybrid orbitals are more stable than those formed with pure atomic orbitals.

4. Hybridisation necessarily involves atomic orbitals of the same atom.

5. Effective hybridisation occurs only when the orbitals undergoing hybridisation are of comparable energy.

6. Hybrid orbitals generally form either a sigma bond or contain a lone pair of electrons.

7. The hybrid orbitals are associated with higher energy than the pure atomic orbitals from which they are formed. The greater stability of bonds formed by the hybrid orbitals is due to *enhanced overlapping capacity* of such orbitals.

Shapes of Hybrid Orbitals. A reference to Figs. 2, 3, 5 and 8 indicates that the shapes of hybrid orbitals are different from those of the parent orbitals. For example, *s* orbital is spherical and *p* orbital is dumb-bell shaped and, thus, the shape of the bigger lobe of ***sp* hybrid orbital** which results from the mixing of one *s* and one *p* orbital, is different. It has the characteristics of both the mixing orbitals,and thus has an oval shape, as illustrated in Figs. 2 and 3. The bigger lobes of ***sp*^{2} hybrid orbitals** which result from the combination of one *s* and two *p* orbitals are pear-shaped because of the greater contribution of the two dumb-bell shaped *p* orbitals, as shown in Fig. 5. In the case of ***sp*^{3} hybrid orbitals** which result from the mixing of one *s* and three *p* orbitals, the contribution of the three *p*-orbitals predominates over the contribution of one *s* orbital. The resulting shape of their bigger lobes, therefore, is practically the same as that of the parent *p* orbitals except for the fact that the lobes in *sp*^{3} hybrid orbitals are somewhat more spread and are somewhat shorter in length than the pure *p* orbitals, as shown in Fig. 8. As can be seen, one lobe of the hybrid orbital in each type of hybridisation is considerably bigger in size than the other lobe. It is the bigger-sized lobe of the hybrid orbital of an atom which overlaps with the orbital of another atom to maximise the overlap to form a stable chemical bond.

Wave Functions for Hybrid Orbitals. We shall now illustrate the construction of wave functions for some common hybrid orbitals, namely, *sp*, *sp*^{2} and *sp*^{3} hybrid orbitals.

We shall first give **rules for constructing wave functions for hybrid orbitals.** These rules are :

1. The wave functions of hybrid orbitals are constructed by taking into consideration the linear combination of the wave functions of the appropriate AOs. Thus, the wave function of the *i*th hybrid orbital formed from *s* and *p* AOs is

$$\psi_i = a_i\phi_s + b_i\phi_{p_x} + c_i\phi_{p_y} + d_i\phi_{p_z}$$

where $\phi_s, \phi_{p_x}, \phi_{p_y}, \phi_{p_z}$ are the atomic orbital wave functions which constitute an *orthonormal* set. Two wave functions ϕ_m and ϕ_n are said to form an orthonormal set if

$$\int_{-\infty}^{+\infty} \phi_n\phi_n \, d\tau = 1, \quad \int_{-\infty}^{+\infty} \phi_m\phi_m \, d\tau = 1 \text{ and } \int_{-\infty}^{+\infty} \phi_m\phi_n \, d\tau = 0$$

The coefficients of wave functions a_i, b_i, c_i, d_i can be calculated by observing the following three conditions :

(*i*) Each wave function of a hybrid orbital is normalized, that is,

$\int_{-\infty}^{+\infty} \psi_i^2 \, d\tau = 1$. It can be shown that for such a normalised wave function ψ_i,

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1$$

(*ii*) Each hybrid orbital in the set of hybrid orbitals is orthogonal to the other hybrid orbitals, *i.e.*, $\int_{-\infty}^{+\infty} \psi_i \psi_j \, d\tau = 0$. From this relation, it can be shown that

$$a_i a_j + b_i b_j + c_i c_j + d_i d_j = 0$$

(*iii*) The squares of the coefficients of component wave functions which give contributions of the component wave functions to the hybrid orbital wave functions summed over all the hybrid orbitals wherein they participate, equal unity, *i.e.*,

$$\Sigma a_i^2 = 1$$

This is because the pure orbitals must be completely utilised in the formation of hybrid orbitals.

2. In order to obtain the equivalent hybrid orbitals, we specify a cartesian co-ordinate system and place one of the *i*th hybrid orbitals along one co-ordinate axis (usually +Z axis) and as many of other hybrid orbitals as possible in the plane containing this axis and the other co-ordinate axis (usually XZ plane). This simplifies the procedure for (*i*) constructing wave functions for hybrid orbitals (*ii*) for calculating angles between hybrid orbitals and (*iii*) for determining orientations of hybrid orbitals in space around the central atom.

3. Since the *s* orbital is spherically symmetric, each equivalent hybrid orbital of a set contains $1/\sqrt{n}$ of the *s* orbital distributed in *n* hybrid orbitals, that is, the coefficient of ϕ_s in each hybrid orbital is $1/\sqrt{n}$.

Problem 1. Construct the wave functions for the *sp* hybrid orbitals.

Procedure. Since one of the *sp* hybrid orbitals is to be placed along the +Z axis, we shall invoke the hybridisation of *s* and p_z orbitals. The wave functions for the two *sp* hybrid orbitals are :

$$\psi_1 = a_1\phi_s + b_1\phi_{p_z} \quad ...(i)$$

$$\psi_2 = a_2\phi_s + b_2\phi_{p_z} \quad ...(ii)$$

Since the *s* orbital is equally distributed between the two hybrid orbitals and since the square of the coefficient of a wave function gives its contribution to the hybrid orbital, we have

$$a_1^2 = a_2^2 = 1/2$$

$$\therefore \quad a_1 = a_2 = 1/\sqrt{2}$$

Since ψ_1 is normalized, we have

$$\int \psi_1^2 d\tau = \int (a_1\phi_s + b_1\phi_{p_z})^2 d\tau$$

$$= a_1^2 \int \phi_s^2 d\tau + b_1^2 \int \phi_{p_z}^2 d\tau + 2a_1b_1 \int \phi_s\phi_{p_z} d\tau = 1$$

Since the atomic orbital wave functions are orthogonal and individually normalized, we have

$$\int \psi_1^2 d\tau = a_1^2(1) + b_1^2(1) + 2a_1b_1(0) = a_1^2 + b_1^2 = 1$$

Since $a_1 = 1/\sqrt{2}$, hence $b_1 = 1/\sqrt{2}$.

Again, since ψ_1 and ψ_2 are orthogonal,

$$a_1a_2 + b_1b_2 = 0$$

Substituting for a_1, a_2 and b_1, we have

$$(1/\sqrt{2})\ (1/\sqrt{2}) + (1/\sqrt{2})b_2 = 0. \text{ Hence } b_2 = -1/\sqrt{2}$$

Thus, from Eqs. (*i*) and (*ii*), the two ***sp* hybrid orbital wave functions** are :

$$\psi_1 = (1/\sqrt{2})\ (\phi_s + \phi_{p_z})$$

$$\psi_2 = (1/\sqrt{2})\ (\phi_s - \phi_{p_z})$$

Problem 2. Derive the wave functions for the *sp*^{2} hybrid orbitals.

Procedure. Since one of the *sp*^{2} hybrid orbitals is to be placed along the +*Z* axis, we shall invoke the hybridisation of *s*, p_z and p_x orbitals so that the resulting hybrid orbitals are in the *XZ* plane. The

wave functions for the three sp^2 hybrid orbitals are :

$$\psi_1 = a_1\phi_s + b_1\phi_{p_z} + c_1\phi_{p_x} \quad ...(i)$$

$$\psi_2 = a_2\phi_s + b_2\phi_{p_z} + c_2\phi_{p_x} \quad ...(ii)$$

$$\psi_3 = a_3\phi_s + b_3\phi_{p_z} + c_3\phi_{p_x} \quad ...(iii)$$

Since the s orbital is equally distributed among the three hybrid orbitals, we have

$$a_1^2 = a_2^2 = a_3^2 = \frac{1}{3}$$

$$\therefore \quad a_1 = a_2 = a_3 = 1/\sqrt{3}$$

Assuming that ψ_1 is pointed towards the +Z-axis, this hybrid orbital will have contribution from s and p_z orbitals only. The contribution of p_x orbital in this case will, therefore, vanish, *i.e.*, $c_1 = 0$.

Now, since ψ_1 is normalized, we have

$$a_1^2 + b_1^2 + c_1^2 = 1 \text{ so that } a_1^2 + b_1^2 = 1 \quad (\because c_1 = 0)$$

Since $a_1 = 1/\sqrt{3}$, we find that $b_1 = (2/3)^{1/2}$

The requirement of orthogonality condition for ψ_1, ψ_2 and ψ_3 gives

$$a_1a_2 + b_1b_2 + c_1c_2 = 0$$

or $$a_1a_2 + b_1b_2 = 0$$

and $$a_1a_3 + b_1b_3 + c_1c_3 = 0$$

or $$a_1a_3 + b_1b_3 = 0$$

Hence, $b_2 = -a_1a_2/b_1 = -(1/\sqrt{3})\ (1/\sqrt{3})/\sqrt{2}/3 = -1/\sqrt{6}$

$$b_3 = -a_1a_3/b_1 = -(1/\sqrt{3})\ (1/\sqrt{3})/\sqrt{2}/3 = -1/\sqrt{6}$$

Again, since ψ_2 is normalized, we have

$$a_2^2 + b_2^2 + c_2^2 = 1$$

$$\therefore \quad c_2^2 = 1 - (a_2^2 + b_2^2) = 1 - (1/3 + 1/6) = 1/2$$

$$\therefore \quad c_2 = \pm 1/\sqrt{2}$$

The normalization requirement of ψ_3 gives

$$a_3^2 + b_3^2 + c_3^2 = 1$$

$$\therefore \quad c_3^2 = 1 - (a_3^2 + b_3^2) = 1 - (1/3 + 1/6) = 1/2$$

$$\therefore \quad c_3 = \pm 1/\sqrt{2}$$

If we choose positive root for c_2, we shall have to choose negative root for c_3 so that ψ_2 and ψ_3 fulfil the condition of orthogonality, *i.e.*, $a_2a_3 + b_2b_3 + c_2c_3 = 0$. Thus, if c_2 is $+\sqrt{1/2}$, c_3 is $-\sqrt{1/2}$.

Thus, the three sp^2 **hybrid orbital wave functions** are

$$\psi_1 = 1/\sqrt{3}\ \phi_s + \sqrt{2/3}\ \phi_{p_z}$$

$$\psi_2 = 1/\sqrt{3}\ \phi_s - 1/\sqrt{6}\ \phi_{p_z} + 1/\sqrt{2}\ \phi_{p_x}$$

$$\psi_3 = 1/\sqrt{3}\ \phi_z - 1/\sqrt{6}\ \phi_{p_z} - 1/\sqrt{2}\ \phi_{p_x}$$

Problem 3. Construct the wave functions for the sp^3 hybrid orbitals.

Procedure. The four sp^3 hybrid orbitals are :

$$\psi_1 = a_1\phi_s + b_1\phi_{p_z} + c_1\phi_{p_x} + d_1\phi_{p_y} \quad ...(i)$$

$$\psi_2 = a_2\phi_s + b_2\phi_{p_z} + c_2\phi_{p_x} + d_2\phi_{p_y} \quad ....(ii)$$

$$\psi_3 = a_3\phi_s + b_3\phi_{p_z} + c_3\phi_{p_x} + d_3\phi_{p_y} \quad ...(iii)$$

$$\psi_3 = a_4\phi_s + b_4\phi_{p_z} + c_4\phi_{p_x} + d_4\phi_{p_y} \quad ...(iv)$$

Since the s orbital is equally distributed among the four hybrid orbitals, we have

$$a_1^2 = a_2^2 = a_3^2 = a_4^2 = 1/4$$

$$a_1 = a_2 = a_3 = a_4 = 1/\sqrt{4} = 1/2$$

Assuming that ϕ_1 is developed along the +Z-axis, this hybrid orbital will have contribution from s and p_z orbitals only. The contributions of ϕ_{p_x} and ϕ_{p_y} orbitals in this case will, therefore, vanish so that we can write

$$c_1 = d_1 = 0$$

Since ψ_1 is normalized, we have

$$a_1^2 + b_1^2 + c_1^2 + d_1^2 = 1$$

or $$a_1^2 + b_1^2 = 1 \quad (\because c_1 = d_1 = 0)$$

$$\therefore \quad b_1 = \sqrt{1 - a_1^2} = \sqrt{1 - (1/4)} = \sqrt{3}/2$$

The requirement of orthogonality condition for ψ_1 and ψ_2 ; ψ_1 and ψ_3 and ψ_1 and ψ_4, gives

$$a_1a_2 + b_1b_2 + c_1c_2 + d_1d_2 = 0 \quad (\because c_1 = d_1 = 0)$$

or $$a_1a_2 + b_1b_2 = 0$$

$$a_1a_3 + b_1b_3 + c_1c_3 + d_1d_3 = 0$$

or $$a_1a_3 + b_1b_3 = 0$$

$$a_1a_4 + b_1b_4 + c_1c_4 + d_1d_4 = 0$$

or $$a_1a_4 + b_1b_4 = 0$$

Hence,

$$b_2 = b_3 = b_4 = -a_1a_2/b_1 = -a_1a_3/b_1 = -a_1a_4/b_1$$

$$= -(1/2)\ (1/2)/\sqrt{3}/2 = -1/2\sqrt{3}$$

Assuming that ψ_2 lies in the XZ plane, the hybrid orbital will have contribution from s, p_z and p_x orbitals only. The contribution of p_y to ϕ_2 would be zero so that $c_2 = 0$..

The normalization requirement for ϕ_2 gives

$$a_2^2 + b_2^2 + c_2^2 + d_2^2 = 1$$

or $$a_2^2 + b_2^2 + d_2^2 = 1 \quad (\because c_2 = 0)$$

or $$d_2^2 = 1 - (a_2^2 + b_2^2) = 1 - (1/4 + 1/12) = 2/3$$

$$\therefore \quad d_2 = \sqrt{2/3}$$

The requirement of orthogonality condition for ϕ_2 and ϕ_3 and for ϕ_2 and ϕ_4 gives

$$a_2a_3 + b_2b_3 + c_2c_3 + d_2d_3 = 0$$

or

$$a_2a_3 + b_2b_3 + d_2d_3 = 0$$

$$a_2a_4 + b_2b_4 + c_2c_4 + d_2d_4 = 0$$

or

$$a_2a_4 + b_2b_4 + d_2d_4 = 0$$

Hence,

$$d_3 = d_4 = -(a_2a_3 + b_2b_3)/d_2$$

or

$$-(a_2a_4 + b_2b_4)/d_2 = -(1/4+1/12)/\sqrt{2/3} = -1/\sqrt{6}$$

The normalization requirement for ϕ_3 gives

$$a_3^2 + b_3^2 + c_3^2 + d_3^2 = 1$$

$$c_3^2 = 1-(a_3^2 + b_3^2 + d_3^2)$$

$$= 1 - (1/4 + 1/12 + 1/6) = 1/2$$

$$\therefore \quad c_3 = +1/\sqrt{2}$$

Proceeding as above, the normalization requirement for ϕ_4 and orthogonality condition for ϕ_3 and ϕ_4 gives $c_4 = -1/\sqrt{2}$

Hence, the four sp^3 **hybrid orbital wave functions** are :

$$\psi_1 = 1/2\phi_s + \sqrt{3}/2\phi_{p_z}$$

$$\psi_2 = 1/2\phi_s - 1/2\sqrt{3}\phi_{p_z} + \sqrt{2/3}\phi_{p_x}$$

$$\psi_3 = 1/2\phi_s - 1/2\sqrt{3}\phi_{p_z} + 1/\sqrt{2}\phi_{p_y} - 1/\sqrt{6}\phi_{p_x}$$

$$\psi_4 = 1/2\phi_s - 1/2\sqrt{3}\phi_{p_z} - 1/\sqrt{2}\phi_{p_y} - 1/\sqrt{6}\phi_{p_x}$$

Orientation of Hybrid Orbitals in Space

The directional characteritsitcs of atomic orbitals of central atom A in the compound AX_n get uniformly distributed in the hybrid orbitals involved in the formation of the compound. Therefore, *the arrangement of hybrid orbitals around A is an automatic consequence of the hybridisation of its atomic orbitals.* This point will become clear from the following discussion.

It follows from the discussion on the topic Angular Wave Functions and Shapes of Orbitals, given in Chapter 1, that the *s* and *p* orbital wave functions of A are :

$$\phi_s = \frac{1}{2\sqrt{\pi}} R(r)_{n,0}$$

$$\phi_{p_x} = \frac{3}{2\sqrt{\pi}} \sin\theta \cos\phi \; R(r)_{n,1}$$

$$\phi_{p_y} = \frac{3}{2\sqrt{\pi}} \sin\theta \sin\phi \; R(r)_{n,1}$$

$$\phi_{p_z} = \frac{3}{2\sqrt{\pi}} \cos\theta \; R(r)_{n,1}$$

For most efficient hybridisation (*i.e.*, mixing) of atomic orbitals of the central atom A, the hybrid orbital wave functions should be maximised by putting their first differential $\partial\psi/\partial\theta$ equal to zero. Let us now consider the wave functions of the various types of hybrid orbitals.

1. Consider the wave function ψ_1 of one of the *sp* hybrid orbitals. As illustrated earlier in Problem 1,

$$\psi_1 = \frac{1}{\sqrt{2}}\phi_s + \frac{1}{\sqrt{2}}\phi_{p_z}$$

In terms of polar coordinates, the above function becomes

$$\psi_1 = \frac{1}{\sqrt{2}} \times \frac{1}{2\sqrt{\pi}} R(r)_{n,0} + \frac{1}{\sqrt{2}} \times \frac{3}{2\sqrt{\pi}} \cos\theta \, R(r)_{n,1}$$

Applying conditions for maximising ψ_1, we get

$$\frac{\partial\psi_1}{\partial\theta} = 0 = 0 + \frac{1}{\sqrt{2}} \times \frac{3}{2\sqrt{\pi}} (-\sin\theta) R(r)_{n,1}$$

or $\sin\theta = 0$ so that $\theta = \mathbf{0°}$ or $\mathbf{180°}$

We get exactly the same result when we consider the wave function ψ_2 of the second *sp* hybrid orbital.

Under the maximising condition, θ is the angle which the directions of the hybrid orbitals ψ_1 and ψ_2 make with +*Z* axis. This automatically means that one of the *sp* hybrid orbitals is aligned along the +*Z* axis (for $\theta = 0$) and the other orbital is aligned along the –*Z* axis (for $\theta = 180°$) so that the angle between the two *sp* hybrid orbitals is 180° (Fig. 2.)

2. Consider the wave functions for the sp^2 hybrid orbitals. If the atomic orbitals invovled in sp^2 hybridisation are *s*, p_z and p_x, then all the three resulting hybrid orbitals would be in the *XZ* plane. Suppose one of the hybrid orbitals with wave function ψ_1 lies along the +*Z* axis. Then, as illustrated above in Problem 2, the wave function ψ_2 of the second hybrid orbital lying in the plane *XZ* would be given by

$$\psi_2 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{p_x}$$

In terms of polar coordinates, ψ_2 takes the form,

$$\psi_2 = \frac{1}{\sqrt{3}} \times \frac{1}{2\sqrt{\pi}} R(r)_{n,0} - \frac{1}{\sqrt{6}} \times \frac{3}{2\sqrt{\pi}} \cos\theta \, R(r)_{n,1} + \frac{1}{\sqrt{2}} \times \frac{3}{2\sqrt{\pi}} \sin\theta \cos\phi \, R(r)_{n,1}$$

The angle ϕ for any orbital in *XZ* plane is 0° so that $\cos\phi = 1$. (ϕ is the angle which the direction of the hybrid orbital makes with +*Z* axis, as shown in Fig. 11)

$$\therefore \quad \psi_2 = \frac{1}{\sqrt{3}} \times \frac{1}{2\sqrt{\pi}} R(r)_{n,0} - \frac{1}{\sqrt{6}} \times \frac{3}{2\sqrt{\pi}} \cos\theta \, R(r)_{n,1} + \frac{1}{\sqrt{2}} \times \frac{3}{2\sqrt{\pi}} \sin\theta \, R(r)_{n,1}$$

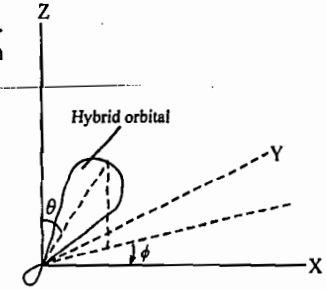


Fig. 11. Polar coordinates θ and ϕ of an sp^2 hybrid orbital.

Applying conditions for maximising ψ_1, we get

$$\frac{\partial\psi_2}{\partial\theta} = 0 = 0 + \frac{1}{\sqrt{6}} \times \frac{3}{2\sqrt{\pi}} \sin\theta\, R(r)_{n,1} + \frac{1}{\sqrt{2}} \times \frac{3}{2\sqrt{\pi}} \cos\theta\, R(r)_{n,1}$$

or $$\tan\theta = -\sqrt{3} \text{ so that } \theta = \mathbf{120°}$$

That is, the second sp^2 hybrid orbital in XZ plane is making an angle of 120° with the $+Z$ axis and hence with the first sp^2 hybrid orbital.

Similarly, $$\psi_3 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_z} - \frac{1}{\sqrt{2}}\phi_{p_x}$$

This function in polar coordinates becomes

$$\psi_3 = \frac{1}{\sqrt{3}} \times \frac{1}{2\sqrt{\pi}} R(r)_{n,0} - \frac{1}{\sqrt{6}} \times \frac{3}{2\sqrt{\pi}} \cos\theta\, R(r)_{n,1} - \frac{1}{\sqrt{2}} \times \frac{3}{2\sqrt{\pi}} \sin\theta \cos\phi\, R(r)_{n,1}$$

Applying the condition for maximising ψ_3 and simplifying the resulting equation, we get

$$\tan\theta = \sqrt{3} \text{ so that } \theta = \mathbf{240°}$$

Thus, the third sp^2 hybrid orbital in XZ plane makes an angle of 240° with the $+Z$ axis and hence with the first sp^2 hybrid orbital. Accordingly, the angle between the second and the third sp^2 hybrid orbitals is also 120° (Fig. 5)

3. Let us now consider the wave functions for the sp^3 hybrid orbitals. One of the hybrid orbitals is supposed to be lying along the +Z axis. Let us find out the angle which any other sp^3 hybrid orbital makes with the +Z axis and hence with the first sp^3 hybrid orbital. Let ψ_2 be the wave function for the second sp^3 hybrid orbital. Then, as illustrated above in Problem 3,

$$\psi_2 = \frac{1}{2}\phi_s - \frac{1}{2\sqrt{3}}\phi_{p_z} + \sqrt{\frac{2}{3}}\phi_{p_x}$$

Since this hybrid orbital utilises p_z and p_x atomic orbitals for hybridisation, it would lie in the XZ plane.

ψ_2, in terms of polar coordinate system, transforms as

$$\psi_2 = \frac{1}{2} \times \frac{1}{2\sqrt{\pi}} R(r)_{n,0} - \frac{1}{2\sqrt{3}} \times \frac{3}{2\sqrt{\pi}} \cos\theta\, R(r)_{n,1} + \sqrt{\frac{2}{3}} \times \frac{3}{2\sqrt{\pi}} \sin\theta \cos\phi\, R(r)_{n,1}$$

Since the hybrid orbital is in XZ plane, the angle ϕ is zero so that $\cos\phi = 1$.

Applying the condition for maximising ψ_2, we get

$$\frac{\partial\psi_2}{\partial\theta} = 0 = 0 + \frac{1}{2\sqrt{3}} \times \frac{3}{2\sqrt{\pi}} \sin\theta\, R(r)_{n,1} + \sqrt{\frac{2}{3}} \times \frac{3}{2\sqrt{\pi}} \cos\theta\, R(r)_{n,1}$$

or $$\frac{1}{2\sqrt{3}} \sin\theta = -\sqrt{\frac{2}{3}} \cos\theta$$

or $$\frac{\sin\theta}{\cos\theta} = \tan\theta = -\sqrt{\frac{2}{3}} \times 2\sqrt{3} = -2\sqrt{2}$$

$\therefore$ $$\theta = \mathbf{109° 28'}$$

Thus, the second sp^3 hybrid orbital makes an angle of 109° 28′ with the $+Z$ axis and hence with the first sp^3 hybrid orbital. We can similarly show that the angle between the first and the third hydrid orbital as also between the first and the fourth sp^3 hybrid orbital is 109°28′. Thus, the sp^3 hybrid orbitals are tetrahedrally spread around the central atom (Fig. 8).

Following the same procedure as discussed above, we can show that the arrangement of dsp^3 hybrid orbitals around the central atom is trigonal pyramidal while that of d^2sp^3 hybrid orbitals is octahedral and so on.

It is clear from the above discussion that the concept of hybridisation alone is sufficient to fix the arrangement of hybrid orbitals in space around the central atom.

VSEPR Theory

We have seen that in the formation of simple covalent molecules, there is one central atom which forms covalent bonds with other atoms. For example, in the formation of a molecule of water, the central atom is oxygen which forms *two* covalent bonds with two hydrogen atoms (*i.e.*, one bond with each hydrogen atom). Similarly, in the formation of a molecule of ammonia, the central atom is nitrogen which forms *three* covalent bonds with three hydrogen atoms and in the formation of a molecule of methane, the central atom is carbon which forms *four* covalent bonds with four hydrogen atoms and so on.

According to the **valence shell electron pair repulsion theory (VSEPR theory)**, the geometry of a covalent compound depends upon the number and arrangement in space of electron pairs present in the valency shell of the central atom. This number is *half* of the summation of electrons present in the valence shell of the central atom and the electrons contributed by the combining atoms. Thus, in the case of H_2O molecule, the number of electron pairs present around the oxygen atom would be $\frac{1}{2}(6+2)$ and in the case of PCl_5 molecule, this number would be $\frac{1}{2}(5+5)$ and so on. These electron pairs occupy the available orbitals around the central atom, each orbital accommodating only one electron pair. These electron pairs experience electrostatic repulsion from one another. Such electron pairs, therefore, tend to keep apart from one another as far as possible so that they may experience minimum electrostatic repulsion. This would result in minimum energy and maximum stability of the molecule.

The charge of a lone pair of electrons is more spread around the central atom than the charge of a bond pair of electrons with the result that the distance between charges of two lone pairs of electrons on the central atom is less than the distance between the charges of a lone pair and a bond pair of electrons which, in turn, is less than the distance between the charges of two bond pairs of electrons. Hence the electrostatic repulsion between lone pair–lone pair of electrons is greater than the repulsion between lone pair–bond pair of electrons which, in turn, is greater than the repulsion between bond pair–bond pair of electrons. Since the repulsion between electron pairs recedes very rapidly with distance between the centres of charges of electron pairs, therefore, in molecules which are capable of existing in more than one geometries, the most stable geometry is determined by assuming that the electrostatic repulsion between any two electron pairs is taken to be negligibly small if the angle between them is more than about 100°.

The VSEPR theory, however, has a weak theoretical basis and is associated with some snags. For instance, if in a compound AX_2, there are two electron pairs around the central atom, one pair would be in the *s* orbital and the other pair would be in the *p* orbital. In the compound AX_2, therefore, the two A–X bonds would be non-equivalent. This is evidently a wrong conclusion. For instance, both the Be – F bonds in BeF_2 molecule are equivalent.

However, we can explain the geometry of molecules more satisfactorily if we assume, before applying principles of VSEPR theory, that in the formation of covalent compounds, the orbitals (containing electron pairs) present around the central atom *undergo hybridisation* before entering into covalent bond

formation with other atoms. Thus, the VSEPR theory would lead to correct conclusions only in combination with the concept of hybridisation. The combination of the two concepts helps us to predict correctly the geometry of covalent molecules. This aspect has been discussed below in adequate details.

GEOMETRY OF COVALENT MOLECULES

We shall first discuss the geometry of molecules in which the central atom has no lone pair of electrons in any of its hybrid orbitals. In such cases if only two electron pairs are present around the central atom, they would be accommodated in the two *sp* hybrid orbitals of equal energy obtained by the hybridisation of *s* and p_z orbitals of the central atom. For minimum energy and maximum stability, these hybrid orbitals arrange themselves at an angle of 180° to each other. The molecule (AB_2) in such a case is thus **linear** and the bond angle is 180°.

If there are three electron pairs around the central atom, they would be accommodated in the three sp^2 hybrid orbitals obtained by the hybridisation of one *s* and two *p* orbitals of the central atom. According to the VSEPR theory, these orbitals are arranged at an angle of 120° to one another. The molecule (AB_3) in such a case is **planar trigonal** and the bond angle is 120°.

If there are four electron pairs around the central atom, they would occupy the four sp^3 hybrid orbitals of the central atom which according to the VSEPR theory are directed towards the four corners of a regular tetrahedron. The molecule (AB_4) in such a case is, therefore, **tetrahedral** and the bond angle is 109·5°.

It can thus be argued that if there are five electron pairs around the central atom, the hybrid orbitals around the central atom containing the electron pairs would be sp^3d hybridised and the molecule (AB_5) adopts **trigonal bipyramidal** geometry. In this geometry, all the bond angles are not equal. Three of the hybrid orbitals are in the same plane at an angle of 120° to one another and form, what are known as, **equatorial bonds.** Of the remaining two hybrid orbitals, one lies above and the other lies below the plane of the equatorial bonds. These orbitals form, what are known as, **axial bonds.** Thus, in this arrangement, the bond angles between equatorial bonds are of 120° each and the bond angles between axial bonds are of 90° each.

If there are six electron pairs around the central atom, the molecule (AB_6) utilises sp^3d^2 hybrid orbitals of the central atom and has **octahedral** geometry. The angles between any two of the six hybrid orbitals are 90° each. Similarly, if there are seven electron pairs around the central atom, the molecule (AB_7) utilises sp^3d^3 hybrid orbitals of the central atom and has **pentagonal bipyramidal** geometry. Like trigonal bipyramidal geometry, all the bond angles in this case also are not equal. Five of the hybrid orbitals are in the same plane at an angle of 72° to one another while the remaining two (one above and one below the plane) are at 90° to the plane.

From the above discussion it is evident that *the geometry of a covalent molecule depends upon the type of hybridisation which the orbitals around the central atom undergo.* If the valency shell orbitals of the central atom containing only shared pairs of electrons undergo *sp* hybridisation, the molecule is *linear*, if they undergo sp^2 hybridisation, the molecule is plane triangular and if they undergo sp^3 hybridisation, the molecule has a *tetrahedral* geometry and so on.

Regular and Irregular Geometry. It may be noted that if the central atom A of a molecule AB_x is surrounded by hybrid orbitals containing only shared pairs of electrons, *i.e., bond pairs* and there are no hybrid orbitals containing lone pairs in the valency shell, the molecule has a **regular geometry.** There is no distortion of the shape. If, however, the central atom is surrounded also by one or more hybrid orbitals containing lone pairs of electrons in the valency shell, the geometry of the molecule is **distorted** to some extent. This is because the repulsive interactions between lone pair–lone pair, lone pair–bond pair and bond pair–bond pair are different. We know that the bond pair between two atoms is under the influence of two nuclei and most of the electron charge cloud is oriented between them. On

the other hand, the lone pair of electrons is under the influence of only one nucleus and, therefore, its electron charge cloud is spread out and tends to occupy more space. For example, in the case of **ammonia**, there are three bond pairs and one lone pair (Fig. 12). Since the lone pair occupies more space around the central atom, it can interact more and, therefore, it will repel the electron pairs in the neighbouring orbitals more strongly whereas the repulsive interactions between the two bond pairs will be less. Thus, it may be concluded that the lone pair–lone pair repulsion is greater than the lone pair–bond pair repulsion which, in turn, is greater than the bond pair–bond pair repulsion, *i.e.,*

Lone pair–Lone pair Repulsion > Lone pair–Bond pair Repulsion > Bond pair–Bond pair Repulsion

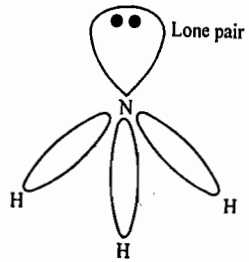


Fig. 12. Lone pair and bond pairs in ammonia molecule.

Accordingly, the presence of one or more hybrid orbitals with lone pairs of electrons has the effect of altering the bond angles to some extent. The molecules now do not retain any regular geometry (such as triangular, tetrahedral, etc.) This type of behaviour is met with, for example, in ammonia and water molecules (Figs. 22 and 23).

We shall now discuss the geometry of some typical covalent molecules resulting from different types of hybridisation of their valence shell orbitals.

Geometry of Molecules Containing only Bond Pairs of Electrons

1. Geometry of beryllium fluoride molecule involving *sp* hybrid orbitals of Be. Beryllium atom, in ground state, has electronic configuration $1s^2\,2s^2$, as shown in Fig. 13(*a*). It has no unpaired electron and, therefore, should be chemically inert. However, in the excited state, it has two unpaired electrons, as represented in Fig. 13(*b*). Beryllium atom can, therefore, form two covalent bonds as, for example, with fluorine atoms to give a molecule of beryllium fluoride, F–Be–F. Since both the bonds are of equal strength, it follows that *s* and *p* orbitals hybridise to give two *sp* hybrid orbitals of equivalent energy. These hybrid orbitals must lie as far apart from each other as possible in order to minimise the force of repulsion between them and thus to have a stable structure. Hence, the two hybrid orbitals point in opposite directions, as shown in Fig. 13. The molecule is, therefore, linear and the F–Be–F bond angle is equal to 180°.

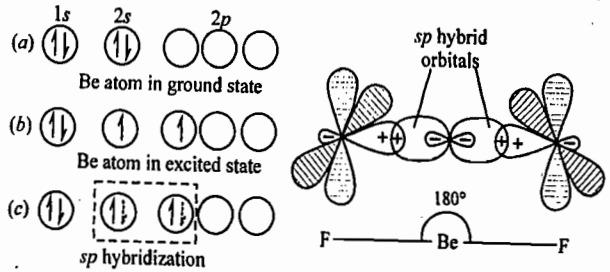


Fig. 13. Linear beryllium fluoride molecule resulting from *sp* hybridisation of valence shell orbitals of the central Be atom. Dotted arrows represent electrons supplied by fluorine atoms.

The molecules such as BeH_2, $BeCl_2$, $ZnCl_2$, $HgCl_2$, etc., have similar geometry.

2. Geometry of boron trifluoride molecule involving sp^2 hybrid orbitals of B atom. The electronic configuration of the central atom, boron, in ground state is $1s^2\,2s^2\,2p^1$. This is shown in Fig. 14(*a*). It has only one unpaired electron and, therefore, it can form only one covalent bond. In the excited state, however, it has three unpaired electrons, as represented in Fig. 14(*b*).

Evidently, now three covalent bonds can be formed, as, for example, with fluorine atoms, giving a molecule of boron trifluoride, BF_3. Since all the three B – F bonds are known to be equivalent, it follows

that the s and p orbitals of boron hybridise to give three sp^2 hybrid orbitals of equivalent energy. According to the VSEPR theory, the three sp^2 hybrid orbitals should be held at an angle of 120° to one another. This arrangement would lower the force of repulsion between electron pairs to the minimum. Since these three hybrid orbitals overlap with orbitals of three fluorine atoms, each F–B–F bond angle would be equal to 120° and the molecule would, therefore, be **trigonal planar**, as shown in Fig. 14.

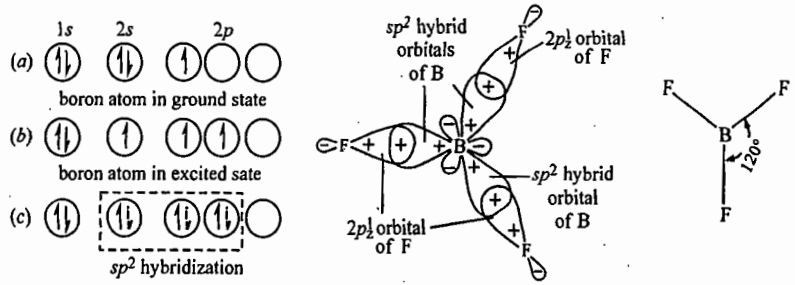


Fig. 14. Trigonal planar molecule of boron trifluoride resulting from sp^2 hybridisation of valence shell orbitals of the central boron atom. Dotted arrows represent electrons supplied by fluorine atoms.

Molecules such as BH_3, BCl_3, etc., have similar geometry.

3. Geometry of methane molecule involving sp^3 hybrid orbitals of C atom. The electronic configuration of carbon atom (the central atom in this case) is $1s^2 2s^2 2p_x^1 2p_y^1$, as shown in Fig. 15(*a*). It has only two unpaired electrons and hence it can form only two covalent bonds. In the excited state, however, it has four unpaired electrons, as represented in Fig. 15(*b*) and, therefore, it can form four covalent bonds with hydrogen atoms to give a molecule of methane. Since all the four C–H bonds are known to be exactly equivalent, it is evident that the s and p orbitals hybridise to give four sp^3 hybrid orbitals of equivalent energy. The orientation of these orbitals should be such as to have minimum repulsion between them. This is possible if the orbitals are directed towards the four corners of a regular tetrahedron. Thus, methane molecule has **tetrahedral geometry**, as shown in Fig. 15. The carbon atom is at the centre of the tetrahedron and four hydrogens are at the four corners. The H–C–H bond angle is 109·5°.

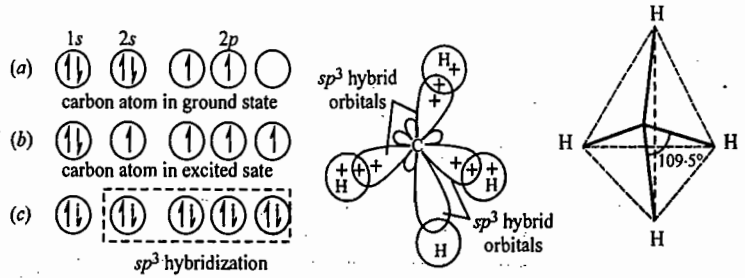


Fig. 15. Tetrahedral molecule of methane resulting from sp^3 hybridisation of valence shell orbitals of the central carbon atom. Dotted arrows represent electrons supplied by hydrogen atoms.

Molecules such as CCl_4, SiF_4 etc., have similar geometry.

4. Geometry of phosphorus pentafluoride molecule involving sp^3d hybrid orbitals of P atom. The outer electronic configuration of phosphorus, the central atom in this case, is $3s^2\ 3p^3$ which may be represented as in Fig. 16(*a*), in accordance with the Hund's rule.

As can be seen from Fig. 16(*a*), phosphorus in its ground state has only three unpaired electrons in the valency shell. Two more unpaired electrons should be made available in order to explain the formation of PF_5. This happens by the unpairing of electrons in the 3s orbitals by the excitation of the atom, as shown in Fig. 16(*b*).

Now five orbitals are available for chemical combination which permit the formation of five covalent bonds with five fluorine atoms to give PF_5 molecule, as shown in Fig. 16 (*d*). These orbitals hybridise to form five sp^3d hybrid orbitals. The d orbital used in sp^3d hybridisation is $3d_{z^2}$. It may be noted that all the five hybridised orbitals are not equivalent. Three of these are oriented towards the three corners of an equilateral triangle making an angle of 120° between them. The bonds formed by these orbitals are called *equatorial bonds*. These three orbitals are planar, as shown. The remaining two orbitals are oriented at right angles to the plane of the first set of three orbitals, as shown in the figure. The bonds formed by these orbitals are called *axial bonds*. Phosphorus pentafluoride thus, has a **trigonal bipyramidal** geometry (Table 1), as shown in Fig. 16. In this molecule, therefore, while the bond angles between equatorial bonds are of 120° each, the bond angles between axial and equatorial bonds are of 90° each. Such unsymmetrical structures are not stable. Consequently, PF_5 is a very reactive molecule.

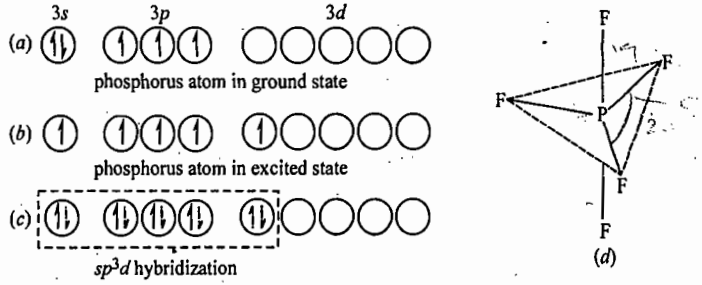


Fig. 16. Trigonal bipyramidal geometry of PF_5 molecule resulting from sp^3d hybridisation of valence shell orbitals of the central P atom. Dotted arrows represent electrons supplied by fluorine atoms.

It has been observed that in trigonal bipyramidal geometry, the axial bonds are slightly longer than the equatorial bonds. This is because of the fact that axial bonds experience greater repulsion from other bonds than the equatorial bonds. The electron pair repulsions decrease very sharply with increase in the bond angle so that the repulsions between bond pairs of electrons where the bond angle is greater than 100° are generally neglected. For the bond pair of electrons of the axial P–F bond, there are *three* bond pair–bond pair repulsions whereas for the bond pair of electrons of the equatorial P–F bond, there are only *two* bond pair–bond pair repulsions. Thus, in the case of PF_5 molecule, the length of each P–F axial bond is 2·19 Å while the length of each P–F equatorial bond is 2·04 Å.

Molecules such as PCl_5 and $SbCl_5$ have similar geometry.

It may be noted that if the d orbital involved in sp^3d hybridisation is the $d_{x^2-y^2}$ orbital, the molecule (AB_5) formed would have a **square pyramidal geometry,** as shown in Fig. 17.

This geometry, however, is less stable than the trigonal bipyramidal geometry unless stabilised by some other factors such as greater probability of pi bonding in the plane containing one A and four B atoms.

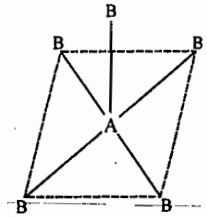


Fig. 17. Square pyramidal geometry of AB_5 molecule resulting from $sp^3d_{x^2-y^2}$ hybridisation of valence shell orbitals of the central atom A.

5. Geometry of sulphur hexafluoride molecule involving sp^3d^2 hybrid orbitals of S atom. Here the central atom is sulphur. Its outer electronic configuration is $3s^2 p_x^2 p_y^1 p_z^1$, as represented in Fig. 18(*a*).

There are only two unpaired electrons. Four more unpaired electrons have to be there in order to explain the formation of SF_6. This happens by the unpairing of 3*s* and 3*p* electrons which move into the 3*d* orbitals, by the excitation of the atom. This is shown in Fig. 18(*b*). Now, six unpaired electrons are available in six orbitals (one *s*, three *p* and two *d* orbitals) for bond formation to give SF_6 molecule, as shown in Fig. 18(*c*). These six orbitals hybridise to form six sp^3d^2 hybrid orbitals. The *d* orbitals used are $d_{x^2-y^2}$ and d_{z^2}. The six hybrid orbitals are now directed towards the six corners of a regular octahedron. Each of these six sp^3d^2 hybrid orbitals overlaps with the half-filled *p* orbital of each fluorine atom to form SF_6 molecule. The sulphur hexafluoride molecule thus has an octahedral geometry, as shown in Fig. 18(*d*).

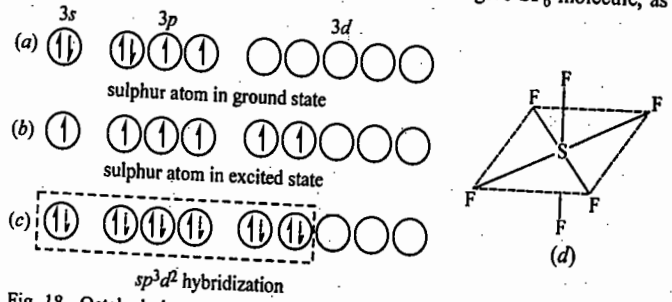


Fig. 18. Octahedral geometry of SF_6 molecule resulting from sp^3d^2 hybridisation of valency shell orbitals of the central S atom. Dotted arrows represent electrons supplied by fluorine atoms.

TeF_6 molecule has also octahedral geometry.

6. Geometry of iodine heptafluoride molecule involving sp^3d^3 hybrid orbitals of I atom. The outer electronic configuration of the central atom, iodine, in the ground state is $5s^2p_x^2p_y^2p_z^1$, as represented in Fig. 19(*a*). On excitation, unpairing of 5*s* as well as of $5p_x$ and $5p_y$ electrons takes place, as shown in Fig. 19(*b*). Now the seven orbitals ($5s$, $5p_x$, $5p_y$, $5p_z$, $5d_{xy}$, $5d_{yz}$ and $5d_{zx}$) hybridise to give seven sp^3d^3 hybrid orbitals. Each of these hybrid orbitals overlaps with the half-filled 2*p* orbitals of each fluorine atom to form IF_7 molecule, as shown in Fig. 19(*d*).

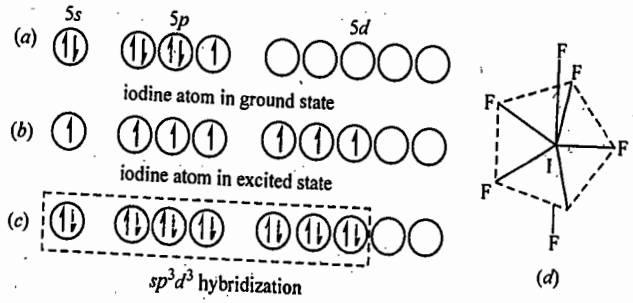


Fig. 19. Pentagonal bipyramidal geometry of IF_7 molecule resulting from sp^3d^3 hybridisation of valence shell orbitals of the central iodine atom. Dotted arrows represent electrons supplied by fluorine atoms.

The resulting molecule acquires **pentagonal bipyramidal** geometry, as shown in Fig. 19. In this molecule, again, all the seven bonds are not equivalent. Five of these are directed towards the vertices of a regular pentagon making an angle of 72° with one another. The remaining two are oriented at right angles to the plane of the first set of five orbitals. Thus, the bond angles in this molecule are of 72° and 90°.

The various kinds of hybridisation of valence shell orbitals discussed above together with the name of one compound formed in each case and the geometry acquired by the molecule, are summed

up in Table 1.

TABLE 1

Geometry of Covalent Molecules involving Different Types of Hybrid Orbitals of the Central Atom

Type of Hybridisation Involved	Name of the Compound	Geometry of the Molecule	Bond Angles ∠ABA
sp	BeF_2	Linear	180°
sp^2	BF_3	Trigonal plannar	120°
sp^3	CH_4	Tetrahedral	109·5°
sp^3d^2	PF_5	Trigonal bipyramidal	120° and 90°
sp^3d^2	SF_6	Octahedral	90°
sp^3d^3	IF_7	Pentagonal bipyramidal	72° and 90°

It may be noted that in the above compounds, all the electron pairs are *bonded* and the geometry and bond angles are exactly the same as expected according to VSEPR theory.

GEOMETRY OF MOLECULES CONTAINING BOND PAIRS AS WELL AS LONE PAIRS OF ELECTRONS

So far we have seen that in a molecule in which central atom has no lone pairs of electrons in any of its hybrid orbitals, the arrangement of hybrid orbitals around the central atom and the geometry of the molecule are the same. But, as already mentioned, the presence of one or more orbitals containing lone pairs in the valency shell cause some distortion in the geometry of the molecule. A few examples of molecules containing bond pairs as well as lone pairs of electrons and involving different types of hybridisation may now be considered. The + and – signs in the overlapping orbitals are not shown in the figures that follow for the sake of simplification.

1. Geometry of $SnCl_2$ Molecule. The outer electronic configuration of the central atom, tin, in this case, is $5s^2p_x^1p_y^1$. There are two unpaired electrons in 5*p* orbitals of tin and these are sufficient to form two bonds with chlorine atoms and, therefore, there is no need of promotion of electrons. The bond formation can take place by the overlapping of the two mutually perpendicular half-filled p_x and p_y orbitals of tin atom with the half-filled *p* orbitals of the two chlorine atoms. The molecule should thus be angular with Cl–Sn–Cl bond angle equal to 90°. However, as revealed by X-ray analysis and other properties, the Cl–Sn–Cl bond angle is quite close to 120°. Hence, it has been postulated that one *s* and two *p* orbitals of tin hybridise to give three sp^2 *hybrid orbitals of equivalent* energy, as shown in Fig. 20.

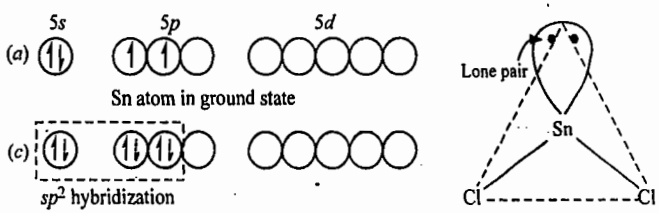


Fig. 20. V-shaped geometry of $SnCl_2$ molecule resulting from sp^2 hybridisation of the valence shell orbitals of Sn atom.

These sp^2 hybrid orbitals are arranged around the central atom in a *trigonal planar* geometry. One of these hybrid orbitals contains a lone pair of electrons while the remaining two contain one unpaired electron each. These two sp^2 hybrid orbitals containing unpaired electrons overlap with the half-filled

$2p$ orbitals of two chlorine atoms to form two Sn–Cl bonds. Thus, the central atom Sn in $SnCl_2$ is surrounded by three orbitals, each containing a pair of electrons. Two of these orbitals contain *shared* pairs while the third contains a *lone pair* of electrons (Fig. 21). The geometry of the molecule should have been V-shaped with bond angle of exactly 120°. However, on account of the fact that lone pair–bond pair repulsion is greater than bond pair–bond pair repulsion, the bond angle is slightly less than 120° although the molecule is still V-shaped.

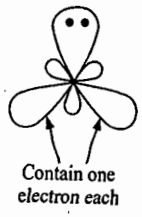


Fig. 21. Three sp^2 hybrid orbitals around tin.

2. Geometry of Ammonia Molecule. In this case, nitrogen is the central atom. Its outer electronic configuration is $2s^2p_x^1p_y^1p_z^1$. All the three p orbitals contain one electron each, in accordance with Hund's rule, as shown in Fig. 22(*a*). There are three unpaired electrons in the $2p$ orbitals and these are sufficient to form three bonds with hydrogen atoms giving ammonia molecule without involving any excitation of the atom. In that case, however, the molecule, utilising only three p orbitals of N atom, would have three mutually perpendicular N–H bonds. But actually it is not so. NH_3 molecule is *pyramidal* in structure with H–N–H bond angle of 107°. This is explained by postulating that one $2s$ and three $2p$ orbitals hybridise to form four sp^3 hybrid orbitals. One of these hybrid orbitals contains a lone pair of electrons while the remaining three contain one unpaired electron each. These three hybrid orbitals of N atom overlap with $1s$ orbitals of hydrogen atoms to form three N–H sigma bonds.

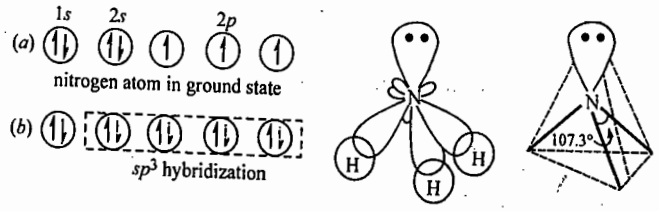


Fig. 22. Pyramidal geometry of ammonia molecule resulting from sp^3 hybridisation of valence shell orbitals of the central N atom. Dotted arrows represent electrons supplied by hydrogen atoms.

According to VSEPR theory, the force of repulsion between a lone pair and a bond pair is greater than the force of repulsion between the bond pairs of electrons. The molecule, therefore, gets a little distorted and the bond angle H–N–H decreases from the tetrahedral angle of 109·5° to 107°. The shape of the molecule is thus **pyramidal** in which the nitrogen atom lies at the centre, three hydrogens form the base and the lone pair of electrons lies at the apex of the pyramid, as shown in the figure.

3. Geometry of Hydronium Ion, H_3O^+. The formation of hydronium ion involving a coordinate covalent bond has been discussed in the last chapter. Since a coordinate covalent bond once formed is indistinguishable from a covalent bond, all the O–H bonds in hydronium ion are equivalent. The number of valence electrons to be accommodated in the orbitals of the central oxygen atom are 6 + 2 = 8. Therefore, four hybrid orbitals are required to accommodate these 8 valence electrons. The orbitals of the central oxygen atom would thus undergo sp^3 hybridisation. Of the four pairs of electrons accommodated in the four sp^3 hybrid orbitals, the three are bond pairs between O and H atoms and the fourth one is a lone pair. Because of the presence of this lone pair, the shape of H_3O^+ molecule becomes **pyramidal.** The positive charge is not confined to a single H atom but is delocalised over the entire hydronium ion so that the ion is better written as $(H_3O)^+$.

4. Geometry of Water Molecule. In water the central atom is oxygen. Its outer electronic configuration is $2s^22p_x^2p_y^1p_z^1$, as represented in Fig. 23 (*a*).

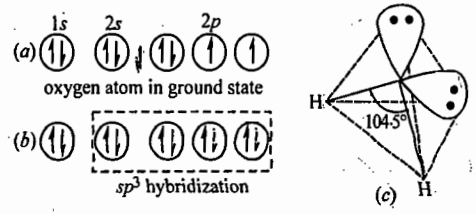


Fig. 23. V-shaped geometry of water molecule resulting from sp^3 hybridisation of valence shell orbitals of the central O atom. Dotted arrows represent electrons supplied by hydrogen atom.

Thus, there are two unpaired electrons which can form two bonds with hydrogen atoms without involving any excitation of the oxygen atom. But, in that case, the H_2O molecule, utilising only two p orbitals should have had H–O–H bond angle of 90°. This is not so actually. Water molecule is known to have a *bent structure* with H–O–H angle of 104·5°. This is explained by postulating that one $2s$ and three $2p$ orbitals of oxygen undergo hybridisation to give four sp^3 hybrid orbitals of equivalent energy. According to VSEPR theory, these hybrid orbitals are arranged *tetrahedrally* around the oxygen atom. Two of these orbitals contain bond pairs and the other two contain lone pairs of electrons. Since, as stated before, the force of repulsion between the two lone pairs of electrons amongst themselves is more than the force of repulsion between a lone pair and a bond pair which, in turn, is more than the force of repulsion between two bond pairs of electrons, there is greater distortion in this molecule than in ammonia. Consequently, the bond angle H–O–H in water is even smaller than the bond angle H–N–H in ammonia. This angle has been found to be 104·5°. The water molecule is thus said to have a **V-shaped geometry** as shown in Fig. 23(*c*).

It is evident from the above discussion that although ammonia and water molecules have essentially tetrahedral arrangement of hybrid orbitals around their central atoms as in methane, yet the four pairs of electrons are not equivalent in each of ammonia and water molecules. The result is that while methane molecule has a symmetrical tetrahedral geometry, ammonia molecule has pyramidal and water molecule has V-shaped geometry.

5. Geometry of Sulphur Tetrafluoride Molecule. In SF_4 molecule, the central atom, sulphur (Z = 16) has the outer electronic configuration $3s^23p_x^2p_y^1p_z^1$, as shown in Fig. 24. In the formation of SF_4 molecule, sulphur needs four half-filled orbitals to overlap with $2p$ orbitals of four fluorine atoms. This happens by the unpairing of the two p_x electrons and movement of one of them into one of the $3d$ orbitals on the excitation of atom [Fig. 24(*b*)]. These five orbitals ($3s$, $3p_x$, $3p_y$, $3p_z$ and $3d$) hybridise to give five sp^3d hybrid orbitals of equivalent energy. The central atom is, therefore, surrounded by five hybrid orbitals. One of these contains a lone pair of electrons while the other four contain one unpaired electron each which overlap with p orbitals of fluorine atoms to form four S – F bonds. According to VSEPR theory, such a molecule should have bond angles of 90°, 120° and 180°. However, due to the presence of a lone pair of electrons, there is distortion in the molecule and the bond angles are 89°, 118° and 177° instead of normal bond angles of 90°, 120° and 180°, respectively. The molecule thus has an irregular tetrahedral geometry.

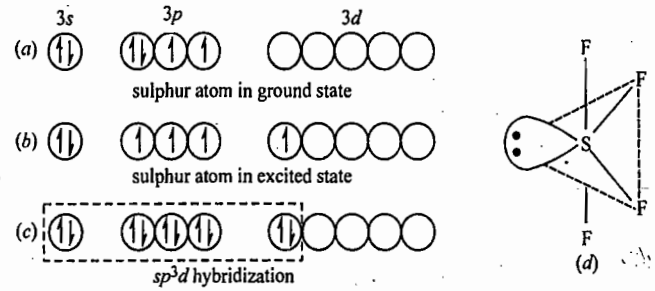


Fig. 24. Irregular tetrahedral geometry of SF_4 molecule resulting from sp^3d hybridisation of valence shell orbitals of the central S atom.

It may be noted that the lone pair in SF_4 structure is present in equatorial position and not in axial position. This may be understood in terms of stability of structure. We have seen that in the case of trigonal bipyramidal geometry (Fig. 16*d*), the electron pair present in axial position experiences more repulsion than the electron pair present in equatorial position. Therefore, in SF_4 molecule, if the lone pair is present in axial position, it would experience greater repulsion and the structure would be unstable. On the other hand, if the lone pair is present in equatorial position, it would experience comparatively less repulsion and the molecular structure would be stable.

6. Geometry of Chlorine Trifluoride Molecule. In ClF_3 molecule, chlorine is the central atom. Its outer electronic configuration is $3s^2 3p_x^2 p_y^2 p_z^1$. In the formation of ClF_3 molecule, chlorine requires three half-filled orbitals to form three Cl – F bonds. This becomes possible by the promotion of one of the electrons of $3p_y$ orbital to one of the vacant $3d$ orbitals as a result of the excitation of the atom. The five orbitals (one $3s$, three $3p$ and one $3d$) hybridise to form five sp^3d hybrid orbitals (Fig. 25 *c*). Two of these hybrid orbitals are occupied by lone pairs of electrons. The remaining three hybrid orbitals contain single electron each and form three sigma bonds with three fluorine atoms. Thus, in ClF_3, the central chlorine atom is surrounded by three bond pairs and two lone pairs of electrons. On the basis of VSEPR theory, the molecule is expected to be T-shaped with *cis* ∠ FClF of 90°. However, due to the presence of lone pairs, there is distortion in the structure and bond angle is 87·6° instead of 90°. Such a structure is also described as **distorted T-shaped** taking into consideration the positions occupied by atoms only.

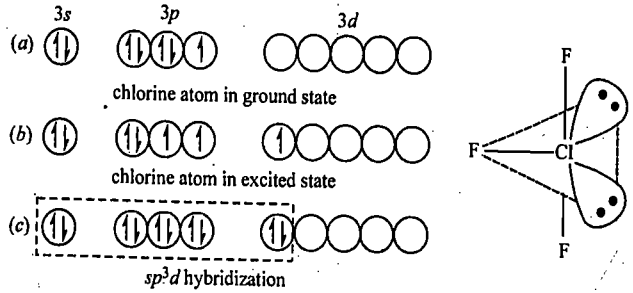


Fig. 25. Distorted T-shaped geometry of ClF_3 molecule resulting from sp^3d hybridisation of valence shell orbitals of the central Cl atom.

7. Geometry of Xenon Difluoride Molecule. The outer electronic configuration of the central atom, xenon, is $5s^2 5p_x^2 p_y^2 p_z^2$, as shown in Fig. 26(*a*). In the formation of XeF_2 molecule, one of the $5p$ electrons of xenon atom gets unpaired and shifts to one of the $5d$ orbitals (Fig. 26 *b*) as a result of the excitation of the xenon atom. One $5s$, three $5p$ and one $5d$ orbitals of Xe hybridise to yield five sp^3d hybrid orbitals of equivalent energy, as shown in Fig. 26 (*c*). Three of these hybrid orbitals contain lone pairs and the remaining two are half-filled. The two half-filled hybrid orbitals overlap with the *p* orbitals of the two fluorine atoms to form two Xe–F bonds. Thus, in XeF_2 molecule, the central atom, Xe, is surrounded by the five completely filled orbitals, two of which contain shared pairs of electrons and the remaining three contain lone pairs of electrons. The molecule is **linear**, as shown in Fig. 26(*d*). This is due to the fact that the three lone pairs are present on equatorial positions to

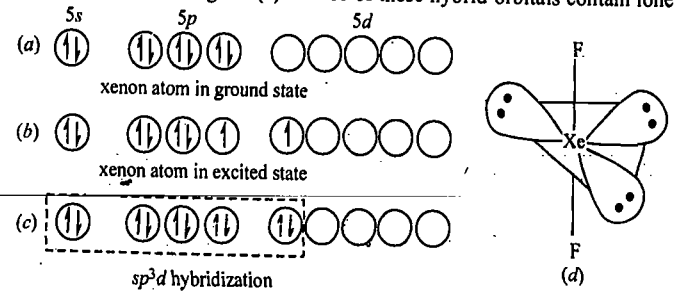


Fig. 26. Linear geometry of XeF_2 molecule resulting from sp^3d hybridisation of valence shell orbitals of the central Xe atom.

minimise electron pair repulsions. Due to symmetrical arrangement of lone pairs around the central xenon atom, the molecule has linear structure.

8. Geometry of Xenon Tetrafluoride Molecule. The outer electronic configuration of the central atom, xenon, in the ground state (*viz.*, $5s^2 5p_x^2 p_y^2 p_z^2$) is represented in Fig. 27 (*a*). In the excited state, two of the $5p$ electrons go to the $5d$ orbitals so that there are now four unpaired electrons (two in $5p$ and two in $5d$ orbitals), as shown in Fig. 27 (*b*). The six orbitals (one $5s$, three $5p$ and two $5d$) hybridise to form six sp^3d^2 hybrid orbitals. Two of these contain lone pairs of electrons. The remaining four contain unpaired electrons which are involved in bonding with four atoms of fluorine, as shown in Fig. 27 (*c*). The central atom, Xe, is thus surrounded by 6 fully filled hybrid orbitals. Four of these orbitals contain shared pairs while the remaining two contain lone pairs of electrons, as shown in Fig. 27 (*d*). The two orbitals containing lone pairs are present in axial position, one above and the other below the plane of the four fluorine atoms. Lone pair orbitals in these positions cause minimum repulsion. The geometry of XeF_4 molecule is **square planar**, as shown in the figure.

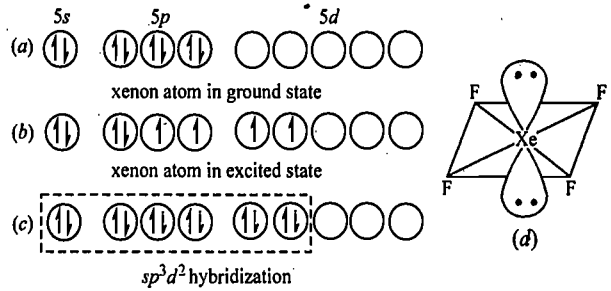


Fig. 27. Square planar geometry of XeF_4 molecule resulting from sp^3d^2 hybridisation of valence shell orbitals of the central Xe atom.

9. Geometry of Iodine Pentafluoride Molecule. The formation of IF_5 molecule involves sp^3d^2 hybridisation, as will be clear on reference to Fig. 28. In the excited state, the central atom, iodine, after combining with five fluorine atoms, is surrounded by six completely filled hybrid orbitals, five of which contain bond pairs and one contains a lone pair of electrons. Its geometry is **square pyramidal**, as shown in Fig. 28(*d*).

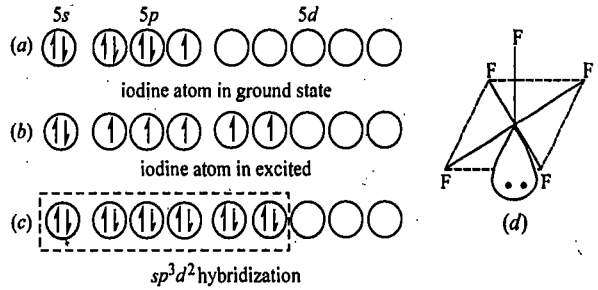


Fig. 28. Square pyramidal geometry of IF_5 molecule resulting from sp^3d^2 hybridisation of valence shell orbitals of the central iodine atom.

General Treatment. If A, B and L represent, respectively, the central atom, the bond pairs of electrons and the lone pairs of electrons, then the stability of a particular geometry would, evidently, depend upon the magnitude and the number of repulsive interactions between the various types of electron pairs. Since the electrostatic repulsion between two like charges decreases sharply with the distance between them, the electron pair repulsion is taken to be negligible and stands rejected if the angle between the electron pairs is more than 100°. The lone pair (L) is shown by an orbital having two electrons which are represented by two dots. Based on the above discussion, the geometry of the various molecules would be as follows.

Molecules of AB_3L Type. This type of molecules in which the sp^3 hybrid orbitals of the central atom are occupied by three bond pairs and one lone pair of electrons would have **pyramidal geometry**, as shown in Fig. 29. Examples are NH_3 and PCl_3. The bond angle BAB in such cases is less than 109·5°.

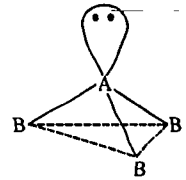


Fig. 29. Geometry of AB_3L type of molecules

Molecules of AB_2L_2 Type. This type of molecules in which the sp^3 hybrid orbitals of the central atom are occupied by two bond pairs and two lone pairs of electrons would have **V-shaped geometry**, as shown in Fig. 30. Examples are H_2O, $SeCl_2$ and NH_2^- ion. The bond angle BAB in this case is less than that in molecules of AB_3L type.

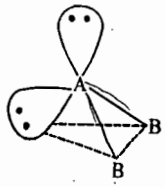
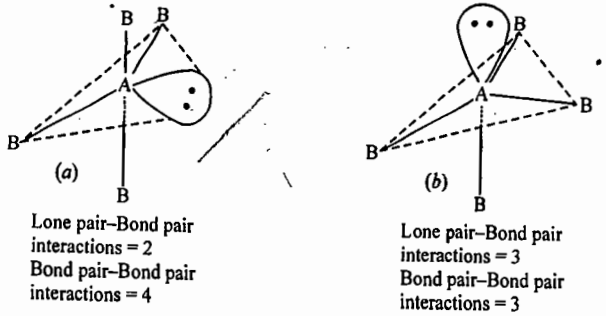


Fig. 30. Geometry of AB_2L_2 type of molecules

Molecules of AB_4L Type. *Molecules having four bond pairs and one lone pair of electrons accommodated in sp^3d hybrid orbitals, of the central atom can have two types of geometry, as shown in Fig. 32.*



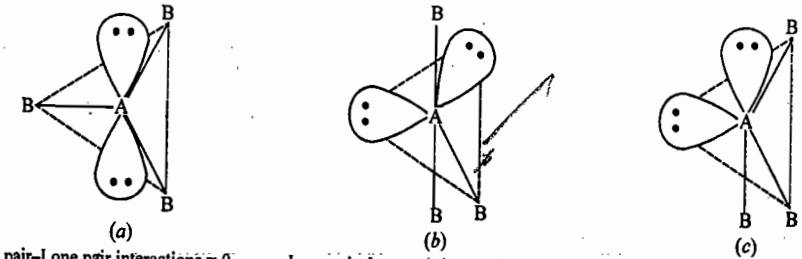
Lone pair–Bond pair interactions = 2
Bond pair–Bond pair interactions = 4

Lone pair–Bond pair interactions = 3
Bond pair–Bond pair interactions = 3

Fig. 31. Geometry of AB_4L type of molecules

The repulsive interactions involved in the above geometries are as indicated above. Since geometry (*a*) involves lesser electronic repulsion, it is more stable than geometry (*b*). Thus, molecules of the type AB_4L would have geometry (*a*).

Molecules of AB_3L_2 Type. Molecules having three bond pairs and two lone pairs accommodated in sp^3d hybrid orbitals of the central atom can have three types of **trigonal bipyramidal** arrangements of orbitals around the central atom, as shown in Fig. 32.

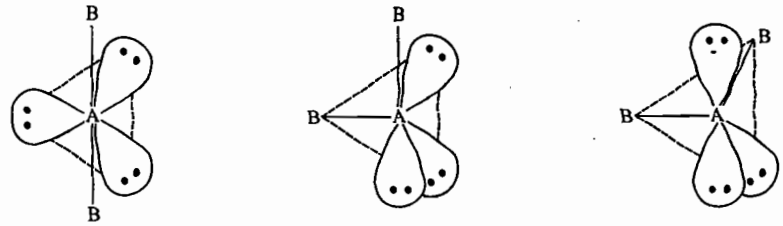


(*a*)	(*b*)	(*c*)
Lone pair–Lone pair interactions = 0	Lone pair–Lone pair interactions = 0	Lone pair–Lone pair interactions = 1
Lone pair–Bond pair interactions = 3 + 3 = 6	Lone pair–Bond pair interactions = 4	Lone pair–Bond pair interactions = 3
Bond pair–Bond pair interactions = 0	Bond pair–Bond pair interactions = 2	Bond pair–Bond pair interactions = 2

Fig. 32. Geometry of AB_3L_2 type of molecules

Neglecting the electron pair repulsions where the angle is greater than 100°, the various repulsive interactions involved in the three types of arrangements are as indicated above. Of the three resulting geometries, geometry (*b*) involves the minimum electronic repulsion. It is, therefore, most stable. The actual geometry of molecules of the type AB_3L_2 is thus geometry (*b*).

Molecules of AB_2L_3 Type. Molecules having two bond pairs and three lone pairs of electrons accommodated in sp^3d^2 hybrid orbitals of the atom can have the following three types of arrangements of orbitals around the central atom, as shown in Fig. 33.

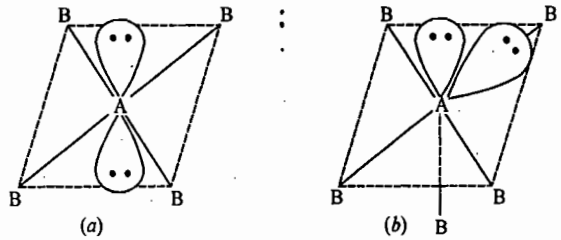


(*a*)	(*b*)	(*c*)
Lone pair–Lone pair interactions = 0	Lone pair–Lone pair interactions = 2	Lone pair–Lone pair interactions = 2
Lone pair–Bond pair interactions = 6	Lone pair–Bond pair interactions = 3	Lone pair–Bond pair interactions = 4
	Bond pair–Bond pair interactions = 1	Bond pair–Bond pair interactions = 0

Fig. 33. Geometry of AB_2L_3 type of molecules

It readily follows from the above that the resulting geometry (*a*), involving minimum electronic repulsion, would be the most stable and most probable geometry of compounds of AB_2L_3 type. It is evidently a linear geometry. Examples are XeF_2 and ICl_2^-.

Compounds of AB_4L_2 Type. Compounds having four bond pairs and two lone pairs of electrons accommodated in sp^3d^2 hybrid orbitals of the central atom can have either of the following two types of arrangements of orbitals around the central atom shown in Fig. 34.



(*a*)	(*b*)
Lone pair–Lone pair interactions = 0	Lone pair–Lone pair interactions = 1
Lone pair–Lone pair interactions = 8	Lone pair–Lone Bond interactions = 6
Bond pair–Lone pair interactions = 4	Bond pair–Lone pair interactions = 5

Fig. 34. Geometry of AB_4L_2 type of molecules

A perusal of various interactions suggests that the resulting geometry (*a*) is more stable than geometry (*b*). Thus, molecules of the type AB_4L_2 would have **a square planar geometry** depicted by (*a*). Examples are XeF_4 and ICl_4.

Molecules of AB_5L Type. Molecules having five bond pairs and one lone pair of electrons accommodated in sp^3d^2 hybrid orbitals of the central atom would have a square pyramidal geometry, as shown in Fig. 35.

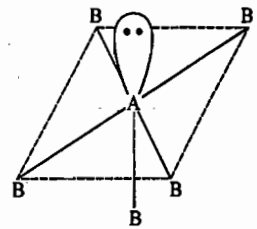


Fig. 35. Geometry of AB_5L type of molecules

Molecules of AB_7 Type. Molecules of the type AB_7 would have **pentagonal bipyramidal** geometry, as already illustrated in Fig. 19.

The geometries of various types of molecules are summed up in Table 3.

TABLE 3

Geometries of Various Types of Molecules

Type of molecules	No. of bond pairs of electrons	No. of lone pairs of electrons	Total number of electron pairs	Type of hybridisation involved	Geometry of molecules	Examples
AB_2	2	0	2	sp	Linear	$BeF_2[Ag(NH_3)_2]^+$
AB_3	3	0	3	sp^2	Trigonal planar	BCl_3, BH_3
AB_2L	2	1	3	sp^2	V-shaped	$SnCl_2$, $PbCl_2$
AB_4	4	0	4	sp^3	Tetrahedral	CH_4, NH_4^+
AB_3L	3	1	4	sp^3	Trigonal pyramidal	NH_3, PX_3
AB_2L_2	2	2	4	sp^3	V-shaped	H_2O, $SeCl_2$, NH_2
AB_5	5	0	5	sp^3d	Trigonal bipyramidal	PF_5, $Fe(CO)_5$
AB_4L	4	1	5	sp^3d	Irregular tetrahedral	SF_4, $TeBr_4$
AB_3L_2	3	2	5	sp^3d	T-shaped	ClF_3
AB_2L_3	2	3	4	sp^3d	Linear	XeF_2, ICl_2^-
AB_6	6	0	6	sp^3d^2	Octahedral	SF_6, $[SbF_6]^-$
AB_5L	5	1	6	sp^3d^2	Square pyramidal	IF_5, ClF_5, $[SbF_5]^{2-}$
AB_4L_2	4	2	6	sp^3d^2	Square planar	XeF_4, ICl_4
AB_7	7	0	7	sp^3d^3	Pentagonal bipyramidal	IF_7

Structure of Carbon Dioxide Molecule. The outer electronic configuration of carbon in ground state is $2s^2 2p_x^1 p_y^1$ and in excited state is $2s^1 2p_x^1 p_y^1 p_z^1$. The outer electronic configuration of oxygen atom in ground state is $2s^2 2p_x^2 p_y^1 p_z^1$. In the formation of CO_2 molecule, hybridisation of orbitals of carbon occurs only to a limited extent involving only one s and one p orbital, as shown in Fig. 36. There is thus sp hybridisation of valence shell orbitals of the carbon atom resulting in the formation of two *sp hybrid orbitals*. The remaining two p orbitals of carbon are excluded from hybridisation.

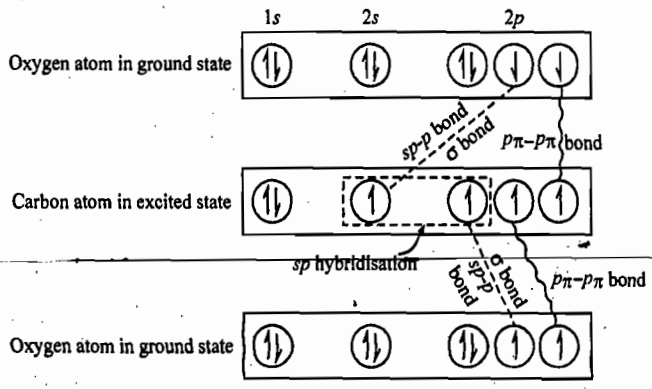


Fig. 36. Linear geometry of CO_2 molecule resulting from sp hybridisation of orbitals of valence shell of the carbon atom.

The two sp hybrid orbitals of carbon atom form sigma bonds with one p orbital of each of the two oxygen atoms, as shown by means of dotted lines. These are, evidently, $sp - p$ bonds. This leaves *two unhybridised* half-filled p orbitals in the carbon atom and one half-filled p orbital in each oxygen atom. This permits *pi bond formation* between the two half-filled p orbitals of carbon atom with the half-filled p orbitals of the two oxygen atoms. This is shown by dotted lines (Fig. 36). These bonds are called $p\pi - p\pi$ bonds.

The formation of CO_2 molecule is shown pictorially in Fig. 37.

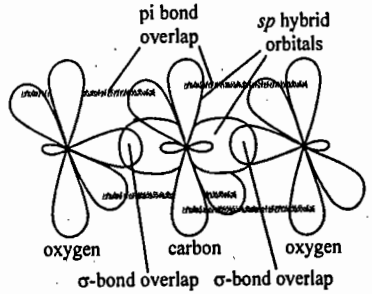


Fig. 37. Pictorial representation of the formation of linear carbon dioxide molecule.

As already mentioned, in CO_2 molecule, the two p orbitals of carbon atom are excluded from hybridisation. This is a case of only sp hybridisation of carbon orbitals and hence the molecule of carbon dioxide is ***linear***.

GEOMETRY OF SOME IONS

The **geometry of an ion** is determined to a large extent by the following two factors :

1. *The number of sigma bonds* involved in the bonding of atoms.
2. The *number of lone pairs of electrons* present around the central atom.

It is to be noted that double bonds, if any, involved in the formation of an ion do not influence the geometry of the ion.

In cases where the central atom forms multiple bonds, the number of orbitals involved in hydridisation is equal to $\frac{1}{2}$ (Number of valence shell electrons of the central atom + Number of electrons gained by the central atom through σ covalent bonding). The π bonds are invariably *excluded* from hybridisation.

We shall now consider geometry of a few common ions.

1. Geometry of Carbonate Ion. The outer electronic configuration of carbon atom in ground state is $2s^2 p_x^1 p_y^1$ and in excited state is $2s^1 2p_x^1 p_y^1 p_z^1$, as shown in Fig. 38.

Since carbonate ion is doubly charged, two of the oxygen atoms carry one additional electron each, so that they contain only one half-filled p orbital each, as shown. The third oxygen atom, however, has the normal outer electronic configuration, *i.e.*, it has two half-filled p orbitals.

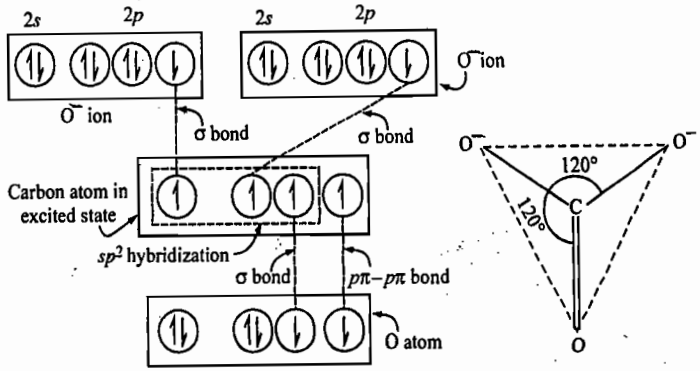


Fig. 38. Geometry of carbonate ion. A trigonal planar geometry results from sp^2 hybridisation of valence shell orbitals of the central atom.

The three orbitals (one $2s$ and two $2p$) of the carbon atom hybridise to form three sp^2 hybrid orbitals. The covalent sigma bonds are formed by overlapping of two of the three sp^2 hybrid orbitals of the carbon atom with the p orbitals of the two oxygen anions each of which contains only one unpaired electron. One more covalent sigma bond is formed by overlapping of the third sp^2 hybrid

orbital of the carbon atom with one of the two half-filled p orbitals of the *third* oxygen atom. Now only one of the p orbitals of the carbon atom and one of the p orbitals of the *third* oxygen atom remain half-filled. These two p orbitals *overlap laterally* forming a *pi bond*. The various types of overlappings are shown in Fig. 38.

Since, as mentioned above, there are three sp^2 hybrid orbitals around the central carbon atom which are involved in the formation of three sigma bonds with the three oxygen atoms, the CO_3^- ion has a **trigonal planar geometry**, as shown in the figure. It is evident that all the three sigma bonds in the carbonate ion are $sp^2 - p$ bonds.

Since all the C – C bonds in CO_3^- ion are equivalent, the actual structure of CO_2 molecule is a resonance hybrid of three resonating structures, as discussed in the previous chapter.

2. Geometry of Nitrate Ion. The outer electronic configuration of nitrogen atom is $2s^2 2p_x^1 p_y^1 p_z^1$ while that of oxygen atom is $2s^2 2p_x^2 p_y^1 p_z^1$. The nitrate ion carries a unit negative charge. This means that one of the oxygen atoms carries an extra electron. The outer electronic configurations of the three oxygen atoms are represented in Fig. 39.

The three orbitals (one $2s$ and two $2p$) of the N atom hybridise to give three sp^2 hybrid orbitals. One of the three sp^2 hybrid orbitals of the N atom contains a lone pair of electrons while the other two contain unpaired electrons. The orbital with lone pair of electrons overlaps with p orbital of oxygen atom which is vacated by rearranging the electrons of this atom. This results in the formation of a sigma dative bond, N→O. A sigma covalent bond is formed between nitrogen and oxygen atoms by the overlapping of one of the sp^2 hybrid orbitals of nitrogen with the *only* half-filled p orbital of the second oxygen atom (which already contains one additional electron). Another covalent bond (σ bond) is formed by the overlapping of another sp^2 hybrid orbital of nitrogen with one of the half-filled p orbitals of the *third* oxygen atom. We still have one unhybridised p orbital of nitrogen atom containing one electron and one half-filled p orbital of the third oxygen atom. These two half-filled p orbitals overlap laterally forming a pi bond.

The various types of overlappings are shown in Fig. 39.

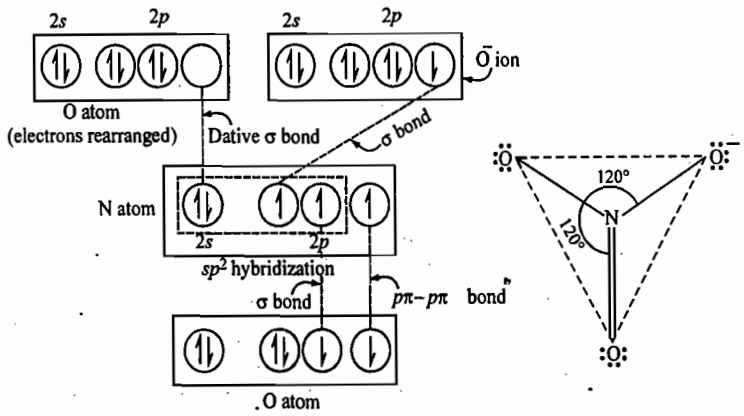
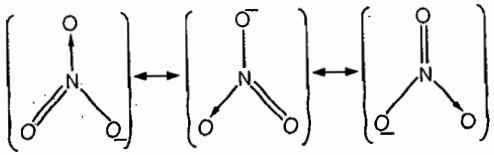


Fig. 39. Geometry of nitrate ion. A trigonal planar geometry results from sp^2 hybridisation of the valence shell orbitals of the central N atom.

Since there are three sp^2 hybrid orbitals around the central N atom which are involved in forming two sigma covalent and one sigma dative covalent bond with the three oxygen atoms, the NO_3^- ion has **trigonal planar geometry**, as shown in Fig. 39. As is evident, all the three covalent bonds in nitrate ion are sp^2–p bonds.

Actually the nitrate ion is a *resonance hybrid* of the three resonating structures given below :



3. Geometry of Sulphate Ion. The outer electronic configuration of sulphur is $3s^2 3p_x^2 p_y^1 p_z^1$, in the normal state and $3s^1 3p_x^1 p_y^1 p_z^1 d_{xy}^1 d_{yz}^1$, in the excited state, as shown in Fig. 40. One $3s$ and three $3p$ orbitals hydridise to produce four sp^3 hybrid orbitals, as shown. The d orbitals are excluded from hybridisation. The sulphate ion carries two units of negative charge. Therefore, two of the oxygen atoms may be considered to have one additional electron each forming O^- ions. These two ions of oxygen marked (a), therefore, have only one half-filled p orbital each. Thus, two of the four sp^3 hybrid orbitals of the sulphur atom overlap with the half-filled orbitals of the two oxygen ions giving rise to two sigma covalent bonds.

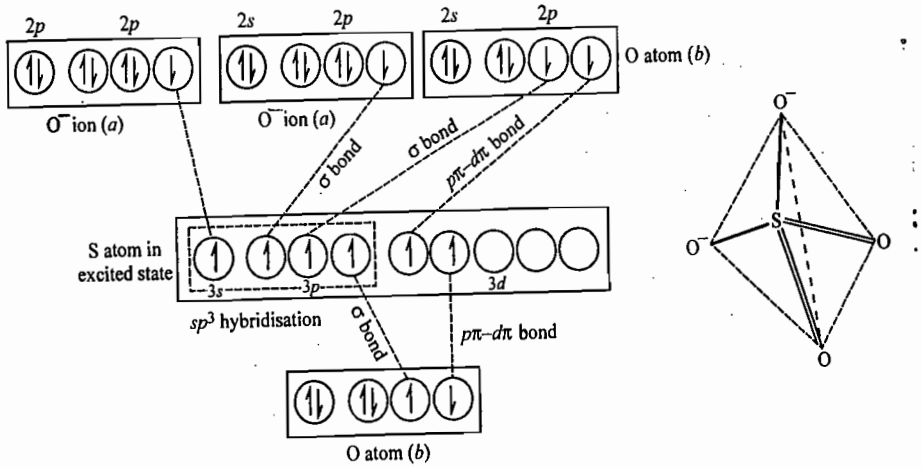


Fig. 40. Geometry of sulphate ion. A tetrahedral geometry results from sp^3 hybridisation of the orbitals of the central S atom.

We are left with two sp^3 hybrid orbitals of sulphur atom. Also we have two oxygen atoms more (marked b), the outer electronic configuration of each of which is $2s^2 2p_x^2 p_y^1 p_z^1$. The two sp^3 hybrid orbitals of sulphur atom form two more *sigma covalent bonds* by overlapping with one half-filled p orbital of each of the two oxygen atoms. Now we are left with two half-filled $3d$ orbitals of sulphur and also with one half-filled p orbital of each of the two oxygen atoms (marked b). The $3d$ orbitals of sulphur, therefore, form π bonds with the two oxygen atoms.

It is evident that all the four sigma bonds in the sulphate ion are $sp^3 - p$ bonds. The SO_4^{2-} ion is actually a resonance hybrid of several structures so that all the S–O bonds are exactly equivalent.

4. Geometry of Perchlorate Ion. The outer electronic configuration of chlorine atom in ground state is $3s^2 3p_x^2 p_y^2 p_z^1$ while in excited state is $3s^1 3p_x^1 p_y^1 p_z^1 d_{xy}^1 d_{yz}^1 d_{xz}^1$. One $3s$ and three $3p$ orbitals hybridise

to give four sp^3 hybrid orbitals. The d orbitals are excluded from hybridisation. This is illustrated in Fig. 41.

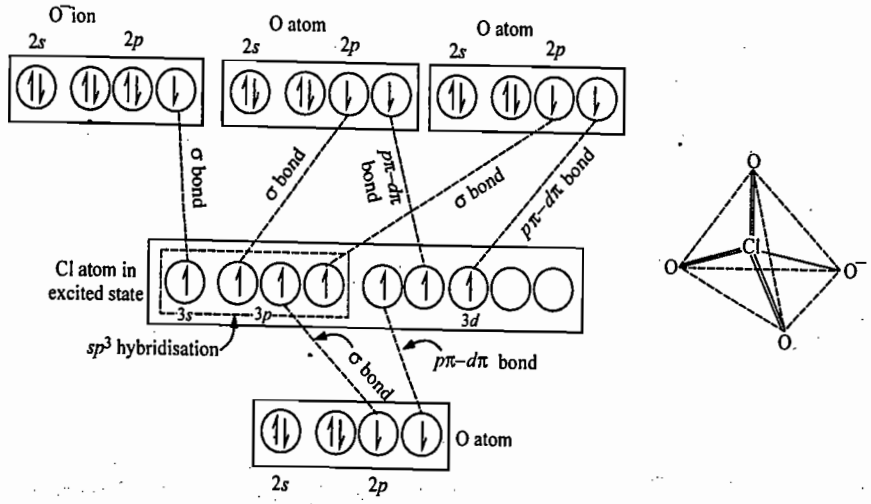


Fig. 41. Geometry of perchlorate ion. A tetrahedral geometry results from sp^3 hybridisation of valence shell orbitals of the central atom.

The outer electronic configuration of oxygen is $2s^2 2p_x^2 p_y^1 p_z^1$. There are four oxygen atoms in ClO_4^- ion. One of these carries an extra electron due to the negative charge on the ClO_4^- ion forming O^- ion. Chlorine forms a sigma covalent bond with this oxygen ion through the overlapping of one of its sp^3 hybrid orbitals with the only half-filled p orbital of the oxygen ion. Chlorine also forms three more sigma covalent bonds with three other oxygen atoms. For this purpose, three half-filled sp^3 hybrid orbitals of chlorine atom overlap with one of the half-filled p orbitals of each of the three oxygen atoms.

Now we have three half-filled $3d$ orbitals of the chlorine atom and one half-filled $2p$ orbital in each of the the three oxygen atoms. The $3d$ orbitals of chlorine atom overlap with the half-filled p orbitals of the three oxygen atoms *laterally*, thus, forming three π bonds, one with each of the three oxygen atoms.

Since there are four sp^3 hybrid orbitals around the central Cl atom which are involved in the formation of four sigma covalent bonds with the oxygen atoms, the ClO_4^- ion has a **tetrahedral geometry,** as shown in the figure.

As can be seen, all the four sigma bonds in perchlorate ion are $sp^3 - p$ bond. The ClO_4^- ion is actually a resonance hybrid of several structures so that all the Cl – O bonds are exactly equivalent.

5. Geometry of Chlorate Ion. The chlorate ion differs from the perchlorate ion in having one oxygen atom less. In this case, the central atom, chlorine, is attached to three oxygen atoms instead of four. One of the oxygen atoms carries an extra electron thus forming O^- ion due to the negative charge on the chlorate ion.

One $3s$ and three $3p$ orbitals of the chlorine atom hybridise to give four sp^3 hybrid orbitals. Chlorine forms three sigma covalent bonds by overlapping of three of the four sp^3 hybrid orbitals with three oxygen atoms and also two π bonds by lateral overlapping of $3d$ orbitals of chlorine with the half-filled p orbitals of two of the oxygen atoms, as shown.

Since the central Cl atom forms three sigma bonds with oxygen atoms, the ClO_3^- ion should have a planar trigonal geometry. But the geometry of chlorate ion is actually **pyramidal.** This is due to the fact that one of the sp^3 hybrid orbitals is occupied by a lone pair of electrons, as is evident from Fig. 42.

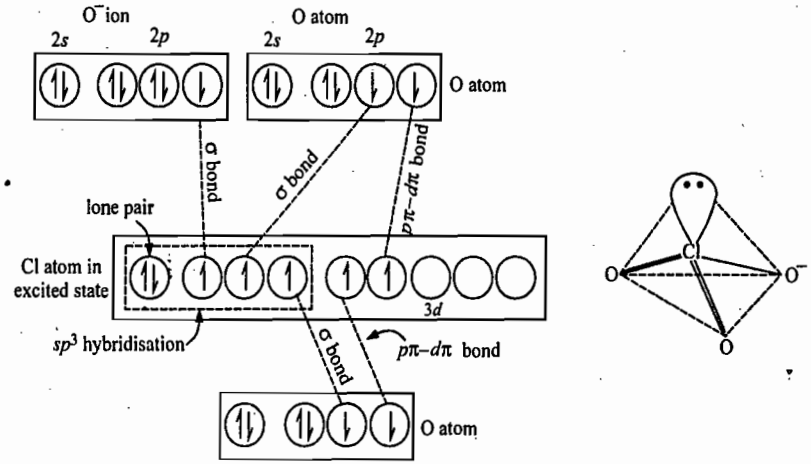


Fig. 42. Geometry of chlorate ion. The molecule is pyramidal because of the presence of a lone pair of electrons on Cl atom.

The ClO_3^- ion is a resonance hybrid of several structures so that all the Cl – O bonds are exactly equivalent.

Problem. (*a*) In the hydrides of Group 16 elements, *viz.*, H_2O, H_2S, H_2Se and H_2Te, the central atom in each case involves sp^3 hybridisation but the bond angles decrease as shown below :

H_2O	H_2S	H_2Se	H_2Te
104·5°	92·5°	91·0°	89·5°

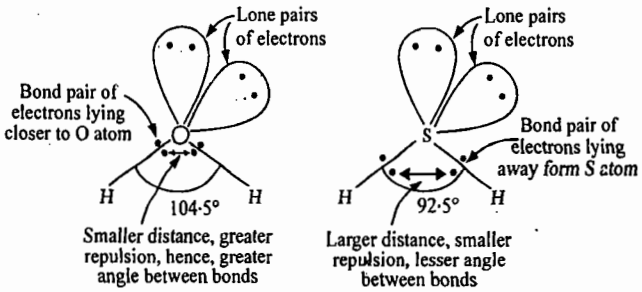
How would you account for this ?

(*b*) Why is the bond angle in F_2O smaller than that in H_2O ?

Answer. (*a*) In the hydrides of Group 16 elements, the orbitals around the central atom in each case undergo sp^3 hybridisation and the atom is surrounded by two lone pairs and two bond pairs of electrons (*cf.* geometry of H_2O molecule, Fig. 23). Since lone pair–lone pair repulsion is greater than the lone pair–bond pair repulsion, the bonded electron pairs are forced closer to each other and, therefore, the bond angle decreases from the normal tetrahedral angle of 109·5°. It is a general observation that the bond angles in the hydrides of the elements belonging to third or higher periods of a group are smaller than the bond angles in the hydrides of the elements of the second period of the same group. For instance, the bond angle in H_2O is 104·5° whereas it is close to 90° in H_2S, H_2Se and H_2Te. Thus it appears that the repulsions between bond pairs around the smaller atoms of an element of a group are stronger than between the bigger atoms of the same group. This may be explained in the following manner :

An orbital containing a lone pair when present in a bigger-sized atom occupies much more space than the lone pair orbital on a smaller-sized atom of an element of the same group. Therefore, the lone pair–bond pair distances are smaller and hence the lone pair–bond pair repulsions are stronger in the hydrides of bigger- sized S, Se and Te atoms compared to the hydride of O atom, *i.e.*, H_2O. Apart from this, the electronegativity goes on decreasing from O to Te. Consequently, the position of the bond pairs

of electrons shifts more and more away from the central atom in moving from H_2O to H_2Te. For example, as shown below, the bond pair is closer to oxygen in O–H bond than it is to sulphur atom in S – H bond. As a result, the force of repulsion between the bonded pairs of electrons in H_2O is more than that in H_2S. The force of repulsion between the bonded pairs of electrons decreases as we move from H_2O to H_2Te. Therefore, the bond angle also decreases in the same order. Since the increase in size and decrease in electronegativity is more significant in going from O to S than from S to Se to Te, the decrease in bond angle is also more significant in going from O to S than from H_2S to H_2Se to H_2Te.



(*b*) In F_2O, the bond pairs of electrons would lie *closer to fluorine atom* because fluorine is more electronegative than oxygen.

In H_2O, the bond pairs of electrons would lie *closer to oxygen atom* because oxygen is more electronegative than hydrogen.

Following the same arguments as advanced for (*a*), it can be easily realised that the bond angle in F_2O would be smaller than that in H_2O.

QUESTIONS

1. (*a*) What do you understand by hybridisation ? Explain giving examples.
   (*b*) What type of geometry is possible for molecules undergoing the following types of hybridisation :
   (*i*) sp (*ii*) sp^2 (*iii*) sp^3 (*iv*) sp^3d (*v*) sp^3d^2 (*vi*) sp^3d^3
2. (*a*) Why do molecules have definite geometry ? In which of the following types of geometry, all the bond angles are not the same :
   (*i*) Octahedral (*ii*) trigonal planar (*iii*) trigonal bipyramidal
   (*iv*) tetrahedral (*v*) pentagonal bipyramidal. [Ans. (*iii*), (*v*)]
   (*b*) Beryllium (Z = 4) has no unpaired electron in its ground state. However, in all its compounds beryllium shows divalency. Explain.
3. (*a*) What is hybridisation ? What are the important characteristics of hybridisation ?
   (*b*) The central atom in the molecules of CH_4, NH_3 and H_2O involves sp^3 hybridisation of its valence shell orbitals. But the bond angles in these molecules are 109·5, 107° and 104·5°, respectively. Account for this.
   (*c*) What shapes are associated with the molecules involving sp^3d^2 and sp^3d^3 hybridisation ?
4. Discuss the stereochemistry of the following molecules on the basis of hybridisation : PF_5, $SnCl_2$, NH_3, ClF_3
5. The ground state electronic configuration of chlorine is $1s^22s^2p^63s^2p^5$. Account for the geometry of the following molecules/ions of chlorine :
   (*a*) ClF_3 (*b*) ClO_4^- (*c*) ClO_3^-
6. On the basis of hybridisation, discuss the geometry of the following molecules :
   SF_6, IF_7, $SnCl_2$, XeF_4, SF_4, H_2O, PCl_5 and NH_3.
7. (*a*) According to electronic configuration, water should have bond angle H – O – H of 90° and ammonia should have three mutually perpendicular N – H bonds but actually both the molecules have unsymmetrical tetrahedral structure. How would you explain this ?
   (*b*) Account for the following decreasing trend of repulsive interactions : lone pair–lone pair > lone pair–bond pair > bond pair–bond pair.

   (*c*) Discuss the geometry of molecules having
   (*i*) two lone pairs and two bond pairs (*ii*) one lone pair and three bond pairs
   (*iii*) one lone pair and four bond pairs (*iv*) one lone pair and five bond pairs
8. Discuss the geometry of the following ions :
   (*a*) NO_3^- (*b*) CO_3^{2-} (*c*) SO_4^{2-} (*d*) ClO_3^- (*e*) ClO_4^-
9. (*a*) Why is it necessary to involve hybrid orbitals while trying to account for the geometry of methane molecule ?
   (*b*) Which of PF_5 or SF_6 does not have symmetrical geometry and why ?
   (*c*) Account for the geometry of PH_3, OF_2 and IF_5 on the basis of concept of hybridisation.
   (*d*) Discuss sp^3d^3 hybridisation with one example.
10. Construct wave functions for sp, sp^2 and sp^3 hybrid orbitals.
11. Involving the wave mechanical treatment, discuss the orientation of hybrid orbitals in space.
12. Discuss the VSEPR theory. Illustrate carefully that VSEPR theory has to be combined with the concept of hybridisation to account for the geometry of covalent molecules.

6 THE STRUCTURE OF SOLIDS

Solids, as is well known, are characterised by *incompressibility, rigidity* and *mechanical strength.* This indicates that the molecules, atoms or ions that make up a solid are *closely packed, i.e.,* they are held together by strong forces and cannot move at random. Thus, *in solids there is well-ordered arrangement of molecules, atoms or ions.* The properties of solids not only depend upon the number and kind of constituents but also on their arrangements.

Solids can be classified into the following two categories.

1. Crystalline Solids. *A substance whose constituents are arranged in an orderly manner in a definite geometric form is called a* **crystalline solid.** X–ray diffraction studies of these solids reveal that the regular arrangement of the constituents (molecules, atoms or ions) *extends over large distances* in three-dimensional network of crystals. In other words, the crystalline solids are said to exhibit *long range order.* Some common examples of crystalline solids are sodium chloride, sulphur, diamond, sugar, etc.

2. Amorphous Solids. *A substance whose constituents are not arranged in an orderly manner is called an* **amorphous solid.** These substances do possess properties such as incompressibility and rigidity to a certain extent but they do not have definite geometric forms. Some amorphous solids may have some orderly arrangement but *it does not extend to more than a few Angstrom units.* Thus, amorphous solids have only *short range order.* Some common examples of amorphous solids are glass, rubber, plastics, etc.

Difference between Crystalline and Amorphous Solids. Crystalline and amorphous solids differ from one another in the following respects.

1. Characteristic Geometry. A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules, atoms or ions in three-dimensional space. An amorphous solid, on the other hand, does not have any pattern or arrangement of its constituents and, therefore, does not have any definite geometric shape.

2. Melting Points. A crystalline substance has a *sharp melting point, i.e.,* it changes abruptly into liquid state at a fixed temperature. An amorphous substance, on the contrary, does not have a sharp melting point. For example, if glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt change into liquid state. Strictly speaking, *solid state refers only to crystalline state, i.e., only a crystalline material can be considered to be a* **true solid.**

3. Isotropy and Anistropy. Amorphous solids differ from crystalline solids in another important respect. *The properties such as electrical conductivity, thermal conductivity, mechanical strength and refractive index of an amorphous solid are the same in all directions.* Amorphous substances are, therefore, said to be **isotropic.** Liquids and gases are also isotropic.

Crystalline solids, on the other hand, are **anisotropic,** *i.e., their physical properties are different in different directions.* For example, the velocity of light passing through a crystal varies with the direction

in which it is measured. Thus, a ray of light entering such a crystal may split up into two components each following a different path and travelling with a different velocity. This phenomenon is known as **double refraction.** Thus, anisotropy in itself is a strong evidence for the existence of ordered molecular arrangement in such materials. This can be shown on reference to Fig. 1 in which a simple two-dimensional arrangement of only two different kinds of atoms is depicted. If the properties are measured along the direction indicated by the slanting line *CD,* they will be different from those measured in the direction indicated by the vertical line *AB.* The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case, each row is made up of one type of atoms only. In amorphous solids, atoms or molecules are arranged at random and in a disorderly manner and, therefore, all directions are identical and all properties are alike in all directions.

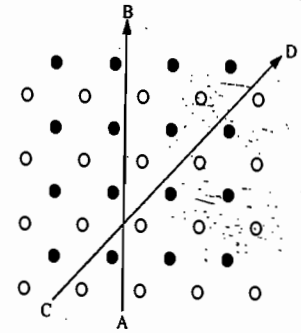


Fig. 1. Anisotropic behaviour of a crystal.

Size and Shape of Crystals. Several naturally occurring solids have definite crystalline shapes which can be recognised easily. There are many other solid materials which occur as powders or agglomerates of fine particles and appear to be amorphous. But when an individual particle is examined under a microscope, it is also seen to have a definite crystalline shape. *Such solids in which the crystals are so small that they can be recognised only under a powerful microscope, are said to be* **microcrystalline.** The size of a crystal depends on the rate at which it is formed ; the slower the rate, the bigger the crystal. This is because time is needed by the ions or atoms or molecules to get into their proper positions in the crystal structure. Thus, large transparent crystals of sodium chloride, silver chloride, lithium chloride, etc., can be prepared by melting these salts and allowing them to cool very slowly at a uniform rate. It is for this reason that crystals of most of the minerals formed by geological processes are often very large.

Interfacial Angles. Crystals are bound by plane faces. *The angle between any two faces is called an* **interfacial angle.** It is measured by an instrument called *goniometer.* It may be noted that the size of the faces or even shapes of the crystals of *one and the same substance* may vary widely with conditions of their formation. Although a crystal may have different shapes yet the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout. This is also known as law of constancy of interfacial angles or law of crystallography. This is illustrated in Fig. 2. Although the external shapes are different yet the interfacial angle is the same.

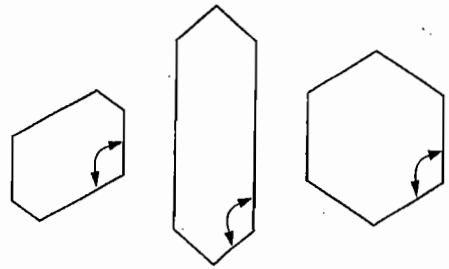


Fig. 2. Interfacial angles in a crystal.

SYMMETRY IN CRYSTALS

Besides the interfacial angles, another characteristic property of crystals is their symmetry. The symmetry of a crystal may be understood in terms of symmetry operation and symmetry elements.

The ***symmetry operation*** *is an operation performed around a line, plane or point on a body so that it yields the same or similar appearance of the body after the operation.* To illustrate this, let us consider a symmetry operation such as rotation around an axis. Suppose we are looking at a cube. If we rotate the cube through 90° about an imaginary axis passing through the centres of the top and bottom faces (Fig. 3), the appearance after rotation is exactly similar to the appearance before rotation. The cube on further rotation presents similar appearance three times more in one complete rotation. Thus, a cube gives similar

appearance by rotation through 90° about an axis passing perpendicularly through the centre. In this example, the *rotation about an axis* is called *symmetry operation* and the *axis of rotation* about which the cube is rotated is called a *symmetry element.*

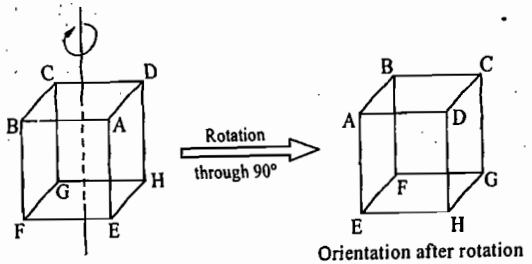


Fig. 3. Illustration of rotation of a cube around an axis. Rotation of a cube through 90° about an axis passing through the centres of the top and bottom faces yields exactly similar appearance.

There are various types of symmetry elements, only three of which will be described here. These are : (1) *Plane of symmetry* (2) *Axis of symmetry* and (3) *Centre of symmetry.*

1. Plane of symmetry. *When an imaginary plane can divide a crystal into two parts such that one is the exact mirror-image of the other, the crystal is said to have a plane of symmetry.*

2. Axis of Symmetry. *An axis of symmetry is an imaginary line about which the crystal may be rotated such that it presents the same or similar appearance more than once during the complete rotation.* For example, in the case of a *cube* (as discussed above), an axis passing *perpendicularly* through the centres is such that when the cube is rotated, it presents similar appearance in four rotations of 90° each and the same appearance after the fourth rotation. Such an axis is called **a four-fold** or **a tetrad axis** of symmetry (Fig. 3). In a cube, there are 3 four-fold axes of symmetry, as shown in Fig. 4.

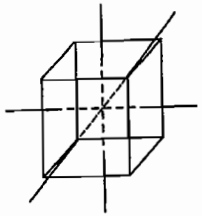
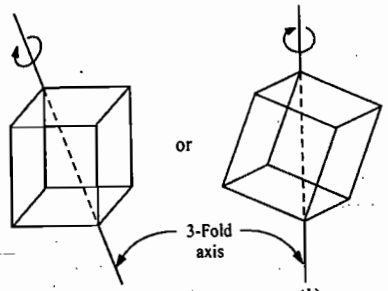


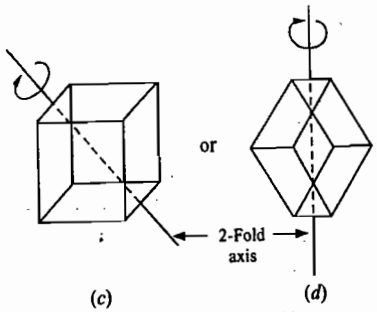
Fig. 4. Three four-fold axes in a cube.

If the same or similar appearance is repeated after an angle of 120°, the axis is called a **three-fold** or **triad axis of symmetry**. One of the three-fold axes in a cube is shown in Fig. 5(*a*). To illustrate the rotation more clearly, it is held as shown in Fig. 5(*b*) and rotated around the body diagonal. Since there are four body diagonals in a cube, it has 4 three-fold axes of symmetry.



Rotation through 120°

Fig. 5. A three-fold axis in a cube.

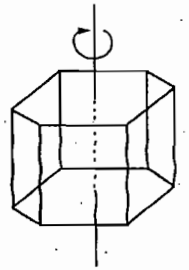


Rotation through 180°

Fig. 6. A two-fold axis in a cube.

Similarly, if the same or similar geometry appears after an angle of 180°, the axis is called a **two-fold** or a **diad axis**. One of the two-fold axes in a cube is shown in Fig. 6(*a*). The rotation can be understood by holding the cube as shown in Fig. 6(*b*). There are, evidently, 2 two-fold axes in a cube.

Likewise, if the same or similar geometry appears after rotation through an angle of 60°, the axis is called a **six-fold** or **hexad axis**. A hexagonal crystal has one six-fold axis (Fig. 7). It is clear from the figure that similar appearance is repeated after rotating the crystal through an angle of 60°.



6-Fold axis

Rotation through 60°

Fig. 7. A six-fold axis in a hexagonal crystal.

In general, if the same or similar appearance of a crystal is repeated on rotating it through an angle of 360°/n around an imaginary axis, the axis is called an **n-fold axis**. A crystal can have only the 2-fold, 3-fold 4-fold and 6-fold axes of rotation. The angle through which the crystal will have to be rotated to get the same or similar appearance, evidently, will be 180°, 120°, 90° and 60°, respectively.

3. Centre of Symmetry. *Centre of symmetry of a crystal is such a point that any line drawn through it intersects the surface of the crystal at equal distances in both directions.*

It may be pointed out that a crystal may have any number of planes or axes of symmetry but *it has only* **one** *centre of symmetry.*

Elements of Symmetry of a Crystal. As mentioned above, there are three different types of symmetry elements which are possible in a crystal. A crystal may have different numbers of each type of symmetry element. *The total number of* **planes, axes** *and* **centres of symmetries** *possessed by a crystal is termed as the* **elements of symmetry** of the crystal. To explain this term further, we may consider the elements of symmetry possessed by a **cubic crystal,** such as NaCl crystal. A cubic crystal possesses **a total of 23 elements of symmetry,** as will be clear from the discussion that follows. These elements of symmetry are :

a. Rectangular planes of symmetry. One rectangular plane of symmetry is shown in Fig. 8(*a*). There will be two more such planes, each of which will be at right angles to the plane shown in the figure. Thus, *there are 3 rectangular planes of symmetry in all.*

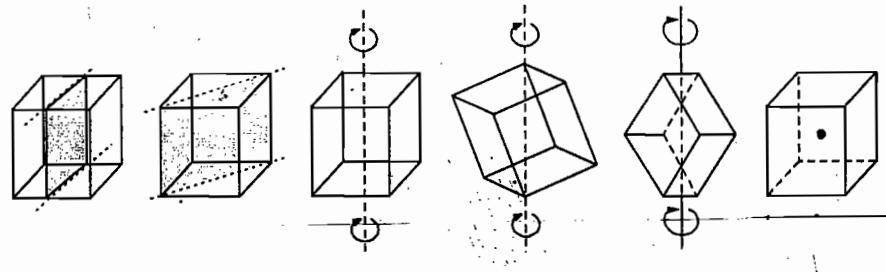
b. Diagonal planes of symmetry. One plane passing *diagonally* through the cube is shown in Fig. 8(*b*). *There can be a total of 6 such planes passing diagonally through the cube.*

c. Axes of four-fold symmetry. One of the four-fold axes is shown in Fig. 8(*c*). Evidently, *there can be a total of 3 such four-fold axes at right angles to one another.*

d. Axes of three-fold symmetry. One such axis passing through opposite corners is shown in Fig. 8(*d*). *There can be a total of 4 such three-fold axes.*

e. Axes of two-fold symmetry. One such axis emerging from opposite edges is shown in Fig. 8(*e*). There are, evidently, *6 such axes of two-fold symmetry.*

f. Centre of symmetry. There is *only one centre of symmetry* lying at the centre of the cube (Fig. 8*f*).



(*a*) A rectangular plane of symmetry
(*b*) A diagonal plane of symmetry
(*c*) An axis of four-fold symmetry
(*d*) An axis of three-fold symmetry
(*e*) An axis of two-fold symmetry
(*f*) Centre of symmetry

Fig. 8. Various elements of symmetry in a cubic crystal.

Thus, the numbers of symmetry elements of various types in a cubic crystal are :

Planes of symmetry $= 3 + 6 = 9$

Axes of symmetry $= 3 + 4 + 6 = 13$

Center of symmetry $= 1$

Total number of symmetry elements $= 23$

Basic Crystal Systems. It can be shown from geometrical considerations that, theoretically, there can be 32 different combinations of elements of symmetry of a crystal. These are called **32 systems.** Some of the systems, however, have been grouped together so that we have only seven differents categories, known as the **seven basic crystal systems.** These are *cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal* and *rhombohedral.*

These systems together with the maximum number of planes of symmetry and axes of symmetry and their examples are given in Table 1.

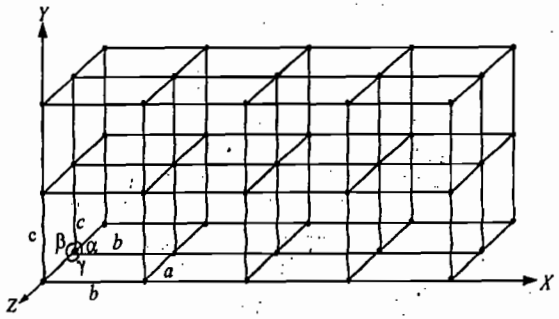
TABLE 1

The Basic Crystal Systems and Their Maximum Symmetry Elements

System	Number of Maximum Axes and Planes of Symmetry	Examples
1. Cubic	Nine planes of symmetry Thirteen axes of symmetry	NaCl, KCl, CaF_2, ZnS, Cu_2O, Diamond, Alums, Pb, Ag, Au
2. Orthorhombic	Three planes of symmetry Three axes of symmetry	KNO_3, K_2SO_4, $BaSO_4$, $PbCO_3$, Mg_2SiO_4, Rhombic sulphur
3. Tetragonal	Five planes of symmetry Five axes of symmetry	SnO_2, TiO_2, $ZrSiO_4$, KH_2PO_4, $PbWO_4$, Sn
4. Monoclinic	One plane of symmetry One axis of symmetry	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, $CaSO_4.2H_2O$, Monoclinic sulphur
5. Triclinic	No plane of symmetry No axis of symmetry	$CuSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3
6. Hexagonal	Seven planes of symmetry Seven axes of symmetry	ZnO, CdS, HgS, Graphite, Ice, PbI_2, Beryl, Mg, Zn, Cd
7. Rhombohedral	Seven planes of symmetry Seven axes of symmetry	$NaNO_3$, ICl, Calcite, Magnesite, Quartz, As, Sb, Bi

Space Lattice and Unit Cell

Crystals have definite orderly arrangements of their constituents (atoms, molecules or ions) in three dimensions. The positions of atoms, molecules or ions in a crystal, relative to one another in space, are designated usually by points. Such a representation is called *space lattice.* A **space lattice** *is an array of points showing how atoms, molecules or ions are arranged at different sites in a three-dimensional space.* An example of an array of points in a three-dimensional space lattice is shown in Fig. 9. Each point represents an identical atom or group of atoms.



If we carefully look at a space lattice, it is observed that the entire lattice can be considered as a *repetition of a small pattern* (or *motif*). This smallest repeating pattern is called a *unit cell.* Thus, a **unit cell** *is the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance.* The crystal may be considered to consist of infinite number of unit cells. Each unit cell in a three-dimensional space has, evidently, three vectors, *a, b* and *c*, as shown in Fig. 9.

Note that these are the *points* and not the lines which constitute the space lattice. The lines joining the points are drawn simply for representing the three axes by means of which the relative positions of the points can be described. For example, in Fig. 9, three imaginary axes, *OX, OY* and *OZ*, which are used to represent the unit cell, have been shown. In order to describe a unit cell, we should know : (*i*) the distances *a, b* and *c* which give the lengths of the edges of the unit cell and (*ii*) the angles α, β and γ which give the angles between the three imaginary axes *OX, OY* and *OZ.*

Knowing the unit cell dimensions, the **theoretical density** of a crystal can be calculated from the relation

$$\rho = n M_m / (N_A V) \qquad ...(1)$$

where n is the number of atoms in the unit cell, M_m is the molar mass, N_A is Avogadro's number and V is the volume of the unit cell.

Bravais Lattices

Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged in a three-dimensional space. Thus, the total number of space lattices belonging to all the seven basic crystal systems put together is only 14, as given in Table 2 (column 2). These are known as **Bravais lattices.**

The crystals have four kinds of Bravais lattices depending upon the shapes of the unit cells. These are :

1. Simple or **primitive lattice** *in which there are points at all the corners of the unit cell.* It is labelled as **P.** A primitive cubic unit cell is shown in Fig. 10 (*a*). This unit cell consists of one atom at each of the eight corners. Since each atom at the corner is shared by 8 unit cells, therefore, only 1/8 th of the atom is within the unit cell. Thus, the number of atoms per unit cell in primitive lattice is $8 \times (1/8) = 1$.

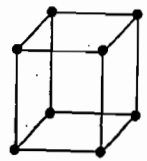


Fig. 10 (*a*). Primitive (*P*) cubic unit cell.

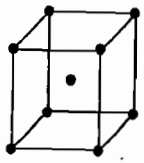


Fig. 10 (*b*). Body centred (*I*) cubic unit cell.

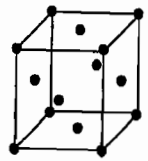


Fig. 10 (*c*). Face centred (*F*) cubic unit cell.

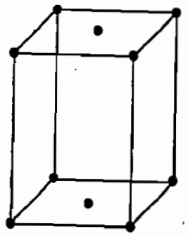


Fig. 10 (*d*). End centred (*C*) orthorhombic unit cell.

2. Body centred lattice *in which there are points at all the corners as well as in the centre of the unit cell.* It is labelled as **I.** For example, in body centred cubic unit cell (Fig. 10 *b*), there are eight atoms at the corners (each shared by 8 unit cells) and one at the centre (belonging to only one unit cell). Therefore, the number of atoms per unit cell is $8 \times (1/8) + 1 = 2$.

3. Face centred lattice *in which there are points at the corners as well as at the centre of each face.* It is labelled as **F.** In a face centred cubic unit cell (Fig. 10 *c*), there are eight atoms at the corners (each shared by 8 unit cells) and six at the faces (each shared by two unit cells). Therefore, the number of atoms per unit cell is $8 \times (1/8) + 6 \times (1/2) = 4$.

4. End centered lattice *in which there are points at the corners and at the centres of two end faces.* It is labelled as **C**. For example, in an end centred orthorhombic unit cell* (Fig. 10 *d*), there are eight atoms at the corners and two at the end faces so that the number of atoms per unit cell is $8\times(1/8)+2\times(1/2)=2$.

The Bravais space lattices associated with various crystal systems are shown in Figs. 11 (*a*), (*b*), (*c*) and (*d*). The unit cell is described by the lengths *a*, *b* and *c* of the three intersecting edges and the angles α, β and γ between the pairs of edges *b*, *c* ; *a*, *c* and *a*, *b*, respectively.

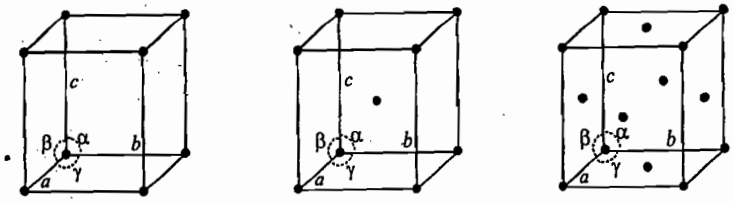


Fig. 11 (*a*). Cubic Space Lattices

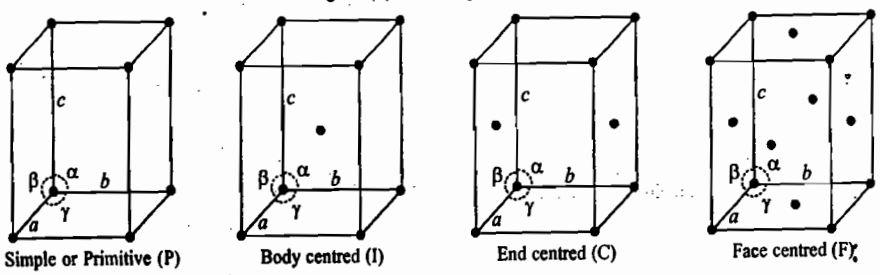


Fig. 11 (*b*). Orthorhombic Space Lattices.

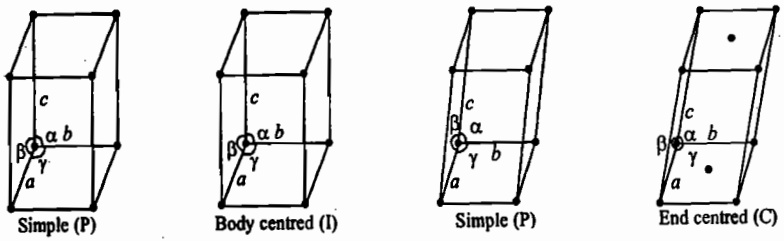


Fig. 11 (c). Tetragonal and Monoclinic Space Lattices

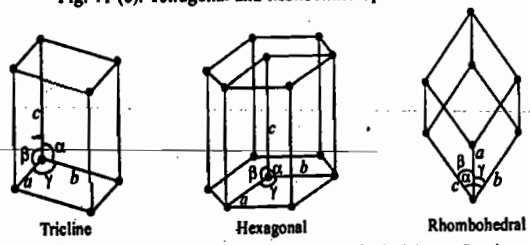


Fig. 11(*d*). Triclinic, Hexagonal and Rhombohedral Space Lattices.

* There is no end centred cubic unit cell.

The actual lattice in a crystal of a given kind consists of a repetition of a unit cell of that kind all over in three-dimensional space. As already mentioned, there can only be a maximum of 32 combinations of elements of symmetry (point groups).

Some detailed descriptions of the seven basic crystal systems and their Bravais lattices are given in Table 2.

TABLE 2

Important Characteristics of the Seven Basic Crystal Systems

Crystal System	Bravais Lattices	Minimum Symmetry Elements	Parameters of Unit Cell	
			Intercepts	Crystal Angles
1. Cubic	Primitive, Face centred, Body centred = 3	Four 3-fold axes Three 4-fold axes	$a=b=c$	$\alpha=\beta=\gamma=90°$
2. Orthorhombic	Primitive, Face centred, Body centred, End centred = 4	Three mutually perpendicular 2-fold axes	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$
3. Tetragonal	Primitive, Body centred = 2	One 4-fold axis	$a=b\neq c$	$\alpha=\beta=\gamma=90°$
4. Monoclinic	Primitive, End centred = 2	One 2-fold axis	$a\neq b\neq c$	$\alpha=\gamma=90°$ $\beta\neq 90°$
5. Triclinic	Primitive = 1	One 1-fold axis	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$
6. Hexagonal	Primitive = 1	One 6-fold axis	$a=b\neq c$	$\alpha=\beta=90°$ $\gamma=120°$
7. Rhombohedral	Primitive = 1	One 3-fold axis	$a=b=c$	$\alpha=\beta=\gamma\neq 90°$
	Total = 14			

The first column gives the name of the crystal system. The second column gives the number and types of space lattices present in the given crystal system. The third column contains information with regard to *minimum symmetry elements* of each system. These are the absolutely essential symmetry requirements of a given crystal system. A crystal belonging to that system may have more symmetry elements but it cannot have less. The unit cell parameters, *viz.*, the intercepts *a*, *b* and *c* and the interfacial angles α, β and γ between the three imaginary axes are given in the last column.

Example 1. A metallic element has a cubic lattice. Each edge of the unit cell is 2·88 Å. The density of the metal is 7·20 g cm^{-3}. How many unit cells will there be in 100 g of the metal ?

Solution : Volume of unit cell $= (2{\cdot}88\ \text{Å})^3 = (2{\cdot}88\times10^{-8}\ \text{cm})^3 = 23{\cdot}9\times10^{-24}\ \text{cm}^3$

$$\text{Volume of 100 g of the metal} = \frac{100\ \text{g}}{7{\cdot}20\ \text{g cm}^{-3}} = 13{\cdot}9\ \text{cm}^3$$

$$\left.\begin{array}{l}\text{Number of the unit cells}\\ \text{in this volume}\end{array}\right\} = \frac{13{\cdot}9\ \text{cm}^3}{23{\cdot}9\times10^{-24}\ \text{cm}^3} = 5{\cdot}82\times10^{23}$$

Example 2. Ferrous oxide (FeO) crystal has a cubic structure and each edge of the unit cell is 5·0 Å. Taking density of the oxide as 4·0 g cm^{-3}, calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell.

Solution : Volume of the unit cell, $V = (5\ \text{Å})^3 = (5\times10^{-8}\ \text{cm})^3 = 1{\cdot}25\times10^{-22}\ \text{cm}^3$

Density of FeO, $\rho = 4{\cdot}0\ \text{g cm}^{-3}$

$\therefore$ Mass of unit cell $= V\times\rho = 1{\cdot}25\times10^{-22}\ \text{cm}^3 \times 4{\cdot}0\ \text{g cm}^{-3} = 5{\cdot}0\times10^{-22}\ \text{g}$

$$\text{Mass of one molecule of FeO} = \frac{\text{Molar mass in grams}}{\text{Avogadro's number}} = \frac{72\ \text{g mol}^{-1}}{6{\cdot}022\times10^{23}\ \text{mol}^{-1}} = 1{\cdot}195\times10^{-22}\ \text{g}$$

$$\therefore\ \text{Number of FeO molecules per unit cell} = \frac{5{\cdot}0\times10^{-22}\ \text{g}}{1{\cdot}195\times10^{-22}\ \text{g}} = 4{\cdot}19 = 4$$

Thus, there are **four Fe^{2+} ions and four O^{2-} ions** in each unit cell.

Example 3. At room temperature, pollonium crystallises in a primitive cubic unit cell. If $a = 3{\cdot}36$ Å, calculate the density of pollonium. Its atomic mass is 209 g mol^{-1}.

Solution : A primitive cubic unit cell contains atoms only at the 8 corners with each corner contributing 1/8th of an atom. Hence, total number of atoms per unit cell $= 8\times(1/8) = 1$.

Volume, $V = a^3 = (3{\cdot}36\ \text{Å})^3 = (3{\cdot}36\times10^{-8}\ \text{cm})^3$

$$\text{From Eq. 1, } \rho = \frac{nM_m}{N_A V} = \frac{(1)(209\ \text{g mol}^{-1})}{(6{\cdot}022\times10^{23}\ \text{mol}^{-1})(3{\cdot}36\times10^{-8}\ \text{cm})^3} = 9{\cdot}15\ \text{g cm}^{-3}$$

Example 4. Lithium borohydride, $LiBH_4$, crystallises in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are : $a = 6{\cdot}81$ Å, $b = 4{\cdot}43$ Å and $c = 7{\cdot}17$ Å . If the molar mass of $LiBH_4$ is 21·76 g mol^{-1}, calculate the density of the crystal.

Solution : Density of the crystal, $\rho = nM_m/(N_A V)$ (Eq 1)

$$= \frac{4\times(21{\cdot}76\ \text{g mol}^{-1})}{(6{\cdot}022\times10^{23}\text{mol}^{-1})(6{\cdot}81\times4{\cdot}43\times7{\cdot}17\times10^{-24}\text{cm})^3} = 0{\cdot}668\ \text{g cm}^{-3}$$

Example 5. An organic compound crystallises in an orthorhombic system with two molecules per unit cell. The unit cell dimensions are 12·05, 15·05 and 2·69 Å. If the density of the crystal is 1·419 g cm^{-3}, calculate the molar mass of the organic compound.

Solution : Molar mass, $M_m = \rho N_A V/n$ (Eq. 1)

$$= \frac{(1{\cdot}419\text{g cm}^{-3})(6{\cdot}022\times10^{23}\ \text{mol}^{-1})(12{\cdot}05\times15{\cdot}05\times2{\cdot}69\times10^{-24}\ \text{cm}^3)}{2}$$

$$= 208{\cdot}4\ \text{g mol}^{-1}$$

Designation of Planes in Crystals : Miller Indices

A number of methods have been suggested to represent the various planes in crystals. The method proposed by W.H. Miller is commonly used. In this method, the planes are described by a set of integers (h, k and l) known as **Miller indices.** *The Miller indices of a plane of a crystal are the reciprocals of the fractional intercepts of that plane on the various axes.*

The procedure for determining Miller indices for a plane is as follows :

1. Prepare a three-column table with the unit cell axes at the tops of the columns.
2. Enter in each column the intercept (expressed as a multiple of a, b or c) of the plane with these axes.

Devide these intercepts by the corresponding lengths a, b, c of axis of unit cell to obtain fractional intercepts on the axis.

3. Invert all numbers.
4. Clear fractions to obtain h, k and l.

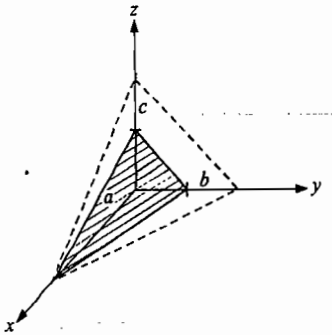


Fig. 12. A plane having Miller indices 122.

The concept of Miller indices may be illustrated as follows :

Consider the shaded plane in Fig. 12. It is clear from the figure that the intercepts of the shaded plane along X, Y and Z axes are :

a $b/2$ $c/2$ and the fractional intercepts are a/a $b/2b$ $c/2c$ or 1 1/2 1/2

$\therefore$ Miller indices (reciprocals of the intercepts) are :

1/1 2/1 2/1 or **1 2 2**

Let us now describe the planes in a cube. It should be remembered that if a plane is parallel to an axis, its intercept with that axis would be infinity. Thus, the Miller index for that plane will be zero ($1/\infty = 0$). For example, consider the shaded plane in Fig. 13. It is clear from the figure that the fractional intercepts of the shaded plane are :

∞ 1 ∞

$\therefore$ Miller indices are

$1/\infty$ 1/1 $1/\infty$ or 0 1 0

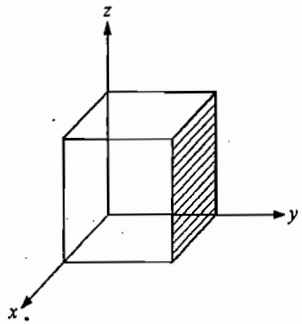


Fig. 13. A plane in a cube having Miller indices 010.

Similarly, the Miller indices of some planes in cubic crystals, shown shaded in Fig. 14 are as given below.

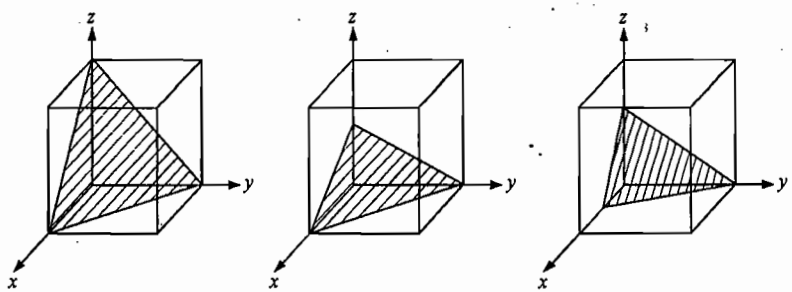


Fig. 14. Miller indices for some planes in cubic crystals.

Fractional intercepts	1	1	1	Fractional intercepts	1	1	1/2	Fractional intercepts	1/3	1	2/3
Miller indices	1/1	1/1	1/1	Miller indices	1/1	1/1	2/1	Miller Indices	3/1	1/1	3/2
	1	**1**	**1**		**1**	**1**	**2**		**6**	**2**	**3**

Example 6. Calculate the Miller indices of crystal planes which cut through the crystal axes at (*i*) (2*a*, 3*b*, *c*) (*ii*) (*a*, *b*, *c*) (*iii*) (6*a*, 3*b*, 3*c*)

Solution : Following the procedure given above, we prepare the table as follows :

(*i*)	*a*	*b*	*c*	
	2	3	1	Fractional Intercepts
	1/2	1/3	1	Reciprocals
	3	2	6	Clear fractions

Hence, the Miller Indices are (326).

(*ii*)	*a*	*b*	*c*	
	1	1	1	Fractional Intercepts
	1	1	1	Reciprocals
	1	1	1	Clear fractions

Hence, the Miller indices are (111).

(iii)

	a	b	c	
	6	3	3	Fractional Intercepts
	1/6	1/3	1/3	Reciprocals
	1	2	2	Clear fractions

Hence, the Miller indices are (122).

Types of Crystals

It is convenient to classify crystals into the following four types depending upon the nature of the units which occupy the lattice points.

1. **Ionic crystals** in which the units are positively and negatively charged ions.
2. **Covalent crystals** in which the units are atoms.
3. **Metallic crystals** in which the units are metal atoms bonded by metallic bonds.
4. **Molecular crystals** in which the units occupying the lattice points are molecules.

1. Ionic Crystals. In ionic crystals, the units occupying lattice points are positive and negative ions. In sodium chloride, for example, the units are Na^+ ions and Cl^- ions. These ions are held together by coulombic forces of attraction. X-ray studies have shown that in ionic crystals, each ion is surrounded by a number of ions of opposite charge. For example, in NaCl, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. Some other common ionic crystals are KNO_3, Na_2SO_4, etc. The coulombic forces of attraction between the oppositely charged ions are very strong and, therefore, the amount of energy required to separate ions from one another is very high. Accordingly, the **ionic crystals** have the following **characteristics :**

1. The heats of vaporisation of ionic crystals are high.
2. The vapour pressures of ionic crystals at ordinary temperatures are very low.
3. The melting and boiling points of ionic crystals are very high.
4. Ionic crystals are hard and brittle.
5. Ionic crystals are insulators in the solid state. The reason is that ions are entrapped in fixed places in the crystal lattice and cannot move when electric field is applied. However, when melted they become good conductors of electricity. This is due to the fact that in the molten state, the well-ordered arrangement of ions in the crystal is destroyed and the ions are in a position to move about freely in the liquid medium when an electric field is applied.
6. Ionic crystals are soluble in water and also in other polar solvents. They are insoluble or very slightly soluble in non-polar solvents such as benzene and carbon tetrachloride.
7. Ionic crystals are good conductors of electricity when dissolved in water. The ions held by coulombic forces fall away from one another when dissolved in water or in any other solvent having high dielectric constant. This is in accordance with the Coulomb's law that forces of attraction between oppositely charged particles vary inversely as the dielectric constant.

2. Covalent Crystals. The lattice in covalent crystals consists of atoms linked together by a continuous system of covalent bonds. The covalent bonds extend in two or three dimensions forming a giant interlocking structure called *network*. **Diamond** furnishes a good example of a covalent crystal. Its structure is represented in Fig. 15.

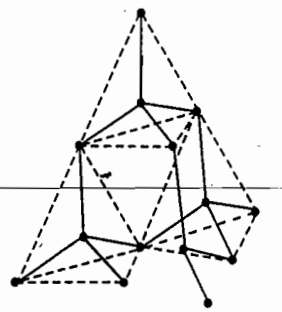


Fig. 15. Structure of diamond.

Each carbon atom in this structure is bonded to *four* other carbon atoms through sp^3 hybrid bonds. Thus, each carbon atom (with complete outer electron octet) is surrounded by four others which lie at the four corners of a regular tetrahedron. This gives rise to a *rigid three-dimensional network*. This is also the reason why diamond is the hardest substance known, with a high density and melting point. The entire crystal is regarded as one large carbon molecule and is called a **macromolecule**. The other examples of covalent crystals are silicon carbide (SiC), quartz (SiO_2) and boron nitride (BN).

The important **characteristics of covalent crystals** are given below.

1. There is a continuous network of covalent bonds forming a giant three-dimensional structure as in diamond and quartz.
2. Due to multi-dimensional network, covalent crystals have generally high melting points.
3. Covalent crystals are generally poor conductors of electricity.
4. They are generally hard. In fact, diamond is the hardest substance known.
5. Covalent crystals are insoluble in polar solvents.
6. Covalent crystals have generally high heats of fusion and low coefficients of expansion.

3. Metallic Crystals. As discussed earlier (Chapter 4), a metallic crystal consists of an assemblage of atoms held together by metallic bonds. The force of attraction between the atoms due to the metallic bond is sufficiently strong and is thus responsible for a compact solid structure of metals.

The important **characteristics of metallic crystals** are given below.

1. Metallic crystals are good conductors of heat and electricity.
2. Most of the metals are quite hard and tough.
3. Metals are malleable and ductile. Due to malleable nature of metals, they can be beaten into sheets and drawn into wires.
4. They exhibit lustre, especially when freshly cut.
5. Except alkali metals, they have very high melting and boiling points.
6. Metals also possess elasticity.
7. Metals have high tensile strength, *i.e.*, they can resist stretching without breaking.

4. Molecular Crystals. In molecular crystals, the lattice positions are occupied by molecules which do not carry any charge. The forces binding the molecules together are of two types : (*i*) *Dipole-dipole forces* (*ii*) *van der Waals forces*. Dipole-dipole forces occur in crystals which consist of polar molecules. Thus, in the case of water molecules (in ice or even in liquid state), the negative end of one molecule attracts the positive end of a neighbouring molecule, as shown in Fig. 16.

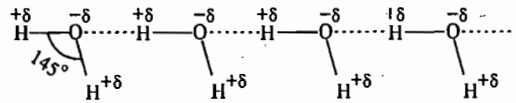


Fig. 16. Dipole-dipole forces of attraction between water molecules.

The van der Waals forces are more general and occur in all kinds of molecular crystals. Both types of molecular forces mentioned above are much weaker than the coulombic forces of attraction between oppositely charged ions existing in ionic crystals. The binding energy in molecular crystals, therefore, is considerably less than in ionic crystals. Accordingly, the **heat of vaporisation**, *i.e., the energy required to separate molecules from one another* in a molecular crystal is very low in comparison to the value for ionic or covalent crystals.

The important **characteristics of molecular crystals** are given below.

1. Molecular crystals are generally soft.
2. They have low melting and boiling points.
3. They are bad conductors of electricity because they consist of neutral molecules in solid as well as in dissolved state.
4. They are volatile and have low heats of vaporisation.

Close Packing of Identical Solid Spheres

In order to understand the packing of atoms, molecules or ions in crystals, let us consider the packing of hard spheres of equal size in two dimensions, *i.e.*, in a layer and extend the arrangement to three dimensions by putting such layers above one another. There can be a number of possible arrangements but the one in *which maximum available space is occupied will be economical*. Such an arrangement is called *close packing*. Hence, the closer the packing, the greater is the stability of the packed system.

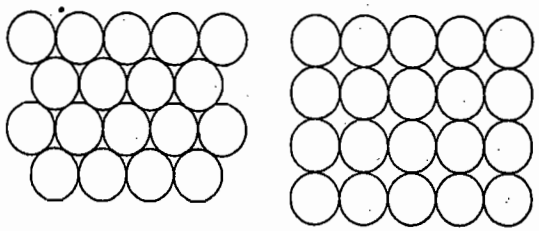


Fig. 17. Two common ways of packing of spheres of equal size. In arrangement I, 60·4% of the volume is occupied and in arrangement II, 52·4% of the volume is occupied.

There are two common ways of packing spheres of equal size in a layer. These are shown in Fig. 17.

A comparison of the two ways of packing of spheres shows that in arrangement I, the spheres are more closely packed than in arrangement II. It has been calculated that in the first arrangement, 60·4% of the available space is occupied by the spheres. The remaining 39·6% of the space is empty and is called **void volume**. In the second arrangement, only 52·4% of the space is filled and 47·6% of the space is empty. Thus, the arrangement I is more economical and it represents a *close packing of spheres*.

It can be seen that in the close packing arrangement, the spheres arrange themselves in such a way that their centres are at the corners of an equilateral triangle. Each sphere is in contact with six other similar spheres shown shaded in Fig. 18. *The number of nearest neighbours with which a given sphere is in contact is called the* **coordination number**. Thus, the coordination number of each sphere packed in the above manner in a layer is 6.

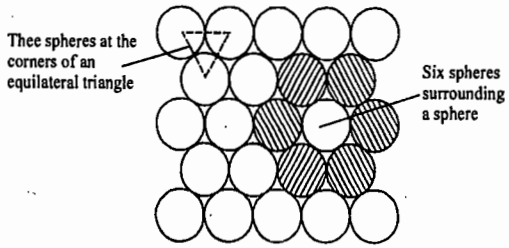


Fig. 18. Close packing of spheres.

The above arrangement can be extended in three dimensions by placing other closest packed layers on the top of hollows (or voids) of the first layer. Let us label the first layer as *A* layer.

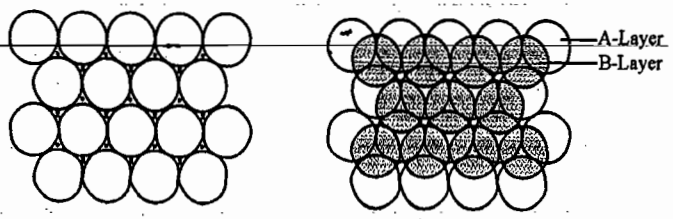


Fig. 19. Building of second layer (*B*, shown shaded) covering hollows marked by dots (·). The hollows marked by crosses (×) remain unoccupied.

There are two types of hollows in the first layer

which are marked by dots (·) and crosses (x). All the hollows are equivalent but the spheres of second layer may be placed either on hollows which are marked by dots or on other set of hollows marked by crosses. It may be noted that it is not possible to place spheres on both types of hollows simultaneously. Let us place spheres on hollows marked by dots to make the second layer which may be labelled as *B* layer (Fig. 19)

When we come to packing of third layer, there are two alternative ways. One way is to put the spheres of third layer on the hollows of the second layer. In that case it is observed that each sphere of third layer (shown as dark spheres in Fig. 20) lies directly above those in the first layer. In other words, the third layer becomes identical to the first layer. This arrangement if continued indefinitely in the same sequence, is represented as *ABABABA*.....

This arrangement of layers, *viz.*, *ABABABA*.... is shown more clearly in Fig. 20(*b*). On examination, this arrangement is found to represent **hexagonal close packing** symmetry. This is abbreviated as ***hcp***. This means that the structure has one 6-fold axis of symmetry. This is illustrated in Fig. 20(*c*). The same or similar appearance is repeated on rotating the crystal through an angle of 60°. It may be noted that the symmetry axis is perpendicular to the layers of close packed spheres.

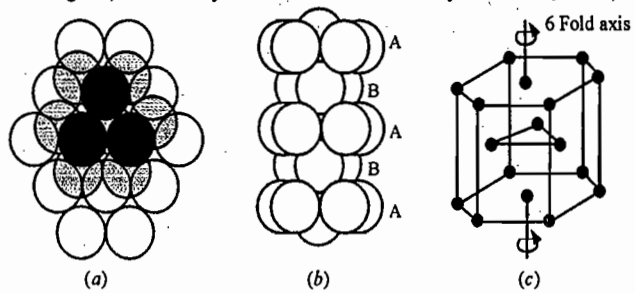


Fig. 20. *ABABABA*..... system of close packing or hexagonal close packing (*hcp*) of spheres.

The second way to pack spheres in third layer is to place them over the unoccupied hollows of the first layer marked by crosses. This will give a different type of close-packed arrangement (Fig. 21*a*). However, it can be shown that now the spheres in the fourth layer will correspond with those in the first layer. This arrangement of stacking, if continued indefinitely, is represented as *ABCABCABCA*... (Fig. 21 *b*). The resulting arrangement has cubic symmetry and, consequently, it is referred to as **cubic close packing** of spheres and is abbreviated as ***ccp***. According to Table 2, this structure has four **3-fold axes** of symmetry which pass through the diagonals of the cube. A closer study of *ABCABC*... system of close packing also shows that there is a sphere at the centre of each face of the unit cube and hence this structure is also known as **face centred cubic structure**. The face-centred cubic arrangement has been shown more clearly in Fig. 21(*c*).

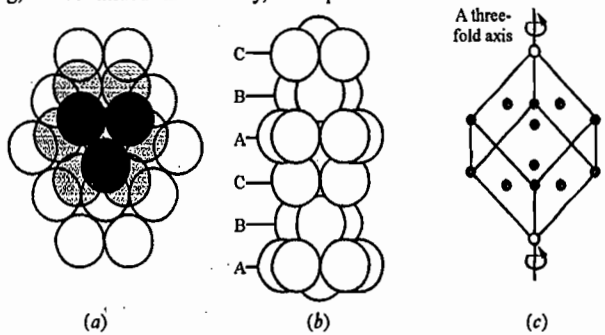


Fig. 21. *ABCABCA*.... system of close packing or cubic close packing (*ccp*) of spheres.

It may be noted that in both the types of structures discussed above, each sphere is surrounded by twelve other spheres. For example, a sphere marked x is in contact with six nearest spheres (marked 1, 2, 3, 4, 5 and 6) in the same layer, as shown in Fig. 22. In addition to this, the sphere marked x is also in contact with three spheres (marked 7, 8, 9) in the layer above and three spheres (marked 10, 11, 12) in the layer

below (shown at some distance for the sake of clarity). Thus, the coordination number in the *hcp* as well as in the *ccp* structure is 12.

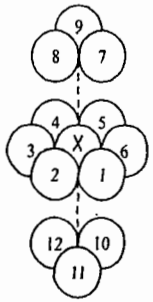


Fig. 22. Coordination number in *hcp* and *ccp* structures.

In addition to the above two close packed arrangements, another arrangement of packing of spheres is the **body centred cubic arrangement**. In this arrangement, the spheres in the first layer of close packing are slightly opened up. As a result, the spheres are not in contact with each other. This is shown in Fig. 23. To build the second layer (shown by dotted spheres in Fig. 23*a*), the spheres are placed at the top of hollows in the first layer. Each sphere in the second layer is in contact with four spheres of the first layer. In the third layer, spheres are placed exactly above the first layer. Thus, each sphere in this system of close packing is in contact with eight spheres, four in the layer below it and four in the layer above it. In other words, coordination number of each sphere is 8. In this arrangement, as can be easily visualised, there are eight spheres at the corners of a cube and one sphere is in the centre (or body) of the cube. Therefore, the structure is known as **body centred cubic** and is abbreviated as ***bcc***.

It can be shown by simple geometry that while the volume occupied in *ccp* arrangement is 74%, that in *bcc* arrangement is 68% of the total volume (see below).

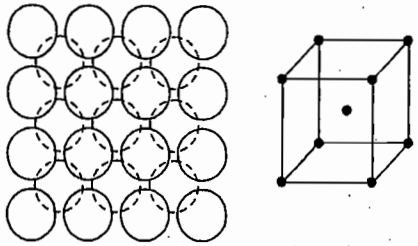


Fig. 23. Body centred cubic packing of spheres.

Volume occupied in *ccp* arrangement. Consider the cubic close packed arrangement, as shown in Fig. 24*. Let the length of each side be a so that the volume of the cube is a^3. Let us now calculate the volume occupied by spheres.

As shown in the figure, there are eight spheres at the corners and six spheres at the faces. But, each sphere at the corner is shared by eight unit cells and its contribution per unit cell is 1/8. Similarly, each sphere in the face is shared by two unit cells and its contribution per unit cell is 1/2 . Thus, the number of spheres per unit cell $= 8\times(1/8) + 6\times(1/2) = 4$.

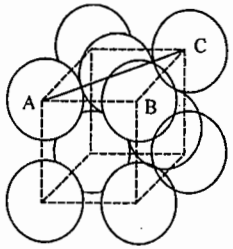


Fig.24. Volume occupied in *ccp* arrangement. Only one face centred sphere is shown here.

Consider Δ ABC. Since it is a right angled triangle, hence

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

$\therefore$ Face diagonal, $AC = \sqrt{2}a$

But, as is evident from the figure, $AC = 4r$ where r is the radius of the sphere.

$$\therefore \quad 4r = \sqrt{2}a \quad \text{or} \quad r = \sqrt{2}\,a/4$$

Since, as mentioned above, there are 4 spheres per unit cell, hence the volume occupied by 4 spheres

$$= 4\times 4/3\,\pi r^3 = 4\times 4/3\,\pi(\sqrt{2}a/4)^3$$

$$\text{Ratio of the volume occupied to total volume} = \frac{\text{Volume occupied by spheres}}{\text{Volume of the cube}}$$

$$= \frac{4\times 4/3\times 22/7\times(\sqrt{2}a/4)^3}{a^3} = 0{\cdot}7406$$

Thus, the volume occupied in *ccp* arrangement = 74·06%

*This is the simplified representation of the arrangement. Actually all the spheres in a face are touching one another. Each face has four spheres at its edges and one sphere in the middle.

Volume occupied in *bcc* arrangement. Consider the body-centred cubic arrangement, as shown in Fig. 25**. As before, let the length of each side be a so that the volume of the cube is a^3.

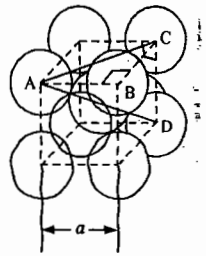


Fig. 25. Volume occupied in *bcc* arrangement.

It is clear from the figure that there are eight spheres at the corners and one in the body of the unit cell. But, each sphere at the corner is shared by eight unit cells and its contribution per unit cell is 1/8. However, the sphere at the body centre of the cube contributes fully to the cube. Thus,

The number of spheres per unit cell $= 8\times(1/8) + 1 = 2$ ...(*i*)

In right angled triangle ABC, $AC^2 = AB^2 + BC^2 = a^2 + a^2$

or $AC^2 = 2a^2$ or $AC = \sqrt{2}a$ ...(*ii*)

Similarly, in right angled triangle ACD, $AD^2 = AC^2 + CD^2 = (\sqrt{2}a)^2 + a^2 = 3a^2$

or $AD = \sqrt{3}a$ ...(*iii*)

But, as is evident from the figure,

the body diagonal $AD = 4r$

where r is the radius of the sphere. ...(*iv*)

From Eqs. (*iii*) and (*iv*), $4r = \sqrt{3}a$ or $r = \sqrt{3}a/4$

Since there are 2 spheres per unit cell (Eq. (*i*), hence,

Volume occupied by 2 spheres $= 2\times 4/3\pi r^3 = 2\times 4/3\times 22/7\times(\sqrt{3}a/4)^3$

Ratio of volume occupied to total volum $= 2\times 4/3\times 22/7\times(\sqrt{3}a/4)^3/a^3 = 0{\cdot}6805$

Thus, the volume occupied in *bcc* arrangement = 68·05%

Interstitial Sites in Close Packing of Spheres

We have seen before that even in the closest packing of spheres, there is some empty space left in between the spheres. This is known as an interstitial site. For example, when the spheres are closely packed in a single plane, the centres of three adjacent spheres lie at the vertices of an equilateral triangle. In between these three spheres, there is some empty space. This empty space (hole or void) is called **triangular** or **trigonal site**. In addition to this, we come across two more common interstitial sites, *viz.*, *tetrahedral* and *octahedral sites*, in closely packed lattices. These are discussed below.

Tetrahedral Sites. If one sphere is placed upon three other spheres which are touching one another, *tetrahedral structure* results. This is shown in Fig. 26. Since the four spheres touch one another at one point only, they leave a small space in between which is called a **tetrahedral site.** The size of the site is much smaller than that of the spheres. However, the bigger the spheres, the larger is the size of the tetrahedral site formed by them. We have seen already that in *hexagonal close packing* (*hcp*) as well as *in cubic close packing* (*ccp*) arrangement, *each sphere* is in contact with *three spheres* in the layer *above* and *three spheres* in the layer *below*. Thus, there would be *two tetrahedral sites associated with each sphere*. One of these sites will be immediately above and the other immediately below the sphere. It may be noted that tetrahedral site does not mean that the shape of

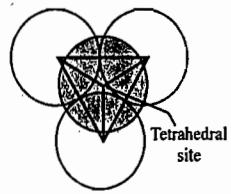


Fig. 26. A tetrahedral site.

**This is the simplified representation of the arrangement. All the spheres in a face are not only touching one another but are also touching the sphere at the centre of the cube.

the site is tetrahedral but it indicates that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron. It is this tetrahedral arrangement of the spheres which gives tetrahedral name to this site.

Octahedral Sites. Another type of interstitial site formed by close packing of spheres in *hcp* as well as in *ccp* systems is called an **octahedral site.** This interstitial site is formed at the *centre of six spheres,* the centres of which lie at the apices of a regular octahedron, as illustrated in Fig. 27.

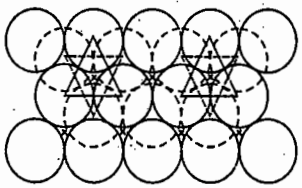


Fig.27. Octahedral interstitial sites formed by close packing of spheres in *hcp* as well as in *ccp* arrangement.

The figure shows two layers of close-packed spheres. The full circles represent the spheres in one plane while the dotted circles represent those in second plane. Two triangles have been drawn. One of these joins the centres of three spheres in one plane while the second (dotted lines) joins the centres of three spheres in the second plane. The octahedral sites, marked by x, are formed where two triangles of different layers are superimposed one above the other. In this position, the apices of these triangles point in opposite direction, as shown. Thus, each octahedral site is created, by two equilateral triangles with apices in opposite direction.

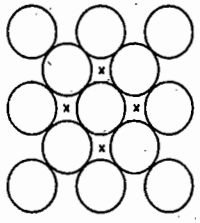


Fig. 28. Cross-section of octahedral interstitial sites in a face centred cubic lattice.

One of the faces of a cubic close packed (*ccp*) lattice is shown in Fig. 28. The cross sections of octahedral sites formed in this lattice are marked by x in the figure.

Sizes of Interstitial Sites in Ionic Crystals. Limiting Radius Ratios

In general, the size of a trigonal site is smaller than the size of a tetrahedral site which, in turn, is smaller than the size of an octahedral site. Further, the size of a site varies with the size of the spheres surrounding it. In the case of ionic crystals, the radius of a cation which may occupy a given site created by anionic spheres can be calculated by simple geometry. This has been done in terms of the ratio of the radius of cation to that of anion (r_+/r_-), also known as **radius ratio.**

In order to acquire minimum energy, the ions are close-packed in such a way that each ion is surrounded by as many ions of opposite charge as possible. The number of ions surrounding an oppositely charged ion is known as the *coordination number*, as already mentioned. The higher the coordination number, the greater would be the stability of the ionic compound, in general.

Only that particular structure will be adopted by the ionic compound which gives it the lowest energy or maximum stability. The energy of an ionic crystal is mainly determined by the resultant of the *energy of attraction* between the cations and anions and *energy of repulsion* between the anions surrounding the cation. Energy of attraction would, evidently, increase with the coordination number of the cation. The energy of repulsion would increase when anions of the same size and charge are squeezed together because the electron charge clouds of the squeezed ions would repel one another.

As already mentioned, the internuclear distance r is taken as the sum of the radii of cations and anions. If cations and anions do not touch each other (*i.e.*, the interstitial site formed by anions is too big for cations, then the internuclear distance would increase and the energy of attraction would decrease.

Thus, the optimum arrangement of cations and anions would be the one in which the required number of anions touch a cation without being squeezed. Such an arrangement would be of minimum energy and maximum stability. The limiting radius ratios for various types of ionic arrangements in crystals are determined by keeping the above principle in view.

a. Limiting radius ratio for trigonal site. A trigonal site is formed when the three anions represented by spheres lie at the vertices of an equilateral triangle and a cation, represented by a small sphere, occupies the trigonal site (Fig. 29). Let r_+ and r_- be the radii of the cation and the anion, respectively. As is evident from the figure, in equilateral triangle EBC,

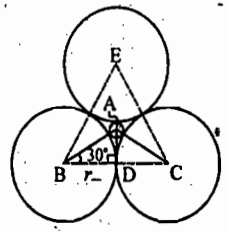


Fig. 29. Size of a trigonal site.

$$BC = CE = BE = 2r_-$$

If A is the centre of the triangle (and hence of the cation), then

$$BD = r_- \text{ and } AB = r_+ + r_-$$

In right angled triangle BDA, cos ∠ABD

$$= BD/AB, \text{ i.e., } \cos 30° = r_-/(r_- + r_+)$$

$$\text{Since } \cos 30° = \sqrt{3}/2, \text{ hence } \sqrt{3}/2 = r_-/(r_- + r_+)$$

On inverting both sides, $2/\sqrt{3} = (r_- + r_+)/r_- = 1 + (r_+/r_-)$

$$\therefore \quad r_+/r_- = 2/\sqrt{3} - 1 = 0{\cdot}155$$

Thus, the **limiting r_+/r_- ratio** for trigonal site is **0·155**.

b. Limiting radius ratio for tetrahedral site. A tetrahedral site is formed by placing one sphere over three spheres which are touching one another. In an ionic crystal such a site can be created by placing the anions at the alternate corners of a cube. Let the cation occupy the tetrahedral site. Suppose a is the length of each side of the cube and r_- and r_+ are the radii of anion and cation, respectively. For simplicity, the cations and anions are shown by separated spheres (Fig. 30). Actually the cations and anions are touching one another so that

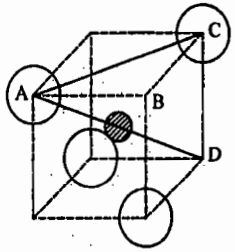


Fig. 30. A tetrahedral site. The spheres actually touch one another though not shown so in the figure for the sake of simplicity.

$$AC = 2r_- \text{ and } AD = 2AO = 2(r_+ + r_-)$$

As can be seen from the figure, the face diagonal,

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}\,a$$

$$\therefore \quad 2r_- = \sqrt{2}\,a$$

or $$r_- = \sqrt{2}\,a/2 = a/\sqrt{2} \qquad ...(i)$$

As is also evident from the figure, the body diagonal

$$AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}\,a \qquad ...(ii)$$

The cation is present at the centre of the body diagonal AD so that half the length of this diagonal is equal to the sum of the radii of the anion and the cation. Thus,

$$r_- + r_+ = AD/2 = \frac{\sqrt{3}\,a}{2} \qquad ...(iii)$$

Dividing Eq. (*iii*) by (*i*), we get

$$(r_- + r_+)/r_- = (\sqrt{3}\,a/2) \times (\sqrt{2}/a) = \sqrt{3}/\sqrt{2}$$

or $$r_+/r_- = (\sqrt{3}/\sqrt{2}) - 1 = (\sqrt{3} - \sqrt{2})/\sqrt{2}$$

$$= (1{\cdot}732 - 1{\cdot}414)/1{\cdot}414 = 0{\cdot}225$$

Thus, the **limiting r_+/r_- ratio** for tetrahedral site is **0·225**

If the radius ratio is less than 0·225, then either the anion is too big or the cation is too small in size. In either case, the anions will have to be squeezed so that the anions and the cation just touch one

another. The squeezing of anions would increase the repulsion between them and, as a result, *the tetrahedral arrangement would become less stable.* The squeezing of anions can be avoided by decreasing the number of anions surrounding the cation, *i.e.*, by decreasing the coordination number of the cation. This would change the structure of the crystal from tetrahedral to planar trigonal. Thus, *the crystal would have a trigonal structure if the radius ratio is less than* 0·225.

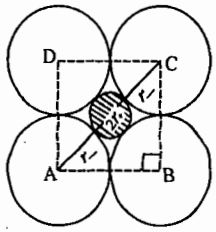


Fig. 31. An octahedral site. Only a cross-section through octahedral site is shown.

c. Limiting radius ratio for octahedral site. An octahedral site is shown in Fig. 31. A cross-section through an octahedral site shows that the four anions are at the corners of a square and the cation is at the centre. One anion at the top and one anion at the bottom of the plane formed by the four anions also touch the cation (the two anions at the top and at the bottom of the plane are not shown in the figure). Suppose each side of the square is a and r_- and r_+ are the radii of the anion and cation, respectively. In right angled triangle ABC,

$$AC = \sqrt{AB^2+BC^2} = \sqrt{a^2+a^2} = \sqrt{2}a$$

But, $$AC = r_- + 2r_+ + r_- = 2r_- + 2r_+$$

$$\therefore \quad 2r_- + 2r_+ = \sqrt{2}a$$

or $$r_- + r_+ = \sqrt{2}\, a/2 \qquad ...(i)$$

As is evident from the figure, $AB = a = 2r_-$

or $$r_- = a/2 \qquad ...(ii)$$

Dividing Eq. (*i*) by (*ii*), we get

$$(r_- + r_+)/r_- = \sqrt{2}a/2\times 2/a = \sqrt{2}$$

or $$r_+/r_- = 1{\cdot}414 - 1 = 0{\cdot}414$$

Thus, the **limiting** r_+/r_- **ratio** for octahedral site is **0·414.**

If the radius ratio is less than 0·414, then either the anion is too big or the cation is too small in size. In either case, the anions shall have to be squeezed so that the cation and the anions just touch one another. This would increase the repulsion between the anions and destabilise the octahedral arrangement of anions. The squeezing of anions can be avoided by decreasing the coordination number of the cation. In other words, the system would prefer to change from octahedral to tetrahedral arrangement of anions. Thus, *ionic crystals with radius ratio less than 0·414 would tend to have a tetrahedral structure.*

d. Limiting radius ratio for cubic site. Consider a cubic site, as shown in Fig. 32. The spheres are not shown touching one another for the sake of clarity. Suppose the length of each side of the cube is a and r_- and r_+ are the radii of the anion and the cation, respectively.

As is evident from the figure, $AB = 2r_- = a$

or $$r_- = a/2 \qquad ...(i)$$

Length of the face diagonal $AC = \sqrt{AB^2+BC^2} = \sqrt{a^2+a^2} = \sqrt{2}\, a$

Length of body diagonal $AD = \sqrt{AC^2+CD^2}$

$$= \sqrt{(\sqrt{2}\,a)^2+a^2} = \sqrt{3}\, a$$

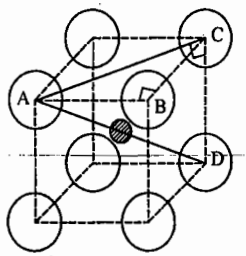


Fig. 32. A cubic site. The spheres are not shown touching for simplicity.

But, the length of the body diagonal $AD = r_- + 2r_+ + r_- = 2r_- + 2r_+$

or $$r_- + r_+ = \sqrt{3}a/2 \qquad ...(ii)$$

Dividing Eq. (*ii*) by (*i*), we get,

$$(r_- + r_+)/r_- = \sqrt{3}\, a/2\times 2/a = \sqrt{3}$$

or $$r_+/r_- = \sqrt{3} - 1 = 1{\cdot}732 - 1 = 0{\cdot}732$$

Thus, the **limiting** r_+/r_- **ratio** for cubic site is **0·732.**

If the radius ratio is less than 0·732, then, as discussed in earlier cases, the arrangement would become unstable. The coordination number of the cation would, therefore, tend to decrease to stabilise the system. In other words, the system would prefer to change from cubic to octahedral arrangement of anions. Thus, *ionic crystals with radius ratios less than* 0·732 *would tend to adopt an octahedral geometry.*

Determination of Ionic Radii. In the ordinary sense, **ionic radius** may be defined as *the distance from the nucleus of an ion up to which the nucleus has influence on the electron charge cloud.* The electron charge cloud, no doubt, may extend theoretically up to a very large distance. Nevertheless, it is essential to characterise the radius of each ion by some specific value. For this purpose, the internuclear distance in an ionic compound is determined from X-ray measurements. *This distance is then taken as the sum of the radii of the two ions involved.* For example, the distance between the nuclei of Na^+ and F^- ions is found from X-ray studies of NaF crystals to be 2·31 Å. Thus, $r_{Na^+} + n_{F^-} = 2{\cdot}31$ Å. The problem remains unsolved unless the radius of one of the ions is known. Several solutions have been suggested in this context. One proposed by Pauling has been most widely followed. He selected four ionic solids, namely NaF, KCl, RbBr and CsI. In each salt, as can be seen, *the cation and anion are iso-electronic, i.e.*, they have the same number of electrons which correspond to a noble gas configuration. In NaF, for example, both Na^+ and F^- ions have 10 electrons each and have $1s^2 2s^2 p^6$ configuration which is the same as that of neon. Pauling proposed that in ionic compounds formed by iso-electronic ions, *the ratio of the two ionic radii should be inversely proportional to the ratio of the effective nuclear charges of the two ions.* The effective nuclear charge (Z_{eff}) is obtained by subtracting a screening constant from the actual nuclear charge. The value of screening constant is evaluated from **Slater's rules**, as discussed in details in Chapter 1. According to these rules, the effective nuclear charges of Na^+ and F^- ions at their perpheries come out to be 6·5 and 4·5, respectively. Hence, according to Pauling's rule

$$\frac{r_{Na^+}}{r_{F^-}} = \frac{Z_{eff}(F^-)}{Z_{eff}(Na^+)} = \frac{4{\cdot}5}{6{\cdot}5} \qquad ...(i)$$

Also, we know that $$r_{Na^+} + r_{F^-} = 2{\cdot}31 \text{ Å} \qquad ...(ii)$$

From Eqs. (*i*) and (*ii*) $$r_{Na^+} = 0{\cdot}95 \text{ Å} \quad \text{and} \quad r_{F^-} = 1{\cdot}36 \text{ Å}$$

Following this procedure, the radii of most of the cations and anions have been determined. The radii of some of the univalent cations and anions, thus calculated, are given in Table 3. These values are quite close to the experimentally observed values for these ions (see Table 7, Chapter 2).

TABLE 3

Calculated Radii of Some Univalent Cations and Anions

Ion	Radius (Å)	Ion	Radius (Å)
Li^+	0·60	Au^+	1·37
Na^+	0·95	Ag^+	1·26
K^+	1·33	F^-	1·36
Rb^+	1·48	Cl^-	1·81
Cs^+	1·69	Br^-	1·95
Cu^+	0·96	I^-	2·16

Example 7. The internuclear distance in KCl is 3·44 Å. Calculate the radii of K^+ and Cl^- ions.

Solution : Since K^+ and Cl^- ions are iso-electronic having 18 electrons each, Pauling's rule can be applied.

According to Slater's rules (cf. Chapter 1),

$$Z_{eff}(K^+) \text{ at the periphery of the ion} = 19 - (8\times0{\cdot}35 + 8\times0{\cdot}85 + 2\times1) = 19 - 11{\cdot}60 = 7{\cdot}40$$

$$Z_{eff}(Cl^-) \text{ at the periphery of the ion} = 17 - (8\times0{\cdot}35 + 8\times0{\cdot}85 + 2\times1) = 17 - 11{\cdot}60 = 5{\cdot}40$$

According to Pauling's rule,

$$\frac{r_{K^+}}{r_{Cl^-}} = \frac{Z_{eff}(Cl^-)}{Z_{eff}(K^+)} = \frac{5{\cdot}40}{7{\cdot}40} \quad ...(i)$$

$$r_{K^+} + r_{Cl^-} = 3{\cdot}44 \text{ (given)} \quad ...(ii)$$

From Eqs. (*i*) and (*ii*),

$$r_{K^+} = 1{\cdot}40 \text{ Å and } r_{Cl^-} = 1{\cdot}94 \text{ Å}$$

Radius Ratio Rule and the Shape of Ionic Crystals

As discussed before, in ionic crystals, the coordination numbers of ions as well as the geometric shapes of crystals depend very largely on the relative sizes of the ions, *i.e.*, on their radius ratios.

In order to study the role played by this ratio in determining the coordination number and the shape of an ionic crystal let us suppose that the coordination number of ion A^+ in an ionic compound AX_3 is 3. Thus, three X^- ions will be in contact with one A^+ ion. This may be represented as in Fig. 33(*a*). Such a structure will be quite stable because the positive ion (A^+) finds three negative ions (X^-) immediately in contact with it. The forces of attraction will be quite strong. At the same time, the negative ions are not at all in contact with one another. The forces of repulsion, therefore, will be quite small. The limiting case of stability with coordination number 3 arises when the negative ions (X^- ions) are in contact with each other, as shown in Fig. 33(*b*). The positive ion, no doubt, is still touching the negative ions and the force of attraction is quite strong. But the negative ions are also touching one another and, therefore, the force of repulsion is stronger than before. As already shown, in such a case, the radius ratio r_+/r_- is 0·155. If the ratio r_+/r_- falls below this value (*i.e.*, if A^+ ion becomes still smaller), the structure will be as shown in Fig. 33(*c*). The positive ion is *not* touching any of the negative ions now. The force of attraction, therefore, is weak. At the same time, the negative ions are in direct contact with one another. The force of repulsion, therefore, will be strong. Hence, such a structure is unstable and, therefore, cannot exist. Evidently, for coordination number 3, the lowest, *i.e.*, the limiting radius ratio r_+/r_- is 0·155.

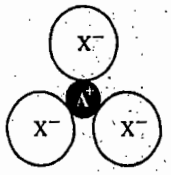


Fig. 33(*a*). A case of stable structure of ionic compound AX_3 with coordination number of A^+ ion 3.

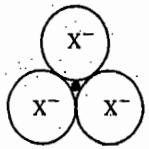


Fig. 33(*b*). Limiting case of stable structure of ionic compound AX_3 with coordination number of A^+ ion 3.

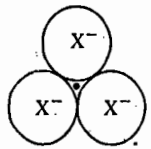


Fig. 33(*c*). Unstable structure of ionic compound AX_3 with coordination number of A^+ ion 3.

Similarly, the limiting radius ratio for the cations to fit in a tetrahedral site is 0·225. In other words, for the radius ratios r_+/r_- ranging between 0·155 to 0·225, trigonal site will be preferred in which the coordination number of cation is 3.

Likewise, as already shown, the limiting radius ratio for the cations to fit into an octahedral site of anions is 0·414. Therefore, tetrahedral sites (C.N. of cation 4) will be preferred between the radius ratio

range 0·255 to 0·414 . In the range 0·414 to 0·732 , octahedral sites (C.N. of cation 6) will be adopted by the cations while above 0·732, cubic sites (C.N. of cation 8) will be favoured.

Thus, *we find that radius ratio is a very important factor in determining the most stable form of arrangement of ions in the crystal lattice of an ionic crystal.*

The permitted coordination numbers and structural arrangements of anions around cations for different r_+/r_- ratios are given in Table 4.

TABLE 4

Limiting Radius Ratios and Shapes of Crystals

Limiting Radius Ratios, r_+/r_-	Permitted Coordination Number	Structural Arrangement	Example
0·155 – 0·225	3	Plane trigonal	Boron oxide
0·255 – 0·414	4	Tetrahedral	ZnS
0·414 – 0·732	6	Octahedral	NaCl
0·732 – 1·00	8	Cubic	CsCl

It would be useful to remember that

In the case of **crystals of the type AB,** if the radius ratios is 0·732 or above, the crystal would have **CsCl type structure,** *i.e., body centred cubic structure in which each ion has a coordination number 8.* If the ratio is less than 0·732 but equal to or greater than 0·414 , the crystal would have **NaCl type structure** *in which each ion has a coordination number 6.* If the ratio is less than 0·414 but equal to or higher than 0·225, the crystal would have a **ZnS type structure** *in which each ion has a coordination number 4.* Lastly, if the ratio is less then 0·225 but equal to or higher than 0·155, the crystal would adopt a **planar trigonal structure** *in which the coordination number of each ion is 3.*

In the case of **crystals of the type AB_2,** if the radius ratio is 0·732 or above, the crystal would have **flourite (CaF_2) type structure** *in which coordination number of cation is 8 and that of anion is 4.* If the ratio lies between 0·414 and 0·732 , the crystal would adopt **rutile (TiO_2) type structure** *in which coordination number of cation is 6 and that of anion is 3.*

Thus, with the help of radius ratios, it is possible to predict the shapes of ionic crystals. Since cations are commonly monovalent and divalent, the ionic crystals are commonly of the type AB and AB_2.

Further Application of Radius Ratio Rule. Some further applications of radius ratio rule have been discussed below.

1. The radius of Na^+ ion is 0·95 Å and that of Cl^- ion is 1·81 Å. Hence, the radius ratio

$$\frac{r_+}{r_-} = \frac{r_{Na^+}}{r_{Cl^-}} = \frac{0{\cdot}95}{1{\cdot}81} = 0{\cdot}524$$

This ratio lies between 0·414 and 0·732 . Hence, Na^+ ions prefer to occupy **octahedral sites** with coordination number 6 in the close-packed lattice of Cl^- ions.

2. The radii of Zn^{2+} and S^{2-} ions are 0·74 Å and 1·84 Å, respectively, so that the radius ratio

$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = \frac{0{\cdot}74}{1{\cdot}84} = 0{\cdot}40$$

This radius ratio lies between 0·225 and 0·414 and, therefore, the Zn^{2+} ions prefer to occupy **tetrahedral sites** with coordination number 4 in close-packed lattice of S^{2-} ions.

3. The radii of Cs^+ and Cl^- ions are 1·69 Å and 1·8 Å, respectively, so that the radius ratio

$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{1{\cdot}69}{1{\cdot}81} = 0{\cdot}93$$

This suggests that Cs^+ ions perfer to occupy **cubic sites** with coordination number 8.

4. The radii of Mg^{2+} and O^{2-} ions are 0·66 Å and 1·40 Å, respectively, so that the radius ratio

$$\frac{r_{Mg^+}}{r_{O^{2-}}} = \frac{0{\cdot}66}{1{\cdot}40} = 0{\cdot}472$$

This suggests a coordination number 6 for Mg^{2+} ions and they perfer to occupy **octahedral sites.**

5. The radii of B^{3+} and O^{2-} ions are 0·23 Å and 1·40 Å, respectively. Hence, the radius ratio

$$\frac{r_{B^{2+}}}{r_{O^{2-}}} = \frac{0{\cdot}23\ \text{Å}}{1{\cdot}40\ \text{Å}} = 0{\cdot}164$$

The ratio lies between 0·155 and 0·225. Hence, boron oxide would tend to have a **plane trigonal structure** (Table 4).

It may be pointed out pertinently that the radius ratio rule applies to only the packing of rigid spheres. Since larger anions are easily polarised, they do not behave as rigid spheres. Because of polarisation they tend to form covalent bonds which are strongly directional. Such ionic crystals, therefore, do not strictly follow the radius ratio rule.

Structures of Metallic Crystals. The metal atoms in a metallic lattice are all identical and can be assumed to have spherical shape. Metals, therefore, crystallise in three forms, *viz., hexagonal close packing, cubic close packing and body centred cubic arrangement.*

1. Hexagonal close packing. This form has *ABABAB*... type of arrangement of layers of metal atoms. Each metal atom is 'touching' 12 other atoms (6 atoms in its own layer, 3 atoms in the layer above and 3 atoms in the layer below), that is, each metal atom has a coordination number of 12. Approximately 74% of the space is occupied in hexagonal close packing. This arrangement has already been shown in Fig. 20. Metals such as Be, Mg, Ti, etc., have this type of arrangement in their crystals at 25°C.

2. Cubic close packing or face centred cubic arrangement. This form has *ABCABCABC*... type of arrangement of layers of metal atoms. Each metal atom has coordination number 12 as in hexagonal close packing. In this arrangement also, about 74% of space is occupied by cubic close packing. This arrangement has been shown earlier in Fig. 21. Metals such as Ni, Cu, Ag, Au, etc., have this type of arrangement. Due to greater ease of sliding of one layer of atoms over the other in *ccp* arrangement, the metals with *ccp* arrangement are found to be more malleable and ductile than the metals having *hcp* arrangement.

3. Body centred cubic arrangement. In this form, each atom has 8 nearest neighbours and 6 next nearest neighbours that are farther away to the tune of 15 per cent. This form is 92 per cent as dense as the *ccp* and *hcp* forms. The body centred cubic (*bcc*) arrangement has already been shown in Fig. 23*a*. Metals such as Li (and all other alkali metals), Ba, Cr, Fe, etc., have *bcc* structure. The metals having this structure in their crystals are considerably malleable and ductile because *bcc* arrangement can be deformed comparatively easily. These metals have comparatively lower densities because only 68% of the space (as compared to 74% in *ccp* or *hcp* arrangement) is occupied in the *bcc* arrangement.

Some metals crystallise in mixed *hcp-ccp* arrangement of the type *ABCABABCAB*... Examples are metal crystals of La, Co, etc.

Structures of some of the metals at 25°C are presented in Table 5.

TABLE 5

Structures of Metals at 25°C

Metal	Structure	Metal	Structure
Li	*bcc*	Co	*hcp-ccp*
Na	*bcc*	Rh	*ccp*
K	*bcc*	Ir	*ccp*
Rb	*bcc*	Zn	*hcp*
Cs	*bcc*	Cd	*hcp*
Be	*hcp*		
Mg	*hcp*	Ti	*hcp*
Ca	*ccp*	Zr	*hcp*
Sr	*ccp*	Hf	*hcp*
Ba	*bcc*		
Al	*ccp*	V	*bcc*
Tl	*hcp*	Nb	*bcc*
		Ta	*bcc*
		Cr	*bcc*
Pb	*ccp*	Mo	*bcc*
		W	*bcc*
Ni	*ccp*	Te	*hcp*
Pd	*ccp*	Re	*hcp*
Pt	*ccp*		
Cu	*ccp*	Fe	*bcc*
Ag	*ccp*	Ru	*hcp*
Au	*ccp*	Os	*hcp*
Sc	*ccp*		
Y	*hcp*		
La	*hcp-ccp*		

It is evident from Table 5 that it is not easy to frame rules which may predict the type of structure the metals would have in a particular group of the periodic table. The only exception appears to be the group of alkali metals all of which have the same structure. The problem is further complicated by the fact that a large number of metals exhibit polymorphism as a function of temperature, *i.e.*, the same metal may have different structures at different temperatures. This is illustrated in Table 6.

TABLE 6

Structures of Some Metals at Different Temperatures

Metal	Temperature (°C)	Structure
Ca	25	*ccp*
	500	*bcc*
Fe	25	*bcc*
	900	*ccp*
	1400	*bcc*
Sr	25	*ccp*
	350	*hcp*
	600	*bcc*
Li	25	*bcc*
	100	*hcp*

Structures of Ionic Crystals

Ionic crystals, as already explained, consist entirely of positively and negatively charged units called *ions*. It is evident that for *maximum stability* the arrangements of ions in a crystal should be such that *forces of attraction are maximum* and the *forces of repulsion are minimum*.

Hence, for maximum stability, the oppositely charged ions should be as close to one another and similarly charged ions as far away from one another as possible.

The structure of an ionic crystal depends, to a large extent, on relative sizes of the cations and anions concerned. If, for example, anions are larger, they form a close-packed arrangement and the cations just fit into (or occupy) the resulting interstitial sites of tetrahedral or octahedral type, as the case may be.

In the case of a substance of general formula AX, like sodium chloride (NaCl) or zinc sulphide (ZnS), in which the number of each kind of ions is the same, the coordination number of the positive ion is the same as that of the negative ion. But in the case of a substance of general formula AX_2 or A_2X (*e.g.*, $CaCl_2$ or Na_2S) in which the number of each kind is not the same, the coordination number of positive ion is different from that of negative ion. In calcium chloride, for example, chloride ions are twice as many as calcium ions. The coordination number of calcium ion, therefore, is *twice* the coordination number of chloride ion.

Let us discuss the structures of a few common crystals of the formula AX and AX_2. The structures can be described in terms of close-packed arrangements of large anions with small cations occupying the interstitial sites such as tetrahedral or octahedral.

CRYSTALS OF THE TYPE AX

Structure of Sodium Chloride (NaCl). The unit cell of sodium chloride crystal is shown in Fig. 34. In this structure, the sodium ions are represented by hollow circles and chloride ions by solid circles.

The salient features of this structure are as follows :

1. The chloride ions are arranged in *cubic close packing* (*ccp*) arrangement. In this arrangement, there are Cl^- ions at the corners of the cube as well as at the centre of each face (*face centred cubic arrangement*).

2. The sodium ions occupy all the *octahedral sites.*

3. There is only one octahedral site per atom in a close packed lattice. Therefore, there will be one Na^+ ion for every Cl^- ion. This corresponds to 1 : 1 stoichiometry of sodium chloride crystal. This stoichiometry can also be understood by counting the number of Na^+ and Cl^- ions which contribute to the unit cell, as discussed below.

It is clear from Fig. 34 that there are eight Cl^- ions at the corners and six at the faces of the unit cell. We can easily understand from the figure that each ion at the corner is shared between eight unit cells and its contribution per unit cell is 1/8. Similarly, each ion on a face is shared by two unit cells so that its contribution per unit cell is 1/2. Therefore, the number of Cl^- ions for the unit cell is equal to $8\times(1/8) + 6\times(1/2) = 4$. The number of sodium ions can also be calculated in a similar way. There are twelve Na^+ ions on the edges and one inside the cell. It can be easily seen that each ion on the edge is shared by four unit cells and its contribution per unit cell is 1/4 , while the ion at

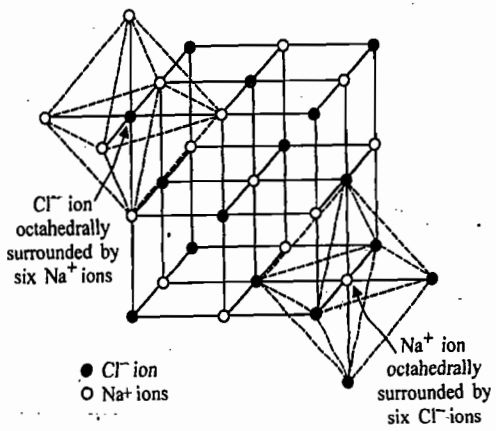


Fig. 34. Unit cell representation of NaCl structure, Hollow circles represent Na^+ ions and solid circles represent Cl^- ions.

the body centre contributes only to one unit cell. Therefore, the number of Na^+ ions for the unit cell is equal to $12 \times (1/4) + 1 = 4$. Thus, the stoichiometry is 1 : 1.

4. In this structure, each Na^+ ion is surrounded by six Cl^- ions which are disposed towards the corners of a regular octahedron. This has also been shown in the figure. Similarly, each Cl^- ion is surrounded by six Na^+ ions. Thus, the coordination number of Na^+ ion as well as that of Cl^- ion is 6.

5. We have seen that for cations to fit into octahedral sites, the radius ratio r_+/r_- should be equal to 0·414 (Table 4). The radius of Na^+ ion is 0·95 Å and that of Cl^- ion is 1·81 Å so that r_{Na^+}/r_{Cl^-} is 0·524 . Therefore, to accommodate somewhat larger sized Na^+ ions, Cl^- ions move apart slightly. In other words, the *ccp* arrangement of Cl^- ions is slightly opened up. This type of structure is adopted by most of the alkali metal halides, the alkaline earth metal oxides and AgF, AgCl, AgBr, NH_4Cl and NH_4 Br, etc.

Structure of Zinc Sulphide (ZnS). It has two types of structures known as

1. Zinc blende Structure *2. Wurtzite Structure*

1. Zinc Blende Structure. The unit cell of zinc blende structure is shown in Fig. 35. In this structure, the zinc ions are represented by hollow circles and the sulphide ions are represented by solid circles. The salient features of this structure are as follows :

1. The sulphide ions are arranged in *ccp* arrangement, *i.e.*, at the corners of the cube and at the centre of each face.

2. The zinc ions occupy half of the tetrahedral sites.

3. Since there are two tetrahedral sites per atom in a close packed lattice, this means that there are two tetrahedral sites per S^{2-} ion. In this arrangement, only half of the tetrahedral sites are occupied by Zn^{2+} ions so that each S^{2-} ion has one Zn^{2+} ion. Therefore, the stoichiometry of the compound is 1 : 1.

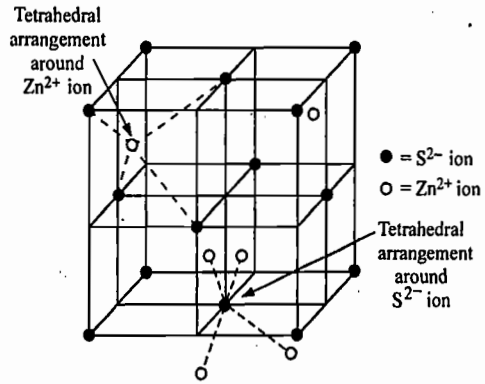


Fig. 35. Unit cell representation of zinc blende structure. Hollow circles represent Zn^{2+} ions and solid circles represent S^{2-} ions.

4. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, each S^{2-} ion is surrounded by four Zn^{2+} ions. The arrangement around one Zn^{2+} ion and one S^{2-} ion is also shown in Fig. 35. Thus, the coordination numbers of Zn^{2+} and S^{2-} ions in zinc blende are described as 4 : 4.

5. In zinc sulphide, the radius ratio r_+/r_- is 0·40. This suggests that the coordination number is 4 (Table 4). This supports the structure presented in Fig. 35.

Zinc blende structure is also adopted by some other compounds such as ZnO, CuCl, CuBr, CuI, etc.

2. Wurtzite Structure. The unit cell for wurtzite structure is shown in Fig. 36 in which each Zn^{2+} ion is represented by a hollow circle and each S^{2-} ion is represented by a solid circle. The wurtzite structure may be described as follows :

1. The sulphide ions are arranged in a hexagonal close packed (*hcp*) arrangement.

2. The zinc ions occupy half of the tetrahedral sites.

3. There are two tetrahedral sites for each S^{2-} ion in the lattice. Since only half of them are occupied by Zn^{2+} ions, the stoichiometry of the compound is 1 : 1.

4. Each S^{2-} ion is surrounded by four Zn^{2+} ions which are disposed towards the corners of a regular tetrahedron. Similarly, each Zn^{2+} ion is surrounded by four S^{2-} ions. The arrangement around one Zn^{2+} ion and one S^{2-} ion is shown in Fig. 36. Therefore, the coordination numbers of Zn^{2+} and S^{2-} ions in wurtzite structure are 4 : 4.

5. The radius ratio r_+/r_- in this structure is 0·40 which also suggests that the coordination number is 4 (Table 4) and that the crystal has a tetrahedral structure. Thus, the radius ratio rule supports the above structure. The compounds such as AgI, ZnO, NH_4F and AlN have wurtzite structure.

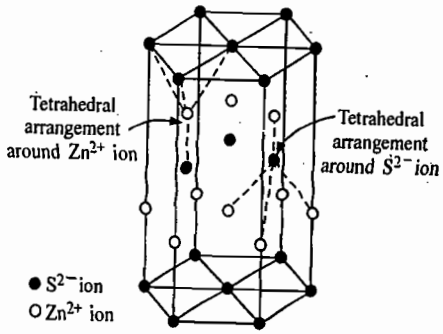


Fig. 36. Unit cell representation of wurtzite structure. S^{2-} ions (solid circles) adopt *hcp* arrangement and Zn^{2+} ions (hollow circles) occupy half of the tetrahedral sites.

It will be noted that the basic difference between *zinc blende* and *wurtzite* structure is that whereas in the former case the sulphide ions are arranged in *ccp* type of packing, in the latter case they are arranged in *hcp* type of packing.

Structure of Cesium Chloride (CsCl). The unit cell of CsCl is shown in Fig. 37. In this structure, cesium ions are represented by hollow circles whereas chloride ions are represented by solid circles. The structure of CsCl may be described as follows :

1. The Cl^- ions form the simple cubic arrangement and the Cs^+ ions occupy the cubic interstitial sites. In other words, the Cl^- ions may be regarded as lying at the corners of a cube and cesium ions are present at the body centre of each cube.

2. Each Cs^+ ion is surrounded by eight Cl^- ions which are disposed towards the corners of a cube. This is clear from Fig. 37(*a*). When the unit cell is extended as shown in Fig. 37 (*b*), it becomes clear that each Cl^- ion is also surrounded by eight Cs^+ ions. Thus, both types of ions are in equivalent positions. Therefore, the coordination numbers of Cs^+ and Cl^- ions are 8 : 8.

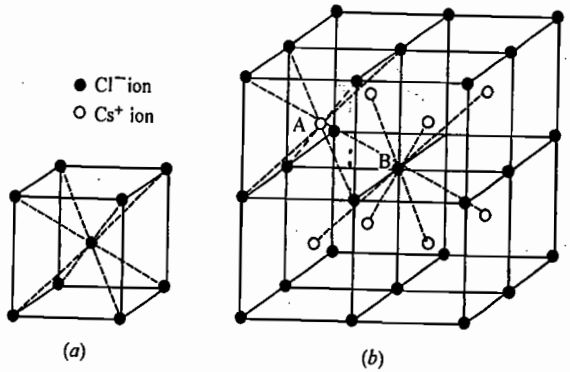


Fig. 37. (*a*) Unit cell representation of CsCl. The Cl^- ions adopt simple cubic arrangement and Cs^+ ions occupy cubic sites. (*b*) The extended unit cell.

The above structure may be described as body centred cubic. But, this would be a misnomer because the body centred cubic structure is one which has the same atoms at the body centre as well as the corners. But in CsCl, the atoms at the corners are different from the atoms at the centre. This type of structure is adopted by CsBr, CsI, TlCl, TlBr, etc.

Since coordination numbers of ions in CsCl (8 : 8) are higher than those in NaCl (6 : 6), we might expect that cesium chloride lattice would be more stable since each ion would have more ions of opposite charge as its neighbours. This is actually the case. The cesium chloride lattice is 1 per cent more stable than the sodium chloride lattice.

Here question arises that if CsCl lattice is more stable then why do the halides of Li, Na, K and Rb not have this lattice ? The answer lies in the radius ratio effect. The radius ratio in the halides of Li, Na,

K and Rb lies between 0·73 and 0·41 and, therefore, the coordination number has to be 6 (Table 4). If an attempt is made to pack 8 halide ions around a *smaller* positive ion, say, Na^+ ion, then some of the negative ions will touch each other sooner than they can approach a positive ion, as shown in Fig. 38. The lattice would thus be unstable. This difficulty can be overcome by packing 6 negative ions around the central positive ion. Hence, the coordination number of 6 is preferred.

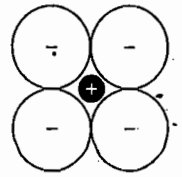


Fig. 38. Cross-section of unstable structure with 8 halide ions around an alkali metal ion other than Cs^+.

CRYSTALS OF THE TYPE AX_2

Structure of Calcium Fluoride (CaF_2). The unit cell of CaF_2 is shown in Fig. 39. The calcium ions are represented by hollow circles and fluoride ions are represented by solid circles. The CaF_2 structure may be described as follows :

1. The Ca^{2+} ions are arranged in *ccp* arrangement so that there are Ca^{2+} ions at all the corners and at the centre of each face of the cube. The fluoride ions occupy all the tetrahedral sites.

2. Since there are two tetrahedral sites for each Ca^{2+} ion and F^- ions occupy all the tetrahedral sites, there will be two F^- ions for each Ca^{2+} ion. Thus, the stoichiometry of the compound is 1 : 2.

3. In this arrangement, each F^- ion is surrounded by four Ca^{2+} ions whereas each Ca^{2+} ion is surrounded by eight F^- ions. Thus, the coordination numbers of Ca^{2+} and F^- ions are 8 : 4.

This structure is adopted by a large number of fluorides such as BaF_2, SrF_2, PbF_2, HgF_2, CuF_2, etc.

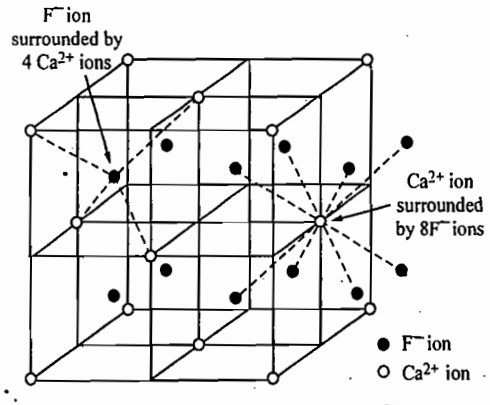


Fig. 39. Unit cell representation of CaF_2. The Ca^{2+} ions adopt *ccp* arrangement and F^- ions occupy all the tetrahedral sites.

Structure of Titanium Dioxide, TiO_2 (Rutile Structure). The unit cell of rutile structure is shown in Fig. 40 in which titanium ions are represented by hollow circles and oxide ions are represented by solid circles.

The structure may be described as follows :

1. The titanium ions are arranged in a *distorted body centred cubic arrangement* in which these ions are present at all the corners and at the centre of the distorted cube. This structure cannot be described as cubic because one of the axes is shorter than the other by 30 per cent. The structure is, therefore, described as **distorted cubic**.

2. As shown in Fig. 40, each titanium ion is surrounded octahedrally by six oxide ions, as, for example, the titanium ion marked A in the figure. On the other hand, each oxide ion is surrounded by three titanium ions disposed towards the corners of an equilateral triangle. Thus, the coordination numbers of Ti^{4+} and O^{2-} ions are 6 : 3.

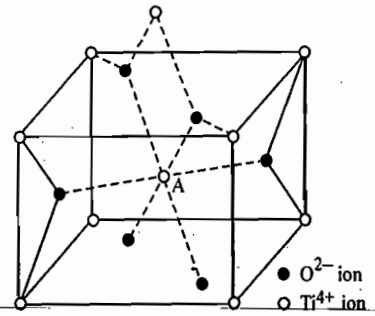


Fig. 40. Structure of titanium dioxide.

Structure of Calcium Carbide (CaC_2). The unit cell of calcium carbide is shown in Fig. 41. The structure of calcium carbide is similar to that of sodium chloride (Fig. 34). Here sodium ions are replaced by

calcium ions and chloride ions by C_2 groups. The carbon atoms are associated in pairs, as shown in Fig. 41, forming the C_2 groups. The C_2 groups are aligned in parallels as shown. The cubic symmetry observed in sodium chloride is, however, distorted considerably in the case of calcium carbide for obvious reasons.

The structure of FeS_2 is similar to that of CaC_2. However, the S_2 units are not aligned in parallels as are the C_2 units in the case of CaC_2.

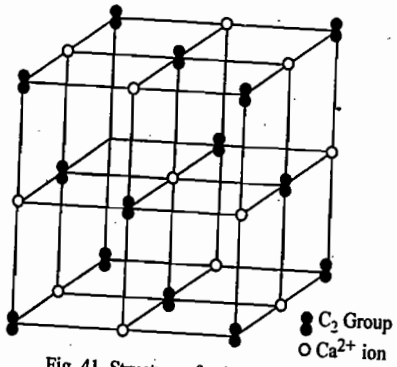


Fig. 41. Structure of calcium carbide.

Structure of Cadmium Iodide (CdI_2) The unit cell of cadmium iodide is shown in Fig. 42 in which Cd^{2+} ions are represented by hollow circles and iodide ions are represented by solid circles.

The salient features of this structure are described below :

1. The iodide ions are arranged in a *hexagonal close packed* (*hcp*) arrangement while cadmium ions lie in *octahedral sites between every two layers of iodide ions*.

2. Each Cd^{2+} ion is surrounded octahedrally by six I^- ions, as shown in Fig. 42. On the other hand, each I^- ion has three Cd^{2+} ions as nearest neighbours. The three Cd^{2+} ions surround the I^- ion in an arrangement in which Cd^{2+} ions form the base of a trigonal pyramid whose apex is the I^- ion.

3. The arrangement of the three layers corresponds to the composition CdI_2.

This arrangement is continued as shown and the structure is referred to as a layer lattice. The forces operating in between the I – Cd – I layers to hold them together are weak. As a result, this compound is flaky and can be easily cleaved.

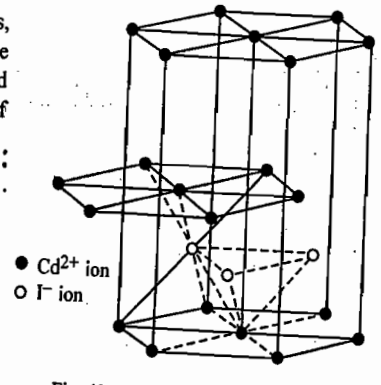


Fig. 42. Structure of cadmium iodide.

Lattice Energy of an Ionic Crystal

The **lattice energy *U* of an ionic crystal** is defined *as the amount of energy released when cations and anions in their gaseous states are brought from infinity to their respective lattice sites in a crystal to form one mole of the ionic crystal.*

The formation of a mole of an ionic crystal from the constituent gaseous ions may be represented as follows :

$$A^+(g) + B^-(g) \xrightarrow{-U} A^+B^-(s) \; ; \qquad U = \text{Lattice energy}$$

With the coming together of positive and negative ions, there is a considerable decrease in potential energy of the system. Hence, in the formation of an ionic crystal from the constituent gaseous ions, as in the above example, there is considerable *release of energy in the form of heat.* Hence, *U* is negative.

It is obvious that the greater the magnitude of the lattice energy of an ionic crystal, the greater would be its stability. Lattice energies of a few ionic crystals are given in Table 7.

TABLE 7

Lattice Energies of Some Common Ionic crystals

Uni-Univalent Crystals		Bi-Bivalent Crystals	
Ionic Crystal	**Lattice Energy (kJ mol^{-1})**	**Ionic Crystal**	**Lattice Energy (kJ mol^{-1})**
LiF	– 1033	CaF_2	– 2581
CsF	– 748	MgF_2	– 2882
NaCl	– 778	MgO	– 3932
LiI	– 140	BeO	– 3125
CsI	– 601	MgS	– 3254
AgCl	– 895	ZnO	– 4032

As can be seen, lattice energies of ionic crystals are quite high. This is on account of strong electrostatic attraction between oppositely charged ions present in the crystals. Since coulombic forces of attraction vary directly as the product of the charges, it follows that the higher the valency (charge) of the ions, the greater would be the lattice energy of the ionic crystals. Thus, lattice energy increases as we move from uni–univalent ionic crystals to uni-bivalent ionic crystals and then to bi-bivalent ionic crystals.

Calculation of Lattice Energies of Ionic Crystals

The lattice energy of ionic crystals can be calculated theoretically on the basis of coulombic interactions between the ions present in the crystals. There are two types of interactions :

1. *Attractive interactions between oppositely charged ions.*
2. *Repulsive interactions because of interpenetration of electron charge clouds.*

1. Attractive Interactions between Oppositely Charged Ions. The potential energy (*P.E.*) of a pair of ions of opposite charges varies inversely as the distance *r* between the ions. This may be expressed as

$$P.E.\ (\text{attraction}) = z_1 z_2 \frac{(+e)(-e)}{r} = -\frac{z_1 z_2 e^2}{r} \qquad ...(2)$$

where *e* is the electronic charge and z_1 and z_2 are the charges on the oppositely charged ions (being, for example, 1 and 1 in the case of NaCl and 2 and 1 in the case of $CaCl_2$).

2. Repulsive Interactions due to Interpenetration of Electron Charge Clouds. As a cation and an anion come very close to each other, there is repulsion between them because of interpenetration of similarly charged electron charge clouds. The potential energy due to this repulsion has been shown to be inversely proportional to the *n*th power of the distance between the ions, *i.e.*,

$$P.E.\ (\text{repulsion}) = b\, e^2 / r^n \qquad ...(3)$$

when *n* is called *Born exponent* while *b* is a constant termed as *repulsion coefficient*. The value of *n* increases with increase in electron charge density around the ions. In the case of ions having Ne configuration (*e.g.*, Na^+ and F^- ions), $n = 7$ while in the case of ions having Ar, Kr and Xe configurations, $n = 9$, 10 and 12, respectively.

The net potential energy for a pair of ions of opposite charges is thus given by combining Eqs. 2 and 3, *i.e.*,

$$P.E.\ (\text{net}) = -z_1 z_2 e^2/r + be^2/r^n \qquad ...(4)$$

Eq. 4 is known as **Born equation.** It gives the potential energy of a system comprising of a cation and an anion which carry z_1 and z_2 as integral charges, as explained above.

It will be seen that the second term, be^2/r^n, *viz.*, the repulsion term in Eq. 4 increases more rapidly than the first term with decrease in the interionic distance r. Born equation gives the *energy released* when a cation and an anion separated by an infinite distance in gaseous state are brought closer together in a crystal at a distance r from each other.

The **application of Born equation** may be illustrated by considering the forces of attraction and repulsion involved in a crystal of sodium chloride. In a crystal, there is not one cation and one anion. Instead, there is a large number of cations and anions arranged together according to a certain specific geometry. It is necessary, therefore, to consider forces of attraction and repulsion between all of them. Thus, in a crystal of sodium chloride (Fig. 43), each sodium ion is surrounded by

(*i*) 6 chloride ions at a distance r

(*ii*) 12 other sodium ions at a distance $\sqrt{2}\,r$

(*iii*) 8 more chloride ions at a distance $\sqrt{3}\,r$

(*iv*) 6 more sodium ions at a distance $\sqrt{4}\,r$

(*v*) 24 more chloride ions at a distance $\sqrt{5}\,r$

(*vi*) 24 more sodium ions at a distance $\sqrt{6}r$, and so on and so forth.

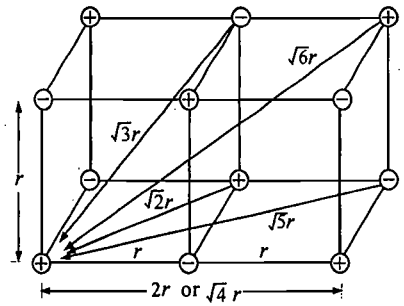


Fig. 43. Interionic distance in NaCl crystal.

The *first term* in Born equation may be calculated from the above data. It is useful to remember that since attraction leads to *fall* and repulsion leads to *rise* in potential energy, the potential energy due to attraction is given a negative sign while that due to repulsion is given a positive sign. Keeping this in view, the potential energy due to the first term in Born equation is obtained by adding up the effect of all the interactions. Thus,

$$(P.E.)_1 = -\frac{6z_1z_2e^2}{r} + \frac{12z_1z_2e^2}{\sqrt{2}r} - \frac{8z_1z_2e^2}{\sqrt{3}r} + \frac{6z_1z_2e^2}{\sqrt{4}r} - \frac{24z_1z_2e^2}{\sqrt{5}r} + \frac{24z_1z_2e^2}{\sqrt{6}r} - \ldots\ldots$$

$$= -\frac{z_1z_2e^2}{r}\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} \ldots\right]$$

For NaCl, a uni-univalent electrolyte, both z_1 and z_2 are equal to unity. The quantity in the brackets is thus summation of an infinite series and is known as the **Madelung constant** for the sodium chloride structure. Its value comes out to be 1·747558. Madelung constant is generally denoted by the symbol A. Any other salt having the same geometrical arrangement of ions as sodium chloride will have the same value of Madelung constant. If it is required to calculate the value in the case of some other salts, it is possible to do so provided the geometrical arrangement of the ions in their crystals is known. Thus, the *first term* may be expressed as

$$(P.E.)_1 = -A\,z_1\,z_2\,e^2/r \qquad \ldots(5)$$

The values of Madelung constants for some of the typical crystal structures are given in Table 8.

TABLE 8

Madelung Constants for Some Typical Crystal Structures

Crystal Structure	Examples of Compounds	Coordination Numbers of Ions	Madelung Constant
Sodium chloride	NaCl	Na^+ : 6 ; Cl^- : 6	1·7475
Cesium chloride	CsCl	Cs^+ : 8 ; Cl^- : 8	1·7627
Zinc blende	ZnS	Zn^{2+} : 4 ; S^{2-} : 4	1·6381
Wurtzite	ZnS	Zn^{2+} : 4 ; S^{2-} : 4	1·6410
Fluorite	CaF_2	Ca^{2+} : 8 ; F^- : 4	5·0388
Rutile	TiO_2	Ti^{2+} : 6 ; O^{2-} : 3	4·8160
Cadmium iodide	CdI_2	Cd^{2+} : 6 ; I^- : 3	4·7100

The *second term* in Born equation may now be considered. As already mentioned, it arises from repulsion between a cation and an anion due to interpenetration of similarly charged electron charge clouds. Since this term varies inversely as r^n, it is enough to consider nearest neighbours only. Others which are farther away will not have any significant effect. In the case of sodium chloride crystal, each sodium ion is surrounded by six chloride ions. The repulsion energy term, therefore, becomes $6be^2/r^n$. The term $6be^2$ is generally replaced by B where B is, evidently, the product of be^2 and the number of nearest neighbours. Therefore, the *second term* becomes B/r^n.

Considering interionic force due to all the neighbouring ions, the potential energy of an ion in a crystal may be written as

$$P.E. = -Az^2e^2/r + B/r^n \qquad \ldots(6)$$

where A is Madelung constant and z^2 has replaced z_1z_2 because $z_1 = z_2 = z$. It is the highest common factor of the ionic charges. The value of n in many common ions varies from 7 to 12.

It is possible to eliminate B from the above equation by realising that an *ion will be in stable equilibrium position when attractive and repulsive forces acting on it are equally balanced.* The potential energy of the ion is then a minimum and $d(P.E.)/dr = 0$. The interionic distance r may then be taken as r_0. By differentiating potential energy with respect to r and equating it to zero, we can eliminate the constant B as follows :

$$P.E. = -Az^2e^2r^{-1} + Br^{-n} \qquad \text{(Eq. 6)}$$

$$d(P.E.)/dr = -Az^2e^2(-1)\,r^{-2} + B(-n)\,r^{(-n-1)}$$

$$= Az^2e^2r^{-2} - nBr^{(-n-1)}$$

Equating $d(P.E.)/dr = 0$ when r is denoted as r_0, we get

$$Az^2e^2r_0^{-2} - nBr_0^{(-n-1)} = 0$$

or $$Az^2e^2r_0^{-2} = n\,Br_0^{(-n-1)}$$

or $$r_0^{n-1} = \frac{nB}{Az^2e^2}$$

or $$r_0 = \left(\frac{nB}{Az^2e^2}\right)^{1/(n-1)} \qquad \ldots(7)$$

and $$B = Az^2r_0^{n-1}e^2/n \qquad \ldots(8)$$

Substituting the value of B in Eq. 6, we have

$$(P.E.)_0 = -\frac{Ae^2z^2}{r_0} + \frac{Az^2e^2}{nr_0^n} r_0^{n-1} = \frac{-Az^2e^2}{r_0} + \frac{Az^2e^2}{nr_0}$$

$$= \frac{Az^2e^2}{r_0}\left(\frac{1}{n} - 1\right) \qquad ...(9)$$

The lattice energy U_0 is defined as the amount of energy released in the formation of a *mole* of a crystal from the constituent gaseous ions separated at infinite distance from one another. Thus,

$$U_0 = N_A \times \text{(Potential energy)} = \frac{N_A Az^2e^2}{r_0}\left(\frac{1}{n} - 1\right) \qquad ...(10)$$

Since n is always more than 1, U_0 would be negative, as expected.

In the above equation, all the quantities are known for a given crystal except the value of n which can be calculated from the compressibility of the crystal if the crystal spacing parameters are known.

The values of lattice energies calculated by means of this equation have been found to be in good agreement with those obtained experimentally, as shown for some of the compounds in Table 9.

TABLE 9

Lattice Energies of Some Common Compounds

Compound	Lattice Energy (kJ mol^{-1})	
	Experimental	Theoretical
MgF_2	– 2882	– 2920
CaF_2	– 2581	– 2585
AgCl	– 895	– 849
AgBr	– 883	– 824
AgI	– 870	– 795

The Born equation leads to the following conclusions :

1. The higher the charge on cation and anion, the greater would be the magnitude of lattice energy and, therefore, the greater would be the stability of the crystal.

2. Since lattice energy is inversely proportional to the interionic distance which is taken as the sum of the radii of the cation and the anion, hence the smaller the size of the ions, the smaller would be the interionic distance, the higher would be the magnitude of lattice energy and the greater would be the stability of the ionic crystal.

3. The lattice energy and hence stability of an ionic crystal is directly proportional to the Madelung constant which depends upon the coordination number of each ion and the geometric pattern of the ions in the crystal lattice of the crystal.

Experimental Determination of Lattice Energy. The Born-Haber Cycle. Since direct experimental determination of lattice energies is not so easy, these are determined indirectly with the help of a thermo-chemical cyclic process known as **Born-Haber cycle**. We would illustrate this by taking into consideration the determination of the lattice energy of NaCl.

The various steps involved in the formation of NaCl (s) in crystalline state are as follows :

1. Conversion of Metallic Sodium into Gaseous Sodium Atoms. The energy required for the conversion of one mole of metallic sodium into gaseous sodium atoms is called **sublimation energy**. It is represented by S.

$$\underset{1\text{ mole}}{Na\,(s)} + S \longrightarrow Na\,(g)\,; \qquad S = \text{Sublimation energy}$$

2. Dissociation of Gaseous Chlorine Molecules into Gaseous Chlorine Atoms. This step involves the dissociation of gaseous chlorine molecules into gaseous chlorine atoms. The amount of energy required to dissociate one mole of gaseous chlorine molecules into gaseous atoms is called **dissociation energy**. It is represented by D.

$$\underset{1\text{ mole}}{Cl_2\,(g)} + D \longrightarrow 2Cl\,(g)\,; \qquad D = \text{Dissociation energy}$$

Evidently, the energy required to produce one mole of gaseous chlorine atoms would be $D/2$.

3. Conversion of Gaseous Sodium Atoms into Sodium Ions. The amount of energy required to convert one mole of gaseous sodium atoms into sodium ions in the gaseous state is called **ionisation energy**. This may be represented by IE.

$$Na(g) + IE \longrightarrow Na^+(g) + e^-\,; \qquad IE = \text{Ionisation energy}$$

4. Conversion of Gaseous Chlorine Atoms into Chloride Ions. The amount of energy released when one mole of gaseous chlorine atoms are converted into chloride ions in the gaseous state is called **electron affinity.** It is represented by EA.

$$Cl\,(g) + e^- \longrightarrow Cl^-\,(g) + EA\,; \qquad EA = \text{Electron affinity}$$

5. Combination of Gaseous Ions to form a Solid Crystal. This step invsolves the combination of gaseous Na^+ and Cl^- ions to give one mole of sodium chloride crystal. The amount of energy released when one mole of solid crystalline compound is formed from gaseous ions of opposite charges is called **lattice energy.** It is denoted by U.

$$Na^+\,(g) + Cl^-(g) \longrightarrow NaCl\,(s) + U\,; \qquad U = \text{Lattice energy}$$

The *overall change* may be represented as

$$Na\,(s) + 1/2\,Cl_2\,(g) \longrightarrow NaCl\,(s)\,; \qquad \Delta H_f = ?$$

The enthalpy change for this reaction is called **enthalpy of formation** of sodium chloride and may be denoted as ΔH_f.

The various steps may be represented in the form of **Born-Haber cycle,** as shown in Fig. 44.

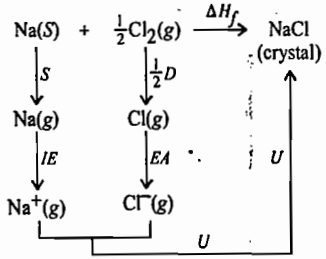


Fig. 44. Born-Haber cycle for the formation of NaCl.

According to Hess's law, the enthalpy of formation of sodium chloride should be the same irrespective of the fact whether it takes place directly in one step or through a number of steps, as illustrated above. Hence,

$$\Delta H_f = S + (1/2)\,D + IE + EA + U$$

Using positive sign for energy *absorbed* and negative sign for *energy released*, we have

Heat of sublimation of sodium (S) = 108·5 kJ mol^{-1}

Dissociation energy of Cl_2 (D) = 243·0 kJ mol^{-1}

Ionisation energy of sodium (IE) = 495·2 kJ mol^{-1}

Electron affinity of chlorine (EA) = – 348·3 kJ mol^{-1}

Enthalpy of formation of NaCl (ΔH_f) = – 381·8 kJ mol^{-1}

Substituting the various values in the above equation, we get

$$-381{\cdot}8\text{ kJ mol}^{-1} = 108{\cdot}5\text{ kJ mol}^{-1} + 1/2\,(243{\cdot}0)\text{ kJ mol}^{-1} + 495{\cdot}2\text{ kJ mol}^{-1} - 348{\cdot}3\text{ kJ mol}^{-1} + U$$

$\therefore$ **Lattice energy of sodium chloride,** $U = -758{\cdot}7$ **kJ mol^{-1}**

Explanation of Some Properties of Ionic Crystals on the Basis of Lattice Energy

1. Solubility of Ionic Crystals in Various Solvents. When an ionic solid goes into solution, *its crystal lattice gets ruptured.* The ions which occupied certain fixed positions in the crystal now move farther apart in the solution. The *question* arises. *How is the energy required to cause the rupture of the lattice obtained ?* The answer is not far to seek. There is a *strong interaction between the solvent and the ions* resulting in the *solvation of the ions.* If water is the solvent, the process is called *hydration of the ions.* The ionic solvation or hydration is an exothermic process releasing a considerable amount of

energy. *It is this energy which is utilised in causing rupture of the crystal lattice.* The liquids which cause solvation of ions and are, therefore, good solvents for ionic solids, have *high dielectric constants.* Thus, water, liquid ammonia, hydrogen fluoride, etc., are good solvents for ionic solids. Liquids with low dielectric constants, such as benzene, carbon tetrachloride, etc., do not solvate the ions and are, therefore, not good solvents for ionic solids. Since solvation of ions does not occur, no energy is released to break down the lattice.

The salts of alkaline earth metals (Mg, Ca, Ba, etc.,) with polyvalent anions such as sulphate, oxalate, phosphate, etc., are much less soluble than the corresponding salts of alkali metals. This has been attributed to their higher lattice energies. The energy released in the solvation of the ions is not sufficiently large to break their crystal lattice to an appreciable extent.

2. Stability of Ionic Compounds. The higher the magnitude of lattice energy, the greater would be the stability of the ionic compound. The higher magnitude of lattice energy means larger energy of attraction between the cations and the anions. The magnitude of properties such as melting point, boiling point, enthalpy of formation, enthalpy of sublimation would be high for ionic compounds having high magnitude of lattice energy.

DEFECT STRUCTURES IN CRYSTALS

The structures of ionic solids described in the preceding pages relate only to *ideal crystals.* An **ideal crystal** *is the one which has the same unit cell and contains the same lattice points throughout the crystal.*

At absolute zero, all ionic crystals show well-ordered arrangements of ions and there are no defects. With rise in temperature, however, there is a chance that one or more of the lattice sites may remain unoccupied by the ions. This constitutes a defect. The number n of such defects per cm^3, at a given temperature T on the absolute scale, is given by the equation

$$n = Ne^{-w/2RT} \qquad ...(11)$$

where N is the total number of sites per cm^3 of the crystal and w is the work (energy) required to produce a defect ; R is the gas constant.

Defects in crystals may be discussed under two heads :

A. Defects in Stoichiometric Crystals

B. Defects in Non-Stoichiometric Crystals.

A. Defects in Stoichiometric Crystals

Stoichiometric crystals are those in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae. For simplicity, we can consider the crystals of the type AB having equal number of A^+ and B^- ions. In these crystals, two types of defects are generally observed. These are called (1) Schottky defect and (2) Frenkel defect.

1. Schottky Defect. This defect arises if *some of the lattice points are unoccupied.* The points which are unoccupied are called *lattice vacancies* or *'holes'*. The existence of two holes, one due to a missing positive ion and the other due to a missing negative ion in a crystal lattice, is illustrated in Fig. 45. It may be noted that the crystal, as a whole, remains neutral because the number of missing positive and negative ions is the same.

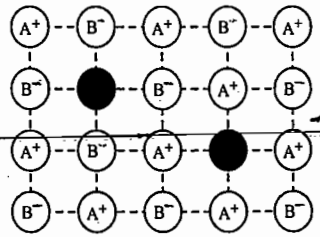


Fig. 45. The Schottky defect in crystals.

Schottky defect appears generally in ionic compounds having a high coordination number and in which the radius ratio, r_+/r_-, is not far below unity, *i.e.*, in which the positive and negative ions do not differ very much in size. Sodium chloride and cesium chloride

which have coordination numbers of 6 and 8, respectively, furnish good examples of ionic crystals in which Schottky defect appears.

2. Frenkel Defect. This defect arises when an ion occupies an interstitial position between the lattice points. This is shown in Fig. 46. It is seen that one of the positive ions occupies a position in the interstitial space rather than at its own appropriate site in the lattice. A 'hole' is thus created in the lattice as shown. It may be noted again that the crystal remains neutral since the number of positive ions is the same as that of the negative ions. Positive ions being smaller are more likely to occupy interstitial positions than the negative ions.

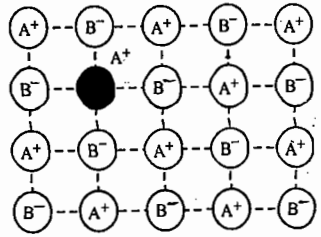


Fig. 46. The Frenkel defect in crystals.

Frenkel defect appears generally in compounds in which the negative ions are much larger than the positive ions, *i.e.*, the radius ratio, r_+/r_-, is low. The coordination number in such compounds is also low (Table 4). Hence, fewer attractive forces between oppositely charged ions have to be broken in causing movement of a positive ion from its appropriate site to the interstitial position.

In silver bromide, AgBr, some of the Ag^+ ions are generally missing from their regular positions and occupy positions in between the other ions in the lattice. The presence of Ag^+ ions in the interstitial spaces of the silver bromide crystal is responsible for the formation of a photographic image on exposure of silver bromide crystals (*i.e.*, photographic plate) to light. Zinc sulphide is another substance in which Frenkel defect appears. Zn^{2+} ions are entrapped in the interstitial spaces leaving 'holes' in the lattice.

Lattice vacancies ('holes') occur in almost all types of ionic crystals. However, Schottky defect appears more often than Frenkel defect. The reason is that the *energy needed to form a Schottky defect is much less than that needed to form a Frenkel defect.* In sodium chloride, the energy required to form a Schottky defect is about 170 kJ per mole. The lattice energy of sodium chloride is – 758·7 kJ per mole so that the energy required to break the NaCl lattice is 758·7 kJ per mole. It is, therefore, far easier to produce a Schottky defect than to break the lattice. The number of Schottky defects increases exponentially with rise in temperature. Thus, as revealed by X–ray diffraction of sodium chloride, while at room temperature this substance has one Schottky defect for 10^{15} lattice sites, the number of defects for the same number of lattice sites rises to such a high value as 10^6 at 500°C and 10^{11} at 800°C.

Consequences of Schottky and Frenkel Defects. Schottky and Frenkel defects in crystals lead to some interesting consequences.

1. The closeness of similar charges brought about by the Frenkel defect (Fig. 46) tends *to increase the dielectric constant of the crystals.*

2. A consequence of both types of defects is that the *crystal is able to conduct electricity to a small extent* by an ionic mechanism. It happens like this. As an electric field is applied, a nearby ion moves from its lattice site to occupy a 'hole'. This results in creating a new 'hole' and another nearby ion moves into it, and so on. This process continues and a 'hole', thereby, migrates from one end to the other end. Thus, it conducts electricity across the whole of the crystal.

3. The presence of 'holes' *lowers the density of the crystal,* as expected.

4. The presence of 'holes' also *lowers the lattice energy* or *the stability of the crystal.* The presence of too many 'holes' may cause a partial collapse of the lattice.

B. Defects in Non-Stoichiometric Crystals

Non-stoichiometric crystals do not obey strictly the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. In other words, there is excess of either positive charge or negative charge in the crystal. However, the crystal as a whole is neutral. If positive charge is in excess, it is balanced by the presence of *extra electrons.* If negative charge is in excess, it is balanced by the presence of *extra positive ions.* The crystal structure, therefore, becomes irregular and this implies the presence of defects. Such

defects are called **non-stoichiometric defects.** These defects may exist in a crystal in addition to Schottky and Frenkel defects already discussed.

Non-stoichiometric defects, evidently, are of two types depending upon whether *positive ions are in excess* or *negative ions are in excess*. These are known as **metal excess defects** and **metal deficiency defects,** respectively.

Metal Excess Defects. In these defects, positive ions are in excess. These defects may arise in *two ways*.

1. A negative ion may be missing from its lattice site leaving a 'hole' which is occupied by an extra electron to maintain the electrical balance, as shown in Fig. 47. There is, evidently, an excess of positive (metal) ions, although the crystal, as a whole, is neutral.

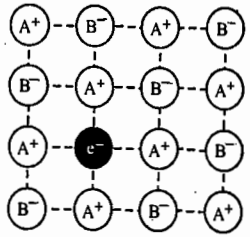


Fig. 47. Metal excess defect casued by a missing negative ion.

This defect is somewhat similar to Schottky defect but differs in having only one 'hole' and not a pair as in the latter case. This type of defect is not very common. It has been observed in those crystals which are likely to form Schottky defect. For example, when sodium chloride is treated with sodium vapour, a *yellow* non-stoichiometric form of sodium chloride is obtained in which there is excess of sodium ions. Similarly, if potassium chloride is exposed to potassium vapour, a *lilac* coloured non-stoichiometric form of potassium chloride is obtained in which there is excess of potassium ions. In each case, the extra positive charge due to extra metal ion is balanced by the presence of a free electron in the lattice.

2. *An extra positive ion occupies an interstitial position in the lattice and to maintain electrical neutrality, an electron also finds a place in the interstitial space*, as shown in Fig. 48.

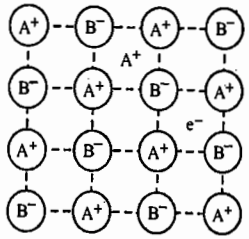


Fig. 48. Metal excess defect due to extra positive ion.

This type of metal excess defect is somewhat similar to Frenkel defect but differs in having no 'holes' and in having interstitial electrons. This kind of defect is more common than the first kind of metal excess defect. It is formed in crystals which are likely to develop Frenkel defect. Zinc oxide crystal is a good example.

Consequences of Metal Excess Defects. 1. The crystals associated with metal excess defects of the first kind or second kind, *contain free electrons* (Figs. 47 and 48). Since these electrons can migrate in an electric field, *such crystals can conduct electricity.* However, since the number of defects and, therefore, the number of electrons is very small, these crystals can conduct only small amounts of current, very much smaller than the current conducted by metals, fused salts or salts dissolved in water. These materials are, therefore, termed as **semiconductors.** Since current, howsoever small, is carried by electrons in *normal way*, these substances are called ***n*-type semiconductors.**

2. The crystals with metal excess defects are generally coloured. This, again, is due to the presence of free electrons. These electrons get excited easily to higher energy levels by absorption of certain wave lengths from the visible white light and, therefore, the compounds appear coloured. Thus, non-stoichiometric sodium chloride is *yellow*, non-stoichiometric potassium chloride is *lilac* in colour. Zinc oxide which is white in cold, *appears yellow when hot.*

Metal Deficiency Defects. There are *two possible ways* in which metal deficiency defects can occur.

1. In the first way, one of the positive ions may be missing from its lattice site. The extra negative charge may be balanced by some nearby metal ion by acquiring an additional positive charge. This is represented in Fig. 49. The metal, obviously, must be in a position to exhibit variable valency. This

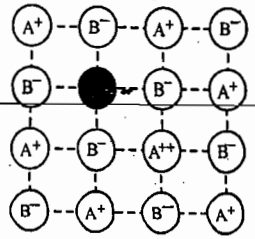


Fig. 49. Metal deficiency defect due to a missing positive ion.

type of defect, therefore, is generally found amongst the compounds of transition metals. Crystals of ferrous oxide, FeO, ferrous sulphide, FeS and nickel oxide, NiO, show this type of defect.

2. In the second way, an extra negative ion may occupy an interstitial position. The extra negative charge is balanced again by means of an extra charge on one of the adjacent metal ions, as shown in Fig. 50. *The metal* in this case also, *should be capable of exhibiting variable valency, i.e.,* it should be one of the transition metals. However, since the negative ions are usually very large, it is not expected that they would be able to fit into the interstitial positions. As a matter of fact, no crystal showing this type of metal deficiency defect is known. The structure represented in Fig. 50, therefore, remains merely a *theoretical possibility.*

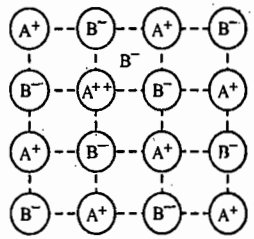


Fig. 49. Metal deficiency defect due to a negative ion.

Consequences of Metal Deficiency Defects. Crystals with metal deficiency defects can also be semiconductors. This property arises from the movement of an electron from one ion to another ion. In this way, the ion, say, A^+, changes into A^{++}. Thus, the movement of an electron from A^+ ion is *an apparent movement of* A^{++} *ion*. This is called *movement of positive 'hole'* and the substances permitting this type of movement are known as ***p*-type semiconductors.**

Thermal Defects. Intrinsic Conduction. Atoms of both germanium and silicon have four electrons in the outer shell. Each atom, therefore, is covalently bonded with four neighbouring atoms through sp^3 hybrid bonds, giving rise to a highly stable tetrahedral structure as in diamond. There are no free or conducting electrons as we have in metals. The electrical conductance, therefore, is very low. Now, suppose a sufficient amount of energy, say, in the form of heat, is supplied to the crystal as a result of which one of the covalent bonds gets broken and the electrons are released. The electrons, thus released, can migrate leaving behind a positive charge, *i.e.,* a 'positive hole', at the site of the missing bond. *The crystal will now be able to conduct electricity* because, when electric field is applied, the electrons migrate in one direction and the 'positive holes' in the other. This type of conduction in known as **intrinsic conduction** as it can be introduced in the crystal without adding an external substance.

Impurity Defects. Certain defects in crystals arise from the presence of chemical impurities. These are known as **impurity defects.** One important application of these defects lies in the use of externally added metal impurities to germanium and silicon crystals to make them act as **semiconductors.** Germanium and silicon belong to Group 14 of the periodic table. These elements, in pure state, have very low electrical conductivity. However, on adding even traces of an element belonging to Group 13 or 15, the electrical conductivity is greatly enhanced. This may be explained as follows :

Suppose, in the first instance, a Group 15 element, like arsenic, is added to a germanium crystal. As a germanium atom is substituted by an atom of arsenic, four of the electrons in arsenic form covalent bonds with the surrounding germanium atoms but the *fifth electron remains free.* In this way, an extra electron, over and above the number required for forming four covalent bonds, gets introduced into the crystal. This extra electron can serve to conduct electricity, *i.e.,* it behaves like a conductor-electron as in metals. Thus, germanium containing traces of arsenic (known as ***arsenic-doped germanium***) begins to exhibit fairly high electrical conductivity. This type of conduction is known as **extrinsic conduction.** It is much greater than the intrinsic conduction discussed above. Since, in this type of conduction, current is carried by excess electrons in the *normal way*, it is called ***n*-type semiconduction.**

Now, suppose a Group 13 element, like indium, having only three electrons in the outer shell, is added in small traces to, say, pure germanium. The atoms of indium, evidently, are not able to complete tetrahedral covalent structures of Group 14 elements because they are one electron short of the requirement. Hence, some of the sites normally occupied by electrons will be left empty. This gives rise to *electron-vacancies.*

The electron-vacant sites are known as 'positive holes' because the net charge at these sites is positive. When electric field is applied, adjacent electrons move into the positive holes and in this way other electron-vacancies (or positive holes) are formed. The migration of positive holes thus continues and current is carried thereby throughout the crystal.

Thus, doping of germanium with traces of indium increases the electrical conductivity of germanium crystal. Since the current, in the present case, is carried by *positive holes*, this type of conduction is called ***p*-type semiconduction.**

It is clear from the above discussion that while doping germanium (or silicon) with arsenic (an element of Group 15) gives rise to *n-type* of semi-conduction, that with indium (an element of Group 13) gives rise to *p-type* of semiconduction. It may be noted that *n-type* as well as *p-type* of semiconductors are electrically neutral because each atom of impurity added is neutral in itself containing, as it does, equal number of protons and electrons. There is, no doubt, a surplus or shortage of one valency electron depending on whether an element of Group 15 or Group 13 is added, but the overall number of electrons remains equal to the number of positive nuclear charges.

Effect of temperature on the conductivity of semiconductors. *The conductivity of semiconductors, unlike that of metals, increases with rise in temperature.* This is due to the fact that extra electron or positive hole, as the case may be, is bound, though weakly, with the crystal and, therefore, some energy in the form of heat is needed to free it from the crystal lattice for the conduction of electricity.

Applications of Semiconductors. The combination of *n* and *p*-type semiconductors (known as ***n–p* junctions**), finds interesting applications in the **fabrication of transistors.** This device can conduct electric current more easily in one particular direction than in the reverse direction and, therefore, can be used as **a rectifier** for changing alternating current into direct current. The device is schematically represented in Fig. 51. The material on the left side of each junction is *n*-type conductor obtained by doping germanium with, say, arsenic. The minus signs represent extra electrons. The material on the right side of the junction is *p*-type conductor obtained by doping germanium with, say, indium. The positive signs represent 'positive holes' arising from the deficiency of electrons at the indium impurity centres. When an external voltage is applied in such a way as to cause motion of electrons (*n*-current) from left to right and motion of positive holes (*p*-current) from right to left (Fig. 51*a*), current is readily conducted. If direction of voltage is reversed so that there is separation of electrons and positive holes as shown in Fig. 51(*b*), there is cancellation of *n* and *p*-currents and hence the conduction stops. Thus, the *n–p* junction permits the current from an outside source to flow *in one direction only.*

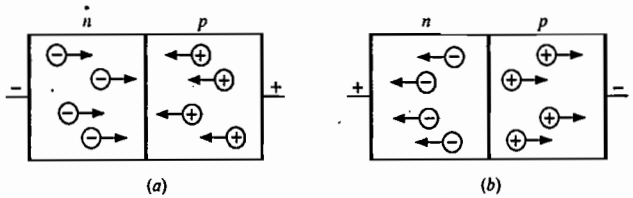


Fig. 51. Semiconductors acting as rectifier.

Fabrication of Transistors

Transistors are obtained either by putting a very thin layer of *n*-type semiconductors between two much thicker layers of *p*-type semiconductors or by putting a very thin layer of *p*-type semiconductors between two much thicker layers of *n*-type semiconductors. The first type is known as *p–n–p* transistors and the second type is known as *n–p–n* transistors.

The fabrication of an *n–p–n* type transistor, for illustration, is described below. It involves the following steps :

1. A small chip of a single *n*-type silicon crystal is oxidised in air or steam to produce a thin coating of SiO_2 over its surface.

2. The SiO_2 film is then coated with a film of a *photosensitive material* known as *'photo-resist'*.

3. A thin film of a *masking material* is then applied over that portion of the photo-resist which is required to be 'protected'. The crystal is then exposed to ultraviolet light which attacks only the unprotected, *i.e.*, the unmasked region. The exposed part of the photo-resist is removed by treatment with an acid. The masked region remains unaffected.

4. The unprotected surface of the crystal is then etched with HF to remove the SiO_2 layer and washed.

5. The etched surface is then exposed to the vapours of a Group 13 element (*e.g.*, indium) so that its atoms diffuse through the exposed silicon surface to form ***p*-type silicon**. The vapours will not diffuse through silicon surface protected by SiO_2.

6. Steps 1 – 4 are repeated using a different mask to selectively expose the desired new areas on the surface of the crystal. The newly exposed areas are then exposed to vapours of a Group 15 element (*e.g.*, arsenic) to produce patterned layers of ***n*-type silicon.**

7. The resulting material is an ***n–p–n* transistor.**

By employing similar technique, we can fabricate ***p–n–p* type transistors.**

A transistor can act as a triode and can thus be used as an *amplifier*, as an *oscillator* and also as a *rectifier.*

QUESTIONS

1. (*a*) How will you distinguish a crystalline solid from an amorphous solid ?
   (*b*) What is meant by elements of symmetry of a crystal ? Discuss the various elements of symmetry in a cubic crystal.
2. (*a*) Explain the terms : isotropy, anisotropy and interfacial angles with respect to crystals.
   (*b*) Explain the difference between cubic and hexagonal close packing.
   (*c*) Represent diagrammatically the unit cells for
   (*i*) a simple cubic lattice (*ii*) face centred cubic lattice (*iii*) body centred cubic lattice
   How many atoms are present per unit cell in these arrangements ? **[Ans. (*i*) 1 (*ii*) 4 (*iii*) 2]**
3. (*a*) What do you understand by axis of rotation ? Show the following axes of rotation in a cubic unit cell :
   (*i*) one 2-fold axis (*ii*) one 3-fold axis (*iii*) one 4-fold axis
   (*b*) Show that the volume of space occupied for a cubic close packed lattice of spheres is 74%.
   (*c*) Out of the seven basic crystal systems which one has (*i*) maximum and (*ii*) minimum symmetry ? **[Ans. (*i*) cubic (*ii*) triclinic]**
4. Calculate the maximum radius ratio r_A/r_B for an atom A to fit in the simple cubic lattice of atom B. **[Ans. 0·732]**
5. Discuss the structure of a compound in which the cation and the anion have 6 coordination numbers.
   (*a*) Calculate the size of tetrahedral and octahedral sites in closed packed structures.
   (*b*) In a close packed array of *N* spheres, how many (*i*) octahedral and (*ii*) tetrahedral sites are present ? **[Ans. (*i*) *N* (*ii*) 2*N*]**
   (*c*) A compound consisting of cation A of radius 0·97 Å and anion B of radius 2·51 Å will probably crystallise in the NaCl form. Is this statement correct ? Justify. **[Ans. Incorrect]**
6. (*a*) Define and explain the terms unit cell and space lattice.
   (*b*) Describe the three types of cubic unit cells among the Bravais lattices ? Calculate the number of atoms per unit cell in each case.
   (*c*) Sketch a two-dimensional lattice of closest packed identical spheres and indicate a suitable unit cell.
7. (*a*) Discuss the classification of crystals on the basis of bonding between the constituent units.
   (*b*) Discuss the radius ratio rule for determining the shapes of ionic crystals.
   (*c*) Sodium chloride has *fcc* structure. How many Na^+ and Cl^- ions are there in the unit cell ? **[Ans. Na^+ = 4, Cl^- = 4]**
8. (*a*) Discuss in details the close packing of identical solid spheres. What is meant by *hcp* and *ccp*?
   (*b*) Draw neat diagrams for NaCl and CsCl structures. What is the basic difference between the two structures ?
   (*c*) At room temperature, sodium crystallises in a body centred cubic lattice with *a* = 4·24 Å. Calculate the theoretical density of sodium. Molar mass of sodium = 23·0 g mol^{-1} **[Ans. 1·0 g mol^{-3}]**
9. (*a*) What is coordination number ? Calculate the coordination number of an atom in
   (*i*) a primitive cubic unit cell (*ii*) a body centred cubic unit cell and
   (*iii*) a face centred cubic unit cell.

(*b*) Show with the help of a diagram that a face centred tetragonal structure is actually a body centred tetragonal structure.

(*c*) Iron (α-Fe) crystallises in a *bcc* system with $a = 2{\cdot}86$ Å. The atomic mass of iron is $55{\cdot}85$ g mol^{-1}. Calculate the density of iron. **[Ans. 7·92 g cm^{-3}]**

10. What are Miller indices ? Sketch the planes in a cube having the Miller indices (*i*) 010 (*ii*) 112 (*iii*) 312 (*iv*) 111

11. Discuss the following structures with diagrams :

(*i*) Rutile structure (*ii*) Calcium fluoride structure

(*iii*) Calcium carbide structure (*iv*) Cadmium iodide structure

12. The ionic radii of Rb^+, Br^- and I^- ions are 1·47, 1·95 and 2·16 Å, respectively. Predict the most probable type of geometry exhibited by RbBr and RbI on the basis of radius ratio rule.

13. (*a*) Draw the structures of zinc blende and wurtzite and show the coordination around each type of ion in these structures. What is the basic difference in these two types of ZnS structures ?

(*b*) If the radius of each close packed sphere is *R*, calculate the radius *r* of the largest sphere that can pack into a tetrahedral hole without disturbing the close packed spheres.

(*c*) What is Madelung constant ? Is the Madelung constant same or different for NaCl and CsCl structures ? **[Ans. Different]**

14. Discuss Born equation for theoretical calculation of lattice energies. What conclusions can be drawn from this equation ?

15. Discuss in details the Born-Haber cycle for experimental determination of lattice energy.

16. What is lattice energy ? How does the solubility of an ionic solid depend upon its lattice energy ?

17. What types of defect are commonly produced in crystals ? Discuss in details the following types of defects in crystals :

(*i*) Schottky defect (*ii*) Frenkel defect (*iii*) Metal deficiency defect (*iv*) Metal excess defect.

18. (*a*) What are non-stoichiometric compounds ? Discuss the defects observed in their structures.

19. (*a*) What type of lattice defects are possible in non-stoichiometric compounds of the type *AB* ? What is the effect of increase in temperature on these detects ?

20. (*a*) What are semiconductors ? Explain what is meant by *n*-type and *p*-type semiconduction. What is the effect sof temperature on semiconduction ?

(*b*) Describe the principle of working and fabrication of a transistor.

7 NON-AQUEOUS SOLVENTS

Solvent. A solvent is defined as a substance which has the power of dissolving other substances. Water is an excellent solvent. On account of its high dielectric constant, it is capable of reducing forces of electrostatic attraction binding the charged ions in electrolytes in the solid state. Thus, salts and other electrolytes get dissociated into ions when they dissolve in water and the solutions conduct electricity. Water has a long liquid range (0° to 100°C) and hence is liquid at ordinary temperatures. It is most easily available and can be easily purified. It is neutral, odourless, non-toxic and non-poisonous. It can, therefore, be handled safely. Due to all these characteristics, water serves as the most useful solvent.

Attempts have been made to find out some other common substances which could serve as good solvents like water and could also have sizeable dielectric constants so that they could have high ionising capacities. Liquid ammonia, liquid sulphur dioxide, anhydrous hydrogen fluoride, anhydrous sulphuric acid and liquid dinitrogen tetroxide are some such solvents.

Classification of Solvents. The various solvents are generally classified as follows :

1. Protonic and aprotic solvents. Solvents from which protons (*i.e.*, H^+ ions) can be derived are called protonic solvents. Common examples are : H_2O, NH_3, HF, etc. Solvents from which protons cannot be ordinarily derived are called aprotic solvents. Examples are : CCl_4, C_6H_6, acetonitrile, etc.

2. Acid solvents, basic solvents and amphiprotic solvents. Solvents which have a strong tendency to give protons are also called acid solvents, *e.g.*, liquid hydrogen fluoride, sulphuric acid and acetic acid. Solvents which have strong affinity for protons are called basic solvents, *e.g.*, liquid ammonia, pyridine, hydrazine, etc. Amphiprotic solvents are those which neither have a strong tendency to gain nor a strong tendency to lose protons. Examples are : water, methyl alcohol, ethyl alcohol, etc.

3. Ionising and non-ionising solvents. Ionising solvents are those which are capable of undergoing auto or self-ionisation. Examples are : water, ammonia, sulphur dioxide, etc. These solvents ionise as follows :

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$$

Solvents which do not ionise at all are non-ionising solvents. Ionising solvents have high dielectric constants and are polar. Non-ionising solvents have low dielectric constants and are non-polar.

Characteristic Properties of a Solvent. Some characteristic physical and chemical properties of a solvent which govern its usefulness as a solvent are given below.

1. Melting point and boiling point. The melting and boiling points of a solvent indicate the range of temperature over which it can exist in the liquid state under atmospheric pressure. The melting and boiling points of various solvents alongwith their critical temperatures and critical pressures are given in Table 1.

TABLE 1

Melting Points, Boiling Points and Critical Constants of Various Solvents

Solvent	M.P./F.P. (°C)	B.P. (°C)	Critical temperature (°C)	Critical pressure (atm)
Sulphuric acid	10·4	300·0	–	–
Water	0	100·0	374·0	217·7
Ammonia	– 77·7	– 33·5	132·4	112·0
Sulphur dioxide	– 75·5	– 10·1	157·5	77·8
Hydrogen fluoride	– 89·4	19·5	230·2	–
Dinitrogen tetroxide	– 11·2	21·1	–	–

Because of the above values while water exists as liquid at ordinary temperature and pressure, ammonia, sulphur dioxide and dinitrogen tetroxide exist as gases under these conditions. These gases, therefore, act as solvents only at low temperatures.

2. Heats of fusion and vaporisation. The heat absorbed by one mole of a substance to change from solid to liquid state is called its molar heat of fusion. Likewise, the heat absorbed by one mole of a substance to change from liquid to vapour state is called its molar heat of vaporisation. These constants for water, ammonia, sulphur dioxide and hydrogen fluoride are given in Table 2.

TABLE 2

Molar Heats of Fusion and Vaporisation of Some Solvents

Solvents	Molar heat of fusion (kJ mol^{-1})	Molar heat of vaporisation at boiling point (kJ mol^{-1})
Water	6·02	40·65
Ammonia	5·65	23·34
Sulphur dioxide	7·40	24·93
Hydrogen fluoride	4·58	30·28

The heats of fusion and vaporisation indicate the nature and strength of forces with which the molecules of the solvent are held together in the solid or the liquid state. A high heat of vaporisation of a liquid indicates that the intermolecular forces in it are strong. A better idea of the intermolecular forces is obtained by dividing the heat of vaporisation by the boiling point. For normal liquids, the ratio of the heat of vaporisation expressed in joules to the boiling point (K) is a constant known as **Trouton constant.** This constant is about 90 J K^{-1} mol^{-1} for normal liquids. Such liquids have single molecules without any bonds between them. A higher value of the constant indicates association of molecules. The molecules of liquids which undergo association are polar. The common solvents like water, ammonia, hydrogen fluoride and alcohols are all associated liquids.

It is evident from Table 2 that heats of fusion for water and ammonia are very nearly the same. This indicates that the forces which hold molecules together in water and ammonia are of the same magnitude. The heat of fusion of sulphur dioxide is comparatively high while that of hydrogen fluoride is comparatively low indicating that while the force holding SO_2 molecules together is stronger, the force holding HF molecules is weaker.

TABLE 3

Dipole Moments and Dielectric Constants of Some Solvents

Solvent	Dipole Moment (Debye Units)	Dielectric Constant
Water	1·85	78·5 (25°C)
Ammonia	1·47	22·0 (– 33·5°C)
Sulphur dioxide	1·61	17·4 (– 20°C)
Hydrogen fluoride	1·90	83·6 (0°C)
Dinitrogen tetroxide	—	2·42 (0°C)

3. Dielectric constant. The coulombic force F between a cation and an anion is given by the expression $F = q_1q_2 / [\varepsilon (r_1+r_2)^2]$ where q_1 and q_2 are the charges for cations and anions, respectively ; r_1 and r_2 are the radii of the two ions and ε is the dielectric constant. A high value of ε indicates that a small

amount of energy will be required to separate the ions and hence it will be easy to dissolve an ionic solute. Thus, dielectric constant, in general, determines the ability of a solvent to dissolve ionic compounds. For example, solvents such as anhydrous hydrogen fluoride and water, which have high dielectric constants, are the best solvents for ionic and polar compounds. On the other hand, solvents like liquid ammonia and liquid sulphur dioxide with low dielectric constants show decreased ability to dissolve ionic compounds especially those containing multi-charged ions. Thus, carbonates, sulphates and phosphates are practically insoluble in liquid ammonia and liquid sulphur dioxide.

The dielectric constant and the polarity of a solvent are closely related. An ionising solvent not only has a large dipole moment but also has a large dielectric constant. This is evident from the data given in Table 3.

Some important **non-aqueous solvents** are described below.

LIQUID AMMONIA

Liquid ammonia is one of the most extensively studied non-aqueous solvents. It is a protonic solvent and its water-like properties have made it a highly useful solvent and a reaction medium for carrying out several types of organic and inorganic reactions.

Liquid ammonia shows a striking resemblance with water in its solvent action. Ammonia molecules are, however, less strongly associated through hydrogen bonding in liquid ammonia. Consequently, the freezing and boiling points of liquid ammonia are lower than those of water. Another similarity with water is the polarity of the ammonia molecule. It has a pyramidal structure which makes it polar. A third similarity is autoionisation of liquid ammonia, similar to the autoionisation of water. Both liquid ammonia and water show comparable autoionisation, represented as below :

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$H^+ + H_2O \rightleftharpoons H_3O^+$$
$$2H_2O \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+} + \underset{\text{Hydroxyl ion}}{OH^-}$$

$$K_w = [H_3O^+][OH^-] = 1{\cdot}0\times10^{-14} \text{ at } 25°C$$

$$NH_3 \rightleftharpoons H^+ + NH_2^-$$
$$H^+ + NH_3 \rightleftharpoons NH_4^+$$
$$\underset{\text{Liquid ammonia}}{2NH_3} \rightleftharpoons \underset{\text{Ammonium ion}}{NH_4^+} + \underset{\text{Amide ion}}{NH_2^-}$$

$$K_b = [NH_4^+][NH_2^-] = 1{\cdot}9\times10^{-33} \text{ at } -50°C.$$

However, the extent of autoionisation of liquid ammonia is much less than that of water (compare the values of K_w and K_b).

Ammonia can, therefore, conduct electricity only to a feeble extent. The dielectric constant of liquid ammonia (22) is much smaller than that of water (78·5) . The lower dielectric constant results in a generally decreased ability of liquid ammonia to dissolve ionic compounds. Liquid ammonia is, therefore, a poor solvent for ionic substances. However, low viscosity of ammonia (0·254 centipoise at – 33·5°C) compared to that of water (0·959 centipoise at 25°C) is expected to promote greater ionic mobilities and thereby compensate to some extent the effect of the comparatively low dielectric constant. The physical properties of water and liquid ammonia are given in Table 4.

TABLE 4

Physical Properties of Water and Ammonia

Properties	Water	Ammonia
Boiling point	100°C	−33·5°C
Freezing point	0°C	−77·7°C
Density	1·0 g ml^{-1} (4°C)	0·68 g ml^{-1} (−33·5°C)
Dielectric constant	78·5 (25°C)	22·0 (−33·5°C)
Specific conductance (ohm^{-1} cm^{-1})	$6{\cdot}0\times10^{-8}$ (25°C)	1×10^{-11} (− 33·5°C)
Viscosity (centipoise)	0·959 (25°C)	0·254 (− 33·5°C)
Dipole moment (Debye)	1·85	1·47
Trouton constant (J K^{-1} mol^{-1})	109	101·2

Chemical Reactions in Liquid Ammonia

As mentioned above, liquid ammonia has water–like properties and hence the reactions which take place in aqueous solutions can also occur in liquid ammonia solutions. Chemical reactions that take place in liquid ammonia are of the following types.

1. Precipitation Reactions. Precipitation reactions normally involve double decomposition. The solubilities of various substances in liquid ammonia and water are different and hence many reactions which are not normally possible in water have been reported to occur in liquid ammonia. Some of these reactions are discussed below.

a. Consider the precipitation of silver chloride in aqueous medium.

$$KCl + AgNO_3 \longrightarrow AgCl\downarrow + KNO_3$$

In liquid ammonia, the direction of the reaction is reversed.

$$AgCl + KNO_3 \xrightarrow{\text{liq. } NH_3} KCl\downarrow + AgNO_3$$

Similarly, a white precipitate of $BaCl_2$ is produced when solutions of silver chloride and barium nitrate in liquid ammonia are brought together.

$$AgCl + Ba(NO_3)_2 \xrightarrow{\text{liq. } NH_3} BaCl_2\downarrow + 2AgNO_3$$

b. Iodides and bromides get precipitated when solutions of various metal nitrates and ammonium halides in liquid ammonia are mixed together.

$$Sr(NO_3)_2 + 2NH_4Br \xrightarrow{\text{liq. } NH_3} SrBr_2\downarrow + 2NH_4NO_3$$

$$Zn(NO_3)_2 + 2NH_4I \xrightarrow{\text{liq. } NH_3} ZnI_2\downarrow + 2NH_4NO_3$$

c. Ammonium sulphide in liquid ammonia is capable of precipitating many metal sulphides from the solutions of nitrates of the metals.

$$(NH_4)_2S + 2AgNO_3 \xrightarrow{\text{liq. } NH_3} Ag_2S\downarrow + 2NH_4NO_3$$

$$(NH_4)_2S + Cu(NO_3)_2 \xrightarrow{\text{liq. } NH_3} CuS\downarrow + 2NH_4NO_3$$

$$(NH_4)_2S + Cd(NO_3)_2 \xrightarrow{\text{liq. } NH_3} CdS\downarrow + 2NH_4NO_3$$

2. Acid–Base Reactions in Liquid Ammonia. There is an interesting comparison between neutralisation reactions in aqueous solution and in liquid ammonia solution. Hydrochloric acid gas dissolves in liquid ammonia giving NH_4^+ ions and Cl^- ions.

$$HCl(g) + NH_3 \longrightarrow NH_4^+ + Cl^-$$

A similar reaction takes place in the case of water.

$$HCl(g) + H_2O \longrightarrow H_3O^+ + Cl^-$$

In aqueous solution, the process of neutralisation of a strong acid by a strong base involves the combination of H_3O^+ and OH^- ions to form practically un-ionised H_2O, the anion of the acid and the cation of the base remaining unchanged. For instance, the neutralisation of hydrochloric acid with potassium hydroxide may be represented as

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$KOH \longrightarrow OH^- + K^+$$

$$H_3O^+ + OH^- \longrightarrow 2H_2O \text{ (Neutralisation)}$$

A similar thing happens in the case of liquid ammonia solution. The process of neutralisation involves combination of NH_4^+ and NH_2^- ions to form un–ionised NH_3. For instance, the neutralisation of ammonium chloride with potassium amide may be represented as

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$KNH_2 \longrightarrow NH_2^- + K^+$$

$$NH_4^+ + NH_2^- \longrightarrow 2NH_3 \text{ (Neutralisation)}$$

Obviously, the role of NH_4Cl in liquid ammonia solution is the same as that of HCl in aqueous solution. Similarly, the role of KNH_2 in liquid ammonia solution is the same as that of KOH in aqueous solution. Thus, NH_4Cl may be regarded as a strong acid and KNH_2 as a strong base in liquid ammonia solution. They are termed as ammono acids and ammono bases, respectively. Some typical reactions of ammono acids and ammono bases are given below.

a. Reactions of Ammono Acids. Ammono acid is a substance which in liquid ammonia furnishes NH_4^+ ion. The following reactions show their behaviour to be similar to that of aqua acids.

1. Neutralisation. This has already been discussed above.

2. Replacement of protons by reactive metals. Acids give out hydrogen with metals in aqueous solutions. Likewise, the solutions of ammonium salts in liquid ammonia react with alkali and other metals to give hydrogen.

$$Na + NH_4^+ \xrightarrow{\text{liq. } NH_3} Na^+ + NH_3 + 1/2\,H_2$$

$$Co + 2NH_4NO_3 \xrightarrow{\text{liq. } NH_3} Co(NO_3)_2 + 2NH_3 + H_2$$

This is analogous to the reaction :

$$Co + H_2SO_4 \longrightarrow CoSO_4 + H_2$$

Ammonium salts decolourise blue solutions of alkali metals in liquid ammonia.

3. Protolysis. Certain compounds like urea, acetamide, sulphamide, etc., which are incapable of donating protons to water, can readily undergo protolysis in liquid ammonia, *i.e.*, they can donate protons to NH_3 in liquid ammonia. Hence organic amides act as acids in liquid ammonia, as illustrated by the following reactions:

$$H_2N(CO)NH_2 + NH_3 \longrightarrow H\bar{N}(CO)NH_2 + NH_4^+$$

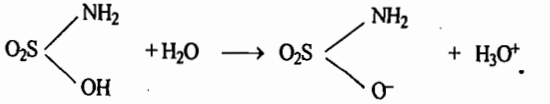
$$H_3C(CO)NH_2 + NH_3 \longrightarrow H_3C(CO)\bar{N}H + NH_4^+$$

$$H_2N(SO_2)NH_2 + NH_3 \longrightarrow H_2N(SO_2)\bar{N}H + NH_4^+$$

Similarly, sulphamic acid behaves as a dibasic acid in liquid ammonia.

$$H_2N(SO_2)OH + 2NH_3 \longrightarrow \bar{O}(SO_2)\bar{N}H + 2NH_4^+$$

However, it acts as a monobasic acid in aqueous solution. This is because NH_2 group cannot donate a proton to water.



h. Reactions of Ammono Bases. Ammono base is a substance which in liquid ammonia furnishes NH_2^- ion. Consequently, amides ($-NH_2$), imides ($=NH$) and nitrides ($\equiv N$) behave as bases in liquid ammonia, as shown below :

$$-NH_2 + NH_3 \longrightarrow -NH_3^+ + NH_2^-$$
$$=NH + NH_3 \longrightarrow =NH_2^+ + NH_2^-$$
$$\equiv N + NH_3 \longrightarrow \equiv NH^+ + NH_2^-$$

Since in all the above reactions, the NH_2^- ion is released, the amide, imide and nitride all behave as ammono bases.

Several species that are considered as strong bases in water, behave as weak bases in liquid ammonia. Extremely strong bases such as H^- and O^{2-} are levelled to NH_2^- ion in liquid ammonia.

$$H^- + NH_3 \longrightarrow \bar{N}H_2 + H_2$$
$$O^{2-} + NH_3 \longrightarrow \bar{N}H_2 + \bar{O}H$$

Since alkaline earth amides and lithium and sodium amides have very low solubility, potassium amide (KNH_2), which is much more soluble, is usually employed as an ammono base. Thus, salts of metals in liquid ammonia are precipitated as amides, imides and nitrides by the addition of a solution of KNH_2.

$$AgNO_3 + KNH_2 \xrightarrow{\text{liq. } NH_3} KNO_3 + AgNH_2 \downarrow$$
$$PbI_2 + KNH_2 \xrightarrow{\text{liq. } NH_3} KI + HI + Pb(NH) \downarrow$$
$$BiI_3 + KNH_2 \xrightarrow{\text{liq. } NH_3} KI + 2HI + BiN \downarrow$$

3. Amphoterism. A compound that dissolves both in acids and bases is said to be amphoteric in character. In aqueous medium, zinc and aluminium hydroxides are amphoteric. In liquid ammonia, zinc amide shows amphoteric behaviour. This is illustrated by the following reactions :

$$Zn(OH)_2 + 2HCl \xrightarrow{H_2O} ZnCl_2 + 2H_2O$$
$$Zn(NH_2)_2 + 2NH_4Cl \xrightarrow{\text{liq. } NH_3} ZnCl_2 + 4NH_3$$
$$Zn(OH)_2 + 2NaOH \xrightarrow{H_2O} Na_2ZnO_2 + 2H_2O$$
$$Zn(NH_2)_2 + 2NaNH_2 \xrightarrow{\text{liq. } NH_3} Na_2Zn(NH)_2 + 2NH_3$$

4. Ammonolysis. Ammonolysis in liquid ammonia is similar to hydrolysis in aqueous medium. Just as in hydrolysis, the concentration of H^+ or OH^- ions increases due to interaction of cations or anions of a salt with H^+ or OH^- ions furnished by autoionizaion of H_2O, in ammonolysis, the concentration of either NH_4^+ or NH_2^- ions increases due to interaction of cations or anions of a salt with NH_4^+ or NH_2^- ions furnished by autoionisation of NH_3. Consider the hydrolysis of $CuSO_4$ and ammonolysis of $SnCl_4$:

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$
$$2H_2O + 2H_2O \rightleftharpoons 2H_3O^+ + 2OH^-$$
$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$$
$$CuSO_4 + 4H_2O \rightleftharpoons \underset{\text{Weak base}}{Cu(OH)_2} + SO_4^{2-} + 2H_3O^+$$

$$SnCl_4 \longrightarrow Sn^{4+} + 4Cl^-$$
$$4NH_3 + 4NH_3 \rightleftharpoons 4NH_4^+ + 4NH_2^-$$
$$Sn^{4+} + 4NH_2^- \longrightarrow Sn(NH_2)_4$$
$$SnCl_4 + 8NH_3 \rightleftharpoons \underset{\text{Weak base}}{Sn(NH_2)_4} + 4NH_4^+ + 4Cl^-$$

In ammonolysis, the atom or ion from the compound undergoing ammonolysis is replaced by $-NH_2$ or $=NH$ or $\equiv N$ group. For example, in excess of liquid ammonia, the ammonolysis of $TiCl_4$ takes place in steps as follows :

$$TiCl_4 \xrightarrow[-HCl]{\text{liq. } NH_3} TiCl_3(NH_2) \xrightarrow[-HCl]{\text{liq. } NH_3} TiCl_2(NH_2)_2 \xrightarrow[-HCl]{\text{liq. } NH_3} TiCl(NH_2)_3 \xrightarrow[-HCl]{\text{liq. } NH_3} Ti(NH_2)_4$$

In the case of organic halides which undergo slow ammonolysis at the boiling point of liquid ammonia, mixtures of primary, secondary and tertiary amines are formed.

$$RX + 2NH_3 \longrightarrow RNH_2 + NH_4X$$
$$RX + RNH_2 + NH_3 \longrightarrow R_2NH + NH_4X$$
$$RX + R_2NH + NH_3 \longrightarrow R_3N + NH_4X$$

where X = Cl, Br or I.

Alkali metal hydrides and oxides also undergo ammonolysis to give amides.

$$NaH + NH_3 \longrightarrow NaNH_2 + H_2$$
$$Na_2O + 2NH_3 \longrightarrow 2NaNH_2 + H_2O$$

5. Ammonation and formation of Ammoniates. Ammonation is a type of solvation reaction in which liquid ammonia is used as a solvent and in which one or more ammonia molecules are attached to a solute species (a cation, an anion or a neutral molecule) by a chemical bond. The products of solvation are called solvates and in the case of ammonation they are known as ammoniates. Solvation in water is called hydration and the products are known as hydrates.

Formation of typical ammoniates is shown below :

$$SO_3 + 2NH_3 \longrightarrow SO_3.2NH_3 \qquad 1:2 \text{ adduct}$$
$$SiF_4 + 2NH_3 \longrightarrow SiF_4.2NH_3 \qquad 1:2 \text{ adduct}$$
$$BF_3 + NH_3 \longrightarrow BF_3.NH_3 \qquad 1:1 \text{ adduct}$$

6. Complex Formation Reactions. Several complex formation reactions in liquid ammonia are known. These are similar to reactions occurring in aqueous systems. The following reactions are given for illustration:

Aqueous System :

$$Zn(NO_3)_2 + 2NaOH \xrightarrow{H_2O} \underset{\text{Insoluble}}{Zn(OH)_2} + 2NaNO_3$$
$$Zn(OH)_2 + 2NaOH \xrightarrow{H_2O} \underset{\text{Soluble hydroxo complex}}{Na_2[Zn(OH)_4]}$$

Liquid Ammonia System :

$$Zn(NO_3)_2 + 2KNH_2 \xrightarrow{\text{liq. } NH_3} \underset{\text{Insoluble}}{Zn(NH_2)_2} + 2KNO_3$$
$$Zn(NH_2)_2 + 2KNH_2 \xrightarrow{\text{liq. } NH_3} \underset{\text{Soluble amide complex}}{K_2[Zn(NH_2)_4]}$$

Similarly, many metal amides, imides and nitrides dissolve in a solution of potassium amide in liquid ammonia forming soluble amide complexes.

$$AgNH_2 + KNH_2 \xrightarrow{liq.\,NH_3} \underset{\text{Soluble amide complex}}{K[Ag(NH_2)_2]}$$

Aluminium salts react with potassium amide solution in liquid ammonia forming soluble amide complexes. Thus,

$$AlCl_3 + 3KNH_2 \xrightarrow{liq.\,NH_3} \underset{\text{Insoluble}}{Al(NH_2)_3} + 3KCl$$

$$Al(NH_2)_3 + KNH_2 \xrightarrow{liq.\,NH_3} \underset{\text{Soluble amide complex}}{K[Al(NH_2)_4]}$$

7. Reduction Reactions. Liquid ammonia serves as an excellent medium for reduction reactions involving inorganic species. For instance, alkali metals dissolve in liquid ammonia giving blue coloured solutions which are strong reducing agents as they can readily supply electrons for reduction processes. Sodium metal in liquid ammonia, for instance, reduces CuI to Cu.

$$CuI + Na \xrightarrow{liq.\,NH_3} Cu + NaI$$

8. Oxidation Reactions. Oxidising action of various oxidising agents is weaker in liquid ammonia than in aqueous solutions. For instance, HNO_3 in liquid ammonia does not act as an oxidising agent. Similarly, $KMnO_4$ in liquid ammonia acts as a very weak oxidising agent. $KMnO_4$ is reduced by a solution of potassium in liquid ammonia to K_2MnO_4 and finally to MnO.

$$K + NH_3 \longrightarrow KNH_2 + 1/2\,H_2$$

$$6KMnO_4 + 6KNH_2 \longrightarrow 6K_2MnO_4 + 4NH_3 + N_2$$

$$K_2MnO_4 + 4K + 3NH_3 \longrightarrow MnO + 3KNH_2 + 3KOH$$

9. Solubility of Substances in Liquid Ammonia. As expected from its very low dielectric constant, liquid ammonia is a poor solvent for ionic substances. Amongst the **inorganic compounds,** nitrates, thiocyanates, perchlorates and most of the cyanides are soluble in liquid ammonia. Oxides, hydroxides, carbonates, phosphates, sulphates and most of the sulphides are insoluble. Most of the iodides are soluble and bromides are less soluble. Fluorides and chlorides (except Be^{2+} and Na^+ chlorides) are practically insoluble. Most of the ammonium salts such as NH_4NO_3, NH_4SCN, CH_3COONH_4 are soluble in liquid ammonia. Most of the metal amides, except those of alkali metals, are insoluble.

Amongst the **organic compounds,** halogen compounds, alcohols, ketones, esters, simple ethers, phenol and its derivatives are soluble. Aromatic hydrocarbons are sparingly soluble. Alkanes are insoluble. Alkenes and alkynes are slightly soluble.

Amongst the **elements,** metals like Mg, Al, Zn, Ca, La, Ce, Mn, etc., have low solubilities in liquid ammonia. Alkali metals and alkaline earth metals are highly soluble in liquid ammonia. The non-metals like sulphur, phosphorus, iodine are soluble and they react with the solvent.

Solutions of Alkali Metals in Liquid Ammonia. The ability to dissolve the alkali metals is one of the striking features of liquid ammonia as a solvent. The alkali metal solutions in liquid ammonia are blue in colour. The **blue solution** is characterised by

(*i*) its colour which is independent of the metal involved.

(*ii*) its density which is similar to that of pure liquid ammonia.

(*iii*) its conductivity which is in the range of conductivities of electrolytes dissolved in liquid ammonia, and

(*iv*) its paramagnetism (*i.e.*, these solutions when placed in a magnetic field are attracted into the field) which indicates the presence of a large number of unpaired electrons.

The alkali metal solutions dissociate to form alkali metal cations and ammoniated electrons.

The dissociation into cation and ammoniated electron accounts for the electrolytic conductivity of the blue coloured dilute solutions. As the concentration of the solution is increased, M^+ and e^--species associate resulting in a decrease of conductivity.

Very dilute solutions of alkali metals in liquid ammonia are metastable and when catalysed they undergo decomposition.

$$[e(NH_3)_x]^- \xrightarrow{Fe_2O_3} NH_2^- + 1/2H_2 + (x-1)NH_3$$

As the concentration of metal increases, the blue colour changes to bronze and finally the colour disappears altogether. On evaporating the alkali metal–ammonia solutions, the alkali metal can be recovered.

The blue colour of dilute metal-ammonia solutions is attributed to the presence of ammoniated cation as well as ammoniated electron.

$$M^+ + xNH_3 \rightleftharpoons \underset{\text{Ammoniated cation}}{M(NH_3)_x^+}$$

$$e^- + yNH_3 \rightleftharpoons \underset{\text{Ammoniated electron}}{e(NH_3)_y^-}$$

Advantages of Liquid Ammonia as a Solvent

1. Dissolution of alkali metals in liquid ammonia without chemical reaction is the greatest advantage of using liquid ammonia as a solvent. The dissolved alkali metals can be recovered from the solution by evaporation.
2. The alkali metal solutions in liquid ammonia are strong reducing agents, even stronger than hydrogen.
3. Ammonium salts dissolved in liquid ammonia find application in preparative chemistry. They can be used to precipitate sulphides, halides, sulphates and alcoholates.
4. The tendency for solvolysis is less in liquid ammonia than in water.

Limitations of Liquid Ammonia as a Solvent

1. Low temperature or high pressure is necessary while working with liquid ammonia. This is because the liquid range for liquid ammonia is from – 33·5°C to – 77·7°C.
2. Liquid ammonia is hygroscopic in nature. Hence, all the reactions are to be carried out in sealed tubes.
3. The use of liquid ammonia as a solvent and as a reaction medium requires special technique as it has an offensive odour.

ANHYDROUS HYDROGEN FLUORIDE

Hydrogen fluoride is one of the most water-like solvents since it is **liquid** at temperatures below 19·4°C upto – 89·4°C. Its boiling point (+ 19·4°C) is very high as compared to the boiling points of other non-aqueous solvents. Its dipole moment (1·90 D) and dielectric constant (83·6 at 0°C) are also quite close to those of water. Because of its high dielectric constant, it serves as an excellent ionising solvent.

However, its use as a non-aqueous solvent has been quite limited because it is poisonous, its specific conductance is low and it can dissolve only a few substances without reacting with them.

The characteristic physical properties of liquid hydrogen fluoride are given in Table 5.

TABLE 5

Some Characteristic Physical Properties of Anhydrous Hydrogen Fluoride

Property	Values
Freezing point	– 89·4°C
Boiling point	19·4°C
Density	0·99 g ml^{-1}
Dielectric constant	83·6 (0°C)
Dipole moment	1·90 D
Viscosity	0·256 centipoise (15°C)
Specific conductance	$1{\cdot}4\times10^{-5}$ ohm^{-1} cm^{-1} (15°C)

Chemical Reactions in Liquid Hydrogen Fluoride. Some of the important chemical reactions taking place in anhydrous hydrogen fluoride are discussed below briefly.

1. Precipitation Reactions. Sulphates, perchlorates and periodates of non-alkali metals get precipitated when their fluorides dissolved in liquid hydrogen fluoride are treated with solutions of sulphates, perchlorates and periodates of alkali metals.

$$Na_2SO_4 + NiF_2 \longrightarrow \underset{\text{Ppt.}}{NiSO_4} + 2NaF$$

$$NaClO_4 + TlF \longrightarrow \underset{\text{Ppt.}}{TlClO_4} + NaF$$

$$KIO_4 + AgF \longrightarrow \underset{\text{Ppt.}}{AgIO_4} + KF$$

Another important precipitation reaction involves the precipitation of $AgBF_4$.

$$AgNO_3 + BF_3 + 2HF \longrightarrow \underset{\text{Ppt.}}{AgBF_4} + H_2NO_3F$$

2. Acid-Base Reactions. The high specific conductance of anhydrous hydrogen fluoride suggests a relatively large degree of its autoionisation :

$$3HF \rightleftharpoons \underset{\text{(Acid)}}{H_2F^+} + \underset{\text{(Base)}}{HF_2^-}$$

Thus, any substance which can yield H_2F^+ ion would behave as an acid and any substance which can yield HF_2^- or F^- ion would behave as a base. Accordingly, *even strong acids* such as HNO_3 and H_2SO_4 *behave as bases* in hydrogen fluoride since they release F^- ions.

$$\underset{\text{Base}}{HNO_3} + \underset{\text{Acid}}{HF} \longrightarrow H_2NO_3^+ + F^-$$

$$\underset{\text{Base}}{H_2SO_4} + \underset{\text{Acid}}{HF} \longrightarrow H_3SO_4^+ + F^-$$

Perchloric acid, which behaves as the strongest acid in aqueous solution, exhibits an amphoteric character in liquid hydrogen fluoride. Thus,

$$\underset{\text{Base}}{HClO_4} + HF \longrightarrow H_2ClO_4^+ + F^-$$

$$\underset{\text{Acid}}{HClO_4} + HF \longrightarrow ClO_4^- + (H_2F)^+$$

Only a few substances such as BF_3, AsF_5, SbF_5 and SnF_4, which behave as Lewis acids in aqueous solutions, function as acids in anhydrous hydrogen fluoride. Thus,

$$\underset{\text{Acid}}{SbF_5} + 2HF \longrightarrow SbF_6^- + H_2F^+$$

$$\underset{\text{Acid}}{BF_3} + 2HF \longrightarrow BF_4^- + (H_2F)^+$$

$$\underset{\text{Acid}}{SnF_4} + 4HF \longrightarrow SnF_6^{2-} + 2(H_2F)^+$$

3. Protonation of Organic Compounds. Organic compounds such as benzene, ethanol, alkanes get protonated when dissolved in HF. Thus,

$$C_6H_6 + HF \longrightarrow C_6H_7^+ + F^-$$

$$C_2H_5OH + HF \longrightarrow C_2H_5OH_2^+ + F^-$$

(*i*) $$(CH_3)_3CCH_3 + HF \longrightarrow (CH_3)_3CCH_4^+ + F^-$$

(*ii*) $$(CH_3)_3CCH_4^+ \longrightarrow (CH_3)_3C^+ + CH_4$$

Because of the formation of ions, organic compounds mentioned as above, give conducting solutions in HF. The aromatic hydrocarbons give coloured solutions in HF and their solubilities can be increased further by adding fluoride acceptors such as BF_3 and SbF_5. The protonated species can be isolated as crystalline salts of BF_4^- and SbF_6^-.

4. Formation of Addition Compounds. Metallic fluorides form addition compounds with HF. Examples are : *KF.2HF*, *KF.3HF*, *NH_4F.HF*, etc.

ANHYDROUS SULPHURIC ACID

The characteristic physical properties of non-aqueous sulphuric acid are given in Table 6.

The viscosity of anhydrous H_2SO_4 is about 25 times higher than that of water. Therefore, solutes dissolve very slowly in sulphuric acid and are also difficult to crystallise from H_2SO_4.

TABLE 6

Some Characteristic Physical Properties of Sulphuric Acid

Properties	Values
Freezing point	10·4°C
Boiling point	300°C
Density	1·84 ml^{-1} (25°C)
Dielectric constant	110
Viscosity (centipoise)	24·54 (20°C)

Chemical Reactions of anhydrous Sulphuric Acid

1. Autoionisation. Anhydrous sulphuric acid autoionises to give $H_3SO_4^+$ and HSO_4^- ions :

$$2\,H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

Therefore, any chemical species producing HSO_4^- ions will act as a base and any chemical species producing $H_3SO_4^+$ ion acts as an acid in H_2SO_4.

2. Acid–Base Reactions. Some typical acid–base reactions of anhydrous H_2SO_4 are given below :

(*a*) $KHSO_4$ acts as a base in anhydrous sulphuric acid.

$$KHSO_4 \rightleftharpoons K^+ + HSO_4^-$$

(*b*) Species that are basic in water are also basic in H_2SO_4.

$$OH^- + 2H_2SO_4 \longrightarrow 2HSO_4^- + H_3O^+$$

$$NH_3 + H_2SO_4 \longrightarrow NH_4^+ + HSO_4^-$$

(*c*) Water behaves as a base in anhydrous sulphuric acid.

$$H_2O + H_2SO_4 \longrightarrow HSO_4^- + H_3O^+$$

(*d*) Species containing lone pair of electrons easily accept a proton from H_2SO_4 and act as bases. Thus, amides (like urea, etc). which act as acids in liquid NH_3, are neutral in water and behave as bases in anhydrous H_2SO_4.

$$H_2N(CO)NH_2 + H_2SO_4 \longrightarrow HSO_4^- + [H_2N(CO)NH_3^+]$$

(*e*) Acids which behave as weak acids or even as strong acids in water behave as bases in anhydrous H_2SO_4.

$$CH_3COOH + H_2SO_4 \longrightarrow HSO_4^- + CH_3COOH_2^+$$

$$HNO_3 + 2H_2SO_4 \longrightarrow 2HSO_4^- + NO_2^+ + H_3O^+$$

(*f*) Even very strong acids like perchloric acid behave as weak acids in anhydrous H_2SO_4.

$$HClO_4 + H_2SO_4 \longrightarrow H_3SO_4^+ + ClO_4^-$$

3. Dehydrating Action. H_2SO_4 acts as a strong dehydrating agent and extracts water even from chemical compounds. Thus,

$$C_{12}H_{22}O_{11} \xrightarrow[-11\,H_2O]{H_2SO_4} 12C$$

4. Super Acids. The acids which behave as *strong acids* in strong acid solvents are termed as super acids. For example, $[HB(HSO_4)_4]$, hydrogen [tetrakis(hydrogen sulphato) borate] whose solutions can be prepared in sulphuric acid, behaves as an exceptionally strong acid.

The super acid $HB(HSO_4)_4$ has not been isolated as such. Only its solutions can be prepared. The other super acids are $H_2Sn(HSO_4)_4$ and $H_2Pb(HSO_4)_4$ in H_2SO_4 solution.

LIQUID DINITROGEN TETROXIDE

Dinitrogen tetroxide, N_2O_4, has been studied extensively as a non-protonic non-aqueous solvent. The physical properties of this solvent are given in Table 7.

Much of the chemistry in this solvent can be rationalised in terms of an autoionisation equilibrium of the type

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

Although there is no physical evidence for the above type of autoionization occurring in N_2O_4, it has been found that the electrical conductance of N_2O_4 increases on adding a donor or a polar solvent to it. This may perhaps be due to increased stabilisation of cations and anions (NO^+ and NO_3^-) of N_2O_4 as a result of the ion–dipole interaction of these ions with the molecules of the added donor or polar solvent.

TABLE 7

Some Characteristic Physical Properties of Liquid Dinitrogen tetroxide

Properties	Values
Freezing point	– 11·2°C
Boiling point	21·1°C
Density	1·493 g ml^{-1} (0°C)
Dielectric constant	2·42
Viscosity	0·527 centipoise (0°C)
Specific conductance	$1{\cdot}3\times10^{-13}$ ohm^{-1} cm^{-1} (0°C)

Thus, assuming that N_2O_4 undergoes autoionisation as mentioned above, it can be said that any chemical species which gives the cation NO^+ in this solvent will behave as an acid and any chemical species which gives the anion NO_3^- in this solvent will behave as a base. Thus, NOCl behaves as an acid in N_2O_4, as is evident from the following reaction :

$$2NOCl \xrightleftharpoons{N_2O_4} 2NO^+ + 2Cl^-$$
$$2NO^+ + Sn \rightleftharpoons 2NO + Sn^{2+}$$
$$Sn^{2+} + 2Cl^- \rightleftharpoons SnCl_2$$
$$\overline{2NOCl + Sn \rightleftharpoons 2NO + SnCl_2}$$

Thus, the acid behaviour of NOCl in N_2O_4, when it reacts with Sn, is parallel to the behaviour of HCl in water when it reacts with Zn as is apparent from the following reaction :

$$2HCl + 2H_2O \xrightleftharpoons{H_2O} 2H_3O^+ + 2Cl^-$$
$$2H_3O^+ + Zn \rightleftharpoons Zn^{2+} + 2H_2O + H_2$$
$$Zn^{2+} + 2Cl^- \rightleftharpoons ZnCl_2$$
$$\overline{Zn + 2HCl \rightleftharpoons ZnCl_2 + H_2}$$

The compound $[EtNH_3]^+[NO_3]^-$ releases NO_3^- anion in N_2O_4. It, therefore, acts as a base in N_2O_4. A

typical reaction of $[EtNH_3]^+[NO_3^-]$ with zinc metal in N_2O_4 is similar to the reaction of zinc with $NaNH_2$ in liquid ammonia, as is evident from the following reactions :

$$2N_2O_4 \rightleftharpoons 2NO^+ + 2NO_3^- \text{ (autoionisation)}$$
$$Zn + 2NO^+ \rightleftharpoons Zn^{2+} + 2NO$$
$$\overline{2\,[EtNH_3]^+[NO_3]^- + Zn^{2+} + 2NO_3^- \rightleftharpoons [EtNH_3]_2^+[Zn(NO_3]^{2-} + 2NO}$$
$$Zn + 2N_2O_4 + 2[EtNH_3]^+[NO_3]^- \rightleftharpoons [EtNH_3]_2^+[Zn(NO_3)_4]^{2-} + 2NO$$
$$4NH_3 \rightleftharpoons 2NH_4^+ + 2NH_2^- \text{ (autoionisation)}$$
$$Zn + 2NH_4^+ \rightleftharpoons 2NH_3 + H_2 + Zn^{2+}$$
$$Zn^{2+} + 2NaNH_2 + 2NH_2^- \rightleftharpoons Na_2[Zn(NH_2)_4]$$
$$\overline{Zn + 2NH_3 + 2NaNH_2 \rightleftharpoons Na_2[Zn(NH_2)_4] + H_2}$$

The solvolysis of metal oxides in N_2O_4 is similar to their solvolysis in liquid ammonia, as shown below :

$$2N_2O_4 \rightleftharpoons 2NO^+ + NO_3^- \text{ (autoionisation)}$$
$$CaO + 2NO^+ \rightleftharpoons Ca^{2+} + N_2O_3$$
$$Ca^{2+} + 2NO_3^- \rightleftharpoons Ca(NO_3)_2$$
$$\overline{CaO + 2N_2O_4 \rightleftharpoons Ca(NO_3)_2 + N_2O_3}$$
$$4NH_3 \rightleftharpoons 2NH_4^+ + 2NH_2^- \text{ (autoionization)}$$
$$Na_2O + 2NH_4^+ \rightleftharpoons 2NH_3 + H_2O + 2Na^+$$
$$2Na^+ + 2NH_2^- \rightleftharpoons 2NaNH_2$$
$$\overline{Na_2O + 4NH_3 \rightleftharpoons 2NaNH_2 + 2NH_3 + H_2O}$$

In fact, solvolysis of the halides of metals in N_2O_4 provides an excellent method for preparing anhydrous metal nitrates which are otherwise extremely difficult to prepare. Thus,

$$2N_2O_4 \rightleftharpoons 2NO^+ + 2NO_3^-$$
$$ZnX_2 + 2NO^+ \rightleftharpoons 2NOX + Zn^{2+}$$
$$Zn^{2+} + 2NO_3^- \rightleftharpoons Zn(NO_3)_2$$

The NOX produced in the reaction decomposes to NO and X_2 and, therefore, it does not participate in the reverse equilibrium reaction. The overall reaction is, thus,

$$2N_2O_4 + ZnX_2 \rightleftharpoons 2NO + X_2 + \underset{\text{(anhydrous)}}{Zn(NO_3)_2}$$

Several metal carbonyls are also solvolysed in a similar manner. Thus,

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$
$$\overline{(OC)_5Mn\text{–}Mn(CO)_5 + NO^+ + NO_3^- \rightleftharpoons Mn(CO)_5(NO_3) + Mn(CO)_4NO + CO}$$
$$(OC)_5Mn\text{–}Mn(CO)_5 + N_2O_4 \rightleftharpoons Mn(CO)_5NO_3 + Mn(CO)_4NO + CO$$

Similarly,

$$3N_2O_4 \rightleftharpoons 3NO^+ + 3NO_3^-$$

$$Fe(CO)_5 + 3NO_3^- \rightleftharpoons Fe(NO_3)_3 + 5CO + 3e^-$$

$$3NO^+ + 3e^- \rightleftharpoons 3NO$$

$$Fe(CO)_5 + 3N_2O_4 \rightleftharpoons Fe(NO_3)_3 + 5CO + 3NO$$

N_2O_4 is also known to form solvated species of the type shown below :

$$2N_2O_4 \rightleftharpoons 2NO^+ + 2NO_3^-$$

$$Ca + 2NO^+ + 2NO_3^- + N_2O_4 \longrightarrow [Ca(NO_3)_2.N_2O_4] + 2NO$$

$$Ca + 3N_2O_4 \longrightarrow [Ca(NO_3)_2.N_2O_4] + 2NO$$

Quite often, however, the solvated species formed as above are found to be nitrosonium nitrate compounds. For example, $Sc(NO_3)_3.2N_2O_4$ and $2Fe(NO_3)_3.3N_2O_4$ are actually $[NO^+]_2[Sc(NO_3)_5]^{2-}$ and $[NO^+]_3[Fe(NO_3)_4]_2^-[NO_3]^-$, respectively.

There are certain reactions which cannot be explained on the basis of the autoionisation of N_2O_4 proposed as above. For instance, the reaction of N_2O_4 with BF_3 yields $[NO_2]^+[ONOBF_3]^-$ and $[NO_2]^+[F_3BONOBF_3]^-$, which can be explained better by assuming the following autoionisation of N_2O_4 :

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$$

It is worthwhile mentioning here that neither the two proposed ionisations of N_2O_4 nor the partial equations written for various chemical reactions occurring in liquid N_2O_4 are essentially an experimental reality. Nevertheless, the two proposed auto-ionisations and the various partial equations described as above do explain satisfactorily the chemistry of reactions occurring in liquid dinitrogen tetroxide.

LIQUID SULPHUR DIOXIDE

Liquid sulphur dioxide is also a non-protonic solvent as it does not yield a proton (H^+) on ionisation. It is widely used for carrying out a number of chemical reactions.

Under normal temperature and pressure, sulphur dioxide is a gas but it can be readily liquefied. It has a wide liquid range (– 10·°C to – 75·5°C) and hence can serve as a good solvent. Its use as a non-aqueous solvent is rapidly increasing due to its low cost and ease of its handling. Its dielectric constant is small (17·4 at – 20·0°C) which makes it a good solvent for covalent compounds but a poor solvent for electrovalent compounds.

The characteristic physical properties of liquid sulphur dioxide are given in Table 8.

TABLE 8
Some Characteristic Physical Properties of Liquid Sulphur Dioxide

Properties	Values
Freezing point	– 75·5°C
Boiling point	–10·1°C
Density	1·46 g ml^{-1} (– 10°C)
Dielectric constant	17·4 (– 20°C)
Dipole moment	1·61 Debye
Viscosity	0·428 centipoise (– 10°C)
Specific conductance	4×10^{-8} ohm^{-1} cm^{-1} (– 10°C)

Autoionisation. By analogy with water and liquid ammonia, autoionisation of sulphur dioxide takes place as under :

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$$

The thionyl ion (SO^{2+}) is analogous to the hydronium ion (H_3O^+) and ammonium ion (NH_4^+) while sulphite ion (SO_3^{2-}) corresponds to hydroxyl ion (OH^-) and amide ion (NH_2^-) of the aqueous and liquid ammonia systems, respectively.

Sulphur dioxide solutions are not as good electrical conductors as are liquid ammonia solutions or aqueous solutions.

Solubility of Substances in Liquid Sulphur Dioxide. Amongst the **inorganic compounds**, iodides and thiocyanates are the most soluble. Metal sulphates, sulphides, oxides and hydroxides are practically insoluble. Many of the ammonium, thallium and mercuric salts are soluble. Liquid sulphur dioxide is an excellent solvent for covalent compounds. Substances such as IBr, PBr_3, CCl_4, $SiCl_4$, $SnCl_4$ are soluble in it. **Metals** are insoluble in liquid sulphur dioxide.

Amongst the **organic compounds**, benzene and alkenes dissolve in it freely. Pyridine, quinoline, ethers, halogen derivatives and acid chlorides also dissolve in liquid sulphur dioxide. Alkanes are insoluble.

Reactions in Liquid Sulphur Dioxide. Chemical reactions that occur in liquid sulphur dioxide are of the following types :

1. Acid–base Reactions or Neutralisation Reactions. Comparing the autoionisation of liquid sulphur dioxide with that of water, it can be seen that thionyl ion (SO^{2+}) is analogous to hydronium ion (H_3O^+) and sulphite ion SO_3^{2-} is analogous to hydroxyl ion (OH^-). Hence, all compounds containing or making available SO_3^{2-} ions in liquid sulphur dioxide will act as bases in this medium. Similarly, all compounds which make available SO^{2+} ions in liquid sulphur dioxide will act as typical acids in liquid sulphur dioxide.

Typical acid–base or neutralisation reactions in liquid sulphur dioxide are given below.

Reaction between thionyl chloride and cesium sulphite :

$$\underset{\text{Acid}}{SOCl_2} + \underset{\text{Base}}{Cs_2SO_3} \xrightarrow{liq.SO_2} \underset{\text{Salt}}{2CsCl} + \underset{\text{Solvent}}{2SO_2}$$

Reaction between thionyl thiocynate and potassium sulphite.

$$\underset{\text{Acid}}{SO(SCN)_2} + \underset{\text{Base}}{K_2SO_3} \xrightarrow{liq.SO_2} \underset{\text{Salt}}{2K(SCN)} + \underset{\text{Solvent}}{2SO_2}$$

2. Solvolytic Reactions. Only a limited number of salts undergo solvolysis in liquid sulphur dioxide. Some common reactions are given below.

Ammonium acetate is solvolysed in liquid sulphur dioxide.

$$2CH_3COONH_4 + 2SO_2 \longrightarrow (NH_4)_2SO_3 + (CH_3COO)_2SO$$

$$(CH_3COO)_2SO \longrightarrow SO_2 + (CH_3CO)_2O$$

Binary halides such as PCl_5, UCl_6, WCl_6 undergo solvolysis in liquid sulphur dioxide.

$$PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$$

$$UCl_6 + 2SO_2 \longrightarrow UO_2Cl_2 + 2SOCl_2$$

$$WCl_6 + SO_2 \longrightarrow WOCl_4 + SOCl_2$$

The formaion of solvates, *i.e.*, the addition compounds with the solvent, is also known. Typical solvates formed are $NaI.4SO_2$, $RbI.4SO_2$, $KBr.4SO_2$, $CaI_2.4SO_2$, $BaI_2.4SO_2$, $SrI_2.4SO_2$, $AlCl_3.2SO_2$, etc.

3. Precipitation Reactions. A large number of precipitation reactions can be carried out in liquid sulphur dioxide due to specific solubility relationships. Some of these reactions are given below.

$$2CH_3COOAg + SOCl_2 \xrightarrow{liq.SO_2} 2AgCl\downarrow + \underset{\text{Thionyl acetate}}{SO(CH_3COO)_2}$$

$$2KI + SOCl_2 \xrightarrow{liq.SO_2} 2KCl\downarrow + SOI_2$$

$$SbCl_3 + 3LiI \xrightarrow{liq.SO_2} SbI_3\downarrow + 3LiCl$$

$$PbF_2 + Li_2SO_4 \xrightarrow{liq.SO_2} PbSO_4\downarrow + 2LiF$$

$$AlCl_3 + 3NaI \xrightarrow{liq.SO_2} 3NaCl\downarrow + AlI_3$$

4. Complex Formation Reactions. A large number of complex formation reactions of liquid sulphur dioxide have been reported. For instance, the solubility of iodine in liquid sulphur dioxide is greatly increased by the addition of potassium or rubidium iodide. This is due to the formation of the complex KI_3 or RbI_3.

$$KI + I_2 \xrightarrow{liq.SO_2} KI_3$$

$$RbI + I_2 \xrightarrow{liq.SO_2} RbI_3$$

Similarly, the increase in the solubility of cadmium iodide and mercuric iodide in liquid sulphur dioxide is attributed to the formation of complexes.

$$HgI_2 + 2KI \xrightarrow{liq.SO_2} K_2[HgI_4]$$

Some other examples of complex formation are as follows :

$AlCl_3$ reacts with SO_3^{2-} ions to form a precipitate of $Al_2(SO_3)_3$ which redissolves in excess of SO_3^{2-} ions forming the complex ion $[Al(SO_3)_3]^{3-}$.

$$2AlCl_3 + 3SO_3^{2-} \rightleftharpoons Al_2(SO_3)_3\downarrow + 6Cl^-$$

$$Al_2(SO_3)_3 + 3SO_3^{2-} \rightleftharpoons \underset{\text{Soluble complex ion}}{2[Al(SO_3)_3]^{3-}}$$

Similarly,

$$SbCl_3 + 3KCl \xrightarrow{liq.SO_2} K_3[SbCl_6]$$

$$SbCl_5 + KCl \xrightarrow{liq.SO_2} K[SbCl_6]$$

$$SbCl_5 + NOCl \xrightarrow{liq.SO_2} NO[SbCl_6]$$

5. Amphoteric Behaviour. Various salts show amphoteric behaviour in liquid sulphur dioxide. The reaction of $AlCl_3$ with NaOH in aqueous medium can be compared with the reaction of $AlCl_3$ with tetramethyl ammonium sulphite in liquid sulphur dioxide. In aqueous solution, the reaction takes place as follows.

$$AlCl_3 + 3NaOH \xrightarrow{H_2O} \underset{\text{Gelatinous ppt.}}{Al(OH)_3} + 3NaCl$$

$$Al(OH)_3 + NaOH \xrightarrow{H_2O} \underset{\text{Soluble complex}}{Na[Al(OH)_4]}$$

From the soluble complex, $Al(OH)_3$ can be reprecipitated by the addition of HCl.

$$Na[Al(OH)_4] + HCl \longrightarrow NaCl + H_2O + Al(OH)_3\downarrow$$

In liquid sulphur dioxide medium, an identical reaction takes place between $AlCl_3$ and tetramethyl ammonium sulphite :

$$2AlCl_3 + 3[N(CH_3)_4]_2SO_3 \xrightarrow{liq.SO_2} 6[N(CH_3)_4]Cl + \underset{\text{Gelatinous ppt.}}{Al_2(SO_3)_3}$$

$$Al_2(SO_3)_3 + 3[N(CH_3)_4]_2SO_3 \xrightarrow{liq.SO_2} \underset{\text{Soluble complex}}{2[N(CH_3)_4]_3[Al(SO_3)_3]}$$

From the soluble complex, $Al_2(SO_3)_3$ can be reprecipitated by adding the acid, $SOCl_2$.

$$2[N[CH_3)_4]_3[Al(SO_3)_3] + 3SOCl_2 \xrightarrow{liq.SO_2} 6[N(CH_3)_4]Cl + 6SO_2 + Al_2(SO_3)_3\downarrow$$

The behaviour of $GaCl_3$ is similar to that of $AlCl_3$.

6. Redox Reactions. Liquid sulphur dioxide does not have any strong oxidising or reducing properties. It serves only as a medium for redox reactions. For instance, liquid sulphur dioxide cannot reduce iodine. However, a sulphite in liquid sulphur dioxide reduces iodine to iodide. Thus,

$$I_2 + 2K_2SO_3 \xrightarrow{liq.SO_2} K_2SO_4 + 2KI + SO_2$$

KI is oxidised to free iodine by $SbCl_5$ in liquid sulphur dioxide.

$$6KI + 3SbCl_5 \xrightarrow{liq.SO_2} 3I_2 + SbCl_3 + 2K_3[SbCl_6]$$

MOLTEN SALTS AS NON-AQUEOUS SOLVENTS

The molten salts which act as non-aqueous solvents can be divided into two categories, *viz.*,

1. High Temperature Molten Salts *2. Room Temperature Molten Salts*

1. High Temperature Molten Salts. This category contains melts of compounds containing mainly ionic bonds, *e.g.*, alkali halides. The coordination number of the ions drops from 6 in solids to 4 in their melts. The long range lattice symmetry is destroyed in the molten state of such salts but the short range symmetry around the ions still exists. Ionic compounds can be dissolved in such melts giving rise to highly conducting solutions. The cryoscopic technique can be applied to determine the number of ions of the solute. For example, the number of ions of KF in molten sodium chloride is 2 and of BaF_2 is 3. But the number of ions of NaF in molten NaCl comes out to be 1 by the cryoscopic method because the Na^+ ion of solute is common with the Na^+ ion of molten NaCl solvent.

Another type of molten salts are melts of covalently bonded compounds although some autoionisation may occur in such compounds also. The example is the autoionisation of molten HgX_2 :

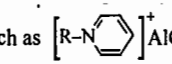
$$2HgX_2 \rightleftharpoons HgX^+ + HgX_3^-$$

Thus, any substance which increases the concentration of HgX^+ behaves as an acid and any substance which increases the concentration of HgX_3^- behaves as a base. Other examples are :

$$Hg(ClO_4)_2 + HgX_2 \longrightarrow 2\,HgX^+ + 2ClO_4^- \qquad (Hg(ClO_4)_2 \text{ acts as an acid})$$

$$KX + HgX_2 \longrightarrow K^+ + HgX_3^- \qquad (KX \text{ acts as a base})$$

$$Hg(ClO_4)_2 + 2KX \longrightarrow 2K^+ + 2ClO_4^- + HgX_2 \qquad (\text{neutralisation})$$

2. Room Temperature Molten Salts. Some chloroaluminates such as  $AlCl_4^-$ are liquids at

room temperature and can be used as solvents for many ionic compounds. But a serious limitation of such liquid chloroaluminate solvents is that they are highly hygroscopic and hydrolyse readily. The hydrolysed chloroaluminates may further react with the dissolved salts to produce their oxidised products.

$$AlCl_4^- + H_2O \longrightarrow [AlCl_2O]^- + 2HCl$$

$$[AlCl_2O]^- + [TiCl_6]^{2-} \longrightarrow [TiOCl_4]^{2-} + AlCl_4^-$$

However, the oxygen of the oxidised product can be quantitatively removed by passing phosgene into the solution of the salt in the chloroaluminate melt.

$$[TiOCl_4]^{2-} + COCl_2 \longrightarrow TiCl_6^{2-} + CO_2 \uparrow$$

Another salt which is liquid at room temperature is obtained by reacting $Et_2NH^+Cl^-$ with CuCl.

$$Et_2NH^+Cl^- + CuCl \longrightarrow Et_2NH^+[CuCl_2]^- \xrightarrow{Et_2NH^+Cl^-} (Et_2NH)_2[CuCl_3]^{2-}$$

$$\xrightarrow{CuCl} (Et_2NH)[Cu_2Cl_3]^-$$

The low melting point of the product obtained by the above reaction is due to the presence of a mixture of salts such as $Et_2NH^+[CuCl_2]^-$, $(Et_2NH^+)_2[CuCl_3]^{2-}$, in the product. This solvent can be easily reduced and can also be easily oxidised.

$$CuCl_2^- + e^- \longrightarrow Cu + 2Cl^-$$

$$CuCl_2^- \longrightarrow CuCl_2 + e^-$$

Therefore, the species which are even mildly oxidising or mildly reducing cannot be studied in this solvent. Moreover, all reactions to be studied in this solvent have to be carried out in the absence of air.

Utility of Molten Salts as Solvents

1. The highly reacting solutes which cannot be studied in reactive solvents can be studied in molten salts. For example, the halogens which cannot be studied in water can be conveniently studied in molten halides.

2. Molten halides are used for the production of halogens.

$$NaCl\ (molten) \xrightarrow{Electrolysis} Na + 1/2\ Cl_2$$

3. Molten salts are used in metallurgy to remove silica as slag which is in molten state at the temperature required for extraction of the metal.

$$CaO\ (flux) + SiO_2\ (impurity) \longrightarrow CaSiO_3\ (slag)$$

4. Molten alkali metal halides can dissolve any amount of the corresponding alkali metal. However, molten halides of Zn, Cd, Hg dissolve the corresponding metal to a smaller extent. It is assumed that the metal dissolved in metal halides loses electrons so that the solution becomes reducing. That is why Cd and Hg reduce a part of molten $HgCl_2$ and $CdCl_2$.

$$Hg + HgCl_2 \longrightarrow Hg_2Cl_2$$

$$Cd + CdCl_2 \longrightarrow Cd_2Cl_2$$

5. The molten salts provide a medium in which the concentration of anionic ligands can be much more than is possible in their aqueous solutions. For example, $CrCl_6^{3-}$, $TiCl_6^{3-}$ cannot be isolated from aqueous solutions as these species *immediately* hydrolyse. But, these species can be easily prepared by using molten metal chlorides as solvent medium.

$$CrCl_3 + 3Cl^- \longrightarrow [CrCl_6]^{3-}$$

$$TiCl_4 + 2Cl^- \longrightarrow [TiCl_6]^{2-}$$

QUESTIONS

1. (*a*) What do you understand by ionising and non-ionising solvents ? Give examples.
2. (*a*) Discuss the chemistry of liquid ammonia as a solvent.
   (*b*) What are the advantages and disadvantages of liquid ammonia as solvent ?
3. Describe the following reactions in liquid ammonia giving suitable examples : (*i*) Acid–base reactions (*ii*) Precipitation reactions (*iii*) Complex formation reactions (*iv*) Ammonolysis.
4. Discuss the nature and applications of metal ammonia solutions.
5. Compare the acid–base neutralisation and protolysis reactions of liquid ammonia and water.
6. What are protic and aprotic solvents ? Give examples. Is liquid HF a protic or an aprotic solvent ?
7. Discuss the merits and demerits of liquid hydrogen fluoride as a non-aqueous solvent. Discuss briefly the chemical reactions which take place in this solvent.
8. Discuss briefly the reactions which take place in non-aqueous sulphuric acid.
9. Give the important physical constants of liquid N_2O_4. Discuss the various reactions which occur in this solvent.
10. (*a*) Discuss the following reactions in liquid sulphur dioxide giving two examples of each type :
    (*i*) Acid–base reactions (*ii*) Solvolytic reactions (*iii*) Complex formation reactions
    (*b*) What are the advantages and disadvantages of liquid SO_2 as a solvent ?
11. "Dielectric constants, dipole moments and autoionisation play a significant role in explaining solubilities of substances in various solvents." Discuss.
12. Explain giving reasons :
    (*i*) Strong oxidising agents do not exist in liquid ammonia.
    (*ii*) Solutions of alkali metals in liquid ammonia are coloured.
    (*iii*) A strong acid like HNO_3 behaves as a base in hydrogen fluoride.
    (*iv*) Covalent compounds such as C_6H_6 and C_2H_5OH give conducting solutions in liquid hydrogen fluoride.
13. Discuss the role played by molten salts as non-aqueous solvents.

8 ACIDS AND BASES

Different concepts have been put forth by different investigators to characterise acids and bases. While some of the concepts are quite narrow in their approach, others are fairly comprehensive. Some important concepts of acids and bases are discussed below.

Arrhenius Concept

According to Arrhenius concept, *an* **acid** *is a substance that dissociates to give hydrogen ions when dissolved in water.* Thus, hydrogen chloride gas is an acid because when dissolved in water, it gives hydrogen ions.

$$HCl\,(g) + \text{water} \rightleftharpoons H^+\,(aq) + Cl^-\,(aq)$$

The symbol *aq* indicates that the ions are hydrated, *i.e.*, associated with one or more molecules of water.

According to Arrhenius concept, *a* **base** *is a substance which dissociates into hydroxyl ions when dissolved in water.* Thus, NaOH is a base because it furnishes hydroxyl ions in aqueous solution.

$$NaOH + \text{water} \rightleftharpoons Na^+\,(aq) + OH^-\,(aq)$$

The high dielectric constant of water lowers the force of attraction between the oppositely charged ions and thus causes the dissociation of the electrolyte.

Hydronium ion. Hydrogen ion is merely a proton. It is a unique ion in the sense that it has no electron. It is the smallest ion known and, therefore, has a strong tendency to get hydrated. It exists largely as attached to a molecule of water forming H_3O^+ ion, *viz.*, the **hydronium ion.**

Although the proton in aqueous solution is known to be largely hydrated, with H_3O^+ as its probable structure, it is customary to represent it as $H^+\,(aq)$, for the sake of convenience.

Due to simplicity, Arrhenius concept was widely accepted and used. However, this concept has a serious limitation that it can be applied only to aqueous solutions. It fails to account for the behaviour of acids and bases in solvents other than water, *viz.*, non-aqueous solvents.

Proton Transfer Theory. Concept of Lowry and Bronsted

Lowry and Bronsted suggested a more general definition of acids and bases which applies to aqueous as well as to non-aqueous solutions. According to this concept, an **acid** is defined as a substance which has a tendency to donate a proton to any other substance and a **base** as a substance which has a tendency to accept a proton from any other substance. In other words, an **acid** is a proton-donor and a **base** is a proton-acceptor.

When an acid loses a proton, the residual part of it has a tendency to regain the proton. Therefore, it behaves as a base. An acid and a base may, therefore, be defined by the general equation

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

Consider ionisation of acetic acid in water which may be represented as

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{CH_3COO^-}$$

It is evident that acetic acid *donates a proton* to water and thus acts as an *acid*. Water *accepts* a proton and, therefore, acts as a *base*. In the reverse reaction, hydronium ion (H_3O^+) *donates* a proton to the acetate ion and, therefore, acts as an *acid*. The acetate ion *accepts* a proton and, therefore, behaves as a *base*.

Such pairs of substances which can be formed from one another by the gain or loss of a proton are known as **conjugate acid–base pairs.** Thus, acetic acid is the conjugate acid of acetate ion and acetate ion is the conjugate base of acetic acid. Similarly, water is the conjugate base of hydronium ion and hydronium ion is the conjugate acid of water.

The ionisation of hydrochloric acid in water may be represented as

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{Cl^-}$$

Evidently, hydrochloric acid is the conjugate acid of chloride ion and chloride ion is the conjugate base of hydrochloric acid.

The following points emerge out of the above discussion :

1. Firstly, it is evident that a substance is able to show its acidic character only if another substance capable of accepting a proton (i.e., a base) is present. For example, acetic acid or hydrogen chloride solution in benzene is not acidic because benzene is not in a position to take up protons. But, a solvent like water can take up protons and, therefore, acetic acid or hydrochloric acid can ionise in water, as shown in the above examples.

2. Secondly, hydrogen ion in aqueous solution does not exist as H^+ ion but as hydrated ion, H_3O^+.

3. Thirdly, not only molecules but even ions may act as acids or bases. Thus, in the above examples, acetate (or chloride) ion acts as a base as it can accept a proton to form acetic acid (or hydrochloric acid). In fact, anion of any acid is the conjugate base of the acid.

As can be seen from the ionisation of acetic acid or hydrochloric acid represented above, there is one acid and one base on each side of the equation. Suppose, acetic acid is designated as $Acid_1$, then the acetate ion, its conjugate base, may be designated as $Base_1$. Similarly, if water is referred to as $Base_2$, then the hydronium ion, its conjugate acid, may be designated as $Acid_2$. The ionization of acetic acid in water may thus be represented as

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1 \qquad ...(4)$$

$Acid_1$ and $Base_1$ is a **conjugate acid–base pair** and so is the pair of $Acid_2$ and $Base_2$.

In general, the ionisation of an acid HA in water may be represented as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Just as an acid requires a solvent that can take up a proton (*i.e.*, can act as a base) for its ionization, a base requires a solvent that can give up a proton (*i.e.*, that can act as an acid) for its ionization. Water possesses both basic and acidic properties. Therefore, acids as well as bases can ionize in water. Thus, water acts as an acid (a proton-donor) towards ammonia and as a base (a proton-acceptor) towards acetic acid. Such substances are said to be **amphiprotic.**

Consider ionisation of ammonia in water which may be represented as

$$\underset{Base_1}{NH_3} + \underset{Acid_2}{H_2O} \rightleftharpoons \underset{Acid_1}{NH_4^+} + \underset{Base_2}{OH^-}$$

Now ammonium ion (NH_4^+) is the conjugate acid (say, Acid $_1$) to the base NH_3 (Base$_1$) and hydroxyl ion (OH^-) is the conjugate base (Base$_2$) to the acid H_2O (Acid$_2$).

Relative Strengths of Acid–Base Pairs. The *strength of an acid*, according to the above concept of Lowry and Bronsted, depends upon its *tendency to lose protons* and the *strength of a base* depends upon its *tendency to gain protons*. If an acid, such as hydrochloric acid, is a strong acid, it will have a strong tendency to donate protons. Thus, the equilibrium

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

lies very much to the right and the reverse reaction, representing the gain of protons by the chloride ions leading to the reformation of HCl, takes place to a very small extent. Accordingly, Cl^- ion is a weaker base than H_2O since the latter has a greater tendency to take up a proton.

Acetic acid, on the other hand, has considerably less tendency to donate protons and is, therefore, a much weaker acid. It ionises to a small extent, *i.e.*, the equilibrium

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

lies mostly towards the left. It follows, therefore, that CH_3COO^- ion has a much greater tendency to gain protons and hence it is a much stronger base than H_2O.

In the above reaction, acetic acid and hydronium ion may be regarded as two acids competing with each other to donate protons. Again, since the equilibrium is known to lie towards the left, it follows that hydronium ion is more successful in this attempt than acetic acid. Hence, the former is a stronger acid. In short, while acetate ion is a stronger base than water, its conjugate acid, acetic acid, is a weaker acid than hydronium ion.

Thus, as a general rule, *the stronger an acid, the weaker must be its conjugate base and vice versa.* If an acid (*e.g.*, HCl) is strong, its conjugate base (Cl^- ion) is weak. If a base (*e.g.*, CH_3COO^-) is strong, its conjugate acid (CH_3COOH) is weak.

Water is a weak base because its conjugate acid, hydronium ion (H_3O^+), is a strong acid. At the same time, water is a very weak acid because its conjugate base, hydroxide ion (OH^-), is a very strong base.

It may be pointed out that while strong acids like HCl, HNO_3, H_2SO_4, etc., being *covalent* compounds, get ionised only in a solvent like water which can take up protons, strong bases such as NaOH, KOH, $Ba(OH)_2$, etc., being *electrovalent* compounds, exist as ions even in the solid state. The basic character of these compounds is exclusively due to the presence of hydroxyl ion which is always there (even without a solvent) and, therefore, no interaction with a solvent like water is necessary in such cases.

Lux–Flood Concept

This concept was proposed by Lux and extended by Flood. It considers the acid–base reaction in terms of the specific reaction of the oxide ion and is mainly used for molten oxides at high temperatures. According to this concept, an **acid** is a substance which accepts the oxide ion and a **base** is a substance which donates the oxide ion. In other words, an **acid** is an oxide ion-acceptor and a **base** is an oxide ion-donor. For example, in the reaction

$$\underset{\text{Base}}{CaO} + \underset{\text{Acid}}{SiO_2} \longrightarrow CaSiO_3,$$

calcium oxide is a base and silicon dioxide is an acid. Similarly, in the reaction

$$PbO + SO_3 \longrightarrow PbSO_4$$

PbO is a base while SO_3 is an acid.

This concept, however, has only a limited scope.

The Solvent–System (or Autoionization) Concept

According to solvent–system concept put forth by Fanklin, an **acid** is a substance which, in a solvent, increases the concentration of a cation charateristic of that solvent and a **base** is a substance which, in a solvent, increases the concentration of an anion characteristic of that solvent. The characteristic cations and anions of the solvent are the ions produced during its autoionization.

Autoionization of water, for instance, is represented as

$$2H_2O \rightleftharpoons \underset{\text{Solvent cation}}{H_3O^+} + \underset{\text{Solvent anion}}{OH^-}$$

Thus, in water, substances giving H_3O^+ ions are acids and those giving OH^- ions are bases.

Liquid ammonia undergoes autoionization as follows :

$$2NH_3 \rightleftharpoons \underset{\text{Solvent cation}}{NH_4^+} + \underset{\text{Solvent anion}}{NH_2^-}$$

According to solvent–system concept, in liquid ammonia, substances which give ammonium ions (NH_4^+) act as acids while those giving amide ions (NH_2^-) act as bases. For example, ammonium chloride acts as an acid while potassium amide acts as a base in liquid ammonia.

$$NH_4Cl \overset{\text{liq. } NH_3}{\rightleftharpoons} NH_4^+ + Cl^-$$

$$KNH_2 \overset{\text{liq. } NH_3}{\rightleftharpoons} K^+ + NH_2^-$$

The acid–base neutralisation reaction of NH_4Cl and KNH_2 in liquid NH_3 is analogous to that of HCl and NaOH in water.

$$NH_4Cl + KNH_2 \longrightarrow KCl + 2NH_3$$

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Consider the autoionization of liquid nitrogen tetroxide :

$$N_2O_4 \rightleftharpoons \underset{\text{Solvent cation}}{NO^+} + \underset{\text{Solvent anion}}{NO_3^-}$$

According to solvent–system concept, in liquid nitrogen tetroxide, the substances which furnish nitrosyl ions (NO^+) behave as acids and those which furnish nitrate ions (NO_3^-) behave as bases. Accordingly, NOCl behaves as an acid and $NaNO_3$ behaves as a base, in this solvent.

$$NOCl \overset{\text{liq. } N_2O_4}{\rightleftharpoons} NO^+ + Cl^-$$

$$NaNO_3 \overset{\text{liq. } N_2O_4}{\rightleftharpoons} Na^+ + NO_3^-$$

Autoionization of sulphuric acid is represented as

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

Thus, any species giving $H_3SO_4^+$ ion acts as an acid and any species giving HSO_4^- ion acts as a base.

Just as ionic product of H_2O is written as $K_w = [H_3O^+][OH^-]$, similarly, the ionic product of any solvent AB ionising as $AB \rightleftharpoons A^+ + B^-$, may be written as $K_{AB} = [A^+][B^-]$. Just as the convenient scale for indicating H^+ ion concentration in aqueous media is the ***p*H scale** and the point of neutrality is given by $-1/2 \log K_w$ (*i.e.*, $pH = 7$), similarly, we can construct a convenient scale for indicating the acidity of the solvent AB, the point of neutrality being given by $-1/2 \log K_{AB}$.

Limitations of Solvent–System (or Autoionization) Concept. The solvent–system concept lays too much stress on ionic reactions and chemical properties of the solvent. This concept totally ignores the physical properties of the solvent. The limitations of the concept can be understood more clearly by taking into consideration certain specific examples.

Solvent $POCl_3$ undergoes autoionization as

$$POCl_3 \rightleftharpoons \underset{\text{Acid ion}}{POCl_2^+} + \underset{\text{Base ion}}{Cl^-}$$

In $POCl_3$, $(CH_3)_4N^+Cl^-$ and $FeCl_3$ ionise as follows :

$$(CH_3)_4N^+Cl^- \longrightarrow (CH_3)_4N^+ + Cl^-$$

$$FeCl_3 + POCl_3 \longrightarrow FeCl_4^- + POCl_2^+$$

According to the solvent–system concept, therefore, $(CH_3)_4N^+Cl^-$ is a *base* and $FeCl_3$ is an *acid* in $POCl_3$ and the net reaction between these two species is a typical neutralisation reaction which may be represented as

$$\underset{\text{Acid ion}}{POCl_2^+} + \underset{\text{Base ion}}{Cl^-} \longrightarrow POCl_3$$

The above view receives support from the fact that $FeCl_3$ can be titrated quantitatively against $(CH_3)_4N^+Cl^-$ in $POCl_3$ as the solvent conductometrically as well as spectrophotometrically and the *end point is sharp.*

The same reaction occurs between $FeCl_3$ and $(CH_3)_4N^+Cl^-$ in $OP(OEt)_3$ as the solvent giving the same product $FeCl_4^-$. However, this solvent cannot autoionize to give Cl^- ion. In fact, there is no evidence for the autoionization of the solvent $OP(OEt)_3$ at all. The solvent–system concept thus fails to explain the reaction between $FeCl_3$ and $(CH_3)_4N^+Cl^-$ in $OP(OEt)_3$.

Autoionization of liquid SO_2 is supposed to occur as follows :

$$2SO_2 \rightleftharpoons \underset{\text{Acid ion}}{SO^{2+}} + \underset{\text{Base ion}}{SO_3^{2-}}$$

The compound $SOCl_2$ is supposed to ionize in liquid SO_2 as follows :

$$SOCl_2 \overset{\text{liq. } SO_2}{\rightleftharpoons} SO^{2+} + 2Cl^-$$

According to the solvent–system concept, therefore, $SOCl_2$ is an acid.

Cs_2SO_3 ionises in liquid SO_2 as follows :

$$Cs_2SO_3 \overset{\text{liq. } SO_2}{\rightleftharpoons} 2Cs^+ + SO_3^{2-}$$

According to the solvent–system concept, therefore, Cs_2SO_3 is a *base.*

Evidently, the net reaction between $SOCl_2$ and a sulphite would be a neutralisation reaction as per the solvent–system concept.

$$SO^{2+} + SO_3^{2-} \rightleftharpoons 2SO_2$$

Such a reaction does occur between $SOCl_2$ and Cs_2SO_3 .

The explanation for the above reaction is, obviously, based on the autoionization of liquid SO_2. But, autoionization of liquid SO_2 has not been established at all. Liquid SO_2 has a very low dielectric constant which does not favour its ionization. Nonionization of liquid SO_2 is fully supported by the following experiment :

$SOCl_2$ is dissolved in liquid SO_2 labelled with radioactive ^{35}S. According to the solvent–system concept, the following reactions are supposed to occur :

$$2\,{}^{35}SO_2 \rightleftharpoons {}^{35}SO^{2+} + {}^{35}SO_3^{2-}$$
$$SOCl_2 \rightleftharpoons SO^{2+} + 2Cl^-$$
$${}^{35}SO^{2+} + 2Cl^- \rightleftharpoons {}^{35}SOCl_2$$

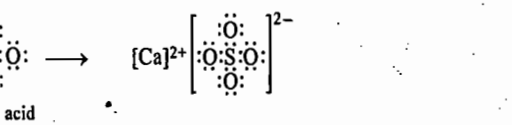
If autoionization of liquid SO_2 actually occurs, the labelled and unlabelled SO^{2+} ions would compete with each other to combine with the Cl^- ion to form $SOCl_2$. As a result, a considerable amount of ^{35}S would get incorporated in $SOCl_2$ within a very short time. But this does not happen. The half-life for the exchange of ^{35}S in this reaction is found to be about 2 years ! This rules out the possibility of autoionization of liquid SO_2. In other words, the reaction between $SOCl_2$ and Cs_2SO_3 cannot be explained on the basis of solvent–system concept.

It may thus be concluded that the solvent–system concept is useful only when the ionic species formed in solution are definitely known. The concept should not be stretched for solvents which are not conducive towards ion formation and also for solvents the nature of whose ions or even the existence of whose ions is not definitely known.

Lewis Concept

In 1923, G.N. Lewis, in order to cover all types of neutralization reactions, gave more broad based definitions of acids and bases. According to Lewis concept, a **base** is defined as a substance which can donate electrons whereas an **acid** is a substance which can accept electrons. In other words, while a **base** is an electron-donor, an **acid** is an electron-acceptor.

In the light of these definitions, the combination of calcium oxide with sulphur trioxide to form calcium sulphate is represented as below :



Lewis base Lewis acid

A lone pair of electrons from oxide ion of calcium oxide is donated to sulphur trioxide.

Lewis definition of a base covers all substances which have unshared electrons in the outer energy levels. These would also be classed as bases according to Lowry–Bronsted's concept. On the other hand, Lewis acids include all substances which have vacant orbitals to accept electrons. These include the following types of substances :

1. *All cations are regarded as Lewis acids* because they can accept electrons. While larger cations such as Na^+, K^+, Ba^{2+}, Ca^{2+}, etc., behave as weak Lewis acids, smaller cations such as H^+, Ag^+, Fe^{2+}, etc., behave as strong Lewis acids. The smallest cation, *viz.*, H^+ ion, behaves as the strongest Lewis acid.

$$H^+ + NH_3 \longrightarrow NH_4^+$$

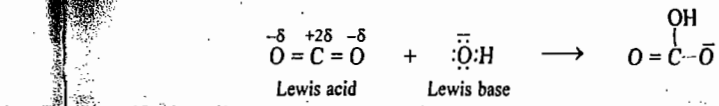
2. *Electron-deficient compounds in which the central atoms can expand their valence shells are regarded as Lewis acids.* For example, in molecules such as BF_3, BCl_3, $AlCl_3$, etc., the central atoms have only six electrons around them and, therefore, have a tendency to accept an electron pair to complete their octet. For example,

$$F_3B + :NH_3 \longrightarrow F_3B:NH_3$$

3. *Molecules in which the central atoms have vacant d orbitals may also behave as Lewis acids by extending their valency shells beyond the octet.* For example, in molecules such as $SnCl_4$, SiF_4, SbF_5, etc., the central atoms have vacant *d* orbitals and, therefore, they extend their valency shells beyond the octet, as shown below :

$$\underset{\text{Lewis acid}}{SiF_4} + \underset{\text{Lewis base}}{2F^-} \longrightarrow [SiF_6]^{2-}$$
$$SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$$
$$SbF_5 + F^- \longrightarrow [SbF_6]^-$$

4. *Molecules in which the central atom is bonded to atoms of different electronegativities through one or more multiple bonds also behave as Lewis acids.* For example, C atom in CO_2 behaves as a Lewis acid because in this molecule, carbon is bonded to more electronegative oxygen atoms through double bonds. As the Lewis base approaches the less electronegative carbon atom, the pi electron charge density gets displaced away from the carbon atom towards oxygen atoms. This results in development of a partial positive charge on carbon atom and a partial negative charge on oxygen atoms. In other words, the electron charge density on carbon atom decreases and, therefore, carbon atom in carbon dioxide acts as an electron-acceptor.



Lewis acid Lewis base

Similarly, S atom in SO_2 acts as a Lewis acid towards OH^- ion.

Sulphur trioxide also acts as a Lewis acid. Its electronic structure is as shown before. It has a double bond between S and one of the O atoms. The oxygen atom, being more electronegative than sulphur atom, pulls the pi electrons towards itself leaving a partial positive charge on sulphur atom which, thereby, acts as an *electron-deficient centre.* As a result, a Lewis base like O^{2-} would donate its electron pair to S atom of SO_3 leading to the formation of SO_4^{2-} ion, as mentioned before.

Limitations of Lewis Concept. The Lewis concept has several limitations, the most significant of which are discussed below :

1. The Lewis concept is *too general* and includes all reactants which can form coordination bonds. Even metals in their zero oxidation state (*e.g.,* Fe, Ni, Co, Mn) are termed as Lewis acids in their complexes with pi acceptor ligands such as CO, cyclopentadiene and olefins.

2. The relative strengths of acids and bases cannot be explained on the basis of Lewis concept.

RELATIVE STRENGTHS OF ACIDS AND BASES

There are several factors which affect the relative strengths of acids and bases. The effects of some of these factors are discussed below.

1. Effect of Solvent on Relative Strengths of Acids and Bases

Effect of Solvent on Acid Strength. *Acid strength* is a relative term. According to the concept of Lowry and Bronsted, the strength of an acid depends on the substance which acts as a base. Consider the general equation

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

Evidently, the capacity of the acid to ionise (*i.e.*, to donate protons) depends upon the base strength (*i.e.*, the capacity to accept protons) of the solvent which acts as a base. To illustrate this point, ionization in three solvents, namely, glacial acetic acid, water and liquid ammonia of increasing basic character may be considered.

Ionization in acetic acid. Although acetic acid is normally an acid, it is also able, to some extent, to accept a proton and thus act as a base as well. The ionization of a strong acid HA in this medium may thus be represented as

$$\underset{\text{Acid}}{HA} + \underset{\text{Base}}{CH_3COOH} \rightleftharpoons \underset{\text{Acid}}{CH_3COOH_2^+} + \underset{\text{Base}}{A^-}$$

But, the equilibrium cannot lie very much to the right since acetic acid has only a small tendency to accept protons. Therefore, *even strong acids are only feebly ionised in acetic acid.*

The degrees of ionization of a number of acids when dissolved in glacial acetic acid have been determined from conductance measurements. Taking these as a measure of their relative strengths, some of the common acids have been arranged in the following order of decreasing strength :

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

This is the correct order of decreasing strengths of these acids.

Ionisation in water. Water is a much stronger base than acetic acid, *i.e.,* it has a much greater tendency to accept protons than acetic acid. Therefore, the ionisation equilibrium of a strong acid in water, represented as

$$\underset{\text{Acid}}{HA} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{A^-}$$

lies very much to the right. All the five acids mentioned in the above series, therefore, react almost completely with water to form, in every case, hydronium ion, H_3O^+. Therefore, *all strong acids in aqueous solutions appear almost equally strong.* Obviously, their relative strengths in aqueous solutions cannot be compared. This phenomenon is known as the **levelling effect.**

However, the ionic equilibria do not proceed that far in the case of weak acids like formic, acetic, propionic, lactic, tartaric and phosphoric acids. It is, therefore, possible to distinguish between their relative strengths, as will be shown a little later.

Ionisation in liquid ammonia. Liquid ammonia has such a strong basic character (*i.e.,* it has such a strong tendency to take up protons) that even a weak acid, like acetic acid, ionises to a considerable extent in liquid ammonia and thus behaves as a strong acid. The ionic equilibrium represented below, lies very much to the right :

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{CH_3COO^-}$$

By conductance measurements it has been found that all acids, which in aqueous solution behave stronger than acetic acid, appear to be of about the same strength when dissolved in liquid ammonia. Thus, such strong acids as hydrochloric and nitric and such weak acids as acetic and propionic, appear to be of almost equal strength when dissolved in liquid ammonia.

Ionisation in hydrogen fluoride. Hydrogen fluoride has strong acidic properties and no basic, *i.e.,* proton-accepting, properties at all. Consequently, even the strongest acid is incapable of ionising as an acid when dissolved in hydrogen fluoride. As a matter of fact, many substances, which are normally acids but have some tendency to accept protons as well under certain conditions, ionise as bases when dissolved in hydrogen fluoride. Thus, nitric acid ionises slightly as a base in hydrogen fluoride solution :

$$\underset{\text{Base}}{HNO_3} + \underset{\text{Acid}}{HF} \rightleftharpoons \underset{\text{Acid}}{H_2NO_3^+} + \underset{\text{Base}}{F^-}$$

It is thus interesting to note that even *a strong acid* like HNO_3 *behaves as a base* (a very weak base though) when dissolved in HF.

Acetic acid, which has comparatively greater tendency to accept a proton, ionises comparatively more readily as a base in hydrogen fluoride solution :

$$\underset{\text{Base}}{CH_3COOH} + \underset{\text{Acid}}{HF} \rightleftharpoons \underset{\text{Acid}}{CH_3COOH_2^+} + \underset{\text{Base}}{F^-}$$

Thus, acetic acid behaves as a stronger base than nitric acid when dissolved in hydrogen fluroride.

Effect of Solvent on Base Strength. The nature of the solvent plays an equally important role in the ionization and relative strengths of bases as well. If the solvent is a weak acid, such as water, it will be possible to compare the strengths of different bases as they will ionise to different extents. But if the solvent is even a slightly stronger acid, *e.g.,* acetic acid, it will not be possible to distinguish between the strengths of different bases.

For example, aniline, a very weak base and sodium hydroxide, a very strong base in water, *appear to be equally strong when acetic acid is used as the solvent* **(levelling effect).** Sometimes advantage is taken of this fact in volumetric estimations of bases which are too weak in aqueous solution to be titrated against acids.

Explanation of levelling effect on the basis of solvent–system concept. The levelling effect can be explained by invoking the solvent–system concept of acids and bases. According to this concept, *all acids and bases stronger than the characteristic cation and the anion of the solvent would be levelled to the characteristic cation and anion of the solvent. Acids and bases weaker than the characteristic cation and anion of the solvent would remain in equilibrium with them.* The above concept would become clear from the following illustration.

The three strong acids, $HClO_4$, HCl and HNO_3 ionise in water as follows :

$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$$

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

All the three acids are stronger acids than the characteristic cation of the solvent (water), *viz.,* the H_3O^+ ion. These acids would, therefore, be *completely levelled* (or converted) to the characteristic cation H_3O^+ of the solvent and thus behave as being equally strong. A solvent in which various strong acids appear equally strong is known as a **levelling solvent.**

Now consider an acid such as CH_3COOH which is weaker than H_3O^+, in water. It would remain in equilibrium with H_3O^+, as shown below :

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The strength of such an acid would depend upon the concentration of the characteristic cation of water, *viz.*, the H_3O^+ ion at equilibrium.

For measuring relative strengths of strong acids, we must select a solvent whose characteristic cation is a stronger acid than the acids whose strengths are to be measured. One such solvent is CH_3COOH. Consider autoionization of acetic acid represented as

$$2CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$$

The strong acid HA dissociates in acetic acid as follows :

$$HA + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + A^-$$

The characteristic cation of acetic acid, *viz.*, $CH_3COOH_2^+$ ion, is stronger than HA. Hence, HA and $CH_3COOCH_2^+$ ion will remain in equilibrium. The strength of HA in acetic acid would thus be determined by the concentration of $CH_3COOH_2^+$ ion at equilibrium.

The solvents in which strong acids ionise to different extents so that the relative strengths of these acids can be measured, are known as **differentiating solvents.** Thus, acetic acid is a *differentiating solvent* while water is a *levelling solvent* for strong acids such as $HClO_4$, HBr, H_2SO_4, HCl, HNO_3.

Levelling effect is observed in the case of strong bases as well. If a base is stronger than the characteristic anion of the solvent, it would be levelled (or converted) into the anion of the solvent. Thus, all strong bases would appear to be equally strong in water as they get completely converted into OH^- ion, the characteristic anion of the solvent (water).

According to the solvent-system concept, the behaviour of a species as an acid or a base would depend upon the *acidic* or *basic nature of the solvent.* For example, acetic acid behaves as a weak acid in water, a strong acid in ammonia and as a base in sulphuric acid, as illustrated below :

In water :

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

There is only a small concentration of H_3O^+ ions in solution. Therefore, acetic acid behaves as a weak acid in water.

In ammonia :

$$CH_3COOH + NH_3 \longrightarrow NH_4^+ + CH_3COO^-$$

Acetic acid is almost completely converted to NH_4^+ ion which is a characteristic cation of the solvent. Therefore, acetic acid behaves as a strong acid in ammonia.

In sulphuric acid :

$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3COOH_2^+ + HSO_4^-$$

There is considerable concentration of HSO_4^- in solution which is the characteristic anion of sulphuric acid. Hence, acetic acid behaves as a base in sulphuric acid.

Similarly, urea behaves as a weak acid in ammonia but as a strong base in concentrated sulphuric acid, as illustrated below :

$$H_2NCONH_2 + NH_3 \rightleftharpoons H_2NCONH^- + NH_4^+$$
$$H_2NCONH_2 + H_2SO_4 \longrightarrow H_2NCONH_3^+ + HSO_4^-$$

Sulphuric acid is such a strong acid solvent that even a strong acid like HNO_3 behaves as a base (though very weak) in it according to the equation

$$HNO_3 + H_2SO_4 \rightleftharpoons HSO_4^- + H_2O + NO_2^+$$

2. Effect of Polarity and Dielectric Constant on Relative Strengths of Acids and Bases

The polarity and dielectric constant of a solvent influence considerably the acidic and basic strength of ionic species dissolved in that solvent. According to Coulomb's law, the force of attraction between two oppositely charged ions is given by

$$F = q_1q_2/\varepsilon r^2 \quad ...(1)$$

where q_1 and q_2 are the charges on the ions, r is the distance between the two ions and ε is the dielectric constant of the solvent. The higher the dielectric constant of the solvent, the lower is the magnitude of F. In solvents with low dielectric constants, the force of attraction between the ions of the solute will be relatively large and consequently the dissociation (separation of ions) of the solute would be small. In solvents with high dielectric constants, the force of attraction between the ions would be small and the extent of dissociation would be large. In other words, the acidic or basic strength of a species would increase with an increase in the dielectric constant of the solvent. The dielectric constant and the dipole moment are known to be directly related. Hence, the greater the polarity of a solvent, the greater would be the acidic or basic strength of the species dissolved in that solvent.

3. Effect of Substituents on Relative Strengths of Acids and Bases

The substituents present in acids and bases have a marked effect on their relative strengths. The increase or decrease in acid or base strength depends upon the nature of the substituents, their number and the type of bonding involved in them. This is illustrated below.

a. Electron-releasing or Electron-withdrawing Nature of Substituents. Since an acid is an electron-acceptor and a base is an electron-donor, the nature of substituents (whether electron-releasing or electron-withdrawing) present in them would affect their acidic or basic strength considerably. An electron-withdrawing substituent would increase and an electron-releasing substituent would decrease the acid strength of a species . Thus, chloroacetic acid is stronger than acetic acid while propionic acid is weaker than acetic acid. This is because Cl is an electron-withdrawing and CH_3 is an electron-releasing group.

Similarly, an electron-releasing substituent would increase and an electron-withdrawing substituent would decrease the basic strength of a species. Thus, while NH_3 is basic, NF_3 is almost neutral. Likewise, $(CH_3)_2NH$ is more basic than CH_3NH_2 and NH_3. The CH_3 group, being electron-releasing, increases the basic character of ammonia.

The inductive effect decreases as the substituent moves away from the COOH group. This is the reason why 1-chloro propionic acid ($CH_3CHClCOOH$) is a stronger acid than 2-chloropropionic acid ($ClCH_2CH_2COOH$).

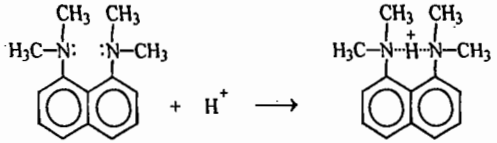
b. Steric and Solvation Effects. The inherent basic character of a species in gas phase is determined from its proton affinity. The proton affinities (kJ/mol) of NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ are 870, 920, 950 and 970, respectively. Proton affinity of a species is defined as the amount of *energy released* when one mole of H^+ ions get attached to one mole of the base. It is always taken as a positive quantity. Therefore, basicity increases in the order : $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ in *gas* phase, as expected from electron-releasing nature of CH_3 group.

In trisubstituted amines in the gas phase, the basicity decreases with increase in the bulk of the substituent. Thus, the basicity of trialkyl amines decreases in the order :

$$N(CH_3)_3 > N(CH_2CH_3)_3 > N(CH(CH_3)_2)_3$$

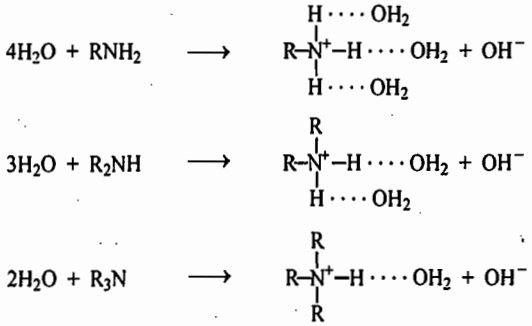
As the bulk of the substituent goes on increasing, the approach of an electron acceptor (acid) towards the electron pair on N atom of amine goes on becoming more and more difficult due to more and more steric evercrowding around the electron pair. *It is to be emphasised here that the same base may act in different ways while reacting with acids having substituents of different bulk.* Thus, $N(CH_2CH_3)_3$ will behave as a weaker base towards $B(CH_2CH_3)_3$ than towards $B(CH_3)_3$ because the bulkier C_2H_5 groups of $B(C_2H_5)_3$ will face more steric hindrance from the substituents on N atom of the base than the CH_3 groups of $B(CH_3)_3$, making the approach of the electron-acceptor B atom of $B(C_2H_5)_3$ more difficult than the approach of B atom of $B(CH_3)_3$ towards the electron pair on N atom of the base.

However, there are some compounds in which the steric effects stabilise the H^+–base adduct. For example, the four methyl groups of bis (dimethylamino) naphthalene sterically hinder one another. Also, the lone pairs of electrons on the two N atoms are too close and repel each other. Both these factors destabilise the base. The reaction of such a base with H^+ ion gives high stability to the adduct in the following manner :



Such compounds are highly basic and are termed as **'proton sponges'** because it is very difficult to remove protons from such adducts.

The order of basicities of amines in water is different from the order observed in gas phase. This is because of the reason that apart from the electronic effects which determine the basicity of amines in gas phase, the solvation effects also determine their basicities. It can be seen from the following reactions that the extent of hydration of amines through hydrogen bonding is in the order : $RNH_2 > R_2NH > R_3N$.



(Water in the above reactions also acts as an acid towards amines. R stands for CH_3 group)

Since solvation releases energy and stabilises the amine, it follows that solvation will stabilise primary amines to the maximum extent and tertiary amines to the minimum extent. Thus, the electronic factors (as in gas phase) and the solvation factors (as in solution phase) impart opposite order to the basicities of amines in water.

The combination of the two factors renders R_3N least basic and R_2NH most basic in water (R is CH_3) . Thus, the true order of the basicities of methyl substituted amines in water is observed to be :

$$(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

c. Type of Bonding Involved in Substituents. The presence of a pi bond in a substituent alters the acidic or basic character of the species. For instance, although fluorine is more electron-withdrawing than chlorine or bromine yet BF_3 is *less acidic* than BCl_3 or BBr_3 . This may be explained as follows : In a B–F bond in BF_3, one of the filled *p* orbitals of fluorine of proper symmetry forms a pi bond by overlapping with a vacant *p* orbital of boron, causing a shift of electronic charge from fluorine to boron. This decreases the electron-accepting power of boron in BF_3 . The *p* orbitals of Cl or Br are much higher in energy and are not suited for pi bonding with boron. Thus, the shift of electronic charge from Cl or Br to boron is much less. Therefore, the electron-accepting power of boron in BCl_3 or BBr_3 is more than that in BF_3 .

4. Additional Factors Influencing Relative Strengths of Acids and Bases

The influence of solvents as well as the effect of substituents on relative strengths of acids and bases

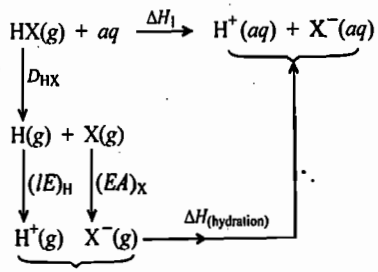
have been discussed above in some details. Apart from these, the following factors also influence the relative strengths of acids and bases :

a. Charge on the species. All other factors remaining constant, an increase in the positive charge would increase the acidic strength of the species and an increase in the negative charge would increase the basic strength of the species. This is because an increase in positive charge increases the electron-accepting capacity and an increase in negative charge increases the electron-donating capacity of the species.

b. Electronegativity. *In the species HX, the higher the electronegativity (electron-pulling capacity) of X, the easier would be the release of proton (H^+) from HX. In other words, the acid strength (proton-releasing capacity) of HX would increase with increase in the electronegativity of X. For example, the electronegativity of non-metals of the second period are in the order C < N < O < F . The acid strength of their hydrides also varies in the same order, i.e., $CH_4 < NH_3 < H_2O < HF$. Thus, within a period of the periodic table, the higher the electronegativity of a non-metal X, the greater would be the acid strength of HX.*

c. Hydration and other energy factors. Electronegativity is not the sole factor which determines the acid strength of a species. On the basis of electronegativities of the halogens, the strength of the halogen acids should change in the order HI < HBr < HCl < HF. But, actual order is just the reverse, *i.e.*, HF < HCl < HBr < HI . This anomaly may be explained as follows :

The ionization of HX (X = halogen) in an aqueous solution, in fact, involves a number of energy factors. We can write the following cycle similar to Born–Haber cycle, for the ionization of HX into $H^+(aq)$ and $X^-(aq)$ ions :



From Hess's law,

$$\Delta H_1 = D_{HX} + (IE)_H - (EA)_X - \Delta H_{hydration}$$

where ΔH_1 = Enthalphy of ionization of HX in water

D_{HX} = Dissociation energy of HX(*g*)

$(IE)_H$ = Ionization energy of H atom

$(EA)_X$ = Electron affinity of X atom

$\Delta H_{hydration}$ = Enthalpy of hydration of H^+ and X^- ions.

Both $(EA)_X$ and $\Delta H_{hydration}$ are energy-releasing processes and are written with negative signs in the Hess's law expression for ΔH_1.

Evidently, the ionization of HX, *i.e.*, the acid strength of HX, would be favoured if ΔH_1 has a large negative value. To this end, while D_{HX} should be small, $(EA)_X$ and $\Delta H_{hydration}$ should be large since $(IE)_H$ is a constant factor. The enthalpies of ionization of the various halogen acids determined as above, fully support the variation of their strengths in the order HF < HCl < HBr < HI .

d. Oxidation number of central atom. In oxoacids, the higher the oxidation number of the central atom, the greater would be the strength of the acid. This is as expected. A higher oxidation number of central atom

increases its electron-pulling capacity and thus makes the release of H atom as H^+ ion easier. This is the reason why the strength of various oxoacids of chlorine varies in the order.

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

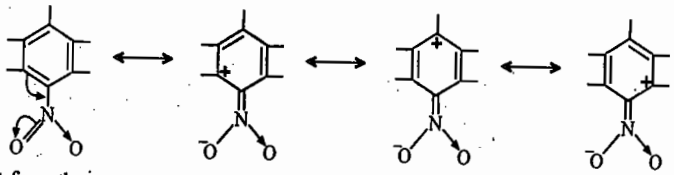
The oxidation number of chlorine in these oxoacids is +7, +5, +3 and +1, respectively.

In oxoacids of similar structures, the acid strength increases with increase in the *electronegativity* of the central atom. Thus, the acid strength of the oxoacids of the three halogens varies in the order

$$HClO_3 > HBrO_3 > HIO_3$$

e. Resonance effect. We shall take aromatic carboxylic acids as a model to explain the effect of resonance. It has been observed that electron-withdrawing groups capable of forming pi bonds with the benzene ring (*e.g.*, NO_2 group) placed at ortho and para positions increase the strength of aromatic carboxylic acids to a greater extent than when such groups are placed at meta position. Further, these groups when placed ortho to the carboxylic group, increase the acid strength to a greater extent than when placed para to the carboxylic group. It may be noted that the increase in acid strength in the above cases is much more than expected from the inductive effect of the NO_2 group *alone. The extra increase in strength is attributed to the resonance effect.*

The various resonance structures of benzene containing the NO_2 group are shown below :



It is evident from these resonance structures that ortho and para positions become **electron-deficient** whereas the meta position retains the original electron density. Therefore, the release of a proton from COOH group attached to an electron-deficient centre, *i.e.*, attached at ortho or para position with respect to the position of the NO_2 group, would be easier. Hence, ortho and para nitrobenzoic acids would be *stronger* than benzoic acid whereas *meta* nitrobenzoic acid would have practically the same strength as benzoic acid.

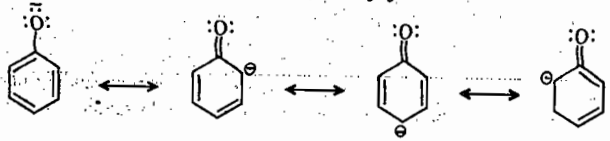
It has been further observed that ortho nitro benzoic acid is relatively stronger than para nitro benzoic acid although the electron deficiency caused by resonance effect is the same at the two positions. A question aries : Why is it so ? The answer is as follows :

In the case of nitrobenzoic acid, both the inductive as well as the resonance effects are operative. Although the resonance effect is the same, yet the inductive effect in ortho and para derivatives is different. This is because the inductive effect of NO_2 group decreases with increase in the number of bonds separating the NO_2 group from the COOH group. Hence, ortho nitrobenzoic acid is stronger than para nitrobenzoic acid.

Electron-donating substituents when placed at ortho and para positions decrease the acid strength of aromatic carboxylic acids to a greater extent than when placed at meta position. This can also be explained easily on the basis of resonance as a result of which the electron density increases at ortho and para positions making the release of proton from the COOH group more difficult.

Another interesting example, showing the effect of resonance, is furnished by the difference in the acidity of the OH group in phenol and ethanol. In phenol, the phenoxide anion formed by deprotonation is stabilised through resonance, thus, favouring the deprotonation reaction.

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$



The ethoxide anion $C_2H_5O^-$ formed by deprotonation of ethanol is not stabilised through resonance. It is, therefore, unstable and readily recaptures the proton to form C_2H_5OH which is much more stable than the $C_2H_5O^-$ ion. This explains why phenol exhibits an *acidic character* whereas ethanol is *neutral*.

Measurement of Acid-Base Strength in Gas Phase

As already mentioned, the basic character of a species in gas phase is measured in terms of its proton affinity. The proton affinity is the amount of energy released (ΔH) for the reaction

$$H^+(g) + :B^-(g) \longrightarrow H:B(g)$$

Although the energy released is given a negative sign according to thermodynamic convention, the proton affinity is always taken as positive or zero, as already mentioned. The higher the proton affinity of a species, the higher is the amount of energy released and the greater is the basic character of the species.

Similarly, the acidic character of a species in gas phase is measured in terms of the enthalpy of the reaction.

$$HX(g) \longrightarrow H^+(g) + X^-(g)$$

The more endothermic the above reaction, the weaker is the acidic character of the specie. For example, the enthalpies of dissociation of HF, HCl, HBr, HI (in gas phase) into $H^+(g)$ and $X^-(g)$ are 1550 kJ/mol, 1400 kJ/mol, 1350 kJ/mol and 1300 kJ/mol, respectively. Therefore, the order of their acidities in gas phase is :

$$HF(g) < HCl(g) < HBr(g) < HI(g)$$

The acidities of metal cations in gas phase can be measured from their electron affinities. For example, $K^+(g)$ has lower electron affinity (420 kJ/mol), compared to first electron affinity of $Ca^{2+}(g)$ (1150 kJ/mol). Therefore, the former is a weaker acid compared to the latter in gas phase.

Generalised Acid–Base Concept for Cations and Anions

According to this concept, the positivity of a cation can be measured in terms of its capability to polarise electron charge cloud of an anion and the negativity of an anion can be measured in terms of the capability of its electron charge cloud to get polarised by a cation. The magnitude of positivity of a cation determines its strength as an acid and the magnitude of negativity of an anion determines its strength as a base.

According to the above definition, a 'free' proton, which has highest charge/size ratio and hence highest polarising power, should be the strongest acid. But a proton never occurs freely. Similarly, a 'free' electron which is not bound by any nucleus and has maximum polarizability of its charge cloud by a cation should be the strongest base. Such a 'free' electron in the solvated state exists in solutions of alkali metals in liquid ammonia, THF, etc.

Calculation of Enthalpies of Acid–Base Reactions from Some Empirical Parameters

Drago and coworkers assigned numerical values to a few empirical parameters such as E_A, C_A, E_B, C_B for acidic and basic species from which the enthalpies of reactions between acids and bases can be calculated. The parameters E_A and E_B are a measure of the *susceptibility* of the reacting acidic and basic species, respectively, to undergo *electrostatic interactions* and the parameters C_A and C_B are a measure of the *susceptibility* of the reacting acidic and basic species, respectively, to undergo *covalent interactions*.

According to Drago and coworkers, the enthalpy of an acid–base reaction is given by the empirical relation :

$$-\Delta H = E_A E_B + C_A C_B$$

The enthalpies of reactions calculated by the above equation are found to be quite close to the experimental values for acid–base reactions involving molecular acidic and basic species. However, the calculated values are found to differ considerably from the experimental values for acid–base reactions involving ionic species. Drago *et al* suggested that the difference is due to the transfer of charge from base to acid during the formation of the acid–base adduct. They proposed the following modified equation for such

reactions :

$$-\Delta H = E_A E_B + C_A C_B + R_A T_B$$

where the parameter R_A reflects the receptance of electronic charge of the acid and the parameter T_B reflects the transference of electronic charge of the base. The numerical values assigned to the various parameters in kcal are available in standard books on this subject and are not reproduced here. Nevertheless, we shall illustrate the application of Drago's equation with reference to the reaction :

$$H_2O + H^+ \longrightarrow H_3O^+ ; \qquad \Delta H_{exp} = -166 \text{ kcal mol}^{-1}$$

$$\Delta H_{cal} = -(E_H^+ E_{H_2O} + C_H^+ C_{H_2O} + R_H^+ T_{H_2O})$$

$$= -(45 \times 2{\cdot}3 + 13 \times 0{\cdot}1 + 130 \times 0{\cdot}43) = -160{\cdot}7 \text{ kcal mol}^{-1}$$

As can be seen, ΔH (calculated) is quite close to ΔH (experimental).

It is pertitent to mention here that acids with large E_A form stabler adducts with bases having large E_B compared with those having small E_B. Similarly, acids with large C_A form stable adducts with bases having large C_B.

HARD AND SOFT ACIDS AND BASES. PEARSON CONCEPT

The coordination chemists have known for quite some time that while certain ligands tend to form stable complexes with heavier ions such as Ag^+, Hg^{2+}, Pd^{2+}, Pt^{2+}, etc., some other ligands prefer to form stable complexes with lighter ions such as Li^+, Be^{2+}, Al^{3+}, Sc^{3+}, etc. Based on this preferential tendency to form stable complexes, the ions as well as ligands have been classified into two categories each. While the cations (*i.e.*, Lewis acids) are categorised as **hard and soft acids**, the anions and neutral ligands are categorised as **hard and soft bases.**

A general classification of some common metal cations (*viz.*, Lewis acids) into hard and soft acids is presented in Table 1.

A general classification of some common anions (*viz.*, Lewis bases) into hard and soft bases is presented in Table 2.

A little consideration shows that while hard bases are species which cannot be easily polarised, soft bases are species which can be easily polarised. For example, the I^- ion (a soft base) has a very high polarisability. Ammonia is a hard base. However, the presence of easily polarisable aromatic ring makes both aniline and pyridine to behave as nearly soft bases.

TABLE 1

Classification of Some Common Lewis Acids as Hard and Soft Acids

Hard Acids	Soft Acids
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Hg^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, Tl^{3+}, Pt^{4+}
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	I^+, Br^+, HO^+, RO^+
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ce^{3+}	O, Cl, Br, I, N
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}	M^0 (metal atom)
UO_2^{2+}, VO_2^{2+}, MoO^{3+}	

TABLE 2

Classification of Lewis Bases as Hard and Soft Bases

Hard Bases	Soft Bases
NH_3, RNH_2, N_2H_4	H^-, R^-, C_2H_4, C_6H_6
H_2O, OH^-, O^{2-}, ROH, RO^-	CN^-, RNC, CO
CH_3COO^-, CO_3^{2-}, NO_3^-	$S_2O_3^{2-}$, SCN^-, R_3P
PO_4^{3-}, SO_4^{2-}, ClO_4^-, F^-, Cl^-	R_3As, I^-

R stands for an aryl radical

It may be pointed out that all the species mentioned in any category *are not equally hard or soft*. Thus, Cu^{2+} ion behaves as a harder acid than Mn^{2+} ion because of the smaller size of the former. Similarly, Li^+ ion is a harder acid than Cs^+ ion because of the smaller size of the former. Similarly, bases such as $C_6H_5NH_2$, $(C_6H_5)_2NH$, N_3^-, NH_3, C_6H_5N, all containing nitrogen, are not equally hard. For example, NH_3 is harder than $C_6H_5NH_2$ which, in turn, is harder than $(C_6H_5)_2NH$. In fact, $(C_6H_5)_2NH$ is a soft base.

To sum up :

Hard acids are Lewis acids which are small in size and whose electron charge clouds are not easily polarizable. These are mostly light metal ions generally associated with high positive oxidation states.

Soft acids are Lewis acids which are comparatively larger in size and whose electron charge clouds are easily polarisable. These are mostly heavy metal ions generally associated with low (or even zero) positive oxidation states.

Hard bases are Lewis bases which prefer to coordinate with hard acids. These are anions or neutral molecules which are not easily polarizable.

Soft bases are Lewis bases which prefer to coordinate with soft acids. These are anions or neutral molecules which are easily polarizable.

It is important to note, however, that there is no sharp line of demarcation between soft and hard species and a number of border line cases also exist. For instance, transition metal ions such as Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} behave as border line acids. Metals and non-metals in lower oxidation states behave as soft acids while the same species in higher oxidation states behave as hard acids.

Bonding in Hard–Hard and Soft–Soft Combinations. Since hard acids have generally vacant *d* orbitals, they can accept electrons from hard bases so that the bonding between hard acids and hard bases is predominantly *ionic*. Interaction between soft acids and soft bases occurs mostly through pi bonding so that the bonding between soft acids and soft bases is largely *covalent*.

It must be clearly understood that hardness and softness of acids and bases refer only to hard–hard and soft–soft interactions. It has no relation with their strengths. For instance, both OH^- and F^- ions are hard bases but OH^- ion is several million times more basic than F^- ion. Similarly, SO_3^{2-} ion and Et_3P are both soft bases but Et_3P is 10^7 times more basic than SO_3^{2-}.

HSAB Principle. As already mentioned, in the formation of coordination complexes, *hard acids prefer to combine with hard bases whereas soft acids prefer to combine with soft bases*. This is known as **HSAB principle**. This principle does not state, however, that hard–soft or soft–hard combinations cannot exist. It only states that if there is a choice, a hard–hard or a soft–soft combination would be preferred to a soft–hard or hard–soft combination.

Applications of HSAB Principle. The HSAB principle has several applications, some of which are discussed below.

1. Stability of Complexes. Pearson (1963) explained the relative stability of complexes on the basis of HSAB principle. A complex A : B formed as follows :

$$\underset{\text{Lewis acid}}{A} + \underset{\text{Lewis base}}{:B} \longrightarrow \underset{\text{Complex}}{A:B}$$

would be more stable if A and B are either both hard or both soft.

The complex would be less stable if A is hard and B is soft or vice versa. For example, while AgI_2^- exists as a stable compound, AgF_2^- does not. The reason is as follows :

Ag^+ ion is a *soft acid*. Its interaction with I^- ion, a *soft base*, yields a stable complex AgI_2^- whereas its interaction with F^- ion, a *hard base*, yields an unstable complex, AgF_2^-.

$$\underset{\text{Soft acid}}{Ag^+} + \underset{\text{Soft base}}{2I^-} \longrightarrow \underset{\text{Stable complex}}{AgI_2^-}$$

$$\underset{\text{Soft acid}}{Ag^+} + \underset{\text{Hard base}}{2F^-} \longrightarrow \underset{\text{Unstable complex}}{AgF_2^-}$$

With similar reasoning we can explain why $[CoF_6]^{3-}$ is more stable than $[CoI_6]^{3-}$.

2. Prediction of Coordination in Complexes of Ambidant Ligands. We can predict the formation of various metal ion complexes with *ambidant ligands*. An **ambidant ligand** *is one which, although unidentate, may coordinate to the metal ion through either of its two coordinating atoms*. For example, $[SCN]^-$ is an ambidant ligand ; it coordinates through N atom to form the complex $[Co(NCS)_4]^{2-}$ whereas it coordinates through S atom to form the complex $[Pd(SCN)_4]^{2+}$. The reason for the above is as follows : Pd^{2+} is a *soft acid* so that it prefers to coordinate through the *softer* species S atom to form Pd–SCN linkage. Co^{2+} is a *hard acid* so that it prefers to coordinate through the *harder* species N atom to form the Co–NCS linkage.

3. Predicting Feasibility of a Reaction. The reaction between LiI and CsF to give LiF and CsI is an interesting example of preferential combination of soft – soft and hard – hard species :

$$\underset{\text{hard-soft}}{LiI} + \underset{\text{soft-hard}}{CsF} \longrightarrow \underset{\text{hard-hard}}{LiF} + \underset{\text{soft-soft}}{CsI}; \qquad \Delta H = -138 \text{ kJ}$$

Another example is :

$$\underset{\text{soft-hard}}{HgF_2} + \underset{\text{hard-soft}}{BeI_2} \longrightarrow \underset{\text{hard-hard}}{BeF_2} + \underset{\text{soft-soft}}{HgI_2}; \qquad \Delta H = -397 \text{ kJ}$$

Combination of hard ligands or of soft ligands with a metal ion is more favourable than the combination of a mixture of hard and soft ligands with the metal ion. With this, it is easy to understand why the complexes $[Co(CN)_5I]^{3-}$ and $[Co(NH_3)_5F]^{2+}$ are stable while the complexes $[Co(CN)_5F]^{3-}$ and $[Co(NH_3)_5I]^{2+}$ are unstable. It may be recalled that CN^- and I^- are both soft bases while NH_3 and F^- are both hard bases.

4. Prediction of Hardness and Softness. Consider a base B whose hardness or softness is to be predicted. If the equilibrium :

$$[BH]^+ + \underset{\text{Soft acid}}{[CH_3Mg]^+} \rightleftharpoons [CH_3MgB]^+ + \underset{\text{Hard acid}}{H^+}$$

shifts towards the right, then B is a *soft base* because it shows more affinity for the *soft acid* $[CH_3Mg]^+$ (*soft-soft interaction*). If the equilibrium shifts towards the left, then it is a *hard base* since it exhibits more affinity for the *hard acid* H^+ (*hard-hard interaction*).

Symbiosis. Soft ligands have a tendency to combine with a centre which is already associated with soft ligands and hard ligands have a tendency to combine with a centre which is already associated with hard ligands. This tendency has been termed as **symbiosis**. Thus, F^- ion, a hard ligand, readily combines with BF_3 to form a stable complex BF_4^-. Similarly, H^- ion, a soft ligand, readily combines with BH_3 to form a stable complex BH_4^- :

$$BF_3 + F^- \longrightarrow BF_4^-$$

$$BH_3 + H^- \longrightarrow BH_4^-$$

Mixed substituents are generally not preferred. Thus, compounds such as BF_3H^- and BH_3F^-, having mixed substituents, interact spontaneously to yield BH_4^- and BF_4^-, *i.e.*, compounds with the same substituents :

$$BH_3F^- + BF_3H^- \longrightarrow BH_4^- + BF_4^-$$

Likewise, the following reaction occurs spontaneously :

$$CH_3F + CHF_3 \longrightarrow CH_4 + CF_4$$

Basis for Hard–Hard and Soft–Soft Interactions. Several views have been put forth to explain the basis for hard–hard and soft–soft interactions. However, no single view is completely satisfactory.

According to the most accepted view, the cause of *hard–hard interaction* is an electrostatic interaction.

As already discussed, bonding between hard acids and hard bases is predominantly ionic. The electrostatic energy between a positive and a negative ion pair is inversely proportional to the internuclear distance. Therefore, the smaller the ions, the lesser would be the internuclear distance and the greater would be the electrostatic attraction between the two ions. Consequently, the resulting compound would be highly stable.

Electrostatic interaction cannot explain the *soft–soft interaction* because the sizes of soft species are comparatively very large. Polarisation of the species, however, plays an important role in explaining their interactions. Most of the soft acids have 6 to 10 *d* electrons in their electronic configurations. These electrons get easily polarised favouring covalent bonding between them and the soft bases which are also easily polarisable (recall covalent bonding between Li^+ and I^- ions due to polarisation of I^- ion). Thus, bonding between soft acids and soft bases is assumed to be *largely covalent*.

Considering hard–hard interactions as ionic and soft–soft interactions as covalent, Misons and coworkers (1967) proposed the following relation which can tell whether a given species is hard or soft :

$$pK = -\log K = aX + bY + c$$

where K is the equilibrium constant for the dissociation of the metal–ligand (*i.e.*, acid–base) complex ; X, Y are parameters for the metal ions, *i.e.*, acids ; a, b are parameters for the ligands *i.e.*, bases and c is a constant required to adjust the pK values in such a way that all of them lie on the same scale.

The values of parameter Y for some of the cations are given below :

Hard acids :	Li^+,	Al^{3+},	Mg^{2+},	Na^+,	Ca^{2+},	Fe^{3+},	Co^{2+},	Cs^+,	Co^{2+}
	0·36	0·70	0·87	0·93	1·62	2·37	2·56	2·73	2·96
Soft acids :	Sn^{2+},	Tl^{3+},	Cu^+,	Pb^{2+},	Tl^+,	Hg^{2+},	Au^+		
	3·17	3·2	3·45	3·58	3·78	4·25	5·95		

If the value of Y is less than 2·8 , the acid is hard and if the value is more than 3·2 , the acid is soft.

The value of parameter b for some of the bases are given below :

Hard Bases			Soft Bases		
OH^-	NH_3	Cl^-	Br^-	I^-	$S_2O_3^{2-}$
0·40	1·08	2·49	5·58	7·17	12·4

The value of b, evidently, increases with the softness of the base. If the value is less than 3, the base is hard and if the value is more than 5, the base is soft.

In a similar manner, the values of X and a also give rough information about the hardness and softness of the species.

In **soft–soft interactions**, the contribution of pi bonding is also important. Soft acids are generally metals in low oxidation states and thus have a strong tendency to form pi bonds with soft bases which are also good pi bonding ligands. The polarizability of soft acids and soft bases further favours pi bonding.

To sum up : *While hard–hard interactions are ionic, soft–soft interactions are predominantly covalent involving pi bonding as well.*

QUESTIONS

1. (*a*) How are acids and bases defined in terms of (*i*) Arrhenius concept and (*ii*) Bronsted–Lowry concept ? Give suitable examples.

   (*b*) Comment on the statement, "All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases."

2. (*a*) What do you understand by conjugate acid–base pairs ? Show that a strong acid has a weak conjugate base and a weak acid has a strong conjugate base.

(*b*) Give examples to show that water can behave both as an acid and a base under suitable conditions.

3. (*a*) Discuss briefly the solvent–system concept of acids and bases. What are the limitations of this concept ?

(*b*) The liquid ammonia solution of phenolphthalein is colourless but becomes red on the addition of $NaNH_2$. Explain.

(c) Define an acid and a base according to Lux–Flood concept.

4. (*a*) What is Lewis concept of acids and bases ?

(*b*) Which of the following can act as Lewis acids :

(*i*) H_2O (*ii*) $CaCl_2$ (*iii*) SO_3 (*iv*) OH^- (*v*) CO_2 (*vi*) Ag^+

5. (*a*) What are Lewis acids ? Arrange the following in the order of increasing acid strength :

(*i*) BCl_3, BI_3, BF_3 (*ii*) $SnCl_2$, $SnCl_4$ (*iii*) BF_3, B_2H_6, BPh_3

(*b*) What are Lewis bases ? Arrange the following in the order of decreasing base strength :

(*i*) NH_3 , PH_3 , AsH_3 (*ii*) NH_3, NCl_3 , NF_3

(*c*) NH_3, $(CH_3)_2NH$, CH_3NH_2, $(CH_2)_3N$

6. Illustrate the effect of substituents on relative strengths of acids and bases.

7. Discuss the effect of solvent on relative strengths of acids and bases.

8. What is meant by levelling effect ? Explain this effect on the basis of solvent-system concept of acids and bases.

9. (*a*) Explain Person's concept of hard and soft acids. Give examples.

(*b*) What are the characteristics of a hard acid, soft acid, hard base and soft base ?

10. Explain HSAB princple. Discuss its applications.

11. (*a*) Explain clearly why hard acids coordinate with hard bases and soft acids coordinate with soft bases.

(*b*) What is symbiosis ? Give examples. What are its applications ?

12. Give reasons for the following :

(*i*) AgI_2^- complex is stable but AgF_2^- is not. (*ii*) $[Co(NH_3)_5F]^{2+}$ complex is stable while $[Co(NH_3)_5I]^{2+}$ complex is unstable. (*iii*) CsF reacts with LiI even though both are ionic. (*iv*) BF_3 readily combines with F^- to form stable complex BF_4^-. (*v*) CH_3F and CHF_3 react to form CH_4 and CF_4.

13. (*a*) "While hard–hard interactions are generally ionic, soft—soft interactions are generally covalent." Why is it so?

(*b*) Discuss the contribution of pi bonding in soft–soft interaction.

9 OXIDATION AND REDUCTION

The concept of oxidation and reduction is very important because oxidation and reduction reactions are frequently encountered in our daily life. Rusting of iron articles, generation of electricity in batteries, extraction and purification of metals, etc., are common examples of such reactions.

According to classical concepts, oxidation is defined as a reaction which involves addition of oxygen (or any other electronegative element) or removal of hydrogen (or any other electropositive element). In a general sense, **oxidation** is defined as a reaction which involves loss of electrons by an atom or a group of atoms and **reduction** is defined as a reaction which involves gain of electrons by an atom or a group of atoms. A substance which can accept one or more electrons is called an **oxidising agent** and a substance which can furnish one or more electrons is called a **reducing agent.** The substance which loses electrons is said to be *oxidised* and a substance which gains electrons is said to be *reduced.*

Oxidation Number (Oxidation State)

The term oxidation number (or oxidation state) is now used instead of valency to describe the combining capacity of an element in a compound. The **oxidation number** (or **oxidation state**) of an element is defined as the charge which an atom of the element appears to have when the electrons on the atom are counted according to the following conventions :

1. Electrons shared between two like atoms are divided equally between the sharing atoms.

2. Electrons shared between two unlike atoms are counted with the more electronegative atom.

In the case of electrovalent compounds, the oxidation number of an element is the same as the charge on its ion. As a general rule, the algebraic sum of oxidation numbers of all the atoms in the formula for any electrovalent compound is zero.

Based on the above conventions, the following **operational rules** have been derived which permit easy calculation of oxidation numbers :

1. The oxidation number of each element in the uncombined state is zero.

2. The oxidation number of an ion is the same as its charge.

3. The sum of the oxidation numbers of all the atoms in the formula for a neutral compound is zero.

4. In all hydrogen compounds (except hydrides of active metals), the oxidation number of hydrogen per atom is +1.

5. In all oxygen compounds (except hydrogen peroxide and other peroxides and superoxides), the oxidation number of oxygen per atom is – 2.

A given species is said to be oxidised if its oxidation number increases and is said to be reduced if its oxidation number decreases.

Galvanic Cells. A galvanic cell is a device in which chemical energy *is converted into electrical energy.* Such a cell, usually, consists of two electrodes immersed in one or more suitable electrolytes. When the electrodes are connected externally through a copper wire and internally through a salt bridge, a chemical reaction occurs in the cell involving *oxidation* at one electrode and *reduction* at the other electrode. According to the latest convention, the electrode at which oxidation occurs is called the **anode** while the electrode at which reduction occurs is called the **cathode.**

Consider, for instance, a copper rod dipping in a solution of copper sulphate and a zinc rod dipping in a solution of zinc sulphate, as in the **Daniell cell.** The two metal rods are connected through an ammeter and the two solutions are connected through a salt bridge, *i.e.*, an inverted U-shaped glass tube filled with a solution of potassium chloride, as shown in Fig. 1.

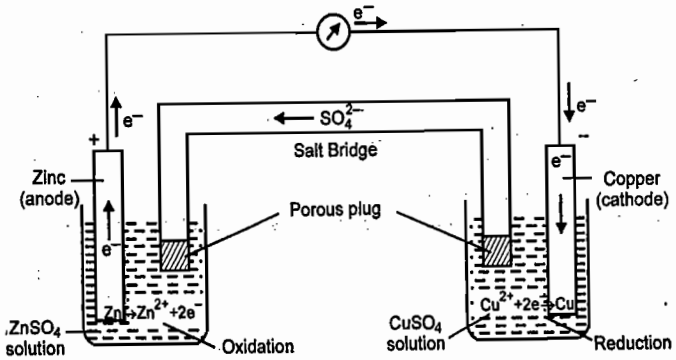


Fig. 1. Production of electricity in a galvanic cell.

As soon as the circuit is closed, current starts flowing which is indicated by deflection in the ammeter. The flow of current is accompanied by the following processes :

The zinc metal passes into the solution as Zn^{2+} ions liberating two electrons ($Zn \longrightarrow Zn^{2+} + 2e^-$). The process involves *oxidation*. The liberated electrons move into the ammeter and then enter the copper rod. Cu^{2+} ions extract two electrons each from the copper rod and are discharged as copper metal on the copper electrode ($Cu^{2+} + 2e^- \longrightarrow Cu$). The process involves *reduction*. The overall chemical reaction taking place in the cell, usually called the **cell reaction**, is, thus,

$$Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

Since in this case electrons are generated at the zinc electrode and consumed at the copper electrode, the flow of electrons in the cell is from the zinc electrode to the copper electrode as shown. The SO_4^{2-} ions left unpaired due to the discharge of their partners (*viz.*, the Cu^{2+} ions) as copper, migrate to the other side through the salt bridge as shown in Fig. 1 and become available there for pairing with the Zn^{2+} ions produced by the oxidation of zinc. Thus, while electrons move from the zinc rod to the copper rod in the outside circuit, the SO_4^{2-} ions move through the salt bridge in *opposite* direction as shown. This completes the electric circuit of the cell.

With the passage of time there is more and more depletion of Cu^{2+} ions due to their reduction to Cu and more and more generation of Zn^{2+} ions due to the oxidation of Zn. Both these factors push the cell reaction backwards (Le Chatelier's principle). Ultimately, a state of equilibrium is reached after which the flow of electricity from the cell stops. In order to rejuvinate the cell, we add more of $CuSO_4$ and/or replace $ZnSO_4$ partly by H_2SO_4.

Single Electrode Potential

As is well known, each galvanic cell is made up of two electrodes. At one electrode, oxidation takes place, *i.e., electrons are evolved.* At the other electrode, reduction takes place, *i.e., electrons are taken up.*

The **tendency** *of an electrode to lose or gain electrons when it is in contact with its own ions in solution,* is called **electrode potential.** Since the tendency to gain electrons means also the *tendency to get reduced,* this tendency is called **reduction potential.** Similarly, the *tendency to lose electrons* means *the tendency to get oxidised.* Hence, this tendency is called **oxdiation potential.** Needless to mention that oxidation potential is the reverse of reduction potential. Thus, if the reduction potential of an electrode under given conditions is 1·5 volts, then its oxidation potential is taken as – 1·5 volts and *vice-versa.*

It is not possible to determine experimentally the potential of a single electrode (*i.e.*, of a half-cell). It is only the difference of potentials between the two electrodes that we can measure by combining them to give a complete cell. By arbitrarily fixing potential of one electrode as zero (just as the freezing point of water at atmospheric pressure is arbitrarily fixed as zero on the temperature scale), it is possible to assign numerical values to potentials of the various other electrodes. Conventionally, the potential of a reversible hydrogen electrode in which the gas at one atmospheric pressure is bubbled through a solution of hydrogen ions of unit activity (or, to be approximate, 1 M concentration) has been fixed as zero. This electrode is known as **standard hydrogen electrode** and is represented as

$$Pt\,;\,H_2\,(g)\,(1\text{ atm}),\ H^+\,(aq)\,(c = 1\text{ M})$$

All other single electrode potentials measured with respect to standard hydrogen electrode are referred to as *potentials on the hydrogen scale.*

If it is required to find the electrode potential of, say, zinc electrode dipping in a solution of zinc sulphate (*i.e.*, Zn, Zn^{2+} electrode), all that is needed is to combine it with the standard hydrogen electrode so as to have a complete cell represented as :

$$Zn,\ Zn^{2+}\text{ solution}\,||\,H_2\,(g)\,(1\text{ atm})\,;\,H^+\,(aq)\,(c = 1\text{ M})\,;\,Pt$$

The EMF of the cell, determined potentiometrically, gives the potential of the zinc electrode (on the hydrogen scale) since potential of the standard hydrogen electrode is taken as zero.

Sign of Electrode Potential. According to the latest convention adopted by IUPAC (International Union of Pure and Applied Chemists), the electrode potential is given a *positive sign* if the electrode reaction involves *reduction* when connected to the standard hydrogen electrode and a *negative sign* if the electrode reaction involves *oxidation* when connected to the standard hydrogen electrode whose potential is taken arbitrarily as zero.

Thus, when copper electrode (copper rod dipping in a solution of a copper salt) is connected with a standard hydrogen electrode, *reduction* takes place at the copper electrode. The electrode reactions are as follows :

Copper electrode : $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu\,(s)$ (Reduction)

Hydrogen electrode : $H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$ (Oxidation)

Hence, according to the above convention, the potential of copper electrode is taken as *positive.* Thus, $E_{(Cu^{2+},Cu)}$ is positive.

However, if zinc electrode is connected with the standard hydrogen electrode, *oxidation* takes place at the zinc electrode. The electrode reactions are now as follows :

Zinc electrode : $Zn\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2e^-$ (Oxidation)

Hydrogen electrode : $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ (Reduction)

Hence, the potential of the zinc electrode is taken as *negative.* Thus, $E_{(Zn^{2+},Zn)}$ is negative.

Standard Electrode Potentials. The Electrochemical Series

The potential of an electrode, at a given temperature, depends upon the concentration of the ions in the surrounding solution. If the concentration of the ions is unity and the temperature is 25°C, the potential of the electrode is termed as the **standard electrode potential,** E°_{el}). Further, it is assumed that the electrode is working in a thermodynamically reversible manner.

The standard electrode potentials of a number of electrodes are given in Table 1. These values are said to be **on hydrogen scale** since in these determinations the potential of the standard hydrogen electrode, used as the reference electrode, has been taken as zero. The standard reversible electrode potentials arranged in the decreasing order as shown in Table 1 is called the **electrochemical series.**

Adopting the latest convention, the electrode reactions, *i.e.*, the half-cell reactions are written as reduction reactions. The oxidised and reduced species involved in a half-cell reaction (such as Cu^{2+}, Cu ; H^+, H_2, Zn^{2+}, Zn, etc.) are termed as **redox couples.** It may be mentioned, however, that in inorganic chemistry, the discussions are based on oxidation potentials rather than on reduction potentials.

TABLE 1
Electrochemical Series. Standard Electrode Potentials

Electrodes	Electrode Reactions	E°_{el} (volts)
$F_2(g)$, $2F^-$	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2·87
Co^{3+}, Co^{2+} ; Pt	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1·82
Ce^{4+}, Ce^{3+} ; Pt	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	+1·71
Mn^{2+}, MnO_4^- ; Pt	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1·51
Au^{3+}, Au	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1·50
$Cl_2(g)$, $2Cl^-$; Pt	Cl_2 (g, 1atm) $+ 2e^- \rightleftharpoons 2Cl^-$	+1·36
Cr^{3+}, $Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1·33
$Br_2(l)$, $2Br^-$: Pt	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1·06
Hg^{2+}, Hg_2^{2+} : Pt	$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0·92
Ag^+, Ag	$Ag^+ + e^- \rightleftharpoons Ag$	+0·80
Fe^{3+}, Fe^{2+} : Pt	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0·77
$Hg_2SO_4(s)$, SO_4^{2-} ; Hg	$Hg_2SO_4(s) + 2e^- \rightleftharpoons 2Hg + SO_4^{2-}$	+0·61
$I_2(s)$, $2I^-$; Pt	$I_2(s) + 2e^- \rightleftharpoons 2I^-$	+0·53
Cu^+, Cu	$Cu^+ + e^- \rightleftharpoons Cu$	+0·52
Cu^{2+}, Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0·34
$Hg_2Cl_2(s)$, Cl^-; Hg	$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	+0·28
AgCl (s), Cl^-; Ag	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0·22
Sn^{4+}, Sn^{2+} ; Pt	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0·15
Cu^{2+}, Cu^+	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0·15
$Hg_2Br_2(s)$, Br^-; Hg	$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg + 2Br^-$	+0·13
AgBr (s), Br^-; Ag	$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	+0·07
$2H^+$, $H_2(g)$; Pt	$2H^+ + 2e^- \rightleftharpoons H_2$ (g, 1atm)	0·00
Pb^{2+}, Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0·13
Sn^{2+}, Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0·15
AgI (s), I^-; Ag	$AgI(s) + e^- \rightleftharpoons Ag + I^-$	−0·15
Ni^{2+}, Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0·24

(*Continued*)

Electrodes	Electrode Reactions	E°_{el} (volts)
Co^{2+}, Co	$Co^{2+} + 2e^- \rightleftharpoons Co$	−0·27
Cd^{2+}, Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0·40
Fe^{2+}, Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0·44
Cr^{3+}, Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0·74
Zn^{2+}, Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0·76
Mn^{2+}, Mn	$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1·18
Al^{3+}, Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1·66
Mg^{2+}, Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2·52
Na^+, Na	$Na^+ + e^- \rightleftharpoons Na$	−2·71
Ca^{2+}, Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	−2·87
Ba^{2+}, Ba	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	−2·90
K^+, K	$K^+ + e^- \rightleftharpoons K$	−2·92
Li^+, Li	$Li^+ + e^- \rightleftharpoons Li$	−3·04

Nernst Equation

As mentioned above, the standard electrode potentials given in Table 1 are those when the concentration of the ions in solution is 1 M. The electrode potential would be different if the concentration is different from 1 *M*.

The EMF (*E*) of a reversible cell involving the cell reaction

$$lL + mM \rightleftharpoons xX + yY$$

is given by the relation :

$$E = E^\circ - \frac{RT}{nF} \ln Q \qquad ....(1)$$

where $Q = [X]^x[Y]^y / [L]^l[M]^m$ is called the **reaction quotient** of the concentrations of the reactants and the products at any stage of the cell reaction. E° is the standard EMF of the cell when the concentrations of the species involved are 1 M each.

The electrode potential E_{el} of a metal M in contact with M^{n+} ions involving the electrode reaction :

$$M^{n+} + ne^- \rightleftharpoons M(s)$$

would thus be given by

$$E_{el} = E^\circ_{el} - \frac{RT}{nF} \ln \frac{[M(s)]}{M^{n+}(aq)} \qquad ...(2)$$

$$= E^\circ_{el} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \qquad [(\because [M(s)] \text{ is taken as unity})]$$

$$= E^\circ_{el} + \frac{RT}{nF} \ln [M^{n+}] = E^\circ_{el} + \frac{0{\cdot}0591}{n} \log [M^{n+}] \text{ at } 25°C \qquad ...(3)$$

where E°_{el} is the standard electrode potential of the electrode M^{n+},M and *n* is the number of electrons involved in the redox reaction. The above equation which gives the effect of concentration of M^{n+} ions on the potential of M^{n+},M electrode is known as the **Nernst equation.**

Thus, for the hydrogen electrode for which the half-cell reaction is

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g)$$

the potential of the electrode is given by

$$E_{el} = E^{\circ}_{el} + 0{\cdot}0591 \log [H^+]$$

$$= 0{\cdot}0591 \log [H^+] = -0{\cdot}0591\, pH \text{ at } 25°C \qquad ...(4)$$

because E°_{el} for hydrogen electrode is arbitrarily taken as zero.

Similarly, for silver electrode for which the half-cell reaction is

$$Ag^+ (aq) + e^- \rightleftharpoons Ag (s),$$

the potential of the electrode is given by

$$E_{el} = E^{\circ}_{el} + 0{\cdot}0591 \log [Ag^+]$$

where $E^{\circ}_{el} = 0{\cdot}80$ V (Table 1).

Source of Electrical Energy in a Galvanic Cell

The electrical energy produced by a galvanic cell is given by the product of its electromotive force and the quantity of electricity which passes. If EMF is measured in volts and quantity of electricity in coulombs, the electrical energy is obtained in volt-coulombs or joules (volt-coulomb = joule). Till about the middle of the nineteenth century it was generally believed that electrical energy of a reversible cell originated from the *decrease in the enthalpy* ($-\Delta H$) of the cell reaction. This view received support from the fact that the enthalpy of the reaction :

$$Zn (s) + Cu^{2+} (aq) \rightleftharpoons Zn^{2+} (aq) + Cu (s)$$

taking place in the Daniell cell is about 210000 joules which is quite close to the value 212300 joules obtained by the product of EMF (1·1 volt) and the quantity of electricity passed (2×96500 coulombs). However, it was pointed out by Gibbs, and independently by Helmholtz, that the **electrical energy** in a galvanic cell originates from the *decrease in free energy* of the reaction occurring in the cell.

Suppose, n is the number of electrons involved in a particular cell reaction. Then, evidently, n faradays of electricity will be generated in the complete reaction. If E is the EMF of the cell, then

Electrical energy supplied by the cell = nFE

If $-\Delta G$ is the decrease in the free energy of the cell reaction, then

$$-\Delta G = nFE \qquad ...(5)$$

If $E°$ is the standard EMF of the cell, then the standard decrease in free energy would be given by

$$-\Delta G° = nFE° \qquad ...(6)$$

Application of Electrochemical Series to check Feasibility of Chemical Reactions

1. Suppose we want to know whether zinc and silver would react with dilute sulphuric acid or not. The reaction of zinc with dilute sulphuric acid may be represented as

$$Zn + H_2SO_4 \rightleftharpoons ZnSO_4 + H_2 (g)$$

or

$$Zn (s) + 2H^+ (aq) \rightleftharpoons Zn^{2+} (aq) + H_2 (g)$$

The above reaction may be split into two half-cell reactions, as represented below :

Oxidation half-cell reaction : $Zn (s) \rightleftharpoons Zn^{2+} (aq) + 2e^-$

Reduction half-cell reaction : $2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$

Since, as a convention, in a galvanic cell, oxidation occurs at the left hand electrode and reduction at the right hand electrode, the cell involving the above reaction is written as

$$Zn, Zn^{2+} (aq) \parallel H^+ (aq), H_2 (g) ; Pt$$

Therefore, the EMF of the cell would be given by

$$E° = E^{\circ}_R - E^{\circ}_L = 0 - (-0{\cdot}76 \text{ V}) = +0{\cdot}76 \text{ V} \qquad \text{(Table 1)}$$

Since $E°$ is positive, $\Delta G°$ ($= -nFE°$) is *negative*. Hence, the reaction of zinc with sulphuric acid *is feasible, i.e.*, Zn will react with H_2SO_4.

Now let us consider the reaction of silver with dilute sulphuric acid :

$$2Ag + H_2SO_4 \rightleftharpoons Ag_2SO_4 + H_2 (g)$$

or

$$2Ag (s) + 2H^+ (aq) \rightleftharpoons 2Ag^+ (aq) + H_2 (g)$$

Following the same procedure as given above, the cell involving above reaction should be written as

$$Ag, Ag^+ (aq) \parallel H^+ (aq), H_2 (g) ; Pt$$

$$\therefore \quad E° = E^{\circ}_R - E^{\circ}_L = 0 - (+0{\cdot}08 \text{ V}) = -0{\cdot}80 \text{ V} \qquad \text{(Table 1)}$$

Since $E°$ is negative, value of $\Delta G°$ ($= -nFE°$) is *positive*. Hence, the reaction of silver with sulphuric acid is *not feasible, i.e.*, Ag will not react with H_2SO_4.

2. Suppose we want to know whether on mixing H_2O_2 with Fe^{2+} (*aq*), the oxidation of Fe^{2+} (*aq*) to Fe^{3+} (*aq*) will take place or not.

The reaction involving the oxidation of Fe^{2+} (*aq*) to Fe^{3+} (*aq*) with H_2O_2 may be represented as follows :

$$H_2O_2 + 2H^+ (aq) + 2e^- \rightleftharpoons 2H_2O ; \qquad E^{\circ}_{el} = +1{\cdot}77 \text{ V}$$

$$Fe^{2+} (aq) \rightleftharpoons Fe^{3+} (aq) + e^- ; \qquad E^{\circ}_{el} = -0{\cdot}77 \text{ V}$$

Overall reaction would be

$$H_2O_2 + 2H^+ (aq) + 2Fe^{2+} (aq) \rightleftharpoons 2H_2O + 2Fe^{3+} (aq) ; \qquad E° = +1{\cdot}00 \text{ V}$$

Since $E°$ is positive, $\Delta G°$ would be negative. Hence, oxidation of Fe^{2+} (*aq*) to Fe^{3+} (*aq*) will be feasible.

Hydrogen Overvoltage

Consider electrolysis of a solution which is 1 M with respect to H^+ ions. As can be seen from Table 1, the reversible standard potential of hydrogen is zero. Hence, H^+ ions should be discharged at zero potential to liberate hydrogen gas. However, this does not happen. The potential at which H_2 gas is actually evolved using any of the common metals as cathode is considerably higher than the reversible potential of hydrogen electrode. *The difference between the potential of the electrode at which H_2 gas is actually evolved and the theoretical (i.e., reversible) potential of hydrogen electrode is called* ***hydrogen overvoltage.***

Hydrogen overvoltage varies from metal to metal. Thus, hydrogen overvoltage on nickel, lead and mercury is 0·22 V, 0·64 V and 0·80 V, respectively. The origin of this phenomenon is not exactly known.

Problem. A zinc rod is placed in 1M aqueous solution of $ZnSO_4$. Hydrochloric acid is added to this solution. Will there be evolution of H_2 gas if the concentration of H^+ ions in solution is (*A*) 1 M, (*B*) 10^{-4} M at 25°C ?

Solution : The reaction involved in the evolution of H_2 gas is

$$Zn (s) + 2H^+ (aq) \rightleftharpoons Zn^{2+} (aq) + H_2 (g)$$

Case *A* : The two half-cell reactions in this case can be written as

(*i*) $\underset{1\,M}{2H^+ (aq)} + 2e^- \rightleftharpoons H_2 (g) ;$ $\quad E = E° = 0$ (Table 1)

(*ii*) $\underset{1\,M}{Zn^{2+} (aq)} + 2e^- \rightleftharpoons Zn (s) ;$ $\quad E = E° = -0{\cdot}76$ V (Table 1)

Subtracting Eq. (*ii*) from Eq. (*i*) and rearranging, we get

$$2H^+(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + H_2(g); \qquad E = 0 - (-0{\cdot}76) = +0{\cdot}76\ V$$

Since E for the reaction is positive, hence ΔG (= $-nFE$) is negative and, therefore, the reaction is thermodynamically feasible. Since the overvoltage of H_2 on zinc is about 0·70 V, there would be rapid evolution of H_2 gas.

Case *B* : The two half-cell reactions in this case are :

(*i*) $$\underset{(10^{-4}\ M)}{2H^+(aq)} + 2e^- \rightleftharpoons H_2(g); \qquad E = E^\circ + \frac{0{\cdot}0591}{2}\log(10^{-4})^2$$

$$= 0 + \frac{2 \times 0{\cdot}0591}{2} \times (-4) = -0{\cdot}2364\ V$$

(*ii*) $$\underset{1\ M}{Zn^{2+}(aq)} + 2e^- \rightleftharpoons Zn(s); \qquad E = E^\circ = -0{\cdot}76\ V$$

Subtracting Eq. (*ii*) from Eq. (*i*) and rearranging, we get

$$2H^+(aq) + Zn(s) \rightleftharpoons Zn(aq) + H_2(g); \ E = -0{\cdot}2364 - (-0{\cdot}76) = +0{\cdot}5236\ V$$

Although the reaction is thermodynamically feasible (since E is positive and hence ΔG is negative), yet there would be no reaction between Zn(*s*) and H^+ ions, *i.e.*, there would be no evolution of H_2 gas (in spite of the solution being acidic) because the hydrogen discharge potential (0·5236 V) is lower than the hydrogen overvoltage (~ 0·70 V).

Oxygen Overvoltage

The evolution of oxygen on metal anodes also involves overvoltage. The value varies from metal to metal. Thus, oxygen overvoltage on iron, platinum and lead is 0·24, 0·43 and 0·32 V, respectively.

Redox Stability in Water

The stability of an ion or a molecule in a solution depends upon the solvent as also on other solutes including oxygen that may be present in the solution. This is because the ion or the molecule may be destroyed by oxidation or reduction brought about by the solvent or by the other species present in the solution. For instance, metals such as Na, K, Ca, Sc, etc., get oxidised by water or H^+ions liberating hydrogen :

$$M(s) + H_2O(l) \longrightarrow M^+(aq) + \tfrac{1}{2}H_2(g) + OH^-(aq)$$

$$M(s) + H^+(aq) \longrightarrow M^+(aq) + \tfrac{1}{2}H_2(g)$$

and ions such as Co^{3+} get reduced by water liberating oxygen :

$$4\,Co^{3+}(aq) + 2H_2O(l) \longrightarrow 4Co^{2+}(aq) + 4H^+(aq) + O_2(g)$$

It follows from above that water can act as an oxidising agent as well as a reducing agent. In the former case, it is reduced to H_2 and in the latter case it is oxidised to O_2.

The reduction of water, in effect, means reduction of H^+ ions which, in accordance with Nernst equation, may be represented as

$$2H^+(aq) + 2e^- \longrightarrow H_2(g); \qquad E = -(0{\cdot}0591\ V)\,pH \quad \text{(Eq. 4)} \qquad ...(7)$$

Since there is hydrogen overvoltage, E required for the liberation of H_2 would be a little more negative than – 0·6591V at $pH = 1$ and a little more negative than – 0·6 V at $pH = 0$. This means that the species with redox potentials more negative than – 0·6591 V at pH=1 as, for example, Na (E = – 2·71 V), Ca (E = –2·87 V), Li (E = – 3·04V), would get oxidised by water or H^+ ions.

When water acts as a reducing agent, it itself gets oxidised to oxygen ($2H_2O(l) \longrightarrow O_2 + 4H^+ + 4e^-$), as already mentioned. Following the convention of writing all half-cell reactions as reduction reactions, the above reaction may be represented as

$$O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O(l); \qquad E = 1{\cdot}23\ V - (0{\cdot}0591\ V)\,pH \qquad ...(8)$$

$$= 1{\cdot}23\ V \text{ at } pH = 0$$

(since E° in this reaction is +1·23 V)

Since there is oxygen overvoltage, the value of E required for the liberation of O_2 would be accordingly higher. This means that species with redox potentials higher than about + 1·5 V at $pH = 0$ [as, for example, the redox couples Co^{3+},Co^{2+} (E = + 1·82 V) and Ce^{4+},Ce^{3+} (E = + 1·71 V)] would get reduced by water.

The variation of reduction potential of H^+ ions to give H_2 and of oxidation potential of H_2O to give O_2 with change in pH of the solution, not taking into consideration hydrogen overvoltage or oxygen voltage, is shown in Fig. 2 by full lines *CD* and *AB*, respectively.

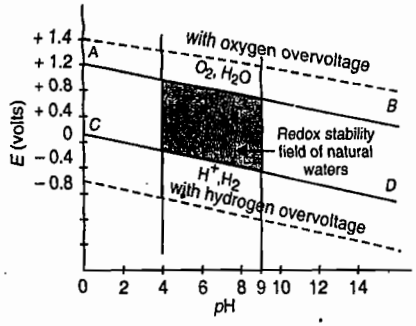


Fig. 2. The redox stability field of natural waters.

It readily follows that redox couples whose redox potentials lie above the upper line *AB* would oxidise water liberating oxygen and redox couples whose redox potentials lie below the line *CD* would reduce water (H^+ ions) liberating hydrogen. Thus, any species having redox potential higher than that given by Eq. 8 would oxidise H_2O to O_2. Similarly, any species having redox potential more negative than that given by Eq. 7, would reduce H^+ ions to H_2. Two vertical lines are drawn at pH 4 and pH 9 which mark the limits on pH values that commonly prevail in water obtained from lakes and rivers (natural waters). The stability field of water shown by shaded area in the figure depicts the range of values of redox potentials and pH values for which water is thermodynamically stable towards both oxidation and reduction. This shows that redox couples whose redox potentials and pH values lie within the stability field of water are stable. They are not destroyed by the oxidising or the reducing action of water.

If hydrogen overvoltage and oxygen overvoltage are also taken into consideration, the stability field of water would get extended on the upper as well as on the lower side, as shown in the figure by broken lines.

Disproportionation

Disproportionation is defined as a reaction in which the oxidation number of an element is raised and lowered simultaneously. In other words, the element undergoing disproportionation acts as its own oxidising and reducing agent. $Cu^+(aq)$, for instance, disproportionates into $Cu^{2+}(aq)$ and Cu(*s*) :

$$Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$$

The above reaction is the difference of the following two reduction half reactions of the cell $Cu^+, Cu^{2+} \| Cu^+, Cu$

$$Cu^+(aq) + e^- \longrightarrow Cu(s); \text{ (at Reduction half cell)} \qquad E^\circ_{cl} = 0{\cdot}52\ V$$

$$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq); \text{ (at Oxidation half cell)} \qquad E^\circ_{cl} = 0{\cdot}16\ V$$

Since E° (= 0·52 – 0·16 = 0·36 V) is positive, the disproportionation reaction is spontaneous. This explains why Cu^+ ion is unstable in aqueous solution.

Oxidation by Atmospheric Oxygen

When a solute in solution is exposed to atmosphere, there is need to consider the possibility of reaction between the solute and the dissolved oxygen. Consider, for instance, a solution containing $Fe^{2+}(aq)$ out of contact with air. Since the standard redox potential of Fe^{3+}, Fe^{2+} couple lies within the stability field of water (Fig. 1), it follows that $Fe^{2+}(aq)$ should be stable in water. This is actually the case. The situation, however, becomes different if the solution is exposed to air (O_2) because there is now a possibility that $Fe^{2+}(aq)$ may get oxidised to $Fe^{3+}(aq)$ by atmospheric oxygen. Let us explore this possibility.

The reaction

$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \longrightarrow 4Fe^{3+}(aq) + 2H_2O(l)$$

is the difference of the following two reduction half-reactions of the cell $Fe^{2+}, Fe^{3+} \parallel O_2(g), O^{2-}$:

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)\text{; (at reduction half cell)} \quad E_{cl} = 1{\cdot}23\ V - (0{\cdot}0591)\,pH$$

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)\text{; (at oxidation half cell)} \quad E_{cl} = +0{\cdot}77\ V$$

Accordingly, E for the complete oxidation reaction given above $= 1{\cdot}23 - 0{\cdot}77 = +0{\cdot}46$ V at $pH = 0$. Since E is positive, the oxidation of $Fe^{2+}(aq)$ by O_2 is spontaneous. Atmospheric oxidation of $Fe^{2+}(aq)$ is feasible even in neutral solution ($pH = 7$) because the potential for the reaction involving oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$, although very very small, being $+0{\cdot}05$ V, is still positive. This explains why $Fe^{3+}(aq)$ is the most common form of iron present in the Earth's crust as also in sediments deposited from aqueous environments.

Consider now the atmospheric oxidation of copper in damp environment. The reaction

$$2Cu(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Cu^{2+}(aq) + 2H_2O(l)$$

is the difference of the following two reduction half reactions of the cell $Cu, Cu^{2+} \parallel O_2(g), O^{2-}$:

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)\text{; (at reduction half cell)} \quad E_{cl} = 1{\cdot}23\ V - (0{\cdot}0591)\,pH$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu\text{; (at oxidation half cell)} \quad E_{cl} = +0{\cdot}34\ V$$

Evidently, for the complete oxidation reaction given above, $E = 1{\cdot}23 - 0{\cdot}34 = +{\cdot}89$ V at $pH = 0$ and $+0{\cdot}48$ V at $pH = 7$.

Hence, the oxidation of copper to Cu^{2+} is spontaneous in solutions which are neutral ($pH = 7$) or acidic ($pH = 0$). If the atmosphere contains CO_2 and SO_2, Cu^{2+} ions would be converted to $CuCO_3$ and $CuSO_4$, respectively. Thus, the copper roofs get covered by a green layer of a mixture of $CuCO_3$ and $CuSO_4$ in damp environments.

Oxidation of magnesium and aluminium in moist air is also spontaneous. However, these metals can last for years in the presence of air and water. This is due to the formation of impervious layers of oxides on their surface which protect the metals from further attack. In such cases, the metals are said to be **passivated.**

Role of Redox Potentials in the Extraction of Metals. This aspect has been discussed in details with the help of the Ellingham diagram in the next chapter on Metals and Metallurgy.

Diagrammatic Presentation of Potential Data

There are several diagrammatic presentations which give summaries of useful redox potential data depicting relative stabilities of compounds in which one element exists in a series of different oxidation states. Two such diagrammatic presentations are the **Latimer diagrams** and the **Frost diagrams.** These diagrams furnish a good deal of information in a compact form.

Latimer Diagrams

As mentioned above, a Latimer diagram for an element presents redox potential data for a series of compounds of an element in which the element is in different states of oxidation. The most highly oxidised form of the element is placed on the left. In species placed on the right the element has successively lower oxidation states. The **Latimer diagram for chlorine** in acidic solution, for example, is

$$\underset{+7}{ClO_4^-} \xrightarrow{+1{\cdot}20} \underset{+5}{ClO_3^-} \xrightarrow{+1{\cdot}18} \underset{+3}{HClO_2} \xrightarrow{+1{\cdot}65} \underset{+1}{HClO} \xrightarrow{+1{\cdot}67} \underset{0}{Cl_2} \xrightarrow{+1{\cdot}36} \underset{-1}{Cl^-}$$

The redox potentials for the couples involved are written over the arrows and the oxidation numbers are written below the spieces, as shown above. The notation $ClO_4^- \xrightarrow{+1{\cdot}20} ClO_3^-$, for instance, represents the reduction half-cell reaction :

$$ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_3^-(aq) + H_2O(l)\text{;} \quad E^\circ = +1{\cdot}20\ V$$

Similarly, the notation $HClO \xrightarrow{+1{\cdot}67} Cl_2$ represents the reduction half-reaction :

$$2HClO(aq) + 2H^+(aq) + 2e^- \longrightarrow Cl_2(g) + 2H_2O(l)\text{;} \quad E^\circ = +1{\cdot}67\ V$$

A Latimer diagram is, thus, converted into a reduction half-cell reaction by including the predominant species present in acidic solution, (*viz.*, H^+ ion and H_2O) and balancing the equation by adding appropriate number of electrons. The solution in the above cases is **acidic** with $pH = 0$.

In **basic solution** corresponding to $pH = 14$ ($pOH = 0$), the Latimer diagram for chlorine is :

$$ClO_4^- \xrightarrow{+0{\cdot}37} ClO_3^- \xrightarrow{+0{\cdot}30} ClO_2^- \xrightarrow{+0{\cdot}68} ClO^- \xrightarrow{+0{\cdot}42} Cl_2 \xrightarrow{+1{\cdot}36} Cl^-$$

The notation $ClO^- \xrightarrow{+0{\cdot}42} Cl_2$ in Latimer diagram represents the reaction :

$$2ClO^-(aq) + 2H_2O(l) + 2e^- \longrightarrow Cl_2(g) + 4OH^-(aq)\text{;} \quad E^\circ = 0{\cdot}42\ V$$

In basic solution, the predominant species are OH^- and H_2O. Hence, these species are included to balance the equation for the half-cell reaction, as shown above.

To illustrate the application of Latimer diagram, we may consider the disproportionation of H_2O_2 into O_2 and H_2O under acid conditions :

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The Latimer diagram for O_2 including other species involved in the above reaction is

$$\underset{0}{O_2} \xrightarrow{+0{\cdot}70} \underset{-1}{H_2O_2} \xrightarrow{+1{\cdot}76} \underset{-2}{H_2O}$$

The half-cell reactions for the notations $H_2O_2 \xrightarrow{+1{\cdot}76} H_2O$ and $O_2 \xrightarrow{+0{\cdot}70} H_2O_2$ may be written as

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)\text{; (at reduction half cell)} \quad E^\circ = +1{\cdot}76\ V$$

$$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)\text{; (at oxidation half cell)} \quad E^\circ = +0{\cdot}70\ V$$

The difference of the two half-cell reactions (of the cell $H_2O_2, O_2 \parallel H_2O_2, H_2O$) gives

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)\text{;} \quad E^\circ = +1{\cdot}06\ V$$

Since E° is positive, the disproportionation reaction is spontaneous. This explains why an aqueous solution of H_2O_2 in acidic solutions decomposes spontaneously to give H_2O and O_2.

A Latimer diagram can also help in calculating E° for a redox reaction which involves non-adjacent members of the Latimer diagram.

Suppose we want to find out E° for the reaction,

$$\underset{+7}{HClO_4} + 4H^+ + 4e^- \longrightarrow \underset{+3}{HClO_2} + 2H_2O$$

The two half-cell reactions as written above in the Latimer diagram for chlorine can be rewritten along with ΔG° values as follows :

$$\underset{+7}{HClO_4} + 2H^+ + 2e^- \longrightarrow \underset{+5}{HClO_3} + H_2O\text{;} \quad E^\circ = 1{\cdot}20\ V\text{;}\ \Delta G^\circ = -2 \times F \times 1{\cdot}20$$

$$\underset{+5}{HClO_3} + 2H^+ + 2e^- \longrightarrow \underset{+3}{HClO_2} + 2H_2O\text{;} \quad E^\circ = 1{\cdot}18\ V\text{;}\ \Delta G^\circ = -2 \times F \times 1{\cdot}18$$

Adding the two half-cell reactions, we get

$$\underset{+7}{HClO_4} + 4H^+ + 4e^- \longrightarrow \underset{+3}{HClO_2} + 2H_2O\text{;} \quad \Delta G^\circ = (-2{\times}F{\times}1{\cdot}20) + (-2{\times}F{\times}1{\cdot}18)$$

$\Delta G°$ for the overall reaction can also be written as :

$$\Delta G° = -nF(E')° = -4F(E')°$$

where $(E')°$ is the potential for the overall reaction.

$$\therefore \quad -4F(E'°) = (-2 \times F \times 1{\cdot}20) + (-2 \times F \times 1{\cdot}18)$$

$$(E')° = 1{\cdot}19\,V$$

Frost Diagrams

Suppose an element X forms a redox couple, X(n),X(0), in which the element has oxidation number n in oxidised state and zero in reduced state. The **frost diagram** for element X is the plot of $nE°$ for the couple against oxidation number n. Since $-\Delta G° = nFE°$ (Eq. 6), hence $nE° = -\Delta G°/F$. This means that the plot of $nE°$ versus n is the same as a plot of $-\Delta G°$ versus n. Obviously, the most stable oxidation state of an element corresponds to the species which occupies the lowest position in its Frost diagram, as shown in Fig. 3.

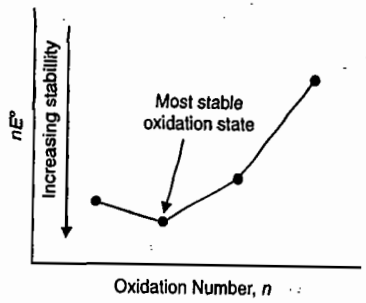


Fig. 3. Plot of $nE°$ vs n showing the most stable oxidation state of an element.

The Frost diagram for nitrogen under standard conditions (pH = 0) is shown in Fig. 4.

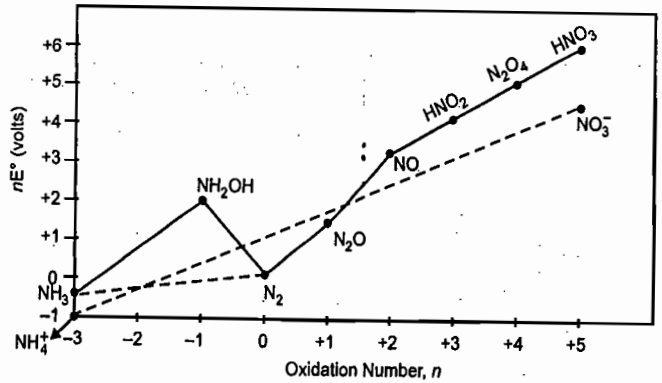


Fig. 4. The Frost diagram for nitrogen.

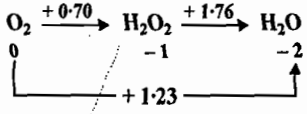
For analysing this diagram, we make use of the fact that if the point for a species lies *above* the line connecting two points which represent two other species, one on each side of the species under consideration, then that species would be thermodynamically *less stable* than the two neighbouring species and if the said point lies *below* the connecting line, then that species would be thermodynamically *more stable* than the two neighbouring species. Since the point for NH_2OH lies above the line connecting points for NH_3 and N_2, hence NH_2OH is thermodynamically less stable than NH_3 and N_2. This explains why NH_2OH decomposes readily into NH_3 and N_2 even at room temperature.

$$3NH_2OH \longrightarrow NH_3 + N_2 + 3H_2O,$$

Likewise, since the point for N_2O lies below the line connecting points for NH_4^+ and NO_3^- ions, hence N_2O is thermodynamically more stable than NH_4^+ and NO_3^- ions. This explains why NH_4NO_3 decomposes on heating into N_2O and H_2O.

If in the Frost diagram, three consecutive points representing three species lie more or less on a straight line, then the three species would be almost equally stable. Thus, NO, HNO_2 and N_2O_4 are almost equally stable.

Problem. Construct a Frost diagram for oxygen from the Latimer diagram given below :



Solution. The oxidation numbers of O in the above diagram are 0, – 1 and – 2 in the three species. For the change of oxidation number from 0 to – 1, *i.e.*, for the change of O_2 to H_2O_2, $E° = 0{\cdot}70$ V and $n = -1$ so that $nE° = -0{\cdot}70$ V. Since the oxidation number of O in H_2O is – 2, $n = -2$ and $E°$ for the formation of H_2O from O is + 1·23 V. Hence $nE° = -2{\cdot}46$ V. These results are plotted in Fig. 5.

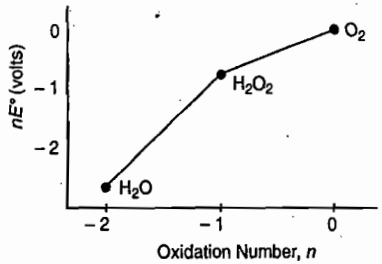


Fig. 5. Frost diagram for oxygen in acidic solution.

It follows from the above discussion that the steeper the line joining the two points in a Frost diagram, the higher is the standard potential of the corresponding couple.

Suppose, the plot of $nE°$ vs n in a particular case is as shown in Fig. 6. The line CD is steeper than the line BC. This shows that the couple corresponding to points C and D would have higher reduction potential than the couple corresponding to points B and C. This indicates that the species represented by the point D would be liable to undergo reduction while the species represented by the point B would be liable to undergo oxidation.

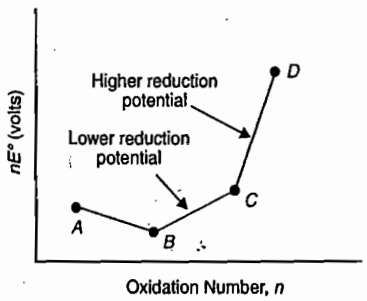


Fig. 6. Frost diagram depicting higher and lower reduction potentials of a species.

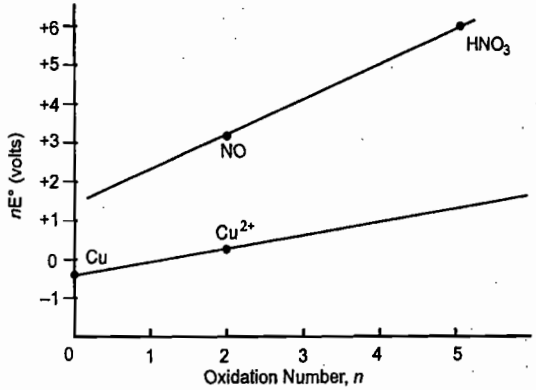


Fig. 7. Plot of $nE°$ vs oxidation number for HNO_3–NO and Cu–Cu^{2+} systems.

We can thus make use of the Frost diagram to predict whether a particular oxidant would oxidise a particualr species or not. The deciding factor which follows from the above discussion is that an oxidant occupying a position in $nE°$ vs n plot with a more positive slope would easily oxidise a species occupying a position in a similar plot with a less positive slope. Thus, as can be seen from Fig. 7, the HNO_3 – NO line has distinctly more positive slope than the Cu – Cu^{2+} line. Hence, HNO_3 would easily oxidise Cu to Cu^{2+} and would itself get reduced to NO ($3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$).

Pourbaix Diagrams

A Pourbaix diagram is a map depicting the conditions of potential and *p*H under which a given metal species is thermodynamically stable towards oxidation or reduction. As an illustration, we may consider the Pourbaix diagram for iron species in natural waters (Fig. 8). The various reactions that would be involved in the construction of this diagram would be as follows :

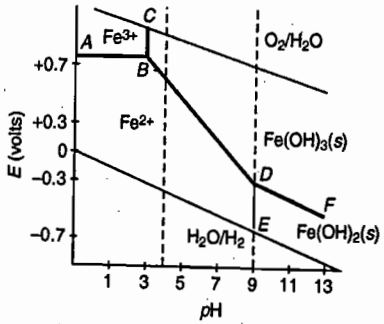


Fig. 8. Pourbaix diagram for iron species in natural waters.

1. The reduction half-cell reaction

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq); \qquad E^\circ = +0{\cdot}77$$

Since this reaction does not involve H^+ ions, it would be independent of *p*H. This is represented by the horizontal line *AB*. If the solution of the iron species contains a redox couple whose redox potential lies above the line *AB*, the Fe^{3+} ions would retain their identity. There would be no Fe^{2+} ions in solution. The line *AB* thus forms a boundary between the regions in which Fe^{3+} and Fe^{2+} ions dominate.

2. Another reaction which is needed to be considered is :

$$Fe^{3+}(aq) + 3H_2O(l) \longrightarrow Fe(OH)_3(s) + 3H^+(aq)$$

This reaction, evidently, is not a redox reaction as there is no change in the oxidation number of any species during the reaction. Since, however, H^+ ions are liberated in this reaction, it does depend upon *p*H. The formation of $Fe(OH)_3(s)$ is favoured by high *p*H whereas the continuation of $Fe^{3+}(aq)$ in solution is favoured by low *p*H. The vertical line *BC* represents the *p*H at which the Fe^{3+} ions remain dominant. At higher *p*H, $Fe(OH)_3(s)$ is formed :

3. The third reaction which is required to be considered is the reduction half-cell reaction :

$$Fe(OH)_3(s) + 3H^+(aq) + e^- \longrightarrow Fe^{2+}(aq) + 3H_2O(l)$$

Since H^+ ions are involved in this reaction, it is dependent on *p*H. The variation of potential with change in *p*H is given by Nernst equation as

$$E = E^\circ - (0{\cdot}0591)\log[Fe^{2+}] - (3 \times 0{\cdot}0591)\,pH$$

The potential falls linearly with increase in *p*H, as shown by the line *BD*. The regions of potential and *p*H that lie above the line *BD* corrrespond to conditions in which the oxidised species $Fe(OH)_3(s)$ is stable. The regions below the line *BD* correspond to conditions under which the reduced species $Fe(OH)_2(s)$ is stable.

4. Let us consider the reaction

$$Fe^{2+}(aq) + 2H_2O(l) \longrightarrow Fe(OH)_2(s) + 2H^+(aq)$$

which is also involved in the Pourbaix diagram. This is, evidently, not a redox reaction. Since H^+ ions are liberated in this reaction, it depends upon *p*H. While the presence of Fe^{2+} ions is favoured by low *p*H, the formation of $Fe(OH)_2$ is favoured by high *p*H. Thus, the vertical line *ED* at *p*H = 9, divides the regions in which the reactants and the products of the above reaction dominate.

5. We may consider yet another reaction

$$Fe(OH)_3(s) + H^+(aq) + e^- \longrightarrow Fe(OH)_2(s) + H_2O(l)$$

involved in Pourbaix diagram. This reaction is, obviously, dependent on *p*H. The variation of potential with change in *p*H is given by Nernst equation as

$$E = E^\circ - (0{\cdot}0591)\,pH$$

The line *DF* separates the region in which $Fe(OH)_2(s)$ and $Fe(OH)_3(s)$ are stable.

The Pourbaix diagram shows that Fe^{3+} ions can exist in water if the environment is oxidising. Hence, where O_2 is plentiful and the *p*H is low (less than 4), iron will be present as Fe^{3+} ions. Since the *p*H of natural waters varies between 4 and 9, there is very little possibility of the presence of Fe^{3+} ions in natural waters. Iron will be present almost entirely in the form of insoluble $Fe(OH)_3$.

If the conditions of the water are as represented by the regions falling below the sloping line *BD*, the iron present as insoluble Fe_2O_3, gets reduced to FeO which then goes in solution as Fe^{2+} ions. At higher *p*H, Fe_2O_3 would change into Fe^{2+} ions only if strong reducing agents are present. Thus, the formation of Fe^{2+} ions is very unlikely in oxygen–rich water. Organic matter consumes lot amount of oxygen for its bio-degradation which means that organic matter has a strong reducing character. Therefore, in organic matter–rich water logged soils with *p*H around 4·5, the insoluble Fe_2O_3 present gets reduced and dissolves in the form of Fe^{2+} ions. Thus, while oxygen rich–waters contain Fe^{3+} ions, the organic matter–rich water logged soils contain Fe^{2+} ions.

QUESTIONS

1. Define oxidation and reduction in terms of electron transfer and change in oxidation number.
2. Explain the term single electrode potential. How is this quantity measured ? How do we assign a negative or a positive sign to electrode potential ?
3. What is meant by Electrochemical series ? Discuss one important application of this series.
4. State and explain Nernst equation for giving the effect of concentration of an electrolyte on electrode potential.
5. What is a galvanic cell ? What is the source of electrical energy in a galvanic cell ?
6. What is hydrogen overvoltage ? What is its significance ?
7. Explain the term stability field of water. Explain why metals such as Na, K, Ca react with water to liberate hydrogen.
8. Explain why ions such as Ce^{4+} and Co^{3+} are not stable in aqueous solution.
9. How would you account for the disproportionation reaction : $Cu(I) \longrightarrow Cu(II) + Cu$
10. How would you explain the following :
    (*i*) Fe^{3+} is most common form of iron present in Earth's crust.
    (*ii*) Iron present in sediments deposited from aqueous environments is mostly in the form of Fe^{3+}.
    (*iii*) Copper roofs get covered by a green layer of a mixture of $CuSO_4$ and $CuCO_3$ in damp environments.
11. What are Latimer diagrams ? Explain how a Latimer diagram is converted into reduction half-cell reactions in acidic and basic solutions.
12. How would you account for the disproportionation of H_2O_2 with the help of a Latimer diagram ?
13. What are Frost diagrams ? To what use are they put ? Explain giving examples.
14. What are Pourbaix diagrams ? To what use are they put ? Explain giving examples.

10 METALS AND METALLURGY

Elements have been broadly divided into *metals* and *non-metals* on the basis of their physical and chemical properties. Metals have generally low ionisation energies, low electron affinities and low electronegativities which are responsible for their high electrical and thermal conductivities, high malleability and ductility, metallic lustre and hardness. Of the 108 elements known at present, about 70 are metals. In the present chapter, we shall study the occurrence and general methods used for the extraction of metals from their ores.

Occurrence of Metals

Metals occur in nature sometimes free but mostly in the combined state. The earth's crust is the biggest source of metals. Some soluble salts of metals are also found in sea water.

Noble metals which have little or no affinity for oxygen and which resist the attack of water and other chemical reagents, occur in the free, *i.e.*, the **native state.** Thus, metals such as silver, gold and platinum occur in nature in native state along with alluvial impurities such as clay and sand. Sometimes lumps of pure metals are also found. These are called **nuggets.**

The standard electrode potentials (*i.e.*, reduction potentials) of noble metals are always *positive* which means that the ions of such metals have a tendency to accept electrons and get reduced to the corresponding metals. That is why these metals occur in metallic, *i.e.*, native state.

The standard electrode potentials of active metals, on the other hand, are *negative* which means that these metals have a tendency to get oxidised to their ions. In other words, the ions of such metals are reluctant to get reduced to the metallic state. That is why the active metals occur in nature in the form of their compounds, *i.e.*, in the **combined state**. These compounds are known as **minerals.**

The minerals from which metals can be conveniently and economically extracted are referred to as **ores.**

Active metals occur in the form of the following categories of ores :

Sulphide ores. Metals such as iron, mercury, copper, etc., occur as their sulphides, *e.g., iron pyrites* (FeS), *galena* (PbS), *cinnabar* (HgS), *copper pyrites* ($CuFeS_2$), *zinc blende* (ZnS), etc.

Oxide ores. Metals such as iron, aluminium, manganese, tin, zinc, etc., occur as their oxides, *e.g., haematite* (Fe_2O_3), *bauxite* ($Al_2O_3.2H_2O$), *pyrolusite* (MnO_2), *cassiterite* (SnO_2), *zincite* (ZnO), etc.

Carbonate ores. The important carbonate ores are of magnesium, iron, copper, zinc and lead, *e.g., magnesite* ($MgCO_3$), *dolomite* ($CaCO_3,MgCO_3$), *siderite* ($FeCO_3$), *malachite* [$Cu(OH)_2.CuCO_3$], cerussite ($PbCO_3$), calamine ($ZnCO_3$), etc.

Halide ores. Chloride ores are the most common among the halide ores. The chlorides of sodium, potassium and magnesium are found in salt beds on the surface of the earth and in sea water. *Carnallite* ($KCl.MgCl_2.6H_2O$), *rock salt* (NaCl) and *horn silver* (AgCl) are common examples of chloride ores.

Bromides and iodides of potassium and magnesium are present in small amounts in sea water. The fluoride ores include *fluorspar* (CaF_2) and *cryolite* ($AlF_3.3NaF$).

Sulphate ores. Many sulphide ores get converted into sulphates by atmospheric oxidation. The common sulphate ores are *barytes* ($BaSO_4$), *anglesite* ($PbSO_4$), *epsomite* ($MgSO_4.7H_2O$), *anhydrite* ($CaSO_4$), etc.

Metallurgy

The process of extracting metals from their ores is called **metallurgy.** The metallurgical process would necessarily depend upon the nature of the ore which is to be worked out for the extraction of the metal. It is not possible to chalk out a universal scheme for the extraction of all metals since the extraction of each metal involves individual procedure depending upon its nature and properties. However, heavy metals such as copper, iron, zinc, lead, tin, etc., are extracted from their ores by the conventional 'Roasting and Smelting' processes. The active metals such as alkali metals, magnesium, calcium, aluminium, etc., are obtained by the electrolysis of their chlorides, oxides or hydroxides in fused state and the noble metals such as gold and silver are obtained by the amalgamation or the cyanide process.

Various Steps Involved in Metallurgical Processes. The various steps essentially involved in the extraction of pure metals from their respective ores are as follows.

1. Concentration of the Ore

Metallic ores are often found mixed with rocky material, *e.g.*, quartz, felspar, mica and other silicates. These impurities are known as **gangue.** Before the ore is subjected to metallurgical process, it is necessary to remove these unwanted impurities mechanically. This operation is known as concentration of the ore. The common methods of concentration are as follows :

a. Hand picking. Quite often, the ore is separated from the main stock in a sufficient degree of purity by simply picking it by hand and then eliminating the adhering rocky material by breaking with hammer.

b. Gravity separation. The ore can be concentrated by taking advantage of the differences in the specific gravities of metallic ore and the earthy impurities. The ore, after grinding, is washed with a running stream of water. The heavy ore settles down rapidly while the lighter earthy material (gangue) is washed away. The two common techniques of gravity separation are described below.

Hydraulic Classifier. Finely powdered ore is dropped into a conical reservoir, called *hydraulic classifier,* from the top. A powerful stream of water is introduced from the bottom of the reservoir. The gangue, being lighter, is carried away by water and the heavier ore particles accumulate at the apex of the cone. The conical shape of the reservoir helps in reducing the velocity of water and thus prevents the ore particles from being carried away along with the stream of water.

Wilfley Table. Wilfley table is a wooden table having a slanting floor on which long wooden strips called cleats or riffles are fixed. The powdered ore is suspended in a stream of water and delivered at the upper end of the table which is then given a bumping motion. The heavier ore particles are obstructed by the cleats while the lighter impurities pass over and are carried away by the stream of water. The ore particles which collect behind in the cleats move to one side as a result of the motion of the table and are collected.

c. Magnetic separation. Ferromagnetic ores, as of iron, that are affected by a magnet, are separated from the non-magnetic impurities by means of magnetic separators. A magnetic separator consists of a leather belt moving over two rollers, one of which is magnetic. The powdered ore is dropped on the belt at one end. At the other end, the magnetic portion of the ore is attracted by the magnetic roller and falls nearer to the roller while the non-magnetic impurities fall farther off.

d. Electrostatic separation. This method is based on the fact that the particles which are good conductors of electricity become electrically charged as soon as they are brought into an electrostatic field and are consequently repelled by the electrode carrying the like charge. Lead sulphide and zinc sulphide ores which occur together in nature are separated by this technique. The mixed ore, after grinding, is fed upon a roller in a thin layer and subjected to the influence of an electrostatic field. Lead sulphide ore, being a good conductor, gets charged immediately and is thrown away from the roller due to electrical repulsion. The zinc sulphide ore which is a poor conductor is not charged and hence drops vertically from the roller.

e. Froth flotation. This process is based on the principle of *preferential wetting of solids by liquids*. Metallic sulphides, for instance, are wetted by certain oils, like pine oil, but not by water.

The finely divided ore is put in water to which a small quantity of oil (*e.g.*, pine oil) has been added. The water is agitated violently with air (Fig. 1) when froth is formed at the air–water interface. The ore which is preferentially wetted by the oil rises to the surface along with the foam while the stony matter (gangue) which is preferentially wetted by water remains in the water below the foam, as shown on the right of the figure. The foam separates out and, in due course, settles down as shown on the left of the figure. This process is known as **froth flotation process.**

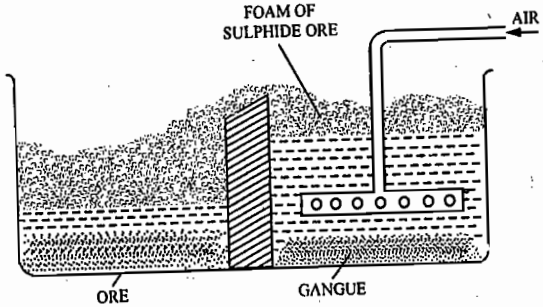


Fig. 1. Froth flotation process.

f. Leaching. This is a chemical method for the concentration of ores. In this method, the powdered ore is treated with some suitable reagent which may dissolve the ore but not the impurities. The impurities are filtered off and the ore is recovered from the solution by suitable chemical methods. For example, during the extraction of aluminium from bauxite ($Al_2O_3.2H_2O$) ore, the finely divided ore is treated with hot sodium hydroxide solution. Alumina present in the ore dissolves forming soluble sodium metaaluminate but impurities are left behind as such and are filtered off.

2. Calcination

Calcination is a process in which the ore is heated in a limited supply of air at a temperature insufficient to melt it. During calcination, organic matter, volatile impurities and moisture present in the ore are expelled and the remaining mass becomes porous. Calcination is also done to remove water from hydrated oxide ores or carbon dioxide from a carbonate ore. For example, when limestone is heated, carbon dioxide is given off and limestone is said to be calcined. When bauxite is calcined, water is removed and anhydrous alumina is left behind. Similarly, iron ores on calcination give anhydrous iron oxide. The various chemical changes are represented below :

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O$$

$$2Fe_2O_3.3H_2O \longrightarrow 2Fe_2O_3 + 3H_2O$$

Calcination is generally done in a reverberatory furnace (Fig. 2). It renders the ore porous and easily workable in subsequent stages.

3. Roasting

Roasting is a wider term used to denote the process in which the ores (usually sulphide ores) either

alone or with the addition of other materials, are subjected to the action of heat in the presence of air, at temperatures well below their melting points, in order to bring about their oxidation.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

Sometimes, during roasting, oxidation of sulphides takes place only upto sulphates. For example,

$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

During roasting, the non-volatile impurities like sulphur, arsenic, phosphorus, etc., are removed in the form of their volatile oxides which escape as gases through the chimney.

$$S + O_2 \longrightarrow SO_2 \uparrow$$

$$4As + 3O_2 \longrightarrow 2As_2O_3 \uparrow$$

$$P_4 + 5O_2 \longrightarrow 2P_2O_5 \uparrow$$

Roasting is carried out either in a reverberatory furnace or in a blast furnace. In a reverberatory furnace (Fig. 2), the charge is placed on the hearth and heated by the flames deflected from its roof. The reverberatory furnace is used in roasting the ores of copper, tin, lead, etc.

Blast furnace is a long vertical furnace (Fig. 3), made of steel plates, lined inside with fire clay bricks. It is provided with an arrangement for blowing in air near the base, as shown in the figure. It is also provided with a hole for removing the slag and a tapping hole for taking out the metal.

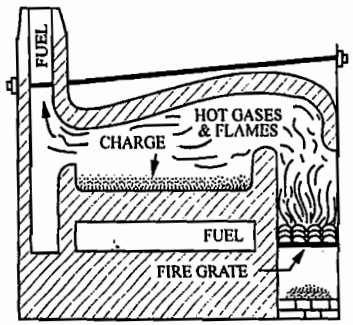


Fig. 2. A reverberatory furnace.

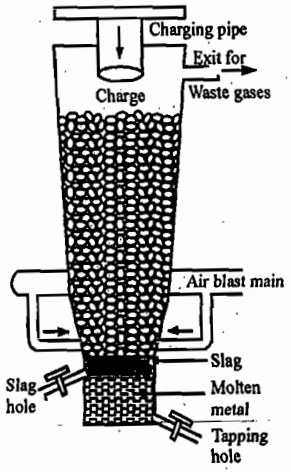


Fig. 3. A blast furnace.

4. Smelting. Reduction of Metal Oxides by Carbon

A large number of metal oxides obtained during roasting can be reduced to metals by heating with carbon at elevated temperatrues (> 1000°C). This process is called **smelting.**

The roasted ore is mixed with a suitable quantity of carbon (coal or coke) and heated to a high temperature above the melting point of the metal. Carbon and carbon monoxide (produced by the

incomplete combustion of carbon) reduce the oxide to the free metal. For example,

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$
$$PbO + C \longrightarrow Pb + CO$$
$$PbO + CO \longrightarrow Pb + CO_2$$

During reduction, an additional substance, called the *flux*, is added to the ore. It combines with impurities to form easily fusible product known as **slag**.

$$\underset{\text{(Present in the ore)}}{\text{Impurities}} + \text{flux} \longrightarrow \underset{\text{Slag}}{\text{fusible product}}$$

Slag is not soluble in molten metal. Being lighter, it can be easily skimmed off from the surface of the molten metal.

The choice of flux depends upon the impurities present in the ore. For example, if the ore contains acidic impurities such as SiO_2, P_2O_5, then basic fluxes like lime (CaO), magnesite ($MgCO_3$), haematite (Fe_2O_3), etc., are used.

$$\underset{\text{Acidic impurity}}{SiO_2} + \underset{\text{Basic flux}}{CaO} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

On the other hand, if the ore contains basic impurities such as CaO, FeO, $MgCO_3$, then acidic fluxes like sand and borax are used.

$$\underset{\text{Basic impurity}}{FeO} + \underset{\text{Acidic flux}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

Smelting is generally carried out in a **reverberatory furnace** (Fig. 2) or a **blast furnace** (Fig. 3) in a controlled supply of air.

In the case of metals which are volatile in nature (for example, zinc), smelting cannot be done in an open furnace. In such cases, reduction of the oxide ore is carried out in fire-clay retorts. The vertical retort, which is now in common use, is shown in Fig. 4. Heating is done by producer gas.

It is to be noted that reduction with carbon is practical only if the required temperature is achieved conveniently which may not be so always.

Reduction by controlled heating in air. In the case of less active heavy metals whose oxides are unstable towards heat, only roasting in air is enough for the separation of the metal. For example, roasting of the sulphide ore of mercury (*cinnabar*) gives the metal rather than its oxide.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

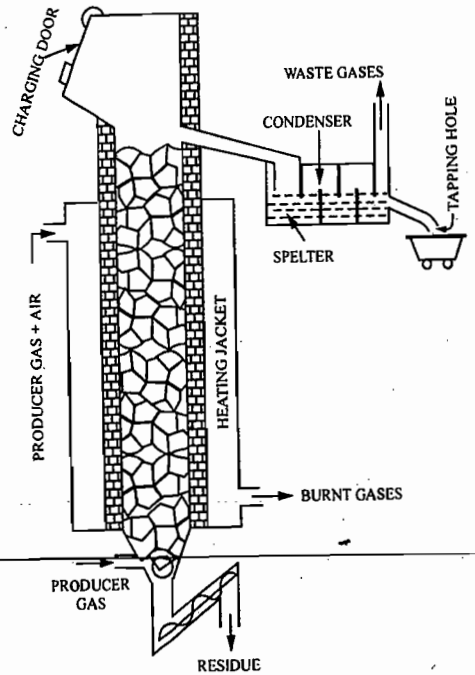


Fig. 4. A vertical retort furnace for the smelting of zinc ore.

Mercury vapours are condensed to the liquid state in the condensing chambers. This process is known as **air reduction** process. The Idrian furnace commonly used for the process is shown in Fig. 5.

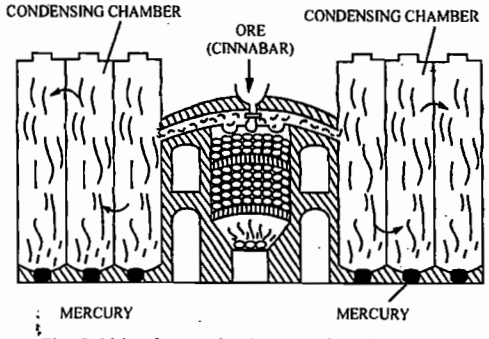


Fig. 5. Idrian furnace for the extraction of mercury.

Sulphide ores of several metals such as Pb, Cu, Sb, may be first roasted in a limited supply of air to partially convert them to oxides. These are further roasted in the absence of air when the sulphides and the oxides formed react to give the metals. For instance,

$$Cu_2S \xrightarrow[\text{in limited supply of air}]{\text{Roasting}} \underbrace{Cu_2S + Cu_2O} \xrightarrow[\text{absence of air}]{\text{Roasting in}} Cu + SO_2$$

This process is known as **self reduction**.

Electrometallurgy. The carbon reduction methods are not applicable for the chemically active metals such as alkali metals, alkaline earth metals, aluminium, etc. The oxides of these metals are very stable and have to be heated very strongly with carbon in order to reduce them to metals. But at high temperatures, these metals combine with carbon to form carbides. Hence, these metals are extracted by the electrolysis of their oxides, hydroxides or chlorides in fused state. The metal is liberated at the cathode.

Other Methods for Reduction of Oxides of Metals. If the temperature required for the reduction of the oxide by carbon is not easily attainable, then reduction is carried out by another metal such as aluminium. This is called **Goldschmidt thermite process.** Examples are :

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$
$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

In a few cases, as for example, in the case of Ag_2O, reduction is carried out by thermal decomposition alone. Such cases have been dealt with below on the basis of the **Ellingham diagram.** The thermodynamics of carbon reduction process and the electrolytic process have also been discussed with the help of this diagram.

Thermodynamics of the Oxidation of Metals to Metal Oxides. The Ellingham Diagram

Consider a general oxidation reaction of a metal M in which $2x/y$ moles of the metal react with one mole of oxygen to form the oxide M_xO_y :

$$\underset{\text{solid}}{(2x/y)\,M} + \underset{\text{gas}}{O_2} \longrightarrow \underset{\text{solid}}{2/y\,M_xO_y}$$

Thermodynamically, the oxidation reaction would be feasible and the oxide formed would be stable if the free energy change ΔG of the oxidation reaction is negative. Free energy change of a

reaction is given by the well known thermodynamic relation $\Delta G = \Delta H - T\Delta S$ where ΔH is the enthalpy change and ΔS is the entropy change accompanying the reaction. Since oxygen, being a gas, has higher entropy than the metal and the metal oxide, there would be a decrease in entropy in going from the reactants to the product. In other words, ΔS for the oxidation reaction would be negative. Obviously, the term $T\Delta S$ would become more and more negative and thereby ΔG would become less and less negative with increase in temperature. If the temperature is very high, ΔG may become zero and even positive in which case the oxidation reaction would no longer remain feasible. The variation of ΔG with increase in temperature for the oxidation of some common metals to their oxides (using one mole of oxygen in each case) is represented in Fig. 6. This figure is known as the **Ellingham diagram.** Similar diagrams can be drawn for the conversion of metals to metal sulphides or metal halides using one mole of sulphur or the halogen, as the case may be.

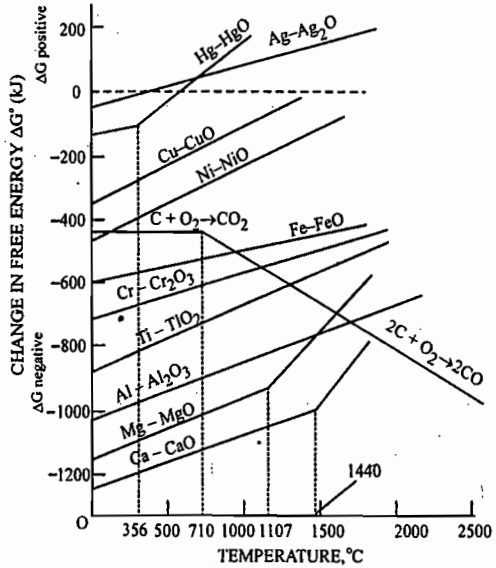


Fig. 6. Ellingham diagram showing the change in free energy ΔG with temperature for metal–metal oxide reactions, based on one mole of oxygen in each case.

Consider the relation,

$$\Delta G = \Delta H - T\Delta S$$

Differentiating with respect to T (assuming that ΔH does not vary with change in temperature), we get

$$d(\Delta G)/dT = -\Delta S$$

Thus, for a reaction with *negative* ΔS, the slope of the line obtained by plotting ΔG vs T will be *positive* while the slope of a similar line for a reaction with *positive* ΔS will be *negative*. Since for the reaction of metals with oxygen to give metal oxides, ΔS is negative, the slope of the lines obtained by plotting ΔG vs T, will be *positive*. Since for a reaction such as $C(s) + O_2(g) \longrightarrow CO_2(g)$, ΔS is zero, the slope of the line will be zero and the plot of ΔG vs T will be parallel to the temperature axis. The slope of the line for the reaction $2C(s) + O_2(g) \longrightarrow 2CO(g)$, for which ΔS is obviously positive, has to be *negative*, as actually observed.

The Ellingham diagram for the oxidation of metals to metal oxides, represented in Fig. 6, has a number of significant features :

1. All the ΔG vs T lines slope upward since ΔG becomes less and less negative with increase in temperature.

2. The ΔG vs T graphs are straight lines upto the temperatures at which the metals remain in solid state. There is a large change in entropy when the metals undergo fusion or vaporisation. This considerably changes the slopes of ΔG vs T lines. Thus, the slopes of Hg – HgO, Mg – MgO and Ca – CaO lines change appreciably at 356°, 1107° and 1440°C which are, respectively, the boiling points of Hg, Mg and Ca.

3. With continuous increase in temperature, a state would be reached when the ΔG vs T graphs cross the $\Delta G = 0$ line. Below these temepratures, ΔG is negative, *i.e.*, the heats of formation of the oxides are negative and hence the oxides formed are stable. Above these temperatures, ΔG would be

positive and the oxides formed would, therefore, be unstable and would decompose to give the metals and oxygen. According to the Ellingham diagram, all oxides should decompose to give the metal and oxygen provided the temperatures are sufficiently high at which ΔG becomes positive. Such temperatures are, in practice, not easily attainable. The Hg – HgO and Ag – Ag_2O lines, however, cross the $\Delta G = 0$ line at temperatures which are easily attainable. These oxides, therefore, decompose easily to give the metals. This is the reason why Hg and Ag are obtained by thermal decomposition of their oxides.

4. Quite frequently, one metal is used to reduce the oxide of another metal. For example, aluminium is used to reduce Cr_2O_3 to Cr. Any metal would reduce the oxides of other metals which lie above it in the Ellingham diagram. This has been illustrated below.

Consider the following reactions taking place at a particular temperature :

$$4/3\ Cr + O_2 \longrightarrow 2/3\ Cr_2O_3\ ; \qquad \Delta G = -x\ kJ \qquad ...(1)$$

$$4/3\ Al + O_2 \longrightarrow 2/3\ Al_2O_3\ ; \qquad \Delta G = -y\ kJ \qquad ...(2)$$

We see from the Ellingham diagram that the ΔG vs T line for Al – Al_2O_3 system lies below the ΔG vs T line for Cr – Cr_2O_3 system so that $|y| > |x|$. Subtracting Eq. 1 from Eq. 2, we get

$$4/3\ Al - 4/3\ Cr \longrightarrow 2/3\ Al_2O_3 - 2/3\ Cr_2O_3\ ; \qquad \Delta G = -y - (-x)\ kJ \qquad ...(3)$$

or

$$4/3\ Al + 2/3\ Cr_2O_3 \longrightarrow 4/3\ Cr + 2/3\ Al_2O_3\ ; \qquad \Delta G = (x - y)\ kJ \qquad ...(4)$$

Since $|y| > |x|$, hence $(x - y)$ is negative, that is, ΔG accompanying reaction (4) is negative. Reaction (4) is, therefore, thermodynamically feasible, *i.e.*, Al would reduce Cr_2O_3 to Cr.

Now subtracting Eq. 2 from Eq. 1, we get

$$4/3\ Cr + 2/3\ Al_2O_3 \longrightarrow 2/3\ Cr_2O_3 + 4/3\ Al\ ; \qquad \Delta G = (y - x)$$

Since $y - x$ and hence ΔG for the above reaction is positive, it would not occur, *i.e.*, Cr would not reduce Al_2O_3 to Al. However, Mg – MgO line lies below the Al – Al_2O_3 line in Ellingham diagram. Hence, Mg would reduce Al_2O_3 to Al.

5. As can be seen from the Ellingham diagram, the ΔG vs T graph for the oxidation of carbon is typical in itself.

Two reactions are possible for the reaction of carbon with oxygen :

$$C + O_2 \longrightarrow CO_2$$

$$2C + O_2 \longrightarrow 2CO$$

In the first reaction, there is pratically no change in entropy because the volume of CO_2 produced is the same as the volume of O_2 used. As a result, the ΔG vs T graph for $C \longrightarrow CO_2$ reaction is practically horizontal, as shown. The second reaction is accompanied by an increase in entropy because one volume of O_2 produces two volumes of CO. Since ΔS is positive, hence ΔG (= $\Delta H - \Delta S$) goes on becoming more and more negative with increase in temperature. As a result, the ΔG vs T graph for the second reaction slopes downward, as shown. The two graphs cross at about 710°C. Below this temperature, carbon reduces metal oxides to metals which lie above the horizontal line in Ellingham diagram, carbon itself being oxidised to CO_2. Above 710°C, reduction of oxides results in the formation of CO. Since the ΔG line for $C \longrightarrow CO$ slopes downwards, it would eventually cross all other metal–metal oxide graphs and would lie below all of them. This implies that, in principle, carbon can be used for reducing any metal oxide to metal provided a sufficiently high temperature is made available for the purpose. But, sometimes it is difficult to attain such high temperatures and, therefore, other techniques are used for the reduction of the metal oxides.

It can thus be concluded from the above discussion that *HgO and Ag_2O can be reduced to their respective metals simply by heating* since the temperatures at which ΔG for the decomposition reactions of these oxides becomes positive are easily attainable. The process in which the metal is obtained simply by heating the oxide ore to an easily attainable temperature is called **pyrometallurgical process.**

The extraction of other metals simply by heating their oxides is difficult since the temperatures at which ΔG for the decomposition reactions of their oxides becomes positive, are not easily attainable. In such cases, the metal oxide is reduced by heating it with coke to temperatures at which C – CO line in the Ellingham diagram lies below the metal–metal oxide line. Thus, iron is obtained from its oxide ore by heating it with C at temperatures around 1000°C at which the C – CO line lies below the Fe – FeO line (Fig. 6).

The reduction of SiO_2 with C is extremely difficult as the temperature at which C can reduce SiO_2 is very high, *viz.*, around *1500°C* (the *Si – SiO_2 line is not shown in the diagram*).

If the temperatures at which the reduction of metal oxides with C can be affected are difficult to achieve, then reduction is carried out electrolytically. In this technique, the process of reduction of the oxide gets coupled with the electrolytic process for which ΔG is sufficently negative so as to make the overall ΔG for the coupled process decidedly *negative*. The process, therefore, becomes feasible. Thus,

$$\Delta G = \Delta G \text{ (reduction process)} + \Delta G \text{ (from external cell)}$$

$$= \Delta G \text{ (reduction process)} - (nFE_{\text{external}})$$

(E_{external} is the potential difference applied across the two electrodes of the electrolytic cell).

In order that ΔG (overall) is negative so that the reduction process becomes feasible, the factor [ΔG (reduction process) – nFE_{ext}] should be negative, *i.e.*, nFE_{ext} should be greater than ΔG (reduction process), Thus, E_{ext} should be greater than ΔG (reduction process)/nF.

A question may arise in reader's mind : Why do we almost invariably convert metal sulphides into metal oxides before reducing them with carbon ? Why can't we directly reduce metal sulphides with carbon ? The answer is that there is no compound CS analogous to CO for which ΔG vs T graphs slope downwards. Therefore, the sulphide ores are first converted into the oxides and then reduced by carbon.

Hydrogen is of limited use as a reducing agent for extracting metals from their oxides. This is because of two reasons. Firstly, the ΔG vs T line for the oxidation of hydrogen ($2H_2O + O_2 \longrightarrow 2H_2O$) runs parallel to most of the metal–metal oxide lines so that only a very few metals, having metal–metal oxide lines above the hydrogen line, can be reduced by hydrogen. The increase in temperature will not be of any use because at elevated temperatures hydrogen reacts with many metals forming hydrides.

The thermodynamic treatment discussed above has two limitations as well. These are :

1. The treatment is based on the assumption that the reactants and products are in a state of equilibrium which is often not true.

2. The treatment only predicts the feasilibty of the reaction. It gives no information about the rate of the reaction.

Specialised Techniques for the Extraction of Metals

Some specialised techniques are also employed for the extraction of metals in specific cases. These techniques include amalgamation, hydrometallurgy, solvent extraction and ion-exchange chromatography.

a. Amalgamation. This process is used for the extraction of gold which occurs native. The finely crushed auriferous quartz is brought into contact with mercury which takes up the metal forming an amalgam. The metal is then recovered by distilling the amalgam.

b. Hydrometallurgy. Hydrometallurgy involves bringing the metal in solution by the action of suitable chemical reagents, *e.g.*, sodium cyanide solution. This is followed by the recovery of the metal by the use of suitable precipitating agents. For example, native silver or poor ores of silver are suspended in dilute solution of sodium cyanide and air is blown through it. The native silver or silver ore goes into

solution as the argentocyanide complex from which the metal is precipitated by adding zinc turnings.

$$4Ag + 8NaCN + O_2\text{ (air)} + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

or

$$AgCl + 2NaCN \longrightarrow Na[Ag(CN)_2] + NaCl$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$$

c. Solvent Extraction. Solvent extraction is a technique in which the solution of a solute in a solvent is brought into contact with a second solvent which is essentially immiscible with the first solvent in order to bring about the transfer of the solute into the second solvent. It can be shown in a smiple manner that with a given volume of the extracting liquid, the extraction is more complete if it is used in a number of instalments than if the whole of it is used in a single operation. The efficiency of the process largely depends upon the partition coefficient which tells how many times the solute is more soluble in the extracting liquid.

The solvent extraction process is successfully employed in the desilverization of lead by zinc (Parke's process). In this process, argentiferous lead is melted and heated to 800°C. Molten zinc is then added. Molten lead and molten zinc behave as two immiscible liquids in contact with each other and silver behaves as a solute which is more soluble in zinc than in lead, the partition coefficient being of the order of 300 at 800°C. Silver, therefore, passes readily from the heavier lead layer into the lighter zinc layer which is separated. By repeating the process three or four times, almost the entire amount of silver passes into the zinc layer from which it can be recovered by distilling off zinc.

d. Ion exchange Chromatography. This technique is effectively employed for the separation of lanthanides. This has been discussed in details in Chapter 25.

5. Refining or Purification

After various metallurgical operations, the metal first obtained is usually impure. The impurities largely consist of

(*i*) other metals produced by the simultaneous reduction of their respective oxides originally present in the ore.

(*ii*) unreduced oxides and sulphides of the metals and

(*iii*) substances such as residual slag, flux, etc.

The impure metal is, therefore, subjected to certain purifying processes which depend upon the metal under treatment and the nature of the impurities to be removed. The usual refining processes are :

a. Liquation process. This process is employed when the impurity is less fusible than the metal itself. The impure metal is placed on the sloping hearth of a furnace and gently heated. The metal melts and drains away leaving behind the infusible material on the hearth.

b. Distillation process. This process is employed for purification of volatile metals like mercury, zinc and cadmium. The impure metal is heated in a retort and its vapours are condensed in a receiver. While the pure metal distils over, the non-volatile impurities are left behind in the retort.

c. Oxidation processes. Oxidation processes are employed for refining when impurities consisting of other metals get oxidized more readily than the metal itself. The impure metal is exposed in a molten state to the oxidizing influence of air in a suitable furnace. The oxides of other metals which are formed are removed from the surface by skimming. Sometimes, the oxide of the metal itself is added which provides the oxygen to the impurities. Thus, copper oxide is added to impure molten copper to provide oxygen required for the oxidation of impurities.

d. Thermal decomposition of suitable compounds. In this method, the impure metal is converted into some volatile compound which decomposes easily to yield the pure metal. Two examples are given below.

(*i*) *Mond Process.* Impure nickel is treated with CO at 50°C when $Ni(CO)_4$ gas is produced which

when heated to 250°C in a closed vessel decomposes to give CO and pure nickel. CO is recycled to react with more of the impure nickel. This process is known as Mond process.

(*ii*) *Van Arkel-de-Boer Process*. This method is used for ultrapurification of Zr and Ti. The impure metal is heated with iodine to give volatile MI_4 (M = Ti, Zr). The iodide is then heated electrically in a closed container when MI_4 decomposes to give the metal which deposits on the tungsten filament of the electric heater. The iodine liberated is recycled to react with further quantity of the impure metal. The tungsten filament is then drilled out leaving behind the hollow bar of pure titanium or zirconium, as the case may be.

e. Electrorefining. A large number of metals are refined electrolytically. The impure metal in the form of blocks is made the anode of an electrolytic cell while the cathode is a thin plate of the pure metal. A solution of a suitable salt of the metal is used as the electrolyte. On passing the electric current, the pure metal dissolves from the anode and is deposited on the cathode. The soluble impurities go into solution while the insoluble matter settles down at the bottom and is called the *anode mud*.

f. Zone refining. This technique is employed for preparing extremely pure metals. This is based on the principle that when the melt of an impure metal is allowed to cool, the pure metal crystallizes out while the impurities remain in the melt. In this technique, the impure metal is converted into a bar which is heated *at one end* with a moving circular heater. The impure metal melts at this end and forms a molten zone. As the heater is moved slowly along the length of the rod, the pure metal cystallizes out of the earlier molten zone while the impurities pass into the adjacent newly created molten zone. This process is carried out throughout the length of the rod. As a result, the impurities are completely driven to one end of the rod which is cut off and discarded. The process is carried out in an inert atmosphere to prevent oxidation of the metal.

QUESTIONS

1. How do metals occur in nature ? Describe the general procedure of extracting a metal from its ores.
2. What is meant by the term metallurgy ? Describe the various steps involved in getting a pure metal from its sulphide ore.
3. Explain the terms : Mineral, Ore, Gangue, Flux and Slag. Give examples.
4. Write short notes on :
   (1) Dressing of the ore (2) Electrometallurgy
   (3) Hydrometallurgy (4) Electrorefining (5) Zone refining
5. What is meant by the term concentration of the ore ? Describe the various methods used for the purpose.
6. Describe the various methods employed for the refining of crude metals.
7. Differentiate between
   (*i*) mineral and ore
   (*ii*) calcination and roasting
   (*iii*) gangue and flux
8. Discuss briefly the various methods used for the reduction of the roasted ores to the metallic state.
9. Give a brief description of specialised techniques for the extraction of metals.
10. What is an Ellingham diagram. Discuss briefly the applications of this diagram.
11. Explain how with the help of an Ellingham diagram, we can fix the criterion for each of the following reactions :
    (*i*) Reduction of a metal oxide by carbon at a given temperature.
    (*ii*) Reduction of an oxide X_2O_3 by a metal Y.
    (*iii*) Reduction of a metal oxide by hydrogen.

11 HYDROGEN

Position of Hydrogen in the Periodic Table. Hydrogen is the first element in the periodic table. Its atomic number is 1 and atomic mass 1·008 a.m.u. The nucleus of the hydrogen atom contains one proton but no neutron. There is only one planetary electron arranged in the *s* orbital of the *K* shell. The hydrogen atom has a tendency to lose this electron and change into H^+ ion. Hydrogen, therefore, has an electropositive character like alkali metals. The hydrogen atom has also a tendency to gain an electron to complete the 1*s* subshell and thus has an electronegative character like the halogens. Thus, in some respects it resembles alkali metals (Group 1) while in some other respects it resembles the halogens (Group 17). The points of resemblance and the points of difference of hydrogen with alkali metals on one hand and the halogens on the other hand are discussed below.

Resemblance with Alkali Metals. 1. Like alkali metals (*i.e.*, elements of Group 1), hydrogen has only one electron in its outer shell.

2. The atoms of alkali metals have a strong tendency to lose the solitary electron from their outer shell and change into positive ions (*i.e.*, Li^+, Na^+, K^+, Rb^+, Cs^+). Hydrogen also has a tendency, though not as strong as the alkali metals, to lose the solitary electron to change into H^+ ion.

3. The normal valency of hydrogen as well as of alkali metals is 1.

4. Hydrogen forms a stable oxide, H_2O. Alkali metals also form stable oxides, *e.g.*, Na_2O, K_2O. Hydrogen forms a peroxide, H_2O_2. Alkali metals also form peroxides, *e.g.*, Na_2O_2.

5. Alkali metals are good reducing agents and so is hydrogen.

Although hydrogen resembles alkali metals in many respects, yet it has some **differences** also. For example, the ionization energy of hydrogen is very high in comparison with alkali metals. This is because the 1*s* electron of hydrogen atom is tightly held by the nucleus because of its small size.

The size of H^+ ion is extremely small in comparison with the sizes of alkali metal ions.

Resemblance with the Halogens. 1. Hydrogen has also a tendency to gain one electron more so as to complete its outer *K* shell and acquire helium configuration and thus change into negative ion, H^-. The halogens (the elements of Group 17) have seven (ns^2p^5) electrons in their outer shells, hence their atoms also have a strong tendency to gain one electron more so as to acquire stable noble gas configurations and thus form negative ions.

2. The ionization energy of hydrogen (1312 kJ mol^{-1}) is of the same order as that of the halogens, as shown below :

Halogens	F	Cl	Br	I
Ionization energy (kJ mol^{-1})	1680·8	1255·5	1140·1	1008·8

3. Hydrogen molecule is diatomic and so are the molecules of the halogens.

4. Hydrogen forms hydrides with carbon (*e.g.*, CH_4, C_2H_2). Halogens also form well known halides with carbon (*e.g.*, CCl_4, $CHCl_3$).

5. Hydrogen in organic compounds can be substituted by halogens by suitable means :

$$C_6H_6 + Cl_2 \xrightarrow[FeCl_3]{\text{Catalyst}} C_6H_5Cl + HCl$$

However, there are some **points of difference** also. Hydrogen differs from the halogens in the fact that it has a much smaller tendency to form the anion H^-. Its electron affinity (72·8 kJ mol^{-1}) is smaller than those of the halogens which are greater than 295 kJ mol^{-1}. It forms stable hydrides only with strongly electropositive metals like sodium and calcium yielding NaH and CaH_2.

In view of the anomalous behaviour of hydrogen, it is difficult to assign any definite position to it in the periodic table. It is customary to include it in Group 1 as well as in Group 17, although it would be preferable to place it in a group of its own. It differs from the alkali metals in being much less electropositive and from the halogens in being much less electronegative. The position of hydrogen in the periodic table thus remains enigmatic.

HYDROGEN

Hydrogen occurs most commonly in the combined state in the form of water, hydrocarbons and carbohydrates. All organic matter contains hydrogen in combination with carbon, nitrogen and oxygen.

Preparation. On a small scale, the gas is prepared by the action of metals such as Na, K, Ca on cold water ; Mg on hot water ; Fe, Zn on superheated steam, Al, Sn, Zn on caustic alkalies and Fe, Zn, Al on dilute acids.

On a commercial scale, the gas is prepared by (*i*) electrolysis of acidulated water (*ii*) reduction of steam with carbon or iron and (*iii*) partial catalytic oxidation of crude naphtha and natural gas (methane).

Properties. Hydrogen forms covalent compounds with a number of non-metallic elements such as oxygen, nitrogen, fluorine, chlorine, bromine, etc. But at ordinary temperatures hydrogen exists in molecular state and in molecular hydrogen, the atoms have the stable helium structure (H : H), *i.e.*, both the H atoms acquire stable $1s^2$ configuration of He. It combines with oxygen, sulphur, nitrogen, bromine, iodine, etc., only when energy is supplied in the form of heat. With oxygen, for example, the reaction $2H_2 + O_2 \longrightarrow 2H_2O$, is not perceptible even at 300°C. The reaction is extremely slow even at 500°C. It is only at 700°C that the reaction becomes almost instantaneous. At higher temperatures it becomes explosive. It is believed that when energy is supplied to the gaseous mixture in the form of heat, some of the H_2 molecules get dissociated into atoms which combine more readily. Further, as the reaction is exothermic, the heat produced dissociates more molecules into atoms and a cumulative effect is thus produced. This explains the instantaneous and explosive nature of the reaction.

The combination with sulphur resulting in the formation of H_2S also takes place at high temperatures, though not so vigorously.

The combination with nitrogen requires a high temperature (450–500°C) besides a high pressure (200 atm) and the presence of a catalyst (finely divided iron with molybdenum as promoter). The product is ammonia.

Hydrogen combines with strongly electropositive metals such as Li, Na, K, Ca, etc., when heated, to form hydrides which are electrovalent compounds (hydrogen forming an anion) which have high melting points and conduct electricity when fused. The metal hydrides find many industrial applications. Calcium and lithium hydrides, for example, are used in **portable hydrogen generators** since they evolve large amount of hydrogen when added to water. The hydrides are also good reducing agents.

Hydrogen gas acts as a reducing agent. The oxides of the less electropositive metals, such as those of Cu, Zn, Pb, Fe, etc., are reduced when they are heated and hydrogen is passed over them. The oxides

of strongly electropositive metals, such as those of alkali metals and alkaline earths, are not reduced by hydrogen. Certain chlorides also get reduced by hydrogen.

Uses of Hydrogen. From the above discussion of physical and chemical properties it is easy to follow the important uses to which hydrogen has been put at various times.

1. *Hydrogen Generators.* The metallic hydrides, such as NaH and LiH, are used in portable hydrogen generators since, when put in water, they release large amounts of hydrogen. Tin and silicon hydrides have high heats of combustion. They are being examined as rocket fuels. The complex borohydrides, such as sodium borohydride, $NaBH_4$, on account of their solubility in organic solvents, are used as reducing agents in a number of organic reactions.

2. *Hydrogenation Processes.* Hydrogen gas is largely used in hydrogenation processes, that is, *processes in which hydrogen gas is added as such to compounds in the presence of a catalyst.* A few examples are given below.

(*i*) Vegetable oils, such as coconut oil, groundnut oil, cotton seed oil, which are liquid at ordinary temperatures, are treated with hydrogen at 170°C in the presence of finely divided nickel. They take up hydrogen and change into semi-solid fats which are used as a cooking medium in several countries.

(*ii*) Carbon monoxide takes up hydrogen under pressure in the presence of a catalyst consisting of a mixture of zinc oxide and finely divided copper, to give methyl alcohol.

$$CO + 2H_2 \xrightarrow{\text{Catalyst}} CH_3OH$$

(*iii*) Hydrogen is used in the production of synthetic petroleum. In the Bergius process, for example, the hydrogenation of coke is carried out at moderately high temperatures and extremely high pressures when several compounds of carbon and hydrogen which constitute different petroleum products, such as gasoline, kerosene and lubricating oils, are produced.

3. *Oxy-Hydrogen Flame and Atomic Hydrogen Flame.* When hydrogen is burnt in oxygen, a very hot flame known as oxy-hydrogen flame with a temperature of about 2000°–2500°C is produced. This temperature is sufficient to melt platinum and to cause a stick of lime to glow with a dazzling light, known as lime light. It is used in welding and other allied processes. The apparatus in which this flame is produced is known as *oxy-hydrogen torch.*

Langmuir, in 1927, devised another torch known as *atomic hydrogen torch* which gives a flame with temperature twice as high as that of oxy-hydrogen torch. It makes use of the heat liberated by the change of atomic hydrogen into molecular hydrogen. The molecular hydrogen is made to pass through an electric arc of tungsten when it absorbs energy and gets heated to a very high temperature between 3500 – 4000°C. As a result of this, the hydrogen molecules break down into atoms. $\Delta H_D = 458{\cdot}1$ kJ/mol. As soon as these atoms come out of the arc, they immediately reunite to form molecules. A large amount of heat equal to 458·1 kJ per mole of hydrogen is liberated in this process. The development of a very high temperature is not only due to the cumulative effect of the union of hydrogen atoms to form molecules but also due to the burning of hydrogen in oxygen.

Recently, a flame giving as high a temperature as 4000°C has been produced by burning fluorine in hydrogen.

4. *Reducing Agent.* Hydrogen is used in the reduction of metallic oxides in metallurgical processes. Molybdenum and tungsten, for instance, are prepared by the reduction of their oxides by hydrogen.

5. *Production of Ammonia.* Appreciable quantities of hydrogen are used in the production of ammonia by direct combination with nitrogen under pressure by Haber process. Ammonia is used as a refrigerant and as a source of fertilizers and explosives. At present, more hydrogen is being used in the manufacture of ammonia than for any other purpose.

NASCENT HYDROGEN

Hydrogen gas cannot reduce acidified solutions containing ferric, permanganate, dichromate or chlorate ions. But, if a small zinc piece is added to such solutions, these ions are reduced to ferrous,

manganous, chromic and chloride ions, respectively, by the hydrogen produced by the action of zinc on the acid present. Thus, hydrogen at the moment of its formation is more active than the ordinary hydrogen gas. *The hydrogen produced in contact with the substance to be reduced is known as* **nascent hydrogen.**

Theories of Nascent Hydrogen. A number of theories have been proposed to explain the superior activity of nascent hydrogen. Some of these are briefly discussed below.

a. Atomic hydrogen theory. Initially it was considered that at the moment of its liberation, hydrogen exists as atoms which are ready to react. In ordinary hydrogen, the atoms have already combined into molecules (H_2) which require extra energy to separate into atoms prior to chemical combination. Hence, nascent hydrogen is more active than ordinary (molecular) hydrogen. The theory, however, fails to explain why nascent hydrogen obtained from different sources is not equally reactive. Thus, chlorates are not reduced by nascent hydrogen generated by the action of sodium amalgam and water although they are easily reduced by nascent hydrogen produced by the action of zinc and dilute sulphuric acid. Again, hydrogen liberated during electrolysis at a lead cathode is more reactive than that set free at a silver cathode.

b. Energy association theory. According to this theory, it is believed that a part of the energy set free in a given reaction producing hydrogen, becomes associated with the liberated hydrogen and thus makes it hyperactive. Since the energy changes involved in different chemical reactions producing nascent hydrogen are different, the difference in the chemical reactivity of nascent hydrogen from different sources is understandable.

This theory also explains the difference in the reducing powers of hydrogen produced by electrolysis using cathodes of different metals. It has been, in general, observed that the higher the voltage required by the metallic cathode to liberate hydrogen, the greater is the reactivity of the nascent hydrogen formed. Here again some of the extra energy supplied becomes associated with the hydrogen and enhances its chemical activity.

c. Pressure theory. It has been shown by Ipatiev that the activity of ordinary hydrogen can be increased by applying a high pressure on it. The hydrogen gas at the moment of its liberation is in the form of very minute bubbles having a very high internal pressure. In the light of Ipatiev's work, this high internal pressure of gas bubbles may be responsible for the high chemical activity of the nascent hydrogen.

It may, however, be pointed out that none of the theories described so far is entirely satisfactory to explain the behaviour of nascent hydrogen.

ACTIVE HYDROGEN

When a stream of hydrogen gas at ordinary temperatures is subjected to silent electric discharge at the voltage of about 30,000 volts, an active variety of hydrogen is obtained. It is marked by its great chemical activity. For example, it combines directly at ordinary temperatures with lead and sulphur forming their hydrides. It also reduces copper oxide at ordinary temperatures.

The half-life period of this active hydrogen is only one-third of a second though some believe that it can be extended upto 10 seconds. It has been suggested that this active hydrogen exists either in the form of atoms or as H_3 molecules like ozone (O_3). But neither of these views has been finally accepted.

ATOMIC HYDROGEN

Atomic hydrogen can be prepared by exposing ordinary hydrogen at a low pressure to a high-tension electric discharge. The apparatus used is shown in Fig. 1. It consists of an S-shaped discharge tube fitted with water-cooled aluminium electrodes *A* and *B*. The discharge tube is about one and a half metre long and about 2 cm in diameter. Hydrogen is admitted into the tube at a low pressure (1 mm or less) while a high-tension discharge is passed by means of the electrodes *A* and *B*. Some of the hydrogen molecules get dissociated into atoms.

The action of atomic hydrogen on various substances can be studied by placing them in the gas current at *C*.

Atomic hydrogen can also be obtained by passing molecular hydrogen through an electric arc set up between tungsten rods. The temperature of the arc is maintained at 3500°–4000°C. In order to get maximum formation of atomic hydrogen, the pressure of the hydrogen gas led into the arc should be close to the atmospheric pressure.

In another more recent method, hydrogen containing mercury vapour is subjected to radiations emitted from a mercury vapour arc in a discharge tube. The radiation energy is first absorbed by the mercury vapour and then transferred from the mercury vapour to the hydrogen molecules which get dissociated into atoms.

$$Hg + h\nu \longrightarrow \underset{\text{Excited atom}}{Hg^*}$$

$$H_2 + Hg^* \longrightarrow 2H + Hg$$

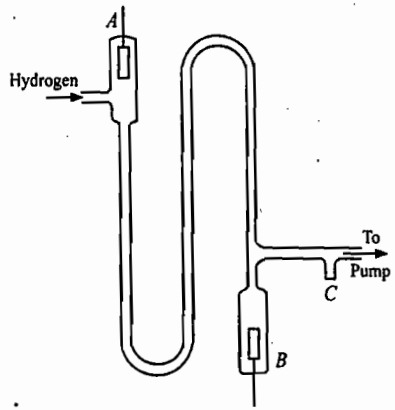


Fig. 1. Production of atomic hydrogen.

Properties of Atomic Hydrogen. 1. Unstable character and reactivity. Atomic hydrogen is highly unstable. Its half-life period is only 0·3 second. The atoms combine readily to form hydrogen molecules liberating a large amount of heat ($\Delta H_f = -458{\cdot}1$ kJ mol^{-1}).

The combination of hydrogen atoms takes place still more readily in the presence of metals like platinum, tungsten and molybdenum.

The half-life period of hydrogen increases considerably at very low pressures. This is due to the fact that at very low pressures, the atoms of hydrogen remain at considerable distances and take lot more time to come in contact with one another to form H_2 molecules. In other words, the atoms retain their identity for a longer period.

2. Combination with non-metals. Atomic hydrogen combines readily at ordinary temperatures with sulphur, phosphorus, arsenic, antimony and bismuth to form their hydrides. However, it does not combine with nitrogen. It also combines with halogens in cold and dark and reduces them to their hydracids. It combines readily with oxygen even at a very low temperature forming hydrogen peroxide.

3. Combination with metals. It combines with metals such as lithium, sodium, calcium at ordinary temperatures, producing their hydrides. It combines with silver and mercury at –180°C to form their hydrides, AgH and HgH_2.

4. Reducing action. Atomic hydrogen is an energetic reducing agent. The various reduction reactions of atomic hydrogen are described below.

It reduces the oxides, chlorides and sulphides of certain metals (*e.g.*, Cu, Ag, Hg and Bi) to free metals at ordinary temperatures. It also reduces barium sulphate to barium sulphide.

However, the more stable oxides like those of aluminium, magnesium, chromium and zinc, remain unaffected.

It reduces carbon dioxide to formic acid and carbon monoxide to formaldehyde.

$$CO_2 + 2H \longrightarrow HCOOH$$

$$CO + 2H \longrightarrow HCHO$$

It reduces phosphorus pentoxide to phosphine.

$$P_2O_5 + 16H \longrightarrow 2PH_3 + 5H_2O$$

Alkali metal salts, such as nitrates, amides and cyanides, are reduced to the free metals. Thus,

$$NaX + H \longrightarrow Na + HX; \quad X = NO_3^-, NH_2^-, CN^-$$

However, the sulphates and halides of these metals are unaffected.

Atomic hydrogen reduces benzene to cyclohexadiene and reduces olefins and acetylenes to the corresponding saturated hydrocarbons.

5. Hydrogenation. Atomic hydrogen immediately hydrogenates unsaturated fatty acids to saturated ones.

Uses of Atomic Hydrogen. It is used as a strong reducing agent. It is used in the preparation of certain metallic hydrides such as AgH and HgH_2. It is also used in the hydrogenation of certain unsaturated organic compounds.

ORTHO AND PARA HYDROGEN

It is now fully established that each particle in the nucleus of an atom is spinning either in clockwise or anticlockwise direction. This phenomenon is similar to the spinning of extra-nuclear electrons. The aggregate of all the spins of particles present in the nucleus gives a net spin to the nucleus called **nuclear spin**. It is represented by I. Each nuclear particle (proton or neutron) has a spin $\frac{1}{2}$. Since the nucleus of hydrogen atom contains only one particle, *i.e.*, a proton, its nuclear spin would be $\frac{1}{2}$. Thus, the nucleus of each of the two atoms of hydrogen in a H_2 molecule would have a nuclear spin $= \frac{1}{2}$.

The spins of the two nuclei may be parallel or antiparallel.

1. If the spins of the two nuclei in hydrogen molecule are *parallel, i.e.*, in the same direction, the total spin I of the nuclei would be $\frac{1}{2} + \frac{1}{2} = 1$. This type of hydrogen molecule in which *the total nuclear spin* is 1, is called **ortho hydrogen** (Fig. 2 *a*).

2. If the spins of the two nuclei in hydrogen molecule are *antiparallel, i.e.*, in opposite direction, total spin I of the nuclei would be $\frac{1}{2} - \frac{1}{2} = 0$. This type of hydrogen molecule in which *the total nuclear spin is zero*, is called **para hydrogen** (Fig. 2 *b*).

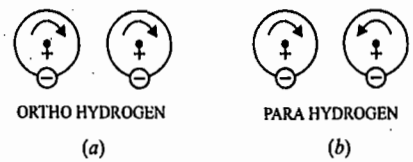


Fig. 2. Ortho and para hydrogen.

The Ratio of Ortho to Para Hydrogen. Ordinary hydrogen gas is an equilibrium mixture of ortho and para hydrogen :

$$\text{Ortho hydrogen} \rightleftharpoons \text{Para hydrogen}$$

The ratio of ortho to para hydrogen varies with temperature, as shown in Fig. 3. Evidently, this ratio increases with rise in temperature upto a temperature of about 300 K (*i.e.*, 27°C) and remains almost constant thereafter.

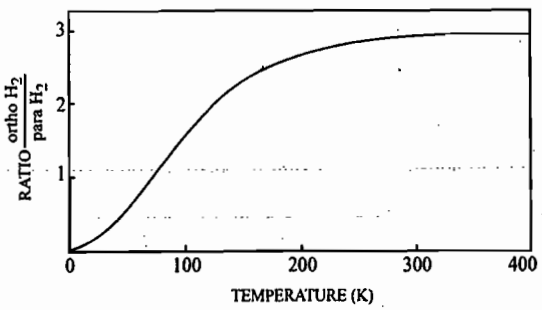


Fig. 3. Variation of the ratio of ortho to para hydrogen with temperature.

The ratio of ortho to para hydrogen at 300 K and above is 3 : 1. This means

that it is not possible to get pure ortho hydrogen at ordinary temperatures or above. The equilibrium

$$\text{Ortho hydrogen} \rightleftharpoons \text{Para hydrogen}$$

shifts toward the right on lowering the temperature, *i.e.*, the proportion of ortho hydrogen decreases and of para hydrogen increases on lowering the temperature. Thus, it has been possible to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature close to about 20 K. This evidently means that while we *can get pure para hydrogen* by lowering the temperature, we *cannot get pure ortho hydrogen* at any temperature.

The occurrence of ortho and para hydrogen in the ratio of 3:1 at room temperature and above may be explained as follows :

Any spinning nucleus or nuclei with nuclear spin $I > 0$, would generate spin angular momentun which is a vector quantity of the magnitude $\sqrt{(I(I+1)}\ h/2\pi$. The angular momentun vector is quantized in space, *i.e.*, it is allowed $(2I + 1)$ orientations in space with respect to any direction. *Each of these orientations corresponds to a particular energy state for the nucleus.* As mentioned above, the total nuclear spin I for *ortho hydrogen* is 1. Hence, the spin angular momentum vector has $(2\times1 + 1) = 3$ orientations with respect to, say, the Z-direction with $I_z = M_I \doteq +1, 0, -1$ which would generate three nuclear energy states, as shown in Fig. 4.

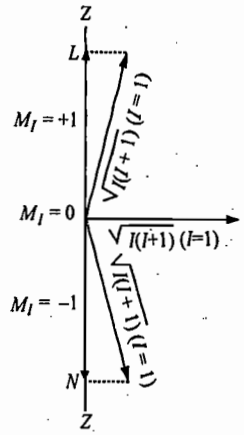


Fig. 4. The orientations of spin angular momentum vector $I = 1$. $I_z (= M_I)$ has the value +1, 0 or −1, according as the vector is parallel, perpendicular or antiparallel to the Z-axis. I_z is the z-component of the angular momentum vector for any of its orientations.

In the absence of an external magnetic field, all the three nuclear energy states are *degenerate, i.e.*, of equal energy. *The population of the molecules of ortho hydrogen would thus be the same in all the three energy states.*

The total nuclear spin I for *para hydrogen*, as mentioned above, is zero, *i.e.*, $I = 0$. Therefore, the spin angular momentum vector would have only one orientation $(2\times0 + 1) = 1$ with $I_z = M_I = 0$ with respect to the Z-direction. This would generate only one nuclear energy state. Hence, *all the molecules of para hydrogen would be populated in this lone energy state.*

Because of the differences in the nuclear spin interactions encountered in ortho and para hydrogen, the nuclear energy state of para hydrogen would have *lower energy* and the three degenerate nuclear energy states of ortho hydrogen would have *higher energy*, as shown in Fig. 5, although, ΔE, the energy difference between states I and II is quite small.

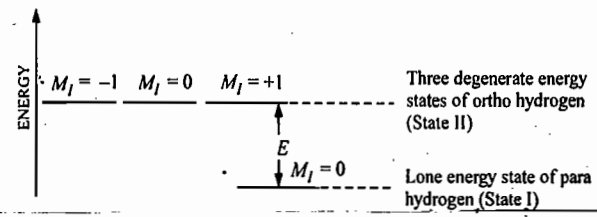


Fig. 5. The energy states of ortho and para hydrogen.

Hydrogen molecules at very low temperatures would mostly occupy state I of lower energy in the form of para hydrogen. The equilibrium

$$\text{Para hydrogen} \rightleftharpoons \text{Ortho hydrogen}$$

remains almost entirely towards the left. As the temperature is gradually increased, more and more of the molecules would get excited from the lower energy para hydrogen state to yield ortho hydrogen which would occupy state II of higher energy. Since state II comprises of three energy states of equal energy, molecules of ortho hydrogen get distributed equally in all the three states. With further increase in temperature, the equilibrium shifts more and more towards the right yielding more and more of ortho hydrogen. Ultimately, at room temperature the amount of ortho hydrogen produced is such that its population in each of the three degenerate energy states II becomes equal to that of para hydrogen in lower energy state I. In other words, *all the four energy states are now occupied by hydrogen to almost the same extent.* Of these four energy states, there are three energy states for the occupancy of ortho hydrogen and only one energy state for the occupancy of para hydrogen. Hence the ratio of ortho to para hydrogen becomes 3 : 1. The ratio would remain the same irrespective of any further increase in temperature because the occupancy of all the four states would now be equally affected by the increase of temperature.

Preparation of Para Hydrogen. 1. The best method of obtaining para hydrogen in almost pure state consists in adsorbing hydrogen gas on activated charcoal contained in a quartz vessel and gradually lowering the temperature of the vessel to 20 K. After the lapse of some time interval the gas is pumped off and is found to consist of 99·8% of para hydrogen.

2. Para hydrogen can also be prepared by keeping ordinary hydrogen under high pressure at liquid air temperature for several days.

Preparation of Ortho Hydrogen. Preparation of ortho hydrogen in pure form is very difficult as, at room and higher temperatures, it is always mixed with the para form and at lower temperatures, the equilibrium, para $\rightleftharpoons$ ortho, shifts towards para form. However, when molecular hydrogen is brought in contact with materials containing unpaired electrons, like Fe, Ni, O_2, NO, etc., reasonably pure ortho form is obtained.

Properties of Ortho and Para Hydrogen. The two forms resemble each other in their chemical properties. However, the parallel and antiparallel nuclear spins lead to different internal energies of the two forms. This results in differences in some of their physical properties like boiling point, specific heat and thermal conductivity. These differences have been used in measuring the proportion of ortho and para forms in a sample of ordinary hydrogen.

Ionised Forms of Hydrogen. The known ionised forms of hydrogen are H^+, H_2^+, H_3^+ and H^-. We are too familiar with H^+ to discuss it here. However, it is pertinent to add that it is a very very strong acid so much so that it combines in gaseous state even with helium atom to form HeH^+. The species H_2^+ is highly unstable with H – H bond distance of 1·06 Å. The species H_3^+ was first detected by J. J. Thomson when a high voltage electric discharge was passed through hydrogen gas and has a bent structure formed by a $3c-2e$ bond resulting from the angular overlap of three $1s$ orbitals of H atoms. H_3^+ is also a shortlived species. The species H^-, however, exists in a number of hydrides. The chemistry of hydrides is discussed below in some details.

HYDRIDES

Hydrogen combines with a number of other elements including metals and non-metals to form compounds called *hydrides*. Based on their physical and chemical properties, the hydrides have been classified into three main categories :

1. *Ionic or Salt-like Hydrides*
2. *Molecular or Covalent Hydrides* and
3. *Interstitial Hydrides.*

Another category, named as *Indermediate Hydrides*, is also known.

1. Ionic Hydrides. These are formed by metals which are more electropositive than hydrogen. Such metals are located towards the left of the periodic table. The examples are alkali metals and alkaline earth metals except Be and Mg. These are formed by transfer of electrons from metals to hydrogen atoms and contain hydrogen as H^- ion, *e.g.*, lithium hydride (Li^+H^-) and calcium hydride ($Ca^{2+}2H^-$). These are white crystalline solids, have ionic lattices and behave like salts. They have high melting and boiling points and conduct electricity in fused state liberating hydrogen at the anode. The reaction

$$\tfrac{1}{2}H_2(g) + e^- \longrightarrow H^-(g); \qquad \Delta H = +146{\cdot}4 \text{ kJ mol}^{-1}$$

is evidently *endothermic*. Therefore, unless the element with which hydrogen combines is highly electropositive (*i.e.*, has a high tendency to lose electrons), the ionic hydride formed would be unstable. This is the reason why only alkali and alkaline earth metals, which can readily lose electrons to yield cations, form stable ionic hydrides.

Ionic hydrides are prepared by direct combination of the metals with hydrogen at high temperatures, usually close to 700°C. They are strong reducing agents, as shown below.

$$2CO + NaH \longrightarrow HCOONa + C$$
$$SiCl_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$$
$$PbSO_4 + 2CaH_2 \longrightarrow PbS + 2Ca(OH)_2$$

They burn spontaneously in air on heating on account of their decomposition into hydrogen (*e.g.*, $CaH_2 \longrightarrow Ca + H_2$) which is inflammable.

They are strong bases. When dissolved in water they form hydroxides and evolve hydrogen.

$$NaH + H_2O \longrightarrow NaOH + H_2$$

They form complexes, *e.g.*, lithium aluminium hydride, $Li[AlH_4]$ and sodium borohydride, $Na[BH_4]$.

$$LiH + AlH_3 \longrightarrow Li[AlH_4]$$
$$NaH + BH_3 \longrightarrow Na[BH_4]$$

The complexes are also good reducing agents.

The thermal stabilities of alkali metal hydrides decrease and their chemical reactivities increase from LiH to CsH. The alkaline earth metal hydrides behave similarly.

Uses. The ionic hydrides and their complexes are used as reducing agents. Since they evolve hydrogen when heated and, therefore, ignite spontaneously, they are used as solid fuels.

2. Molecular or Covalent Hydrides. Beryllium and magnesium of Group 2 form hydrides which have considerable covalent character in their M–H bonds. The hydride MgH_2 has a *rutile* structure. It has lower enthalpy of formation and is thermally less stable than the true saline hydrides. In fact, MgH_2 represents a state of transition between pure ionic hydrides and pure covalent hydrides. Bonding in BeH_2, on the other hand, is predominantly covalent. It has a polymeric structure with hydrogen atoms forming bridges between the Be atoms as in boranes. Both BeH_2 and MgH_2 are prepared by direct action of the metal with hydrogen at elevated temperatures.

The hydrides formed by elements of Groups 13 to 17 are predominantly covalent although in some cases, as, for example, in HF, the bonds are partly ionic.

The hydrides of Group 13 elements (*i.e.*, BH_3 and AlH_3) are electron-deficient compounds and exist in polymerised forms [*e.g.*, B_2H_6, B_4H_{10} and $(AlH_3)_n$]. Hydrides of B and Al are employed as efficient reducing agents.

Carbon of Group 14 forms polynuclear hydrides in which two or more atoms of the element are directly bonded to each other as well as to hydrogen thus giving numerous hydrocarbons. Silicon and some other non-metal elements of Group 14 also show this property but to a very limited extent. Silicon, for example, gives hydrides such as Si_2H_6, Si_3H_8, Si_4H_{10}, etc. Sn and Pb also form hydrides which are rather unstable.

The covalent hydrides of As, Sb, Bi are also known.

The hydrides of elements after Group 13 become increasingly acidic in character on moving from left to right along a given row in the periodic table. Thus, while NH_3 is a weak base, H_2O is neutral and HF is acidic. Similarly, in the next row, while PH_3 is a weak base, H_2S is a weak acid and HCl is highly acidic.

In covalent hydrides, the H–X bond energies generally *decrease* with increase in atomic number (and hence atomic size) of the element within a group. The lesser the bond energy, the lesser is the stability of the H–X bond. This readily accounts for the *instability* of the hydrides of heavier elements of Groups 14 and 15. In fact, PbH_4 and BiH_5 are so unstable that these can be prepared only in traces.

Within a group, the boiling points of covalent hydrides (barring the hydride of the first element) *increase regularly with increase in atomic number of the element and the molar mass of the hydride.* Thus, boiling points of hydrides of elements of Group 15, 16 and 17 (with the exception of top elements) increase as we move down the groups, as shown in Table 1.

TABLE 1

Boiling Points of Hydrides of Elements of Groups 15, 16 and 17

Group 15		Group 16		Group 17	
Hydride	b.p. (°C)	Hydride	b.p. (°C)	Hydride	b.p. (°C)
NH_3	– 33·0	H_2O	+ 100	HF	+ 19·4
PH_3	– 84·6	H_2S	– 59·6	HCl	– 85·0
AsH_3	– 55·1	H_2Se	– 42·0	HBr	– 67·1
SbH_3	– 17·0	H_2Te	– 1·8	HI	– 35·5

The boiling points of the hydrides of top elements, *viz.*, NH_3, H_2O and HF are abnormally high. This is because of the association of these molecules through hydrogen bonding. These molecules, thus, have long polymeric structures.

The electronegativity difference in carbon (the first element of Group 14) and hydrogen is very small. There is thus no association of CH_4 molecules through hydrogen bonding. It has, therefore, the lowest boiling point amongst the hydrides of Group 14 elements. As expected, the boiling points of these hydrides vary in the order :

$$CH_4 < SiH_4 < GeH_4 < SnH_4$$

3. Transition and Inner Transition Metal Hydrides. Interstitial Hydrides. The transition metal hydrides are almost invariably non-stoichiometric compounds with varying composition. Ti, Zr and Hf, for instance, form hydrides with compositions $TiH_{1\cdot7}$, $ZrH_{1\cdot9}$ and $HfH_{1\cdot8}$, respectively. The M–H distances in all these non-stoichiometric compounds are different. Cr and Cu form hydrides approximating to CuH and CrH. The transition metals V, Nb and Ta form hydrides which are also non-stoichiometric. These hydrides are unstable and have *extensive range of composition.*

The transition metal hydrides are strong reducing agents and are used as such in metallurgical processes.

There is lot of ambiguity in the nature of bonding in non-stoichiometric transition metal hydrides. The arrangements of metal atoms in transition metal hydrides remain the same as in the corresponding metals although the densities of the hydrides are less than the densities of the corresponding metals. This suggests that *hydrogen occupies interstitial sites in the metallic lattices.* These hydrides are, therefore, sometimes called **interstitial hydrides.** Some research workers consider these hydrides as mere *solid solutions.* There is, however, strong evidence to suggest that there is some sort of association between the metal and the interstitial hydrogen in these hydrides.

The **inner transition metal hydrides** are of varying composition which falls between the limiting formulae MH_2 and MH_3. These hydrides are formed when the inner transition metals react with hydrogen slightly above the room temperature at atmospheric pressure. Lanthanides Yb and Eu give hydrides of stoichiometry approximating to YbH_2 and EuH_2. These two lanthanides do not form hydrides approximating to MH_3. There is evidence to suggest that the bonding in YbH_2 and EuH_2 is *predominantly ionic* and the two hydrides contain Yb^{2+} ($4f^{14}$) and Eu^{2+} ($4f^7$) ions. YbH_2 is known to absorb more hydrogen to give a non-stoichiometric hydride approximating to $YbH_{2\cdot5}$ in which probably both Yb^{2+} and Yb^{3+} ions are present.

Other lanthanides also form hydrides approximating to the formula MH_2. The bonding in these hydrides is also *predominantly ionic* in which the lanthanide ion is present as M^{3+} and not as M^{2+}. The third valence electron of the metal in such hydrides is located in a metallic conduction band so that these hydrides have considerable conductivity. For instance, LaH_2 is a dark coloured material with a conductivity of about 10 ohm^{-1} per centimetre in which the 5*d* electron enters the La metallic conduction band. With further uptake of hydrogen, the stoichiometry approaches LaH_3 in which all the three valence electrons (*i.e.*, $5d^1s^2$) are used up in bonding and there is thus no valence electron to be contributed to the La metallic conduction band. As a result, there is 100-fold decrease in the conductivity of LaH_3 compared to that of LaH_2.

A number of actinides form stoichiometric and non-stoichiometric hydrides out of which UH_3 is the most studied. It can be prepared by reacting uranium directly with hydrogen. It exists in two crystalline forms α and β. Both the forms are highly reactive and are thus used for the preparation of other compounds of uranium.

Occlusion of Hydrogen by Palladium and Palladium Alloys. If red hot palladium is cooled in the atmosphere of hydrogen, it absorbs or occludes about 1000 times its own volume of hydrogen. As the gas is absorbed, the metallic conductivity falls till the material becomes a semiconductor at a composition approximating $PdH_{0\cdot5}$. Palladium does not lose its ductility unless the amounts of hydrogen absorbed are very large.

In the process of occlusion, hydrogen is first chemisorbed at the surface of Pd and at increased pressures it enters the metal lattice. The precise nature of the metal–hydrogen interaction is not clear although there is some evidence to suggest that a disordered, non-stoichiometric palladium hydride approaching the composition PdH is formed. The occluded hydrogen has high mobility inside the metal lattice and diffuses rapidly through the metal.

Alloys of palladium such as Pd-Ag and Pd-Au occlude greater amount of hydrogen than the palladium metal.

ISOTOPES OF HYDROGEN

Hydrogen has three isotopes with mass numbers 1, 2 and 3. These are described below.

1. Protium or Ordinary Hydrogen. This isotope is the most common and constitutes 99·984 per cent of total hydrogen available in nature. The molecule of ordinary hydrogen is diatomic. The nucleus of the hydrogen atom ^1_1H which consists of a solitary proton (mass number = 1) has no neutron at all. There is a solitary electron outside the nucleus (atomic number = 1).

2. Deuterium or Heavy Hydrogen. Deuterium constitutes only about 0·016 per cent of total hydrogen occurring in nature. In other words, in nature there are roughly 6000 atoms of hydrogen for every 1 atom of deuterium. The molecule of deuterium or heavy hydrogen is diatomic. The nucleus of the heavy hydrogen atom ^2_1H or ^2_1D contains a proton and a neutron (mass number = 2). There is, however, a solitary electron outside the nucleus as expected (atomic number = 1).

3. Tritium. Tritium is formed in the upper atmosphere by certain nuclear reactions which are induced by cosmic rays. It constitutes only 10^{-15} per cent of total natural hydrogen. The molecule of tritium is diatomic. The nucleus of tritium atom ^3_1H or ^3_1T consists of one proton and two neutrons

(mass number = 3). There is a solitary electron outside the nucleus as expected (atomic number = 1). It is radioactive in character.

All the three isotopes have similar chemical properties. However, they differ from one another in the rates of their reactions. Their physical properties differ appreciably from one another on account of differences in their mass numbers.

HEAVY HYDROGEN OR DEUTERIUM

History of Discovery. The discovery of heavy hydrogen or deuterium was the result of the discrepancy observed between the very exact physical and chemical atomic masses of hydrogen. Aston was the first to show this discrepancy and the difference between the two values led Birge and Menzel, in 1931, to predict the existence of a heavier hydrogen isotope. In the same year, Urey, Brickwedde and Murphy obtained, by fractional evaporation of liquid hydrogen, a heavy residue which was examined spectroscopically and was found to contain an isotope of mass number 2. They called it deuterium and gave it the symbol D. Urey was awarded Chemistry Nobel Prize in 1934.

Methods of Preparation

1. Separation from Ordinary Hydrogen. There are several methods by which deuterium can be separated from ordinary hydrogen. Some of these are described below.

a. By diffusion process. Deuterium can be isolated from ordinary hydrogen by taking advantage of different rates of diffusion of the two isotopes. Protium (^1_1H), which is lighter, diffuses more readily than deuterium. This method, though slow and tedious, has been found to give spectroscopically pure deuterium. The diffusion is carried out under reduced pressure. The lower the pressure, the greater is the efficiency of the process.

b. By fractional distillation of liquid hydrogen. Deuterium can be separated from ordinary hydrogen by careful fractional distillation of liquid hydrogen. Heavy hydrogen boils at – 249·5°C while protium boils at a lower temperature of –252·8°C. Hence, fractional distillation of liquid hydrogen can result in enrichment of the last fraction in deuterium. This fraction, very much enriched in deuterium, can be used for recovery of deuterium by the diffusion process described above.

c. By adsorption on charcoal. Protium is adsorbed more readily and more strongly on solid surfaces in general and on charcoal surface in particular. Thus, when a mixture of the two isotopes is led over charcoal kept at liquid air temperature, most of the protium gets adsorbed while most of the deuterium passes out unchanged.

d. By chemical methods. The lighter isotope (protium) is more reactive than the heavier isotope (deuterium). Thus, when ordinary hydrogen is passed over red hot copper oxide, the lighter component is consumed more than the heavier one in the reaction involving the reduction of CuO. In this way enrichment of ordinary hydrogen in deuterium is possible. Deuterium is then isolated by the process of diffusion, discussed above.

2. From Heavy Water. a. By electrolysis of heavy water, D_2O. The first step in this method is to get higher concentration of D_2O (heavy water) in ordinary water. It may be noted that ordinary water contains a very small proportion (about 1 part in 5000) of the oxide of heavy hydrogen, *i.e.*, D_2O. Although the boiling point of D_2O (101·42°C) is only slightly higher than that of H_2O (100°C), yet it has been found that a partial separation of the heavy water can be affected by fractional distillation of water. This method of getting a higher concentration of heavy water was used, originally, by Urey, Brickwedde and Murphy.

The concentration of heavy water can also be increased by fractional freezing of water. Heavy water freezes at 3·8 °C while ordinary water freezes at 0°C at 1 atm pressure.

The residual water left after prolonged electrolysis of water is also richer in D_2O.

In the **second step,** heavy water along with ordinary water is electrolysed to give a mixture of deuterium and ordinary hydrogen (protium). The deuterium content in the mixture is very much higher than that in ordinary hydrogen. Deuterium can be obtained from this mixture by the *diffusion process* already discussed.

b. By chemical methods. Deuterium is obtained from heavy water by the action of sodium metal.

$$2D_2O + 2Na \longrightarrow 2NaOD + D_2$$

However, in this method a part of heavy water changes into sodium deuteroxide and, therefore, complete recovery is not possible.

Deuterium can also be obtained by passing vapour of heavy water over heated metals such as zinc or tungsten (the metals are converted into their oxides in the process).

Physical Properties. Deuterium, like hydrogen, is a colourless, odourless and tasteless gas. It is insoluble in water and is a bad conductor of heat and electricity. Some of the physical constants of deuterium are presented in Table 2 in which, for comparison, the corresponding figures for ordinary hydrogen have also been given.

TABLE 2

Some Physical Constants of Hydrogen and Heavy Hydrogen

Property	Ordinary hydrogen, H_2 (Protium)	Heavy hydrogen, D_2 (Deuterium)
Boiling point	– 252·8°C	– 249·5°C
Melting point (or Triple point)	– 259·2°C	– 254·3°C
Heat of vaporisation	904 J mol^{-1}	1226 J mol^{-1}
Heat of fusion	117 J mol^{-1}	219 J mol^{-1}
Vapour pressure (at triple point)	5·4 mm Hg	5·8 mm Hg
Molar volume of solid	26·14 cm^2	23·17 cm^2
Dissociation energy	435·1 kJ mol^{-1}	438 kJ mol^{-1}

Chemical Properties 1. Burning in oxygen. Like hydrogen, deuterium is combustible and burns in air or oxygen forming deuterium oxide, D_2O.

2. Action with halogens. It combines with halogens under suitable conditions forming their *deuterides* which are analogous to the halogen hydracids. For example, D_2 reacts with F_2 in dark to produce D_2F_2. However, it reacts with Cl_2 in the presence of light to produce DCl.

3. Combination with nitrogen. Deuterium combines with nitrogen in the presence of a catalyst and forms nitrogen deuteride (ND_3) which is similar to ammonia. ND_3 is also known as deutero ammonia.

4. Combination with metals. Like hydrogen, deuterium combines with alkali metals at high temperature (363°C) forming deuterides which closely resemble metallic hydrides in their chemical properties as well as crystalline structures.

5. Addition reactions with unsaturated hydrocarbons. Deuterium, like hydrogen, gives addition reactions with unsaturated hydrocarbons. Thus, when a mixture of deuterium and ethylene is passed over heated nickel, ethylene deuteride, $C_2H_4D_2$, is formed which is a saturated hydrocarbon like ethane.

6. Exchange reactions. The deuterium and hydrogen atoms undergo ready exchange. Thus, detuerium reacts with H_2, NH_3, H_2O and CH_4, at high temperatures and exchanges its hydrogen partially or completely to give products such as HD, ND_3, D_2O, CD_4, etc. The exchange reactions, in general, are catalysed by finely divided nickel or chromium.

Uses of Deuterium. 1. Accelerated deuterons (nuclei of deuterium atoms) are employed for bombarding atoms in nuclear transformations and artificial radioactivity.

2. Since the replacement of an ordinary hydrogen atom in a compound by a deuterium atom causes an increase in the density of the compound, deuterium has been found useful as a *tracer element* in chemical and biological research and in understanding mechanisms of various reactions.

TRITIUM

Tritium occurs very very rarely in nature and constitutes only a negligibly small fraction (10^{-15} per cent) of the total hydrogen. Its atom is denoted by the symbol $^{3}_{1}T$. The molecule of tritium is diatomic. T_2O is present in water in extremely minute traces and, therefore, its recovery from water is of no practical interest.

Production of Tritium. Tritium has been obtained in small quantities by nuclear reactions, as shown below.

1. By bombardment of beryllium with deuterium.

$$^{9}_{4}Be + ^{2}_{1}D \longrightarrow \underset{\text{Isotope of beryllium}}{^{8}_{4}Be} + \underset{\text{Tritium}}{^{3}_{1}T}$$

2. By bombardment of boron, nitrogen or lithium by slow moving neutrons.

$$\underset{\text{Boron}}{^{10}_{5}B} + \underset{\text{neutron}}{^{1}_{0}n} \longrightarrow \underset{\text{Isotope of boron}}{^{11}_{5}B} \longrightarrow \underset{\text{Tritium}}{^{3}_{1}T} + \underset{\alpha\text{ particles}}{2\,^{4}_{2}He}$$

$$\underset{\text{Nitrogen}}{^{14}_{7}N} + \underset{\text{neutron}}{^{1}_{0}n} \longrightarrow \underset{\text{Isotope of nitrogen}}{^{15}_{7}N} \longrightarrow \underset{\text{Tritium}}{^{3}_{1}T} + \underset{\alpha\text{ particles}}{3\,^{4}_{2}He}$$

$$\underset{\text{Lithium}}{^{6}_{3}Li} + \underset{\text{neutron}}{^{1}_{0}n} \longrightarrow \underset{\text{Tritium}}{^{3}_{1}T} + \underset{\alpha\text{ particle}}{^{4}_{2}He}$$

Properties of Tritium. Tritium is a radioactive isotope of hydrogen. The half-life period of tritium atom is 12·4 years. It undergoes β transformation yielding an isotope of helium of mass number 3.

$$^{3}_{1}T \longrightarrow \underset{\text{Isotope of helium}}{^{3}_{2}He} + \underset{\beta\text{ particle}}{^{0}_{-1}n}$$

The molecule of tritium is diatomic and is written as T_2

Some of the physical constants of tritium are : Boiling point = – 248·1°C ; Melting point = –252·4°C ; Vapour pressure at the triple point = 162·0 mm, Heat of vaporisation at the boiling point = 139·3 kJ mol^{-1}

Being an isotope of hydrogen, it shows the same reactions as hydrogen and deuterium. For example, when burnt in oxygen, it forms tritium oxide, T_2O. Tritium hydride is obtained by treating lithium hydride with tritium.

$$LiH + T_2 \longrightarrow LiT + TH$$

However, the rate at which it reacts is very slow.

Uses. 1. It is used in several tracer experiments. 2. Tritium hydride is used in preparing a large number of organic compounds containing this radioactive isotope.

HEAVY WATER

The oxide of heavy hydrogen is called **heavy water.** It was discovered by Urey (1932). He showed that ordinary water contains small proportion (about 1 part in 5000) of the oxide of heavy hydrogen, *i.e.*, D_2O.

Preparation of Heavy Water

Heavy water is finding increasing applications in scientific research and as a moderator for slowing down neutrons in nuclear reactions. It is, therefore, being prepared in large amounts. The main source of heavy water is ordinary water from which it is isolated either by prolonged electrolysis or by fractional distillation.

1. By Prolonged Electrolysis of Water. The apparatus designed by Brown, Dagget and Urey for electrolysis of water consists of a steel cell about 45 cm long and 10 cm in diameter (Fig. 6). The cell itself serves as the cathode while the anode consists of a cylindrical sheet of nickel with a number of holes punched in it. A large number of such cells are used for electrolysis of water in several stages. The gases obtained from each stage are separately burnt and the water thus formed is returned to the previous stage. The heavy water gradually concentrates in the residue left behind. The process usually consists of five stages, as described below.

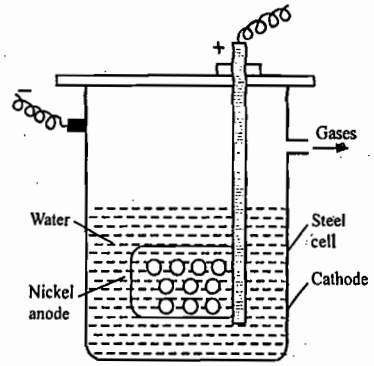


Fig. 6. Electrolytic cell for the preparation of heavy water.

First stage. Thirty electrolytic cells, described above, are used in the first stage. Each cell is charged with three litres of a 3 per cent solution of sodium hydroxide in ordinary water. An electric current at 110 volts is used for electrolysis. The evolved gases containing light hydrogen ($^{1}_{1}H$) and oxygen are discarded. When the electrolysis has been going on for about 72 hours, the total charge gets reduced to 1/6th of its volume and contains about 2·5% heavy water.

Second stage. In the second stage, the residue from the first stage is electrolysed using 6 cells till the content of heavy water increases to about 12%. The gases evolved evolved are burnt and the water formed is returned to the first stage cells.

Third stage. The residue from the second stage is further electrolysed and the content of heavy water is raised to nearly 60%. The gases evolved are burnt and the water formed is returned to the second stage cells.

Fourth stage. The residue from evolved the third stage is further subjected to electrolysis and nearly 99·5% heavy water is obtained. The gases evolved are burnt, as usual and sent to the third stage cells.

Fifth stage. The nearly 99·5% heavy water obtained from the fourth stage is freed from alkali and other impurities by distillation and the distillate is then electrolysed. The hydrogen evolved is pure deuterium. This, when burnt in oxygen, yields 100% pure D_2O.

2. By Fractional Distillation of Water. A partial separation of heavy water from ordinary water can be affected by fractional distillation. Advantage is taken of small difference in boiling points of protium oxide and deuterium oxide (Table 3).

TABLE 3

Physical Properties of Water and Heavy Water

Property	H_2O	D_2O
Density at 20°C (g cm^{-3})	0·988	1·017
Freezing point (°C)	0	3·82
Boiling point (°C)	100	101·42
Temperature of maximum density (°C)	4	11·6
Maximum density	1·000 (4°C)	1·1073 (11·6°C)
Heat of fusion (kJ mol^{-1})	6·01	5·68
Heat of vaporisation (kJ mol^{-1})	40·5	41·9
Surface tension (dyn cm^{-1}) at 20°C	72·8	67·8
Refractive index at 20°C	1·3330	1·3284
Dielectric constant	82·0	80·5
Viscosity (millipoises) at 20°C	10·09	12·6
Solubility of NaCl (g per litre)	350	805
Dissociation constant at 25°C	$1·0\times10^{-14}$	$0·3\times10^{-14}$
Ionic mobilities ($cm^2\,s^{-1}\,V^{-1}$) at 18°C :		
of K^+ ions	64·2	54·4
of Cl^- ions	65·5	55·3

Since the boiling points do not differ much, it is necessary to use a very long column and to repeat the process several times.

Properties of Heavy Water. Physical Properties. Heavy water, like ordinary water, is a colourless, odourless and tasteless mobile liquid. However, there is a marked difference between physical properties of ordinary water and heavy water, as shown in Table 3.

Higher viscosity of heavy water is responsible for lower solubility of ionic solids like NaCl and smaller mobilities of ions. Density of heavy water is expected to be higher on account of higher molar mass of this compound.

Chemical Properties. Heavy water differs only slightly from ordinary water in its chemical properties. However, the reactions of D_2O are slower than those of H_2O. Some of the important chemical reactions of heavy water are given below. All these reactions are given by ordinary water with a much greater vigour.

1. Action with metals. D_2O reacts slowly with alkali and alkaline earth metals producing deuteroxides and liberating heavy hydrogen.

2. Action with metallic oxides. Basic oxides of metals like sodium and calcium dissolve in D_2O and form heavy alkalies such as NaOD and $Ca(OD)_2$.

3. Action with acid anhydrides. D_2O dissolves acid anhydrides or acidic oxides of non-metals like P_2O_5, SO_3, etc., to form the corresponding acids containing heavy hydrogen, *e.g.*, D_2SO_4, D_3PO_4, etc.

4. Action with metallic carbides. Like H_2O, heavy water reacts with metallic carbides and forms deutero-hydrocarbons.

$$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + 3CD_4$$

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

5. Action with metallic nitrides, phosphides and arsenides. Heavy water decomposes metallic nitrides, phosphides, etc., forming deutero ammonia, deutero phosphine, etc.

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$

$$Ca_3P_2 + 6D_2O \longrightarrow 3Ca(OD)_2 + 2PD_3$$

$$Na_3As + 3D_2O \longrightarrow 3NaOD + AsD_3$$

The melting and boiling points of deutero-compounds are higher than those of the corresponding compounds of hydrogen. Thus, the melting and boiling points of ND_3 are higher than those of NH_3.

6. Electroysis. Heavy water containing dissolved P_2O_5 (to make it a good conductor) on electroysis decomposes into deuterium and oxygen which are liberated at the cathode and anode, respectively.

7. Formation of deuterates. Like ordinary water, D_2O may be associated with salts and other compounds as water of crystallization. The hydrates so formed are termed **deuterates** *e.g.*, $CuSO_4.5D_2O$, $Na_2SO_4.10D_2O$, $NiCl_2.6D_2O$, etc.

8. Exchange reactions. When compounds containing hydrogen are treated with D_2O, hydrogen undergoes an exchange for deuterium. If the compounds contain ionically bound hydrogen, the exchange reactions take place almost instantaneously, *e.g.*,

$$NaOH + D_2O \longrightarrow NaOD + HOD$$

$$HCl\,(aq) + D_2O \longrightarrow DCl + HOD$$

$$NH_4Cl + 4D_2O \longrightarrow ND_4Cl + 4HOD$$

In the case of compounds containing non-ionic hydrogen, the exchange reactions take place slowly and require the presence of a catalyst.

9. Biological properties. The biological properties of heavy water are still in dispute although it is established that heavy water retards the growth of living organisms, plants and animals. Lewis had shown that tobacco seeds do not grow in heavy water. Also, pure heavy water kills small fish, tadpoles and mice when fed upon it. Certain moulds have, however, been found to develop better in heavy water.

Uses of Heavy Water. 1. Heavy water is used for slowing down the fast moving neutrons. Neutrons are used for bringing about fission of uranium atoms. But, for this purpose their speed should be slowed down. This is done by passing them through heavy water.

2. Heavy water is commonly employed as a *tracer compound* for studying the mechanisms of many chemical reactions for confirming the structures of compounds. For example, when hypophosphorous acid, H_3PO_2, is treated with D_2O, only one ionic hydrogen of the acid is found to exchange for deuterium. Since deuterium is known to exchange only with ionic hydrogen, it can be safely inferred that H_3PO_2 contains only one ionizable hydrogen and, therefore, it is a monobasic acid.

3. Heavy water is used as one of the *references* in nuclear magnetic resonance spectroscopy.

OTHER COMPOUNDS OF DEUTERIUM

A brief description of some other deuterium compounds is given below.

1. Deuterium peroxide, D_2O_2. This compound is prepared by treating barium peroxide with dilute deutero sulphuric acid (D_2SO_4) dissolved in D_2O.

2. Deutero ammonia, ND_3. This is prepared by the action of heavy water on magnesium nitride, as already shown.

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$

ND_3 boils at 242 K whereas NH_3 boils at 238·5 K.

3. Deuterium chloride, DCl. It is prepared by a number of methods, for instance, by reducing silver chloride with deuterium, by treating NaCl with D_2SO_4 or by the action of D_2O on thionyl chloride.

$$2AgCl + D_2 \longrightarrow 2Ag + 2DCl$$

$$2NaCl + D_2SO_4 \longrightarrow Na_2SO_4 + 2DCl$$

$$SOCl_2 + 2D_2O \longrightarrow D_2SO_3 + 2DCl$$

4. Deutero methane, CD_4. It is most conveniently prepared by the action of D_2O on aluminium carbide.

$$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + 3CD_4$$

5. Deutero acetylene, C_2D_2. It can be prepared by treating calcium carbide with heavy water.

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

QUESTIONS

1. Discuss the position of hydrogen in the periodic table. Describe its important properties and uses.
2. Describe the preparation of nascent hydrogen. Discuss the theories of nascent hydrogen.
3. How is atomic hydrogen prepared ? Why is atomic hydrogen more reactive than molecular hydrogen?
4. What do you understand by ortho and para hydrogen ? How and why does the ratio of ortho to para hydrogen vary with temperature ? How can para hydrogen be obtained ?

5. Differentiate carefully between ortho and para hydrogen. Explain clearly why the ratio of ortho to para hydrogen at room temperature and above is 3 : 1.
6. Describe the methods for the preparation of ortho and para hydrogen. Give important properties of these two forms of hydrogen.
7. What are hydrides ? How are they classified ? Discuss briefly the ionic hydrides, covalent hydrides and interstitial hydrides.
8. Name the three isotopes of hydrogen. Give their electronic structures.
9. Describe the methods of preparation, properties and uses of deuterium and tritium.
10. (*a*) What is meant by heavy hydrogen ? How is it separated from ordinary hydrogen ? Discuss the important chemical properties of heavy hydrogen.

    (*b*) Write a note on spin isomerism of hydrogen.
11. What is meant by heavy water ? How is it obtained on a large scale ? Compare its properties with those of ordinary water.
12. What is heavy water ? How does it differ from ordinary water ? Give at least four chemical reactions of heavy water.

12 THE MAIN GROUP ELEMENTS. GENERAL CHARACTERISTICS

The *s* **and** *p* **block elements** taken together are known as the **main group elements** and as such they include the elements belonging to Groups 1, 2, 13 to 18. The elements belonging to Groups 1 and 2 which have one or two electrons in their outermost s orbitals preceded by noble gas configurations are known as *s* **block elements** while the elements belonging to Groups 13 to 18 which have one, two, three, four, five and six electrons, respectively, in the outermost *p* orbitals constitute the *p* **block elements.** In all these elements, the inner orbitals are completely filled. Thus, while the general outer electronic configuration of *s* block elements is $\mathbf{n}\,s^{1-2}$, that of *p* block element is $\mathbf{n}\,s^2p^{1-6}$.

GENERAL CHARACTERISTICS OF THE MAIN GROUP ELEMENTS

Atomic radii, ionic radii, ionization energies, electron affinities and **electronegativities** of the main group elements have already been discussed in details in Chapter 2. Other characteristics of these elements are discussed below.

Metallic Character

Metals have a tendency to lose electrons yielding positive ions : $M \longrightarrow M^{z+} + ze^-$. This tendency gives rise to what is known as the **metallic character** of an element. The greater the tendency to lose electrons, the greater is the metallic character of the element.

The tendency of an element to lose electrons is closely connected with the ionisation energy of the element. The smaller the ionisation energy of an element, the greater will be its tendency to lose electrons, *i.e.*, the greater will be its metallic character. Further, since it is easier to remove an electron from a larger atom than from a smaller atom, it follows that *metallic character increases as we move down from top to bottom in a given* **group** *of the periodic table.* For example, in Group 13, the metallic character increases as we move down from boron towards thallium. The effect is more striking in Groups 14 and 15. For example, in Group 14 , while carbon, the element at the top, is a non-metal, silicon and germanium, the next two elements, show some metallic character while tin and lead, the last two elements, have distinctly metallic character. In Group 15, nitrogen, the top element, is non-metallic while bismuth, the last element, has distinctly metallic character.

Further, since the ionisation energy increases on moving across a period from left to right on account of decrease in atomic radius, as already discussed in Chapter 2, *metallic character decreases on moving from left to right in a given* **period.** Consequently, the main group elements with strong metallic character are located mostly in the left or lower left portion while those with strong non-metallic character are found in the right or top right portion of the periodic table. Somewhere in between these two extremes, lie a number of other elements which show characteristics of both metals and non-metals. These are called **metalloids** or **semi-metals.** The division of elements into the three categories is

represented in Table 1.

TABLE 1
Division of Elements into Metals, Non-metals and Metalloids

s Block Elements		*p* Block Elements					
1	2	13	14	15	16	17	18
				NON-METALS			
H						H	He
Li	Be		C	N	O	F	Ne
Na	Mg			P	S	Cl	Ar
K	Ca	Ga			Se	Br	Kr
Rb	Sr	In	Sn			I	Xe
Cs	Ba	Tl	Pb	Bi		At	Rn
Fr	Ra						
	Metals				Metalloids		

It may be pointed out, however, that since the electrical properties are generally a function of the crystal structure of the element concerned, the classification of elements into metals, non-metals and metalloids (or semi-metals) becomes somewhat enigmatic because of the existence of some of the elements in more than one allotropic forms having different electrical properties. For example, white tin (or β tin) is metallic in character and is rightly placed in Table 1. However, grey tin (or α tin) having a diamond-like structure resembling that of Si and Ge, shows semi-metallic properties and, therefore, should find a different place in this table. Similarly, one allotropic form of Se consists of eight-membered rings, Se_8 and is non-metallic like S_8 whereas the other allotrope of Se, having a chain structure, has electrical properties of a semi-metal. Likewise, white phosphorus (having P_4 units) and red phosphorus do not conduct electricity and are thus non-metallic whereas black phosphorus having a sheet-like structure conducts electricity to a limited extent and thus behaves as a semi-metal or metalloid. It follows, therefore, that unless we know the crystal structure, it is difficult to unequivocally classify elements into metals, non-metals or semi-metals.

Metallic elements have a crystal structure with high coordination number of 12 (in close-packed lattice) or 8 (in body centred cubic lattice) whereas non-metals exist generally as volatile molecular solids. The semi-metals, generally, have either a three-dimensional network or a layer or a long chain structure. The coordination number in crystals of semi-metals is small compared to metallic crystals.

Polarizing Power and Polarisability

The distortion of the electron charge cloud of an anion by a cation is termed as **polarization.** The distortion of the electron charge cloud occurs due to the *attraction* between the positive charge of cation and the electrons of the anion and the *repulsion* between the electrons and between the positively charged nuclei. *The extent to which a cation can distort the electron charge cloud of an anion is known as the* **polarizing power of the cation** and *the ease with which the electron charge cloud of an anion gets distorted by a cation is known as the* **polarizability of the anion.**

Fajan suggested the following rules to estimate the extent to which a cation can polarize an anion. These are commonly known as **Fajan's rules.**

1. *The cations with high charge and small size have high polarizing power, i.e.*, they can distort the electron charge cloud of an anion highly effectively. In other words, the polarizing power of a cation is directly proportional to its charge and inversely proportional to its size. The polarising power of a cation is generally expressed in terms of a parameter called **ionic potential** which is the *ratio of the effective nuclear charge of the cation and its size.* The higher the ionic potential of a cation, the greater would be its polarizing power.

2. *The anions possessing high negative charge and large size are easily polarizable.* Both these factors would decrease the hold of the nucleus of the anion on its electron charge cloud which, therefore, can be easily distorted by a cation. Thus, anions such as I^- and Se^{2-} are easily polarizable because of their large size. Similarly, anions such as As^{3-} and P^{3-} sare easily polarizable because of their high charge.

3. As we know, the *d* electrons shield the nucleus poorly as compared to *s* and *p* electrons (Chapter 1). If we have two cations of the same size and charge, the cation having a configuration with *d* electrons

would have more effective nuclear charge due to poorer screening of the nucleus by the *d* electrons and would have more ionic potential or polarizing power than the cation having a configuration with no *d* electrons in the *penultimate shell.* For example, Hg^{2+} and Ca^{2+} ions have the same charge and nearly the same size (the ionic radii being 1·16 Å and 1·14 Å, respectively), yet Hg^{2+} ion with $[Xe]4f^{14}5d^{10}6s^0$ configuration has more polarizing power than Ca^{2+} ion with $[Ar]4s^0$ configuration.

It may be noted that these are not only the anions which get polarized; the cations also get polarised though the polarisation is much less due to their smaller size.

Consequences of Polarisation. ***1. Diagonal relationship.*** The ionic potentials of some simple cations are given below.

Cation	Ionic Potential	Cation	Ionic Potential	Cation	Ionic Potential
Li^+	17	Be^{2+}	64	B^{3+}	150
Na^+	10	Mg^{2+}	31	Al^{3+}	60
K^+	8	Ca^{2+}	20	Ga^{3+}	48

The above data clearly show that ionic potential or polarizing power of cations generally *increases* as we move from left to right within a period and *decreases* as we move from top to bottom within a group (cations with charge higher than + 3 generally do not exist).

It is well known that the *first* element in any given group of the periodic table resembles the *second* element of the *next group.* Thus, Li forms organometallic compounds like Mg. None of the other elements of Group 1 forms such compounds. Similarly, the chemistry of Be is similar to that of Al despite the difference in their oxidation states. *This type of relationship of the first element of a group with the second element of the next group is known as* **diagonal relationship.** The cause of similarity in the pairs of such elements can be understood by considering a few examples.

If we move from Be^{2+} to B^{3+}, the charge increases and the size slightly decreases. The polarising power or ionic potential of B^{3+} is thus more than that of Be^{2+}. If, now, we move down from B^{3+} to Al^{3+}, the size increases and, therefore, the polarizing power of Al^{3+} is less than that of B^{3+}. If we make both the moves together, it would amount to moving *diagonally* from Be^{2+} to Al^{3+}. The overall change in charge and size in the above movement is such that they give rise to almost the same ionic potential of Be^{2+} and Al^{3+}, *viz.*, 64 and 60, respectively. Thus, Be^{2+} and Al^{3+} ions have similar polarizing powers and, therefore, have similar properties. Likewise, Li^+ and Mg^{2+} ions have similar polarizing powers and, therefore, have similar properties. Thus, the phenomenon of polarization satisfactorily explains the cause of diagonal relationship in elements of the first three groups of the periodic table. In subsequent groups, the diagonal relationship can be explained on the basis of electronegativities of elements. This aspect would be discussed at an appropriate place in this chapter.

2. Melting points of halides. Let us consider the melting points of $BeCl_2$ (405°C) and $CaCl_2$ (772°C). The anion Cl^- is common in both the compounds. Both the cations belong to Group 2 of the periodic table and carry two units of positive charge each. Because of its small size, Be^{2+} ion has greater polarizing power than the Ca^{2+} ion. As a result, the electron charge cloud of Cl^- ion is pulled towards Be^{2+} and there is considerable overlap of electron charge clouds of Cl^- and Be^{2+} ions. Consequently, the bond formed between Be and Cl atoms is *polar covalent* rather than ionic. In $CaCl_2$, the extent of distortion of electron charge cloud of Cl^- by Ca^{2+} is less. The extent of overlap of electron charge clouds of Ca^{2+} and Cl^- ions is negligible so that the bond formed between Ca and Cl atoms is *mainly ionic* and only negligibly covalent. This explains the lower melting point of $BeCl_2$ which has a polar covalent bond between Be and Cl and higher melting point of $CaCl_2$ in which the bonding is predominantly ionic.

Let us now consider compounds with cations of different charges but of nearly the same size, as, for example, NaBr (m.p. 755°C), $MgBr_2$ (m.p. 700°C) and $AlBr_3$ (m.p. 498°C). The polarizing power of Al^{3+} ion is greater than that of Mg^{2+} ion which, in turn, is greater than that of Na^+ ion. Therefore, NaBr has the least covalent character and highest melting point whereas $AlBr_3$ has maximum covalent character and lowest melting point of the three compounds.

Finally, let us consider anions of different sizes forming compounds with the same cation, *viz.*, LiF (m.p. 870°C), LiCl (m.p. 613°C), LiBr (m.p. 547°C) and LiI (m.p. 466°C). Because of differences of sizes, the polarizability of the anions is in the order : $I^- > Br^- > Cl^- > F^-$. Hence, LiI has the maximum and LiF has the minimum covalent character. As a result, LiI has the lowest and LiF has the highest melting point of all the compounds.

3. Solubilities of silver halides. AgF is soluble in water whereas AgCl is not. This is because the Cl^- ion, due to its large size, is polarised by Ag^+ ion to a greater extent than the F^- ion. As a result, the bonding in AgCl is predominantly covalent whereas in AgF it is mainly ionic. Therefore, AgF being an ionic compound, is soluble in water whereas AgCl, being a covalent compound, is insoluble in water.

4. Decomposition of carbonates. The temperatures at which the various metal carbonates decompose to give metal oxides and CO_2 gas, according to the reaction $MCO_3 \longrightarrow MO + CO_2$, are given below :

Metal Carbonate	Decomposition Temperature (°C)	Metal Carbonate	Decomposition Temperature (°C)
$BeCO_3$	100	$BaCO_3$	1360
$MgCO_3$	400	$CdCO_3$	~ 350
$CaCO_3$	900	$PbCO_3$	~ 350
$SrCO_3$	1290		

From the data on the decomposition of alkaline earth carbonates, it is clear that the greater the size of the cation, the higher is the decomposition temperature of the carbonate. The cations with large size will not be able to polarise the electron charge cloud of the carbonate ion so effectively, with the result that bonding in carbonates with larger cations would be mainly *ionic*. On the other hand, the cations with smaller size would distort the electron charge cloud on the oxygens of the carbonate ion very effectively so that the carbonate ion would get split into CO_2 and O^{2-} ion to form the metal oxides more easily, *i.e.*, at a lower temperature.

It may be observed, however, that although Cd^{2+}, Pb^{2+} and Ca^{2+} ions have nearly the same size, yet the carbonates of Cd^{2+} and Pb^{2+} decompose at a much lower temperature (~ 350°C) than $CaCO_3$ (decomposition temperature 900°C). This is explained as follows : The outer electronic configurations of Cd^{2+}, Pb^{2+} and Ca^{2+} are, respectively, $4s^2p^6d^{10}$, $4f^{14}\,5s^2p^6d^{10}\,6s^2$ and $3s^2p^6$. Thus, while Cd^{2+} and Pb^{2+} ions have *d* electrons in the penultimate shells, Ca^{2+} ion does not have any *d* electron in its electronic configuration. Since *d* electrons have a poorer screening effect than *s* and *p* electrons, therefore, the *effective nuclear charge* in case of Cd^{2+} and Pb^{2+} ions would be more than in Ca^{2+} ions. Consequently, Cd^{2+} and Pb^{2+} ions would have greater polarising power than Ca^{2+} ions. The electron charge cloud on the oxygens of CO_3^{2-} ion would get distorted more in the case of Pb^{2+} and Cd^{2+} ions than in the case of Ca^{2+} ion. The CO_3^{2-} ion would , therefore, get split *more easily* to give CO_2 and O^{2-} ion in the case of $CdCO_3$ and $PbCO_3$ than in the case of $CaCO_3$.

Melting Points and Boiling Points

The metallic character of elements also affects their melting as well as boiling points. As the metallic character *increases*, the melting and boiling points generally *decrease*. This is illustrated in the case of elements of Group 14, the melting and boiling points of which are given in Table 2.

TABLE 2

Melting and Boiling Points of Elements of Group 14

Elements	C	Si	Ge	Sn	Pb
Melting Points (°C)	3727	1410	937·5	231·8	327·4
Boiling Points (°C)	4830	2680	2830	2270	1725

We know, for example, that the metallic character *increases* on moving from carbon to lead in the same group. Hence, the melting and boiling points generally *decrease* in the same order. The melting point of tin is exceptionally low.

The metallic character *decreases* as we move from lithium to carbon in the same period. The melting and boiling points, therefore, *increase* in the same order. The boiling point of boron, however, is comparatively low (Table 3). The remaining four elements (namely, N, O, F and Ne) of this period are gases at ordinary temperatures.

TABLE 3

Melting and Boiling Points of the First Four Elements of the Second Period

Elements	Li	Be	B	C
Melting Points (°C)	181	1277	2030	3727
Boiling Points (°C)	1330	2770	2550	4830

Oxidising and Reducing Properties

It may be recalled that an **oxidising agent** is a substance which is in a position to *gain electrons* and a **reducing agent** is a substance which is in a position to *lose electrons*. Since elements with low ionization energies can easily undergo loss of electrons, they are good reducing agents.

Since ionization energies decrease on moving down a group, it is evident that *reducing character* of elements in a given group increases with increase in atomic number. Conversely, the *oxidising character* of elements in a group decreases with increase in atomic number. Thus, amongst the elements of Group 1, while the first element, lithium, is a *moderate* reducing agent, the last element, cesium, is a *strong* reducing agent. Similarly, in case of Group 14 elements, while the first element, carbon, is a *weak* reducing agent, the last element, lead, is a *strong* reducing agent.

Further, since ionisation energy increases on moving across a period from left to right, it follows that reducing character decreases while oxidising character increases with increase in atomic number in a given period. For example, while the first element of the third period, sodium, is *a reducing agent*, the last element of the same period, chlorine, is an *oxidising agent*.

Electrode Potentials. Electropositive Character

Electrode potential is defined *as the potential developed on a metal when it is immersed in a solution of its own ions*. If the concentration of the ions is *one molar*, the potential developed is called **standard electrode potential**. Standard electrode potentials of some of the main group elements are given in Table 4.

According to the latest convention, the electrode reactions are written in the form of reduction, *i.e.*,

TABLE 4

Standard Electrode Potentials (in volts) of Redox Couples involving Some Important Main Group Elements (on Hydrogen Scale)

H^+, H 0						
Li^+, Li − 3·04	Be^{2+}, Be − 1·85	Be^{3+}, B − 0·87			O_2, OH^- + 0·44	1/2 F_2, F^- + 2·87
Na^+, Na − 2·71	Mg^+, Mg − 2·52	Al^{3+}, Al − 1·66			S, S^{2-} + 0·49	1/2 Cl_2, Cl^- + 1·36
K^+, K − 2·92	Ca^{2+}, Ca − 2·87	Ga^{3+}, Ga − 0·52		As^{3+}, As + 0·25		1/2 Br_2, Br^- + 1·06
Rb^+, Rb − 2·99	Sr^{2+}, Sr − 2·89	In^{3+}, In − 0·34	Sn^{2+}, Sn − 0·15	Sb^3, Sb + 0·21		1/2 I_2, I^- + 0·53
Cs^+, Cs − 3·02	Ba^{2+}, Ba − 2·90	Tl^+, Tl − 0·34	Pb^{2+}, Pb − 0·13	Bi^{3+}, Bi + 0·23		

consumption of electrons. Accordingly, the half-cell reaction for Li^+, Li electrode is written as

$$Li^+ + e^- \longrightarrow Li\,(s)\ ; \qquad E^\circ_{el} = -3{\cdot}04\ V$$

Since negative reduction potential implies positive oxidation potential, we may write the above reaction as

$$Li\,(s) \longrightarrow Li^+ + e^-\ ; \qquad E^\circ_{oxid} = +3{\cdot}04\ V$$

Since a reducing agent is a substance which is capable of *losing* electrons, it is evident that elements with **positive oxidation potentials** (*viz.*, negative standard electrode potentials) are capable of acting as **reducing agents** in aqueous solution. Conversely, the elements with negative oxidation potentials (*viz.*, positive standard electrode potentials), are capable of acting as **oxidising agents**. Accordingly, the elements in Groups 1, 2 and 13 are reducing agents while those in Groups 15, 16 and 17 are oxidising agents.

In general, the reducing character tends to decrease and oxidising character tends to increase as we move across a period from left to right in the periodic table. Lithium is, thus, the strongest reducing agent while fluorine is the strongest oxidising agent.

Elements having *negative reduction potentials* or *positive oxidation potentials* are said to be **electropositive** since they have a greater tendency than hudrogen to chang into **positive ions** ($M \longrightarrow M^+ + e^-$). The greater the positive oxidation potential (or negative standard electrode potential), the greater is the electropositive character of the element. Lithium, evidently, is the *strongest electropositive elements* and fluorine is, accordingly, the *strongest electronegative element.*

The electropositive character is seen to decrease on moving across a period from left to right. The trends on moving down a group, though not so definite, indicate, in general, an increase in electropositive character. In the case of the first group, the values are fairly close. In the case of the second group, the electropositive character shows gradual increase on moving down the group. In the third group, electropositive character increases from boron to aluminium but decreases on moving to the next higher elements, namely, gallium, indium and thallium. The reason is that while boron and aluminium follow the *s* block elements, gallium, indium and thallium follow the *d* block elements. The *d* electrons provide much less shielding of the nucleus and, therefore, the orbital electrons are held more firmly by the nucleus and are thus difficult to be knocked out. These elements, therefore, are less electropositive.

Oxidation States

The oxidation states which various elements can have in forming compounds are closely connected with the number of valency electrons. Since this number changes periodically, it is expected that *the oxidation states of elements will also change periodically.* This is illustrated in Table 5 in which the maximum positive and negative oxidation states of the first 18 elements have been listed.

TABLE 5
Periodicity of Oxidation States

	Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
Element	H							He
Electrons in shells	1							2
Highest oxidation states	−1 +1							0
Element	Li	Be	B	C	N	O	F	Ne
Electrons in shells	2, 1	2, 2	2, 3	2, 4	2, 5	2, 6	2, 7	2, 8
Highest oxidation states	+1	+2	+3	+4 −4	+5 −3	−2	−1	0
Element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
Electrons in shells	2, 8, 1	2, 8, 2	2, 8, 3	2, 8, 4	2, 8, 5	2, 8, 6	2, 8, 7	2, 8, 8
Highest oxidation states	+1	+2	+3	+4 −4	+5 −3	+6 −2	+7 −1	0

It is evident that with each unit increase in atomic number, the oxidation state changes by one unit, the change, of course, proceeds in cycles. The noble gases, having zero oxidation state, are followed by elements having + 1 oxidation state (alkali metals) and these, in turn, are followed by elements having + 2 oxidation state (alkaline earth metals), and so on. Negative oxidation states are usually exhibited by elements in Groups 14 to 17.

It is also seen that while positive oxidation state increases, negative oxidation state decreases with increasing atomic number on moving across the period from left to right.

In a group, the *s* block elements show only one stable oxidation state (+1 for alkali metals and +2 for alkaline earth metals). However, *p* block elements generally show more than one stable oxidation state. The maximum oxidation state shown by a *p* block element is equal to the total number of *s* and *p* electrons in the valence shell. In addition to this, some of the *p* block elements show oxidation states which differ from the group oxidation state by steps of two. For example, the elements of Group 14 exhibit two oxidation states of + 4 and + 2. The + 4 state is more important in the first two elements carbon and silicon. The + 2 state becomes more and more stable as we go down the group. Thus, the compounds in which the last two elements tin and lead are in + 2 state, are more stable than those in which these elements are in + 4 state.

Similarly, the elements of Group 13 show + 3 and + 1 oxidation states. As we go down the group, the + 1 oxidation state becomes more and more stable. Thus in the case of heavier elements In and Tl, + 1 oxidation state is more stable than the + 3 oxidation state.

It is evident from the above description that if the elements in a group show variable oxidation state, *the heavier elements of that group* (*e.g.*, elements Sn and Pb of Group 14 and elements In and Tl of Group 13) *show reluctance to exist in higher oxidation state and prefer to stay in lower oxidation state.* The outer electronic configurations of 13th and 14th group elements are ns^2p^1 and ns^2p^2, respectively. Since the valence *p* electrons have lesser probability of being nearer to the nucleus than the valence *s* electrons, the former are easier to be removed or excited to higher orbitals than the latter. Because of this, the two *s* electrons were thought to be inert, *i.e.*, they remained paired and did not take part in bonding especially in heavier elements. This concept was given the name **inert pair effect.** As a result of this effect, the stable oxidation states of such elements were two units less than the total number of valence electrons. Thus, Sn ($5s^2p^2$) and Pb ($6s^2p^2$) have more stable oxidation state of $4 - 2 = 2$ while In ($5s^2p^1$) and Tl ($6s^2p^1$) have more stable oxidation state of $3 - 2 = +1$. However, *the concept of inert pair effect has several lacunae* which we shall discuss a little later in this chapter.

An alternative explanation for the stability of lower oxidation states in heavier elements is as follows : Since the atomic sizes of heavier elements are comparatively large, a sideways overlap to form pi bonds is not favoured. Thus, only sigma covalent bonds are formed in the case of heavier elements. In contrast, the lighter elements, because of their smaller size, are capable of forming both sigma and pi bonds. In other words, comparatively *fewer* valence electrons are involved in bond formation in the case of heavier elements. This accounts for the stability of *lower* oxidation states in these elements.

Diagonal Relationship

As we move diagonally across the periodic table, the elements, although belonging to different (adjacent) groups, show certain similarities. These similarities, though weaker than those within a group, are, nevertheless, quite well prononuced particularly in the following pairs of the main group elements :

Group 1	Group 2	Group 13	Group 14
Li	Be	B	C
Na	Mg	Al	Si

The reason for this diagonal similarity, as already discussed, is as follows : On moving from left to right across a period, the ionic charge increases while the ionic size decreases, thus causing an increase in its polarising power (Fajan's rule). On the other hand, on moving down a group, the ionic charge

remains the same while the ionic size increases and, therefore, the polarising power decreases. When we move diagonally, these two effects partly balance each other and, therefore, there is no marked change in their properties.

Diagonal relationship is also exhibited by elements of Groups 15, 16 and 17. Thus, C shows diagonal relationship with P ; N with S and O with Cl. The diagonal effect in the case of non-metals (C, P, N, S, O, Cl) cannot be explained on the basis of the ionic charge. This is because these elements have no metallic character and, therefore, the explanation of *similarity in their properties on the basis of their polarising power, generally expressed in terms of ionic potential, viz.*, cationic charge/cationic size ratio, has no meaning.

However, the diagonal effect in non-metals can be explained on the basis of similarity in electronegativities of diagonal elements. Consider the electronegativities of elements, as shown :

C	N	O	F
(2·5)	(3·0)	(3·5)	(4·0)
Si	P	S	Cl
(1·8)	(2·1)	(2·5)	(3·1)

As can be seen, the electronegativities *decrease* on moving down a group and *increase* on moving across a period. These two effects balance each other on moving diagonally so that the diagonal elements have similar electronegativities and hence similar chemical properties. Thus, the pairs of elements C, P ; N, S and O, Cl have similar electronegativities and, therefore, have similar chemical properties. It may, however, be emphasised that the similarities in electronegativities of the diagonal non-metal elements are not as close as the similarities in the polarizing powers (ionic potentials) of the diagonal metal elements.

COMPOUNDS OF MAIN GROUP ELEMENTS

OXIDES

Almost all the main group elements form oxides which can be classified into ***three categories*** : 1. *Basic oxides* which react with acids 2. *Acidic oxides* which react with bases and 3. *Amphoteric oxides* which react with both acids and bases. The products in all cases are termed as *salts*.

Periodic Trends in Acid-Base Character of Oxides. Generally speaking, on moving across a period, *the acid-base character of the oxides gradually changes from basic to amphoteric and finally to acidic*. Thus, on moving across the third period, it is observed that while Na_2O is strongly basic, MgO is less basic, Al_2O_3 is amphoteric, SiO_2 is weakly acidic, P_2O_5 is acidic, SO_3 is strongly acidic and Cl_2O_7 is even more strongly acidic. On moving down a group, it is observed that the oxides exhibit gradually *increasing basic character* or *decreasing acidic character*. This may be illustrated by considering oxides of Group 13 elements. Thus, while B_2O_3 is weakly acidic, Al_2O_3 and Ga_2O_3 are amphoteric whereas In_2O_3 and Tl_2O_3 show increasing basic character.

Type of Bonding in Oxides. The type of bonding in oxides depends considerably on the difference in the electronegativities of the element and oxygen. If this difference is large, the oxide generally has ionic structure. For example, the oxides of alkali metals have an ionic antifluorite structure in which each metal ion is surrounded by four oxide ions and each oxide ion is surrounded by eight metal ions. Alkaline earth metal oxides with the general formula MO have an ionic NaCl type structure (Chapter 6).

If the electronegativity differences are small, the bonds formed are predominantly *covalent*. Thus, oxides of non-metals whose electronegativity is close to that of oxygen, exist as discrete molecules and not as ions. Examples are NO, F_2O, etc.

The oxides of *heavier* non-metals and semi-metals have *complex* crystal structures in solid state. Thus, while CO_2 exists as a discrete molecule, SiO_2 has an infinite three-dimensional network in which each Si atom is *covalently bonded* with four oxygen atoms. GeO_2 and SnO_2 also have complex three-

dimensional structures containing Ge–O and Sn–O covalent bonds. Oxides of N, P and As have simple molecular structures whereas oxides of Sb and Bi have complex three-dimensional net work containing Sb–O and Bi–O covalent bonds. In Group 16, oxides of sulphur have simple molecular structures whereas SeO_2 and TeO_2 have infinitely long-chain structures.

Stability of Oxides. Almost every main group element (with the exception of halogens, nitrogen and noble gases) forms *at least one oxide which has a negative free energy of formation and is thus stable*. The stabilities of M–O bonds are represented by the magnitude of their molar enthalpies of formation or better by their equivalent enthalpies of formation. The equivalent enthalpy of formation of an oxide M_xO_y is obtained by dividing the molar enthalpy of formation by $2y$. The equivalent enthalpies of formation of various oxides when plotted as a function of the positions of the elements in the periodic table, give a curve as shown in Fig. 1.

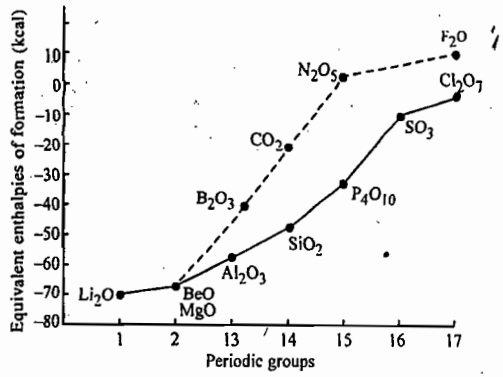


Fig. 1. Equivalent enthalpies of formation of various oxides (in kcal) as a function of the positions of the elements in the periodic table.

It is apparent from this figure that oxygen forms compounds of greater stability with elements that are farther off from it in the periodic table. Thus, while Li_2O, with a high negative enthalpy of formation, is the most stable, F_2O with a positive enthalpy of formation, is the least stable oxide.

According to Fig. 1, the order of stability of oxides of elements from Mg to Cl is as follows :

$$MgO > Al_2O_3 > SiO_2 > P_4O_{10} > SO_3 > Cl_2O_7$$

HYDRIDES

Hydrogen combines with a number of other elements including metals and non-metals to form compounds called *hydrides*. Based on their physical and chemical properties, the hydrides have been classified into three main categories, *viz.*, *1. Ionic or Salt-like Hydrides 2. Molecular or Covalent Hydrides* and *3. Interstitial Hydrides*. The preparation, properties and uses of these hydrides have already been discussed in details in the last chapter on 'Hydrogen.'

HALIDES

The main group elements form halides which can be classified as *1. Ionic or Salt-like Halides 2. Covalent or Acid Halides 3. Complex Halides*. However, due to a wide difference of electronegativities amongst the halogens, the classification is just arbitrary. The line of demarcation between ionic and covalent halides is not very sharp. Therefore, the discussion based on this classification is in no way comprehensive and complete.

1. Ionic or Salt-like Halides. These halides exist as ionic or semi-ionic crystals in solid state. They are generally characterised by (*i*) their comparatively high melting and boiling points (*ii*) their solubility in polar solvents and (*iii*) their high conductivity in fused state or in solutions. The magnitude of these properties, however, varies considerably because of factors such as charge and size of the metal ion, electropositive character of the metal and electronegative character of the halogen involved. True ionic character is, however, limited to the halides of alkali and alkaline earth metals. The anhydrous halides of other elements are more covalent than ionic in solid state although they dissolve in polar solvents to give ionic solutions.

The increase in oxidation number and decrease in size of cation increases the polarising power of a cation and promotes covalent character in halides (see Fajan's rules discussed earlier in this chapter). For example, in the fourth period, ionic character goes on decreasing and covalent character goes on

increasing as we move from $KCl \longrightarrow CaCl_2 \longrightarrow ScCl_3 \longrightarrow TiCl_4$. The last halide, $TiCl_4$, is essentially covalent in character.

The covalent character in halides of a particular element increases with increase in size and decrease in electronegativity of the halogen. Thus, there is a distinct decrease in ionic character as we move from $LiF \longrightarrow LiCl \longrightarrow LiBr \longrightarrow LiI$. Similarly, amongst the halides of aluminium, AlF_3 is essentially ionic, $AlCl_3$ has an intermediate character while $AlBr_3$ and AlI_3 exist as covalent dimers. The fluorides of metallic elements are essentially ionic whereas the other halides may or may not be so.

In the case of a metal showing more than one oxidation state, the ionic character of the metal halides decreases with increase in the oxidation state. For example, while $PbCl_2$ is largely ionic, $PbCl_4$ is largely covalent.

Salt-like halides vary widely in their solubility in water. Although many fluorides are soluble, the fluorides of lithium and alkaline earths are insoluble owing to their large lattice energies. Chlorides, bromides and iodides are generally soluble and the solubility increases with increase in the size of the halide ion. The reverse is true of halides in which covalent bonding is appreciable.

The halide ions are oxidisable to free halogens, the ease of oxidation increasing with increase in the size of the halide ion. Thus, out of all halides, the iodides are most easily oxidisable. They undergo oxidation even by aerial oxygen in acidic solutions.

2. Covalent or Acid Halides. These halides generally exist as discrete molecules and are derived from either non-metals, or metals with high charge/size ratios. As a convention, the non-metal halogen compounds containing oxygen, sulphur or nitrogen as a third element (as, for example, $POCl_3$) are also included in this class. The covalent halides have low boiling points, *i.e.*, they are volatile. They are soluble in non-polar solvents and are liable to undergo solvolytic reactions when brought in contact with polar solvents. In the series of halides derived from a particular non-metal, melting points generally increase with increase in their molar masses as is generally the case with characteristic covalent compounds.

The hydrogen halides deserve a special mention here. All of them dissolve in water owing to the following reaction :

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

These halides, therefore, act as acids in water.

Hydrogen fluoride undergoes association because of hydrogen bonding, as already mentioned. In solid state, it exists as an infinite linear zig-zag chain of molecules. The association of HF molecules occurs in liquid and vapour phase as well. Other hydrogen halides show very little hydrogen bonding and very little association of their molecules.

3. Complex Halides. Entry of halide ions into the coordination sphere of a metal ion is a common phenomenon. Fluoride ion forms stable complexes with *smaller cations* such as Ba^{2+}, Al^{3+}, Si^{4+} because of strong electrostatic attraction and high energies of the resulting bonds.

In contrast, the fluoride ion does not form stable complexes with *larger cations*. The stability of halide complexes formed with larger cations increases in the order : Iodide > Bromide > Chloride. These complexes are easily polarisable. Some common halogen complexes of main group elements are : $[BeX_4]^{2-}$, $[BX_4]^-$, $[AlX_6]^{3-}$, $[GaX_6]^{3-}$, $[InX_6]^{3-}$, $[TlX_6]^{3-}$, $[AsX_6]^{3-}$, $[GeX_6]^{2-}$, $[SnX_6]^{2-}$, $[SbX_6]^-$, $[AsX_6]^-$, $[PX_6]^-$.

SOME SPECIAL CHARACTERISTICS OF *p* BLOCK ELEMENTS

The *p* block elements differ from *s* block elements in several respects and exhibit some special characteristics which are a consequence of their size, effective nuclear charge, polarising power and polarisability, the extent of involvement of *p* orbitals in pi bonding and of *d* orbitals in sigma and pi bonding. It may be noted that there are some distinct features which make conspicuous distinction not only between *s* and *p* block elements but also between the lighter and the heavier *p* block elements

themselves. While the differences between *s* and *p* block elements are largely due to differences in their electronic configurations, the differences between lighter and heavier *p* block elements are largely due to differences in their sizes. We know that the atomic size goes on *decreasing* as we move across a period. Also the effective nuclear charge goes on *increasing* with increase in atomic number. Because of these factors, ionization energies, electron affinities, electronegativities and polarising powers of the lighter *p* block elements become considerably different from those of the heavier *p* block elements.

Some **typical properties of *p* block elements** are discussed below.

1. Ionization Energies. As discussed in Chapter 2, ionization energies *decrease regularly* as we move down the groups of *s* block elements. But, *this is not the case in p block elements*. For instance, the ionization energies of Group 13 elements change in an oscillating manner, the values for B, Al, Ga, In and Tl, being 800·1, 577·4, 579·0, 558·2 and 589·2 kJ mol^{-1}, respectively. Evidently, ionization energy *decreases* from B to Al, *increases* from Al to Ga, again *decreases* from Ga to In and again *increases* from In to Tl. Irregularities in the trends of ionization energies are also shown by Group 14 elements. For instance, ionization energies *decrease* as we move from C to Sn (the values being 1086·2, 786·4, 760·4 and 708·5 kJ mol^{-1} for C, Si, Ge and Sn, respectively) but it *increases* as we move from Sn to Pb, the value for Pb being 715· 6 kJ mol^{-1}. The irregularities in ionization energies of elements of Groups 13 and 14 may be attributed to differences in their atomic sizes and electronic configurations, as illustrated below.

The ionisation energy of boron is the highest in the group since its atomic size is the smallest and the shielding effect is the lowest. The sharp decrease from B to Al is due to an appreciable increase in atomic size and the effective shielding of the nuclear charge by the intervening *s* and *p* electrons. In the case of Ga, there are ten *d* electrons in its inner electronic configuration. Since *d* electrons shield the nuclear charge less effectively than the *s* and *p* electrons (Chapter 1), the outer electron is held fairly strongly by the nucleus. As a result, the ionisation energy remains practically the same in spite of an increase in atomic size as we move from Al to Ga. In the case of In, the number of *d* electrons and hence their screening effect remains the same as in Ga. However, since there is an increase in atomic size as we move from Ga to In, there is a noticeable decrease in ionisation energy. The last element, Tl, has fourteen *f* electrons in its inner electronic configuration. Since the shielding effect of *f* electrons is much smaller than that of *d* electrons and also since there is only a marginal increase in atomic size (from 1·44 Å to 1·48 Å) as we move from In to Tl, the outer electron in Tl is held quite firmly and hence there is considerable increase in its ionisation energy.

As for the elements of Group 14, the ionization energy of carbon, the first element, is quite high. This is understandable in view of the small size of the carbon atom. There is a sharp decrease in ionization energy as we move from carbon to the next element silicon. This is due to an appreciable increase in the size of the Si atom. There is, however, a very small decrease in ionization energy as we move from Si to Ge to Sn. This is because the *d* electrons which are now present in the inner configurations of Ge and Sn, shield the nuclear charge less effectively than is done by the *s* and *p* electrons. The outer electrons are, therefore, held strongly by the nucleus and hence, in spite of a sizeable increase in atomic radius, there is only a small decrease in ionization energy as we move from Si to Sn. In the last element, Pb, there are fourteen *f* electrons in its inner configuration which shield the nuclear charge less effectively than even the *d* electrons. Also there is only a marginal increase (of 0·03 Å) in the atomic radius as we move from Sn to Pb. Because of these two factors, the ionization energy of Pb, instead of decreasing, shows a marginal increase.

2. Electron Affinities. Electron affinities of *s* block elements decrease regularly as we move down the groups. *This is, however, not true in the case of p block elements.* There is distinct irregularities in trends as we move down the groups of *p* block elements and also when we move along the periods (Table 10, Chapter 2). These irregularities have already been explained in details in Chapter 2.

Heavier *p* block elements differ from their lighter cogeners also in showing reluctance to exhibit maximum oxidation state, reluctance to involve *p* orbitals for pi bonding but allowing full participation of *d* orbitals in sigma and pi bonding. All these aspects have been discussed below in some details.

3. Reluctance of Heavier *p* Block Elements to Show Maximum Oxidation States. As discussed earlier, the *s* block elements and the lighter *p* block elements show only one oxidation state which is equal to the number of valence *s* electrons in the case of *s* block elements and to the total number of valence *s* and *p* electrons in the case of lighter *p* block elements of Groups 13 and 14. The lighter *p* block elements of Groups 15, 16 and 17 show oxidation states which are equal to 8 minus the sum of *s* and *p* electrons in the valence shells. The situation in the case of heavier *p* block elements of Groups 13, 14 and 15 is, however, different. These elements are reluctant to show the maximum oxidation state. For example, Tl (Group 13) and Bi (Group 15) prefer to exist in their lowest oxidation states of +1 and +3, respectively. Similarly, Sn and Pb (Group 14) are far more stable in their lower oxidation state of +2 instead of +4. It was previously thought that the valence *s* electrons of heavier elements do not take part in bonding, *i.e.*, they remain paired and inert because of greater difficulty in their removal or their excitation **(inner pair effect)**. The heavier elements, therefore, prefer to exist in an oxidation state 2 units lower than their maximum oxidation state.

There is, however, concrete evidence to show that inert pair effect is *not the exact cause* of stabilisation of lower oxidation states in the case of heavier *p* block elements. The following points pertinently support this contention :

1. The oxidation state of Sn in $SnCl_2$ is undoubtedly + 2. But, this molecule has a bent structure with Cl–Sn–Cl angle of about 120° indicating sp^2 hybridisation for Sn. If *s* electrons had been inert and only *p* electrons had taken part in chemical bonding, the Cl–Sn–Cl angle would have been close to 90° and not 120°. This shows clearly that the valence *s* electrons are certainly involved in bonding contrary to the idea of their being inert.

2. The summations of second and third ionisation energies in the case of Group 13 elements and those of third and fourth ionization energies in the case of Group 14 elements are given below :

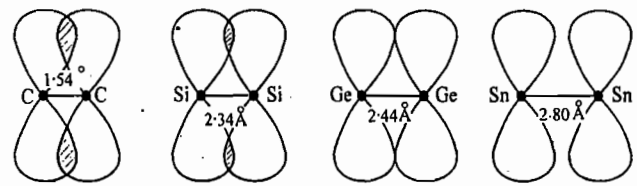
Elements of Group 13	$(IE)_2 + (IE)_3$ (kJ mol^{-1})	Elements of Group 14	$(IE)_3 + (IE)_4$ (kJ mol^{-1})
B ($2s^2 2p^1$)	6090	C ($2s^2 2p^2$)	10820
Al ($3s^2 3p^1$)	4550	Si ($3s^2 3p^2$)	7580
Ga ($4s^2 4p^1$)	4940	Ge ($4s^2 4p^2$)	7710
In ($5s^2 5p^1$)	4520	Sn ($5s^2 5p^2$)	6870
Tl ($6s^2 6p^1$)	4840	Pb ($6s^2 6p^2$)	7160

Evidently, $(IE)_2 + (IE)_3$ is the sum of ionization energies for the removal of both the *s* electrons of Group 13 elements while $(IE)_3 + (IE)_4$ is the summation for the removal of both the *s* electrons of Group 14 elements. According to the data given above, the energy required for the elimination of the pair of valency *s* electrons in heavier elements is *in no way higher* than that required in lighter elements in each group. This implies that the ease with which the *s* electrons can take part in chemical bonding is more or less the *same* in all the elements of a particular group. If at all any element is to show reluctance for bonding, it is the lightest first element in each group and not the heavier elements. This is because the ionization energy summation is the highest in the case of the first element in each group. The ionization energy data thus *negate the contention* that the reluctance of heavier elements to show maximum oxidation states is due to the inert pair effect. A *plausible explanation* for the reluctance of heavier elements to show maximum oxidation state is that the heavier *p* block elements have considerable covalent bond character in their compounds. Since the atomic size of heavier elements is large, a sideways overlap of *p* orbitals is not favoured. These elements, therefore, form only sigma bonds and no pi bonds. This is in contrast to the behaviour of the lighter members of the groups which form both sigma and pi bonds with equal ease. Thus, *fewer valence electrons are involved in bonding in the case of heavier elements. This accounts for the lower oxidation state of these elements.*

4. Reluctance of Heavier *p* Block Elements to Involve *p* Orbitals for pi Bonding. The lighter non-metals, especially of the second period of the *p* block elements, frequently form doubly or triply bonded structures involving *p* orbitals, such as C = C, N ≡ N, O = O, etc. Such structures are very rare

for heavier *p* block elements. For example, while nitrogen exists as N ≡ N, phosphorus exists as P_4 in which all the phosphorus atoms are singly bonded. Similarly, while oxygen exists as O=O, sulphur exists as S_8 in which all the sulphur atoms are singly bonded. Pi bonding through *p* orbitals is quite common in the chemistry of boron but it is not so in the chemistry of aluminium. Thus, while pi bonding through *p* orbitals is quite common in lighter *p* block elements such as B, C, N and O, it is quite rare in heavier *p* block elements although recently some compounds of silicon with Si=Si structure involving $p\pi$–$p\pi$ bonding have been prepared. Because of the reluctance of heavier *p* block elements to form $p\pi$–$p\pi$ bonds, the analogous compounds of lighter and heavier elements in a group tend to have different structures. Thus, while CO_2 has a double bond structure, *viz.*, O=C=O, involving $p\pi$–$p\pi$ bond and is a monomer, SiO_2 is a three-dimensional single-bonded polymer consisting of a large number of Si atoms in which each Si atom is tetrahedrally bonded to four oxygen atoms.

A probable reason for the non-existence or instability of doubly-bonded structures involving $p\pi$–$p\pi$ bonding in heavier elements is that the bigger length of the sigma bond in a heavier element reduces or even excludes the sideways overlapping of *p* orbitals. This is illustrated in Fig. 2 by depicting the effect of the length of C–C, Si–Si, Ge–Ge and Sn–Sn sigma bonds on the sideways overlapping of *p* orbitals of these elements.



Considerable overlapping of orbitals | Very small overlapping of orbitals | No overlapping of orbitals

Fig. 2. Effect of the length of sigma bond on the sideways overlapping of *p* orbitals

A very small overlap implies a very weak $p\pi$–$p\pi$ bond and if no overlap is possible, there is no formation of $p\pi$–$p\pi$ bond at all.

We mentioned above that in SiO_2, each Si atom is attached to four oxygen atoms through sigma bonds. Millikan, however, postulated that all the Si–X bonds (where X stands for O, N, halogens, etc.) have small double bond character as well. This occurs through back bonding involving fully filled $p\pi$ orbitals of X and vacant *d* orbitals of silicon. Thus, each Si–X bond has a partial double bond character. This bond would evidently be stronger than a single sigma bond and more than half as strong as the hypothetical double bond involving $p\pi$–$p\pi$ bonding. A similar situation would exist in compounds of other heavier elements.

5. Participation of *d* Orbitals in Sigma Bonding. The *p* block elements of the second period have only *s* and *p* orbitals whereas the elements of third and higher periods have *d* orbitals also in their valence shells. The elements of the second period, therefore, show a maximum covalency of 4 corresponding to sp^3 hybridisation of their valence shell orbitals. In contrast, the elements of third and higher periods (*e.g.*, Si, P, S, etc.) show a covalency higher than 4 due to the involvement of valence *d* orbitals also in hybridisation. Thus, while the covalency of C in CCl_4, CF_4, etc., involving sp^3 hybridisation is 4, that of Si in $[SiF_6]^{2-}$ involving sp^3d^2 hybridisation is 6. Similarly, while the covalency of N in NF_3 is 3, that of P in PF_5 involving sp^3d hybridisation is 5.

The exhibition of higher covalency by elements in higher periods is fully justified by their atomic sizes. Since the elements in higher periods are bigger in size, they have more space to accommodate substituents around themselves. As a result, a larger number of substituents can be connected with the central element through sigma bonds which implies a higher covalency of the element.

The hydrolysis of tetrahalides of silicon and pentahalides of phosphorus can be explained only on the basis of the involvement of *d* orbitals in sigma bonding. Water acts as a nucleophile in the hydrolytic

reaction. The lone pair of electrons of H_2O is easily accommodated in the vacant *d* orbitals of Si or P thereby facilitating the hydrolysis, Thus,

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

$$PCl_5 + H_2O \xrightarrow{-2HCl} POCl_3 \xrightarrow{+3H_2O} OP(OH)_3 + 3HCl$$

Since carbon has no *d* orbitals, CCl_4 does not undergo hydrolysis at all.

6. Participation of *d* Orbitals in Pi Bonding. a. It is a common experience that trialkyl and triaryl phosphine oxides, *viz.*, (RR′R″)PO, are much more stable than the corresponding amine oxides. The bond dissociation energy of P→O bond is in the range of 500 – 600 kJ mol^{-1} compared to that of N→O bond which is in the range of 200–300 kJ mol^{-1}. This shows that P and O are linked together through more than one bond.

If the bonding between P and O is represented merely as P→O, then, the greater the combined electronegativity (electron attracting power) of (RR′R″), the lesser would be the strength of P→O bond and the greater would be the length of P→O bond. The actual situation is just the reverse, *i.e.*, the greater the combined electronegativity of (RR′R″), the greater is the strength of P→O bond and the shorter is the length of P→O bond. The above facts can be explained only if we assume pi back bonding from fully filled $p\pi$ orbitals of oxygen to vacant $d\pi$ orbitals of phosphorus in phosphine oxide. Accordingly, the structure of the oxide would be as shown in Fig. 3.

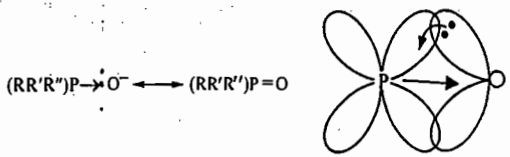


Fig. 3. $p\pi$–$d\pi$ bonding in trialkyl phosphine oxides.

Since nitrogen does not have any *d* orbitals, there would be no $p\pi$–$d\pi$ bonding between N and O in the amine oxides. These compounds would, therefore, have a simple structure, *viz.*, RR′R″N→O. The pi back bonding in phosphine oxides thus readily accounts for their greater dissociation energy and, therefore, greater stability as compared to amine oxides.

It can be easily visualised that the greater the combined electronegativity of (RR′R″), the greater would be the partial positive charge created on P and hence the greater would be the flow of $p\pi$ electronic charge from O to P. This would impart a greater double bond character to the bond between P and O resulting in the shortening of the PO bond and thereby increasing the stability of the phosphine oxide.

b. The electronegativity difference between P and O is more than that in N and O. On the basis of this difference *alone* (*i.e.*, in the absence of any pi back bonding), amine oxides should have been less polar than the corresponding phosphine oxides. But, actually the situation is just the reverse. Phosphine oxides are less polar than the analogous amine oxides. For instance, the dipole moment of $(CH_3)_3PO$ is 4·4 debye whereas the dipole moment of $(CH_3)_3NO$ is 5·0 debye. The pi back bonding, *i.e.*, $p\pi - d\pi$ bonding in the PO bond shifts back some of the charge to P and thus decreases the dipole moment of phosphine oxide. The PO bond should thus be represented as P⇐O and not merely as P→O (the NO bond would be represented merely as N→O). The dipole moment is the product of the amount of charges separated and the distance between the separated charges. On account of $p\pi$–$d\pi$ back bonding, the distance between P and O and also the separated charges on P and O, decrease. As a result there is a decrease in the dipole moment of phosphine oxide.

c. Trimethyl amine, $(CH_3)_3N$, is known to have a distorted tetrahedral structure with C–N–C angle of 107·9° whereas $(SiH_3)_3N$ is a planar molecule with Si–N–Si angle of 120°. Such a large difference in bond angles can be explained only on the basis of pi back bonding between N and Si. The N atom

in $(CH_3)_3N$ molecule involves sp^3 hybridisation of valence shell orbitals of N whereas in $(SiH_3)_3N$ molecule, it involves sp^2 hybridisation. In the latter molecule, the third *p* orbital of N containing a lone pair of electrons is of proper symmetry to overlap with the vacant *d* orbital of Si to form a $p\pi$–$d\pi$ bond. Thus, while in $(CH_3)_3N$ molecule, there are only sigma bonds between N and C atoms, in case of $(SiH_3)_3N$ molecule, there is a sigma and a $p\pi$–$d\pi$ bond between Si and N atoms. The structure of this molecule may thus be represented as shown in Fig. 4.

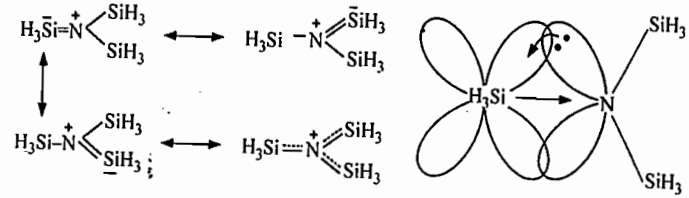


Fig. 4. The structure of trisilylamine molecule.

As discussed earlier, the electropositive character increases and electronegative character decreases as we move down a group. Hence, Si should be more electropositive than carbon. Accordingly, because of the inductive effect, $(SiH_3)_3N$ should be more basic than $(CH_3)_3N$. But, actually it is just the reverse. This can be explained on the basis of $p\pi$–$d\pi$ bonding between N and Si. Since in $p\pi - d\pi$ bonding, N donates its electronic charge to the vacant *d* orbitals of Si, the tendency of N atom in $(SiH_3)_3N$ molecule to lose electrons to an acid solvent becomes less, implying thereby that $(SiH_3)_3N$ is less basic than $(CH_3)_3N$..

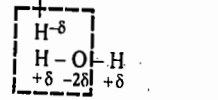
7. Electronegativities. As can be seen from Table 11, Chapter 2, electronegativities of *s* block elements decrease **regularly** as we go down a group. Electronegativities of *p* block elements, however, show **irregular trends.** This is particularly so in the case of elements of Groups 13 and 14. These irregular values, however, are fully supported by the chemical behaviour of some typical compounds of these elements. This is illustrated below.

(*i*) The energy of Ge–X bond is found to be smaller than that of Si–X bond where X stands for a halogen. Because of this, it is more difficult to dissociate a Si–X bond compared to a Ge–X bond. This is evidenced by the fact that while the Ge–X undergoes reduction with Zn and HCl to give Ge–H (Ge – + 2H ⟶ Ge–H + HX), Si–X does not. The Si–X bond would be stronger if it is more polar than Ge–X bond so that the former has higher ionic–covalent resonance energy than the latter and this, in turn, would be possible only if the electronegativity difference between Si and X is more than that between Ge and X or if Si has lower electronegativity than Ge, as is actually the case.

(*ii*) Silane (SiH_4) readily undergoes hydrolysis in the presence of catalytic amounts of OH^- ions whereas germane and stannane do not do so even in the presence of large amounts of OH^- ions. This can be explained only on the assumption that electronegativities of Ge and Sn are higher than that of Si as is actually the case. Since the electronegativities of Ge and Sn are closer to that of H (2·1), the bonds Ge–H and Sn–H would be almost non-polar. But there is considerable electronegativity difference between Si and H so that Si–H bond is *polar* with partial positive charge on Si. It is because of this partial positive charge on Si that silane undergoes hydrolysis readily in the presence of OH^- ions in the following manner :

$$SiH_4 + 2OH^- \longrightarrow [SiH_4(OH)_2]^{2-}$$

$$[H_3\overset{+\delta}{Si}(OH)_2]^{2-} \longrightarrow [H_3Si(OH)_3]^{2-} + H_2$$



$$[H_3Si(OH)_3]^{2-} \xrightarrow{3H_2O} Si(OH)_4 + 2OH^- + 3H_2$$

Further hydrolysis

(Ultimate product)

Since Ge – H and Sn – H bonds are non-polar because of small electronegativity difference between H and the metal, germane, GeH_4 and stannane, SnH_4 do not undergo hydrolysis.

However, R.S. Drago maintains that electronegativity of each of Si, Ge, Sn and Pb is the same, *i.e.*, ~1·8, the conventionally accepted value for Sn and Pb (Table 11, Chapter 2). Therefore, all the four elements should exhibit similar chemical behaviour. But, actually, it is not so. He explained the difference in the chemical behaviour of Si on the basis of its *d* orbital participation in both sigma and pi bonding. According to Drago, the 3*d* orbitals of Si are energetically better suited for bonding than 4*d*, 5*d* and 6*d* orbitals of Ge, Sn and Pb. As a result, the chemistry of Si shows dissimilarities with the chemistry of Ge, Sn and Pb having *d* orbitals with unfavourable energies for participation in bonding.

QUESTIONS

1. What are the main group elements ? Discuss briefly their general characteristics.
2. Explain what is meant by polarising power of a cation and polarizability of an anion. State and explain Fajan rules for estimating the extent to which a cation can polarise an anion.
3. Explain the term polarisation of an anion. Illustrate how the concept of polarisation can account for the diagonal relationship in the main group elements.
4. Illustrate the effect of polarisation on the following :
   (*i*) Melting points of halides of main group elements.
   (*ii*) Solubilities of halides of silver.
   (*iii*) Decomposition of metal carbonates.
5. Discuss the variation of the following properties as we move (*a*) down a group (*b*) along a period amongst the main group elements :
   (*i*) Oxidising and reducing properties.
   (*ii*) Redox potentials. Electropositive character.
   (*iii*) Oxidation states.
6. What is meant by diagonal relationship ? How would you account for this relationship amongst the metallic and non-metallic elements of *s* and *p* block elements ?
7. (*a*) What is meant by oxidation and reduction ? "The oxidising character of elements increases and reducing character decreases as we move from left to right in a period." How would you explain this behaviour ?
   (*b*) "The oxidising character decreases and reducing character increases as we move down a group." How would you explain this trend ?
8. (*a*) How would you account for the diagonal relationship in elements arranged in the periodic table ?
   (*b*) Discuss the variation of oxidation states of elements as we move from left to right in a period.
9. What do you understand by the term redox potential ? How does this quantity change as we move across a period from left to right and down a group and why ?
10. Discuss the trend in the following aspects of the chemistry of *p* block elements in a group and in a period :
    (*a*) Acidic and basic character of oxides.
    (*b*) Ionic and covalent character of halides.
    (*c*) Oxidising and reducing properties of elements.
11. What are acidic, basic and amphoteric oxides ? Discuss the type of bonding which occurs in the various oxides. On what factors does the stability of oxides depend ?
12. "There are some distinctive features not only between *s* and *p* block elements but also between lighter and heavier *p* block elements." How would you justify this statement ?
13. While the ionization energies of *s* block elements decrease regularly as we move down a group, it is not the case in *p* block elements. Why is it so ?
14. Ionization energies in kJ mol^{-1} of elements of Group 13 and Group 14 are as follows :

B	Al	Ga	In	Tl	C	Si	Ge	Sn	Pb
800	577	579	558	589	1086	786	760	708	716

How would you account for these irregular values ?

15. The heavier *p* block elements are reluctant to show maximum oxidation states. How would you account for it ? Explain clearly that this reluctance is not because of inert pair effect.
16. The heavier *p* block elements are reluctant to involve *p* orbitals for pi bonding. Why is it so ?
17. There is a distinct participation of *d* orbitals in sigma bonding in heavier *p* block elements. Illustrate this statement.
18. How would you account for the following :
    (*i*) The elements of the second period can show a maximum covalency of 4 while elements of the third and higher periods can show a maximum covalency higher than 4.
    (*ii*) CCl_4 does not undergo hydrolysis whereas $SiCl_4$ and PCl_5 are easily hydrolysed.
    (*iii*) CO_2 is a monomer while SiO_2 is a three-dimensional giant molecule.
19. There is distinct participation of *d* orbitals in pi bonding in heavier *p* block elements. Illustrate this statement.
20. How would you account for the following :
    (*i*) The dissociation energy of PO bond in (RR′R″)PO is in the range of 500 – 600 kJ mol^{-1} while that of (RR′R″)NO is in the range af 200 – 300 kJ mol^{-1}. (R in an alkyl or aryl radical).
    (*ii*) The dipole moment of $(CH_3)_3PO$ is less than that of $(CH_3)_3NO$.
    (*iii*) $(CH_3)_3N$ has C – N – C bond angle of 107·9° while $(SiH_3)_3N$ has Si – N – Si bond angle of 120°.
    (*iv*) $(CH_3)_3N$ is more basic than $(SiH_3)_3N$?
21. Electronegativities of elements of Group 14 are as follows :

C	Si	Ge	Sn	Pb
2·5	1·9	2·0	1·8	1·8

Show that these irregular values are fully supported by (*i*) the reduction of the halides of these elements (*ii*) hydrolysis of the hydrides of these elements.

22. How would you account for the following :
    (*i*) Ge–X is easily reduced by Sn–HCl to give Ge–H whereas Si–X is not.
    (*ii*) SiH_4 readily undergoes hydrolysis in the presence of catalytic amounts of OH^- ions whereas GeH_4 and SnH_4 are not hydrolysed even in the presence of large amounts of OH^- ions.

13 THE ELEMENTS OF GROUP 1

The *s* Block Elements. The elements of Groups 1 and 2 of the periodic table constitute the ***s* block elements.** The electronic configurations of these elements are given in Table 1.

TABLE 1

Electronic Configurations of *s* Block Elements

Group 1 (Alkali Metals)			Group 2 (Alkaline Earth Metals)		
Element	Atomic number	Electronic configuration	Element	Atomic number	Electronic configuration
Lithium, Li	3	[He] $2s^1$	Beryllium, Be	4	[He] $2s^2$
Sodium, Na	11	[Ne] $3s^1$	Magnesium, Mg	12	[Ne] $3s^2$
Potassium, K	19	[Ar] $4s^1$	Calcium, Ca	20	[Ar] $4s^2$
Rubidium, Rb	37	[Kr] $5s^1$	Strontium, Sr	38	[Kr] $5s^2$
Cesium, Cs	55	[Xe] $6s^1$	Barium, Ba	56	[Xe] $6s^2$
Francium, Fr	87	[Rn] $7s^1$	Radium, Ra	88	[Rn] $7s^2$

It is evident from Table 1 that while the outer electronic configuration of Group 1 elements is ns^1, that of Group 2 elements is ns^2.

The elements constituting **Group 1** are reactive metals and form *strongly alkaline* oxides and hydroxides. Therefore, they are called **alkali metals.** The last element, francium, is radioactive.

The elements belonging to **Group 2** are also metals and are commonly known as **alkaline earth metals.** The oxides of some of these metals were known much earlier than the metals themselves and they were called *alkaline earths* since they were alkaline and existed in the earth. Later, when these elements were discovered, they began to be called **alkaline earth metals.** The last member of the group, radium, being a radioactive element, is studied separately alongwith other radioactive elements.

THE ELEMENTS OF GROUP 1

The elements, **lithium, sodium, potassium, rubidium, cesium** and **francium,** constitute Group 1 of the periodic table. They are highly reactive and readily decompose water even at room temperature yielding metal hydroxides which are strong alkalies. These elements are, therefore, known as **alkali metals,** as stated above.

GENERAL CHARACTERISTICS

The general characteristics of alkali metals have already been discussed while describing the properties of main group elements, in Chapter 12. However, a brief discussion has been made in this chapter also.

Physical Properties

All the elements of Group 1 are silvery-white, soft and light metals. Some of their important physical constants are summed up in Table 2.

TABLE 2

Physical Properties of Alkali Metals

Property	Lithium	Sodium	Potassium	Rubidium	Cesium
Atomic number	3	11	19	37	55
Molar mass (g mol^{-1})	6·94	22·99	39·10	85·48	132·91
Density at 20°C (g cm^{-3})	0·634	0·972	0·859	1·530	1·903
Molar volume (cm^3 mol^{-1})	12·97	23·68	45·36	55·80	69·95
Melting point (°C)	180·0	97·8	64·0	38·9	28·5
Boiling point (°C)	1326	883	756	688	670
Atomic radius (Å)	1·34	1·54	1·96	2·11	2·25
Ionic radius (Å) M^+ ion	0·60	0·98	1·33	1·48	1·67
Heat of atomisation (kJ mol^{-1})	159·0	108·1	90·2	82·1	78·2
Ionization energy (kJ mol^{-1})	520·1	495·2	418·7	403·0	375·7
Electronegativity (Pauling's values)	1·0	0·9	0·8	0·8	0·7
Flame coloration	Crimson red	Golden yellow	Violet	Violet	Violet

1. Density. Density of a metallic element depends upon the type of packing of atoms in the metallic phase as also on their size. Group 1 elements have close packing of metal atoms in their lattices and because of the comparatively large size of these atoms, they have low densities. As can be seen from Table 2, density gradually *increases* in moving down from lithium towards cesium. Potassium, however, is lighter than sodium. Lithium, sodium and potassium are even lighter than water. The reason is that these metals have much larger molar volumes and hence much larger atomic radii than most other metals.

2. Molar Volumes. The ratio of molar mass (g mol^{-1}) and density (g cm^{-3}) is known as the molar volume (cm^3 mol^{-1}) of the element. Molar volume is seen to *increase* in moving down the group from Li to Cs. This is to be expected in view of increase in atomic radius in the same order, as shown in Table 2.

3. Melting Points. All the alkali metals are soft and have low melting points. This is due to the fact that they have only one valency electron per metal atom. Hence the energy binding the atoms in the crystal lattice of the metal is relatively low. The melting points invariably decrease in moving down from lithium towards cesium. Lithium, the first element, melts at 180·0 °C while cesium, the last element, melts at 28·5°C. Thus, the melting point decreases with increase in the size of the atom of the element.

4. Boiling Points. The boiling points also *decrease* in the same order as the melting points. The boiling point of lithium is 1326°C while that of cesium is 670°C.

5. Atomic and Ionic Radii. Atomic and ionic radii *increase* on moving down the group from lithium to cesium, as shown in Table 2. This is on account of the presence of an extra shell of electrons as we move down from one element to the other within the group.

An alkali metal changes into a positive ion by the loss of the solitary *s* electron of the outer shell. This leads to the elimination of the outer shell itself. At the same time, the charge on the nucleus becomes greater than the number of electrons and, therefore, the electrons are attracted all the more

strongly towards the nucleus. As a result of both these effects, a positive ion is smaller than the corresponding atom. Ionic radii of all the alkali metals are thus smaller than the corresponding atomic radii.

The electronic configurations of the alkali metal ions would evidently be similar to those of the noble gases, *viz.*, s^2 (for Li^+) or s^2p^6 (for Na^+, K^+, Rb^+, Cs^+). Since they have no unpaired electrons, these ions are *diamagnetic* and *colourless*.

6. Heat of Atomisation. *Heat* of atomization measures the strength of metal–metal bond in the lattice of an element. Heat of atomisation is maximum in the case of lithium and is much lower in the case of the next element which is sodium. The fall in the case of the subsequent elements is relatively small. Thus, metal–metal bond strength is maximum in the case of lithium.

7. Ionisation Energies. The solitary *s* electron in the outer shell of these elements can be taken out relatively easily. Consequently, the ionisation energies of these elements are relatively low. Further, as the atomic radius increases on moving down the group, the outer electron gets farther and farther away from the nucleus and, therefore, *ionisation energy decreases on moving down from lithium towards cesium.*

8. Electropositive Character. On account of their low ionisation energies, these metals have great tendency to lose their outermost electron and thus change into positive ions :

$$M \longrightarrow M^+ + e^-$$

These elements are, therefore, said to have strong *electropositive* character. Since ionisation energy decreases on moving down the group, *the electropositive character increases on moving down the group from lithium towards cesium.*

These elements are so highly electropositive that they emit electrons even when exposed to light (**photoelectric effect**). This property is responsible for their use in photoelectric cells. Cesium and potassium are used, in particular, for this purpose.

9. Formation of Univalent Positive Ions. As already mentioned, on account of relatively low ionisation energies, these elements have a strong tendency to change into M^+ ions. Hence, they form mostly ionic compounds. The chemistry of these elements, therefore, is the chemistry of M^+ ions (Li^+, Na^+, etc.). Since the ions have the stable noble gas configuration, *viz.*, ns^2 or ns^2p^6, in the valency shell, the energy required to pull out another electron from the valency shell is very high. Therefore, the second ionisation energies of alkali metals are very high. Under ordinary circumstances, therefore, there is no possibility for the formation of M^{2+} ions in any of their compounds. The alkali metals are thus *univalent* and form *ionic compounds.*

However, in certain cases, they do form covalently bonded diatomic molecules like Li_2 (Li:Li), Na_2 (Na:Na) and Cs_2 (Cs:Cs). Li also forms covalently bonded organometallic compounds due to its high polarizing power.

10. Hydration of Ions. The alkali metal ions are *extensively hydrated.* The smaller the size of the ion, the greater is the degree of hydration. Thus, Li^+ ion, which is smallest in size and has the highest charge/size ratio amongst the alkali metal ions, gets much more hydrated (*i.e.*, holds more water molecules in its hydration sphere) than Na^+ ion and the latter gets more hydrated than K^+ ion and so on. The degree of hydration decreases on moving down the group from Li^+ to Cs^+. As a result of the difference in degree of hydration, ionic radii of hydrated alkali metal ions *decrease* from Li^+ to Cs^+, *i.e.*, Li^+ ion, which should have been smallest, is actually largest in size in aqueous solutions. Thus, the ionic radii in aqueous solutions decrease in the order :

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

It is for this reason that Li^+ ion has the lowest and Cs^+ ion has the highest mobility in an electric field.

11. Oxidation States. All the alkali metals exhibit an oxidation state of +1. This is because these metals can lose their solitary outermost electron easily. The second ionisation energy is so high that the second electron is very rarely lost.

12. Electronegativities. Since these metals are highly electropositive, their electronegativities, *i.e.*, their tendencies to attract electrons, are very low. Further, since electropositive character increases on moving down the group, *the electronegativity decreases in the same order.* When these elements react with other elements having high electronegativities (*e.g.*, the halogens), the compounds formed are ionic in character.

13. Reducing Properties, Oxidation Potentials. As is well known, **oxidation** *is a process in which electrons are lost* and **reduction** *is a process in which electrons are gained.* An *oxidising agent,* therefore, is a substance which can *accept* electrons while a *reducing agent* is a substance which can *lose* electrons. Consider the formation of sodium chloride by burning of sodium in chlorine. Sodium, on account of its low ionisation energy, can *lose* an electron readily while chlorine, on account of its high electron affinity, can *accept* it readily.

$$\begin{aligned}
Na\,(s) &\xrightarrow{heat} Na\,(g) \\
Na\,(g) &\longrightarrow Na^+(g) + e^- \\
1/2\,Cl_2\,(g) + e^- &\longrightarrow Cl^-(g) \\
Na^+(g) + Cl^-(g) &\longrightarrow Na^+Cl^-(s) \\
\hline
Na\,(g) + 1/2\,Cl_2\,(g) &\longrightarrow Na^+Cl^-(s)
\end{aligned}$$

Thus, sodium is a reducing agent while chlorine is an oxidising agent. Evidently, an element which is a *reducing agent* must have *low ionisation energy* while an element which is an *oxidising agent* must have *high electron affinity.* Since ionisation energy decreases on moving down from lithium to cesium, the reducing properties increase in the same order.

The tendency of an element to lose an electron *in solution* is measured by the standard oxidation potential of the element. The standard oxidation potentials of the alkali metals are given in Table 3.

TABLE 3
Standard Oxidation Potentials of Alkali Metals

Element	Oxidation Reaction	Standard Oxidation Potential (volts)
Lithium	$Li \longrightarrow Li^+ + e^-$	3·04
Sodium	$Na \longrightarrow Na^+ + e^-$	2·71
Potassium	$K \longrightarrow K^+ + e^-$	2·92
Rubidium	$Rb \longrightarrow Rb^+ + e^-$	2·99
Cesium	$Cs \longrightarrow Cs^+ + e^-$	3·02

These high values indicate that alkali metals have a strong tendency to lose electrons and thus act as strong reducing agents and that lithium is the strongest of them all. However, if we look at the ionisation energies of these elements (Table 2), it is seen that lithium has the highest value indicating that it holds its electron most tightly. This, at first sight, seems to be contrary to the maximum value of oxidation potential of lithium which indicates that lithium gives off its electron most readily. This anomaly can be explained if we recall that ionisation energy is the property of *isolated atom in the gaseous state* while oxidation potential concerns itself with *the metal as it goes into solution in the form of its ions.*

Thus, ionisation energy involves only the following change :

$$M(g) \longrightarrow M^+(g) + e^-$$

Oxidation potential, on the other hand, involves the process

$$M(s) \longrightarrow M^+(aq) + e^-$$

which is considered to take place in three consecutive steps given below :

$$M(s) \longrightarrow M(g)$$

$$M(g) \longrightarrow M^+(g) + e^-$$
$$M^+(g) + H_2O \longrightarrow M^+(aq)$$

In the first step, the metal (solid) is evaporated to the gaseous state in which the atoms get isolated from one another and become independent of one another. The energy required in this process is known as **sublimation energy** which is quite low and about the same for all the alkali metals. In the second step, the outer electron is pulled off from an isolated gaseous atom. The energy required for this change is the **ionisation energy** which, as mentioned above, is the highest for lithium. In the third step, the gaseous ion gets hydrated. In this process, energy, known as **hydration energy**, gets *liberated*. The oxidation potential which gives the tendency for the overall change to occur, naturally depends on the *net effect of all the three steps*. Lithium ion is hydrated to the maximum extent because of its highest charge/size ratio and, therefore, the energy *liberated* in the third step is maximum in the case of Li^+ ion. *The hydration energy of lithium ion (released in step 3) is so large that it more than compensates the sublimation energy (step 1) and the energy required to knock off the electron (step 2).* This explains the highest oxidation potential of lithium, *i.e.*, the greatest ease with which the overall change, $Li(s) \longrightarrow Li^+(aq) + e^-$ takes place. In other words, the greatest strength of lithium as a reducing agent lies in its greatest hydration energy.

14. Characteristic Flame Colouration. All the alkali metals give *characteristic colours* in bunsen flame. The reason is that when an alkali metal or any of its compounds is heated in a bunsen flame, the electrons get excited to higher energy levels. When these electrons return to their original (ground) level, the *excitation energy* which had been absorbed by them, is *released* in the form of light in the visible region of the spectrum. Now for the same excitation energy, the energy level to which the electron in Li rises is lower than that to which the electron in Na rises and this, in turn, is lower than the level to which the electron in K rises and so on. These differences are on account of differences in the forces of attraction between the nucleus and the outermost electron. Consequently, when the electron returns to the ground state, energy released is lowest in Li and increases in the order Li $\longrightarrow$ Cs. As a result of this, the frequency of the light emitted when the compound is placed in the bunsen flame will be minimum in the case of lithium. It increases in the order Li $\longrightarrow$ Cs. Thus, the colour of the flame is crimson red in the case of Li, golden yellow in the case of Na, violet in the case of K and almost the same in the case of Rb and Cs.

15. Lattice Energies. Salts of alkali metals consist of cations and anions only and are, therefore, called *ionic solids*. The **lattice energy of an ionic solid** is defined as *the energy released when cations and anions in gaseous state are brought from infinity to their respective crystal sites to form one mole of the ionic crystal*. Thus, we have

$$Li^+(g) + Cl^-(g) \longrightarrow Li^+Cl^-(s); \qquad \Delta H = \text{Lattice energy of } Li^+Cl^-$$
$$Cs^+(g) + Cl^-(g) \longrightarrow Cs^+Cl^-(s); \qquad \Delta H = \text{Lattice energy of } Cs^+Cl^-$$

Lattice energies of ionic solids are quite high. This is to be expected in view of *strong* electrostatic attraction between oppositely charged ions. When such ions come close together, the system acquires *minimum energy* and, therefore, a large amount of energy is released to the surroundings. Since coulombic forces of attraction vary directly as the product of the charges, it follows that the higher the charge on the ions (*i.e.*, the higher the valency of the ions), the greater should be the lattice energy of the ionic solid. Thus, lattice energy increases as we move from uni-univalent ionic solids like lithium flouride (Li^+F^-) to uni-bivalent solids like calcium fluoride ($Ca^{2+}2F^-$) and to bi-bivalent solids like magnesium sulphide ($Mg^{2+}S^{2-}$).

For cations of the same valency, lattice energy of ionic solids having the same anion, *decreases with increase in the size of the cation*. Thus, lattice energy of Li^+F^- is 1034 kJ mol^{-1} while that of Cs^+F^- is 743·9 kJ mol^{-1}. Similarly, *lattice energy of Li^+I^- is 718·4 kJ mol^{-1} while that of Cs^+I^- is* 584·5 kJ mol^{-1}. Since the fluoride ion in the first case and the iodide ion in the second case is common,

the higher values for lithium salts are due to the smaller size of Li^+ ion as compared to that of Cs^+ ion (Table 2) in the respective ionic solids. We may thus conclude that, as a general rule, lattice energies of salts of alkali metals having a given anion decrease with increase in atomic number of the alkali metal.

Chemical Properties

The alkali metals exhibit high chemical reactivity which is due to their low ionisation energies and relatively low heats of atomisation. The important chemical properties and their trends are discussed below.

1. Relative Reactivity. The reactivity of alkali metals goes on increasing in the following order :

$$Li < Na < K < Rb < Cs$$

2. Action of Air. All the alkali metals tarnish rapidly on exposure to air due to the formation of oxides at the surface. The oxides may further react with moisture and atmospheric CO_2 to form a layer of carbonates at the surface of alkali metals. They are, therefore, always kept under kerosene or paraffin oil to protect them from the action of air.

They burn vigorously in air or oxygen forming oxides. Lithium forms the monoxide, Li_2O; sodium forms a mixture of the monoxide Na_2O and the peroxide, Na_2O_2 and the rest of the elements form superoxides, MO_2.

3. Action of Water. The alkali metals react readily with water forming hydroxides and evolving hydrogen. For example,

$$2Li(s) + H_2O \longrightarrow 2LiOH + H_2$$

The reactivity with water increases on descending the group from lithium to cesium. This is because the electropositive character increases in this order. With potassium, rubidium and cesium, the reaction is so vigorous that the evolved hydrogen catches fire spontaneously.

These metals also react with alcohol giving oxides and evolving hydrogen. For example,

$$2Li + 2C_2H_5OH \longrightarrow 2C_2H_5OLi + H_2$$

The reactivity towards alcohol also increases on moving down the group.

4. Action of Acids. All alkali metals react with acids to produce hydrogen.

$$2M + 2HX \longrightarrow 2MX + H_2$$

5. Action with Hydrogen. The alkali metals react with hydrogen forming hydrides which are ionic in character and in which hydrogen is present as an anion. The hydrides are, therefore, represented as M^+H^-, where M is an alkali metal. The ease with which the alkali metals form hydrides decreases in moving down from lithium towards cesium.

6. Action with Halogens and Sulphur. The alkali metals combine readily with halogens and sulphur forming the halides and sulphides . These are ionic compounds.

7. Action with N_2. Only Li, out of all alkali metals, reacts with N_2 to produce Li_3N.

8. Reactions with NH_3 (gaseous). When ammonia gas is passed over alkali metals, the corresponding amides are formed.

$$2M + 2NH_3 \longrightarrow 2MNH_2 + H_2$$

The alkali amides are also formed when the solutions of alkali metals in liquid NH_3 are evaporated.

9. Solubility in Mercury. The alkali metals dissolve readily in mercury forming what are called **amalgams**. The process is highly *exothermic*.

10. Solubility in Liquid Ammonia. All the alkali metals dissolve in anhydrous liquid ammonia giving deep blue solutions. The colour deepens with increase in concentration of the solution. The concentrated solutions are bronze in colour and possess *metallic lustre*. The solutions are *good conductors*

of electricity and are *paramagnetic* in nature. The paramagnetic character decreases with increase in concentration.

The dissolution of the metal is accompanied by its ionisation :

$$M \longrightarrow M^+ + e^-$$

When the alkali metals are dissolved in liquid ammonia, the ammonia molecules solvate the cation as well as the electron, as represented below.

$$M + NH_3 \text{ (in excess)} \longrightarrow M^+(NH_3)_x + e^-(NH_3)_y$$

The values of x and y depend upon the extent of solvation of the alkali metal ion and the electron, respectively. The exact mechanism for the solvation of electrons is not clear. It is argued, however, that the electron released by the alkali metal causes polarisation of the charge of the electrons of the surrounding ammonia molecules and the repulsion between the electron released by alkali metal and the electrons of the surrounding ammonia molecules causes a 'hole' in which the released electron is trapped. It is the *ammoniated electron which is responsible for the blue colour of the solution.* The electrical conductivity is due to the ammoniated cation as well as the ammoniated electron. The dilute solutions are *paramagnetic* because they contain free electrons. The decrease in paramagnetic character with increase in concentration suggests that in concentrated solutions the ammoniated electrons associate to form electron pairs :

$$2e^-(NH_3)_y \longrightarrow [e^-(NH_3)_y]_2$$

The alkali metal solutions in liquid ammonia are stable and decompose only slowly liberating hydrogen. The presence of transition metals (such as Fe, Pt, Zn, etc.) even in traces, catalyses the reaction.

Due to the presence of the free or ammoniated electrons, these solutions behave as **strong reducing agents** as is evident from the following reactions :

These solutions reduce aerial oxygen to superoxide and peroxide ions without causing cleavage of O – O bond.

$$O_2 \xrightarrow{e^-(NH_3)_y} O_2^- \xrightarrow{e^-(NH_3)_y} O_2^{2-}$$

These solutions reduce metal ions to their unusually low oxidation states.

$$K_2[Ni(CN)_4] + 2K \xrightarrow{e^-(NH_3)_y} K_4[Ni(CN)_4] \quad \text{(Ni is in 0 oxidation state)}$$

$$Mn_2(CO)_{10} + 2K \xrightarrow{e^-(NH_3)_y} 2K[Mn(CO)_5] \quad \text{(Mn is in –1 oxidation state)}$$

$$Fe(CO)_5 + 2Na \xrightarrow{e^-(NH_3)_y} Na_2[Fe(CO)_4] + CO \quad \text{(Fe is in –2 oxidation state)}$$

The alkali metal solutions in liquid ammonia can reduce protonic species like acetylenes to liberate H_2.

$$RC \equiv CH \xrightarrow[Na]{e^-(NH_3)_y} RC \equiv C^-Na^+ + 1/2\ H_2$$

In some of the reactions in liquid ammonia solutions, a reducing species may absorb more than one electron. For example,

$$S_8 + 2e^-(NH_3)_y \longrightarrow S_8^{2-} + 2yNH_3$$

$$Ge_2H_6 + 2e^-(NH_3)_y \longrightarrow 2GeH_3^- + 2yNH_3$$

Sometimes, a specie after getting reduced reacts further with liquid ammonia solvent as follows :

$$(i) \quad N_2O + 2e^-(NH_3)_y \longrightarrow (N_2 + O^{2-}) + 2yNH_3$$

$$(N_2 + O^{2-}) + 2y(NH_3) \longrightarrow N_2 + OH^- + NH_2^- + (2y-1)NH_3$$

$$(ii) \quad C_2H_5Br + 2e^-(NH_3)_y \longrightarrow (Br^- + C_2H_5^-) + 2yNH_3$$

$$(Br^- + C_2H_5^-) + 2y(NH_3) \longrightarrow Br^- + C_2H_6 + NH_2^- + (2y-1)NH_3$$

The alkali metals are also soluble in a number of aliphatic amines, ethylene glycol, dimethyl ether, etc. These solutions are also coloured and have strong reducing properties similar to the liquid ammonia solutions of alkali metals.

11. Ionic Conductance. The alkali metal ions in aqueous solution have high electrical conductance. The electrical conductance of Li^+ ion, which is the smallest of alkali metal ions, is expected to be the highest. Since ionic size increases on moving from Li to Cs, the ionic conductance is expected to decrease in the order :

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

However, we find by experiment that ionic conductance of Cs^+ is the highest and that of Li^+ is the lowest. Thus, ionic conductance actually decreases in the order :

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

This is evidently the *reverse* of what we expect. This anomaly arises from the fact that *alkali metal ions are hydrated to different extents.* The Li^+ ion is hydrated to the maximum extent due to its high charge/size ratio compared to other alkali metal ions. The extent of hydration *decreases* on moving from Li^+ to Cs^+. Thus, Cs^+ ion is the least hydrated. As a result of the variation in the extent of hydration, Li^+ ion due to heavy hydration is the biggest while Cs^+ ion due to much smaller hydration is the smallest. Thus, the ionic size in aqueous solutions, instead of increasing, *actually decreases* on moving from Li^+ to Cs^+ as a result of which the ionic mobility *increases* as we move from Li^+ to Cs^+. Hence, *the ionic conductance,* instead of decreasing, *actually increases on moving from* Li^+ *to* Cs^+.

The ionic radii, radii of hydrated ions and ionic conductances of different alkali metal ions at infinite dilution are given in Table 4.

TABLE 4

Ionic Radii, Radii of Hydrated Ions and Ionic Conductances of Alkali Metal Ions

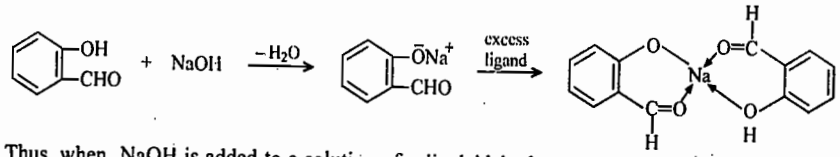
Property	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radii (Å)	0·60	0·98	1·33	1·48	1·67
Radii of hydrated ions (Å)	3·40	2·76	2·32	2·28	2·28
Ionic conductance at infinite dilution ($ohm^{-1}\ cm^2\ mol^{-1}$)	33·5	43·5	64·6	67·5	68·0

Complexes of Alkali Metals

Alkali metal ions with the exception of Li^+ have very little polarising power due their large size and only a unit positive charge. As a result, they have only a weak tendency to form complexes with unidentate ligands. The common unidentate ligands with which the alkali metal ions form somewhat stable complexes are H_2O, NH_3, Ph_3PO, CH_3CONH_2, dioxane and C_5H_5N(py). Thus, there is concrete evidence for the existence of $[M(H_2O)_4]^+$ (where M is Li^+, Na^+ and K^+) and $[M'(H_2O)_6]^+$ (where M' is Rb^+ and Cs^+, in aqueous solutions. Also, lithium iodide reacts with liquid ammonia to produce $[Li(NH_3)_4]^+$. Similarly, lithium iodide, nitrate and perchlorate react with Ph_3PO to yield complex cation $[Li(Ph_3PO)_4]^+$. The complexes $[LiCl(H_2O)(py)_2]$ and $[LiCl(C_4H_8O_2)]_n$ are also reasonably stable. The complex

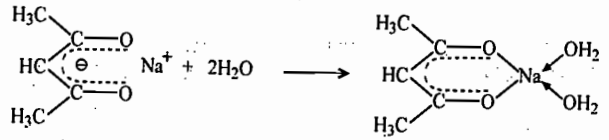
$[LiCl(C_4H_8O_2)]_n$ is polymeric containing Cl and dioxane bridges in which each Cl and each dioxane is coordinated to two lithium atoms. All the complexes mentioned above contain four-coordinated tetrahedral lithium ion. However, polymeric complex $[NaBr(CH_3CONH_2)_2]_n$ (obtained by heating NaBr with acetamide) has each sodium atom surrounded by two bromine atoms (which are trans to each other) and four planar oxygen atoms of acetamide molecule. The polymeric character of the complex is due to the presence of oxygen and bromine bridges in the structure so that the aggregate formula of the complex is as mentioned above.

However, alkali metal ions form reasonably stable complexes with some of the bidentate and polydentate ligands such as salicylaldehyde, β-diketones, nitro phenols, α-nitroso β-naphthol, etc.

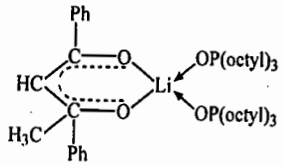


Thus, when NaOH is added to a solution of salicylaldehyde, a neutral complex is formed which is soluble in organic solvents.

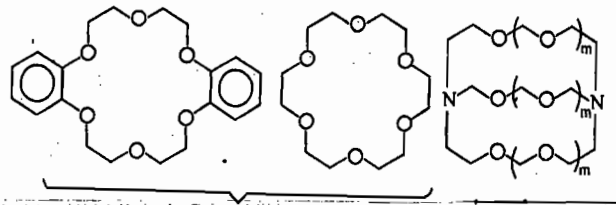
Similarly, the anhydrous sodium derivative of acetylacetone takes up water to produce a hydrated complex which is also soluble in organic solvents.



Quite often it may happen that a particular ligand is better suited to form complex with a particular metal ion. This fact is made use of for the separation of a particular alkali metal ion from others. For instance, the lithium-complex shown is more stable than similar complexes formed by other alkali metals. It is soluble in paraxylene. Through the formation of the above complex, therefore, Li^+ can be easily extracted from an aqueous solution containing a mixture of various alkali metal ions.



The 'Wrap Around' Complexes. Polydentate ligands such as *crown ethers* and *cryptates* are the most important ligands which form *highly stable complexes with alkali metal ions.* These ligands are also *highly selective* in complex formation.



The cause of selectivity lies in the size of the 'hole' available in a polydentate ligand of the type mentioned above. Only that alkali metal ion which *exactly fits into the 'hole'*, forms stable complex. The cations which are either too small or too big to fit in the hole, would not form stable complexes. For example, the 'hole' in cryptate-222 is just of the right size for the K^+ ion to fit in whereas Li^+ and Na^+ ions are *too small* to make contact with the oxygen atoms of the ligand. On the other hand, Rb^+ and Cs^+ ions are *too big* in size to fit in the hole without causing steric strain. The K^+ complex of cryptate-222 is thus most stable. Similarly, Na^+ complex of cryptate-221 is most stable out of all the alkali metal ion complexes formed with this ligand.

The above mentioned macrocyclic ligands 'wrap' the metal ions completely and thus protect them from coming into contact with the solvent molecules. This is the additional cause of the stability of these complexes which are also known as **'wrap around' complexes.**

A number of macrocyclic compounds such as valinomycin and ennatin-B are present in biological systems which are responsible for the transportation of Na^+ and K^+ ions through the hydrophobic lipid by-layers of the cell membranes.

Comparison of Lithium with Other Members of the Family Lithium, no doubt, has most of the characteristic properties of the metals of Group 1 *but it differs from them in many respects.* This is mainly due to the small size of the Li atom and the Li^+ ion. The small size of Li^+ ion is responsible for the highest polarising power of this ion amongst all the alkali metal ions. Lithium differs from the other alkali metals in the following respects.

1. Lithium is much harder than the rest of the alkali metals. Its melting and boiling points are also higher (Table 2).

2. Lithium is the least reactive of the alkali metals towards the various chemical reagents except hydrogen. Thus, it decomposes water only slowly at 25°C whereas sodium does so vigorously. The reaction with potassium, rubidium and cesium is so vigorous that the evolved hydrogen catches fire spontaneously.

3. Lithium is the only alkali metal which reacts with nitrogen to give lithium nitride, Li_3N.

4. Lithium hydride, LiH, is much more stable than any other hydride. Its heat of formation is the highest. However, lithium combines with hydrogen at 700 – 800°C whereas the other alkali metals do so at 350–430°C. Thus, lithium is not so reactive towards hydrogen as the other alkali metals although its hydride is most stable.

5. Lithium reacts with bromine very slowly. Other alkali metals react violently.

6. When burnt in air or oxygen, lithium gives only the monoxide Li_2O which does not react further to give higher oxides. However, the rest of the metals give the peroxides, M_2O_2. Potassium, rubidium and cesium also give the superoxides, MO_2.

7. Lithium hydroxide decomposes at red heat forming Li_2O. The other alkali metal hydroxides do not decompose even at red heat. Also, lithium hydroxide has the lowest solubility among the hydroxides of the alkali metals.

8. The carbonate of lithium is thermally less stable and decomposes into oxide on moderate heating.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

Other alkali metal carbonates are highly stable towards heat. The reason for this behaviour is that Li_2O lattice is more stable than Li_2CO_3 lattice. Other M_2O lattices are less stable than the M_2CO_3 lattices.

9. Its monoxide, Li_2O, is much less basic than the oxides of other alkali metals. Also, it dissolves in water much less readily than sodium or potassium monoxide.

10. Lithium hydroxide is a much weaker base than sodium hydroxide or potassium hydroxide. Its solubility is comparable with that of calcium hydroxide.

11. Lithium fluoride, phosphate, oxalate and carbonate are sparingly soluble in water like the corresponding salts of magnesium. The corresponding salts of sodium and potassium are freely soluble in water.

12. Lithium chloride and lithium nitrate are soluble in alcohol while the corresponding salts of other alkali metals are insoluble in alcohol.

13. Bromide and iodide of lithium are soluble in organic solvents. The corresponding salts of sodium and potassium are not soluble.

14. Lithium chloride separates out from aqueous solution as hydrated crystals, $LiCl.2H_2O$. Sodium and other alkali metal chlorides do not form hydrates at ordinary temperatures. Lithium chloride is deliquescent.

15. Lithium chloride undergoes hydrolysis in hot water though to a small extent but sodium and potassium chlorides do not hydrolyse at all.

16. Lithium nitrate evolves nitrogen dioxide and oxygen on heating leaving behind lithium oxide.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

Sodium and potassium nitrates evolve only oxygen, leaving behind nitrites. For example,

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

17. Lithium sulphate, Li_2SO_4, unlike sulphates of other alkali metals, does not form alums.

18. Lithium ion, Li^+, on account of its small size and consequently high charge density, has a high polarising power as discussed in details in the last chapter. The Li^+ ion thus polarises the electron charge cloud of water molecules more effectively than is done by other alkali metal ions. The Li^+ ion is, therefore, *most extensively hydrated*. The degree of hydration decreases with increase in the ionic size as we move from Li^+ to Cs^+. For the same reason, several lithium salts are hydrated (*e.g.*, $LiClO_4.3H_2O$) whereas the salts of other alkali metals are not hydrated.

Due to excessive hydration, the effective size of Li^+ ion in aqueous solution is larger even than that of Cs^+ ion.

19. High polarising power of Li^+ ion is also responsible for lowering the ionic character of bonds formed in lithium compounds in general and in lithium halides in particular. Assuming, for example, that the bond in lithium iodide is fully ionic (Li^+I^-), the dipole moment of the compound in the gaseous state should be 11·5 debyes but the experimental value is 3·25. This departure is attributed to polarisation, *viz.*, the distortion of electron charge cloud of the iodide ion by the lithium ion (Fig. 1) which results in a partial overlap of orbitals of Li^+ and I^- ions and hence the formation of partial covalent bond in addition to the electrostatic attraction between the two ions. Since the process of overlapping involves filled valence orbital of I^- ion and empty valence orbital of Li^+ ion, the flow of electric charge occurs from I^- to Li^+ ion decreasing thereby the dipole moment of Li – I bond. Thus, the observed dipole moment of LiI is much less than the calculated value which is based on complete transference of one electron from lithium to iodine atom.

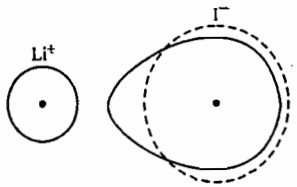


Fig. 1. Polarisation of electron charge cloud of iodide ion by lithium ion.

Diagonal Relationship of Lithium with Magnesium. As already mentioned, lithium differs from the rest of its family members in many respects. However, it shows resemblance with magnesium, the second element of Group 2. This is a case of **diagonal relationship** in which the first element of a group shows similarities with the second element in the next group of the periodic table, as indicated below.

Group 1	Group 2	Group 13	Group 14
Li	Be	B	C
Na	Mg	Al	Si

This diagonal relationship is due to *similar polarising powers* of Li^+ and Mg^{2+} ions despite the occurrence of different charges on these ions. This aspect has already been discussed in the last chapter.

Resemblance of Lithium and Magnesium

Because of the diagonal relationship, lithium resembles magnesium in several respects, as illustrated below.

1. Atomic radius of lithium is 1·34 Å while that of magnesium, being 1·364 Å, is not very much different.

2. The radii of Li^+ ion (0·60 Å) and Mg^{2+} ion (0·65 Å) are not much different from each other.

3. Polarising powers of Li^+ ion and Mg^{2+} ion are about the same.

4. Electronegativities of Li and Mg, being 1·0 and 1·3, respectively, are not much different from each other.

5. Like magnesium, lithium decomposes water only slowly liberating hydrogen.

6. Like magnesium, lithium hardly reacts with liquid bromine.

7. Lithium reacts with nitrogen to give lithium nitride, Li_3N. Magnesium also reacts with nitrogen to give magnesium nitride, Mg_3N_2

8. Lithium forms only the monoxide, Li_2O. Magnesium also prefers to form only the monoxide, MgO.

9. Lithium hydroxide, like magnesium hydroxide, is very slightly soluble in water.

10. Lithium hydroxide, like magnesium hydroxide, is a weak base.

11. Lithium fluoride, phosphate, oxalate and carbonate, like the corresponding salts of magnesium, are sparingly soluble in water.

12. Lithium chloride, like magnesium chloride ($MgCl_2.6H_2O$), separates out from aqueous solutions as hydrated crystals, $LiCl.2H_2O$.

13. Lithium chloride, like magnesium chloride, is deliquescent.

14. Lithium chloride, like magnesium chloride, undergoes hydrolysis in hot water though to a smaller extent than magnesium chloride.

15. Lithium, nitrate, like magesium nitrate, evolves nitrogen dioxide and oxygen on heating, leaving behind the oxide.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$
$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$

Uses of Alkali Metals. Alkali metals are too expensive and too reactive to be used for ordinary purposes where other metals, less expensive and less reactive, can be used with almost the same results. These metals are used only for special purposes as mentioned below.

1. The alkali metals in the liquid state are excellent conductors of heat and are used in this state *for conducting heat from the centre of a nuclear reactor to the outside of the reactor* where it can be converted into useful work.

2. The alkali metals have low ionisation energies, *i.e.*, have relatively greater tendency to emit electrons. This tendency increases on moving from lithium to cesium, as already explained. Thus, electrons can be ejected most readily from cesium. This can happen even by the action of light. This metal, therefore, finds application in the fabrication of *photoelectric cells*.

3. Alkali metals are *strong reducing agents*, as already discussed. These are used in a number of reactions for reduction purposes. Thus, sodium is used as a reducing agent for the preparation of several metals from their chlorides.

4. Alkali metals are also used in the manufacture of several compounds, such as NaH, Na_2O_2, NaCN, $NaNH_2$.

5. Sodium metal is used in the manufacture of Na-Pb alloy required for the manufacture of anti-knocking materials such as $(C_2H_5)_4Pb$ and $(CH_3)_4Pb$ for gasoline.

EXTRACTION OF ALKALI METALS

Extraction of Lithium Lithium is fairly widely distributed in nature and is about twice as plentiful as lead. However, the amount present in any mineral is always small and the extraction is not so easy. The important lithium-bearing minerals are :

1. *Lepidolite or lithia mica* $(Li,Na,K)_2Al_2(SiO_3)_3,(F, OH)_2$ containing up to 1·5% of lithium.

2. *Petalite*, $LiAl(Si_2O_5)_4$, containing 2·7 to 3·7% of lithium.

3. *Spodumene*, $LiAl(SiO_3)_2$ containing 4 to 6% of lithium.

4. *Triphylite*, $(Li,Na)_3PO_4.(Fe,Mn)_3(PO_4)_2$ containing up to 4% of lithium.

Lithium salts also occur in certain spring waters and in some plants such as tobacco, beet and sugar-cane.

The procedure for the extraction of lithium from its silicate mineral *lepidolite* involves the following steps :

1. Preparation of lithium chloride. The silicate mineral, lepidolite, is first of all converted into lithium chloride by any one of the following methods.

a. Acid Treatment Method. The silicate mineral is finely powdered and boiled with sulphuric acid. The insoluble silica (SiO_2) thus formed is filtered off. The solution is treated with the requisite amount of sodium carbonate to precipitate aluminium and iron. Excess sodium carbonate is then added to the filtrate to precipitate lithium as the carbonate. The precipitate is separated by filtration and dissolved in hydrochloric acid to obtain lithium chloride which is purified by extraction with alcohol.

b. Fusion Method. The powdered silicate mineral is fused with a mixture of barium carbonate, barium sulphate and potassium sulphate. The fused mass is separated into two layers : the upper layer containing the sulphates of alkali metals and the lower layer containing barium sulphate along with alumina and silica. The upper layer is separated, dissolved in water and the solution treated with barium chloride solution. Barium sulphate gets precipitated while the chlorides of lithium, sodium and potassium remain in solution. The filtrate is evaporated to dryness and the residue is extracted with pyridine in which only lithium chloride dissolves. Pyridine is distilled off while lithium chloride is left behind.

2. Electrolysis of lithium chloride. A mixture of dry lithium chloride and potassium chloride is fused and electrolysed in an electrolytic cell shown in Fig. 2. The addition of potassium chloride increases the conductivity of lithium chloride and lowers its melting point. The cell is operated at a temperature close to 400°C and a voltage equal to 8 – 9 volts is applied.

The following reactions take place :

$$LiCl \rightleftharpoons Li^+ + Cl^-$$

$$Li^+ + e^- \longrightarrow Li \quad \text{(at cathode)}$$

$$2Cl^- - 2e^- \longrightarrow Cl_2 \quad \text{(at anode)}$$

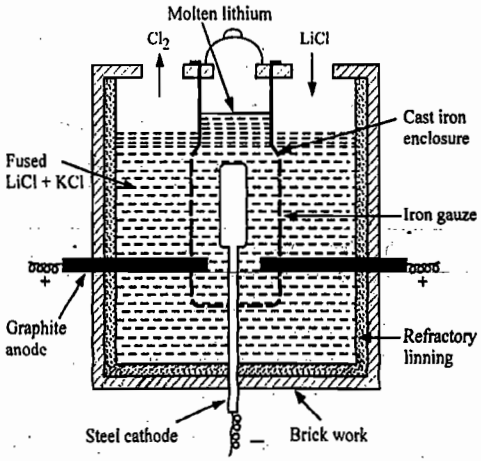


Fig. 2. Electrolytic preparation of lithium.

Chlorine gas liberated at the anode leaves the cell through an exit and the molten lithium metal rises to the surface of the fused electrolyte and collects in the cast iron enclosure surrounding the cathode.

Extraction of Sodium. Sodium occurs in nature in the form of its salts such as NaCl (*rock salt*), $NaNO_3$ (*chile saltpetre*), $Na_2CO_3.NaHCO_3.2H_2O$ (*sodium sesquicarbonate*) and Na_3AlF_6 (*cryolite*).

The metal is extracted by the electrolysis of fused sodium chloride in the presence of calcium chloride and alkali fluorides which themselves do not decompose at the voltage applied but lower the melting point of NaCl from 800° to about 600°C at which the corrossive action of sodium and chlorine is also reduced considerably. Chlorine is a valuable by-product.

Extraction of Potassium. Potassium, like sodium, occurs in nature in the form of its salts such as $KCl.MgCl_2.6H_2O$ (*carnallite*), $K_2SO_4.MgSO_4.CaSO_4.2H_2O$ (*polyhalite*), $KCl.MgSO_4.3H_2O$ (*kainite*), $K_2SO_4.MgSO_4.6H_2O$ (*schonite*), KNO_3 (*saltpetre*) and $K_2SO_4.2MgSO_4$ (*langbenite*).

However, the metal is not extracted from any of the above salts. It is obtained by heating potassium fluoride with calcium carbide in steel cylinders at about 1000°C :

$$2KF + CaC_2 \longrightarrow 2K + CaF_2 + 2C$$

Extraction of Rubidium. Rubidium is a scarce element although it occurs fairly widely in nature alongwith other alkali metals. Carnallite contains up to 0·04 per cent of rubidium chloride, RbCl and is probably the most important source of the metal. *Lepidolite* may contain up to about 1 per cent of rubidium. Other lithium ores like *tryphylite* also contain traces of rubidium.

The metal is extracted either by the electrolysis of *fused* RbCl or RbOH, or by the reduction of rubidium carbonate or hydroxide by aluminium or magnesium.

Extraction of Cesium. Cesium, like rubidium, is a rare element. The chief ores of cesium are *pollucite* ($Cs_4Al_4Si_9O_{26}.6H_2O$) which contains about 27 per cent of cesium ; *lepidolite*, a lithium ore, which contains 0·2 to 0·7 per cent of cesium and *beryl*, a beryllium ore, which contains about 3 per cent of cesium.

The metal is obtained from *pollucite* by heating the mineral with calcium metal at 900°C. About 85% of the cesium formed volatilises. The vapour of the metal are cooled and the crude condensate purified by sublimation in vacuum at 350 – 400°C to get the pure metal.

Cesium metal can also be obtained by the reduction of the hydroxide or the carbonate with Al or Mg in an atmosphere of hydrogen or by heating CsCl with Ca.

Preparation of Francium. This element was discovered by Mlle Perry in 1939 who showed that actinium-237 undergoes an α-ray radioactive change producing a new element which she named francium (after France).

$$^{237}_{89}Ac \longrightarrow ^{233}_{87}Fr + ^{4}_{2}He$$

Francium is a radioactive element with a half-life period of 21 minutes.

PROPERTIES OF ALKALI METALS AND THEIR USES

Properties of Lithium. Lithium is a silvery-white metal. It is harder than sodium or potassium but is soft enough to be cut with a knife. It is the lightest metal known (density 0·634 g cm^{-3}). It has higher melting point (180°C) and a higher boiling point (1326°C) than any of the other alkali metals. When volatilized, it imparts a crimson red colour to the flame. Chemical properties of lithium have already been described along with the properties of other alkali metals.

a. Uses of lithium metal. 1. Lithium forms a number of alloys which are highly useful in industry. For example, lithium-lead alloy (0·05% Li) is used for making bearings and sheaths for electric cables. Lithium-aluminium alloy possesses great tensile strength and elasticity like that of mild steel. 2. Since lithium combines readily with oxygen and nitrogen, it is used for removing the last traces of oxygen and

nitrogen from copper and nickel. 3. Lithium is used for producing thermonuclear energy required for propelling rockets and guided missiles.

b. Uses of lithium compounds. 1. *Lithium carbonate* is used in making a special variety of glass which is very strong and resists weather. 2. *Lithium chloride* is used in air-conditioning plants to regulate the humidity. It is also used in Ni – Fe accumulators. 3. *Lithium salicylate* and *bicarbonate* have been used in medicine for the treatment of rheumatism since the resulting lithium urate is highly soluble. 4. *Lithium bromide* is used in medicine as a sedative. 5. *Lithium hydride* and *lithium aluminium hydride* ($LiAlH_4$) are used in synthetic organic chemistry as reducing agents.

Properties of Sodium. Sodium is a soft, silvery-white metal. It is lighter than water, its density being .0·972 g cm^{-3}. It melts at 97·8°C and boils at 883°C. It is sufficiently malleable and ductile and, like other metals, is a good conductor of heat and electricity. Chemical properties of sodium have already been described along with properites of other alkali metals.

Uses of Sodium. 1. Sodium is used in the manufacture of a number of chemicals like sodium peroxide, sodium cyanide and sodamide. 2. Sodium is largely used in industry for the production of artificial rubber, dyes, drugs, etc. 3. In the laboratory, sodium is employed as a reducing agent in the form of sodium amalgam as well as in the synthesis of many organic compounds. It is also used for detecting nitrogen, halogens and sulphur in organic compounds. 4. It is used in the extraction of boron and silicon. 5. Because of its lightness and high thermal conductivity, it is employed for filling exhaust valves of aeroplane engines.

Properties of Potassium Potassium resembles sodium in its physical as well as chemical properties. However, it is softer and chemically more reactive. Thus, it reacts with water more violently and the heat of reaction is so high that the hydrogen evolved catches fire. When burnt in excess of oxygen, it forms the super oxide, KO_2 (sodium under similar conditions gives the peroxide, Na_2O_2). Potassium is slightly radioactive owing to the presence of traces of the radioactive isotope, $^{40}_{19}K$.

Uses. Very few uses have been found for metallic potassium. It is occasionally used in photoelectric cells and in the synthesis of organic compounds.

Properties of Rubidium, Cesium and Francium.

Rubidium is a soft white metal with low melting point (38·9 °C) and low boiling point (688°C). It is more reactive than potassium. It catches fire spontaneously in air and reacts vigorously with water.

Cesium is a soft white metal with very low melting point (28·7°C). When exposed to air, it first melts and then bursts into flame. It decomposes cold water with great violence forming the hydroxide CsOH which is the strongest of all the bases.

Francium, as already mentioned, is a radioactive element with a half-life period of 21 minutes only. Because of its very short life, chemistry of francium has been studied by radio-chemical methods. Our knowledge of its chemistry is derived almost entirely from the researches of Mlle Perry which show that francium has properties that might be expected of the heaviest alkali metal.

COMPOUNDS OF ELEMENTS OF GROUP 1

I. A Comparative Study

All the common compounds of alkali metals are ionic in character and contain the alkali metals as colourless electropositive monovalent ions. Most of the compounds are soluble in water. With the exception of a few lithium salts, all the alkali metal salts are insoluble in alcohol. The alkali metal cations are extremely stable because of noble gas configurations. The compounds of alkali metals are colourless except those having coloured anions, like MnO_4^-, CrO_4^{2-}, etc.

Oxides. When the alkali metals are burnt in air, they form oxides. Different kinds of oxides are formed depending upon the alkali metal. Thus, lithium forms monoxide Li_2O (and some peroxide Li_2O_2) when burnt in oxygen. Sodium forms peroxide Na_2O_2 (and some oxide Na_2O). Potassium, rubidium and cesium form superoxides of the type MO_2 (where M = K, Rb and Cs) when burnt in air.

The normal oxides contain O^{2-} ion, the peroxides contain O_2^{2-} ion and superoxides contain O_2^- ion. The peroxides and superoxides become more stable with increase in atomic number of the alkali metal. The formation and stability of these oxides can be explained on the basis of their *lattice energy* (Chapter 6). Li^+ ion being a small ion has a strong positive field around it and can stabilize only a small anion, O^{2-}, whereas Na^+ ion being a large cation can stabilize a large anion and so on. Thus, smaller cation can stabilize smaller anion and larger cation can stabilize larger anion.

Oxides of any required type can, however, be prepared by dissolving the metal in ammonia and treating the solution with the required amount of oxygen. Ozonides of the formula MO_3 are also formed on treatment with ozone.

The typical oxides are the monoxides, M_2O, which are strongly basic and highly soluble in water. They give strongly alkaline solutions due to formation of hydroxides, M^+OH^-, which are very largely ionised.

The higher oxides, *viz.*, peroxides and superoxides are important oxidising agents. They react with dilute acids forming hydrogen peroxide and oxygen, respectively.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

$$4KO_2 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2H_2O + 3O_2$$

Structures of oxides. Lithium, sodium and potassium oxides are said to have *anti-fluorite* structure which is similar to the structure of calcium fluoride (called *fluorite structure*). The specific difference is that whereas in calcium fluoride, the fluoride ions are tetrahederally surrounded by Ca^{2+} ions (Chapter 6), in lithium oxide and sodium oxide, etc., the metal ions (Li^+, Na^+, etc.) are surrounded by O^{2-} ions. Thus, alkali metal oxides have the same structure as calcium fluoride with the difference that positions of positive and negative ions have been interchanged. This structure is, therefore, known as *anti-fluorite structure*.

Due to high electropositive character of the alkali metals, their oxides get excessively hydrolysed by water yielding hydroxides. The hydroxides, being strong bases, ionise to yield OH^- ions.

$$M_2O + H_2O \longrightarrow 2M^+ + 2OH^-$$

Hydroxides. The hydroxides of alkali metals have the general formula MOH. These are white crystalline solids, highly soluble in water as well as in alcohol. They act as strong bases in aqueous solutions, as shown above. Since electropositive character of the alkali metals increases on moving from Li to Cs, their hydroxides become more and more basic on moving down the group. Thus, out of the hydroxides of lithium, sodium and potassium, lithium hydroxide is the weakest and potassium hydoxide is the strongest alkali.

All the hydroxides are stable towards heat and this stability increases on moving from Li to Cs. They melt without decomposing and are good conductors of electricity in the fused state.

The hydroxides sublime at about 400°C giving vapours which consist of dimers, $(MOH)_2$.

Halides. Halides of alkali metals have, generally, high melting points. They are good conductors of electricity in fused state and are readily soluble in water.

Their structure is determined by the radius ratio and lattice energy effects. The radius ratio M^+/Cl^- for chlorides of various alkali metals are given in Table 5. The coordination number expected from a given radius ratio, as discussed in Chapter 6, is shown in the next column. The actual coordination numbers as observed from X-ray structure of the crystals, are shown in the last column.

TABLE 5

Radius Ratios and Coordination Numbers of Alkali Metal Halides

Formula of chloride	Radius ratio $M^+ : Cl^-$	Coordination number expected from the radius ratio	Observed coordination number
LiCl	0·338	4	6
NaCl	0·524	6	6
KCl	0·732	6	6
RbCl	0·822	8	6 or 8
CsCl	0·930	8	8

Thus, while the observed coordination numbers for Na, K, Rb and Cs are according to expectations, that for Li is higher. The anomaly in the case of Li is due to the fact that higher coordination number leads to higher lattice energy and, therefore, adds to the stability of the crystal.

The alkali metal halides have essentially ionic character. Lithium halides, however, have partly covalent character in addition to ionic character. This is due to the polarisation of the halide ion by the lithium ion, as has already been discussed.

Carbonates and Bicarbonates. Since the alkali metals are highly electropositive, their carbonates (M_2CO_3) and in most cases, also the bicarbonates ($MHCO_3$), are highly stable to heat. As the electropositive character increases on moving down the group, the stability of the carbonates and bicarbonates increases in the same order. Thus, lithium carbonate is not so stable to heat as the other alkali metal carbonates. Lithium bicarbonate does not exist as solid.

Hydrides. As already mentioned, hydrides of alkali metals contain hydrogen as an anion and are represented as M^+H^-. Hydrogen, in these compounds, gets liberated at the anode, on electrolysis. The hydrides are not very stable. They react with water readily liberating hydrogen. These hydrides are, therefore, used as reducing agents.

Lithium aluminium hydride, $Li[AlH_4]$, is a strong reducing agent and is used as such in organic chemistry.

Organometallic Compounds. Alkali metals, especially lithium, form a number of organometallic compounds which are frequently employed in the synthesis of a variety of organic compounds.

Organolithium compounds are generally synthesised as follows :

(*i*) $Li(n\text{-}C_3H_7) + C_6H_5I \xrightarrow[\text{ether}]{\text{Solvent}} Li(C_6H_5) + n\text{-}C_3H_7I$

(*ii*) $4Li(C_6H_5) + Sn(CH_2-CH_2=CH_2)_4 \xrightarrow[\text{ether}]{\text{Solvent}} 4Li(CH_2-CH=CH_2) + Sn(C_6H_5)_4$

(*iii*) $2Li + C_2H_5I \xrightarrow[\text{ether}]{\text{Solvent}} LiI + Li(C_2H_5)$

Organometallic compounds of other alkali metals such as $Na(C_6H_5)$, $Ph_2C(Na)C(Na)Ph_2$, $CsCH_2CH_2Cs$, are also known. These are generally prepared from the corresponding mercury compounds, as, for example,

$$2K + HgR_2 \longrightarrow Hg + 2KR$$

The monomeric organometallic compounds of alkali metals are not very stable thermodynamically. However, polymeric compounds are comparatively stable. For example, some polymeric lithium alkyls do not decompose even up to 100°C.

Lithium alkyls are extensively used in the synthesis of organic compounds and organometallic

compounds of other elements, as is evident from the following reactions :

(*i*) $3LiR + BCl_3 \longrightarrow 3LiCl + BR_3$

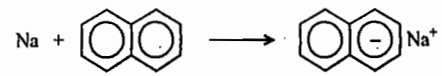
(*ii*) $Li(C_6H_5) + (CH_3C_6H_4)_2CO \longrightarrow (CH_3C_6H_4)_2C(C_6H_5)OLi \xrightarrow{H_2O} (CH_3C_6H_4)_2C(OH)C_6H_5 + LiOH$ (Tertiary carbinol)

(*iii*) $Li(C_6H_5) + CO_2 \longrightarrow [C_6H_5CO_2Li] \xrightarrow{H_2O} C_6H_5COOH + LiOH$ (Carboxylic acid)

(*iv*) $LiR + R'CON(CH_3)_2 \longrightarrow LiN(CH_3)_2 + R'COR$ (Ketones)

Alkyl and aryl compounds of lithium are polymeric having considerable covalent character in their Li – C bonds whereas such organometallic compounds of other alkali metals have predominantly ionic character so that these can be represented as M^+R^-. The alkyl and aryl sodium, potassium, etc., are much more reactive than the corresponding alkyls and aryls of lithium. For instance, the former catch fire in air more violently compared to alkyl or aryl compounds of lithium.

A particular ionic organometallic compound of sodium is formed when the metal is shaken with naphthalene or phenanthrocene in a nonaqueous solvent. The solution is paramagnetic and has strong reducing properties like the solution of Na metal in liquid ammonia. The reaction can be represented as



The electron of sodium metal is captured by partially filled $p\pi$ orbitals which are delocalised on all the carbon atoms of naphthalene or phenanthrocene.

The student is advised to consult Chapter 34 on Organometallic Compounds for the structures of alkyls and aryls of alkali metals.

II. Some Important Compounds of Elements of Group 1

Lithium Monoxide, Li_2O. It may be prepared by burning lithium in oxygen. It is obtained in the pure state by heating carbonate or hydroxide in an atmosphere of hydrogen (to prevent the formation of Li_2O_2)

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

Lithium oxide is a white solid that reacts slowly with water to form lithium hydroxide.

$$Li_2O + H_2O \longrightarrow 2LiOH$$

It resembles other alkali metal hydroxides in possessing caustic properties and in its power to absorb carbon dioxide.

Lithium Peroxide, Li_2O_2. It is prepared by adding hydrogen peroxide and alcohol to a concentrated solution of lithium hydroxide. A white precipitate having the composition $Li_2O_2.H_2O_2.3H_2O$ is obtained.

When dehydrated over phosphorus pentoxide, it loses both water and hydrogen peroxide and leaves behind Li_2O_2.

Lithium Hydroxide, LiOH. It is usually prepared by the action of baryta water ($Ba(OH)_2$ solution) on lithium sulphate.

$$Li_2SO_4 + Ba(OH)_2 \longrightarrow 2LiOH + BaSO_4$$

The filtrate is evaporated when $LiOH.H_2O$ crystallises out from the solution. On heating these crystals in an atmosphere of hydrogen, a white mass of lithium hydroxide, LiOH, remains.

Lithium hydroxide is less soluble (about 80 g per litre at room temperature) than the other alkali metal hydroxides and is also much less thermally stable. On strong heating it decomposes forming the oxide.

$$2LiOH \longrightarrow Li_2O + H_2O$$

Lithium Hydride, LiH. *It is obtained by heating lithium metal in a current of hydrogen.*

$$2Li + H_2 \longrightarrow 2LiH$$

Lithium hydride is a white solid which melts at 680°C. If electrolysed at temperatures slightly below its melting point, hydrogen is given off at the anode indicating that lithium hydride is an electrovalent compound and contains Li^+ and H^- ions. It reduces carbon dioxide to carbon and reacts vigorously with water with the liberation of hydrogen.

Lithium Aluminium Hydride, $LiAlH_4$. It is obtained by the action of anhydrous aluminium chloride on lithium hydride in ethereal solution.

$$4LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl \downarrow$$

It is a powerful reducing agent and reduces a number of covalent halides to the hydrides. Thus, silicon tetrachloride is reduced to silane, SiH_4.

A detailed description of this salt has been given in Chapter 15.

Lithium Carbonate, Li_2CO_3. It is prepared by adding ammonium carbonate to a solution of a soluble salt of lithium in the presence of ammonia.

$$2LiCl + (NH_4)_2CO_3 \longrightarrow Li_2CO_3 + 2NH_4Cl$$

Lithium carbonate, being sparingly soluble, gets precipitated. It is filtered and dried.

It is a white stable powder which decomposes to oxide and CO_2 on heating to above 600°C ($Li_2CO_3 \longrightarrow Li_2O + CO_2$). Li_2CO_3 dissociates into Li_2O more easily than other alkali metal carbonates. The is due to the fact that Li_2O is more stable than other alkali metal oxides. Because of its small size, Li^+ ion has greater polarising power than the other alkali metal cations. It, therefore, polarises the electron charge cloud of O^{2-} ion towards itself to a considerable extent. This allows partial overlap between the orbitals of Li^+ and O^{2-} ions introducing some covalent character in Li – O bond apart from the ionic character in Li_2O. This gives extra stability to Li_2O. The other alkali metal oxides, M_2O, are almost entirely ionic in character. Lithium carbonate, as already stated, is only sparingly soluble in water like the carbonates of calcium and magnesium. On passing carbon dioxide through a suspension of lithium carbonate, the latter dissolves due to the formation of soluble lithium bicarbonate.

The solution of lithium bicarbonate is used in medicine as a remedy for gout and rheumatism under the name *lithia water*. Lithium carbonate is used in glass industry.

Sodium Cyanide, NaCN. It is a chemical of industrial importance and is, therefore, prepared on a large scale by the following methods.

1. From Sodium. Dry ammonia gas is passed over fused metallic sodium in iron retorts when sodamide is first formed.

$$2NH_3 + 2Na \longrightarrow 2NaNH_2 + H_2$$

The liquid sodamide formed is taken to another chamber and dropped on red hot charcoal to yield sodium cyanide.

$$NaNH_2 + C \longrightarrow NaCN + H_2$$

2. From Calcium Cyanamide. Crude calcium cyanamide is mixed with sodium carbonate or sodium chloride and heated with coke.

$$CaN.CN + Na_2CO_3 + C \longrightarrow 2NaCN + CaCO_3$$

$$CaN.CN + 2NaCl + C \longrightarrow 2NaCN + CaCl_2$$

3. From Gas Works. A good deal of sodium cyanide is obtained as a by-product in the purification of coal gas which contains some hydrocyanic acid and ammonia. The crude coal gas is passed through copper sulphate solution when ammonium tricyanocuperate(I) is formed.

$$2CuSO_4 + 8NH_3 + 8HCN \longrightarrow \underset{\text{Ammonium tricyano cuperate (I)}}{2(NH_4)_2[Cu(CN)_3]} + 2(NH_4)_2SO_4 + \underset{\text{Cyanogen}}{(CN)_2}$$

When all the copper salt has been converted into the complex cyanide, the coal gas is turned on to a second vessel. Dilute sulphuric acid is added to the first vessel and the hydrocyanic acid gas evolved is absorbed in caustic soda solution to form sodium cyanide.

$$(NH_4)_2[Cu(CN)_3] + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2HCN + CuCN$$

$$HCN + NaOH \longrightarrow NaCN + H_2O$$

When all the complex cyanide has been decomposed by dilute sulphuric acid, the coal gas is turned again into the first vessel where ammonium tricyanocuperate (I) is formed again and the reaction goes on continuously.

$$CuCN + 2HCN + 2NH_3 \longrightarrow (NH_4)_2[Cu(CN)_3]$$

Properties. Sodium cyanide is a colourless solid readily soluble in water. The solution is alkaline due to hydrolysis of the cyanide ion.

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

It is highly poisonous and has a characteristic smell like that of bitter almonds.

It forms soluble complex cyanides with salts of transition metals like copper, silver, gold, cadmium, zinc and iron. Thus,

$$CdSO_4 + 4NaCN \longrightarrow Na_2[Cd(CN)_4] + Na_2SO_4$$

A dilute solution of sodium cyanide can dissolve gold and silver in the presence of air or oxygen forming soluble complex cyanides.

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow \underset{\text{Sodium dicyano-aurate (I)}}{4Na[Au(CN)_2]} + 4NaOH$$

Uses. Large quantities of sodium cyanide are used in the extraction of silver and gold. It is also employed in electroplating of gold and silver which involves the electrolysis of their complex cyanides. In the laboratory it is used for preparing other cyanides and as a reducing agent in the synthesis of organic compounds. On account of its highly poisonous character it is used as a germicide in spraying over fruit trees.

Sodium Amide or Sodamide, $NaNH_2$. It is prepared by passing a stream of dry ammonia gas over metallic sodium at 300 – 400°C, contained in an iron vessel.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

Sodamide is a waxy solid melting at 210°C. It gets hydrolysed on being treated with water.

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3$$

It reacts with dry hydrogen at 150 — 300°C to give sodium hydride.

$$NaNH_2 + H_2 \longrightarrow NaH + NH_3$$

When warmed with carbon monoxide it gives sodium cyanide.

$$2NaNH_2 + CO \longrightarrow NaCN + NaOH + NH_3$$

With carbon dioxide it gives cyanamide $CN.NH_2$

$$2NaNH_2 + 2CO_2 \longrightarrow Na_2CO_3 + H_2O + CN.NH_2$$

With nitrous oxide it gives sodium azide.

$$NaNH_2 + N_2O \longrightarrow \underset{\text{Sodium azide}}{NaN_3} + H_2O$$

Potassium Cyanide, KCN. It is obtained by heating dry potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, to white heat or better by heating it with metallic potassium.

$$K_4[Fe(CN)_6] \longrightarrow 4KCN + Fe + 2C + N_2$$

$$K_4[Fe(CN)_6] + 2K \longrightarrow 6KCN + Fe$$

It can also be obtained by fusing potassium hexacyanoferrate (II) with potassium carbonate when a mixture of potassium cyanide and potassium cyanate, KCNO, is produced.

$$K_4[Fe(CN)_6] + K_2CO_3 \longrightarrow 5KCN + KCNO + Fe + CO_2$$

Potassium cyanide is a white crystalline solid, m.p. 635°C. It is highly hygroscopic and very soluble in water. The aqueous solutions are alkaline to litmus because of hydrolysis.

$$KCN + H_2O \rightleftharpoons K^+ + OH^- + HCN$$

Potassium cyanide is a **deadly poison !**

Potassium cyanide is extensively used in electroplating and extraction of gold and silver. It is also used as a laboratory reagent.

Role of Na^+ and K^+ ions in Biological Systems. Sodium cation is a major cation of extracellular fluids of animals including human beings which is known to activate certain enzymes in the animal body. Sodium ions are relatively harmless except when present in excess amounts in which case they may cause hypertension. The saline water containing excessive amounts of NaCl is harmful to plant and aquatic life because of the toxicity of Na^+ ions.

The potassium ion is essential to all organisms with the possible exception of blue green algae. It is a major cation of intracellular fluid of animal cells. It is moderately toxic to mammals but only when injected intravenously.

The sodium and potassium ions, taken together, constitute what is known as **'Na^+–K^+ pump'** or simply as **'sodium pump'.** The functioning of this pump is actually a biological process which goes on occurring in each and every cell of all animals. Although the discussion of the exact mechanism of the functioning of this pump is beyond the scope of the book yet it may suffice to say that it transfers Na^+ ions from the intracellular fluids to the extracellular fluids with the help of 'carrier proteins'. Simultaneously it transfers K^+ ions from the extracellular fluids to the intracellular fluids. Since each operation of the pump (*i.e.*, each cycle of this biological process) pumps out larger number of sodium ions from the cell than the number of K^+ ions that it pumps into the cell, the interior of the cell acquires an excess negative charge and the exterior of the cell acquires an excess positive charge. This results in the development of electrical potential gradient across the cell membrane which is responsible for the transmission of nerve signals in animals. The Na^+–K^+ pump also maintains the volume of the cell. Without the existence of the Na^+–K^+ pump in the cell, the latter would have swelled in volume and ultimately bursted.

QUESTIONS

1. (*a*) What are *s* block elements ?
   (*b*) Why are the elements of Group 1 called the alkali metals ? Give their electronic configurations. Why are they so reactive ?
2. (*a*) Explain why the elements of Group 1 are soft, electrically conducting, good reducing agents and form univalent ions.

   (*b*) Account for the fact that alkali metals form basic hydroxides and their basic strength increases on descending the group.
   (*c*) 'Alkali metals lose electrons even when exposed to light'. How would you account for this behaviour ?
3. (*a*) Discuss the general trends in Group 1 metals with respect to
   (*i*) melting point (*ii*) density (*iii*) ionisation energy (*iv*) atomic and ionic radii (*v*) chemical reactivity.
   (*b*) With the help of electronic configurations, how would you account for different colours produced by alkali metals in bunsen flame ?
4. (*a*) Explain the terms oxidation potential and ionisation energy.
   'An element having high oxidation potential will normally have low ionisation energy and vice versa.' How would you explain this ?
   (*b*) Amongst the alkali metals, lithium has the highest ionisation energy but at the same time it has the highest electrode potential. How would you explain this contradictory behaviour
5. Why and in what ways does Li resemble Group 2 metals ?
6. (*a*) Discuss the important characteristics of alkali metals. How would you explain the various properties on the basis of their electronic configurations ?
   (*b*) Why are the hydroxides (MOH) of alkali metals so strongly basic in character ? Why does the basic strength increase as we move down the group ?
7. The extent of hydration of alkali metal ions decreases as we move down the group. How would you account for it?
8. On the basis of ionic size we expect that the ionic conductance of alkali metal ions should decrease in the order $Li^+ > Na^+ > K^+ > Kb^+ > Cs^+$. But actually the trend is just the *reverse*. How would you explain this anomaly ?
9. (*a*) Give a detailed account of the complexes of alkali metals formed with polydenate ligands.
   (*b*) How would you account for the unusual stability of complexes of alkali metals formed with polydenate ligands such as crown ethers and cryptates. Why are these ligands so selective in complex formation.
10. Account for the following :
    (*a*) Li forms normal oxide, Na forms peroxide and K, Rb and Cs form superoxides.
    (*b*) In spite of the fact that lithium is an alkali metal, its halides are covalent.
    (*c*) All alkali metals give flame colouration.
    (*d*) The alkali metals dissolve in liquid ammonia to give paramagnetic and blue coloured solutions.
11. (*a*) How does lithium differ from its congeners ?
    (*b*) Conductivity of Li^+ ion in water is less than that of Cs^+ ion although their sizes suggest an opposite order. Explain.
    (*c*) Give important uses of alkali metals.
12. (*a*) Lithium iodide is quite soluble in nonpolar solvents, the order of solubility in such solvents decreases in the order : LiI > LiBr > LiCl > LiF. How would you account for this ?
    (*b*) Why does the chemical reactivity of the alkali metals increase from Li to Cs ?
13. What is meant by diagonal relationship ? In what respects does lithium resemble magnesium?
14. Give the names of important minerals containing lithium. How is lithium recovered from the silicate minerals ? In what respects do lithium and its compounds differ from other alkali metals and their compounds ?
15. Give a brief account of the oxides and hydroxides of alkali metals. Comment on the structures of the oxides.
16. From the radius ratio, the coordination number of lithium in LiCl should be 4. But actually it is 6. How would you account for it ?
17. Give the preparation and properties of the following :
    Lithium monoxide, lithium peroxide, lithium hydroxide, lithium hydride, lithium carbonate, sodium cyanide, sodamide, potassium cyanide.

14 THE ELEMENTS OF GROUP 2

The elements, **beryllium, magnesium, calcium, strontium, barium** and **radium**, constitute Group 2 of the periodic table.

As mentioned in the previous chapter, all these elements are metals. The oxides of calcium, strontium and barium were known much earlier than the metals themselves and they were called **alkaline earths** since they were alkaline and existed in the earth. Later, when the elements were discovered, they were named as **alkaline earth metals**. Radium corresponds to the alkaline earth metals in its chemical properties but, being a radioactive element, it is studied separately along with the other radioactive elements. The electronic configurations of these elements have been given in Table 1 in the last chapter.

GENERAL CHARACTERISTICS

The general characteristics of alkaline earths have already been discussed in details while describing the properties of the main group elements in Chapter 12. Only a brief discussion has been made in this chapter.

TABLE 1

Some Important Physical Properties of Alkaline Earth Metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Molar mass (g mol^{-1})	9·01	24·31	40·08	87·67	137·34	226·05
Molar volume (cm^3 mol^{-1})	4·90	13·97	25·91	34·54	36·72	38·00
Density (g cm^{-3})	1·84	1·74	1·55	2·54	3·75	6·00
Melting point (°C)	1277	650	838	768	714	~ 700
Boiling point (°C)	2770	1107	1440	1380	1640	1140
Atomic radius (Å)	0·90	1·36	1·74	1·92	1·98	–
Ionic radius (Å)	0·31	0·65	0·99	1·10	1·29	1·32
Heat of hydration of ions (kJ mol^{-1})	2494	1921	1577	1443	1305	–
Heat of atomisation (kJ mol^{-1})	78·2	35·2	42·5	39·1	42·2	–
Ionisation energy (kJ mol^{-1}) First	899·3	737·6	589·8	549·3	502·6	509·0
Ionisation energy (kJ mol^{-1}) Second	1757	1450	1146	1064	965	979
Electronegativity (Pauling's values)	1·5	1·3	1·0	1·0	0·9	0·9
Flame coloration	None	None	Brick red	Crimson	Grassy green	Crimson
Oxidation state	+2	+2	+2	+2	+2	+2

Physical Properties

Some of the important physical properties and other constants of alkaline earth metals are given in Table 1.

1. Metallic Properties. Elements of Group 2 have typical metallic properties. They show good metallic lustre and high electrical as well as thermal conductivity.

2. Metallic Bonding. While in alkali metals (Group 1), there is a single valence electron per atom, in alkaline earth metals (Group 2), there are two valence electrons per atom. Hence metallic bonding in Group 2 elements is stronger than that in Group 1 elements. As a result, the elements of Group 2 are *harder* and *denser* and have *higher melting* and *boiling points* than the elements of Group 1. As already explained in Chapter 4 on Chemical Bonding, the filled valence *s* energy band in these elements overlaps with the empty valence *p* energy band so that valence electrons can easily jump from filled energy levels of valence *s* energy band to empty energy levels of valence *p* energy band. These elements are, therefore, good conductors of heat and electricity.

3. Hardness. The alkaline earth elements are moderately hard. Although they are harder than alkali metals yet they can be cut with a sharp knife.

4. Molar Volume. Molar volume is seen to increase regularly in moving from beryllium to radium. This is to be expected in view of increase in atomic radius (due to increase in the number of shells) on moving down the group in the same order.

5. Density. Density is seen to decrease slightly on moving down the group upto calcium but it increases considerably thereafter upto radium. These metals are seen to be considerably denser than the corresponding alkali metals of Group 1.

6. Melting Points and Boiling Points. Melting points and boiling points do not show regular trends. However, these are higher than those of alkali metals.

7. Atomic and Ionic Radii. The atoms of these elements are smaller than those of the corresponding elements of Group 1. This is due to higher nuclear charge of these atoms which tends to draw the orbital electrons inwards, *i.e.*, towards the nucleus. On account of the smaller atomic size, these elements are harder, have higher densities and higher melting points than the elements of Group 1.

The ionic radii are seen to be smaller than the atomic radii. This is to be expected in view of the removal of two orbital electrons in the formation of the bivalent cation (*e.g.*, Mg^{2+}, Ca^{2+}, Ba^{2+}) accompanied by the disappearance of the *M* shell.

The electronic configurations of the ions are similar to those of noble gases, *i.e.*, s^2p^6 configuration (s^2 for Be^{2+}), in the outer shell. They have also no unpaired electrons. Accordingly, these ions, like the alkali metal ions, are *diamagnetic* and *colourless*. The outer configurations of the ions being highly stable, they resist the elimination of another electron. Hence, the valency of the alkaline earth metals remains 2, *i.e.*, the oxidation state remains +2 in all ionic compounds.

Atomic as well as ionic radius is seen to increase on moving down the group from Be to Ra on account of the presence of an extra shell of electrons at each step.

8. Heat of Atomisation. Heat of atomisation is seen to fall considerably on moving from Be to Mg. The subsequent change is rather small. This shows that metal–metal bond strength is maximum in the case of beryllium.

9. Ionisation Energies. The first as well as the second ionisation energy is seen to *decrease* on going down the group from beryllium to barium. This is to be expected on account of increase in the atomic radius and, therefore, greater distance between the nucleus and the outer electrons as we move down the group.

The ionisation energy of radium, however, is slightly higher than that of barium. It has not been possible to offer any satisfactory explanation for this.

The second ionisation energy in each case is higher than the first, as expected.

In view of the lower value of first ionisation energy, it would appear that the alkaline earth metals should prefer to form + 1 ions (M^+) rather than + 2 ions (M^{2+}). However, in actual practice, these metals give only + 2 ions, *e.g.*, Mg^{2+}, Ca^{2+}, etc. If ionisation energy was the only factor involved, we would have got the monovalent ions (*e.g.*, Mg^+, Ca^+, etc.,) rather than the divalent ions (*e.g.*, Mg^{2+}, Ca^{2+}, etc.). This anomaly may be explained by taking into consideration the magnitude of energy changes involved, say, in the formation of CaCl and $CaCl_2$.

Let us first calculate the enthalpy of formation of CaCl(*s*) from its elements in their standard states from the data given below.

$$Ca\,(s) \longrightarrow Ca\,(g)\text{ ; (Sublimation energy)} \qquad \Delta H_1 = S\text{ kJ mol}^{-1}$$
$$Ca\,(g) \longrightarrow Ca^+\,(g) + e^-\text{ ; (Ionization energy)} \qquad \Delta H_2 = 600\text{ kJ mol}^{-1}$$
$$1/2\,Cl_2\,(g) \longrightarrow Cl\,(g)\text{ ; (Dissociation energy)} \qquad \Delta H_3 = 120\text{ kJ mol}^{-1}$$
$$Cl\,(g) + e^- \longrightarrow Cl^-\,(g)\text{ ; (Electron affinity)} \qquad \Delta H_4 = -350\text{ kJ mol}^{-1}$$
$$Ca^+\,(g) + Cl^-\,(g) \longrightarrow CaCl\,(s)\text{ ; (Lattice energy)} \qquad \Delta H_5 = -720\text{ kJ mol}^{-1}$$
$$\therefore\quad Ca\,(s) + 1/2\,Cl_2\,(g) \longrightarrow CaCl\,(s)\text{ ; (Heat of formation)} \qquad \Delta H_f = (-350 + S)\text{ kJ mol}^{-1}$$

Let us now calculate the enthalpy of formation of $CaCl_2$ (*s*) from its elements in standard states from the data given below.

$$Ca\,(s) \longrightarrow Ca\,(g)\text{ ; (Sublimation energy)} \qquad \Delta H_1 = S\text{ kJ mol}^{-1}$$
$$Ca\,(g) \longrightarrow Ca^{2+}\,(g) + 2e^-\text{ ; (Ionization energy)} \qquad \Delta H_2 = 1800\text{ kJ mol}^{-1}$$
$$Cl_2\,(g) \longrightarrow 2Cl\,(g)\text{ ; (Dissociation energy)} \qquad \Delta H_3 = 240\text{ kJ mol}^{-1}$$
$$2Cl\,(g) + 2e^- \longrightarrow 2Cl^-\,(g)\text{ ; (Electron affinity)} \qquad \Delta H_4 = -700\text{ kJ mol}^{-1}$$
$$Ca^{2+}\,(g) + 2Cl^-\,(g) \longrightarrow CaCl_2\,(s)\text{ ; (Lattice energy)} \qquad \Delta H_5 = -2200\text{ kJ mol}^{-1}$$
$$\therefore\quad Ca\,(s) + Cl_2\,(g) \longrightarrow CaCl_2\,(s)\text{ ; (Heat of formation)} \qquad \Delta H_f = (-860 + S)\text{ kJ mol}^{-1}$$

Now, consider the transformation reaction :

$$2CaCl\,(s) \longrightarrow CaCl_2\,(s) + Ca\,(s)$$

For this reaction, $\Delta H_{Transformation} = \Delta H_{f(Products)} - \Delta H_{f(Reactants)}$

$$= [(-860 + S) + 0] - [2\,(-350 + S)] = -(160 + S)\text{ kJ mol}^{-1}$$

Evidently, the enthalpy of transformation is a *negative quantity* indicating that the conversion of CaCl (*s*) to $CaCl_2$ (*s*) is *spontaneous*. It follows from above that $CaCl_2$ is more stable than CaCl in the solid state. The lattice energies of CaCl(*s*) and $CaCl_2$(*s*), calculated with the help of Born equation (Chapter 6) come out to be –720 and –2200 kJ mol^{-1}, respectively. This clearly shows that $CaCl_2$(*s*) is more stable than CaCl(*s*). Thus, calcium would prefer to form Ca^{2+} ion rather than Ca^+ ion. The same is true of other alkaline earth metals.

A perusal of energy data given above reveals that the factor which tilts the balance in favour of the formation of $CaCl_2$ is the high lattice energy of $CaCl_2$ (– 2200 kJ mol^{-1}) compared to that of CaCl (– 720 kJ mol^{-1}).

The ease of formation of Ca^+ ion due to lower ionization energy is also counterbalanced by the higher heat of hydration of Ca^{2+} ion compared to that of Ca^+ ion.

$$Ca^+\,(g) \xrightarrow{H_2O} Ca^+\,(aq)\text{ ;} \qquad \Delta H = -320\text{ kJ mol}^{-1}$$
$$Ca^{2+}\,(g) \xrightarrow{H_2O} Ca^{2+}\,(aq)\text{ ;} \qquad \Delta H = -1650\text{ kJ mol}^{-1}$$

This makes Ca^{2+} ion more stable in aqueous solution than Ca^+ ion.

Similarly, it can be seen from the following data that Mg^{2+} ion is more stable than Mg^+ ion in its aqueous solutions.

$$Mg\,(s) + Cl_2\,(g) \longrightarrow MgCl_2\,(s)\text{ ;} \qquad \Delta H_f = -642\text{ kJ mol}^{-1}$$
$$2Mg\,(s) + Cl_2\,(g) \longrightarrow 2MgCl\,(s)\text{ ;} \qquad \Delta H_f = -250\text{ kJ mol}^{-1}$$

Rearranging and adding the two equations, we have

$$2MgCl\,(s) \longrightarrow 2Mg(s) + Cl_2 \qquad \Delta H_f = +250\text{ kJ mol}^{-1}$$
$$Mg\,(s) + Cl_2 \longrightarrow 2MgCl_2\,(s) \qquad \Delta H_f = -642\text{ kJ mol}^{-1}$$
$$2MgCl\,(s) \longrightarrow Mg\,(s) + MgCl_2\,(s) \qquad \Delta H_f = -392\text{ kJ mol}^{-1}$$

Also the heat of hydration is greater in magnitude for Mg^{2+} ion than for Mg^+ ion.

Thus, MgCl formed, if any, will at once get converted into $MgCl_2$.

The compounds of alkaline earth metals are more extensively hydrated than those of alkali metals. For example, magnesium chloride and calcium chloride crystals exist as $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$ whereas sodium chloride and potassium chloride, under ordinary conditions, do not form any hydrate.

10. Hydration of Ions. As is evident from the heats of hydration of alkaline earth metal cations given in Table 1, the extent of hydration of these ions decreases with increase in atomic number and molar mass.

11. Electropositive Character. Ionisation energies of these elements are higher than those of the alkali metals and do not permit the change

$$M \longrightarrow M^{2+} + 2e^-$$

to occur readily. Hence these elements, although fairly strongly electropositive, are not as strongly electropositive as the metals of Group 1. For example, unlike the alkali metals, these elements do not emit electrons on exposure to light. Since ionisation energy decreases on moving down the group, the electropositive character increases on moving down the group.

TABLE 2.
Standard Oxidation Potentials of Alkali Metals

Element	Oxidation Reaction	Standard Oxidation Potential (volts)
Be	$Be \longrightarrow Be^{2+} + 2e^-$	1·85
Mg	$Mg \longrightarrow Mg^{2+} + 2e^-$	2·37
Ca	$Ca \longrightarrow Ca^{2+} + 2e^-$	2·87
Sr	$Sr \longrightarrow Sr^{2+} + 2e^-$	2·89
Ba	$Ba \longrightarrow Ba^{2+} + 2e^-$	2·90

12. Reducing Properties. Oxidation Potentials. All the alkaline earth metals have a tendency to release electrons and change into bivalent cations :

$$M \rightleftharpoons M^{2+} + 2e^-$$

Hence, *they are strong reducing agents.*

The oxidation potential which is a measure of the tendency of an element to lose electrons (*i.e.*, a measure of its electropositive character and strength as a reducing agent) increases on moving down the group, as shown in Table 2.

Hence the electropositive character as well as the strength as a reducing agent increase on moving from beryllium to barium. However, these oxidation potentials are lower than those of alkali metals. Hence, the alkaline earth metals are less electropositive and weaker reducing agents than the alkali metals.

13. Electronegativities. Since these elements have strong electrospositive character, as mentioned above, they have low electronegativities which decrease on moving down the group, as shown in Table 1. The value for calcium, however, is an exception.

Trends in electronegativities of alkaline earth metals have already been discussed in details in Chapter 2.

14. Flame Coloration. When energy is supplied to these elements in a flame, their electrons are excited to higher energy states, as is the case with alkali metals under similar conditions. As the electrons drop back to the original energy level, the extra energy is emitted in the form of visible light with characteristic

colours as given below :

Ca : *brick red* Sr : *crimson* Ba : *grassy green* Ra : *crimson*

Beryllium and magnesium atoms are smaller. The electrons in these atoms are, therefore, more strongly bound. Hence these are not excited by the energy of the flame to higher energy states. These elements, therefore, do not give any colour in bunsen flame.

Chemical Properties

The important chemical properties of elements of Group 2 are given below.

1. Action of Air and Water. The alkaline earth metals, being less electropositive than the alkali metals, are less reactive. Thus they are only slowly oxidised on exposure to air. However, they burn in oxygen to form ionic oxides, MO. Calcium burns in air to give a mixture of the oxide CaO and the nitride Ca_3N_2.

These metals react slowly with water liberating hydrogen and forming metal hydroxides. It is not certain if beryllium reacts with water at all. Magnesium reacts only with hot water. The other metals do react with cold water but not as energetically as the alkali metals.

2. Action with Hydrogen. All the elements, except beryllium, combine with hydrogen to form hydrides, MH_2.

Beryllium hydride cannot be prepared by direct combination of beryllium and hydrogen. It can, however, be produced by reacting beryllium chloride with lithium aluminium hydride.

$$2BeCl_2 + Li[AlH_4] \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

Beryllium and magnesium hydrides are covalent compounds while calcium, strontium and barium hydrides are largely ionic compounds.

The small size and high charge make Be^{2+} a highly polarising ion which effectively polarises the electron charge cloud of H^- ion permitting partial overlapping of orbitals of H^- and Be^{2+} ions. This induces considerable covalent character in BeH_2. The same is true in MgH_2 but to a lesser extent. Ca, Sr and Ba have very weak polarising power so that little or no covalent character is imparted to the otherwise ionic hydrides.

3. Action with Halogens. All the alkaline earth metals combine with the halogens at elevated temperatures forming halides, MX_2. Beryllium halides are covalent while the rest are electrovalent and readily soluble in water. The solubility of the halides (except fluorides) decreases on moving down the group.

4. Formation of Amalgams and Alloys. They form amalgams with mercury and alloys with other metals.

5. Action with Acids. These metals, on account of their high oxidation potentials, readily liberate hydrogen from dilute acids. Beryllium reacts very slowly as its oxidation potential is very low. However, Be becomes *passive* when exposed to concentrated or dilute nitric acid.

6. Action with Nitrogen. These elements burn in nitrogen to form nitrides, M_3N_2, which react with water to liberate ammonia.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

Gradation in Properties. On account of gradual increase in size and mass of the atoms of Group 2 elements, we expect a regular gradation in their properties. The gradation in some of the properties is discussed below :

1. The atomic and ionic radii increase on going from beryllium to barium.
2. The first as well as second ionisation energies decrease on moving from beryllium to barium.
3. The electropositive character as well as the reducing action and chemical reactivity increase gradually on moving down the group. These trends can be attributed to the gradual decrease in ionisation energies of these elements.

4. The oxides of all the metals dissolve in water to form basic hydroxides. The heat of formation of the hydroxides increases from beryllium to barium.
5. The basic character of the hydroxides increases gradually on moving down the group.
6. The tendency to form higher oxides, such as peroxides, increases on moving down the group.
7. The stability of the carbonates of the alkaline earth metals increases on moving down the group. This is illustrated by the temperature at which the carbonates decompose :

$BeCO_3$: < 100°C $MgCO_3$: 540°C $CaCO_3$: 900°C

$SrCO_3$: 1290°C $BaCO_3$: 1360°C

8. Beryllium and magnesium have hexagonal close packed (hcp) structure while calcium and strontium have face-centred cubic (fcc) structure

Comparison of Beryllium with Other Elements of Group 2. Beryllium, the first element of Group 2, differs considerably from the rest of the elements of this group. This is partly due to its *small size* and partly due to its *relatively high electronegativity*. The main points of difference are as follows.

1. Tendency to form ionic compounds. Ionisation energy of beryllium (899 kJ mol^{-1}) is the highest. Consequently, it has the lowest tendency to form the ion, Be^{2+}. Accordingly it does not form ionic compounds readily.

2. Tendency to form covalent compounds. Electronegativity of beryllium (1·5) is more than that of any other element of the family (Table 1). Hence, its compounds with oxygen, chlorine, nitrogen, sulphur, etc., are more **covalent** in character than the corresponding compounds of magnesium, calcium, strontium and barium.

3. Reaction with water. Beryllium does *not* react with water even at elevated temperatures. Its reaction with steam forming beryllium oxide, BeO and liberating hydrogen is doubtful.

4. Oxidation potential. Beryllium has the lowest oxidation potential (Table 2) which indicates that it has the lowest electropositive character. Consequently, BeO and $Be(OH)_2$ are not at all basic in character. They are, in fact, amphoteric and dissolve in acids to form salts and in alkalies to form beryllates, Na_2BeO_2.

The oxides and hydroxides of the other metals are basic in character. The basic character increases on moving down the group. Magnesium hydroxide is weakly basic while calcium, strontium and barium hydroxides are distinctly basic, their strengths increasing in the order of their mention.

5. Reaction with acids. Beryllium, on account of its relatively lower oxidation potential, does not liberate hydrogen from acids so readily as the rest of the metals of Group 2 do.

6. Reaction with hydrogen. Beryllium does not combine directly with hydrogen to give the hydride. All other elements of the group do. Beryllium hydride is a covalent compound. Magnesium hydride is also a covalent compound. The hydrides of the remaining elements are, however, electrovalent in character.

7. Reaction with halogens. All the metals of this group form halides by direct combination with the halogens at appropriate temperatures. Beryllium halides are, however, covalent while the other halides are electrovalent compounds.

8. Reaction with nitrogen. All the elements of this group react with nitrogen to give nitrides, M_3N_2, as already stated. However, beryllium nitride is volatile while the other nitrides are not.

9. Formation of carbides. All the elements, from magnesium to barium, give ionic carbides, MC_2, when the metals or their oxides are heated with carbon. Beryllium, on the other hand, gives Be_2C and not BeC_2 when heated with carbon. Beryllium carbide, Be_2C, evolves methane on treatment with water while the other carbides evolve acetylene.

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

10. Formation of complexes. The alkaline earth metal ions do not form many complexes. However, beryllium ion, on account of its small size, gives a number of stable complexes, such as $[BeF_3]^-$ and $[BeF_4]^{2-}$.

The tendency to form complexes decreases on moving down the group. Thus, barium forms very few complexes.

Diagonal Relationship between Beryllium and Aluminium. Beryllium differs from other alkaline earth metals, as has already been discussed. It shows some similarities with aluminium, the second element of the next (third) group, a case of *diagonal relationship*. The polarising power of Be is comparable with that of Al. This is the main cause of the diagonal relationship, as explained in Chapter 12.

The similarities in the chemistry of Be and Al are given below.

1. Beryllium atom is small and, therefore, has a high charge density. It has, therefore, a strong tendency to form covalent compounds. Aluminium, too, has a strong tendency to form covalent compounds.
2. Standard oxidation potentials of these elements are quite close to each other.
3. Beryllium, like aluminium, is rendered passive on treatment with concentrated nitric acid.
4. Beryllium, like aluminium, forms many complexes.
5. Beryllium oxide, like aluminium oxide, is amphoteric. It dissolves in acids as well as in alkalies.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$
$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$
$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$
$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

6. Beryllium and aluminium both react with sodium hydroxide liberating hydrogen.

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$$
$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

7. Beryllium carbide Be_2C and aluminium carbide (Al_4C_3) both evolve methane on treatment with water.

$$Be_2C + 2H_2O \longrightarrow CH_4 + 2BeO$$
$$Al_4C_3 + 6H_2O \longrightarrow 3CH_4 + 2Al_2O_3$$

8. Halides of beryllium and aluminium are similar in their solubilities.

Uses of Alkaline Earth Metals. Pure beryllium and beryllium oxide are used in nuclear reactors. Beryllium is also used in alloys. It causes hardening of metals, notably of copper, when added in traces.

Magnesium is used as structural material because of its lightness and its property to form alloys with other metals. Its alloys with aluminium, manganese and zinc are particularly important as structural materials. It forms Grignard reagents, RMgX, which are important reagents in organic chemistry. Finely divided magnesium burns brightly emitting intense white light.

Calcium, strontium and barium when exposed to air get oxidised and after sometime the oxides strip off exposing fresh surface again to air and so on. This property makes them useful as deoxidisers in the manufacture of steel. Radio tubes have generally an inner lining of barium metal so as to eliminate any oxygen that may be present in the tube.

EXTRACTION OF ALKALINE EARTH METALS

Extraction of Beryllium. Beryllium occurs mostly in complex silicates like felspar and mica. The mineral *beryl*, which is a crude emerald of composition [$Be_3Al_2(SiO_3)_6$], is the only important source of the element.

The first step in the extraction of beryllium is to obtain BeO from the mineral *beryl*. For this purpose, the mineral is pulverised and the powder treated with sulphuric acid when beryllium sulphate and aluminium sulphate are formed. Aluminium sulphate is removed by the addition of ammonium sulphate when the

double salt of aluminium sulphate and ammonium sulphate crystallises out. Beryllium sulphate alone remains in solution. It is separated and calcined in a rotary kiln at 1450°C to get beryllium oxide.

BeO is then reduced with carbon and copper in an electric arc furnace shown in Fig. 1. The lower part of the furnace is made of carbon and serves not only as a receptacle for the charge but also acts as one of the electrodes for the arc. The other carbon electrodes are held vertically and dip in the charge. They can be lowered or raised to a desired extent so as to strike the arc in the furnace. Beryllium oxide is well powdered and mixed with powdered coke and charged in the furnace through the door shown on the right. When the temperature of the furnace rises, carbon takes away oxygen of the oxide forming carbon monoxide which escapes through the outlet shown on the left. The metal beryllium is removed through the tapping hole at the bottom of the furnace.

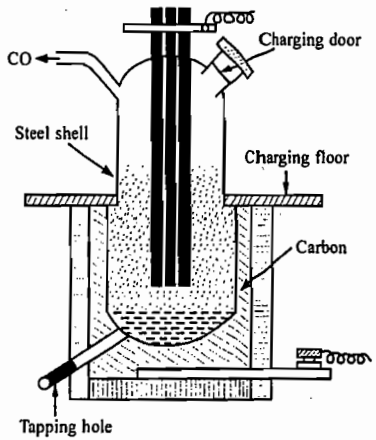


Fig. 1. Extraction of beryllium.

Extraction of Magnesium. Magnesium is widely distributed in nature. Its important ores are *Magnesite*, $MgCO_3$; *dolomite*, $MgCO_3.CaCO_3$; *carnallite*, $KCl.MgCl_2.6H_2O$; *asbestos*, $CaMg_3(SiO_3)_4$, etc. It is an essential constituent of chlorophyll, the green colouring matter of plants. Halides of magnesium are found in sea water.

The metal is usually extracted by the electrolysis of *fused* magnesium chloride or magnesium oxide. Carnallite ore is used as the source of $MgCl_2$ and magnesite ore is calcined to get MgO. $MgCl_2$ can also be obtained from sea water in which magnesium is present as $MgSO_4$ and $MgCl_2$. These salts are first precipitated as $Mg(OH)_2$ by treatment with slaked lime and $Mg(OH)_2$ is then converted to $MgCl_2$ by treatment with HCl.

From MgO, the metal can also be obtained by its reduction by carbon, silicon or aluminium at about 2000°C in vacuum. The metal is distilled away and condensed.

Extraction of Calcium. Calcium occurs largely in the form of carbonates and sulphates. Calcium carbonate occurs in a number of forms, the more important of which are *limestone, chalk, calcite, marble, spardolomite, stalactite, stalacmite,* etc. As sulphate, it occurs in the form of *gypsum* ($CaSO_4.2H_2O$) and *anhydrite* ($CaSO_4$).

Calcium also occurs as phosphate, $Ca_3(PO_4)_2$, in the phosphorite rock and in bones ; as fluoride, CaF_2, in *fluorspar* and as calcium silicate, $CaSiO_3$, in many complex rocks. Calcium is an essential constituent of bones, teeth, sea shells and egg shells. Its soluble compounds are found in sea water and are assimilated by sea animals and changed into calcium carbonate which forms their outer protective shells.

The metal is extracted by the electrolysis of *fused* calcium chloride mixed with about 10 per cent of calcium fluoride in a graphite vessel using iron cathode and graphite anode.

Extraction of Strontium. Strontium occurs as $SrSO_4$ in the mineral *celestine* and as $SrCO_3$ in the mineral *strontianite*.

The metal is obtained by the electrolysis of a *fused* mixture of strontium chloride and ammonium chloride using iron cathode and graphite anode.

Extraction of Barium. Barium occurs as $BaCO_3$ in the mineral *witherite* and more widely as $BaSO_4$ in the mineral *barytes*.

The metal is obtained by the electrolysis of *fused* barium chloride using mercury cathode and graphite anode when barium amalgam separates out. On distilling, mercury volatilises off leaving behind barium.

Extraction of Radium. All uranium minerals contain radium in minute quantities. *Pitchblende* and *carnotite*, the two important uranium ores, are the chief sources of radium.

The metal is obtained by the electrolysis of *fused* radium chloride using a platinum-iridium anode and a mercury cathode. The radium amalgam formed is distilled at 400 – 600°C when mercury distils off leaving behind radium.

PROPERTIES AND USES OF ALKALINE EARTH METALS

Properties of Beryllium. Physical Properties. Beryllium is a steel-grey, light and hard metal. It has the highest melting point (1277°C) and boiling point (2770°C) of all the elements of Group 2. Be is slowly oxidised in moist air. On heating in air it burns with dazzling light. The other chemical properties of beryllium have already been discussed along with general properties of alkaline earth metals.

Uses. Beryllium, although a rare metal, finds many applications. Its importance has increased all the more due to its use in nuclear reactors. The most important uses of beryllium are : *1. In Making Alloys.* A large number of alloys containing beryllium are being used in industry. The presence of 0·005 per cent of beryllium in magnesium greatly reduces its combustibility and thus renders casting much easier. Addition of 0·2 per cent of beryllium improves the casting properties of aluminium. The addition of 0·1 per cent of beryllium to platinum gives an alloy as hard as is obtained by the addition of 10 – 15 per cent of iridium. *2. In X-ray Tubes.* Because of its high permeability to X-rays, beryllium sheets are used for windows of the X-ray tubes. *3. In Nuclear Reactors.* Beryllium salts are used as a source of neutrons. When a beryllium salt is bombarded with alpha particles, neutrons are produced.

$$^{9}_{4}Be + ^{4}_{2}He\ (\alpha \text{ particles}) \longrightarrow ^{12}_{6}C + ^{1}_{0}n$$

Properties of Magnesium. Magnesium is a silvery-white metal which soon becomes dull in air. It is a light metal with a specific gravity of 1·74. It is fairly malleable and ductile. It melts at 650°C and boils at 1107°C.

Magnesium is a fairly reactive metal although much less reactive than calcium, strontium and barium of the same group.

It is stable in dry air but is slowly tarnished in moist air due to the formation of a film of the oxide, MgO. It burns in oxygen or air with a dazzling light forming a dense white smoke of the oxide.

On account of its great affinity for oxygen, magnesium keeps burning even in carbon dioxide.

$$2Mg + CO_2 \longrightarrow 2MgO + C$$

Magnesium forms a number of organometallic compounds which are of special importance in the synthesis of organic compounds. These are discussed in details in Chapter 34 on Organometallic Compounds.

The other chemical properties of Mg have already been discussed along with general properties of alkaline earth metals.

Uses of Magnesium. Magnesium, on account of its lightness, great affinity for oxygen and toughness, is used for many purposes in industry as well as in laboratory. It is thus used 1. *For Making Alloys.* Magnesium is used in making a number of useful alloys which are light but strong and durable. They are used for many purposes as in automobile industry and engineering, fabrication of aircraft and optical instruments and so on. *2. For Extraction of Boron and Silicon.* Magnesium is used for the extraction of boron and silicon by the ignition of the metal in the presence of B_2O_3 and SiO_2. *3. In Aluminothermic Process.* Magnesium ribbon is used for igniting the thermite in aluminothermic process. *4. As a Deoxidizer.* It is used as a deoxidizer for removing last traces of oxygen from copper, steel, etc. *5. As Grignard Reagents.* Magnesium in the form of Grignard reagents is largely used for synthesis of many organic compounds.

Properties of Calcium. Calcium is a greyish white crystalline metal with silvery lustre. It is harder than lead and is malleable. It may be stored without any special precaution. However, moisture should be

kept away from it. Chemical properties of calcium have already been described while discussing properties of alkaline earth metals in general.

Uses. The metal is used in preference to sodium in removing traces of water from alcohol because, unlike sodium, it does not react with alcohol. It is used as a deoxidiser for copper, cast iron and steel and a desulphurizer in oil refining. When alloyed with lead it is used as a cable covering. When alloyed with aluminium it is used in casting and forging. It is also used in reducing oxides and fluorides of beryllium, uranium, plutonium, thorium, etc.

Properties of Strontium, Barium and Radium. ***Strontium*** is a soft silvery-white metal of specific gravity 2·54, melting at 768°C. It is malleable and ductile. It closely resembles calcium both in physical and chemical properties although it is more reactive.

Barium resembles calcium and strontium in its physical as well as chemical properties although it is most reactive of the three metals. It decomposes water more readily and combines with oxygen more easily than either calcium or strontium. When in the powdered state it catches fire spontaneously on exposure to air. It is malleable at 850°C. Its specific gravity is 3·75.

Radium, in many of its physical and chemical properties, resembles barium. It is a silvery-white metal. It melts at about 700°C and vaporizes at a slightly higher temperature. It is thus more volatile than barium. Radium at once turns black when exposed to atmosphere because of the formation of a film of radium nitride, Ra_3N_2. The metal decomposes water forming the hydroxide and liberating hydrogen.

The most outstanding property of radium is the spontaneous emission of radiations, *viz.*, alpha, beta and gamma rays. This is the well known phenomenon of radioactivity. Radium and its salts are strongly radioactive.

COMPOUNDS OF ALKALINE EARTH METALS

I. A Comparative Study

Oxides. The oxides are formed either by heating the metals in oxygen or by heating carbonates at high temperature.

Beryllium oxide is a very hard solid. It can scratch even quartz. Beryllium oxide has a wurtzite structure with 4 : 4 coordination while the rest of the oxides have NaCl type lattices with 6 : 6 coordination. The oxides are highly stable due to large ionic crystal lattice energies. The values are so high in the case of oxides of beryllium and magnesium that these compounds are almost insoluble in water. The oxides of the rest of the elements react with water to yield hydroxides which are basic in character.

Beryllium oxide is amphoteric while the oxides of the rest of the elements are basic in character. Magnesium oxide and calcium oxide (lime) are used as basic linings in furnaces.

In addition to the oxides MO (M = alkaline earth metal), peroxides MO_2 of Ca, Ba, Sr are also known. There is also some evidence for the existence of superoxides $Ca(O_2)_2$ and $Sr(O_2)_2$.

The ozonides $Ba(O_3)_2$ and $Ca(O_3)_2$ have also been reported.

Hydroxides. The oxides, except beryllium oxide and magnesium oxide, dissolve in water forming hydroxides evolving a large amount of heat.

The hydroxides though basic in character are less basic than the hydroxides of alkali metals. The basic character, however, increases on moving down the group. $Be(OH)_2$ is amphoteric in character.

The solubility of the hydroxides increases with increase in atomic number of the element. Thus, beryllium hydroxide and magnesium hydroxide are almost insoluble in water. The hydroxides of other metals are slightly soluble and the solubility increases on moving down the group, as shown by their solubility products (Table 3).

Sulphates. Beryllium sulphate is slightly soluble in water. However, solubility of sulphates *decreases* regularly on going down the group so much so that barium sulphate and radium sulphate are practically insoluble. The solubility products of the various sulphates at ordinary temperatures are given in Table 3.

TABLE 3
Solubility Products of Hydroxides and Sulphates of Alkaline Earth Metals

Hydroxides	Solubility Product	Sulphates	Solubility Product
$Be(OH)_2$	$1{\cdot}6\times10^{-26}$	$BeSO_4$	very high
$Mg(OH)_2$	$8{\cdot}9\times10^{-12}$	$MgSO_4$	high
$Ca(OH)_2$	$1{\cdot}3\times10^{-4}$	$CaSO_4$	$2{\cdot}4\times10^{-5}$
$Sr(OH)_2$	$3{\cdot}2\times10^{-4}$	$SrSO_4$	$7{\cdot}6\times10^{-7}$
$Ba(OH)_2$	$5{\cdot}4\times10^{-2}$	$BaSO_4$	$1{\cdot}5\times10^{-9}$
		$RaSO_4$	$4{\cdot}0\times10^{-11}$

Magnesium sulphate is available in the form of its heptahydrate, $MgSO_4.7H_2O$ (*epsom salt*) and is used in medicine as a purgative.

Calcium sulphate occurs as the mineral *gypsum* ($CaSO_4.2H_2O$). When heated carefully, it gets partially dehydrated giving *plaster of paris*, $CaSO_4.1/2\ H_2O$. The semihydrate is also written as $(CaSO_4)_2.H_2O$.

Barium sulphate, $BaSO_4$, is used as a white pigment.

Comparison of solubility products of hydroxides and sulphates. It may be interesting to note that the solubility products of the hydroxides of these metals increase on going down the group (Table 3). Then, why do the solubility products of the sulphates follow the reverse order ?

The solubility of an ionic solid in water depends upon two factors : *Lattice energy, i.e.,* the energy with which the ions of the solid are held together in a crystal and (*ii*) *hydration energy, i.e.,* the energy evolved as heat when the ions of the solid get hydrated. These two factors tend to oppose each other. If lattice energy is high, it would imply that the ions are packed tightly in a crystal and, therefore, the solubility will be low. If hydration energy is high, the ions will have a greater tendency to be hydrated and, therefore, the solubility will be high.

In the case of the sulphates of alkaline earth metals, the lattice energies are about the same. The sulphate ion itself is so large (radius ≈ 3Å) that relatively small changes in metallic ionic sizes from Be^{2+} to Ba^{2+} do not make any material difference. However, the hydration energies of the metal cations, from Be^{2+} to Ba^{2+}, *decrease* in this order (Table 1). Hence, the solubilities of the sulphates decrease in the same order, *i.e., the solubilities decrease with increase in ionic size.*

In the case of the hydroxides, the lattice energies are different because hydroxide ion is not large and, therefore, even small changes in metallic ionic sizes do make a difference. Thus, as the metallic ionic size increases on moving from beryllium to barium, the lattice energy decreases. This tends to enhance the solubility and to overcome the counter-effect produced by the decrease in hydration energy. Hence, *the solubilities of the hydroxides increase on moving down the group.*

Hydrides. Beryllium hydride is prepared by reducing beryllium chloride with lithium aluminium hydride.

$$2BeCl_2 + Li[AlH_4] \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

The rest of the metals form hydrides when heated with hydrogen.

The hydrides are white powders and react with water liberating hydrogen. Calcium hydride thus serves as a portable supply of hydrogen.

BeH_2 is covalent while MgH_2 is partly covalent and partly ionic. The remaining hydrides are largely ionic.

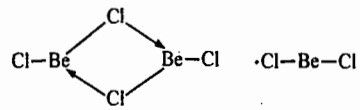
Carbonates and Bicarbonates. The carbonates of these metals are insoluble in water and, therefore, occur as solid rock minerals in nature. Limestone is the most important mineral containing calcium carbonate.

The carbonates, however, dissolve in water containing carbon dioxide yielding bicarbonates.

The soluble bicarbonates of calcium and magnesium impart hardness to water. This type of hardness is known as temporary hardness since it disappears on heating on account of the precipitation of the carbonates.

The bicarbonates are *stable only in solution.* Their decomposition to carbonates is responsible for the formation of *stalactites* and *stalagmites.*

Halides. The metals combine directly with halogens on heating at appropriate temperatures forming halides, MX_2. The halides can also be obtained by reacting metal carbonates with dilute halogen acids. Beryllium halide $BeCl_2$ in which Be orbitals are *sp* hybridised, has zero dipole moment. The structures of dimeric and monomeric beryllium chloride are given below :



Most of the anhydrous halides have fluorite-type structure.

Carbides. Metals from magnesium to barium or their oxides, when heated with carbon, give carbides with formula, MC_2. For example,

$$CaO + 3C \longrightarrow CaC_2 + CO$$

Beryllium under similar conditions gives beryllium carbide with formula Be_2C.

$$2BeO + 3C \longrightarrow Be_2C + 2CO$$

The carbides with formula MC_2 (*e.g.,* CaC_2) react with water to yield acetylene while Be_2C under similar conditions yields methane.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$

Organometallic Compounds of Group 2 Elements

These have been discussed in details in Chapter 34 on Organometallic Compounds.

II. Some Important Compounds of Group 2 Elements

Beryllium oxide, BeO. It is prepared by burning beryllium in air or by heating beryllium hydroxide, carbonate or nitrate.

Beryllium oxide is a white powder and is insoluble in water. It is amphoteric and, when freshly prepared, it dissolves in both acids and alkalies. On fusion, it changes to a very hard mass which is difficult to dissolve in acids or alkalies.

It remains unchanged by heating in air. When strongly heated with carbon, silicon or boron, it yields the carbide, Be_2C_2 ; silicide, Be_2Si or the boride, Be_3B_2.

Because of its very high melting point (2570°C), beryllium oxide is used as refractory material.

Beryllium Chloride, $BeCl_2$. It is prepared by burning the metal in an atmosphere of chlorine or by the action of hydrogen chloride on the metal.

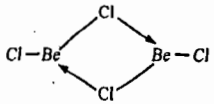
Beryllium chloride is a white crystalline solid, melting at 44°C. It fumes in air like PCl_5 and is very readily hydrolysed in the presence of water.

$$BeCl_2 + H_2O \longrightarrow BeO + 2HCl \ ; \ BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

Beryllium chloride dissolves freely in water with the evolution of heat. The ion $[Be(H_2O)_4]^{2+}$ is formed and on crystallization, the salt $[Be(H_2O)_4]Cl_2$ is deposited. It holds its water of crystallisation so strongly that it is not dehydrated at all even by several month's exposure to P_2O_5.

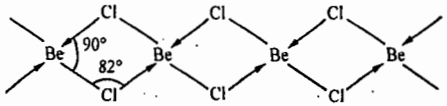
$BeCl_2$ in vapour phase at above 900°C is *monomeric* having a linear structure Cl – Be – Cl. The bonding in $BeCl_2$ is covalent and Be atom accommodates 2 + 2 = 4 electrons in the two *sp* hybrid orbitals.

Below 900°C, beryllium chloride in vapour phase exists as a mixture of monomer $BeCl_2$ and dimer Be_2Cl_4. The dimer has the bridge structure, as shown :



Apart from this, each Be atom in Be_2Cl_4 dimer has two Be – Cl bonds. Thus, each Be atom in Be_2Cl_4 utilises three sp^2 hybrid orbitals to accommodate $2 + 2\times1 + 1\times2 = 6$ electrons.

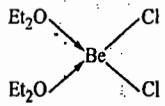
In solid state, $BeCl_2$ has a polymeric structure as shown below :



In this structure, each Be atom is covalently bonded to two Cl atoms. Two of the bridging Cl atoms from two different Cl bridges coordinate with each Be atom donating $2\times2 = 4$ electrons for the Be←Cl bond formation. Thus, each Be atom utilises four sp^3 hybrid orbitals to accommodate $2 + 2\times1 + 2\times2 = 8$ electrons and the geometry around each Be atom is tetrahedral.

$BeCl_2$ in Solution. When solid $BeCl_2$ is dissolved in a coordinating solvent, the infinitely long bridge structure breaks down to liberate $BeCl_2$ monomers in solution. If the solvent molecules are weak coordinators, $BeCl_2$ forms species of the type L_2BeCl_2 where L represents the weak coordinating solvent molecule. Thus, we have

$$BeCl_2 + 2Et_2O \rightleftharpoons$$



The structure of L_2BeCl_2 formed is tetrahedral and the Be atom utilises the four sp^3 hybrid orbitals to accommodate $2 + 2\times1 + 2\times2 = 8$ electrons.

If, however, the solvent molecule is comparatively a stronger coordinator, $BeCl_2$ forms an ionic species of the type $[BeL_4]^{2+}2Cl^-$ where L is NH_3 or H_2O. Thus, we have

$$BeCl_2 + 4H_2O \longrightarrow [Be(H_2O)_4]^{2+}2Cl^-$$

Each coordinated atom donates two electrons to Be^{2+} ion so that the central ion requires four sp^3 hybrid orbitals to accommodate $0 + 4\times2 = 8$ electrons. The geometry of $[BeL_4]^{2+}$ ion would, evidently, be tetrahedral.

Beryllium Sulphate, $BeSO_4.4H_2O$. It is prepared by dissolving beryllium oxide in hot concentrated sulphuric acid. It crystallizes from an aqueous solution as the tetrahydrate, $BeSO_4.4H_2O$.

Beryllium sulphate tetrahydrate loses water at 400°C to give the anhydrous salt. The anhydrous beryllium sulphate does not decompose below 500°C. On heating beyond this temperature, it decomposes to form the oxide.

The tetrahydrate is highly soluble in water but the anhydrous sulphate is almost insoluble in cold water. With hot water, however, the anhydrous salt reacts to form the tetrahydrate which dissolves freely.

All the four water molecules in $BeSO_4.4H_2O$ are, in fact, coordinated to Be^{2+} ion and the actual structure is $[Be(H_2O)_4]^{2+}SO_4^{2-}$. The Be^{2+} ion utilises four sp^3 hybrid orbitals to accommodate 8 electrons from the coordinating water molecules and the structure of $[Be(H_2O)_4]^{2+}$ ion is thus tetrahedral.

Basic Beryllium Acetate. When BeO or $Be(OH)_2$ reacts with acetic acid, it gives a compound of the formula $Be_4O(CH_3COO)_6$ which is known as basic beryllium acetate. This compound is a white crystalline solid and is readily soluble in organic solvents. It is insoluble in polar solvents indicating that it is not an ionic compound.

The structure of basic beryllium acetate contains a tetrahedral Be_4 cluster with an O atom at the centre of this tetrahedron. The six edges of the Be_4 tetrahedron are occupied by the six acetato groups in such a way that each Be atom is also tetrahedrally coordinated to four O atoms of the acetato groups, as shown in Fig. 2. The solid lines between the atoms in Fig. 2. simply show the association between the atoms and *not the exact bond order*.

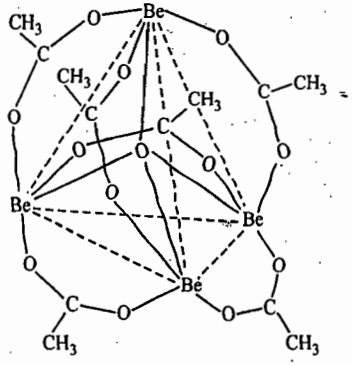


Fig. 2. Structure of basic beryllium acetate, $Be_4O(CH_3COO)_6$.

Basic beryllium acetate melts at 285°C and boils at 333°C. It is slowly hydrolysed by hot water. It is rapidly decomposed by mineral acids to give the corresponding salts and free acetic acid.

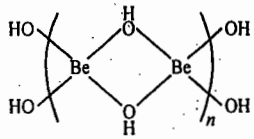
$$Be_4O(CH_3COO)_6 + 8HCl \longrightarrow 4BeCl_2 + H_2O + 6CH_3COOH$$

Basic Beryllium Nitrate. When $BeCl_2$ is heated with N_2O_4, the product is $[Be_4O(NO_3)_6]$. This is called basic beryllium nitrate.

$$4BeCl_2 + 7H_2O + 6N_2O_4 \longrightarrow [Be_4O(NO_3)_6] + 8HCl + 6HNO_2$$

The structure of basic beryllium nitrate is similar to that of basic beryllium acetate with the only difference that while the basic beryllium acetate contains acetato bridges Be – O – C(CH_3)– O – Be, the basic nitrate contains the nitrato bridges Be – O – N(O) – O – Be. The lines between the atoms in both the types of bridges do not indicate the exact bond order.

Tetrahydroxo Beryllate Ion, $[Be(OH)_4]^{2-}$. Beryllium salts hydrolyse readily in the presence of an alkali to give hydroxo complexes of ill-defined composition. Further addition of alkali redissolves the precipitated hydroxo complexes to give hydroxo bridged structures of the type shown :



Still further addition of alkali breaks the hybroxo bridge by adding more OH^- ions per Be atom and leads to the formation of $Be[(OH)_4]^{2-}$ complex ion in which Be atom is tetrahedrally bonded to four OH^- ions.

Calcium Carbide, CaC_2. This is one of the most important compounds of calcium. It is manufactured by heating lime with powdered coke at about 3000°C in an electric furnace.

$$CaO + 3C \longrightarrow CaC_2 + CO$$

The furnace is made of fire-clay bricks and has a thick layer of graphite at the bottom. This serves as one electrode. A block of graphite suspended from the middle serves as the second electrode. Calcium carbide formed in the molten state is taken out from a tapping hole provided near the bottom of the furnace.

Calcium carbide is a hard crystalline solid. The pure product is white but the commercial product is generally grey, the depth of the colour increasing with the extent of impurities.

It reacts with water yielding acetylene.

It reacts with nitrogen at red heat to yield calcium cyanamide.

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

The mixture of calcium cyanamide and carbon is used as such as a fertilizer under the name **nitrolim**. It gets hydrolysed supplying ammonia to the soil :

$$CaNCN + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Calcium carbide is used for the preparation of acetylene gas and for the manufacture of calcium cyanamide which is used as a fertilizer.

Calcium carbide is an ionic solid. Its lattice consists of Ca^{2+} and $(C\equiv C)^{2-}$ ions. The radius ratio $Ca^{2+}/(C\equiv C)^{2-}$ is 0·52 which is close to Na^+/Cl^- ratio in sodium chloride. Its structure, therefore, should be essentially similar to that of sodium chloride, *i.e.*, with coordination number equal to 6. Thus, each Ca^{2+} ion should be surrounded by six carbide ions which should lie at the six corners of a regular octahedron. The shape of the carbide ion itself, however, is such that the unit cell undergoes some elongation in one direction.

Calcium Cyanamide, $CaCN_2$. It is prepared by heating calcium carbide in nitrogen at 1000°C, in an electric furnace. The reaction is highly exothermic evolving a considerable amount of heat.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C; \qquad \Delta H = -304{\cdot}2\ kJ$$

Calcium cyanamide, mixed with carbon, as obtained in the reaction, is used as a nitrogenous fertilizer as mentioned above. In the soil it first changes into calcium carbonate and cyanamide.

$$CaCN_2 + H_2O + CO_2 \longrightarrow CaCO_3 + \underset{\text{Cyanamide}}{H_2N.CN}$$

The cyanamide then hydrolyses in two stages ultimately giving ammonia.

$$H_2N.CN + H_2O \longrightarrow \underset{\text{Urea}}{CO(NH_2)_2}$$

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3$$

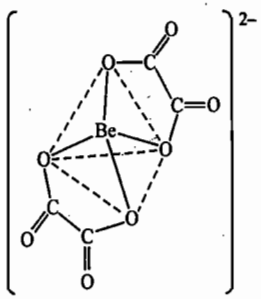


Fig. 5. Structure of beryllium oxalate, $[Be(Ox)_2]^{2-}$ ion.

Ammonia is converted into nitrates through the agency of nitrifying bacteria. On account of its slow conversion into ammonia and nitrates, calcium cyanamide is a valuable fertilizer as its effects are of a prolonged nature. The formation of calcium carbonate in the process is also useful from agricultural point of view.

Calcium cyanamide is also used in the manufacture of ammonia on treatment with superheated water.

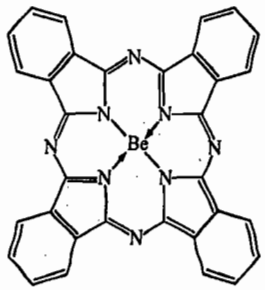
$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

(superheated)

Complexes of Beryllium

Complexes with highly conjugated planar ligands. Although the complexes of beryllium containing Be–X and Be–O bonds are quite common, its complexes with N-containing ligands are quite rare. However, highly conjugated N-containing ligands form fairly stable complexes with Be. The rigid, planar ring system of the ligand imposes upon Be a square planar geometry of BeN_4.

The Be complex of one such ligand is known to have the structure as shown.



This complex readily picks up two water molecules, one of which coordinates from above the plane of the chelate ring and the other from below it so that the N→Be bonds in the complex are replaced by two H_2O→Be bonds in such a way that a tetrahedral BeN_2O_2 structure is obtained.

Halide Complexes of Beryllium. Be, because of its small size, forms stable complexes with halogens, as, for example, $[BeF_3]^-$ and $[BeF_4]^{2-}$.

The complex ion, $[BeF_3]^{2-}$, involves sp^2 hybridisation and, therefore, has a planar trigonal structure, as shown in Fig. 3.

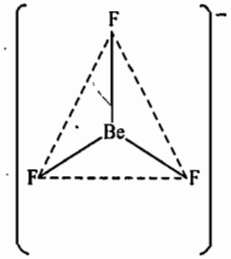


Fig. 3. Planar trigonal structure of $[BeF_3]^-$ complexion.

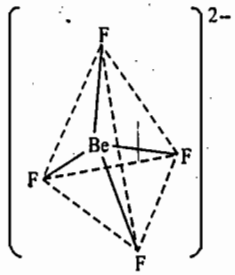
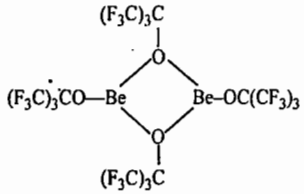


Fig. 4. Tetrahedral structure of $[BeF_4]^{2-}$ complexion.

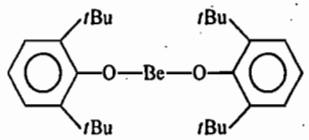
The complex ion $[BeF_4]^{2-}$ involves sp^3 hybridisation and hence has a tetrahedral structure (Fig. 4.).

Beryllium also forms a complex compound with oxalic acid. The complex anion $[Be(OX)_2]^{2-}$ is known to have a tetrahedral structure.

Although the coordination number of Be in its complexes is usually four, it can reduce its coordination number to three or even to two if there is crowding of the ligands to prevent the adjustment of four ligands around the Be atom. The structures of two complexes in which the bulk of the ligands reduces the coordination number of Be are given below :



(Be has a coordination number 3)



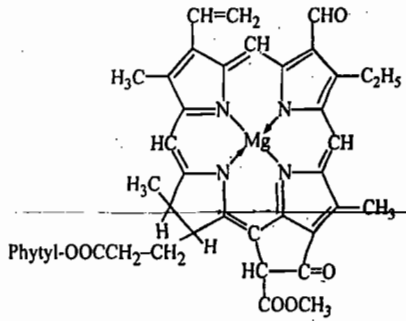
(Be has a coordination number 2)

Complexes of Magnesium. Magnesium forms tetrahedral halide complexes of the type $[(C_2H_5)_4N]_2[MgCl_4]$. The chelates of magnesium with EDTA and pyrophosphates are also known. However, the most important complex of magnesium is the naturally occurring **chlorophyll,** the green pigment present in plants, which photosensitises the synthesis of carbohydrates in nature from CO_2 and H_2O :

$$6CO_2 + 6H_2O \xrightarrow[\text{sunlight}]{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2$$

The structure of chlorophyll is as shown. The macrocyclic ligand involved is derived from the parent tetrapyrrole molecule, porphylin.

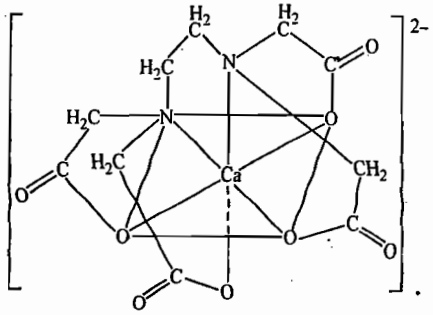
The Mg atom in chlorophyll lies slightly above the plane of the rigid chelate ring structure. The chlorophyll molecule can add to it one or two water molecules axially. Such coordinated water molecules then help in associating other chlorophyll molecules through hydrogen bonding.



Structure of chlorophyll

Complexes of Calcium, Strontium and Barium. Amongst the complexes of Ca^{2+}, Sr^{2+} and Ba^{2+}, the water soluble complex of Ca^{2+} with EDTA is the most important because of its analytical application. Its

structure is as shown :



Ca^{2+}, Sr^{2+} and Ba^{2+} also form complexes with certain specific crown ethers and cryptates.

PORTLAND CEMENT

Portland cement is one of the most important building materials at the present time. It was first discovered in England in the last century. As on setting it hardened to a stone-like mass, it was likened to the famous Portland rock of England and named as Portland cement. It is essentially a mixture of calcium silicates and calcium aluminates with small amounts of added gypsum. The essential constituents are lime, silica, aluminium oxide, magnesium oxide and ferric oxide. The approximate composition is :

Calcium oxide	(CaO) =	50 – 60 per cent
Silica	(SiO_2) =	20 – 25 per cent
Alumina	(Al_2O_3) =	5 – 10 per cent
Magnesium oxide	(MgO) =	2 – 1 per cent
Ferric oxide	(Fe_2O_3) =	1 – 2 per cent
Sulphur trioxide	(SO_3) =	1 – 2 per cent

The essential **raw materials** used are lime stone and clay. Lime stone provides calcium oxide and clay provides silica as well as alumina and ferric oxide. The ratio of silica to alumina lies between 4 and 2·5 while that of calcium oxide to silica + alumina + ferric oxide, should be as close to 2 as possible. If lime is in excess, the cement cracks during setting. If lime is less than required by the above ratio, the cement is weak in strength. There is very little free lime in the cement. Almost the entire amount of it is present in the combined state as calcium silicates and calcium aluminates.

Manufacture. The raw meterials, limestone and clay, are first crushed separately in a suitable machine. The clay is washed with water in a wash mill to remove the foreign material and then powdered lime is added and the two ingredients are finely ground and homogenised. This slurry, containing about 40 per cent of water is introduced into the upper end of the rotary kiln (Fig. 5) which consists of an inclined steel rotating cylinder, 150—200 feet long and 10 feet in diameter lined with bricks. The rotary kiln is heated by coal gas.

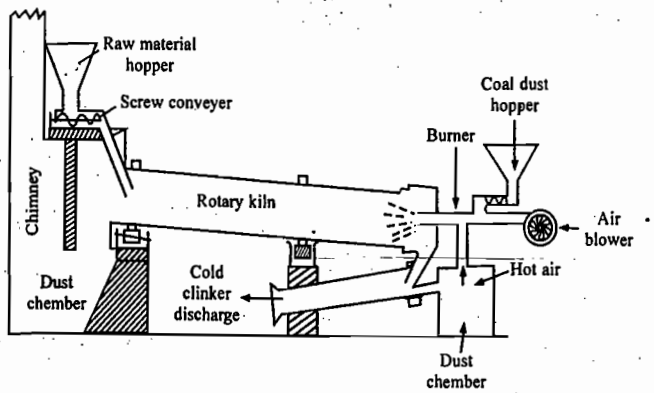


Fig. 5. Manufacture of Cement

In the upper portion of the kiln, the material is heated to about 750°C whereby its moisture is completely eliminated. In the middle portion, the temperature of the material rises to 1000°C. Here the limestone decomposes to give calcium oxide. At the lower end, the temperature rises to 1600°C. At this temperature, the mixture is partly fused and sintered. Chemical combinations occur between lime, alumina, ferric oxide and silica resulting in the formation of calcium aluminates and silicates.

$$2CaO + SiO_2 \longrightarrow \underset{\text{Dicalcium silicate}}{2CaO.SiO_2}$$

$$3CaO + SiO_2 \longrightarrow \underset{\text{Tricalcium silicate}}{3CaO.SiO_2}$$

$$3CaO + Al_2O_3 \longrightarrow \underset{\text{Tricalcium aluminate}}{3CaO.Al_2O_3}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{Tetracalcium alumino ferrite}}{4CaO.Al_2O_3.Fe_2O_3}$$

The reactions are exothermic in nature. The temperature has to be properly controlled in order to avoid excessive vitrification of the mass.

Out of the above compounds, the most important is tricalcium silicate. This substance has the property of setting quickly and developing considerable strength within a few days. It usually constitutes about 50 per cent of cement.

Dicalcium silicate sets only slowly and develops appreciable strength after a fortnight or so.

Tricalcium aluminate sets instantaneously in the presence of water. The internal strength acquired by cement is primarily due to the setting of tricalcium aluminate.

Tetracalcium aluminoferrite also sets rapidly but not as rapidly as tricalcium aluminate.

The product is known as *cement clinker*. After cooling, it is mixed with 2–3 per cent gypsum and ground to a fine powder. The function of gypsum is to slow down the setting of the cement so that it gets sufficiently hardened.

Setting of Cement. Cement has the property of **setting** to a hard mass after being mixed with water. The exact mechanism of this process has not been fully understood. But it is known that it involves many complicated reactions. This is also shown by the fact that while the first setting takes place within 24 hours, the subsequent hardening requires about a fortnight. The absorption of carbon dioxide by lime or by any other constituent is not involved at all. This is supported by the fact that subsequent hardening of the cement takes place when it is covered by a layer of water.

Primarily, the reactions involved are the hydration of calcium aluminates and calcium silicates which change into their colloidal gels. At the same time, some calcium hydroxide and aluminium hydroxide are formed as precipitates due to hydrolysis. Calcium hydroxide binds the particles of calcium silicate together while aluminium hydroxide fills the interstices rendering the mass impervious.

The various reactions involved may be represented as below.

1. *Hydration of tricalcium aluminate to give hydrated colloidal gel.*

$$\underset{\text{Tricalcium aluminate}}{3CaO.Al_2O_3} + 6H_2O \longrightarrow \underset{\text{Hydrated colloidal gel of tricalcium aluminate}}{3CaO.Al_2O_3.6H_2O}$$

2. *Hydrolysis of tricalcium silicate to liberate free lime.*

$$\underset{\text{Tricalcium silicate}}{3CaO.SiO_2} + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Dicalcium silicate}}{2CaO.SiO_2}$$

3. *Hydration of dicalcium silicate to give a hydrated colloidal gel* (a slow process).

$$2CaO.SiO_2 + x\,H_2O \longrightarrow \underset{\text{Hydrated colloidal gel of dicalcium silicate}}{2CaO.SiO_2xH_2O}$$

4. *Partial hydrolysis of tricalcium aluminate to liberate free aluminium hydroxide.*

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2Al(OH)_3$$

5. *Hydration of tetracalcium aluminoferrite to give hydrated tricalcium aluminate,* a colloidal gel.

$$4CaO.Al_2O_3.Fe_2O_3 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3$$

6. *Role of gypsum.* Gypsum combines with tricalcium aluminate to form calcium sulphoaluminate.

$$3CaO.Al_2O_3 + 3CaSO_4 + 2H_2O \longrightarrow \underset{\text{Calcium sulphoaluminate}}{3CaO.Al_2O_3.3CaSO_4.2H_2O}$$

The removal of the fast-setting tricalcium aluminate results in slowing down the setting process.

A quick setting results in the formation of crystalline hydrated calcium aluminate whereas a comparatively slow setting yields the colloidal gel which imparts much greater strength to the set mass.

Heat of hydration. The hydration of calcium aluminates and calcium silicates involved in the setting of cement is an exothermic process. Hence cement structures have to be cooled during setting. In the case of small structures, heat of hydration is removed by sprinkling water. In the case of bigger structures such as dams, the cement-concrete mixtures are prechilled to avoid excessive rise of temperature otherwise uneven expansion of the mass due to heat of hydration is liable to produce cracks in the structure. As an additional safeguard, cold water is circulated through pipes embedded in the concrete mass.

Concrete. It is a mixture of cement with sand and ballast or aggregates of crushed stone. Water is added to get a proper consistency. It sets to a hard solid mass and is used in foundations, floors and walls of buildings as well as on roads. It is also used in building roofs, piers for bridges, dams and canal locks.

Role of Mg^{2+} and Ca^{2+} Ions in Biological Systems

Magnesium is an important constituent of chlorophyll which initiates the process of photosynthesis in green plants as discussed earlier.

Magnesium ions are concentrated more in intracellular than in extracellular fluids in animal bodies. The presence of Mg^{2+} ions is a necessary requirement for the activation of phosphate transfer enzymes which participate in the energy releasing biochemical process occurring in animal body. Magnesium ions are also required for carbohydrate metabolism.

Mg^{2+} and Ca^{2+} ions are also responsible for the transmission of electrical impulses along the nerve fibre and for the contraction of muscles.

Calcium ions are essential for the formation of bones and teeth and for maintaining rythem of heart and for clotting of blood. The enamel on teeth is also a double salt of calcium, $3Ca_3(PO_4)_2.CaF_2$.

QUESTIONS

1. (*a*) Give the electronic configurations of the alkaline earth metals. Why are they so reactive ?
   (*b*) Compare the properties of the alkaline earths with those of alkali metals.
2. (*a*) Why does beryllium differ so much from the rest of the alkaline earths ? Discuss the main points of difference.
   (*b*) Compare and contrast the properties of beryllium and aluminium.
3. (*a*) Why are the alkaline earth metals harder and denser than the alkali metals ? Why do they have higher melting points than the alkali metals ?
   (*b*) The first ionisation energies of alkaline earths are very low as compared to the second ionisation energies. How would you account for it ?
   (*c*) In view of much lower first ionisation energies, the alkaline earth metals should prefer to form +1 ions (M^+) rather than + 2 ions (M^{2+}). But actually these metals give only M^{2+} ions. How would you explain this behaviour ?
4. (*a*) What are alkaline earth metals ? Why are they so called ? Discuss their general physical and chemical properties.
   (*b*) How would you account for different colours produced by alkaline earth metals in the bunsen flame ?.
5. Explain giving reasons why :
   (*a*) Beryllium shows covalency whereas other members of the family show electrovalency ?

   (*b*) NaOH is stronger base than $Ba(OH)_2$?
   (*c*) Na is more electropositive than Ba ?
   (*d*) K is much more reactive than Ca ?
6. (*a*) The solubilities of sulphates of alkaline earths decrease whereas the solubilities of their hydroxides increase on moving down the group. How would you explain this behaviour ?
   (*b*) Calcium imparts brick red, strontium imparts crimson and barium imparts grassy green colour to bunsen flame. How would you explain this behaviour ?
   (*c*) Be and Mg do not impart any colour to bunsen flame ? Why is it so ?
7. Give an account of the occurrence, esxtraction and uses of beryllium.
8. Compare the alkaline earth metals with alkali metals with regard to the following properties :
   (*a*) ionisation energies (*c*) solubilities of compounds
   (*b*) melting and boiling points (*d*) reducing behaviour.
9. (*a*) Indicate with reasons in which direction the following changes occur in Group 2 elements :
   (*i*) The cations become more strongly hydrated.
   (*ii*) The hydroxides become less soluble in water.
   (*iii*) The standard oxidation potentials decrease.
   (*iv*) The size of M^{2+} ions decreases.
10. (*a*) The first ionisation energy of beryllium is greater than that of lithium but the position is reversed in the case of second ionisation energy. Why ?
    (*b*) What is the structure of $BeCl_2$ in the gaseous and solid state ?
    (*c*) Compare the reactions of Group 1 and Group 2 metals with water.
    (*d*) Which alkaline earth metal ion has lowest ionic mobility in water and why ?
11. Explain why
    (*a*) The chemistry of alkaline earth metals is the chemistry of their dipositive ions.
    (*b*) Alkaline earth metal oxides are less basic than those of alkali metals.
    (*c*) Calcium is more reactive than magnesium
    (*d*) The hydroxides of Group 2 metals are less basic than those of Group 1.
    (*e*) The metals of Group 2 are harder and have higher melting points than those of Group 1.
12. Give a brief account of the chemistry of beryllium, bringing out clearly why does it differ from the rest of its family members.
13. How does beryllium occur in nature ? How is it extracted from the mineral beryl ? How does beryllium differ from the rest of the alkaline earths and why ?
14. Write a brief note on complexes of beryllium with highly conjugated planar ligands.
15. (*a*) Give the preparation and properties of $BeCl_2$. In which form does it exist
    (*i*) in vapour phase (*ii*) in solution (*iii*) in solid state.
    (*b*) Write down the structure of chlorophyll.
16. (*a*) How is calcium carbide obtained on a commercial scale ? How can it be converted into calcium cyanamide ? Give the important properties and uses of calcium cyanamide.
    (*b*) Discuss the preparation and structure of calcium carbide.
    (*c*) Draw the structures of beryllium oxalate and basic beryllium acetate.
17. Discuss the stereochemistry of the halide complexes of beryllium. What type of complexes are formed with highly conjugated planar ligands. Give at least one example.
18. Give the approximate composition of Portland cement. Give details of its manufacture. Explain the chemistry of the process of setting of cement.
19. How does magnesium occur in nature ? How is the metal extracted ? Give the important properties and used of the metal.

15 THE ELEMENTS OF GROUP 13

Group 13 of the periodic table contains five elements, namely, **boron, aluminium, gallium, indium** and **thallium.** Aluminium is the most abundant of these elements. Boron occurs rather sparsely. Gallium, indium and thallium are not found in concentrated deposits and do not find much of commercial applications.

Electronic Configurations. The electronic configurations of the various elements of this family are shown in Table 1.

The general outer electronic configuration of the elements of this group may thus be written as ns^2p^1.

TABLE 1

Electronic Configurations of Elements of Group 13

Element	Atomic Number	Electronic Configuration
Boron, B	5	[He] $2s^2p^1$
Aluminium, Al	13	[Ne] $3s^2p^1$
Gallium, Ga	31	[Ar] $3d^{10}\,4s^2p^1$
Indium, In	49	[Kr] $4d^{10}\,5s^2p^1$
Thallium, Tl	81	[Xe] $4f^{14}\,5d^{10}\,6s^2p^1$

GENERAL CHARACTERISTICS

General characteristics of *p* block elements have already been discussed in Chapter 12 while describing the properties of the main group elements. However, we shall briefly discuss these properties in this chapter also. Some of the important properties of Group 13 elements are given in Table 2.

1. Density, Melting Point, Boiling Point and Heat of Sublimation. *Density* increases on moving down the group. Aluminium, however, has an exceptionally low density. *Melting point* decreases considerably on moving down the group upto Ga and increases again in the case of In and Tl. *Boiling point*, however, follows a more regular trend. It decreases regularly on moving down the group. *Heat of sublimation* also follows the same trend. This indicates that the atoms of the elements are held less and less closely as we move down the group.

TABLE 2

Some Important Properties of Group 13 Elements

Property	Boron	Aluminium	Gallium	Indium	Thallium
Atomic number	5	13	31	49	81
Molar mass (g mol^{-1})	10·81	26·98	69·72	114·82	204·37
Density (g cm^{-3})	3·30	2·70	5·91	7·31	11·90
Melting point (°C)	2030	659	29·8	156·4	303
Boiling point (°C)	2550	2450	2237	2000	1457
Atomic radius (Å)	0·82	1·18	1·26	1·44	1·48
Molar volume (cm^3 mol^{-1})	4·62	10·0	11·8	15·1	17·2
Radius of trivalent ion (Å)	0·20	0·50	0·61	0·81	0·91
Ionisation energy (kJ mol^{-1})	800	577	579	558	589
Electronegativity (Pauling's values)	2·0	1·6	1·6	1.8	1·8*
Oxidation states	+3	+3	+1, +3	+1, +3	+1, +3
Heat of sublimation (kJ mol^{-1})	564·8	324·3	273·2	241·4	179·1

2. Ionisation Energies. The Group 13 elements have two *s* electrons and one *p* electron in their outermost (valency) shell. Since *p* electrons are invariably held less tightly than *s* electrons, the ionisation energy of each element is rather low as compared to the ionisation energies of *s* block elements of the same period.

As can be seen from Table 2, the ionisation energy is the highest in the case of boron. It decreases sharply from B to Al, remains practically the same in Ga, again decreases in In and increases in the last element Tl. Normally, there should have been a regular decrease in ionisation energy as we move down the group from B to Tl, as happens in the case of *s* block elements. The anomalous behaviour has already been explained in details in Chapter 12 dealing with the general characteristics of the main group elements. Although ionization energy depends on several factors and an exact explanation is not so easy, yet the trends in ionisation energy may be broadly explained in the following manner.

The ionisation energy of boron is the highest in the group since its atomic size is the smallest and the shielding effect is the lowest. The sharp decrease from B to Al is due to an appreciable increase in atomic size and the effective shielding of the nuclear charge by the intervening *s* and *p* electrons. In the case of Ga, there are ten *d* electrons in its inner electronic configuration. Since *d* electrons shield the nuclear charge less effectively than the *s* and *p* electrons (Chapter 1), the outer electron is held fairly strongly by the nucleus. As a result, the ionisation energy remains practically the same in spite of the increase in atomic size as we move from Al to Ga. In the case of In, the number of *d* electrons and hence their screening effect remains the same as in Ga. However, since there is an increase in atomic size as we move from Ga to In, there is a noticeable decrease in ionisation energy. The last element, Tl, has 14 *f* electrons in its inner electronic configuration. Since the shielding effect of *f* electrons is much smaller than that of *d* electrons and also since there is only a marginal increase in atomic size (from 1·44 Å to 1·47 Å) as we move from In to Tl, the outer electron in Tl is held quite firmly and hence there is a considerable increase in its ionisation energy.

The second and third ionisation energies also follow the same trend.

Since the total of the three successive ionisation energies of the elements of this group is known to be very large, these elements have very little tendency to form trivalent ions, M^{3+}.

3. Oxidation States. Boron shows consistently +3 oxidation state in its compounds. The rest of the elements, however, show +1 as well as +3 oxidation states. The +1 oxidation state becomes more and more stable as we move down the group from B to Tl. As a matter of fact, the compounds in which thallium is univalent, are more stable than those in which it is trivalent. The compounds of Tl(I) show close resemblance to those of alkali metals. For example, TlOH is highly soluble and is a strong base like NaOH ; Tl_2O_3 is also soluble and resembles the corresponding sodium and potassium compounds.

The cause of stability of lower oxidation states of heavier elements of Group 13 has already been discussed in details in Chapter 12.

Gallium, the third element of the group, appears to be bivalent in a few of its compounds, *e.g.*, $GaCl_2$. However, it is believed that this compound has the structure $Ga^+[GaCl_4]^-$ which contains the univalent and trivalent gallium ions, Ga^+ and Ga^{3+}.

4. Electropositive (Metallic) Character. Electropositive (metallic) character increases from boron to aluminium. Boron, in fact, is regarded as a *semi-metal*. It is closer to non-metals than to metals in its properties. It has high ionisation energy and is also a poor conductor of electricity. Aluminium and the rest of the elements are typically metallic and have more or less an equal electropositive character. This is indicated by their first ionisation energies which differ only slightly from one another.

5. Tendency to form Ionic Compounds. From the electronic configurations of the elements (Table 1), it might be expected that all of them would form +3 ions. However, the second and third ionisation energies of boron are so high that this element has little tendency to form B^{3+} ion. This ion in any case is not stable and is not important chemically. The other members of the family, because of comparatively lower ionisation energies involved in the change $M \rightarrow M^{3+}$, have a relatively higher tendency to form Al^{3+}, Ga^{3+} and In^{3+} ions under suitable conditions.

6. Tendency to form Covalent Compounds. The trivalent boron ion, B^{3+}, is exceedingly small. Such an ion would exert large *polarizing effect* on neighbouring atoms, *i.e.*, it would *tend to pull off electrons from neighbouring atoms.* This would result in the transference of electrons to the boron ion from its neighbours resulting in electron sharing and covalent bonding. According to Fajan's rule also, *the smaller the size of the cation, the greater is the tendency for covalent bonding.* Thus, while boron, generally, forms covalent compounds, the other elements form electrovalent compounds also.

7. Action of Air and Water. Pure boron is almost unreactive at ordinary temperatures. It reacts with air only when heated. It does not react with water. Aluminium reacts readily in air, even at ordinary temperatures, forming a layer of the oxide. The impervious oxide film protects it from further action of air.

Aluminium decomposes boiling water to give hydrogen. Gallium and indium are attacked neither by cold nor by hot water unless oxygen is present. Thallium is a little more reactive than gallium and forms an oxide on the surface.

Diagonal Relationship between Boron and Silicon. Boron resembles silicon, the second element of the next group in the next period of the periodic table. This is a case of **diagonal relationship**. Boron, in fact, shows more resemblance with silicon than with aluminium. The various points of resemblance between boron and silicon are discussed below.

1. Non-metallic character. Both boron and silicon have non-metallic character. Both of them have high melting points, high ionisation energies and are bad conductors of electricity.

2. Densities and Boiling points. Both have nearly equal densities ($B = 3{\cdot}30$ g cm^{-3} and $Si = 3{\cdot}52$ g cm^{-3}). Both boil at temperatures which are close to each other, *i.e.*, 2550°C and 2680°C, respectively.

3. Occurrence. Neither boron nor silicon occurs free in nature. Both occur in combined state.

4. Stability of cations. Boron and silicon do not form stable cations normally.

5. Tendency to form covalent compounds. Most of the compounds of boron and silicon are covalent in nature.

6. Oxides and oxoacids. Boron and silicon form stable oxides, B_2O_3 and SiO_2. These oxides are weakly acidic. In water they yield the corresponding weak acids, namely, *boric acid* (H_3BO_3, $K_a = 6{\cdot}0\times10^{-10}$) and *silicic acid* ($H_4SiO_4$, $K_a = 1\times10^{-10}$).

7. Formation of borates and silicates. The oxides, B_2O_3 and SiO_2, being weakly acidic, dissolve in strong alkalies forming metaborates and metasilicates.

$$B_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium meta-silicate}}{Na_2SiO_3} + H_2O$$

8. Formation of esters. Orthoboric acid and orthosilicic acid form esters when treated with alcohols in the presence of sulphuric acid. Thus,

$$H_3BO_3 + 3C_2H_5OH \xrightarrow[-3H_2O]{H_2SO_4} \underset{\text{Triethyl borate}}{(C_2H_5)_3BO_3}$$

The ester burns with a green edged flame. This is used as a qualitative test for borates.

Similarly, orthosilicic acid forms tetraethyl ester with ethyl alcohol.

$$H_4SiO_4 + 4C_2H_5OH \xrightarrow[-4H_2O]{H_2SO_4} \underset{\text{Tetraethyl silicate}}{(C_2H_5)_4SiO_4}$$

9. Formation of hydrides. Hydrides of boron and silicon are formed in almost identical manner, *e.g.*, by the reduction of their halides with lithium aluminium hydride.

$$4BCl_3 + 3LiAlH_4 \longrightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$$

$$SiCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + SiH_4$$

10. Hydrolysis of halides. Halides of boron and silicon get readily hydrolysed to yield orthoboric and orthosilicic acid, respectively. In each case, hydrogen halide is also formed in solution. Thus,

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

$$SiF_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HF$$

If boron trifluoride is added in excess, it dissolves in the hydrofluoric acid formed yielding **hydrofluoboric acid, $H[BF_4]$.**

$$BF_3 + HF \longrightarrow H[BF_4]$$

If SiF_4 is present in excess, fluosilicic acid, H_2SiF_6, results.

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

EXTRACTION OF ELEMENTS OF GROUP 13

Extraction of Boron. Boron occurs in the form of salts of boric acid. Some of these are : (*i*) *Borax* ($Na_2B_4O_7.10H_2O$), (*ii*) *Colemanite* ($Ca_2B_6O_{11}.5H_2O$), (*iii*) *Panderinite* ($Ca_2B_6O_{11}.3H_2O$), (*iv*) *Boracite* ($2Mg_3B_8O_{15}.MgCl_2$) and (*v*) *Boronatrocalcite* ($CaB_4O_7.NaBO_2.H_2O$). Boron is generally obtained from borax.

Extraction. The following steps are involved in getting boron from borax.

a. Preparation of boric anhydride. When hot concentrated hydrochloric acid is added to borax, the sparingly soluble boric acid formed is slowly thrown down which on subsequent heating gives boric anhydride, B_2O_3.

$$(i)\ Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + H_2B_4O_7 + 4H_3BO_3$$

$$(ii)\quad 2H_3BO_3 \xrightarrow{\text{Heat}} B_2O_3 + 3H_2O$$

b. Reduction of boric anhydride. The boric anhydride is then heated with sodium, potassium or magnesium powder in a crucible when it is reduced to boron.

$$B_2O_3 + 6K \longrightarrow 2B + 3K_2O$$

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

Pure boron is prepared by striking an electric arc between water-cooled copper electrodes in an atmosphere of hydrogen and boron trichloride vapour in a glass globe.

$$2BCl_3 + 3H_2 \longrightarrow 2B + 6HCl$$

Boron obtained in this manner is a brown amorphous mass.

Pure boron can also be obtained by heating BBr_3 with hydrogen over a heated tantalum filament at temperatures between 1000 – 1200°C.

Extraction of Aluminium. Next to silica and oxygen, aluminium is the most widely distributed element. It is present to the extent of 7·3 per cent in the earth's crust. The important ores are : (*i*) *Bauxite*, $Al_2O_3.3H_2O$ (*ii*) *Cryolite*, Na_3AlF_6 and (*iii*) *Corundum*, Al_2O_3. Aluminium is generally obtained from the bauxite ore.

The bauxite ore is powdered and digested with sodium hydroxide in an autoclave under pressure at 130°C for several hours when alumina of the ore dissolves as sodium meta aluminate whereas impurities

such as ferric oxide, silica, etc., being insoluble in NaOH, settle down. The sodium meta aluminate solution is then stirred with carbon dioxide gas when a precipitate of $Al(OH)_3$ is obtained. It is ignited at 1500°C to get pure alumina Al_2O_3 which is dissolved in molten cryolite at 800 – 1000°C and the melt electrolysed to get the pure metal.

Extraction of Gallium, Indium and Thallium. Gallium, indium, and thallium occur in nature very rarely. They are usually obtained by the electrolysis of aqueous solutions of their salts.

PROPERTIES OF ELEMENTS OF GROUP 13

Properties of Boron. Physical Properties. Boron exists in amorphous and crystalline forms. Amorphous boron is a brown powder of specific gravity 2·34. It melts at 2030°C and volatilises appreciably even at 1600°C.

Chemical Properties. 1. Action of air. Boron burns brilliantly when heated in oxygen giving boric anhydride (B_2O_3). When heated in air at 700°C, it forms boric anhydride (B_2O_3) and boron nitride (BN).

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

$$2B + N_2 \longrightarrow 2BN$$

2. Action of acids. It is not attacked by hydrochloric acid but is oxidised by nitric acid and sulphuric acid to boric acid.

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

3. Action of alkalies. Boron reacts with fused alkali metal hydroxides forming borates and evolving hydrogen.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

However, extra pure boron is not attacked by aqueous NaOH or fused NaOH upto 500°C.

4. Action with metals. Boron combines with many metals on heating to give the corresponding borides, *e.g.*,

$$3Mg + 2B \longrightarrow Mg_3B_2$$

5. Action with non-metals. Boron combines with nitrogen when heated in air giving boron nitride.

It also combines with halogens at high temperatures to yield covalent boron trihalides, *e.g.*, BF_3, BCl_3.

It combines with carbon at high temperatures to give boron carbide, B_4C.

Crystalline boron is very hard and heat-resistant. It can be ignited with difficulty in air. Its specific gravity is 3·3. It is not acted upon by nitric acid and sulphuric acid. It is a bad conductor of electricity.

Uses. Boron is used, in the form of its salts such as calcium boride, as a deoxidiser. Borax and boric acid are also important technically.

Properties of Aluminium. Physical Properties. Aluminium is a bluish-white metal having a brilliant lustre which, however, is soon destroyed due to the formation of an oxide layer. It is malleable and ductile and can be rolled into sheets, foils and wires. It is a very light metal (specific gravity 2·7). It is a good conductor of heat and electricity. It melts at 659°C and boils at 2450°C.

Chemical Properties. 1. Action of air. Aluminium is not affected by pure dry air but in moist air a film of oxide is formed at the surface which protects the metal from further corrosion. It burns readily in oxygen giving brilliant light.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3; \qquad \Delta H = -3230 \text{ kJ}$$

The heat evolved in the oxidation of aluminium is used in the *thermite process* for the reduction of oxides of chromium, iron, manganese, etc.

2. Action of water. Pure aluminium is not affected by pure water. However, the impure form is readily corroded by water containing salts. It decomposes boiling water evolving hydrogen.

Aluminium-mercury couple is, therefore, used as a reducing agent.

3. Action of alkalies. Aluminium readily dissolves in alkalies such as sodium and potassium hydroxides evolving hydrogen and forming the corresponding aluminates.

It also dissolves in a hot concentrated solution of sodium carbonate evolving hydrogen,

$$2Al + Na_2CO_3 + 3H_2O \longrightarrow 2NaAlO_2 + CO_2 + 3H_2$$

4. Action of acids. Aluminium dissolves in dilute hydrochloric and sulphuric acids evolving hydrogen. With hot concentrated sulphuric acid, sulphur dioxide is given out. Concentrated nitric acid has no action because the metal is rendered *passive* due to surface oxidation.

5. Action of halogens and nitrogen. Aluminium when heated with halogens and nitrogen gives aluminium halides and aluminium nitride, respectively.

6. Displacement of other metals. Aluminium displaces copper, zinc and lead from the solutions of their salts.

$$3ZnSO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3Zn$$

Uses. 1. Aluminium, being very light, is used in manufacturing household utensils, aeroplane parts, precision and surgical instruments, etc. 2. Since it is unattacked by nitric acid, it is used in chemical plants and also for transporting nitric acid. 3. Mixed with oil, it is used in paints for steam pipes and other metal objects. 4. Aluminium foil is used for packing chocolates, cigarettes, etc. 5. Alums are used as mordants in dyeing and paints. 6. It is used as a reducing agent for the production of certain metals such as chromium, manganese, etc. 7. Alumina is used in making refractory bricks and ultramarine 8. In certain forms such as felspar and mica it is used in the construction of buildings. 9. Along with organic colloids, it is used for sizing of paper. 10. The evolution of enormous quantities of heat in the oxidation of aluminium is made use of in thermite welding of metals.

Properties of Gallium. Gallium is a silvery-white metal and is hard and brittle. It melts at 29·8°C and boils at 2237°C.

It is stable in dry air and does not decompose water, hot or cold, in the absence of free oxygen.

It dissolves in caustic alkalies as well as in hydrochloric acid and sulphuric acid but not in nitric acid. Nitric acid renders it *passive*.

It combines directly with halogens and sulphur but not with nitrogen or hydrogen.

Its chemistry is similar to that of aluminium.

Uses. Gallium, on account of its scarcity, does not find much commercial use. However, since under ordinary pressure it remains liquid over a wide range of temperature (between 29·8°C and 2237°C), it has been used in quartz thermostats for maintaining high temperatures. Liquid gallium, like mercury, does not wet glass or quartz. It is also used in lamps for spectroscopic analysis just as mercury is used in mercury lamps.

Properties of Indium. Indium is a soft white metal and is malleable and ductile. It melts at 156·4°C and boils at 2000°C. It alloys readily with copper, silver and gold.

It is not attacked by dry air at ordinary temperatures but when heated it gets covered with an oxide film.

It does not decompose water in cold or even on heating. However, it decomposes steam evolving hydrogen.

It burns in chlorine and combines with other halogens, sulphur, selenium and tellurium on heating.

It differs from aluminium and gallium in its insolubility in caustic alkalies even on heating. However, it dissolves slowly in cold and dilute acids and quickly in hot and concentrated acids.

Uses. Indium, like gallium, on account of its scarcity, does not find much commercial application. However, its alloys with copper and silver are used in dental work and jewellery.

Properties of Thallium. Thallium is a soft grey metal. It melts at 303°C and boils at 1457°C. It is so soft that it can be scratched even by finger nails. It is malleable but not ductile. It exists in two allotropic forms known as α and β varieties. It alloys with a number of metals including copper, silver, gold, zinc and cadmium.

It is more reactive than indium and gallium. This is due to its tendency to form unipositive ion, Tl^+.

It oxidises in moist air and decomposes steam at red heat.

It dissolves readily in dilute mineral acids except hydrochloric acid, yielding thallium(I) compounds. It does not dissolve readily in hydrochloric acid because of the insolubility of TlCl.

It combines directly with the halogens at ordinary temperatures and with sulphur, selenium and tellurium on heating.

Uses. Thallium does not find any worthwhile application as a metal. But its salts find a number of uses. Thus, thallous salts, being toxic, are used as fungicides, germicides and in ointments used for the treatment of ring worms. Thallium compounds also find application in preparing optical glasses on account of their high refractive indices.

COMPOUNDS OF GROUP 13 ELEMENTS

I. A Comparative Study

1. Hydrides. Boron forms a number of stable covalent hydrides with general formulae B_mH_{m+4} and B_mH_{m+6}. These are called **boranes**. The representative compounds of the two series are B_2H_6 and B_4H_{10}. These will be discussed in details a little later in this chapter.

Aluminium forms a polymeric hydride of formula $(AlH_3)_n$. It decomposes on heating above 200°C into its elements. Gallium hydride, GaH_3, is less stable while indium hydride, InH_3 and thallium hydride, TlH_3, are extremely unstable.

Boron, aluminium and gallium form complex anionic hydrides like lithium borohydride, $Li[BH_4]$, lithium aluminium hydride, $Li[AlH_4]$ and lithium gallium hydride, $Li[GaH_4]$. The formation of these anionic complexes is due to the presence of a vacant *p* orbital in their outermost shells which readily accepts electron pair from the hydride ion (H^-).

$$XH_3 + H^- \longrightarrow [XH_4]^-$$

where X = Al, Ga and also B.

Evidently, in these cases the hydride ion acts an an electron donor while the XH_3 behaves as an electron acceptor.

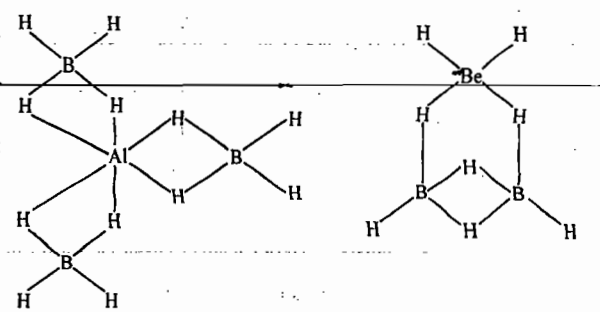
The alkali metal tetrahydridoborates are predominantly ionic in character although $Li[BH_4]$ has some covalent character as well. $Li[BH_4]$ reacts violently with water liberating hydrogen.

$$Li[BH_4] + 2H_2O \longrightarrow LiBO_2 + 4H_2$$

$Na[BH_4]$ reacts only slowly with water whereas $K[BH_4]$ is stable towards water.

$Be[BH_4]_2$, $Al[BH_4]_3$ and many other transition metal tetrahydridoborates have considerable covalent character.

The structures of $Be[BH_4]_2$ and $Al[BH_4]_3$ are as shown :



As can be seen from these structures, the presence of hydrogen bridges in the covalent tetrahydrides, *i.e.*, tetrahydridoborates of Be^{2+} and Al^{3+} is quite a common feature.

Lithium aluminium hydride, $Li[AlH_4]$, is more important of these compounds. It is prepared by reacting lithium hydride with anhydrous aluminium chloride in ether.

$$4LiH + \underset{\text{(anhydrous)}}{AlCl_3} \xrightarrow{\text{Ether}} Li[AlH_4] + 3LiCl$$

The complex hydride $Li[GaH_4]$ can also be prepared by a similar method. The tetrahydridoborates and aluminates are strong reducing agents. Lithium aluminium hydride (or lithium tetrahydridoaluminate) and sodium tetrahydridoborate are used particularly for this purpose.

2. Oxides and Hydroxides. All the elements of this group form oxides of the general formula M_2O_3 in which the elements are in + 3 oxidation state. Examples are B_2O_3, Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3.

Oxides and Hydroxides of Boron. The principal oxide of boron is boron oxide, B_2O_3. It is called diboron trioxide and more commonly boric oxide. It is actually an anhydride of orthoboric acid, H_3BO_3 and is obtained on dehydrating this acid by heating at 100°C.

$$2H_3BO_3 \xrightarrow{100°C} B_2O_3 + 3H_2O$$

It is a highly stable substance but hydrolyses in water yielding boric acid, H_3BO_3.

The trivalent boron ion, B^{3+}, being very small, has high (positive) charge density. Therefore, when placed in water, it tends to pull off electrons from water molecule towards itself sufficiently strongly to rupture the O – H bond. This results in the release of H^+ ion. Hence, hydroxides and oxides of boron, $B(OH)_3$ and B_2O_3, are feebly acidic. They dissolve in strong alkalies forming *metaborates*.

$$B(OH)_3 + NaOH \longrightarrow Na^+BO_2^- + 2H_2O$$

The sodium metaborate is readily hydrolysed and, therefore, orthoboric acid cannot be titrated against sodium hydroxide. However, in the presence of certain polyhydroxy compounds, it behaves as a strong acid and can thus be titrated successfully against strong bases. This aspect would be discussed a little later in this chapter.

Oxides and Hydroxides of Aluminium. The oxide of aluminium, Al_2O_3, is commonly known as alumina. It is obtained on heating aluminium in oxygen. It also occurs in nature in various forms. The two common forms of anhydrous Al_2O_3 are α-Al_2O_3 called corundum and γ-Al_2O_3 called activated alumina. α-Al_2O_3 is stable at high temperatures. It is very hard and is resistant to hydration and to attack by acids. It is used as an abrasive. γ-Al_2O_3 is readily soluble in acids and is used in column chromatography.

Aluminium hydroxide is obtained as a gelatinous precipitate when an alkali solution is added to the solution of an aluminium salt.

$$Al(NO_3)_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaNO_3$$

Aluminium oxide and hydroxide are amphoteric in nature. They dissolve both in acids as well as in alkalies.

Oxides and Hydroxides of Other Elements. Gallium like aluminium forms gallium oxide, Ga_2O_3, which is also amphoteric like alumina. It is formed by direct combination of gallium with oxygen at moderate heat. It is a white solid.

Indium oxide, In_2O_3, is obtained on heating nitrate or sulphate of the metal. It is a yellow solid and is distinctly basic in aqueous medium.

Thallium forms two oxides in which the oxidation state of the metal is +1 and +3. Thallium(I) oxide, Tl_2O, is more stable than thallium(III) oxide, Tl_2O_3. The former is obtained by direct combination of the metal with oxygen. The latter is obtained indirectly by heating thallium(III) hydroxide, $Tl(OH)_3$. It is a

dark brown solid. Being less stable it starts decomposing even below 100°C into Tl_2O and O_2. TlOH is a strong base and is highly soluble in water.

Acidic, Amphoteric and Basic Character of Oxides and Hydroxides. As mentioned above, B_2O_3 and $B(OH)_3$ are acidic, Al_2O_3 and $Al(OH)_3$ and Ga_2O_3 and $Ga(OH)_3$ are amphoteric while In_2O_3 and $In(OH)_3$ are distinctly basic. Thus, on moving down the group, there is a gradual change from acidic to amphoteric and then to basic character of the oxides and hydroxides of the elements. In the case of ***hydroxides**, this behaviour may be explained as follows :*

$B(OH)_3$ in aqueous medium coordinates a molecule of water to form the hydrated species $H_2O{\rightarrow}B(OH)_3$. In this species, B^{3+} ion, because of its small size, exercises a high polarizing power thereby pulling the sigma electron charge of the coordinated O atom towards itself. The coordinated oxygen, in turn, pulls the sigma electron charge of the OH bond of the attached H_2O molecule towards itself. This facilitates the removal of H^+ ion from the O-H bond, as shown below :

$$H_2O{\rightarrow}B(OH)_3 \rightleftharpoons [B(OH)_4]^- + H^+$$

Thus, the solution of $B(OH)_3$ in water acts as a *weak acid*. That is why it reacts with NaOH solution to produce the sodium salt :

$$B(OH)_3 + NaOH \rightleftharpoons Na^+[B(OH)_4]^- \rightleftharpoons \underset{\text{Sodium metaborate}}{Na^+BO_2^-} + 2H_2O$$

Of all the trivalent cations of Group 13 elements, B^{3+} ion has the highest positive charge density (charge/size) and the highest polarizing power. The positive charge density and the polarizing power go on decreasing with increase in the size of the cation. Since the trivalent Al^{3+} and Ga^{3+} ions are relatively larger, their polarizing power is less than that of B^{3+} ion and hence their capacity to release H^+ ions from the hydrated species $H_2O{\rightarrow}Al(OH)_3$ and $H_2O{\rightarrow}Ga(OH)_3$ is relatively smaller. As a result, the oxides and hydroxides of these elements, instead of being acidic, are *amphoteric*. The trivalent In^{3+} and Tl^{3+} ions are even larger than Al^{3+} and Ga^{3+} ions. Their positive charge density and polarizing power are, therefore, so small that they cannot affect the release of H^+ ions from the hydrated species $H_2O{\rightarrow}In(OH)_3$ and $H_2O{\rightarrow}Tl(OH)_3$ at all. Apart from this, the large size of In^{3+} and Tl^{3+} ions and the large energy differences in the sigma orbitals of these cations and the sigma orbitals of the oxygen atoms of OH groups considerably decrease the covalent character of M – O bond and, therefore, increase its ionic character. The hydroxides of In and Tl, in fact, disproportionate in water giving OH^- ions and thus behave as *bases*. This is illustrated below.

(*i*)
$$H_2O + In(OH)_3 \longrightarrow H_2O{\rightarrow}In(OH)_3$$
$$H_2O{\rightarrow}In(OH)_3 \rightleftharpoons [H_2O{\rightarrow}In(OH)_2]^+ + OH^-$$

(*ii*)
$$H_2O + Tl(OH)_3 \longrightarrow H_2O{\rightarrow}Tl(OH)_3$$
$$H_2O{\rightarrow}Tl(OH)_3 \rightleftharpoons [H_2O{\rightarrow}Tl(OH)_2]^+ + OH^-$$

The **oxides** of the elements with formula M_2O_3 (*e.g.*, B_2O_3, Al_2O_3, Ge_2O_3, etc.) may be considered as dehydrated $M(OH)_3$.

$$2M(OH)_3 \longrightarrow M_2O_3 + 3H_2O$$

The acid/base behaviour of the oxides of Group 13 elements can also be explained on similar lines.

3. Halides. The elements of Group 13 form a number of trihalides as well as lower halides. These are discussed below.

Trihalides of Boron. Boron trihalides, BX_3, are covalent compounds. They involve hybridisation of one *s* and two *p* orbitals (sp^2 hybridisation) of boron atom and have, therefore, trigonal planar structure.

All the four halides of boron, namely, boron trifluoride, BF_3, boron trichloride, BCl_3, boron tribromide, BBr_3 and boron triiodide, BI_3 are known. All of them are volatile, highly reactive and monomeric. BF_3 and BCl_3 are gases at room temperature ; BBr_3 is a volatile liquid while BI_3 is a solid.

They do not conduct elecricity in the liquid state. Their boiling points are also very low as compared to the halides of the elements of Groups 1 and 2. These properties are in contrast with those expected from ionically bonded substances. These are the principal reasons for regarding these halides as covalent compounds.

Boron trifluoride, BF_3. This is the most important of the trihalides of boron. It is obtained by heating boron trioxide or borax with calcium fluoride and concentrated sulphuric acid.

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 3H_2O + 2BF_3$$
$$Na_2B_4O_7 + 6CaF_2 + 8H_2SO_4 \longrightarrow 2NaHSO_4 + 6CaSO_4 + 7H_2O + 4BF_3$$

Pure BF_3 can be obtained by thermal decomposition of diazonium tetrafluoroborate.

$$C_6H_5N_2BF_4 \longrightarrow C_6H_5F + N_2 + BF_3$$

It is a colourless pungent gas (m.p. – 127·1°C and b.p. – 99·9°C). It is exceedingly soluble in water and is, therefore, collected over mercury.

It combines with water forming two hydrates, $BF_3.H_2O$ and $BF_3.2H_2O$. The first hydrate melts at 10·18°C and the second at 6·36°C.

It gets hydrolysed in aqueous solution yielding boric acid and hydrofluoric acid:

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

If boron trifluoride is passed in excess, it dissolves in the hydrofluoric acid formed, yielding hydrofluoboric acid, $H[BF_4]$.

$$BF_3 + HF \longrightarrow H[BF_4]$$

Boron trifluoride, being an electron-deficient compound, can accept a lone pair of electrons from ammonia, hydrogen sulphide and also a fluoride ion and thus behaves as a Lewis acid. It is this tendency to accept electrons which makes BF_3 useful as a catalyst in a number of reactions such as alkylation and acylation, in organic chemistry.

Boron trichloride, BCl_3. It is obtained by passing chlorine over a heated mixture of boron trioxide and powdered charcoal at about 500°C.

$$B_2O_3 + 3C + 3Cl_2 \xrightarrow{500°C} 2BCl_3 + 3CO$$

The gases evolved are passed through a U-tube cooled in a freezing mixture. Boron trichloride condenses as a colourless liquid while carbon monoxide and unreacted chlorine pass over.

It can also be prepared by heating boron trioxide with phosphorus pentachloride in a sealed tube at 15°C.

$$B_2O_3 + 3PCl_5 \xrightarrow{15°C} 2BCl_3 + 3POCl_3$$

It is a colourless liquid boiling at 12·5°C and freezing at – 107°C. It fumes in moist air.

It is completely hydrolysed by water yielding boric acid and hydrochloric acid.

Boron tribromide, BBr_3. It is prepared in the same way as boron trichloride with the difference that now bromine, instead of chlorine, is passed over a heated mixture of boron trioxide and powdered charcoal.

$$B_2O_3 + 3C + 3Br_2 \longrightarrow 2BBr_3 + 3CO$$

It is a colourless liquid boiling at 91·3°C and freezing at – 46°C. It fumes in moist air and is completely hydrolysed in aqueous solution.

$$BBr_3 + 3H_2O \longrightarrow H_3BO_3 + 3HBr$$

Boron triiodide, BI_3. It is prepared by the action of iodine on sodium borohydride.

$$4I_2 + NaBH_4 \longrightarrow BI_3 + 4HI + NaI$$

It may also be prepared by the action of hydriodic acid on boron trichloride.

It is a white solid, melting at 49·9°C. It is completely hydrolysed by water, like other boron trihalides.

Relative Strengths of Trihalides as Lewis Acids. Effect of Back Bonding. The relative strengths of trihalides of boron to accept a pair of electrons and thus to act as Lewis acids have been determined by measuring their heats of formation as well as by studying their infra-red spectra. The power to accept an electron pair has been found to decrease in the order :

$$BF_3 < BCl_3 < BBr_3$$

This order is just the *reverse* of what should be expected normally from the electronegativites of the halogens. This *anomalous behaviour* can be explained on the basis of the *tendency of the halogen atom to* **back-donate** *its electrons to the boron atom*, as illustrated below.

In BF_3 molecule, while the $2p$ orbitals of each fluorine atom are fully filled, one of the $2p$ orbitals of the boron atom is *vacant* (Fig. 1). The two $2p$ orbitals involved in the formation of B – F bond, therefore, overlap *laterally* resulting in the transference of the fluorine electrons into the vacant $2p$ orbital of the boron atom. An effective overlapping is easily possible because both the orbitals belong to the same energy level. In other words, an additional $p\pi - p\pi$ **bond** is established between boron and fluorine atoms. The B – F bond, thus, acquires some double bond character. This type of bond formation is known as **back bonding**. This is illustrated in Fig. 1.

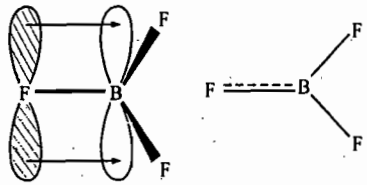


Fig. 1. The phenomenon of back bonding in BF_3 molecule.

Similar structures for the other two B – F bonds are equally probable. The back bonding in BF_3 may, thus, be represented as in Fig. 2.

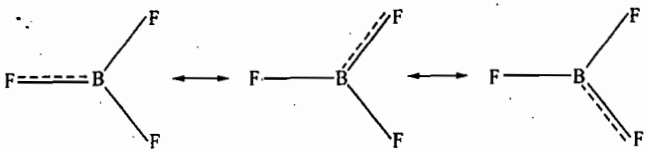


Fig.2. Various resonating structure of BF_3 molecule involving back bonding.

As a result of the **back donation** *of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and, therefore, the Lewis acid character of BF_3 decreases.*

The tendency to form $p\pi - p\pi$ bond is maximum in the case of BF_3 and falls rapidly as we move to BCl_3 and BBr_3. The probable reason for this appears to be the inability of the vacant $2p$ orbital of boron to overlap effectively with the $3p$ orbital of chlorine in B – Cl bond and with the $4p$ orbital of bromine in B – Br bond because of appreciable differences in the energies of the overlapping orbitals.

Trihalides of Aluminium. Trihalides of aluminium with all the four halogens are known. Thus, we have AlF_3, $AlCl_3$, $AlBr_3$ and AlI_3.

Aluminium trifluoride, AlF_3. Metallic aluminium or its oxide or hydroxide when dissolved in excess of hydrofluoric acid, deposits hydrated aluminium fluoride. It is colourless when pure. The common hydrate, $AlF_3.3H_2O$, exists in soluble and insoluble forms. It dissolves in hydrofluoric acid forming *fluo-aluminic acid*, H_3AlF_6, the mineral *cryolite*, Na_3AlF_6, being its sodium salt.

Aluminium trichloride, $AlCl_3$. When aluminium is dissolved in excess of hydrochloric acid, crystals of $Al_2Cl_6.12H_2O$ are deposited. The hydrate on heating decomposes to give alumina.

$$Al_2Cl_6.12H_2O \longrightarrow Al_2O_3 + 6HCl + 9H_2O$$

Anhydrous aluminium chloride is prepared by heating aluminium in a stream of dry chlorine or hydrochloric acid gas.

$$2Al + 3Cl_2\,(dry) \longrightarrow 2AlCl_3$$

$$2Al + 6HCl\,(gas) \longrightarrow 2AlCl_3 + 3H_2$$

The reaction with chlorine is strongly exothermic.

Anhydrous aluminium chloride is also formed when

(*i*) a mixture of aluminium oxide and carbon is strongly heated in dry chlorine gas.

$$Al_2O_3 + 3Cl_2 + 3C \longrightarrow 2AlCl_3 + 3CO$$

(*ii*) a mixture of carbon monoxide and chlorine is passed over heated aluminium oxide.

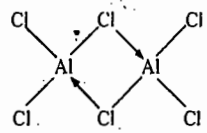
$$Al_2O_3 + 3CO + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

Aluminium chloride is white when pure. It sublimes at 183°C. It is extremely hygroscopic and fumes strongly in moist air due to the formation of hydrogen chloride.

$$2AlCl_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$

Structure of $AlCl_3$. The vapour density measurements show that $AlCl_3$ is *monomeric* above 800°C. The structure of the monomer is *planar triangular* and the bonding is predominantly *covalent*. The Al atom utilises three sp^2 hybrid orbitals to accommodate $3 + 3\times1 = 6$ electrons.

However, below 400°C it exists as a *dimer* with each Al atom utilizing four sp^3 hybrid orbitals to accommodate $3 + 3\times1 + 1\times2 = 8$ electrons (one of the chlorine atoms is coordinated to Al and donates two electrons). The structure of the dimer is as shown.



In the solid state also, aluminium chloride exists as a dimer and is non-conducting. Al_2Cl_6 is the species which exists when aluminium chloride is dissolved in non-polar or less polar solvents. Its solution in such solvents is also non-conducting.

However, when aluminium chloride is dissolved in a polar solvent like water, it dissociates into ions in the following manner and its solution becomes conducting :

$$2AlCl_3 + aq \longrightarrow [AlCl_2(H_2O)_4]^+\,(aq) + [AlCl_4(H_2O)_2]^-\,(aq)$$

The crystallisation of $AlCl_3$ from aqueous solution, therefore, yields an *ionic* solid of composition $[AlCl_2(H_2O)_4]^+[AlCl_4(H_2O)_2]^-.xH_2O$. This compound decomposes at about 190°C to give the *non-ionic* dimer Al_2Cl_6 :

$$[AlCl_2(H_2O)_4]^+[AlCl_4(H_2O)_2]^-.xH_2O \xrightarrow[190°C]{Heat} Al_2Cl_6 + \text{water}$$

The thermal decomposition is accompanied by a *large decrease in density*. This is probably due to the fact that while there is considerable electrostatic attraction between the cations and the anions in the hydrated salt resulting in the decrease of interionic distance in the lattice of $[AlCl_2(H_2O)_4]^+[AlCl_4(H_2O)_2].xH_2O$ crystal, there is no such ionic attraction in the neutral Al_2Cl_6 units which, therefore, lie at a comparatively greater distance in the lattice of solid Al_2Cl_6.

Aluminium chloride is a strong Lewis acid and readily forms adducts with Lewis bases. It is, therefore, used as a catalyst in organic chemistry (Friedel-Crafts reaction). It is also used in the manufacture of dyes, drugs and pharmaceuticals.

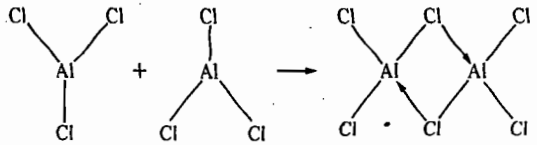
Aluminium tribromide, $AlBr_3$. It is prepared by the direct combination of the elements by passing bromine vapour over heated aluminium. In chemical properties it resembles aluminium chloride. It exists as Al_2Br_6 (*i.e.*, as a dimer) in the crystalline state.

Aluminium triiodide, AlI_3. It is prepared in the same way as aluminium bromide. It reacts with carbon tetrachloride to form aluminium chloride and carbon tetraiodide.

$$4AlI_3 + 3CCl_4 \longrightarrow 4AlCl_3 + 3CI_4$$

It exists as Al_2I_6 (*i.e.*, as a dimer) in the crystalline state.

Characteristic Difference in the Structures of Trihalides of Boron and Aluminium. There is a characteristic difference in the structures of trihalides of boron and aluminium. While the former exist as *monomers*, the latter exist as *dimers*. For example, $AlCl_3$ exists as a dimer, Al_2Cl_6, in non-polar solvents as well as in vapour state between 400 and 800°C. Above 800°C, however, it exists as a monomer. The formation of the dimer is illustrated below :



The arrows indicate donation of electrons to chlorine atoms. The covalency of aluminium increases to 4. The chlorine atoms are arranged tetrahedrally around each aluminium atom.

Such bridge structures are typical of electron-deficient compounds. Boron trihalides, however, do not form dimers. They exist only as *monomers*. This is due to the fact that boron atom is too small to coordinate with four large halide ions such as Cl^-, Br^- and I^-. However, boron atom should be able to coordinate with four fluoride ions which are much smaller in size than other halide ions. Consequently, of the various boron trihalides, the trifluoride at least should exist as a dimer. But actually it is not so. This is because the large amount of energy required for the cleavage of the typical $p\pi - p\pi$ bond in BF_3 to enable dimerisation of BF_3 is not released during the formation of the bridge structure in this case. The boron trifluoride, therefore, exists only as a monomer as do the other halides of boron.

Trihalides of Gallium, Indium and Thallium. The trihalides of gallium, indium and thallium are covalent but the covalent character decreases and ionic character increases on moving from Ga to Tl.

Gallium trichloride ($GaCl_3$) is a white solid, melting at 780°C. The vapours at 500°C consist largely of dimers having the formula Ga_2Cl_6.

Indium trichloride ($InCl_3$), however, does not dimerise. It is relatively more ionic than $GaCl_3$. **Indium triiodide** is, however, dimeric.

Thallium trichloride ($TlCl_3$) also does not dimerise. It is even more ionic than $InCl_3$. It decomposes to TlCl and Cl_2 above 40°C. **TlF_3** is stable upto 500°C. $TlBr_3$ slowly gets converted to $Tl^I[Tl^{III}Br_4]$ at room temperature. TlI_3 is, in fact, an ionic compound of Tl(I) and I_3^-.

Lower Halides of Boron. Several lower halides of boron are known out of which diboron tetrahalides (B_2X_4) are better studied.

When BCl_3 is made to react with mercury, it forms B_2Cl_4.

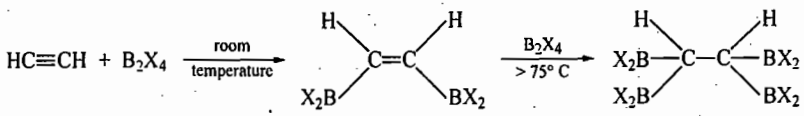
$$2BCl_3 + 2Hg \longrightarrow B_2Cl_4 + Hg_2Cl_2$$

Other diboron tetrahalides are prepared from B_2Cl_4 in the following manner :

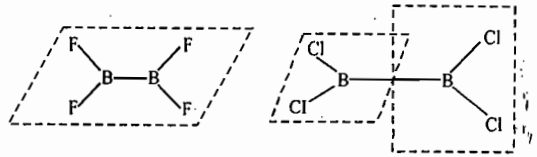
$$B_2Cl_4 \xrightarrow[\text{room temperature}]{SbI_3} B_2F_4 \; ; \; B_2Cl_4 \xrightarrow[-80°C]{BBr_3} B_2Br_4$$

The above diboron tetrahalides burn when brought in contact with air. They react with hydrogen to give BHX_2 and B_2H_6. They are electron-deficient compounds and react with Lewis bases to form stable adducts, $B_2X_4(Base)_2$.

They add to unsaturated hydrocarbons as shown below :



It has been observed that thermal stability of diboron tetrahalides varies with the extent of $p\pi - p\pi$ bonding between B and X. Thus, B_2F_4 which has a planar structure with maximum possibility of $p\pi - p\pi$ bonding is more stable than B_2Cl_4 which has a staggered structure as shown :



Other less studied lower halides of boron are B_4X_4, B_8X_8, B_9X_9, etc. (X = Cl, Br).

Lower Halides of Aluminium, Gallium, Indium and Thallium. All the four elements form monohalides many of which, however, are quite unstable. For instance, AlF, GaF and InF are all unstable gases. AlF, being the most unstable, undergoes quick decomposition into Al and AlF_3

$$3AlF \longrightarrow 2Al + AlF_3$$

Other monofluorides also decompose, though less quickly, in a similar manner.

For a particular element of Group 13, the monohalides of other halogens are more stable than the monofluoride. Thus, gallium(I) chloride, bromide and iodide are thermodynamically more stable than gallium(I) fluoride. The stability of gallium(I) halides, increases with increase in the size of the halide ion. The compound Ga_2Cl_4 is, actually, a mixed halide of Ga(I) and Ga(III) and its correct formula is $[Ga^I[Ga^{III}Cl_4]$. Similarly, indium(I) chloride, bromide and iodide are thermodynamically more stable than indium (I) fluoride. The chloride of indium, In_2Cl_3, appears to have In in the oxidation state of 1·5 but actually it contains both In(I) and In(III) ions and the correct formula of this halide has been shown to be $In_3^I[In^{III}Cl_6]$. Thallium(I) halides are the most stable amongst the monohalides of Group 13 elements. These can be easily prepared by reacting any thallium (I) salt (*e.g.*, $TlClO_4$) with the appropriate alkali halide.

The monohalides, in general, can be prepared by heating the trihalides with the metal.

$$MX_3 + 2M \xrightarrow{Heat} 3MX$$

Indium monohalides can also be prepared by heating indium in a current of the halogen or by heating it with mercuric halide.

$$2In + X_2 \xrightarrow{Heat} 2InX$$

$$2In + 2HgX_2 \xrightarrow{>300°C} Hg_2X_2 + 2InX$$

Several lower halides of thalium are also known (*e.g.*, $TlCl_2$, $TlBr_2$, Tl_2Cl_3, Tl_2Br_3). All these are mixed halides of Tl(I) and Tl(III).

4. Complexes of Group 13 Elements

On account of vacant *p* orbitals, Group 13 elements form a number of complexes. Alkali metal boron hydrides such as $NaBH_4$ and $LiBH_4$ are examples of well known complexes of boron. These contain the complex ion, BH_4^- which is formed by sp^3 hybridisation of the orbitals of boron. It is, therefore, tetrahedral in structure, as shown in Fig. 3.

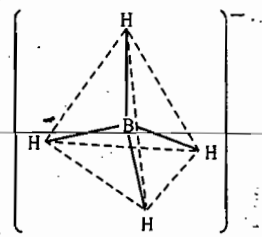
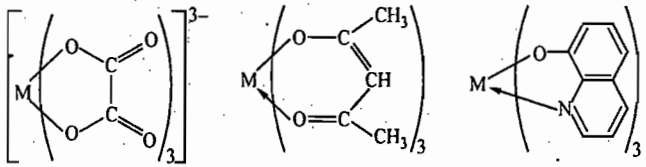


Fig. 3. Tetraheral structure of $[BH_4]^-$ ion.

Similar tetrahderal complexes are formed by other elements of Group 13. Well known examples are $Li[AlH_4]$, $NH_4[AlF_4]$, $Na[GaCl_4]$, $Li[TlBr_4]$, etc.

In addition to the above tetrahderal halide and hydride complexes, many octahedral complexes such as $[GaCl_6]^{3-}$, $[InCl_6]^{3-}$, $[TlCl_6]^{3-}$, etc., are also known. The most important octahedral complexes of Group 13 elements are those which are formed with chelate groups such as oxalate, acetyl acetonate,

8-hydroxyquinoline, etc. Their structures are shown below :



oxalate complex acetyl acetone complex 8-hydroxyquinoline complex

II. Some Important Compounds of Group 13 Elements

BORIDES

Compounds of boron with elements (generally transition metals) which are more electropositive than boron itself are known as **borides.** The borides can be prepared by any of the following methods :

1. By heating the metal with boron.

$$Cr + 2B \xrightarrow{1100°C} CrB_2$$

2. By heating the metal or metal oxide with boron carbide.

$$Eu_2O_3 + 3B_4C \xrightarrow{1600°C} 2EuB_6 + 3CO$$

3. By heating the metal oxide with a mixture of B_2O_3 and carbon.

$$V_2O_5 + B_2O_3 + 8C \xrightarrow{1500°C} 2VB + 8CO$$

4. By heating the metal with a mixture of B_2O_3 and B_4C.

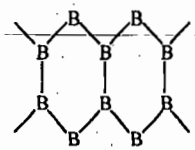
$$7Ti + B_2O_3 + 3B_4C \xrightarrow{2000°C} 7TiB_2 + 3CO$$

5. By electrolysis of a mixture of the metal oxide and B_2O_3 dissolved in a suitable molten salt bath using graphite as the anode and graphite or steel as the cathode. The boride of the metal gets deposited on the cathode.

Structures of Borides. The borides range from metal–rich borides (M_4B, M_5B, etc.) to boron–rich borides (MB_6, MB_{12}, etc.). Some of the salient features of the structures of various categories of borides are discussed below briefly.

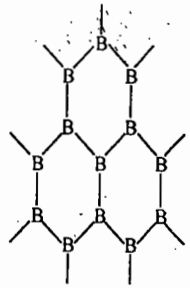
1. Borides having isolated boron atoms. These are metal–rich borides in which the boron atoms occupy the triangular prismatic or square antiprismatic interstices formed by metal atoms. The interstitial boron atoms are not bonded with each other. Examples are Mn_4B, Co_3B, Pd_3B, etc.

2. Borides having chains of boron atoms. As the proportion of boron atoms in borides increases, their tendency to catenate also increases. Thus, in borides M_3B_2 (B : M = 2/3 ; M = V, Nb, Ta), the interstitial boron atoms are present as B_2 units. The borides with the formula MB (B : M = 1 ; M = Ti, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, etc.) have structures with single chains of boron atoms while the borides M_3B_4(B : M = 4 : 3 ; M = V, Nb, Cr, Ta, Mn, etc.) have structures containing double chains of boron atoms, as shown.



3. Borides having extended two-dimensional network. In structures of borides with formula MB_2 (B : M = 2 ; M = Mg, Al, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, etc.), boron atoms further catenate to produce two-dimensional network of boron atoms. This class of borides includes some of the best

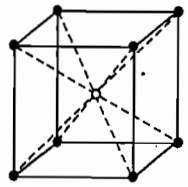
electrically conducting, hardest and highest-melting of all the borides. The structure of borides MB_2 consists of alternating layers of close packed metal atoms and two-dimensional sheets of boron atoms made up of interconnecting B_6 rings, as shown.



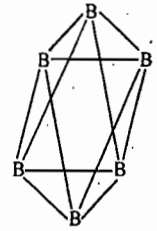
4. Borides with three-dimensional network. Borides with the formulae MB_4, MB_6, MB_{12}, etc., contain a three-dimensional network of boron atoms. The structure of MB_6 (M = La) is similar to that of CsCl. The B_6 octahedra take the place of Cl^- and the metal M takes the place of Cs^+. The B_6 octahedra are linked with each other along the edges of a cube so that there is an infinite three-dimensional network of boron atoms, as shown.

The borides with the general formula MB_{12} (M = Y) have NaCl type structure in which B_{12} cubo-octahedral units, occupy the place of Cl^- and the metal M takes the place of Na^+. The B_{12} units are linked with each other to produce a three-dimensional network of boron atoms. The structure of borides with the general formula MB_4 (M = La) also contain a three-dimensional network of B_6 octahedra interconnected with B_2 units so that the structure can be said to be a transition between the structures of MB_2 and MB_6.

● is B_6 unit
o is metal M



CsCl type structure of MB_6



Structure of B_6 unit

Properties and Uses. Borides possess some unusual properties. They are generally extremely hard, non-volatile refractory substances and are fairly inert chemically. Their electrical and thermal conductivities are many times higher than those of the corresponding pure metals. Their melting points are also much higher than those of the corresponding pure metals.

The borides TiB_2, ZrB_2 and CrB_2, being very hard and very high melting, are used for making turbine blades, combustion chambers and rocket nozzles. The ability of borides to withstand attack by molten metals, slags, salts, etc., makes them useful materials for the fabrication of high temperature reactor vessels, crucibles, etc. The borides are employed as electrodes in high temperature electrolyses due to their inertness to chemical attack at high temperatures and possessing very high electrical conductivity. Since ^{10}B has very high absorption cross-section for thermal neutrons and the products of reaction (n, α) of ^{10}B are stable non-radioactive Li and He, the metal borides are extensively used as neutron shields and control rods in nuclear power plants.

BORON HYDRIDES, BORANES

Boron does not combine directly with hydrogen to form hydrides. Nevertheless, a number of interesting **boron hydrides** are known. These are called **boranes** on analogy with alkanes. These are gaseous substances at ordinary temperatures.

Although it is expected that boron would form the hydride BH_3 yet this compound is unstable at room temperature. However, a large number of higher hydrides of boron are known. These hydrides can be divided into two series depending upon their general formulae which are B_mH_{m+4} and B_mH_{m+6}. Some common compounds belonging to the two series are given below :

B_mH_{m+4}	Series	B_mH_{m+6}	Series
B_2H_6	Diborane (6)	B_4H_{10}	Tetraborane (10)
B_5H_9	Pentaborane (9)	B_5H_{11}	Pentaborane (11)
B_6H_{10}	Hexaborane (10)	B_6H_{12}	Hexaborane (12)
B_8H_{12}	Octaborane (12)	B_8H_{14}	Octaborane (14)
$B_{10}H_{14}$	Decaborane (14)	B_9H_{15}	Enneaborane (15)
		$B_{10}H_{16}$	Decaborane (16)

The numerals in the above names indicate the number of hydrogen atoms present in the borane. The boranes of B_mH_{m+6} series are comparatively less stable.

Several **borane anions** are known which can be assumed to be derived from the three above mentioned series of boranes by the removal of one or two protons. Thus, borane anions can be categorised into $B_mH^-_{m+1}$, $B_mH^{2-}_m$, $B_mH^-_{m+3}$, $B_mH^{2-}_{m+2}$, $B_mH^-_{m+5}$ and $B_mH^{2-}_{m+4}$.

The boranes catch fire spontaneously in air. They are readily hydrolysed yielding boric acid. However, B_9H_{15} and $B_{10}H_{14}$ are quite stable and do not hydrolyse readily. The most important hydride of boron is diborane which has been described below in some details.

Diborane, B_2H_6

Preparation. It is the simplest of the hydrides of boron and can be prepared by the following methods :

1. By the reaction of iodine on sodium borohydride in diglyme.

$$2NaBH_4 + I_2 \xrightarrow{\text{Diglyme}} B_2H_6 + 2NaI + H_2$$

2. By passing silent electric discharge through a mixture of hydrogen and boron trichloride (vapour) at a low pressure.

$$2BCl_3 + 6H_2 \xrightarrow[\text{discharge}]{\text{Electric}} B_2H_6 + 6HCl$$

3. By the reduction of boron trichloride with lithium aluminium hydride.

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

4. By reducing gaseous boron trifluoride with sodium hydride at 180°C.

$$2BF_3 + 6NaH \longrightarrow B_2H_6 + 6NaF$$

Properties. 1. Physical State. Diborane is a colourless gas with a foul smell.

2. Stability. It is stable only at low temperatures. When heated at temperatures between 100°C and 250°C in a closed vessel, it changes to a number of higher hydrides :

$$B_2H_6 \xrightarrow{\text{Heat}} B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, \text{etc.}$$

The process, evidently, involves a series of decompositions and polymerisations, the first step being decomposition of B_2H_6 into BH_3.

3. Action of oxygen. Diborane and other boranes have attracted the attention of technologists on account of a large amount of energy released during their combustion. For example,

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O ; \qquad \Delta H = -2165 \text{ kJ mol}^{-1}$$

4. Hydrolysis. It gets hydrolysed readily yielding boric acid.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

5. Action with alkalies. Diborane dissolves in strong alkali solutions giving metaborates and evolving hydrogen.

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

6. Action with metals. Diborane reacts slowly with active metals such as Na, K, Ca or their amalgams. However, the reaction becomes fast in the presence of ether.

$$2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$$

The anion $B_3H_8^-$ formed as above was the first known polyborane anion.

7. Action with carbon monoxide. It reacts with carbon monoxide at 100°C and 20 atm pressure to form the carbonyl H_3BCO.

$$B_2H_6 + 2CO \longrightarrow 2H_3BCO$$

8. Action with halogens. It reacts with halogens under different conditions to form haloboranes and halodiboranes.

$$B_2H_6 + 6Cl_2 \xrightarrow{\text{low temp.}} 2BCl_3 + 6HCl$$

$$2B_2H_6 + 7Br_2 \xrightarrow{\text{low temp.}} B_2H_5Br + 7HBr + 2BBr_3$$

I_2 does not react with B_2H_6.

9. Action with halogen acids. Diborane reacts with halogen acids to give halodiboranes and evolving hydrogen.

$$B_2H_6 + HX \longrightarrow B_2H_5X + H_2$$

10. Action with hydrides. It combines with hydrides of alkali metals to form complex hydrides.

$$B_2H_6 + 2NaH \longrightarrow 2Na[BH_4]$$

11. Addition to alkenes and alkynes. Diborane adds to alkenes and alkynes in ether at room temperature to form organoboranes.

$$6RCH{=}CH_2 + B_2H_6 \longrightarrow \underset{\text{Organoborane}}{2B(CH_2CH_2R)_3}$$

The reaction is known as hydroboration reaction and has been of great synthetic utility in organic chemistry.

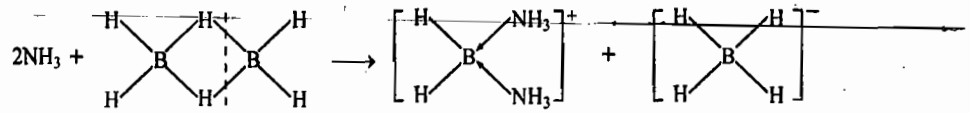
12. Action with ammonia. Diborane reacts with ammonia, the products depending upon the conditions of experiment.

(*i*) $$B_2H_6 + 2NH_3 \xrightarrow{\text{low temp.}} \underset{\text{Diammoniate of diborane}}{B_2H_6.2NH_3}$$

(*ii*) $$nB_2H_6 \xrightarrow[\text{high temp.}]{\text{Excess } NH_3} \underset{\text{Boron nitride}}{(BN)_n}$$

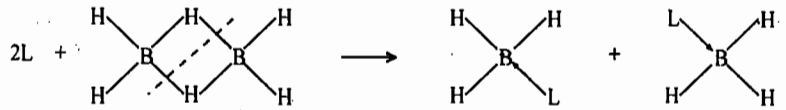
(*iii*) $$3B_2H_6 + 6NH_3 \xrightarrow{200°C} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

The compound $B_2H_6.2NH_3$ obtained in reaction (*i*) is ionic and exists as $[H_3N{\rightarrow}BH_2{\leftarrow}NH_3]^+[BH_4]^-$. Its formation can be explained by assuming unsymmetric cleavage of BHB bridges of B_2H_6, as shown below :



$N(CH_3)_3$ reacts with B_2H_6 to give $Me_3N{\rightarrow}BH_3$. Similar compounds are obtained from the reaction of B_2H_6 with PF_3, Me_2S, Et_2S, etc. These reactions can be explained by assuming symmetric cleavage of

BHB bridges of B_2H_6 by the Lewis bases mentioned above, as shown below :



(L stands for Lewis base such as $N(CH_3)_3$, PF_3, Me_2S, Et_2S).

13. Action with boron halides. Diborane reacts with boron halides to produce halodiborane.

$$B_2H_6 + BBr_3 \longrightarrow B_2H_5Br + BHBr_2$$

14. Methylation of diborane. $B(CH_3)_3$ and $Pb(CH_3)_4$ react with B_2H_6 to give methylated products of the composition $(CH_3)_n B_2H_{6-n}$ (n = 1 to 4).

15. Action with methanol. Diborane reacts with methanol to give methoxy products $B(OCH_3)_3$, $BH(OCH_3)_2$ and $BH_2(OCH_3)$.

Structure of Diborane. Boranes provide interesting examples of *electron-deficient compounds*. We may consider the case of diborane, B_2H_6, as an example. Since boron atom in excited state has three half-filled orbitals, it has three electrons available for sharing. Therefore, it can link to itself three hydrogen atoms. Thus, while each boron atom in diborane can link to itself three hydrogen atoms, there are no electrons left to form a bond between the two boron atoms. Spectroscopic studies reveal that the structure of diborane is as shown in Fig. 4.

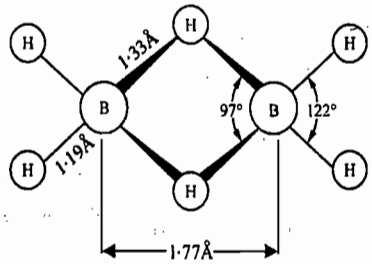


Fig. 4. Structure of diborane molecule.

The various bond distances and angles are as shown.

Four hydrogen atoms, two on the left and two on the right, known as *terminal hydrogens*, are in different environments from the other two hydrogen atoms which are known as the bridging atoms. The two boron atoms and the four terminal hydrogen atoms lie in the same plane while the two boron atoms and the two bridging hydrogen atoms, one above and the other below, lie in a plane perpendicular to this plane.

The **bridge structure** discussed above is supported by the following facts :

1. Heat capacity measurements have shown that the rotation of the two ends of the molecule against each other is very much hindered. This indicates that the bridging hydrogen atoms lie in a plane at right angles to the plane in which the rest of the molecule lies. In a molecule like ethane, in which there are no bridging hydrogen atoms, the hindrance to this type of rotation is very low.

2. Nuclear magnetic resonance and Raman spectra have shown that four hydrogens are of one type and two hydrogens are of another type. In ethane all the six hydrogens are known to be equivalent.

3. Diborane cannot be methylated beyond $(CH_3)_4B_2H_2$. The hydrogens which cannot be methylated, evidently, are in a different environment. These are the bridging hydrogen atoms.

Bonding in Boranes

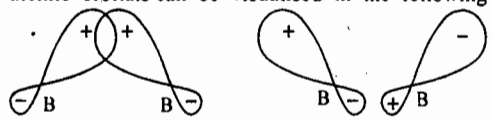
The bonding in boranes may be explained on the basis of an idea of *three centre–two electron* (3c – 2e) types of bonds proposed by Longuet-Higgins in 1949. The idea was later refined by Lipscomb and his coworkers.

Three Centre–two electron Bonds. In molecular orbital theory of covalent bonding, two atomic orbitals of the same symmetry and similar energy linearly combine with each other resulting in the formation of two molecular orbitals by the LCAO method (Chapter 4 on Chemical Bonding).

In a similar manner, if three atomic orbitals of same symmetry and similar energy combine linearly, they would give rise to three molecular orbitals (the number of atomic orbitals which combine linearly is always equal to the number of molecular orbitals formed).

The idea of linear combination of three atomic orbitals can be visualised in the following manner :

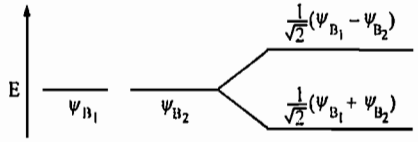
Let ψ_{B_1} be one of the four hybrid orbitals of one boron atom which combines linearly with a hybrid orbital ψ_{B_2} of another boron atom. This results in the formation of two molecular orbitals, *viz.*, $1/\sqrt{2}(\psi_{B_1} + \psi_{B_2})$ and $1/\sqrt{2}(\psi_{B_1} - \psi_{B_2})$. The two linear combinations resulting in the formation of two molecular orbitals are as shown.



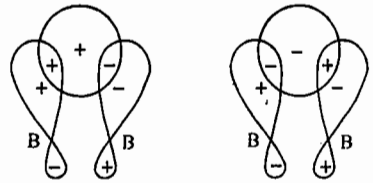
I — $\frac{1}{\sqrt{2}}(\psi_{B_1} + \psi_{B_2})$ Additive combination

II — $\frac{1}{\sqrt{2}}(\psi_{B_1} - \psi_{B_2})$ Subtractive combination

The additive combination I brings the positive lobe of ψ_{B_1} near the positive lobe of ψ_{B_2} making a *positive overlap* possible between ψ_{B_1} and ψ_{B_2}. This results in a decrease of energy of the molecular orbital formed by this combination. The subtractive combination II brings the positive lobe of ψ_{B_1} near the negative lobe of ψ_{B_2} making only *negative overlap* possible between ψ_{B_1} and ψ_{B_2}. This results in an increase in energy of the molecular orbital formed by the combination. The relative energies of the two molecular orbitals are represented as shown.



Let us now combine linearly the atomic orbital of H atom ψ_H with molecular orbital of boron atom which has the same symmetry and similar energy as that of ψ_H. The molecular orbital $1/\sqrt{2}(\psi_{B_1} - \psi_{B_2})$ cannot combine with ψ_H either by addition or by subtraction, as shown.

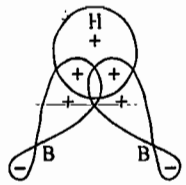


III — Additive combination. Net overlap is zero

IV — Subtractive combination. Net overlap is zero

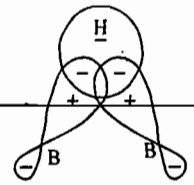
As can be seen, the net overlap in both the cases is zero. Hence, such combinations do not occur.

However, the molecular orbital $1/\sqrt{2}(\psi_{B_1} + \psi_{B_2})$ would easily combine with ψ_H, both by addition as well as subtraction, as illustrated below :



V

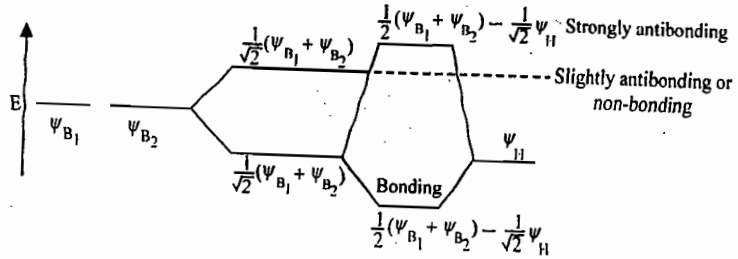
Additive combination of $1/\sqrt{2}(\psi_{B_1} + \psi_{B_2})$ with ψ_H. Net overlap is non-zero and positive. Hence, such a combination is effective and leads to lowering of energy.



VI

Subtractive combination of $1/\sqrt{2}(\psi_{B_1} + \psi_{B_2})$ with ψ_H. Net overlap is non-zero and negative. Hence such a combination is effective in the negative sense and leads to increase in energy.

The normalised linear combination of the *two-centre* molecular orbital $1/\sqrt{2}(\psi_{B_1} + \psi_{B_2})$ with ψ_H to give two 3-centre bonding and antibonding molecular orbitals is shown below :

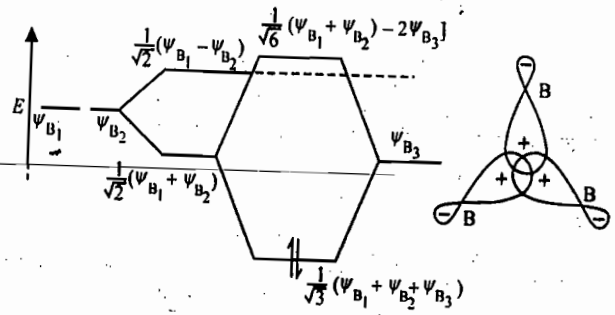


Thus, a linear combination of ψ_{B_1}, ψ_{B_2} and ψ_H results in three molecular orbitals, one of which is *bonding* (V), the other is *slightly antibonding* or *non-bonding* (III or IV) as ψ_H does not affect its energy and the last one is *strongly antibonding* (VI).

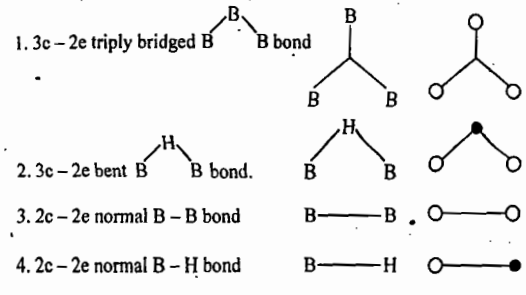
In a molecular orbital wave function obtained by linearly combining a number of atomic orbital wave functions, the square of the coefficient of any atomic orbital wave function gives the contribution of that wave function to the molecular orbital wave function. Since each atomic orbital is completely distributed in the three molecular orbitals, the sum of the squares of the coefficients of the atomic orbital wave functions appearing in the three molecular orbital wave functions is equal to unity. Thus, the contributions of ψ_{B_1} in the bonding, non-bonding and antibonding molecular orbitals are $(1/2)^2$, $(1/\sqrt{2})^2$ and $(1/2)^2$, respectively. The sum of these contributions is, evidently, equal to unity. Also, since each molecular orbital wave function is normalised, the sum of the squares of the coefficients of atomic orbital wave functions in it equals unity. Thus, the sum of the squares of the coefficients of atomic orbital wave functions in the bonding molecular orbital is $(1/2)^2 + (1/2)^2 + (1/\sqrt{2})^2 = 1$. The same is true of the sum of the squares of coefficients of all the atomic orbital wave functions in each of the remaining two molecular orbitals.

The two electrons responsible for the formation of a *three centre-two electron bond* B⟨H⟩B would obviously occupy the bonding molecular orbital.

A similar three centre-two electron bond B⟨B⟩B can be formed by a linear combination of the three hybrid atomic orbitals ψ_{B_1}, ψ_{B_2} and ψ_{B_3} of the three boron atoms of the cluster. The shape of only the resulting bonding molecular orbital in shown below :



The following types of bonds are thus assumed to be involved in bonding in the case of boranes :



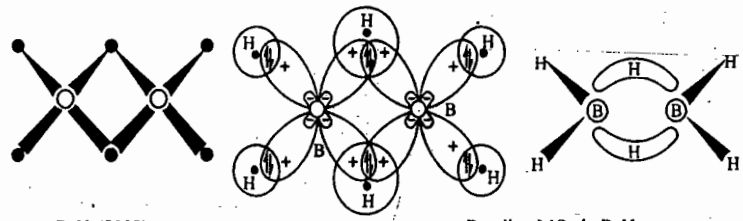
In the above representation and in the ensueing representations of skeletal structures, O denotes B and • denotes H.

The electrons involved in bonding in the framework (skeletal structure) of B_n cluster in boranes are referred to as 'framework electrons'. The B – H – B bonds are considered as part of the B_n framework whereas the terminal B – H bonds are not. Although the framework electrons of B_n cluster are highly delocalised, *i.e.*, they belong to all the boron atoms of the framework, yet the localised 3c – 2e and 2c – 2e molecular orbital approach can explain the main features of the structures of boranes at least qualitatively, as illustrated below.

Each boron atom has three valence electrons of which one electron is used up by each boron atom of the framework in the normal 2c – 2e terminal B – H bond and the remaining two electrons are contributed towards bonding in the B_n framework. However, B atom of each terminal BH_2 group contributes one electron to B_n framework. Thus, overall bonding in boranes is codified as a four digit number, called 'styx' number. The first digit represents the number of 3c – 2e B⟨H⟩B bonds in the structure. The second, third and the fourth digit represents, respectively, the number of the 3c – 2e B⟨B⟩B or B⟨B⟩B bonds, normal 2c – 2e B – B bonds and the terminal BH_2 groups.

Bonding in Boranes. The nature of bonding in some of the boranes is discussed below. The styx number of each borane is also given in brackets.

Bonding in B_2H_6. Valence orbitals of each boron atom in B_2H_6 are sp^3 hybridised. The two terminal BH_2 groups are present in one plane and the bridged B⟨H⟩B part of the molecule is present in a plane perpendicular to the plane containing the two BH_2 groups. Since two valence electrons of each boron atom are used up in BH_2 bonding, the remaining valence electron of each boron atom is used in BHB bonding. Thus, each boron atom contributes one valence electron towards the 3c – 2e BHB bond. The nature of the 3c – 2e BHB bond has already been discussed above in details. The bonding molecular orbitals involved in B_2H_6 and the structure of the molecule are represented below.



B_2H_6(2002) Bonding MOs in B_2H_6

As already mentioned, the B⟨H⟩B bridges are considered as part of the B_n framework. The valence electrons of the two boron atoms can thus be accounted for as follows :

Total number of valence electrons of two boron atoms = 6

Electrons used up in two B⟨H⟩B bridges = 2

Electrons used up in the four terminal B–H bonds = 4

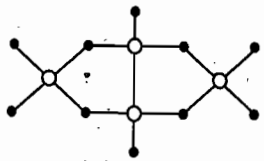
Alternatively,

Total numbers of valence electrons of 2 boron and 6 hydrogen atoms = 6 + 6 = 12

Electrons used up in the two B⟨H⟩B bridges = 4

Electrons used up in the four terminal B – H bonds = 8

Bonding in B_4H_{10}. The boding in B_4H_{10} can be explained more easily by writing the plane projection of its structure, as shown.

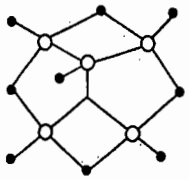


○ B atom ● H atom

Plane projection of the structure of B_4H_{10} (4012)

There are, evidently, four B⟨H⟩B bridges, no B⟨B⟩B or B⟨B⟩B triple bridge, one B – B bond and two terminal BH_2 groups in B_4H_{10}. Hence, out of the 12 valence electrons of 4 boron atoms, 4 electrons are used up in forming the four B⟨H⟩B bridge bonds ; 2 electrons are used up in one B – B bond and the remaining 6 electrons are used up in the six terminal B – H bonds. Alternatively, out of the 22 valence electrons of four boron and ten hydrogen atoms in B_4H_{10}, 8 electrons are used up in the four 3c – 2e B⟨H⟩B bridge bonds, 2 electrons are used up in the single 2c – 2e B – B bond while 12 electrons are used up in the six 2c – 2e B – H bonds.

Bonding in B_5H_9. The bonding in B_5H_9 can be explained conveniently by considering the plane projection of its structure, as shown.

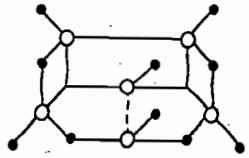


Plane projection of the structure of B_5H_9 (4120).

Out of the 15 valency electrons of five boron atoms, 4 electrons are used up in four B⟨H⟩B bridge bonds, 2 electrons in one B⟨B⟩B triple bridge bond, 4 electrons in the two B – B bonds and the remaining 5 electrons are used up in the terminal five B – H bonds.

Alternatively, out of 24 valence electrons of five boron and nine hydrogen atoms involved in bonding in B_5H_9, 8 electrons are used up in four 3c – 2e B⟨H⟩B bridge bonds, 2 electrons in one 3c – 2e B⟨B⟩B triple bridge bond, 4 electrons in the two 2c – 2e B – B bonds and the remaining 10 electrons in the five 2c – 2e B – H bonds.

Bonding in B_6H_{10}. The bonding in B_6H_{10} can be explained satisfactorily by considering the plane projection of its structure, as shown.

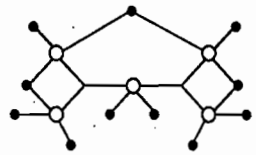


Plane projection of the structure of B_6H_{10} (4220)

Out of the 18 valence electrons of six boron atoms, 4 electrons are used up in four B⟨H⟩B bridge bonds, 4 electrons in two B⟨B⟩B triple bridge bonds, 4 electrons in two B – B bonds and the remaining 6 electrons in the six terminal B – H bonds.

Alternatively, out of a total of 28 valence electrons of six boron and 10 hydrogen atoms in B_6H_{10}, 8 electrons are used up in four 3c – 2e B⟨H⟩B bridge bonds, 4 electrons in two 3c – 2e B⟨B⟩B triple bridge bonds, 4 electrons in two 2c – 2e B – B bonds and the remaining 12 electrons in the six 2c – 2e terminal B–H bonds.

Bonding in B_5H_{11}. The bonding in B_5H_{11} can be explained easily by considering the plane projection of its structure, as shown.

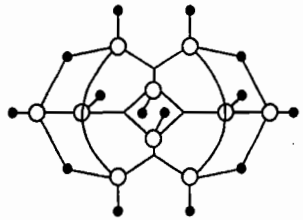


Plane projection of the structure of B_5H_{11} (3203)

There are 15 valence electrons of five boron atoms in B_5H_{11} out of which 3 electrons are used up in three B⟨H⟩B bridge bonds, 4 electrons in two B⟨B⟩B triple bridge bonds and the remaining 8 electrons in the eight terminal B – H bonds.

Alternatively, out of a total of 26 valence electrons of five boron and eleven hydrogen atoms, 6 electrons are used up in three 3c – 2e B⟨H⟩B bridge bonds, 4 electrons in the two 3c — 2e B⟨B⟩B triple bridge bonds and the remaining 16 electrons in the eight terminal B – H bonds.

Bonding in $B_{10}H_{14}$. A plane projection of the structure of $B_{10}H_{14}$ (as shown) explains the bonding in this borane. As can be seen,



Plane projection of the structure of $B_{10}B_{14}$ (4620)

there are four B⟨B⟩B triple bridge bonds and two B⟨B⟩B bent bridge bonds in this structure. Hence, out of the 30 valence electrons of ten boron atoms, 12 electrons are used up in the six B⟨B⟩B bridge bonds, 4 electrons are used up in four B – H bridge bonds and 4 electrons are used in the two B–B bonds. The remaining 10 electrons are used up in the terminal B – H bonds.

Alternatively, out of the 44 valence electrons of ten boron and fourteen hydrogen atoms in $B_{10}H_{14}$, 8 electrons are used up in the four 3c – 2e B⟨H⟩B bridge bonds, 8 electrons in the four 3c – 2e triple bridge B⟨B⟩B bonds, 4 electrons in the two 3c – 2e B⟨B⟩B bent bridge bonds, 4 electrons in the two 2c – 2e B – B bonds and the remaining 20 electrons are used up in the ten terminal 2c – 2e B–H bonds.

Nomenclature. Boranes are named by indicating the number of B atoms with a Latin prefix and the number of H atoms by an arabic numeral in parentheses. Names of anions end in **ate** rather than **ane** and specify the number of H atoms, B atoms and the charge (in that order). The following examples will clarify the nomenclature :

$B_{10}H_{14}$	Nidodecaborane (14)
B_5H_{11}	Arachnopentaborane (11)
$B_{10}H_{10}^{2-}$	Decahydroclosodecaborate (2 –)
$B_{10}H_{14}^{2-}$	Tetradecahydroarachnodecaborate (2 –)

The words closo, nido, arachno indicate a closed skeletal structure, an open skeletal structure and a more open skeletal structure, respectively. The meanings of these words will become more clear to the students when they go through the classification of boranes and carboranes made on the basis of their skeletal structures to be discussed shortly.

Carboranes or Carboboranes

Carboranes or carboboranes are compounds of carbon, boron and hydrogen in which carbon and boron atoms occupy the vertices of a triangular polyhedron. These compounds may be considered to have been derived from boranes by the replacement of BH units by CH units. Carboranes and boranes having the same number of electrons in their bonding frame work, have similar skeletal structures. Three structually different types of carboranes, namely, *closo*, *nido* and *arachno* are known at present (see the next section for this nomenclature). Amongst these the closo carboranes have been studied in greater details. Hence only closo carboranes would be discussed here.

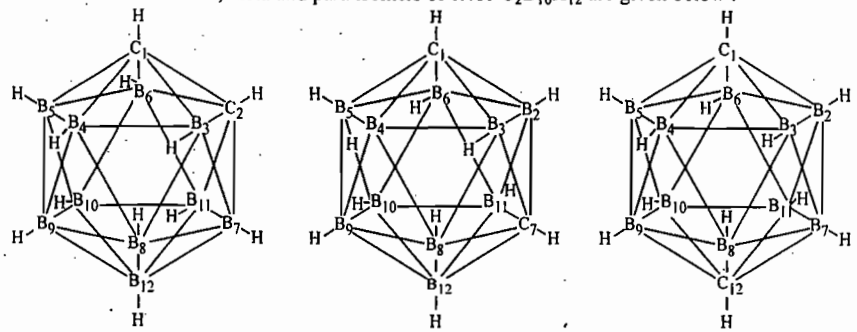
Closo Carboranes. Closo carboranes can be easily prepared from an alkyne and a borane by pyrolysis. Most closo carboranes are stable even upto 400°C. At elevated temperatures they tend to undergo rearrangement to give even more stable isomers.

The most important member of closo carborane family is **dicarbacloso dodecacarborane ($C_2B_{10}H_{12}$)** which has a closed icosachedral structure. The compound occurs in three isomeric forms, *viz.*, ortho, meta and para. All the three isomers are quite stable in air and can be easily prepared as follows :

$$\text{nido } B_{10}H_{14} + 2Et_2S \longrightarrow H_2 + B_{10}H_{12}(SEt_2)_2 \xrightarrow{C_2H_2}$$

$$\underset{\text{(para isomer)}}{\text{Closo } 1,12,\ C_2B_{10}H_{12}} \xleftarrow{700°C} \underset{\text{(meta isomer)}}{\text{Closo } 1,7\ C_2B_{10}H_{12}} \xleftarrow{470°C} \underset{\text{(ortho isomer)}}{\text{Closo } 1,2\ C_2B_{10}H_{12}}$$

The structures of ortho, meta and para isomers of closo $C_2B_{10}H_{12}$ are given below :



(ortho) (meta) (para)

Dicarbacloso dodecacarborane reacts with butyl lithium as shown below :

$$\underset{\text{1, 2 or 1, 7 isomer}}{(CH)_2B_{10}H_{10}} + LiBu \xrightarrow[\text{ether}]{\text{Solvent}} LiC.CHB_{10}H_{10} \xrightarrow[(ii)\ \text{Solvent ether}]{(i)\ LiBu} LiC.CLiB_{10}H_{10}$$

The monolithium and dilithium derivatives can be used for preparing a number of C-substituted derivatives or carboranes as shown.

$$LiC.CLiB_{10}H_{10} \xrightarrow{I_2} (I)_2B_{10}H_{10}$$
$$\xrightarrow{CO_2} (HOOC.C)_2B_{10}H_{10}$$
$$\xrightarrow{NOCl} (C.NO)_2B_{10}H_{10}$$
$$\xrightarrow[H_2O]{HCHO} (C.CH_2OH)_2B_{10}H_{10}$$

Apart from the above derivatives of $(CH)_2B_{10}H_{10}$, a number of polycloso dodecacarboranes have also been synthesised. These derivatives have excellent thermal stability and have important industrial applications.

A number of carborane anions such as $B_9C_2H_{12}^-$, $B_9C_2H_{11}^{2-}$, $B_7C_2H_{11}^{2-}$, are known. These anions form metal complexes with Fe^{2+}, Co^{2+}, Pd^{2+}, etc., which have complicated structures whose discussion is beyond the scope of the book.

Classification of Boranes and Carboranes on the Basis of Their Skeletal Structures. Before we discuss the classification of boranes and carboranes on the basis of their skeletal structures, it would be useful to give Wade's rules for finding out the number of electrons present in the multicentred bonding orbitals of the skeletal structure or framework of a given borane or carborane. Although the concept of localised 3c – 2e and 2c – 2e molecular orbitals satisfactorily explains the bonding in comparatively simple carboranes and boranes, it is not very satisfactory in explaining the bonding in the more complicated boranes and carboranes having highly symmetrical polyhedral structures. In such cases, a molecular orbital description involving completely delocalised molecular orbitals is more useful. Although complete molecular orbital calculations in such cases are tedious, it is possible to give a set of *empirical rules*, called **Wade's rules,** to know the number of electron pairs in the multicentre bonding molecular orbitals of the skeletal structure of a given borane or carborane. These rules are listed below :

Wade's Rules. 1. Each BH unit is assumed to contribute two electrons to the skeletal bonding in a borane or carborane.

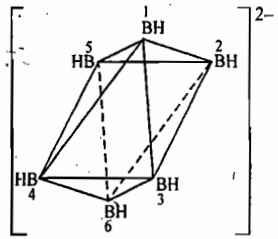
2. The negative charge on a borane or carborane anion is assumed to be used up in skeletal bonding.

3. Each additional H atom in borane or carborane is assumed to contribute one electron to the skeletal bonding.

4. Each CH unit in a carborane is assumed to contribute three electrons to the skeletal bonding.

We shall apply these rules for the classification of boranes and carboranes on the basis of their skeletal structures. On this basis, boranes and carboranes can be classified into the following three types :

A. Closo Boranes and Closo Carboranes. They have a completely closed triangular polyhedral structure in which all the vertices of the triangular polyhedron are occupied by B or C atoms. There are (m+1) electron pairs present in the multicentre bonding orbitals of skeletal structure (or 'cage' or 'framework') of closo boranes and closo carboranes (m is the total number of B and C atoms). The examples are $B_6H_6^{2-}$ and $(CH)_2B_{10}H_{10}$. The structure of $(CH)_2B_{10}H_{10}$ has already been discussed. The structure of closo $B_6H_6^{2-}$ anion is as shown.



In $B_6H_6^{2-}$ anion, m = 6. There are six BH units which according to Wade's rules, contribute 6×2 = 12 electrons to the bonding molecular orbitals of the skeletal structure. The charge of – 2 implies addition of two more electrons to such bonding orbitals. Thus, the total number of electron pairs present in the multicentre bonding orbitals is 6 + 1 = 7 (m + 1 = 7).

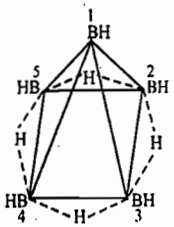
Similarly, in $(CH)_2B_{10}H_{10}$, m is 2+10 = 12. The two CH units, according to Wade's rules, contribute 2×3 = 6 electrons and the ten BH units contribute 10×2 = 20 electrons to the bonding molecular orbitals or the skeletal structure. Thus, there are 13 electron pairs (m + 1 = 13) present in the multicentre bonding orbitals of $(CH_2)B_{10}H_{10}$, commonly written as $C_2B_{10}H_{12}$.

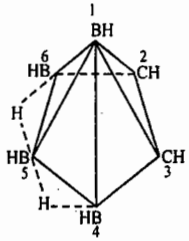
The C and B atoms in the closo structures are numbered in such a manner that the top vertex is given number 1 and the remaining vertices are numbered in a clockwise direction as shown in the structures of $B_6H_6^{2-}$ and $C_2B_{10}H_{12}$.

B. Nido Boranes and Nido Carboranes. These boranes and carboranes may be assumed to be derived from the closo triangular polyhedral structure of a closo borane or closo carborane by the removal of one of the vertices of the polyhedron. The resulting ***nido*** (or ***nestlike***) skeletal structure has (m + 2) electron pairs in its multicentre bonding orbitals. The examples are nido B_5H_9 and nido $C_2B_4H_8$ whose structures are given below :

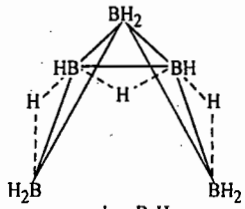
In nido B_5H_9 (m = 5), the five BH units contribute 5×2 = 10 electrons and the four extra hydrogens contribute 4×1 = 4 electrons to the bonding orbitals of the skeletal structure. There are thus 5 + 2 = 7 electron

pairs in the multicentre bonding orbitals of nido B_5H_9. Similarly, in the nido 2, 3, $C_2B_4H_8$ (m = 2 + 4 = 6), the two CH units contribute 2×3 = 6 electrons, the four BH units contribute 4×2 = 8 electrons and the two extra hydrogens contribute 2 electrons to the bonding orbitals of the skeletal structure of nido 2, 3, $C_2B_4H_8$.. Thus, there are 8 electron pairs (m + 2 = 8) in the multicentre bonding orbitals of the skeletal structure of this carborane.


nido B_5H_9

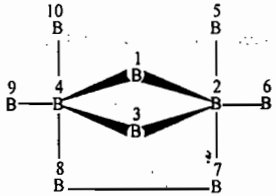

nido 2,3 $C_2B_4H_8$

C. Arachno Boranes and Arachno Carboranes. The structures of this type of boranes and carboranes may be assumed to have been derived from nido structures by the removal of the vertices of these structures. There are (m + 3) electron pairs in the multicentre bonding orbitals of boranes and carboranes. The examples are arachno B_5H_{11} and arachno $C_2B_7H_{13}$. The structure of arachno B_5H_{11} is as shown.


arachno B_5H_{11}

It can be seen by applying Wade's rules that arachno B_5H_{11} contains 5 + 3 = 8 electron pairs and arachno $C_2B_7H_{13}$ contains 9 + 3 = 12 electron pairs in the multicentre bonding orbitals of their skeletal structures.

For numbering the B and C atoms in a nido or an arachno structure, the open face is kept upward and their plane projections (showing only B and C atoms) are drawn viewing them from above. First, the interior B and C atoms of the plane projections are numbered in the clockwise direction followed by the numbering of exterior B and C atoms in the clockwise direction. Thus, for nido $B_{10}H_{14}$, the projections and the numbering of B_5H_{11} atoms are as shown :


Plane Projection of nido $B_{10}H_{14}$

Compounds of Boron with Nitrogen

Boron forms some interesting compounds with nitrogen, most significant of which are *boron nitride* and *borazine*.

Boron Nitride, BN. As already mentioned, boron nitride is obtained by the interaction of ammonia and diborane. Boron nitride is a white crystalline solid and resembles graphite in its structure, as shown in Fig. 5.

A boron atom bonded together with a nitrogen atom has 8 valence electrons, 3 from boron and 5 from nitrogen. This is the same number of electrons as are present in two adjacent carbon atoms in graphite. The structure of boron nitride, therefore, is very similar to that of graphite shown in Fig. 5(*b*). The B — N bonds in boron nitride are formed by the overlapping of sp^2 hybrid orbitals of boron and nitrogen atoms. The remaining electrons form pi bonds. Unlike graphite, where electrons are *completely delocalised* over all the carbon atoms of the lattice, the electrons in boron nitride are only *partially delocalised* over boron atoms leading to *unequal* B — N *bond lengths*. The layers are arranged in such a manner that boron atoms in one layer are immediately above the nitrogen atoms in the adjacent layer. On heating at 1800°C under a pressure of 85 atm, in the presence

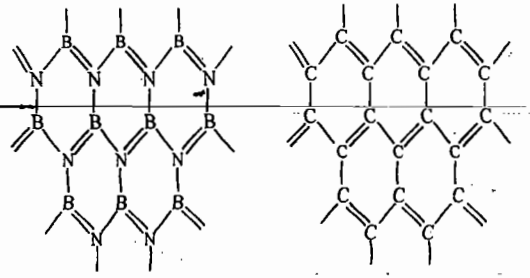

(*a*) Boron nitride (*b*) Graphite

Fig.5. Similarity in the structure of boron nitride and graphite.

of a catalyst, BN gets converted into another modification which, in strcuture, is comparable to diamond.

Borazine or Borazole. Borazine can be prepared by heating together BCl_3 and NH_4Cl. The initial product formed is trichloroborazine which on reducing with $NaBH_4$ yields borazine. It can also be prepared by treating $NaBH_4$ with NH_4Cl.

The **structure** of borazine is similar to that of benzene (Fig. 6).

In this structure, the valence shell orbitals of both boron and nitrogen atoms are sp^2 hybridised. Each nitrogen atom has one lone pair of electrons while each boron atom has an empty *p* orbital. The bonding in borazine is dative and it arises from the sidewise overlapping of fully filled *p* orbitals of nitrogen and empty *p* orbitals of boron. Because of the similarity of the structures of borazine and benzene, borazine is also known as **'inorganic benzene.**

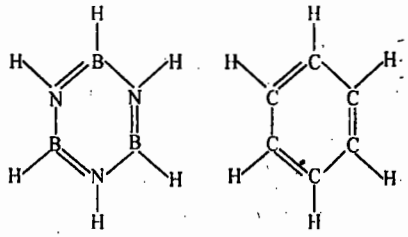

Borazine Benzene

Fig.6. Similarity in the structure of borazine and benzene.

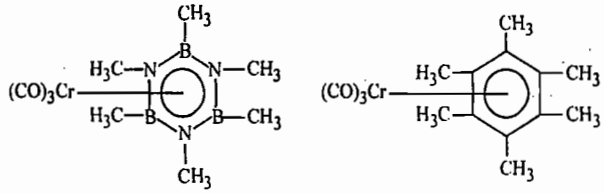
Molecular orbital calculations indicate that the electrons in borazine are only *partially delocalised* unlike benzene in which there is *complete delocalisation*. In fact, complete delocalisation in B_3N_3 ring is not expected either since N-π orbitals are of lower energy than the B-π orbitals. MO calculations indicate that the π electron-drift from N to B is less than the σ electron-drift from B to N due to greater electronegativity of N. These are thus the N atoms which are relatively more electronegative than B atoms in borazine. The π bonding stabilises the planar structure of borazine ring.

The retention of negative charge by nitrogen implies that chemically borazine would be different from benzene. It is thus much more reactive than benzene and readily undergoes addition reactions as, for example,

$$B_3N_3H_6 + 3HX \longrightarrow (H_2N-BHX)_3\ ;\quad X = Cl, OH, OR$$

Borazine undergoes hydrolysis at high temperature to yield NH_3 and $B(OH)_3$. It decomposes slowly on storage.

Borazine resembles benzene in forming similar metal complexes, as illustrated below :


Borazine metal complex Benzene metal complex

Oxo-Compounds of Boron

Ortho Boric Acid, H_3BO_3. Boron forms a number of acids of which ortho boric acid, commonly known as boric acid, is the most important.

Preparation. Boric acid can be prepared by the following methods.

1. From colemanite. A large proportion of the world's supply of boric acid is made from *colemanite*, *viz.*, calcium borate ($Ca_2B_6O_{11}.5H_2O$), occurring in California (U.S.A.) and South America. The mineral is powdered and mixed with boiling water. Sulphur dioxide is passed through the mixture when boric acid and calcium sulphite are formed.

$$Ca_2B_6O_{11} + 2SO_2 + 9H_2O \longrightarrow 2CaSO_3 + 6H_3BO_3$$

On cooling, boric acid crystallises out.

2. From borax. Boric acid is obtained on a large scale from borax. A hot concentrated solution of borax is treated with a calculated quantity of hydrochloric acid or sulphuric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

Properties. 1. It forms soft pearly-white needle-like crystals having a greasy feel.

2. *It is moderately soluble in water. The dissolution is accompanied by absorption of heat which is consistent with the fact that its solubility increases with rise in temperature.*

3. Boric acid is a very weak acid and ionises mainly as a monobasic acid and that, too, to a very limited extent. The dissociation constant of the acid is of the order of $1{\cdot}0\times10^{-9}$. It is not a proton donor but behaves as a Lewis acid, *i.e.*, as an acceptor of a pair of electrons from an $.OH^-$ ion.

As the concentration of aqueous solution increases beyond 0·025 M, the acidity increases. This anomaly has been explained as due to the formation of a polymeric species.

$$3B(OH)_3 \longrightarrow B_3O_3(OH)_4^- + 2H_2O + H^+$$

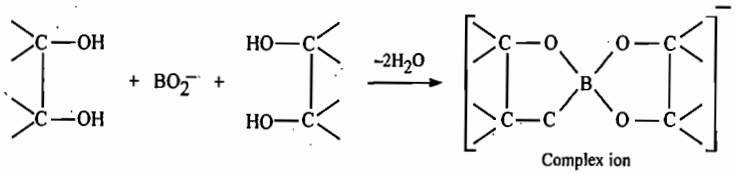
With strong alkalies, it forms salts known as metaborates.

$$B(OH)_3 + NaOH \longrightarrow B(OH)_4^- + Na^+ \longrightarrow \underset{\text{Sod. metaborate}}{Na^+BO_2^-} + 2H_2O$$

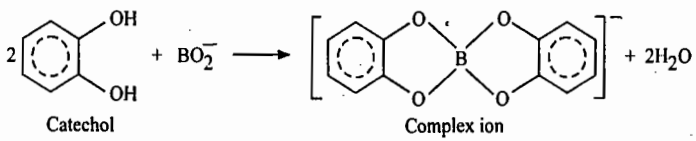
The end point in the titration of boric acid against sodium hydroxide is not sharp on account of excessive hydrolysis of sodium metaborate formed during titration.

$$NaBO_2 + H_2O \rightleftharpoons H_3BO_3 + NaOH$$

However, the addition of certain polyhydroxy compounds such as catechol, mannitol, glycerol or sugars to the titration solution checks the hydrolytic reaction and makes boric acid behave as a strong monobasic acid and the end point can thus be easily detected. The polyhydroxy compounds combine with the metaborate ion to form complex compounds, as illustrated below :



With catechol and mannitol, for instance, the complexation occurs as follows :



$$\underset{\text{Mannitol}}{C_6H_8(OH)_6} + BO_2^- \longrightarrow [C_6H_8(OH)_4BO_4] + 2H^+$$

The elimination of BO_2^- ion in the form of its complexes means no hydrolysis of the end product of the neutralisation reaction. As a result, boric acid ionises freely during titration against a strong alkali thus behaving as a strong acid.

4. On heating at 1000°C or a little above, orthoboric acid loses water to yield metaboric acid.

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$

When metaboric acid is heated at 160°C, tetraboric acid results.

$$4HBO_2 \longrightarrow H_2B_4O_7 + H_2O$$

At still higher temperatures it swells up giving a frothy mass and finally forms a glass of boron trioxide.

$$H_2B_4O_7 \longrightarrow 2B_2O_3 + H_2O$$

5. Boric acid when heated with CaF_2 and concentrated H_2SO_4, *yields boron trifluoride.*

$$3CaF_2 + 3H_2SO_4 + 2H_3BO_3 \longrightarrow 3CaSO_4 + 2BF_3 + 6H_2O$$

6. On heating boric acid with ethyl alcohol, ethyl borate is formed whose vapours burn with green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{Ethyl borate}}{(B(OC_2H_5)_3} + 3H_2O$$

7. $B(OH)_3$ acts as a strong acid in anhydrous H_2SO_4.

$$B(OH)_3 + 6H_2SO_4 \longrightarrow 3H_3O^+ + 2HSO_4^- + [B(HSO_4)_4]^-$$

Uses. 1. Boric acid is used in making enamels, pottery glazes and glass. 2. It is also used in medicines as an eye-wash (eye lotion). 3. It is used as a food preservative.

Structure of boric acid. In order to understand the structure of boric acid let us consider boron atom in ground state as well as in the excited state. It is evident that 3 singly occupied orbitals become available in the excited state which form bonds with three oxygen atoms. This, is, evidently, a case of sp^2 hybridisation.

Since only one electron from each oxygen atom enters into bond formation, the resulting unit is a trivalent ion, BO_3^{3-}, in which each boron atom is bonded to three oxygen atoms arranged at the corners of an equilateral triangle with boron atom lying in the centre.

The triangular BO_3^{3-} units are bonded together through hydrogen bonds into two-dimensional sheets, as shown in Fig. 7.

It is evident that each boron atom remains bonded to three oxygen atoms and each oxygen atom is bonded to a hydrogen atom. Thus, each unit now consists of H_3BO_3. The hydrogens provide the limbs (or bridges) between the oxygen atoms of different BO_3 units, as shown.

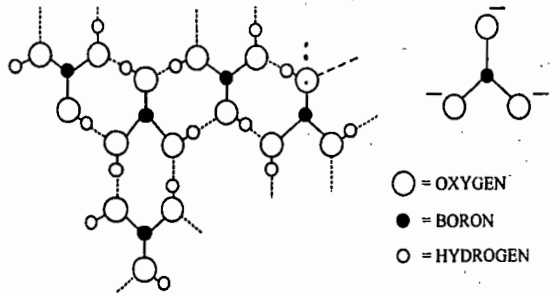


Fig.7. Two-dimensional sl eet structure of boric acid. Dotted lines represent hydrogen bonds.

Lithium Aluminium Hydride, $LiAlH_4$

Preparation. $LiAlH_4$ is prepared by reacting lithium hydride with anhydrous aluminium chloride in ether.

$$4LiH + \underset{\text{anhydrous}}{AlCl_3} \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl$$

On industrial scale, it is prepared by direct combination of the constituent elements under high pressure in the presence of ether.

$$Li + Al + 2H_2 \xrightarrow[\text{140°C, 350 atm}]{\text{ether}} LiAlH_4$$

Alternatively and preferably, $NaAlH_4$ is first prepared by direct synthesis which is then converted

into $LiAlH_4$ by treatment with LiCl.

$$Na + Al + 2H_2 \xrightarrow[140°C,\ 350\ atm]{ether} NaAlH_4$$

$$NaAlH_4 + LiCl \xrightarrow{ether} NaCl\ (s) + LiAlH_4$$

Properties. Lithium aluminium hydride is a white, non-volatile, crystalline solid which is freely soluble in ether and various glymes. It is stable below 120°C.

It is readily attacked by water and ethanol giving hydrogen gas.

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 2H_2$$

$$LiAlH_4 + 3C_2H_5OH \longrightarrow Li(AlH(OC_2H_5)_3] + 3H_2$$

It reacts with ethylene, ammonia, phosphine, arsine as well as primary and tertiary amines.

$$LiAlH_4 + 3C_2H_4 \longrightarrow Li[AlH(CH=CH_2)_3] + 3H_2$$

$$LiAlH_4 + 4NH_3 \longrightarrow Li[(Al(NH_2)_4] + 4H_2$$

$$LiAlH_4 + 4PH_3 \longrightarrow Li(Al(PH_2)]_4 + 4H_2$$

$$LiAlH_4 + 4RNH_2 \longrightarrow LiAl(NHR)_4] + 4H_2$$

$$LiAlH_4 + (CH_3)_3N \longrightarrow (CH_3)_3NAlH_3 + LiH$$

Uses. Lithium aluminium hydride is extensively used in organic as well as inorganic chemistry as a versatile reducing agent.

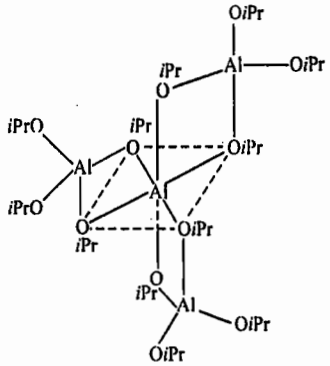
Aluminium Alkoxides, $Al(OR)_3$

These compounds, which are widely used as reducing agents in organic synthesis, can be prepared by the action of aluminium metal on alcohols in the presence of $HgCl_2$ as catalyst or by reacting $AlCl_3$ with sodium alkoxide.

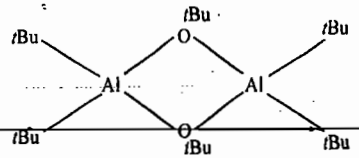
$$Al + 3ROH \xrightarrow{HgCl_2} Al(OR)_3 + 3/2\ H_2$$

$$AlCl_3 + 3RONa \xrightarrow{warm} 3NaCl + Al(OR)_3$$

Actually these alkoxides are complex compounds in which Al has a coordination number 4 and/or 6.



The most widely used aluminium alkoxides for reducing purposes are aluminium isopropoxide and aluminium tertiary butoxide. The former is a tetramer at room temperature whereas the latter is a dimer, as shown below:



Ultramarine. Ultramarine is a complex silicate of aluminium and sodium associated with about 12 per cent of sulphur. It has a fine blue colour and occurs rarely as a mineral. It can be prepared artificially by heating a mixture of kaolin, soda ash, sulphur and charcoal to bright red heat. At first a white mass is formed which in the presence of air changes to green. It is powdered and heated with more sulphur when the *blue* ultramarine, having the composition $Na_5Al_2Si_2S_3O_{12}$ is obtained.

If this product is heated in a stream of chlorine, a *violet* coloured variety of ultramarine is obtained. However, the blue variety is the most popular and is used in laundry for blueing purposes. It is also used in calico printing and in blue paints.

Organometallic Compounds of Group 13 Elements

These have been discussed in details in Chapter 34 on Organometallic Compounds.

QUESTIONS

1. (*a*) Give the electronic configurations of the elements of Group 13.
   (*b*) Why does boron differ from the rest of its family members ? Discuss the main points of difference.
   (*c*) "While Al, Ga, In and Tl form both covalent and electrovalent compounds, boron mostly forms covalent compounds." How would you explain this behaviour ?
2. (*a*) What is meant by diagonal relationship in periodic classification ? Discuss the diagonal relationship of boron with silicon.
   (*b*) $B(OH)_3$ is acidic, $Al(OH)_3$ is amphoteric while $Tl(OH)_3$ is distinctly basic in character. How would you account for this ?
3. (*a*) Account for the trivalency and monovalency of Group 13 elements.
   (*b*) Why is BBr_3 a better Lewis acid than BF_3 ?
   (*c*) How does boric acid ionise in water ? Why is its acidity increased by the addition of catechol?
4. Give the preparation and properties of boron halides. Why are these subtances called Lewis acids ?
5. (*a*) Give an account of the hydrides of boron with special reference to diborane.
   (*b*) Discuss in details the bridge structure of diborane. Bring out clearly the nature of bonds in hydrogen bridges.
   (*c*) Discuss in details the nature of bonding involved in B_2H_6, B_4H_{10}, B_6H_{10}, B_5H_{11} and $B_{10}H_{14}$.
6. Give reasons for the following :
   (*a*) Boron trichloride is monomeric while aluminimum trichloride is dimeric.
   (*b*) BF_3 is a weaker Lewis acid than BCl_3 and BBr_3.
7. (*a*) Discuss the gradation in properties of elements of Group 13 with respect to
   (*i*) oxidation state (*ii*) electron affinity
   (*iii*) metallic character (*iv*) electronegativity.
   (*b*) What is meant by back bonding ? On the basis of back bonding, explain why BF_3 is a weaker Lewis acid than BCl_3.
8. Explain the following :
   (*a*) Aluminium forms $[Al(OH)_6]^{3-}$ but $[B(OH)_6]^{3-}$ is not known.
   (*b*) The +1 oxidation state becomes progressively more stable from boron to thallium.
   (*c*) The B – X (X = F, Cl, Br, I) distance is shorter than what is expected theoretically in BX_3 molecules.
   (*d*) BF_3 is a weaker electron acceptor than BCl_3.
9. (*a*) Normally the ionization energy should decrease regularly as we move along a group. However, the ionisation energies (kJ mol^{-1}) of Group 13 elements are as follows :

B	Al	Ga	In	Tl
800	577	579	558	589

   How much you account for this anomalous behaviour ?
   (*b*) How does the structure of boron nitride differ from that of graphite ?
10. (*a*) How does boron occur in nature ? Describe briefly the extraction of boron.
    (*b*) How does boron react with
    (*i*) nitric acid (*ii*) sodium hydroxide (*iii*) magnesium (*iv*) nitrogen ?
11. (*a*) How is boric acid obtained from *colemanite* ? Discuss in details the structure of the acid.
    (*b*) How does boric acid react with (*i*) ethyl alcohol (*ii*) calcium fluoride in the presence of H_2SO_4 ?
    (*c*) What is the action of heat on boric acid ?
12. What are carboranes ? How are boranes and carboranes classified ?
13. What are Wades' rules ? Discuss the application of these rules in classifying carboranes into closo, nido and arachno carboranes. Discuss briefly how closo carbonanes are prepared.

16 THE ELEMENTS OF GROUP 14

Group 14 contains five elements, namely, **carbon, silicon, germanium, tin** and **lead.** Carbon is an essential constituent of all organic matter. Silicon is an important constituent of inorganic matter. Carbon and silicon are typical non-metals. Germanium has intermediate character while tin and lead are distinctly metals. Carbon occurs hardly upto 0·1 per cent in the earth's crust. However, combined with oxygen and hydrogen it occurs in all living tissues belonging to plant or animal kingdom It occurs as carbon dioxide in the atmosphere and as carbonates in rocks and minerals such as limestone, dolomite, etc. In free state, it occurs as coal, diamond and graphite.

Silicon occurs most abundantly, next only to oxygen, upto about 26 per cent in the earth's crust, as silica and silicates.

Germanium occurs rather sparsely. Tin occurs chiefly as SnO_2 in its ore known as *tin stone* while lead occurs as PbS in its ore known as *galena*.

Electronic Configurations. The electronic configurations of elements of Group 14 are shown in Table 1.

Thus, the general outer electronic configuration of the elements of this group may be written as $\mathbf{ns^2p^2}$.

TABLE 1

Electronic Configurations of Elements of Group 14

Element	At. No.	Electronic Configurations
Carbon, C	6	[He] $2s^2p^2$
Silicon, Si	14	[Ne] $3s^2p^2$
Germanium, Ge	32	[Ar] $3d^{10}4s^2p^2$
Tin, Sn	50	[Kr] $4d^{10}5s^2p^2$
Lead, Pb	82	[Xe] $4f^{14}5d^{10}6s^2p^2$

Carbon and silicon have 8 electrons in the penultimate shell (noble gas kernel) while the rest of the elements have 18 electrons in the penultimate shell. Carbon and silicon contain only *s* and *p* electrons while the rest of the elements also contain fully paired *d* electrons in the penultimate shells.

GENERAL CHARACTERISTICS OF GROUP 14 ELEMENTS

Important physical properties and other physical constants of the elements of Group 14 are shown in Table 2.

TABLE 2

Physical Properties of Elements of Group 14

Property	Carbon	Silicon	Germanium	Tin	Lead
Atomic number	6	14	32	50	82
Molar mass (g mol^{-1})	12·00	28·08	72·59	118·89	207·19
Density (g cm^{-3})	3·52	2·49	5·35	7·30	11·34
Atomic radius (Å)	0·77	1·11	1·22	1·41	1·47
Molar volume (cm^3 mol^{-1})	3·4	11·4	13·6	16·3	18·27
Melting point (°C)	3727	1410	937·5	231·8	327·4
Boiling point (°C) (Pauling's values)	4833	2680	2830	2270	1725
Electronegativity	2·5	1·9	2·0	1·8*	1·8*
Ionization energy (kJmol^{-1})	1086	786	761	708	716
Oxidation states (stable)	+ 4	+ 4	+ 2, + 4	+ 2, + 4	2, + 4

1. Molar volume and atomic radius. Molar volumes and atomic radii, as expected, increase with increase in atomic number.

2. Melting points and boiling points. The melting point as well as the boiling point of carbon, the first element, are exceedingly high. The values decrease as we move from carbon to lead. The melting points of tin and lead are relatively low.

3. Ionization energy. Ionization energy of carbon, the first element, is quite high, being 1086 kJ mol^{-1}. This is understandable in view of the small size of the carbon atom. There is a sharp decrease in the ionization energy as we move from carbon to the next element silicon. This is due to an appreciable increase in the size of the Si atom. There is, however, a very small decrease in ionization energy as we move from Si to Sn. This is because the *d* electrons which are now present in the inner configuration of Ge and Sn, shield the nuclear charge less effectively than is done by the *s* and *p* electrons. The outer electrons are, therefore, held strongly by the nucleus and hence, in spite of a sizeable increase in atomic radius, there is only a small decrease in ionization energy as we move from Si to Sn. In the last element, Pb, there are *f* electrons in the inner configuration which shield the nuclear charge less effectively even than the *d* electrons. Also there is only a marginal increase (of 0·03 Å) in the atomic radius as we move from Sn to Pb. Because of these two factors, the ionization energy of Pb, instead of decreasing, shows a marginal increase.

4. Oxidation states. All the elements have, in common, the oxidation state of + 4. The + 4 state is of much greater importance in carbon and silicon and + 2 state becomes increasingly important for germanium, tin and lead.

5. Metallic and non-metallic character. The change from non-metallic to metallic character with increase in atomic number in the same group, is best illustrated in this group, as already mentioned. The first two elements, carbon and silicon, are distinctly non-metals even though electrical properties of silicon are like those of a semi-metal. The third element, germanium, is partly non-metal and partly metal (*i.e.,* it is a semi-metal) while the last two elements, tin and lead, are distinctly metals in their physical and chemical properties.

6. Electronegativity. Carbon is the most electronegative element of this group. The electronegativity decreases on moving down the group but not after silicon (Table 2). This appears to be due to filling of the *d* orbitals in the case of germanium and tin and also the *f* orbitals in the case of lead.

7. Nature of bonds in their compounds. The elements of Group 14, on account of their high ionisation energies, do not form stable M^{4+} ions. Their electronegativities are also sufficiently low to permit the formation of stable anions. All the same, carbon does have a tendency to form C_2^{2-} ions, as in certain carbides. Thus, calcium carbide is an ionic compound which may be represented as $Ca^{2+}C_2^{2-}$. All the elements, and carbon and silicon in particular, show a covalency of 4.

The last three elements (Ge, Sn and Pb) have a tendency to form M^{2+} ions as well as M^{4+} ions. However, Sn and Pb prefer to form M^{2+} ions. The reason for showing reluctance to exhibit higher oxidation states by the heavier elements of the group have already been discussed in details in Chapter 12. Thus, $Sn^{2+}$and Pb^{2+} exist as stable ions and are much more common than Sn^{4+} and Pb^{4+} ions.

Sn(IV) and Pb(IV) compounds are more covalent than electrovalent in nature. This is to be expected from Fajan's rule according to which the smaller the ion, the greater is its tendency towards covalency. Sn^{4+} and Pb^{4+} ions have much smaller radii than Sn^{2+} and Pb^{2+} ions.

8. Formation of complexes. The tendency of an element to form complexes is favoured by (*a*) small size of its atom or ion, (*b*) high charge and (*c*) availability of vacant orbitals of appropriate energy. Except for the first element carbon, the succeeding elements in this family have vacant *d* orbitals which permit formation of coordinate bonds with other atoms or ions having lone pairs of electrons. For

example, silicon tetrafluoride which is a tetracovalent compound, can form complexes such as $[SiF_6]^{2-}$.

$$2HF + SiF_4 \longrightarrow H_2[SiF_6]$$

Since Si orbitals in $[SiF_6]^{2-}$ undergo sp^3d^2 hybridisation, the complex ion has an octahedral structure. The covalency of silicon thus rises to 6 in this complex ion.

Similarly, other elements of the group can also have a covalency of six due to availability of *d* orbitals, as in $[SnCl_6]^{2-}$ and $[PbCl_6]^{2-}$.

9. Tendency to form chains. Catenation. Carbon exhibits the remarkable property of **catenation**, *i.e., to form chains of identical atoms.* Silicon has much smaller tendency to form chains. Germanium has still smaller tendency while tin and lead have hardly any tendency to do so. Thus, in Group 14 elements, tendency to catenate decreases in the order C > Si > Ge > Sn > Pb.

As a result of catenation, carbon atoms can link together to form linear chains, branched chains and even rings of different sizes. The tendency of an element to form chains depends upon the strength of the element–element bond (bond energy) which is maximum in the case of carbon. The bond energies of C – C, Si – Si, Ge – Ge and Sn – Sn bonds are 354, 222, 167 and 155 kJ mol^{-1}, respectively.

10. Allotropy. Most of the elements of Group 14 show allotropy. Thus, carbon exists in two well-defined crystalline forms known as *diamond* and *graphite*. Besides these, there are microcrystalline forms which were previously regarded as amorphous. These are *coal, coke, charcoal, carbon black*, etc. All these have finely divided graphite structures. Silicon is known to exist in *crystalline* and *amorphous forms*. Germanium also exists in *two crystalline forms*. Likewise, tin exists in three solid forms : *grey tin, white tin* and *rhombic tin*. Grey tin is stable below 18°C, white tin above 18°C and rhombic tin above 161°C. *Grey tin* exists usually in powder form and is a poor conductor of electricity. It, therefore, lacks metallic properties. Its density is 5·75 g cm^{-3}. *White tin*, on the other hand, is soft, ductile and good conductor of electricity. It has, therefore, metallic character. It has also the usual metallic lustre. Being stable at room temperature, it is the most common form of tin. Its density is 7·30 g cm^{-3}.

Unique Character of Carbon. Carbon with smallest atomic radius and lowest molar volume is most compact of all the elements in this group. It has highest melting and boiling points. It has the highest ionisation energy and is the most electronegative element in this group. Also because of the absence of *d* orbitals, it has least tendency to form complex compounds. Its maximum covalency remains 4.

Carbon can form multiple bonds, *i.e.*, double bonds and triple bonds, in a number of its compounds. The most remarkable property of carbon, however, lies in its property of catenation as a result of which it forms thousands of compounds in which carbon atoms are bonded to one another through covalent bonds.

Comparison of Carbon with Silicon. Carbon and silicon, the first two elements of this group, have a number of properties in common. Due to similar electronic configurations, they form similar hydrides (*e.g.*, CH_4, SiH_4 and C_2H_6 and Si_2H_6), similar halides (*e.g.*, CCl_4, $SiCl_4$), similar oxides (*e.g.*, CO_2, SiO_2) and similar oxyacids (*e.g.*, H_2CO_3, H_2SiO_3), etc. In spite of these similarities, the two elements and their compounds differ appreciably from one another in several respects. Most of these differences, though not all, arise from the following factors : 1. Difference in sizes of carbon and silicon atoms, carbon atom being much smaller than silicon atom. 2. Non-availability of *d* orbitals in carbon atom. 3. Carbon having high capacity for catenation, as pointed out above.

Some of the important differences between the two elements are summed up below :

1. Carbon is harder and has higher melting and boiling points than silicon.

2. Carbon in the form of graphite is a good conductor of electricity while silicon is a pair conductor of electricity.

3. Carbon, due to its small atomic size, can form pi bonds with oxygen involving *p* orbitals while silicon due to its large atomic size cannot do so.

4. Due to its high capacity for catenation, carbon forms thousands of compounds. Silicon has much lower capacity for catenation. The number of its compounds is, therefore, limited.

5. Carbon is an essential constituent of living organisms belonging to animal or vegetable kingdom. Silicon is an essential constituent of most of the non-living materials including rocks, hills, clays, soils, ores, etc.

The **compounds of carbon and silicon** also differ in several respects as illustrated below.

1. Hydrides. The hydrides of carbon are numerous (*e.g.*, CH_4, C_2H_6, C_2H_4, C_2H_2, C_6H_6, $C_6H_5CH_3$ and a host of others). Many of these are highly stable. Silicon hydrides (SiH_4, Si_2H_6, etc.) are only a few in number and are not as stable.

2. Oxides. Carbon forms two similar oxides, CO and CO_2, both being *gases* at ordinary temperatures. Silicon forms only one oxide, SiO_2, which is a *solid* with high melting and boiling points. The reason why CO_2 is a gas while SiO_2 is a highly stable solid has been discussed in details in a subsequent section in this chapter dealing with the **structure of silica**.

3. Halides. Carbon tetrachloride does not undergo hydrolysis in water. It also does not form addition compounds. Silicon tetrachloride, however, gets hydrolysed in water and forms addition compounds with ammonia. This is due to the presence of *d* orbitals in silicon. Carbon does not form dihalides while silicon does.

4. Silicones. Silicon is capable of forming cross-linked silicones through hydrolysis of its halides. These compounds are used as lubricants, water repellents and insulators, etc. No such compounds are formed by carbon.

EXTRACTION OF ELEMENTS OF GROUP 14

Recovery of Carbon. Carbon is one of the most widely distributed elements. It occurs naturally in pure forms as diamond and graphite and more abundantly in a contaminated form as coal. The purest form of coal is anthracite which contains about 95 percent carbon. Other varieties of coal are steam coal, bituminous coal, lignite and peat in which the carbon content is respectively, 93, 88, 67 and 60 per cent.

All the naturally occurring forms are recovered as such from their respective mines. Graphite and diamond, are, however, prepared artificially also, as described below.

Artificial diamonds. Artificial diamonds are prepared by Moissan's method. In this method, pure sugar charcoal and iron are heated in a graphite crucible to a temperature of about 3000°C in an electric arc furnace. At this temperature, the iron dissolves an appreciable amount of carbon. The graphite crucible containing the molten mass is *cooled rapidly* by placing it in a bath of molten lead (temperature 327°C). As a result of the solidification of the external surface of the iron, an enormous pressure is exerted on the interior mass (cast iron expands on solidification). Under these conditions, the carbon is thrown out in the form of *minute diamonds*. The mass is cooled and treated with hydrochloric acid to dissolve the iron. The residual carbon is found to contain a number of small diamonds (not more than 0·8 mm in diameter), some transparent and some black.

Artificial graphite. Large amounts of graphite are prepared artificially by Acheson process. A mixture of sand and powdered anthracite (or coke) is heated strongly to about 2500°C in an electric furnace consisting of two carbon electrodes connected by a thin carbon rod. An alternating current is passed and heating continued for 24 – 30 hours. Silicon carbide first formed decomposes into graphite and silicon, the latter volatilises off leaving behind the graphite.

$$SiO_2 + \underset{\text{Coke}}{3C} \longrightarrow 2CO + SiC$$

$$SiC \longrightarrow Si + \underset{\text{graphite}}{C}$$

Extraction of Silicon. Silicon occurs abundantly (26%) in the earth's crust, next only to oxygen (50%). But unlike carbon it does not occur free in nature. As oxide, SiO_2, it is found in sand, quartz of various forms, flint, opal, etc. It is also found as silicates, *e.g., feldspar* ($KAlSi_2O_8$), *mica* [$KH_2Al(SiO)_3$], in rocks and clays.

In laboratory, silicon may be prepared by heating dry powdered silica with magnesium or aluminium.

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

Magnesium oxide and any unreacted silica are removed by treatment with hydrofluoric acid in polythene vessel. Silicon left behind is a *brown amorphous powder.*

On a commercial scale, it is prepared by heating a mixture of finely powdered sand or quartz and carbon in an electric furnace.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Silicon formed in this way is *crystalline* in structure and grey in colour. A small amount of iron is added usually to avoid the formation of silicon carbide (carborundum). In this way, an alloy of iron and silicon, called ferrosilicon, is obtained.

Extraction of Tin. Tin does not occur free in nature. Its chief source is the ore *casseterite*, SnO_2, also known as *tin stone.*

The ore is freed of silicious impurities by froth floation and gravity processes. The magnetic impurity *wolfrom* is removed by electromagnetic means (Chapter 10).

The purified ore is roasted in a rotary furnace. It is then mixed with anthracite and smelted in a reverberatory furnace, using lime as flux. The metal obtained is purified by liquation process.

Extraction of Lead. Small quantities of lead occur native in Sweden. However, its chief ore is *galena*, lead sulphide, which contains about 6 – 8% lead. Galena also contains small quantities of silver (upto 0·1%).

If the ore is rich in lead, it is heated in a reverberatory furnace in a limited supply of air when PbS is partly converted to PbO and partly to $PbSO_4$. The supply of air is then reduced, some more of the ore is added and temperature of the furnace is raised when PbO & PbS and PbS & $PbSO_4$ interact to give lead. If, however, the ore is poor in lead, it is roasted in a free supply of air to convert PbS into PbO which is then reduced on heating with carbon in a blast furnace using lime as flux.

Extraction of Germanium. Germanium occurs rarely. The only relatively rich ore of germanium is *germanite*, GeO_2, which contains nearly 6 per cent of the metal. The ore is strongly heated with hydrochloric acid when the chloride $GeCl_4$ distils off. This is hydrolysed to give pure dioxide, GeO_2, which is dried and then reduced by hydrogen or carbon to give the element.

PROPERTIES OF ELEMENTS OF GROUP 14

Properties of Carbon. Physical Properties. Carbon exists in various allotropic forms, of which *diamond* and *graphite* are crystalline while *coal, wood charcoal, animal charcoal, lamp black, coke* and *gas carbon* are amorphous. The X-ray analysis has revealed, however, that the so-called amorphous carbons are in reality crystalline in structure. However, they consist of extremely fine crystals. These carbons are, therefore, termed as **microcrystalline carbons.** Diamond and graphite are, however, structurally very much different from each other. While diamond has a *three- dimensional tetrahedral structure*, graphite has a *two-dimensional layer structure,* as discussed below.

Structure of diamond. Diamond is a big *three-dimensional polymer* comprising of a large number of carbon atoms arranged *tetrahedrally* by utilising their sp^3 hybrid orbitals. The structure is shown in

Fig. 1. The C – C bond distance is 1·54 Å. It will be seen that each carbon atom lies at the centre of a regular tetrahedron and is linked to four surrounding carbon atoms lying at the corners of the tetrahedron by strong covalent bonds through sharing of their valency electrons. The result is a very big, three-dimensional polymer. Due to high strength of covalent bonds holding numerous carbon atoms together, diamond is very hard and has high density. Since melting of diamond requires breaking of the strong covalent bonds, the melting point of diamond is unusually high, being close to 3500°C. Diamond is the purest form of carbon and is the hardest substance known. It has a very high refractive index (2·417) and a very high density (3·51 g cm^{-3} at 25°C). It is transparent to X-rays and is a bad conductor of heat and electricity.

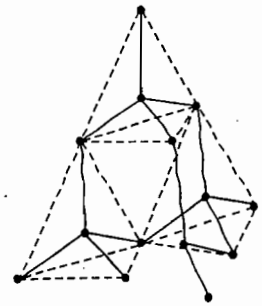


Fig. 1. Structure of diamond.

Structure of graphite. Graphite, unlike diamond, has a *two-dimensional* structure. In this case, only three of the four valency electrons of each carbon atom are involved in bonding. Thus, each carbon atom makes use of its three sp^2 hybrid orbitals forming three covalent bonds with three other carbon atoms in the same plane (unlike the structure of diamond in which each carbon atom is linked to four other carbon atoms through sp^3 hybrid bonds). Thus, the structure of graphite is two-dimensional sheet-like consisting of a number of benzene rings fused together (Fig. 2*a*), unlike that of diamond which is three-dimensional. The sheets or layers are held together by relatively weak van der Waals forces. The C – C covalent bond distance is 1·42 Å. The distance between the two successive layers is 3·36 Å (Fig. 2*b*). This large distance rules out the possibility of covalent bonding between carbon atoms in different layers. Hence, the fourth valency of each carbon atom remains unsatisfied, *i.e.,* the fourth valency electron remains unpaired or free. This free electron can easily move from one carbon atom to another under the influence of applied potential. This permits the passage of electricity through graphite and makes graphite a good conductor of electricity.

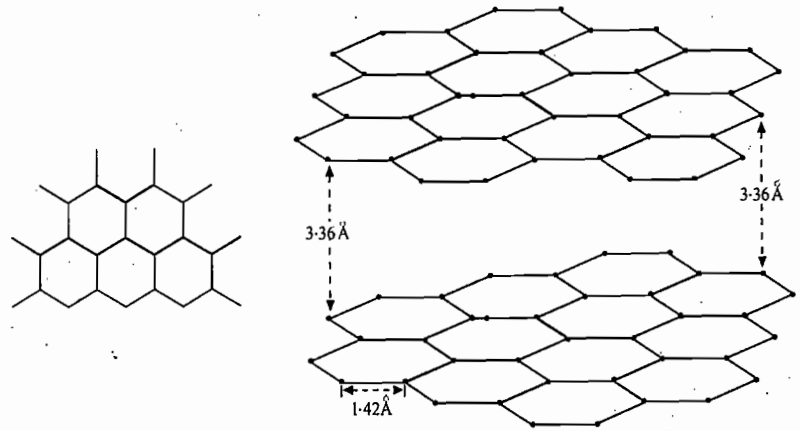


Fig. 2. (*a*) Hexagonal-layer structure of graphite (*b*) Bonding in graphite.

The above layer structure of graphite is less compact than that of diamond. Further, since the bonding between the layers involving only van der Waals forces is weak, these layers can slide over each other. This gives softness, greasiness and lubricating character to graphite.

Graphene. Very recently, Andre Geim and Konstatin Novoselov, Russian scientists working at the University of Manchester (U.K.), succeeded in peeling with an ordinary piece of Scotch tape, the successive two-dimensional layers of carbon from a small chunk of graphite eventually obtaining a layer a single carbon atom thick. They named it **graphene.** Most surprisingly, graphene is 100 times stronger than steel and conducts heat and electricity better than copper.

This remarkable discovery for which the two scientists have been awarded the 2010 Nobel Prize in physics, holds promise for a host of applications, the most significant of which include replacement of carbon fibres in composite materials for the fabrication of lighter air craft and satellites and replacement of silicon in transistors to produce faster electronic devices. The discovery is likely to revolutionize the electronics industry.

The physical characteristics of the various allotropic forms of carbon are shown in Table 3.

TABLE 3

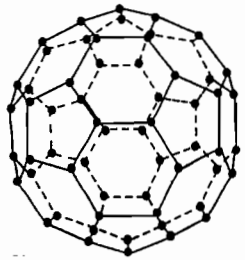
Physical Characteristics of Various Allotropic Forms of Carbon

	Crystalline forms		Microcrystalline forms			
Property	**Diamond**	**Graphite**	**Coal**	**Charcoal**	**Animal charcoal**	**Lamp black**
1. Colour	Colourless transparent	Grey	Black	Black	Black	Black
2. Carbon content	100%	95 – 97%	60 – 90%	68 – 85%	8 – 10%	98 – 99%
3. Density ($g\ cm^{-3}$)	3·51	2·25	–	1·4 – 1·7	–	–
4. Hardness	Hardest substance	Soft, marks the paper	Hard mass	Soft	Soft	Soft
5. Electrical conductivity	Bad conductor	Good conductor	Bad conductor	Bad conductor	Bad conductor	Bad conductor

Fullerenes

Fullerenes are allotropes of carbon having the general formula C_{2n} (n = 30 – 48). These are prepared by passing high voltage current through graphite rods in the inert atmosphere of helium. The graphite of the rods sublimes producing a fluffy mass called 'fullerene soot.' This soot is then dissolved in organic solvents such as benzene and chromatographed when the solutions of pure C_{60} (about 79%) and C_{70} (about 20%) separate out as major fractions. Minor amounts (about 1%) of higher fullerenes comprising of C_{76}, C_{78}, C_{80}, etc., also separate out in the process. The solutions of pure fullerenes, when concentrated, yield crystals containing solvent molecules trapped in the interstices. The sublimation of these crystals in vacuum yields solvent-free fullerene crystals.

The most common of these fullerenes, C_{60}, contains 20 hexagons and 12 pentagons of carbon atoms fused with one another resulting in a spherical **football-like geometry,** as shown.



Spherical foot-ball like geometry of fullerene

There are two types of C – C bonds in the structure of C_{60} one of which is 1·48 Å and the other is 1·38 Å in length. Although the fullerene C_{60} is one of the most strained molecules known so far yet it shows high kinetic stability. Nevertheless, its thermal stability is less than that of graphite and diamond. It starts decomposing at about 700°C.

In the fullerene C_{70}, there are eight distinct types of C – C bonds with lengths varying between 1·39 Å and 1·54 Å. This fullerene has also spherical, football-like structure containing several hexagons and pentagons of carbon atoms fused together. Higher fullerenes have similar football-like structures.

Chemical Properties of Carbon. Of all the allotropic forms, charcoal is the most reactive. It readily burns in air to give carbon dioxide. It reacts with concentrated sulphuric acid and concentrated nitric acid and reduces them readily to SO_2 and NO_2, respectively. It combines with many metals to give carbides, *e.g.*, CaC_2 and Al_4C_3. When heated with sulphur, it forms carbon disulphide.

Chemically, diamond is resistant towards almost all chemical reagents. It burns in air when heated at 900°C giving carbon dioxide. It is slowly oxidised to carbon dioxide by a mixture of potassium dichromate and sulphuric acid at 200°C. It is stable in vacuum up to 1500°C but changes into graphite at 1800°C and more rapidly at 2000°C.

Graphite, like diamond, is not attacked by dilute acids. It is slowly oxidised to CO_2 by chromic acid. It is oxidised by concentrated nitric acid to give graphitic acid, $C_{11}H_4O_5$, which is an insoluble yellowish green substance. With alkaline potassium permanganate, it is oxidised to oxalic acid and mellitic acid, $C_6(COOH)_6$.

Uses. ***Coal*** is used extensively as a fuel in boilers, engines, furnaces, etc. It is also used in the manufacture of coal gas, producer gas, water gas and synthetic petrol. ***Anthracite*** is used as a reducing agent in metallurgical processes and for the manufacture of graphite.

Charcoal (activated) is used as an excellent adsorbent in gas masks and for removing offensive odour from the air used in air-conditioning processes. It is also used for removing fusel oil, in decolourising sugar syrup and for refining of oils, fats, glycerine, etc. It is also used in the treatment of drinking water after chlorination to adsorb the excess of chlorine.

Lamp black is used in making printing inks, paints, shoe polish and as black pigment. The main application, at present, is as a *filler* in making rubber tyres.

Graphite, being a good conductor of electricity, is used in making electrodes and carbon rods and in covering moulds for electrodeposition of copper. It is also used as a solid lubricant. The so-called lead pencils actually contain graphite mixed with a little clay.

Properties of Silicon. Physical Properties. It is a hard and brittle solid with a high melting point (1410°C). It has the same appearance as graphite. Its electrical conductivity is very low compared to that of graphite. It shows allotropy as it exists in two well-defined forms, namely, a *brown amorphous powder* and *a grey crystalline mass*. The amorphous brown powder and crystalline grey varieties differ in particle size and content of impurities. The amorphous variety fuses on strong heating and solidifies on cooling to give the crystalline form.

Chemical Properties. *Amorphous silicon* is chemically more active than the crystalline variety. It unites spontaneously with fluorine at ordinary temperature forming the flouride, SiF_4. When heated in chlorine it burns forming silicon tetrachloride, $SiCl_4$. It also combines with oxygen, bromine, sulphur, nitrogen and carbon at progressively increasing temperatures. It is insoluble in water as well as in acids but a mixture of nitric and hydrochloric acids attacks it. It is also slowly attacked by steam when heated to redness.

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

It dissolves in hot concentrated alkalies to form silicates.

$$Si + 2KOH + H_2O \longrightarrow K_2SiO_3 + 2H_2$$

It also dissolves in fused sodium carbonate displacing carbon.

$$Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$$

It combines with certain metals forming silicides.

$$2Mg + Si \longrightarrow Mg_2Si$$

The *crystalline variety* reacts with halogens and alkalies but not with oxygen even when strongly heated.

Uses. 1. Silicon is added to steel as such or, more usually, in the form of *ferrosilicon* to increase its resistance to attack by acids.

2. Its alloys, such as *silicon bronze* and *manganese-silicon bronze*, possess strength and hardness even greater than steel.

3. Pure silicon is used in the fabrication of transistors.

Properties of Tin. Physical Properties. 1. Tin has a silvery-white lustre which does not tarnish on exposure to air.

2. It exists in three allotropic forms : *grey, white* and *rhombic*. The transition temperatures are as follow :

$$\text{Grey} \overset{18°C}{\rightleftharpoons} \text{White} \overset{161°C}{\rightleftharpoons} \text{Rhombic}$$

The densities of the three forms are 5·74, 7·32 and 6·55 gram per c.c., respectively. White tin is not only the heaviest but also the most stable variety.

The conversion of white tin into grey tin takes place very slowly at 18°C, which is the transition temperature. However, if the temperature is as low as –50°C and a small amount of grey tin is already present, the conversion becomes very rapid. This conversion is known as **tin pest** or **tin disease**.

3. White tin is malleable but not ductile. It becomes brittle when heated to 200°C.

4. When bent, the metal produces a cracking noise which is called **tin cry.** This is due to rubbing of metal crystals over one another.

5. Tin melts at a relatively low temperature of 232°C but boils at a relatively high temperature of 2270°C.

Chemical Properties. 1. Action of air. Air has no action on tin at ordinary temperatures but when heated to whiteness (1500 – 1600°C) in the presence of oxygen it burns with a bright flame giving stannic oxide.

2. Action of halogens and sulphur. If the metal is heated in an atmosphere of chlorine or sulphur vapour, it readily combines to form stannic chloride and stannic sulphide, respectively.

3. Action of acids. Tin is slowly attacked by dilute hydrochloric acid but the reaction becomes rapid on heating with concentrated hydrochloric acid forming stannous chloride and evolving hydrogen.

Dilute sulphuric acid has no action but hot concentrated acid dissolves the metal forming stannous sulphate and evolving sulphur dioxide.

Dilute nitric acid attacks the metal forming stannous nitrate and ammonium nitrate.

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Hot concentrated acid produces copious fumes of nitrogen dioxide and meta stannic acid.

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

Organic acids have no action.

4. Action of alkalies. When the metal is heated with alkali solutions it reacts to evolve hydrogen.

$$Sn + 2NaOH + H_2O \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + 2H_2$$

Uses. 1. Tin is used in the preparation of a number of alloys such as solder, britannia metal, white metal, etc. The names, compositions and uses of some important tin alloys are given in Table 4.

TABLE 4
Some Important Tin Alloys

Name	Percentage Composition	Uses
Solder	Sn 50% Pb 50%	In soldering
Pewter	Sn 75% Pb 25%	In making cups, mugs and other utensils
Babbit metal	Sn 90% Sb 7% Cu 3%	For making bearings for machinery
Britannia metal	Sn 90% Sb 8% Cu 2%	For making table ware
White metal	Sn 82% Sb 12% Cu 6%	For making table ware
Bell metal	Sn 25% Cu 75%	For making bells, gongs, etc.
Rose metal	Sn 28% Pb 22% Bi 50%	For electric fuses

2. It is used in the preparation of collapsible tubes for tooth pastes and various ointments. 3. The metal is extensively used in **tinning** brass utensils. 4. It is largely used in forming a protective coating over iron. The process is known as **tin plating.** It consists in dipping the clean sheets of iron or steel in a bath of molten tin and passing through hot pairs of rollers. A thin coherent film of tin is deposited. Tin coated plates are used in the manufacture of tin cans, kerosene oil containers and other similar articles. 5. Tin amalgam is used in making mirrors. 6. Tin foil is used for wrapping cigarettes and other articles.

Properties of Lead. Physical Properties. Lead is a bluish grey metal and possesses, when freshly cut, a bright metallic lustre which, however, becomes dull on exposure to air due to the formation of a thin layer of the oxide on the surface. It is so soft that it can be cut with a knife and scratched with the finger-nail. It marks paper. It is malleable but not very ductile. The presence of other metals makes it hard and brittle. Its specific gravity is 11·34. It melts as 327·4°C and boils at 1725°C.

Chemical Properties. 1. Action of air. It is not attacked by dry air but gets tarnished in moist air due to the formation of a thin film of the insoluble basic carbonate which prevents it from further action.

2. Action of air and heat. When heated in air or oxygen, lead is oxidised to litharge (PbO) and red lead (Pb_3O_4).

3. Action of water. Lead is not attacked by pure air-free water (except at the boiling point). It slowly decomposes steam at high temperatures. It is readily corroded by water containing dissolved air forming lead hydroxide which is appreciably soluble in water. The solvent action of water, known as 'plumbo solvency' is greater when water contains nitrates, organic acids and ammonium salts. The reaction is, however, retarded by certain salts such as phosphates, carbonates and sulphates since they form a coating of insoluble lead salts on the surface of the metal which protects it from further action. Thus, hard water has no solvent action on lead.

4. Action of acids. Lead is only slightly attacked by dilute hydrochloric acid or dilute sulphuric acid in the cold because a film of insoluble lead chloride or lead sulphate is formed on the surface which prevents further action. Powdered lead is readily dissolved by boiling hydrochloric acid due to formation of the soluble complex, $H_2[PbCl_4]$.

$$Pb + 2HCl \longrightarrow PbCl_2 + H_2$$
$$PbCl_2 + 2HCl \longrightarrow \underset{\text{Chloroplumbous acid}}{H_2[PbCl_4]}$$

Concentrated sulphuric acid dissolves lead readily at 230 – 240°C with the evolution of sulphur dioxide but the action is retarded by the formation of insoluble layer (crust) of lead sulphate on the metal surface.

With cold dilute nitric acid, lead forms lead nitrate and nitric oxide.

With concentrated nitric acid it evolves brown fumes of nitrogen dioxide.

Lead readily dissolves in acetic acid in the presence of oxygen, forming lead acetate.

$$Pb + 2CH_3COOH + 1/2\ O_2 \longrightarrow (CH_3COO)_2Pb + H_2O$$

5. Action of alkalies. It is slowly attacked by caustic alkalies with the evolution of hydrogen.

$$Pb + 2NaOH \longrightarrow \underset{\text{Sodium plumbite}}{Na_2PbO_2} + H_2$$

6. Action of chlorine and sulphur. Lead directly combines with chlorine and sulphur to form lead tetrachloride and lead sulphide, respectively.

Uses. Lead is used 1. For making lead pipes for carrying water. 2. For making telegraph and telephone wires which are to be burried in earth. 3. In fine arts on account of the ease with which it can be worked out, cut and soldered and due to its resistance to water and many acids 4. In making bullets and lead accumulators. 5. In making pigments like chrome yellow, chrome red, red lead, white

lead, etc. 6. In making lead alloys. Some of the important alloys are : *Type metal* (82% Pb, 15% Sb, 3% Sn), used for making printing type ; *Solder* (50% Pb, 50% Sn), used for soldering ; *Pewter* (20% Pb, 80% Sn) used for making utensils.

Wooden tanks lined with lead are frequently used for several chemical operations on a large scale.

Properties of Germanium. Germanium is silvery-white, hard and brittle. It has no allotrope. It is more reactive than silicon. Like silicon, it is used in the fabrication of transistors.

COMPOUNDS OF GROUP 14 ELEMENTS

I. A Comparative Study

1. Hydrides. All the elements of this group form covalent hydrides although the number of the stable hydrides and the ease with which these are formed decreases as we move from carbon to lead.

A brief description of the hydrides of the various elements is given below.

Hydrides of Carbon. Carbon forms a number of hydrides, known as *alkanes* (general formula C_nH_{2n+2}), *alkenes* (general formula C_nH_{2n}), *alkynes* (general formula C_nH_{2n-2}) and a number of aromatic compounds (*e.g.*, benzene, toluene, xylene), etc. The methods of their preparation and properties are discussed fully in organic chemistry books.

Hydrides of Silicon. These compounds are similar to hydrides of carbon but they are much less stable. The number of silicon hydrides is also much less than the number of hydrides of carbon. These are called **silanes** and have the general formula Si_nH_{2n+2}, where n stands for the number of silicon atoms. Silanes with n upto 8 are known. The individual members are known as *silane* (SiH_4), *disilane* (SiH_6), *trisilane*, (Si_3H_8), *tetrasilane*, (Si_4H_{10}), etc. The first two members are colourless gases while the third and subsequent members are liquids. The freezing points and boiling points of these compounds are given below :

	Monosilane (SiH_4)	*Disilane* (Si_2H_6)	*Trisilane* (Si_3H_8)	*Tetrasilane* (Si_4H_{10})
F.P. (°C)	– 185	– 132	– 117	– 89
B.P. (°C)	– 112	– 14	53	107

SiH_4 is stable at room temperature. Thermal stability decreases with increasing chain length.

Silanes are produced by the action of acids on metallic silicides, *e.g.*,

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$

Actually a mixture of silanes is obtained, the composition of the mixture being : SiH_4 (40%), Si_2H_6 (30%), Si_3H_8 (12%), Si_4H_{10} (10%) and others (8%). Monosilane can be separated by fractionating in vacuum.

Pure monosilane is prepared by reacting silicon tetrachloride with lithium aluminium hydride in ether at low temperature.

$$SiH_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3$$

The structures of silanes are analogous to those of alkanes.

The silanes are much less stable than the corresponding alkanes. The lower silanes decompose more readily than the higher ones. Thus, monosilane, SiH_4, decomposes spontaneously on coming into contact with air.

$$SiCl_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

In fact, all the silanes are spontaneously inflammable and explosive in air.

If the gas is bubbled through water, then, as soon as it comes in contact with air, each bubble ignites giving vortex ring of finely divided silica.

They decompose slowly when brought in contact with water.

$$SiH_4 + 3H_2O \longrightarrow H_2SiO_3 + 4H_2$$

Silanes are soluble in strong alkali solutions in the presence of air and evolve hydrogen.

$$SiH_4 + 2NaOH + 1/2\,O_2 \longrightarrow Na_2SiO_3 + 3H_2$$

Silanes, therefore, have *strong reducing properties*. They reduce permanganate to Mn (II) ; mercury (II) to mercury(I) or even mercury(0) ; iron(III) to iron(II) and copper(II) to copper hydride.

They react with chlorine and bromine with explosive violence even at ordinary temperatures. But treatment of SiH_4 with HCl or HBr at 100°C in the presence of aluminium chloride as a catalyst results in the substitution of hydrogen atoms by chlorine or bromine

$$SiH_4 + HCl \xrightarrow{Al_2Cl_6} SiH_3Cl + H_2$$

Halosilanes can also be obtained by reacting silane with solid AgX in a heated flow reactor.

$$SiH_4 + 2AgCl \xrightarrow{260°C} SiH_3Cl + HCl + 2Ag$$

Hydrides of Germanium. The hydrides of germanium (called *germanes*) have the general formula Ge_nH_{2n+2} (n upto 5). Three hydrides of germanium are more commonly known. These are *monogermane*, GeH_4, *digermane*, Ge_2H_6 and *trigermane*, G_3H_8.

These are prepared in the same way as silanes. Thus, treatment of magnesium germanide with dilute hydrochloric acid yields a mixture of mono, di and trigermanes. The individual germanes can be separated by fractional distillation.

Monogermane *alone* can be prepared by the reduction of germanium tetrachloride with lithium aluminium hydride.

The first two compounds are colourless gases while the higher germanes are liquids. Their freezing and boiling points are given below :

	GeH_4	Ge_2H_6	Ge_3H_8	Ge_4H_{10}	Ge_5H_{12}
F.P.(°C)	– 165	– 109	– 106	–	–
B.P. (°C)	– 88	22	110·5	177	234

Germanes are less volatile and less reactive than the corresponding silanes. For example, in comparison to SiH_4, GeH_4 does not ignite when brought in contact with air. Also, unlike silanes, these are not attacked by water. Monogermane, unlike monosilane, is not attacked by alkali (30 per cent NaOH or KOH). Digermane, however, evolves hydrogen under these conditions. At higher temperatures, they decompose to give germanium and hydrogen.

Hydrides of Tin and Lead. Two hydrides of tin, *monostannane* (SnH_4) and *distannane* (Sn_2H_6) are known. SnH_4 is obtained as a gas by reducing tin (IV) chloride with ethereal lithium aluminium hydride. It is also formed by the action of atomic hydrogen on metallic tin or by the action of $SnCl_2$ with aqueous $NaBH_4$.

The freezing and boiling points of monostannane are –146°C and –52°C, respectively. It is not stable and decomposes slowly even at room temperature into tin and hydrogen. It decomposes readily above 145°C. It is resistant to attack by dilute aqueous acids or alkalies. Distannane, Sn_2H_6, is much less stable. Higher homologues are not known.

There is some doubt about the existence of lead hydride although it is claimed that it is formed in minute quantities as a gas when a lead-magnesium alloy is dissolved in dilute acids.

In general, it may be concluded that the stability of the hydrides of elements of Group 14 decreases as we move down the group. Since thermal stability decreases, their tendency to act as reducing agents increases as we move down the group.

2. Halides

Tetrahalides. All the elements of this group form tetrahalides which are mostly covalent.

Amongst the simple tetrahalides, the tetrafluorides of C, Si and Ge (*i.e.*, CF_4, SiF_4 and GeF_4) are gases while the tetrafluorides of Sn and Pb (*i.e.*, SnF_4 and PbF_4) are solids. The last two are more ionic in character than the first three.

Carbon tetrabromide, CBr_4, is a solid while tetrabromides of silicon, germanium and tin (*i.e.*, $SiBr_4$, $GeBr_4$ and $SnBr_4$) are liquids. The tetraiodides of the first four elements (*i.e.*, CI_4, SiI_4, GeI_4 and SnI_4) are solids. $PbBr_4$ and PbI_4 are unknown.

Important tetrahalides of carbon are discussed below.

Carbon tetrafluoride is prepared on a laboratory scale by reacting fluorine and silicon carbide or by fluorinating CO or CO_2 by SF_4. It is a highly stable gas with melting point (–183·5°C) quite close to that of CH_4 (–182·5 °C).

Carbon tetrachloride is prepared on a large scale by passing chlorine into carbon disulphide in the presence of a small amount of iodine.

$$CS_2 + 3Cl_2 \longrightarrow S_2Cl_2 + CCl_4$$

Carbon tetrachloride boiling at 76·7°C can be easily separated by fractional distillation as S_2Cl_2 boils at a higher temperature, *i.e.*, 138°C.

It is a colourless liquid with high density (1·58 g cm^{-3}). It is non-polar and is, therefore, miscible with non-polar solvents. It is a common laboratory and industrial solvent for non-polar materials. It is non- combustible and is used as fire-extinguisher.

It is also used for preparing **freons** such as $CFCl_3$, CF_2Cl_2 and CF_3Cl which are used in refrigeration.

CCl_4 resists hydrolysis. However, CCl_4 does react with water at 300°C to form $COCl_2$

$$CCl_4 + H_2O \xrightarrow{300°C} COCl_2 + 2HCl$$

Moist iron reduces CCl_4 to $CHCl_3$.

$$CCl_4 + 2H \xrightarrow[\text{moisture}]{Fe} CHCl_3 + HCl$$

HF reacts in the catalytic presence of $SbFCl_4$, as follows :

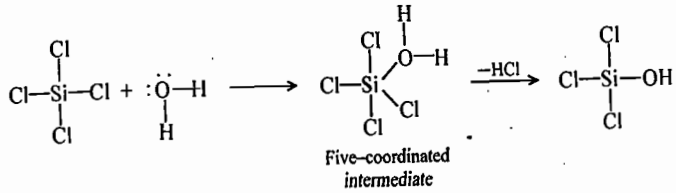
$$CCl_4 + HF \xrightarrow{SbFCl_4} CFCl_3 + HCl$$

$$CCl_4 + HF \xrightarrow{SbFCl_4} CF_2Cl_2 + HCl$$

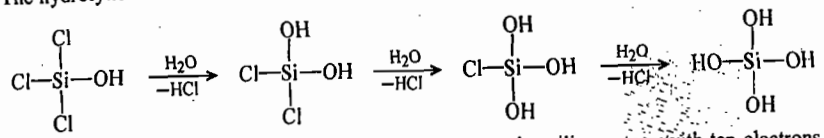
The catalyst $SbFCl_4$ used in the above reactions is obtained by the action of HF on $SbCl_5$.

Differences Between Tetrahalides of Carbon and Tetrahalides of Other Elements of Group 14. The tetrahalides of carbon differ from the tetrahalides of other elements of this group in two respects.

1. Hydrolysis. While tetrahalides of carbon are not hydrolysed by water under normal conditions, the tetrahalides of other elements *are readily hydrolysed*. The hydrolysis of tetrahalides of silicon and other elements is due to the availability of empty *d* orbitals in the valency shells of their central atoms. The *mechanism of hydrolysis of $SiCl_4$* is illustrated below. It involves the nucleophilic attack by water molecule to form a five-coordinated intermediate $SiCl_4(H_2O)$ which then dissociates with the elimination of HCl giving $SiCl_3OH$.



The hydrolytic attack continues till all the chlorine atoms are replaced by *OH* groups.



It can be seen that the five-coordinated intermediate contains silicon atom with ten electrons in its outermost shell. The availability of empty 3*d* orbitals in the outermost shell of silicon permits donation of electrons by oxygen atoms of water molecules to silicon atom to form hydrated intermediate, $SnCl_4.H_2O$. On the other hand, carbon has only *s* and *p* orbitals in its outermost shell and *three are no vacant d orbitals for bond formation*. As a result, it cannot form five-coordinated intermediate and, therefore, the *tetrahalides of carbon are not hydrolysed.*

Hydrolysis of silicon tetrafluoride yields silica and fluosilicic acid.

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6$$

Fluosilicic acid is known only in solution. It is a strong acid and exists largely in the ionised state.

$$H_2SiF_6 + 2H_2O \longrightarrow 2H_3O^+ + [SiF_6]^{2-}$$

The formation of $[SiF_6]^{2-}$ ion involves sp^3d^2 hybridisation of orbitals of Si and has *octahedral structure.*

Stannic chloride on hydrolysis produces the complex compound $H_2[SnCl_3(OH)_3]$.

$$SnCl_4 + 3H_2O \longrightarrow H_2[SnCl_3(OH)_3] + HCl$$

GeF_4 hydrolyses in the same way as SiF_4

$$3GeF_4 + 2H_2O \longrightarrow 2H_2GeF_6 + GeO_2$$

2. Formation of Complexes. Carbon tetrahalides do not form complexes because carbon has no *d* orbitals in the outer shell and cannot increase its coordination number. The tetrahalides of the rest of the elements, however, do form complexes since due to the availability of vacant *d* orbitals in the valency shell, these elements can increase their coordination number from *four* to *six*. The common examples are : $[SiF_6]^{2-}$, $[GeF_6]^{2-}$, $[SnCl_6]^{2-}$

Trihalides. Carbon, silicon and germanium give trihalides of the type $MHCl_3$, *e.g.*, $CHCl_3$, $SiHCl_3$, $GeHCl_3$. Lead and tin do not form such compounds.

Dihalides. Carbon does not form dihalides. Silicon differs from carbon and resembles germanium, tin and lead in forming dihalides.

Silicon dichloride is formed on heating silicon tetrachloride with silicon at temperatures above 1100°C.

$$SiCl_4 + Si \longrightarrow 2SiCl_2$$

Germanium dihalides are formed by passing the tetrahalide vapour over the heated metal.

$$GeX_4 + Ge \longrightarrow 2GeX_2$$

These dihalides are strong reducing agents.

Anhydrous stannous chloride is prepared by heating stannic chloride and tin together.

$$SnCl_4 + Sn \longrightarrow 2SnCl_2$$

Lead dihalides are all sparingly soluble in cold water and are obtained as precipitates by reaction of the type

$$Pb(NO_3)_2 + 2HF \longrightarrow PbF_2 + 2HNO_3$$

The dihalides of germanium, tin and lead are more ionic than covalent in character.

3. Oxides

The elements of this group form two types of oxides, namely, **monoxides** of the formula MO (*e.g.*, CO, SiO, GeO, SnO and PbO) and **dioxides** of the formula MO_2 (*e.g.*, CO_2, SiO_2, GeO_2, SnO_2 and PbO_2). Lead also forms an oxide, Pb_3O_4 which, in fact, is a mixed oxide of PbO and PbO_2, *viz.*, $2PbO.PbO_2$.

Monoxides. Carbon monoxide is obtained by burning carbon in a limited supply of oxygen.

Pure CO can be obtained by heating formic acid with sulphuric acid, the latter acting as a dehydrating agent.

It is a colourless, odourless toxic gas. Its toxic nature is due to its ability to form a complex with haemoglobin in the blood. Carbon monoxide is an essential constituent of gaseous fuels like water gas, producer gas, etc.

The bonding in carbon monoxide may be represented as

$$:C:::O: \quad \text{or} \quad C{\equiv}O:$$

Two pairs of electrons are considered to be shared between carbon and oxygen resulting in a double bond. The oxygen may then be considered to be donating its lone pair of electrons to carbon giving a coordinate bond. The properties of CO can be explained satisfactorily if it is maintained that carbon monoxide is a resonance hybrid of three structures, as shown below :

$$:C::\ddot{O}: \longleftrightarrow :\overset{-}{C}:::\overset{+}{O}: \longleftrightarrow :\overset{+}{C}:\overset{-}{\ddot{O}}:$$

The molecular orbital structure of CO has already been discussed in Chapter 4.

SiO can be obtained by heating silicon dioxide with silicon at about 1300°C in vacuum.

$$SiO_2 + Si \longrightarrow 2SiO$$

Stannous chloride when reacted with weak alkali solutions forms a white precipitate of stannous hydroxide, $Sn(OH)_2$, which on dehydration in the absence of air gives stannous oxide, SnO.

$$Sn(OH)_2 \xrightarrow{-H_2O} SnO$$

GeO can be obtained by dehydrating $Ge(OH)_2$ or by heating Ge and GeO_2 at about 1000°C.

$$Ge(OH)_2 \longrightarrow GeO + H_2O$$

$$GeO_2 + Ge \longrightarrow 2GeO$$

When heated to 700°C and above, GeO undergoes disproportionation to give GeO_2 and Ge.

PbO is obtained by reacting molten lead with air or oxygen above 600°C.

Among the monoxides, CO is *neutral*, GeO is *basic* while SnO and PbO are *amphoteric*.

Dioxides. Carbon dioxide is obtained on burning carbon in excess of air.

In the laboratory, it can be prepared by the action of cold, dilute hydrochloric acid on marble ($CaCO_3$).

It is a colourless gas with a faint pungent odour and slight acidic taste. It dissolves in water to a small extent giving carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

It, therefore, behaves as a *weak acid*. It dissolves in alkalies to form salts.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

Solid carbon dioxide, commonly known as **dry ice**, is a soft, white, snow-like substance with specific gravity 1·53 and melting point – 56·6°C at 5·2 atm pressure. It is manufactured by evaporating liquid carbon dioxide at 20°C and 70 atm pressure to a pressure of less than 5·2 atm. Solid carbon dioxide is used as a refrigerant under the commercial name drikold. It is highly suitable for this purpose as it leaves no residue. It is used as a substitute of ice in cold drinks and in the preparation of ice-cream. Mixed with ether or acetone it provides freezing mixtures with exceedingly low temperatures. It is extensively used in the transport of perishable food-stuffs. It provides cold as well as an inert atmosphere (devoid of oxygen). Both these factors help in killing the undesirable bacteria which otherwise spoil the food.

It is also used in hospitals for surgical operations of sores.

Artificial rain-making has also been accomplished by spraying small pellets of dry ice from aeroplanes over clouds to produce condensation.

The bonding in carbon dioxide is represented as

$$:\ddot{O}::C::\ddot{O}: \quad \text{or} \quad :\ddot{O}{=}C{=}\ddot{O}:$$

However, carbon–oxygen bond length in carbon dioxide is 1·15 Å while the value to be expected for a double bond, C=O, is about 1·20 Å and for a triple bond, C≡O, is 1·10 Å. This shows that the simple double bond formula is inadequate.

It is now maintained that resonance occurs between the three possible structures given below :

$$:\overset{-}{\ddot{O}}{-}C{\equiv}\overset{+}{O}: \longleftrightarrow :\ddot{O}{=}C{=}\ddot{O}: \longleftrightarrow :\overset{+}{O}{\equiv}C{-}\overset{-}{\ddot{O}}:$$

Silicon dioxide, frequently referred to as **silica,** is obtained by heating silicon in oxygen.

$$Si + O_2 \longrightarrow SiO_2$$

Pure silica (amorphous form) can be prepared as a white powder by the action of silicon tetrachloride or tetrafluoride with water.

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

It is insoluble in water and in all acids except HF with which it reacts to form silicon tetrafluoride.

$$SiO_4 + 4HF \longrightarrow SiF_4 + 2H_2O$$

It is acidic and dissolves in hot concentrated alkalies to form sodium silicate.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

Structure of SiO_2.. The study of its crystal structure by X-rays has shown that silica forms 'giant molecules' by linking together of a number of SiO_4 tetrahedra in each of which a silicon atom is linked to four oxygen atoms. This structure, though extending three-dimensionally, may be represented, in a simplified form as shown in Fig. 3.

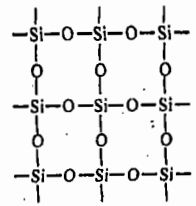


Fig. 3. Structure of SiO_2.

It is to be noted that while CO_2 is a *gas*, SiO_2 is a hard *solid* with a very high melting point. This characteristic difference may be explained as follows : The carbon atom has a small radius (0·77 Å). The positively charged nucleus, therefore, attracts outer electrons very strongly and does not permit the oxygen to combine with another carbon atom. In silica, however, the size of silicon atom (1·17 Å) is fairly large as compared to that of carbon. As a result, the positively charged nucleus cannot attract the outer electrons so strongly and hence the oxygen atom can be shared between two different silicon atoms. This leads to the formation of a giant SiO_2 molecule as shown.

In terms of atomic orbital theory, the formation of double bond between C and O atoms requires the lateral overlapping of $2p$ orbitals of carbon atom with the $2p$ orbitals of oxygen atom. Since the size and energy of the $2p$ orbitals of carbon and $2p$ orbitals oxygen atoms are nearly of the same level, they overlap effectively to form pi bonds between C and O atoms. This permits the formation of monomeric O=C=O molecule.

The formation of double bond between Si and O atoms requires the lateral overlapping of $3p$ orbitals of silicon with $2p$ orbitals of oxygen atom. Due to appreciable differences in the size and energy of these orbitals, $3p$ and $2p$ orbitals cannot overlap effectively to form pi bonds between Si and O atoms. This hinders the formation of Si=O bond in SiO_2 molecule. The tetravalency of silicon is acquired by forming four Si – O bonds. Thus, SiO_2 molecule comprises of a tetrahedron which contains one Si atom surrounded by four oxygen atoms (see central silicon atom in Fig. 3). These tetrahedra are linked together by sharing of the oxygen atoms between the two adjacent tetrahedra.

The crystal structure in silica is highly stable and, therefore, a considerable amount of energy is needed to break it. This explains the hardness and high melting point of silica.

Germanium and **tin dioxides** are obtained by heating germanium and tin with oxygen or air.

$$Ge + O_2 \longrightarrow GeO_2$$

$$Sn + O_2 \longrightarrow SnO_2$$

Lead dioxide is formed by electrolytic oxidation of lead.

The dioxides GeO_2 and SnO_2 are amphoteric. For example, SnO_2 reacts with acids as well as alkalies.

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

It is evident from the above discussion that the acidic character of dioxides decreases and basic character increases as move down the group.

II. Important Compounds of Elements of Group 14

COMPOUNDS OF CARBON

***Metal Carbonyls**

Carbon atom of carbon monoxide has a lone pair of electrons which can be donated to transition metals to form complex compounds called metal carbonyls Thus, **metal carbonyls** *are complex compounds of transition metals with carbon monoxide.* The number of carbon monoxide molecules which get chemically bonded to a metal through coordinate bonds vary with the nature of the metal. For example, the number of CO molecules bonded to nickel in nickel carbonyl, $Ni(CO)_4$, is 4 while in chromium carbonyl, $Cr(CO)_6$, it is 6.

Carbonyls are formed readily with transition metals since they have vacant d orbitals which can accept the donated electron pairs. The number of coordinate bonds that can be formed in this manner depends largely on the number of vacant orbitals. Generally, the number of ligands attached is such that the metal atom appears to possess the same number of electrons as the next noble gas. For example, the atomic number of nickel is 28, *i.e.*, it has 28 electrons. According to the valence bond concept of metal–ligand bonding in coordination complexes, each CO molecule donates one lone pair of electrons to the metal ion to form Ni←CO bond. Four CO molecules donate 8 electrons in all raising the number of electrons in the central atom to 36 which is equal to the number of electrons contained in the next noble gas, krypton. This number is called effective atomic number. *The total number of electrons*

*For a detailed discussion of metal carbonyls, refer to Chapter 32 on Mononuclear Complexes of Pi Acceptor Ligands.

present in the atom of the metal forming the complex, including those gained by sharing in the formation of the complex, is called the **effective atomic number** *of the metal.*

The structure of nickel carbonyl, $NiCO_4$, is represented in Fig. 4.

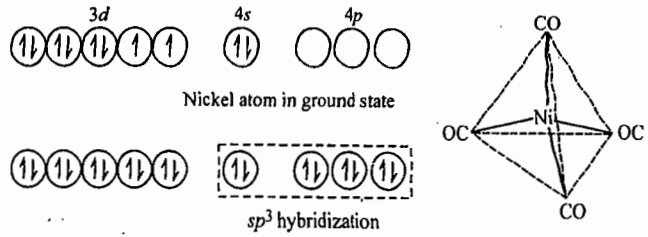


Fig. 4. Tetrahedral structure of nickel carbonyl, $Ni(CO)_4$.

Since the energy of $3d$ and $4s$ electrons is not very much different, the $4s$ electrons can easily go to fill the $3d$ orbitals, *vacating thereby the* $4s$ orbital. Thus, four orbitals (one $4s$ and three $4p$) become available for chemical bonding with four CO molecules to form the complex, $Ni(CO)_4$. Since all the four bonds are known to be exactly identical, it follows that s and p orbitals hybridise to give four sp^3 hybrid orbitals of the same energy. The molecule, $Ni(CO)_4$, has, therefore, a **tetrahedral structure**, as shown.

Some other important carbonyls are $Fe(CO)_5$, $V(CO)_6$, $Cr(CO)_6$, $Mo(CO)_6$, etc. These are called **mononuclear carbonyls** since there is only one metal atom in them. A large number of **polynuclear carbonyls** which contain more than one metal atom are also known. The common examples are $Co_2(CO)_8$, $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, etc. The binuclear carbonyl $Fe_2(CO)_9$ has a *bridged structure* in which bonding between metal atoms occurs through the CO group. The binuclear carbonyl $Co_2(CO)_8$ has a *non-bridged structure* in which the metal atoms are linked directly, *i.e.*, as Co – Co. Trinuclear carbonyls are known to have cyclic structures.

Preparation of Carbonyls. The metal carbonyls can be prepared by the following general methods:

1. By direct interaction of carbon monoxide with finely divided transition metals under suitable conditions of temperature and pressure. For example,

$$Ni + 4CO \xrightarrow[1\,atm]{30°C} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[200\,atm]{200°C} Fe(CO)_5$$

2. By the action of carbon monoxide on a metal oxide or halide in the presence of a reducing agent (generally excess of CO itself). For example,

$$OsO_4 + 9CO \xrightarrow[350\,atm]{250°C} Os(CO)_5 + 4CO_2$$

$$2CrCl_3 + 12CO \xrightarrow[LiAlH_4,\ ether]{115°C,\ 70\,atm} 2Cr(CO)_6 + 3Cl_2$$

3. Metal carbonyls can also be prepared as follows :

$$2CoCO_3 + 2H_2 + 8CO \xrightarrow[120–200°C]{250–300\,atm} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

$$VCl_3 + 6CO + 3Na \xrightarrow[\text{high pressure}]{120°C} V(CO)_6 + 3NaCl$$

4. Polynuclear carbonyls are generally prepared by thermal or photochemical decomposition of simple carbonyls.

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

$$2Co_2(CO)_8 \xrightarrow{70°C} Co_4(CO)_{12} + 4CO$$

Properties of Carbonyls. The simple carbonyls, having only one metal atom, *viz.*, $M(CO)_n$, are generally *colourless* liquids, or solids with low melting points. The well known examples are $V(CO)_5$ which is a *black* solid and $Fe(CO)_5$ which is a *yellow* liquid.

Chemical properties of carbonyls are quite varied. Some of the most important ones are discussed below.

1. The alkaline hydrolysis of $Fe(CO)_5$ gives yellow alkali carbonyl hydride.

$$Fe(CO)_5 + 3NaOH \longrightarrow Na[HFe(CO)_4] + Na_2CO_3 + H_2O$$

2. Reduction of carbonyls by suitable reductants gives carbonylates. For example,

$$CO_2(CO)_8 + 2Na \xrightarrow{\text{Tetrahydrofuran}} 2Na[Co(CO)_4]$$

$$Mn_2(CO)_{10} + 2Li \longrightarrow 2Li[Mn(CO)_5]$$

3. Carbonyls react with the halogens to form the corresponding halides.

$$Mn_2(CO)_{10} + Br_2 \xrightarrow{40°C} 2Mn(CO)_5Br$$

$$Fe(CO)_5 + I_2 \longrightarrow [Fe(CO)_4I_2] + CO$$

4. The CO group can be displaced by other groups such as PF_3, PCl_3, etc. Thus,

$$Ni(CO)_4 + 2PF_3 \longrightarrow Ni(CO)_2(PF_3)_2 + 2CO$$

In addition to the above reactions, each carbonyl gives a number of specific reactions, the discussion of which is, however, beyond the scope of the book.

Metal Cyanides

Metal cyanides may be classified into *ionic, covalent* and *complex cyanides*. A brief description of each type is given below.

1. Ionic Cyanides. Ionic cyanides are generally prepared by neutralising HCN with appropriate alkali.

NaCN can also be prepared by any one of the following high-temperature reactions :

$$2Na + 2C + 2NH_3 + 3/2\ O_2 \xrightarrow{\text{heat}} 2NaCN + 3H_2O$$

$$NaNH_2 + C \xrightarrow{\text{heat}} NaCN + H_2$$

$$Na_2CO_3 + 4C + N_2 \xrightarrow{\text{heat}} 2NaCN + 3CO$$

The bond between the metal and the cyanide group is predominantly *ionic*. The radius of CN^- ion. (1·91 Å) falls in between the radii of Cl^- and Br^- ions (1·81 Å and 1·96 Å, respectively). The crystal structure of the ionic cyanides is similar to that of the alkali metal halides. Sodium, potassium and rubidium cyanides have NaCl-type structure whereas cesium and thallium(I) cyanides have CsCl-type structure. At room temperature, the freely rotating CN^- groups occupy the Cl^- lattice sites. At lower temperatures, the free rotation of CN^- groups ceases and all of them become parallel at their respective lattice sites.

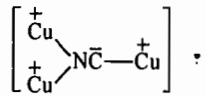
Lithium cyanide has a loosely packed 4-coordinate geometry. That is why LiCN has low density (1·02 g cm^{-3}) and low melting point (157°C)

2. Covalent Cyanides. Metals such as silver, gold, platinum, palladium, nickel and copper form *covalent cyanides*. Examples are : AgCN, $Ni(CN)_2$, $Pd(CN)_2$, etc. X-ray studies on silver cyanide reveal that the compound has a chain-like structure which may be represented as

$$Ag-C\equiv N\cdots\cdots Ag-C\equiv N\cdots\cdots Ag-C\equiv N\cdots\cdots$$

The structure shows the linking of Ag atoms through cyanide bridges. Similar bridges are believed to be present in gold cyanide as well as in some other cyanides.

A cyanide group is mostly bonded to the metal M through the carbon atom. However, the metal cyanide MCN has a tendency to coordinate with another metal atom through N atom as well. An example where a cyanide group is linked to three metal atoms is provided by a cyano complex $[Cu_3CN]^{2+}$ of Cu(I) which has the cyano bridge of the type shown :



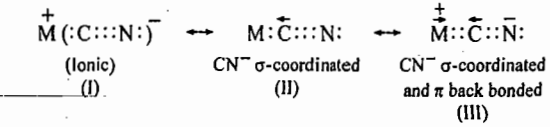
The lines in this structure do not represent exact bond order.

The cyanide group is isoelectronic with CO and has unfilled $\overset{*}{\pi}$ orbitals which may form π bonds with the filled $d\pi$ orbitals of the metal so that the bond order in metal–carbon bond may be greater than one.

3. Complex Cyanides. Cyanides containing discrete groups of the type $[M(CN)_n]^{x-n}$ are called complex cyanides. The metal ion which has been shown to be in $+x$ oxidation state, generally belongs to the transition series or immediately follows the transition series. These complex cyanides have properties quite different from the simple cations from which these are derived. The metal ions in these cyanides sometimes have unusual oxidation states. The coordination number of the metal ion may be 2 as in $[Cu(CN)_2]^-$, 4 as in $[Ni(CN)_4]^{2-}$, 6 as in $[Fe(CN)_6]^{4-}$ or 8 as in $[Mo(CN)_8]^{4-}$.

The bonding in complex cyanides occurs mostly between metal M and C of cyanide group. As already stated, cyanide group is isoelectronic with CO containing two $\overset{*}{\pi}$ orbitals capable of overlapping with $d\pi$ orbitals of the metal. Thus, there is a possibility of $d\pi - \overset{*}{\pi}$ bond formation apart from a normal sigma bond formation between M and C so that the bond order of M – C bond is greater than one.

According to the valence bond approach, the actual structure of M – CN is a resonance hybrid of the following structures :



It may be noted that in resonating structure III, the additional electron pair between M and C is contributed by M through pi back bonding.

Hydrogen Cyanide, HCN

Preparation. 1. Hydrogen cyanide can be prepared by reacting NaCN or KCN with any acid. For example,

$$NaCN + H_2SO_4 \longrightarrow Na_2SO_4 + HCN$$

2. On a large scale, it is prepared from methane.

$$CH_4 + NH_3 + 3/2\ O_2 \xrightarrow[1200\text{–}1300°C]{\text{Pt–Rh, 2 atm}} HCN + 3H_2O \text{ (Andrusson process)}$$

$$CH_4 + NH_3 + 3/2\ O_2 \xrightarrow[1000\text{–}200°C]{\text{Pt}} HCN + 3H_2O \text{ (Degusso process)}$$

Physical Properties. *HCN is a colourless substance which melts at* –134°C and boils at 25·6°C. It is highly poisonous. It has a very high dielectric constant (~ 115 at 20°C). This high value is due to the association of HCN molecules through hydrogen bonding. It is miscible with water, ethanol, ether, etc.

Chemical Properties. 1. HCN has predominantly a covalent character with some ionic contribution in bonding. That is why its aqueous solution is weakly acidic and is neutralised by alkalies. Thus,

$$HCN + NaOH \rightleftharpoons NaCN + H_2O$$

2. HCN is easily oxidised to cyanogen (C_2N_2) or cyanate ion.

$$HCN \rightleftharpoons 1/2\ (C_2N_2) + H^+ + e^-$$

$$HCN + H_2O \rightleftharpoons [CNO]^- + 3H^+ + 2e^-$$

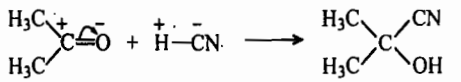
3. It is easily reduced to CH_3NH_2.

$$HCN + 2H_2 \xrightarrow[140°C]{\text{Pd}} CH_3NH_2$$

4. HCN is readily hydrolysed to give HCOOH.

$$HCN \xrightarrow[H_2O]{H^+} \underset{\text{Formamide}}{HCONH_2} \xrightarrow[H_2O]{H^+} HCOONH_4 \longrightarrow HCOOH + NH_3$$

5. It reacts with carbonyl compounds to give cyanohydrins. For example,



Acetone Acetone cyanohydrin

Uses. HCN is used in the manufacture of acrylonitrile, metal cyanides, methyl methacrylate and many other organic compounds. It is also used in the manufacture of insecticides and pesticides.

Metal Carbides

Metal carbides can be divided into the following categories :

1. Salt-like Carbides 2. Covalent Carbides 3. Interstitial Carbides

1. Salt-like Carbides. Carbides of this type are simple compounds of carbon with more electropositive elements, *i.e.*, with metals of Groups 1, 2 and 13. The metal, its oxide or hydride is heated strongly in an electric arc with carbon to get the required carbide. For example,

Be_2C is obtained by heating BeO and C at 1900–2000°C.

$$2BeO + 3C \xrightarrow{1900\text{–}2000°C} Be_2C + 2CO$$

Calcium carbide is obtained by heating lime and coke at 2200–2250°C.

$$CaO + 3C \longrightarrow CaC_2 + CO$$

Aluminium carbide is prepared by heating Al and C in an electric furnace.

$$4Al + 3C \longrightarrow Al_4C_3$$

In general, these compounds exist as transparent crystals and in the solid state they are non-conductors of electricity.

They are readily hydrolysed in water yielding different hydrocarbons. The salt-like carbides are further classified according to the hydrocarbon which they produce on hydrolysis, as illustrated below.

1. *Acetylides.* The carbides which yield **acetylene** on hydrolysis are known as **acetylides**. The examples are MgC_2, BeC_2 and CaC_2.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

They contain C_2^{2-}, *i.e.*, $(C \equiv C)^{2-}$ ions. Some other carbides having similar structures are Cu_2C_2, Ag_2C_2, etc. These, however, are *not* hydrolysed yielding acetylene and are, therefore, *not* regarded as true acetylides.

2. *Methanides.* The carbides such as aluminium and beryllium carbides, Al_4C_3 and Be_2C, which give **methane** on hydrolysis, are known as **methanides**. For example,

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

These carbides contain C^{4-} ions.

3. *Allylides.* Magnesium carbide, Mg_2C_3, is the only carbide which yields **allylene** on hydrolysis.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + \underset{\text{Allylene}}{CH_3C \equiv CH}$$

This carbide is, therefore, classified as an **allylide**.

4. A few carbides, as of thorium and lanthanides, of formula MC_2, yield, on hydrolysis, a mixture of several hydrocarbons including acetylene, olefins and hydrogen.

2. Covalent Carbides. These carbides contain carbon covalently bonded with elements which have the same electronegativity as carbon or a higher value, such as hydrogen, sulphur and chlorine. The covalent carbides can be divided into two categories depending upon their volatility.

(*i*). The first category consists of covalent carbides which contain small discrete molecules. These are formed by combination of carbon with hydrogen or the elements of Groups 16 and 17. The examples are CH_4, CS_2 and CCl_4. These carbides are either gases or volatile liquids and are not thermally stable. In fact, these compounds are not included amongst carbides at all. These are generally included amongst hydrides, sulphides and halides of carbon, respectively.

(*ii*). The second category consists of giant molecules formed by linking together of a large number of simpler units. The common examples are boron carbide, B_4C and silicon carbide, SiC. These are thermally stable, hard and chemically inert solids.

3. Interstitial Carbides. These carbides are prepared, as usual, by the direct combination of metal and carbon or by the reduction of metal oxide with carbon at high temperature close to 2000°C. Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retain their close-packed lattice strcutures and *incorporate carbon atoms in their octahedral interstices* to give MC and M_2C type carbides. The common examples are WC, TaC, V_2C, Nb_2C, Ta_2C, W_2C. These carbides melt at very high temperatures. They are extremely hard refractory materials and have melting points in the range of 3000–4000°C. Since carbon atoms occupy octahedral interstices in close packed lattice of metal atoms, the size of metal atoms must be large enough to form octahedral sites of sufficient size to accommodate C atoms. The limiting radius for metal atoms has been found to be 1·35 Å. Interestitial carbides are very hard and brittle. They are good conductors of electricity and are chemically inert. Due to their extensive hardness and chemical inertness, WC and TaC are used for the manufacture of high speed cutting tools.

Metals with atomic radius below 1·3 Å, as, for example, iron (1·26 Å), chromium (1·27 Å) and manganese (1·27 Å), form carbides which have properties in between those of the salt-like and the interstitial carbides. The carbon atoms in these carbides are located inside the trigonal prisms formed by the metal atoms. These carbides are relatively less stable and are easily decomposed by acids and water.

Applications of Carbides in Industry. The properties of carbides of each type have been described above. Some of these compounds find many applications in industry.

1. Silicon carbide, for example, is used as an *abrasive* under the name *carborundum* and also as a *refractory material*. At high temperatures it has thermal conductivity higher than that of any other refractory material and is, therefore, superior to all of them. It is also very resistant to abrasion and corrosion. It also finds applications in *nuclear reactors* as it provides a good material for making containers for nuclear fuels at high temperatures.

2. Boron carbide, B_4C, which is even harder than silicon carbide, is being used now increasingly as an abrasive. It is also used as a shield against radioactive radiations.

3. Tungsten carbide, WC, is used in making tools and dies.

Carbon Disulphide, CS_2

Preparation. 1. Carbon disulphide is prepared by directly heating sulphur and coke in iron retorts at 750°C – 1000°C.

$$C + 2S \xrightarrow[750\text{–}1000°C]{\text{heat}} CS_2$$

2. It is also prepared from natural gas as follows :

$$CH_4 + 4S \xrightarrow[\text{or } Al_2O_3]{SiO_2 \text{ gel}} CS_2 + 2H_2S$$

Physical Properties. Pure carbon disulphide is a colourless, volatile liquid boiling at 46·2°C. It freezes at – 111·6°C and has a flash point of – 30°C. Its vapour are toxic and have an adverse effect on the nervous system.

Chemical Properties. 1. CS_2 is highly inflammable and burns in air to give CO_2 and SO_2.

$$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$$

2. It combines with metal sulphides to give thiocarbonates.

$$MS + CS_2 \longrightarrow MCS_3$$

where M is a divalent metal.

3. It reacts with aqueous NaOH to give a mixture of Na_2CO_3 and Na_2CS_3 (sodium thiocarbonate).

$$3CS_2 + 6NaOH \longrightarrow Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

4. It reacts with ammonia and primary and secondary amines to give dithiocarbamates.

$$2NH_3 + CS_2 \longrightarrow \underset{\text{Amm. dithiocarbamate}}{NH_4(H_2NCS_2)}$$

$$(C_2H_5)_2NH + CS_2 \xrightarrow{NaOH} \underset{\text{Sodium salt of N, N diethyl dithiocarbamate}}{(H_5C_2)_2N{-}C(=S)S^-\,Na^+}$$

5. Water reacts with CS_2 slowly to give COS and H_2S at 200°C and CO_2 and H_2S at higher temperatures.

$$CS_2 + H_2O \longrightarrow \underset{\text{Thiocarbon dioxide}}{COS} + H_2S$$

$$COS + H_2O \longrightarrow CO_2 + H_2S$$

6. MgO, SO_3, HSO_3Cl convert CS_2 to COS in a similar manner. For example,

$$MgO + CS_2 \longrightarrow COS + MgS$$

$$COS + MgO \longrightarrow CO_2 + MgS$$

7. CS_2 reacts with ethanol in the presence of alkalies to give sodium ethyl dithiocarbonate, also known as *sodium xanthate*.

$$CS_2 + NaOH + C_2H_5OH \longrightarrow \underset{\text{(Sodium ethyl dithiocarbonate)}}{S{=}C(OC_2H_5)(SNa)} + H_2O$$

If, in the above reaction, ethanol is replaced by cellulose, the resulting product is cellulose xanthate which dissolves in aqueous alkali solution to give a viscous solution named as *viscose*. The viscose is treated with an acid to yield *viscose rayon* and *cellophane*. During this treatment, cellulose is regenerated.

8. CS_2 reacts with Cl_2 to give CCl_4, as described earlier.

9. Fluorine reacts with CS_2 to form a variety of fluorinated products such as SF_4, SF_6, S_2F_{10}, etc. The exact nature of the product depends upon the reaction conditions.

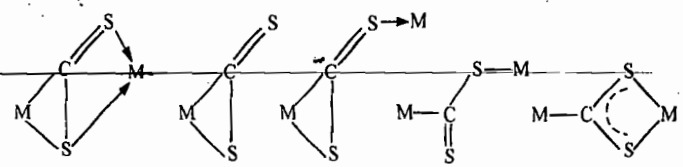
10. It readily undergoes 'insertion reactions' introducing thereby a $-S-\overset{S}{\overset{\|}{C}}-$ group in between a metal–nitrogen bond as also in some other bonds. For example,

$$Ti[N(C_2H_5)_2]_4 + CS_2 \longrightarrow \underset{\text{Tetrakis diethyl-dithiocarbamatotitanium}}{Ti\left[\begin{matrix}-S\\-S\end{matrix}\!\!>C-N<\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right]_4}$$

11. CS_2 is an efficient complexing agent. This is evidenced by the following reaction :

$$Pt(PPh_3)_2X_2 + CS_2 \longrightarrow \begin{matrix}Ph_3P\\Ph_3P\end{matrix}\!\!>Pt<\begin{matrix}C{=}S\\S\end{matrix} + X_2$$

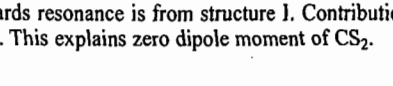
Many complexes of CS_2 with the following types of CS_2 linkages are known :



Uses. Carbon disulphide is used in the manufacture of viscose rayon and cellophane. It is also used in the vulcanization of rubber and for manufacturing insecticides.

Structure of CS_2. Electron diffraction studies show that CS_2 molecule in gaseous phase is *linear* like CO_2. The dipole moment of CS_2 is also zero like that of CO_2. The CS bond distance in CS_2 is found to be 1·54 Å which is quite close to C = S distance. The C – S single bond distance is known to

be 1·8 Å which is obviously far greater than the observed C = S distance in CS_2. Actual structure of CS_2 is maintained to be a resonance hybrid of the following resonance structures :

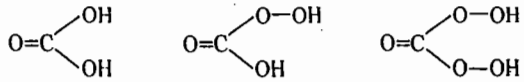


(I) (II) (III)

Major contribution towards resonance is from structure I. Contributions of structures II and III are minor but equal and opposite. This explains zero dipole moment of CS_2.

Percarbonates

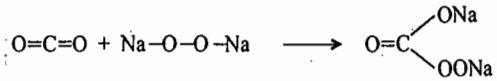
Percarbonates are supposed to be derived from percarbonic acids known as *permonocarbonic acid* and *perdicabonic acid*. The formulae and structures of these acids in relation to carbonic acid are represented as



Carbonic acid Permonocarbonic acid Perdicarbonic acid

These acids have not been isolated so far but their salts, *permonocarbonates* and *perdicarbonates* are known. However, they are not very stable.

Permonocarbonates. Permonocarbonates of sodium and potassium can be prepared by passing carbon dioxide through a solution of the corresponding alkali peroxide. Thus,



These can also be prepared by the action of hydrogen peroxide on the corresponding alkali carbonate. Thus,

$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2CO_4 + H_2O$$

The permonocarbonates when freshly prepared contain water of crystallisation. They are soluble in water, the solution behaving as if it is a mixture of simple carbonate and hydrogen peroxide. The salts, therefore, may be regarded as simple hydrated carbonates containing also hydrogen peroxide as a molecule of crystallisation, the composition of the sodium salt being represented as

$$Na_2CO_3.H_2O_2.H_2O$$

This formula is supported by the fact that the compound slowly liberates iodine from a solution of potassium iodide and that hydrogen peroxide can be extracted by shaking the aqueous solution with ether.

Perdicarbonates. Sodium and potassium perdicarbonate can be prepared by the electrolysis of a concentrated aqueous solution of the corresponding carbonate at a temperature of – 110°. The electrolytic reaction may be represented as

$$K_2CO_3 \longrightarrow K^+ + KCO_3^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : *At anode* :

$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2 \qquad 2KCO_3^- \longrightarrow K_2C_2O_6 + 2e^-$$

Potassium perdicarbonate appears as a bluish precipitate. It is washed with cold water, alcohol and ether and finally dried. It is stable at ordinary temperatures in the absence of moisture. In water it decomposes to give potassium carbonate.

$$2K_2C_2O_6 \longrightarrow 2K_2CO_3 + 2CO_2 + O_2$$

It also decomposes on heating. It acts as an oxidising agent and liberates iodine from potassium iodide.

$$K_2C_2O_6 + 2KI \longrightarrow 2K_2CO_3 + I_2$$

It can also oxidise lead sulphide to lead sulphate.

$$PbS + 4K_2C_2O_6 \longrightarrow PbSO_4 + 4K_2CO_3 + 4CO_2$$

Intercalation Compounds of Graphite

Intercalation means the *insertion of layers of atoms, ions or molecules of a chemical species between the layers of a host material to form 'sandwich' type of compounds.*

In graphite, the interlayer distance (3·36 Å) is considerably greater than the normal C–C covalent bond distance (1·42 Å). The adjacent layers in graphite are, therefore, held together by weak van der Waals forces. It is thus possible for a number of substances to intercalate (*i.e.*, get inserted) between the layers of graphite to give **intercalation compounds** of variable composition depending upon the nature of the species which are inserted between the layers. Some typical types of intercalation compounds of graphite are described below.

1. Intercalation Compounds of Alkali Metals. When graphite is reacted with potassium metal at 300°C, it gives an intercalation compound of composition C_8K.

$$8C\,(\text{graphite}) + K \xrightarrow{300°C} C_8K$$

Rubidium and cesium react in a similar manner to give the intercalation compounds, C_8Rb and C_8Cs, respectively.

Intercalation is difficult with lithium and sodium. However, extra pure sample of graphite reacts with lithium at 500°C to give brass coloured C_6Li and copper coloured $C_{12}Li$. Sodium also reacts with graphite under strictly controlled conditions to form $C_{64}Na$.

The intercalation compound C_8M (where M is K, Rb or Cs) is formed through a number of stages. The compound formed first is $C_{60}M$ (called *fifth stage* intercalation compound) which, in the presence of the alkali metal, gets gradually converted into $C_{48}K$ (called *fourth stage* intercalation compound) and then into $C_{36}M$ (called *third stage* intercalation compound), further into $C_{24}M$ (called *second stage* intercalation compound) and *finally* into C_8M (called **first stage intercalation compound**). Compounds with higher content of alkali metal than that in C_8M are *unstable* probably because of *electrostatic repulsion of intralayers of alkali metal cations.* C_8M is known to have an ionic structure, *viz.*, $C_8^-M^+$.

If the intercalation compound is heated under reduced pressure, the reaction occurs in the reverse direction accompanied by the gradual loss of the alkali metal. Thus, the intercalation compound C_8K changes, on heating, to $C_{24}K$, $C_{36}K$, $C_{48}K$ and finally to $C_{60}K$.

$$C_8K \xrightarrow{heat} C_{24}K \xrightarrow{heat} C_{36}K \xrightarrow{heat} C_{48}K \xrightarrow{heat} C_{60}K$$

1st stage compound (copper coloured) 2nd stage compound (steel blue) 3rd stage compound (dark blue) 4th stage compound (black) 5th stage compound (black)

Structure and Properties. The crystal structure of the *first stage* intercalation compound C_8K contains planar layer of K metal in between two layers of graphite, as shown in Fig. 5. The spacing between K atoms within a layer is twice the spacing between the centres of graphite hexagons in the graphite layers. The C – C distance within a layer of graphite is the same as in pure graphite but the spacing between two graphite layers in C_8K (5·4 Å) is larger than in pure graphite (3·36 Å). This is due to the entry of K atoms in between the two graphite layers. The structures of other intercalation compounds, *viz.*, C_8Rb and C_8Cs are similar to that of C_8K.

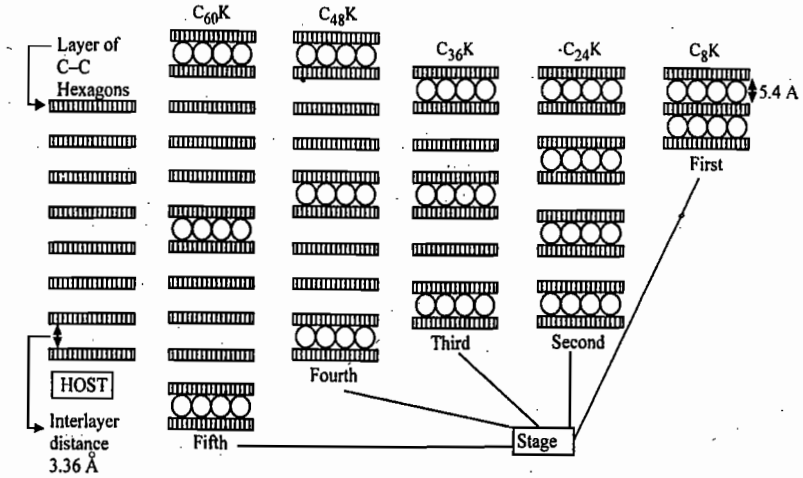


Fig. 5. Structures of intercalation compounds of graphite formed with potassium metal (shown as O) at different stages of intercalation (qualitative).

The structures of compounds formed at other stages of intercalation are arrived at by varying the frequency of occurrence of the intercalated layers containing alkali metal atoms in the host lattice. The structures of *fifth stage* compound $C_{60}K$, *fourth stage* compound $C_{48}K$, *third stage* compound $C_{36}K$, *second stage* compound $C_{24}K$ and first stage compound C_8K are represented in Fig. 5.

The intercalation alkali metal compounds are more conducting than graphite. They are paramagnetic while graphite is diamagnetic. Their electrical conductance decreases with increase in temperature as in metals. These properties indicate that in intercalation compounds bonding occurs through the transfer of electrons from alkali metal atoms to the conduction band of the host element (*i.e.*, graphite) so that the structure of these compounds can be written as $C_n^-M^+$. This very well explains why intercalation compounds are mostly formed by electropositive metals, *i.e.*, alkali metals.

Intercalation compounds of alkali metals are highly reactive. They readily react with water to produce alkali metal hydroxide and hydrogen gas.

$$C_nM + H_2O \longrightarrow MOH + 1/2\,H_2 + \underset{\text{(graphite)}}{nC}$$

2. Intercalation Compounds of Oxoacids and Metal Halides. Besides alkali metals, intercalation compounds are also formed by several oxoacids and metal halides.

Intercalation compounds of oxoacids are formed by reacting graphite with concentrated oxoacids under oxidising conditions, *i.e.*, in the presence of air or oxygen. *These compounds are called lamellar graphite salts.* The formation of these salts is reversible. The formation of the first stage intercalation compound with concentrated H_2SO_4 is as follows :

$$24C + 3H_2SO_4 + 1/2\,O_2 \longrightarrow \underset{\substack{\text{First stage compound}\\ \text{(Blue)}}}{C_{24}^+HSO_4^-.2H_2SO_4} + 1/2\,H_2O$$

The overall stoichiometry is close to the formula $C_8H_2SO_4$ as in C_8M.

A series of graphite nitrates such as $C_{24}^+NO_3^-.2HNO_3$ (blue), $C_{48}^+NO_3^-.3HNO_3$ (black), etc., can also be prepared in a similar manner. Besides HNO_3 and H_2SO_4, several other oxoacids are also known to form intercalation compounds with graphite. The extent of intercalation depends on the strength of the acid and its concentration. The formation of intercalation compounds with oxoacids leads to the swelling and crumbling of graphite electrodes in electrochemical processes conducted in acid media. The graphite electrodes thus need frequent replacement.

Electrical conductivity of intercalated graphite salts is higher than that of the pure graphite.

A non-conducting pale lemon coloured product of variable composition called **graphite oxide** is obtained by treating graphite with fuming nitric acid or concentrated nitric acid containing $KClO_3$ or with a mixture of concentrated nitric acid, concentrated sulphuric acid and $KClO_4$.

Graphite oxide decomposes between 70° – 200°C to CO_2, CO, H_2O and soot. Its structure consists of hexagonal network of C_6 rings in the chair form. It also contains some bridging O atoms, C=O and C – OH groups. The approximate formula of graphite oxide can be written as $C_6O_{1\cdot1-1\cdot7}(OH)_{1\cdot7-2\cdot5}$

Intercalation compounds with metal halides are prepared by reacting metal halides in the presence of the free halogens with graphite. The intercalated halides are all Lewis acids. For example, the first stage intercalated compound of $FeCl_3$ is $C_{6-7}FeCl_3$; second stage compound is $C_{12}FeCl_3$ and third stage compound is $C_{24-30}FeCl_3$.

In the intercalated graphite compounds of oxoacids and metal halides, there appears to be a transfer of electrons from the host (graphite) to the guest species which leads to the formation of intercalation species of the type , $C_{24}^+HSO_4^-.2H_2SO_4$, $C_{24}^+NO_3^-.2HNO_3$ (formed in the presence of oxygen) and $C_{10}^+Cl^-.FeCl_2.5FeCl_3$ and $C_{27}^+AlCl_4^-.2AlCl_3$ (formed in the presence of free chlorine). The formation of positive 'holes' near the top of the valence band of graphite explains the enhanced conductivity of these compounds.

3. Intercalation Compounds of Oxides and Sulphides. A number of oxides and sulphides also intercalate into graphite. Thus, oxides such as SO_3, N_2O_5, Cl_2O_7, CrO_3 and MoO_3 readily intercalate into graphite as do several sulphides such as V_2S_3, Cr_2S_3, WS_2, PdS and Sb_2S_3.

4. Intercalation Compounds of the Halogens. Graphite reacts with fluorine at 400° – 500°C to give **graphite monofluoride** which has a variable composition CF_n, n varying from 0·7 to about 1. The colour of CF_n depends upon the fluorine content and ranges from black ($n \sim 0{\cdot}7$) to transparent white ($n \sim 1$). The intercalation compound $CF_{\sim 1}$ is chemically inert. However, it gradually liberates fluorocarbons when heated to about 800°C. Since all the double bonds in graphite open up to add fluroine atoms during the formation of $CF_{\sim 1}$, it is non-conducting.

When a mixture of fluorine and hydrogen fluoride reacts with powdered graphite at room temperature, a bluish black intercalation compound is predominantly formed whose composition approaches, C_4F. The structure of C_4F comprises of graphite sheets with regularly spaced fluorine atoms above and below each graphite layer. Some C_2F is also formed during the above reaction.

Chlorine and bromine also form intercalated compounds with approximate compositions C_8Cl, C_8Br, $C_{12}Br$, $C_{16}Br$ and $C_{20}Br$.

Several interhalogens such as ClF_3, BrF_3, IF_5, also form a number of intercalation compounds with graphite.

COMPOUNDS OF SILICON

Silicides. These compounds are prepared either by the direct combination of the metal with silicon or by the reduction of SiO_2 with a mixture of the metal and carbon. The melting points of silicides are lower than those of the corrosponding carbides and borides. Several metals, both representative and transition, form silicides. Of these, the silicides of elements of Groups 1 and 2 are quite reactive. They hydrolyse readily to give products which depend upon the stoichiometry of the reacting silicide. Thus, whereas the hydrolysis of Ca_2Si produces $Ca(OH)_2$, SiO_2 and H_2, the hydrolysis of CaSi yields silanes alongwith polysilene and that of $CaSi_2$ gives H_2 and polysilene. The silicides of transition metals are less reactive compared to those of metals of Groups 1 and 2.

Like borides and carbides, the composition of metal silicides cannot be explained by the simple concept of valence. Since boron and silicon are closely related to each other, the silicides are structurally closely related to borides. Some metal-rich silicides M_3Si (M = V, Cr, Mo, Mn) have metal-like structures and like metals, they have good electrical conductivity. However, some other metal-rich silicides M_2Si (M = Mg, Ge, Sn, Pb, Ca, Ru, Ce, Rh, Ni) have non-metallic structures and are non-conductors of electricity. In silicon-rich silicides, atoms have a tendency to catenate into isolated Si_2 units (as in U_3Si_2), Si tetrahedra (as in K_4Si_4), Si chains (as in α USi_2, $ThSi_2$, $TiSi_2$), two-dimensional hexagonal Si nets (as in β USi_2) and three-dimensional Si frame work (as in $SrSi_2$). Many of the metal silicides have typical metallic lustre and hence are used in artificial jewellery.

Silicon Hydrides. These compounds are similar to hydrocarbons but are much less stable. The number of silicon hydrides is also much less than the number of hydrocarbons. These are called **silanes** and have the general formula Si_nH_{2n+2} where *n* stands for the number of silicon atoms. The individual members are known as *silane*, SiH_4, *disilane*, Si_2H_6, *trisilane*, Si_3H_8, etc. The first two members are colourless gases while the third and subsequent members are liquids.

These are produced by the action of acids on metallic silicides, *e.g.*,

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$

Actually a mixture of silanes is obtained. Monosilane can be separated by fractionating in vaccum, as in the case of boron hydrides.

Pure monosilane is prepared by reacting silicon tetrachloride with lithium aluminium hydride in ether.

$$SiCl_4 + LiAlH_4 \xrightarrow{\text{ether}} SiH_4 + LiCl + AlCl_3$$

Monosilane is unstable, decomposing spontaneously on coming in contact with air.

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

If the gas is bubbled through water then, as soon as it comes in contact with air, each bubble ignites giving vortex ring of finely divided silica (cf. phosphine). It decomposes slowly when brought in contact with water.

$$SiH_4 + 3H_2O \longrightarrow H_2SiO_3 + 4H_2$$

Monosilane is soluble in strong alkali solutions in the presence of air.

$$SiH_4 + 2NaOH + 1/2\ O_2 \longrightarrow Na_2SiO_3 + 3H_2$$

Thus, monosilane differs from methane in its reactions with water and sodium hydroxide. However, as in methane, the hydrogen atoms can be substituted by chlorine atoms giving SiH_3Cl (silyl chloride) SiH_2Cl_2 (dichlorosilane), $SiHCl_3$ (silicon chloroform) and $SiCl_4$ (silicon tetrachloride). The trisilylamine, $(SiH_3)_3N$, is not basic, unlike trimethylamine $(CH_3)_3N$.

Silicon Dioxide or Silica, SiO_2. Silica occurs in nature in several amorphous and crystalline forms. The three important crystalline forms are *quartz, tridymite* and *cristobalite*.

Quartz is the most common form. Its specific gravity is 2·648 and it melts in an electric furnace at 1740°C. It can be shaped into vessels such as flasks and beakers, like glass. These vessels have certain advantages over glass as the material is much less soluble in acids or alkalies and its coefficient of expansion is very small and the chances of breakage on sudden heating and cooling are small. Sometimes it occurs as clear colourless hexagonal crystals and is used for optical apparatus. More often it occurs in opaque or coloured masses. Certain coloured varieties are used as gems, *e.g., amethyst* (purple), *jaspar* (red) and *opal* (white).

Quartz is more transparent to ultraviolet light than is glass. It is, therefore, used in all apparatuses where ultraviolet light is to be used. *Sand* is also a crystalline form of quartz which is formed as a result of 'weathering' or disintegration of rocks and further breaking down by violent movements of water.

Quartz is stable below 870°C above which it changes into *tridymite*. Tridymite is stable between 870°C and 1470°C above which it changes into *cristobalite*. Cristobalite melts when heated to 1740°C.

Amorphous forms of silica are *agate, jaspar* and *onyx*.

Silica is also found in certain plants and animals. For example, the hard portions of straw and bamboo contain silica. The skeletons of certain marine organisms (*e.g.*, sponges) consist largely of silica. Claws of animals and finger nails also contain silica.

Pure silica (amorphous form) can be prepared as a white powder by the action of silicon tetrachloride or tetrafluoride with water.

$$SiCl_4.2H_2O \longrightarrow 4HCl + \underset{\text{Silica gel}}{SiO_2}$$

The silica gel is dehydrated by heating.

It is insoluble in water and in all acids, except hydrofluoric acid with which it reacts to form silicon tetrafluoride.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

It dissolves in hot concentrated alkalies to form sodium silicate.

$$SiO_2 + 2NaOH \longrightarrow 2Na_2SiO_3 + H_2O$$

The addition of hydrochloric acid to this mixture reprecipitates the hydrated gelatinous silica.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SiO_2$$

Silica, being a non-volatile substance, displaces volatile acids from their salts on heating to a high temperature, *e.g.*,

$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$

$$Ca_3(PO_4)_2 + 3SiO_2 \longrightarrow 3CaSiO_3 + P_2O_5$$

Apart from the few reactions given above, silica is an inert substance.

Uses. The important uses of the various natural forms of silica may be summarised as follows : 1. Quartz, when transparent, is used in making optical instruments and lenses. 2. The coloured varieties of quartz are used as gems, *e.g.*, amethyst, jaspar and opal. 3. The opaque quartz is used in making vessels which are acid and alkali resistant and can stand sudden changes of temperature and are, therefore, superior to glass vessels 4. Sand is used in the manufacture of glass, mortar and porcelain. It forms an important construction material when mixed with lime or cement. 5. A transluscent variety of glass, known as vitreosil, is obtained by fritting sand with an electrically heated carbon rod or plate. 6. Silica is used in making refractory bricks for furnace linings. 7. Sand (finely ground) is used in the extraction of phosphorus from phosphates.

Silicic Acids. When a dilute solution of sodium silicate, Na_2SiO_3, is poured gradually into a vessel containing excess of dilute hydrochloric acid, the following reaction takes place.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + SiO_2 + H_2O$$

However, no visible precipitate (of silica) is observed although the conductivity of the mixture falls appreciably indicating that the reaction as represented by the above equation has definitely taken place. If the liquid is placed in a dialyser, sodium chloride is seen to diffuse out completely leaving behind a colloidal solution of *silicic acid*, known as **silicic acid hydrosol**. This can be concentrated by evaporation, either by gentle heating or by keeping over concentrated sulphuric acid. The sol is readily coagulated on the addition of a small amount of sodium carbonate or phosphate to give a transparent jelly, known as *silica gel*.

Silicic acid has not been isolated. However, silicates of different compositions are known and may be considered to be derived from different hypothetical silicic acids, the more important of which are *orthosilicic acid*, H_4SiO_4 and *metasilicic acid*, H_2SiO_3. The latter may be considered to be derived from

the former by the loss of one molecule of water.

$$H_4SiO_4 \xrightarrow{-H_2O} H_2SiO_3$$

The other hypothetical acids are disilicic acid and trisilicic acid which contain 2 and 3 silicon atoms per molecule, respectively. Their formation from orthosilicic acid may be represented by the following equations.

$$2H_4SiO_4 \xrightarrow{-2H_2O} \underset{\text{Disilicic acid}}{H_2Si_2O_6} \quad \text{or} \quad 2SiO_2.2H_2O$$

$$3H_4SiO_4 \xrightarrow{-2H_2O} \underset{\text{Trisilicic acid}}{H_6Si_3O_9} \quad \text{or} \quad 3SiO_2.3H_2O$$

Silica Gel. Silica gel may be prepared by hydrolysing silicon tetrachloride or tetrafluoride or by adding a mineral acid such as hydrochloric acid to a fairly concentrated solution of sodium silicate or by adding, gradually, a solution of ammonium sulphate to that of sodium silicate.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SiO_2$$

$$Na_2SiO_3 + (NH_4)_2SO_4 \longrightarrow Na_2SO_4 + 2NH_3 + H_2O + SiO_2$$

In each case, silica separates out as a gel (also called a hydrogel), that is, a colloidal system in which water is dispersed in a solid. The gel is filtered and washed to remove the soluble impurities. It is then dried by heating at 110°C in an air-oven.

Uses. 1. When exposed to moist atmosphere it adsorbs moisture. Hence, dry silica gel is used as an excellent drying agent because it can take up a large amount of water vapour and, at the same time, is chemically inert. Every time, after drying, it can be used over again. 2. It can also adsorb sulphur compounds and is used in removing them from petroleum. 3. When silica gel is heated to fusion and cooled, it changes into a transparent solid known as *silica glass*. It is superior to ordinary glass since it softens at a lower temperature and can be more easily shaped into vessels such as crucibles, dishes, etc. It has low coefficient of expansion and, therefore, an article made of silica glass can withstand sudden changes in temperature. 4. It is also used in making certain types of optical lenses as it transmits ultraviolet light better than ordinary glass.

GLASS

The name **glass** is given to any amorphous and transparent solid which is produced on the solidification of a liquid. The word is generally used for the transparent substance obtained when white sand is fused with oxides and carbonates of alkali and alkaline earth metals and the molten mixture is cooled.

Glass is a mixture of a number of silicates. When it is heated it does not melt at a fixed temperature. On the other hand, it gradually softens and can be moulded into any desired shape. It is this property of glass which makes it a useful material since a number of articles of different shapes and forms can be made out of it. It completely melts into a liquid at a very high temperature.

Manufacture of Glass

Raw Materials. The raw materials required for the preparation of glass are

(*i*) *Silica* (in the form of sand).

(*ii*) *Compounds of alkali metals*, such as Na_2CO_3, Na_2SO_4, $NaNO_3$, K_2CO_3 and KNO_3.

(*iii*) *Compounds of alkaline earth metals*, such as $CaCO_3$, CaO, $BaCO_3$. These are required when glass of high refractive index is needed.

(*iv*) *Oxides of heavy metals*, such as PbO, Pb_3O_4. These are added for getting glass of higher refracting power.

(*v*) *Calcium phosphate*, $Ca_3(PO_4)_2$. This is required when it is desired to produce *opalescent glass*. Arsenic and antimony are also added in such cases, in the form of their oxides.

(*vi*) *Colouring materials*. Certain metallic oxides are added to fused silicates during the manufacture of glass to prepare glass of *different colours*. For example, ferric oxide is added to get yellow colour, chromic oxide to get green colour, manganese oxide to get purple colour and CoO to get blue colour in glass.

Manufacture of Ordinary Glass. The ordinary glass (soda glass), also known as window glass, has approximately the composition : $Na_2O.CaO.6SiO_2$. It is obtained by fusing together in proper proportions sodium carbonate, calcium carbonate and sand or quartz (silica, SiO_2). Each constituent is finely powdered and then mixed intimately with one another. A small amount of 'scrap glass' from a previous run is also added. This acts as a flux. The mixture is then fused in a tank furnace heated by producer gas on the regenerative principle of heat economy. The following reactions take place :

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$

In the early stages, considerable frothing occurs on account of the formation of carbon dioxide. On continued heating the entire amount of carbon dioxide is driven out and a clear viscous fused mass is obtained. This consists of a mixture of Na_2SiO_3 and $CaSiO_3$. It is then poured into moulds or stamped with dies to produce different articles such as bottles, flasks, etc. The articlcs are allowed *to cool gradually* (annealing).

Annealing. The glass if cooled rapidly becomes brittle and fragile and if cooled very slowly it devitrifies and becomes opaque. Therefore, the articles should be cooled neither very slowly nor very quickly. For this purpose, they are made to pass through a long tunnel-like furnace which is very hot at the mouth-end and very cold at the tail-end so that the articles are cooled gradually during their passage through the tunnel. This process is known as **annealing** and takes several days for completion.

Varieties of Glass. 1. Soda glass. The ordinary glass prepared in the above manner is known as **soda glass** or **soft glass**. Its approximate composition is : SiO_2 75%, sodium oxide 15%, calcium oxide 8%, aluminium oxide 2% (as an impurity). This is also called soft glass as it softens at a comparatively lower temperature and can be easily shaped into different forms. It is used in making cheap window panes, bottles, dishes, etc.

2. Potash glass (Hard glass). If sodium carbonate is replaced by potassium carbonate in the above process, a hard glass, which has a higher melting point and can withstand higher temperature, is obtained.

3. Flint glass. If calcium carbonate is replaced in sufficient quantity by lead carbonate or lead oxide (litharge), and sodium carbonate is replaced partly by potassium carbonate, a glass of higher refracting power, known as flint glass, is obtained. Its approximate composition is : silica 45%, sodium oxide 4%, potassium oxide 4%, calcium oxide 3%, lead oxide 44%. It has a higher density and transparency than ordinary glass and is used for making optical instruments as well as for ornamental purposes. It is prepared by fusing litharge, potassium carbonate and silica in proper proportions.

4. Crown glass. A partial replacement of silica by phosphorus pentoxide gives crown glass.

5. Pyrex glass. Addition of certain amounts of boron and aluminium oxides produces a glass with a very low coefficient of expansion, known as *pyrex glass*. This can withstand sudden alterations of temperature very well and is highly suitable for laboratory glass-ware such as flasks, beakers, etc., which are to be heated to high temperatures. Its approximate composition is : silica 80%, sodium oxide 4%, calcium oxide 0·5%, potassium oxide 0·5%, B_2O_3 12%, Al_2O_3 3%.

6. Jena glass. It is obtained by decreasing the alkali content and increasing the alumina content in ordinary soda glass. It also contains barium and zinc oxides and boron trioxide in place of some silica. This glass is stronger than the ordinary glass. At the same time, it is more resistant to the action of acids and alkalies.

7. Crooke's glass. This is a special type of glass used for optical purposes and contains cerium oxide.

8. Bottle glass. It is ordinary soda-lime glass containing MgO to the extent of 3·5 per cent and $Al_2O_3.Fe_2O_3$ to the extent of 0·5 per cent.

9. Ground glass. It is prepared by grinding ordinary soda (soft) glass by emery and turpentine oil or by *sand blasting*.

10. Safety glass. It is used in making wind screens of automobiles, aeroplanes, railway trains, etc. It is prepared by placing a layer of *transparent plastic* (usually a sheet of *vinyl acetate resin*) between two layers of glass by means of a suitable adhesive. The three layers are joined together tightly by the action of heat and pressure.

This glass does not break easily under ordinary impact. This is the reason for the name "safety glass" or "unbreakable glass" given to it. However, it does break under heavy impact. But the particles of glass do not shatter because they are held by the plastic.

Thermoplastics. The main disadvantage of using glass is that it is brittle and fragile. In recent years, it has been replaced, for a variety of purposes, by *transparent plastics*. A plastic consists of highly polymerised substances. It softens on heating and can be given any shape just like glass and is, therefore, sometimes called *thermoplastic*. The interlinking of the molecules in the polymerised materials gives it hardness as well as insolubility.

SILICATES

Silicates occur in earth's crust in abundance in the form of *silicate minerals* and *aluminosilicate clays*. Sodium silicate, Na_2SiO_3, is the only common silicate which is soluble in water. It is prepared by fusing sodium carbonate with silica (SiO_2) at 1500°C. Most of the silicates are insoluble in water. This is due to the great strength of the Si – O bond. This bond can be broken only on treatment with strong reagents like hydrofluoric acid.

The electronegativity of oxygen is 3·5 and that of silicon is 1·9. The electronegativity difference of 1·6 suggests that Si – O bond, though covalent, has an appreciable degree of ionic character.

All silicates comprise of $(SiO_4)^{4-}$ units which are formed by sp^3 hybridisation of Si orbitals. The outer electronic configuration of silicon atom in the excited state is $3s^1p_x^1p_y^1p_z^1$. Thus, it forms four bonds with oxygen atoms by utilising its sp^3 hybrid orbitals and yielding $(SiO_4)^{4-}$ units. The oxygen atoms pick up one electron each from some metal in order to complete their octets. As expected, $(SiO_4)^{4-}$ unit has a **tetrahedral structure,** as shown in Fig. 6. The plane circles represent oxygen atoms and the small dots represents the silicon atoms. As already mentioned, all silicates contain the tetrahedral $(SiO_4)^{4-}$ units. They differ from one another only in the manner in which these units are linked together.

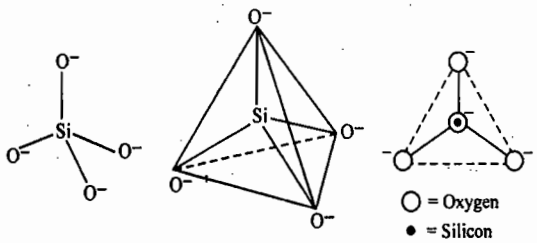


Fig. 6. Tetrahedral structure of $(SiO_4)^{-4}$ ion.

In some cases, several $(SiO_4)^{4-}$ tetrahedral units are bridged together through oxygen atoms of the units. The bridging oxygen atom is covalently bonded to the two Si atoms of the bridging $(SiO_4)^{4-}$ units. The number of oxygen atoms of an $(SiO_4)^{4-}$ unit which form bridges with other $(SiO_4)^{4-}$ units may be one, two, three or all the four. In this way, a number of complex silicates can be formed. The resulting silicate chains are negatively charged anions because any oxygen atom which is not a bridging atom carries a unit negative charge. This negative charge is balanced by a metal cation. Thus, metal

cations such as Li^+, K^+, Ca^{2+}, Al^{3+} are present in silicate minerals. These serve to hold the solid together by ionic attraction.

The structure of silicates has been understood recently with the development of X-ray diffraction techniques.

Different Types of Silicates

Depending upon the linkage of $(SiO_4)^{4-}$ tetrahedral units, the silicates may be classified into the following types.

1. Ortho silicates. These contain discrete $(SiO_4)^{4-}$ units. The common examples are *zircon* ($ZrSiO_4$), *willemite* (Zn_2SiO_4), *phenacite* (Be_2SiO_4). Another important group of orthosilicates is the *garnets* having the general formula $[M_3^{II}M_2^{III}(SiO_4)_3]$, where M^{II} can be Ca^{2+}, Mg^{2+} or Fe^{2+} and M^{III} can be Al^{3+}, Fe^{3+} or Cr^{3+}.

2. Pyrosilicates. These contain disilicate anion, $(S_2O_7)^{6-}$ units. The $(Si_2O_7)^{6-}$ units are formed by joining two tetrahedral $(SiO_4)^{4-}$ units through one oxygen atom, as shown in Fig. 7.

It may be noted that any oxygen atom which does not form a bridge has to pick up an electron from some metal to complete its octet and thus acquire a negative charge. In the present case, there are 6 oxygen atoms which do not form bridges, as shown. Consequently, the Si_2O_7 unit is an anion carrying 6 negative charges and is written as $(Si_2O_7)^{6-}$. The metal atoms from which the electrons are picked up by the oxygen atoms are present in the silicate structure as cations. The number of cations is such that they balance the negative charge on the silicate anion. The most important pyrosilicate is of scandium known as *thortveitite* having the formula $Sc_2(Si_2O_7)$. The 6 negative charges on $(Si_2O_7)^{6-}$ anion are balanced by the same number of positive charges on the two Sc^{3+} ions. The other example of pyrosilicates is *hemimorphite* $[Zn_4(OH)_2Si_2O_7]$.

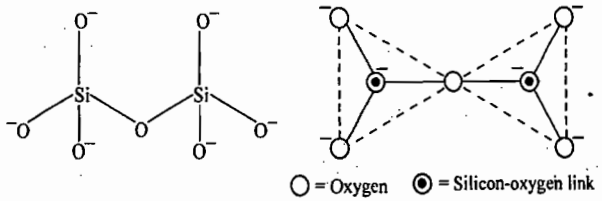


Fig. 7. Structure of $(S_2O_7)^{6-}$ ion in pyrosilicates.

3. Chain Silicates. If there are two bridging oxygens per silicon atom, *i.e.*, there is sharing of two oxygen atoms by each SiO_4 tetrahedron, a simple chain structure, as shown in Fig. 8, results. The remaining two oxygens per silicon atom do not form bridges. The resulting silicate, therefore, is an anion carrying 2 negative charges per silicon atom. The structure given below, for example, contains 5 silicon atoms and, therefore, the silicate ion is an anion carrying 10 negative charges.

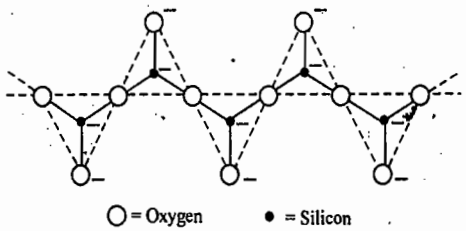


Fig. 8. Structure of chain silicates. The primary unit is $(SiO_3)^{2-}$.

It is eviden from the above structure that there is a total of 3 oxygen atoms per silicon atom. Therefore, the chain silicates contain $(SiO_3)^{2-}$ as the primary units and the general formula of this type of silicates is $[SiO_3)_n^{2-}$. These chains are found in minerals called *pyroxenes*. The common examples are *enstatite*, $MgSiO_3$, *diopside*, $CaMg(SiO_3)_2$ and *spodumene*, $LiAl(SiO_3)_2$.

In certain minerals, double chain structures have been observed. These are formed by further

sharing of oxygen atoms of SiO_4 tetrahedra by half the silicon atoms. The double chain structures (Fig. 9) have the basic unit $(Si_4O_{11})^{6-}$ and are represented by a class of minerals called *amphiboles*. Typical examples of this class are *tremolite*, $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, *amosite*, $(MgFe)_7Si_8O_{22}(OH)_2$ and *crocidolite* $Na_2Fe_3^{II}Fe_2^{III}Si_8O_{22}(OH)_2$.

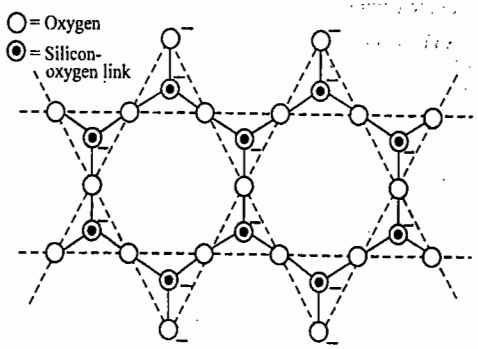


Fig. 9. Structure of double chain silicates. The basic unit is $(Si_4O_{11})^{6-}$.

4. Cyclic Silicates. These are formed by sharing of two oxygens per silicon atom resulting in the formation of a cyclic structure, as shown in Fig. 10. The primary unit in this case also is $(SiO_3)^{2-}$.

The cyclic ion, $(Si_3O_9)^{6-}$, shown in Fig. 10 (*a*), occurs in *wollastonite* $(Ca_2Si_3O_9)$ and *bentonite* $(BaTiSi_3O_9)$ while the cyclic ion $(Si_6O_{18})^{12-}$, shown in Fig. 10 (*b*), occurs in *beryl* $(Be_3Al_2Si_6O_{18})$.

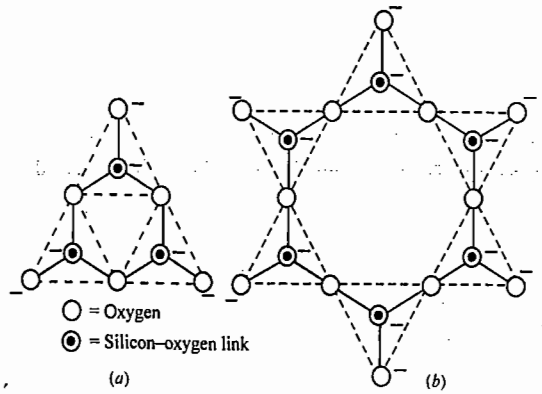


Fig. 10. Structure of cyclic silicates.

5. Sheet Silicates. These are formed by sharing of three bridging oxygens per silicon atom and result in the formation of infinite *two-dimensional sheets*. Each SiO_4 tetrahedron shares three corner oxygen atoms with other tetrahedra, as shown in Fig. 11. The oxygen atom shown around the silicon atom is the one that does not form the bridge and hence carries a negative charge. Actually, this oxygen lies below the plane of the paper. There is one negative charge per silicon atom in such structures. The negative charge on the sheets is neutralised by the positive charge of the 'binding' cations lying in between such sheets. Such substances cleave readily into thin sheets as in micas which are silicates or aluminosilicates of this type.

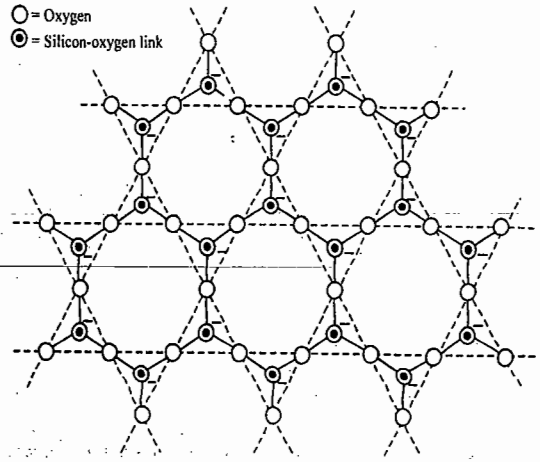


Fig. 11. Two-dimensional structure of sheet silicates.

Some common examples of sheet silicate are *kaolinite*, $Al(OH)_4SiO_5$ and *talc*, $Mg_3(OH)_3Si_4O_{16}$.

Sometimes in these silicates, silicon atoms are partially replaced by aluminium atoms. Examples are : *biotite* $K(MgFe)_3(OH)_3(AlSi_3O_{10})$ and *miscovite*, $KAl_2(OH)_2(AlSi_3O_{10})$

6. Three-Dimensional Silicates. Lastly, there is the extreme case in which four oxygens per silicon atom are bridging atoms. In other words, all the four oxygens of the SiO_4 tetrahedron act as bridge atoms. This results in a *three-dimensional* structure. Since all the oxygens are the bridge atoms, the silicate is neutral. There are no metal cations in this structure. This silicate structure will have the general formula $(SiO_2)_n$, *e.g.*, *quartz, tridymite, cristobalite.*

However, sometimes, $(SiO_4)^{4-}$ unit is replaced by $(AlO_4)^{5-}$ unit in tetrahedral positions in the SiO_2 lattice. In such cases, the presence of an additional monovalent cation is necessary to maintain electrical neutrality. Such replacement results in minerals like *feldspar* $(KAlSi_2O_8)$, *zeolite* $(NaAlSi_2O_6.H_2O)$ etc.

When feldspar is acted upon by carbon dioxide and water of the atmosphere at room temperature it slowly forms potassium carbonate and the clay, *kaolin* $[Al_2O_3.2SiO_2.2H_2O]$. The potassium carbonate, being soluble, becomes available in soil as plant food while kaolin is carried away by water streams to lower levels and is used in making pottery.

Replacement of $(SiO_4)^{4-}$ units with $(AlO_4)^{5-}$ units. Structure of aluminosilicates. The radius ratio rAl^{3+}/rO_2^- is about 0·43. This is close to the limiting radius ratio for coordination numbers 4 to 6. Accordingly, Al^{3+} ion would either fit into the space lattice of tetrahedral $(AlO_4)^{5-}$ ion or an octahedral $(AlO_6)^{9-}$ ion. The $(AlO_4)^{5-}$ ion has roughly the same size as the $(SiO_4)^{4-}$ ion and can thus replace the latter from silicates provided the electrical neutrality is maintained by the adjustment of positive charge elsewhere in the structure.

It is to be kept in mind that Al^{3+} ion can either be a part of $(AlO_4)^{5-}$ unit (in which its coordination number would always remain 4) or it can be present as cation used for binding the chains and sheets in the silicate structure by neutralising the negative charge of the chains or sheets. In the latter role, the coordination number of Al^{3+} cation is generally 6. Such a binding Al^{3+} cation can be replaced by other cations provided the principle of electroneutrality is maintained.

Some of the important **aluminosilicates** are described below.

Micas. Micas are *amphiboles* which are made up of *sheets* of $(SiO_4)^{4-}$ tetrahedra in which some of the $(SiO_4)^{4-}$ tetrahedra are replaced by $(AlO_4)^{5-}$ tetrahedra. In *muscovite*, the sheet composition is $(Si_3AlO_{10})^{5-}$. Two such sheets with their tetrahedral vertices inward are linked by the binding Al^{3+} ions whose octahedral coordination is completed by OH^- ions. The double sheets which have, in consequence, the composition $[Al_2Si_3O_{10}(OH)_2]^-$ are stacked one upon another with sufficient number of K^+ ions between two such double sheets to maintain electrical neutrality. The cleavage of mica is due to the weakness along these layers of K^+ ions. A wide variety of replacement is possible. Thus, the binding Al^{3+} ions may be replaced by Mg^{2+} ions and the 'sandwiched' K^+ ions by Na^+ ions. Micas are tough, elastic and transparent.

They are chemically inert and thermally stable. They also have a high dielectric constant. Due to these characteristic properties micas are used in furnace windows and electrical appliances. The powdered mica is used as a filler for rubbers, plastics and in insulation boards.

Clay. Clays are produced by weathering and decomposition of igneous rocks. They are generally composed of very fine particles. China clay, *i.e.*, *kaoline*, with formula $Al_2O_3.2SiO_2.2H_2O$, more correctly written as $Al_2(OH)_4Si_2O_5$, has a sheet structure in which the sheets are held together by the OH bridges.

When mixed with water, clay becomes plastic-soft and mouldable. The water of plasticity gets eliminated on heating at 100°C when the clay becomes rigid and brittle. Further heating removes structural water of crystallisation and results in oxidation of carbonaceous matter of the clay. At about 900°C, *multite*, $Al_6SiO_2O_{13}$, begins to be formed. This has a *glassy appearance*.

Clay is widely used in making chinaware, fire bricks and many other useful materials.

Fuller's Earth. It is *montmorillonite* in which the principal exchangeable ion is Ca^{2+}. It has a high adsorptive power and pronounced cation exchange properties.

It is widely used as an adsorbent and a cation-exchanger.

Talc. Talc with the formula $Mg_3(OH)_2Si_4O_{10}$ consists of electrically neutral sheets and there are no 'sandwich' type of cations between the sheets. It is soft and smooth and is used as a dry lubricant. It is chemically inert and is used in ceramics, paper manufacture and cosmetics.

Zeolites. Zeolites are alumino-silicates having a three-dimensional network with the general formula $M^{n+}_{x/n}(Al_xSi_yO_{2x+2y})^{x-}.zH_2O$. They are characterised by their open structure which enables them to take up water and other small molecules in their interstices reversibly but not the complex or bigger molecules such as methane and ethane. In zeolites, the cations move freely through the open pore structure and can be exchanged reversibly with other cations. Sodium ions in zeolites, for instance, can be exchanged for calcium ions in hard waters. This explains the use of these materials in water softening operations.

Zeolites as Molecular Sieves. Some crystalline aluminosilicates having open structure with apertures or holes of molecular dimensions can trap small molecules having size smaller than the size of the apertures and can thus act as **'molecular sieves'** for separating such molecules from a mixture of molecules having different sizes. Since the apertures (holes) defined by the cage-like structures of aluminosilicates are highly regular and are of molecular dimensions, these 'molecular sieves' can trap molecules with greater selectivity than do solid adsorbents with large surface areas such as activated charcoal. One such class of compounds is zeolites which can trap cations in their tunnels or interstices of their open structure. Apart from acting as molecular sieves, they can also act as ion exchangers.

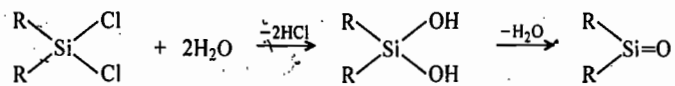
Zeolites are also used in **shape-selective heterogeneous catalysis.** For example, the zeolite ZSM-5 is used as a catalyst in the manufacture of ortho xylene selectively. Meta and para xylenes are not produced in the presence of this catalyst because the catalytic process is controlled by the shape (and size) of the tunnels existing in the structure of this zeolite which permits only the synthesis of ortho xylene.

Silicones

Silicon tetrachloride, $SiCl_4$, when fully hydrolysed, gives silica, SiO_2, which has a stable three-dimensional structure, as mentioned earlier.

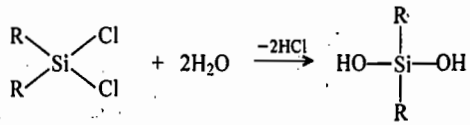
$$SiCl_4 + 4H_2O \xrightarrow{-4HCl} Si(OH)_4 \xrightarrow{-2H_2O} SiO_2$$

However, when an alkyl substituted chlorosilane (which can be obtained from $SiCl_4$ by Grignard reaction) is subjected to similar hydrolysis, *we do not get* the alkyl silicon compound according to the following expected reaction :

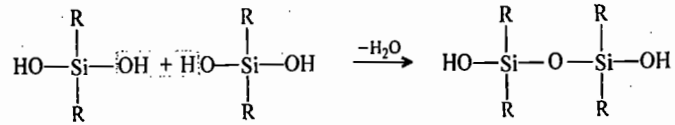


On the contrary, *long chain polymers,* called ***silicones,*** are obtained in this process. For example, in the case of dialkyl dichlorosilane, the reaction proceeds as follows :

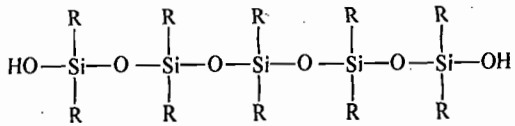
(*i*)



(*ii*)



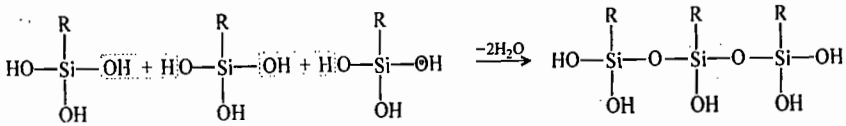
Since an active OH group is left at each end of the chain, polymerisation reaction continues and the length of the chain continues to increase giving a long chain product, as shown below.



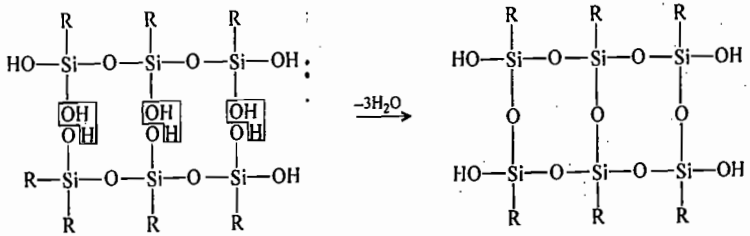
A complex cross-linked polymer is obtained on the hydrolysis of mono alkyl trichlorosilane, $RSiCl_3$, as shown below.

$$RSiCl_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HCl$$

(*i*)



(*ii*)



It is evident that the structure can be extended in two dimensions to any length in any manner.

The silicones are, evidently, **organosilicon polymers.** It may be noted that unlike carbon atom which cannot hold more than one hydroxyl group, the silicon atom in the compound $RSi(OH)_3$ can hold three hydroxyl groups. It is this property of silicon that makes the formation of organosilicon polymers possible.

As mentioned above, the organosilicon polymers grow further by reaction with other molecules containing one silicon atom. Thus, straight chain or cross-linked polymers are obtained. Depending upon the length of the chain and the nature of groups attached to the silicon atom, they can be obtained in the form of oils, viscous fluids, resins or even rubber-like solids.

Properties and Uses of Silicones. Silicone oils are highly stable and non-volatile even on heating. They are, therefore, used for high temperature oil baths, high vacuum pumps, etc. They do not become too viscous on cooling and are, therefore, used for low-temperature lubrication for which purpose hydrocarbon oils which become too viscous on cooling cannot be used. They are also used as greases, varnishes and resins which can be applied even at as low a temperature as – 40°C.

Silicones are also water-repellents and are good insulators. They are, therefore, used for waterproofing and in electrical condensers.

They provide excellent insulators for electric motors and other electric appliances as they can withstand high temperatures.

The rubber-like silicones retain their plasticity even at low temperatures and resist chemical attack. They are mixed in paints to make them damp-resistant. They are also used for waterproofing and for a variety of other purposes.

Silicones are discussed in some greater details in Chapter 35 on Inorganic Polymers.

Silicon Carbide or Carborundum, SiC. Preparation. Silicon carbide is prepared on a commercial scale by heating silica with carbon at a high temperature (around 2000°C) in an electric furnace.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Physical Properties. Pure silicon carbide is a colourless crystalline solid. The colour of the impure compound varies from yellowish to dark brown. SiC is an extremely hard substance. Of all the known binary compounds of silicon, SiC has the largest thermal stability. Its thermal decomposition with loss of silicon becomes appreciable only around 2700°C.

Chemical Properties. 1. Chemical stability. SiC resists the attack of most of the acids including HF but not H_3PO_4. It is slightly oxidised in air above 1000°C. Silica formed during oxidation forms a protective layer on the surface of SiC and inhibits further oxidation.

2. Reaction with molten alkalies. SiC reacts with molten NaOH to form sodium silicate.

$$SiC + 2NaOH + 2O_2 \xrightarrow{heat} Na_2SiO_3 + H_2O + CO_2$$

3. Reaction with chlorine. SiC reacts with chlorine to give silicon tetrachloride and carbon tetrachloride.

$$SiC + 4Cl_2 \xrightarrow{100°C} SiCl_4 + CCl_4$$

Structure of SiC. Silicon carbide exists in three crystalline forms. In each form, it has infinite three-dimensional array of Si and C atoms in which each carbon atom is tetrahedrally surrounded by four silicon atoms and each silicon atom is tetrahedrally surrounded by four carbon atoms.

Uses. 1. Due to its extreme hardness, SiC is used as an abrasive. 2. SiC has very low coefficient of expansion ($\sim 6\times10^{-6}$) and very high thermal and chemical stability. It is, therefore, used as a refractory material. 3. SiC is used as a high-temperature semiconductor in transistor diode rectifiers. 4. It is mostly used in the fabrication of grinding wheels for sharpening metallic tools. 5. It finds application in nuclear reactors because it serves as an excellent material for making containers for nuclear fuel at high temperatures.

Lead Pigments

A few insoluble compounds of lead are used as pigments in the preparation of oil paints. The important ones are described below.

White Lead, $Pb(OH)_2.2PbCO_3$. It can be prepared in laboratory by mixing alkali carbonate with a solution of lead salt.

$$4Na_2CO_3 + 3Pb(NO_3)_2 + 2H_2O \longrightarrow \underbrace{Pb(OH)_2.2PbCO_3}_{\text{Ppt. of white lead}} + 2NaHCO_3 + 6NaNO_3$$

There are three commercial processes for its manufacture.

1. *Dutch Process.* This is a very old process and is based on the action of acetic acid on metallic lead in the presence of carbon dioxide and moist air.

Small perforated buckets of lead are placed in earthenware pots having perforated shelves in which vinegar or dilute (about 2·5 per cent) acetic acid is placed. The pots are partly covered with wooden planks arranged in rows. The space in between the rows is filled by spent tan bark and horse dung.

It is believed that basic lead acetate is formed first and is then decomposed by the carbon dioxide produced during the fermentation of tan bark and horse dung. The following reactions are probably involved.

$$2Pb + O_2(air) + 2H_2O \longrightarrow 2Pb(OH)_2$$

$$2Pb(OH)_2 + 2CH_3COOH \longrightarrow \underbrace{Pb(OH)_2.(CH_3COO)_2Pb}_{\text{Basic lead acetate}} + 2H_2O$$

$$Pb(OH)_2 + Pb(OH)_2.(CH_3COO)_2Pb + 2CO_2 \longrightarrow \underbrace{Pb(OH)_2.2PbCO_3}_{\text{White lead}} + 2CH_3COOH$$

The heat produced during the fermentation of tan bark maintains the temperature at the optimum level of about 40°C.

This process is now being replaced by better ones given below.

2. *Carter's Process.* In this process, molten lead is atomised in wooden cylinders by blowing in a jet of air or superheated steam. The wooden cylinders keep rotating about their horizontal axes. A spray of dilute acetic acid and a current of air mixed with carbon dioxide are admitted into the cylinders. Here they meet the atomised lead and chemical reactions like those which occur in the Dutch process take place between lead, acetic acid and carbon dioxide. As the overall reaction is exothermic, the temperature remains almost constant at 40°C. The reactions are completed in about 7–10 days when lead is converted into the basic lead carbonate.

3. *Chamber Process.* This process has been developed in recent years. Here sheets of lead are suspended horizontally in large chambers into which carbon dioxide and acetic acid vapours are introduced. The reactions take place as in the above processes and are completed in about 7–10 weeks when the basic carbonate is found deposited on the lead sheets.

White lead mixed with linseed oil is used as white paint. It has a large covering power. But it has one serious drawback that it gets blackened if there is hydrogen sulphide in the atmosphere. Other substitutes such as *lithopone* ($BaSO_4 + ZnS$) and *sublimed white lead* ($PbSO_4 + PbO + ZnO$) have been suggested.

Sublimed white lead. It is also used as a white pigment. Its approximate composition is $PbSO_4$ 75%, PbO 20% and ZnO 5%. It is prepared by roasting galena (PbS) mixed with a small amount of zinc sulphide, in a strong blast of air. The fumes given out during the process are collected and condensed in a separate chamber. The sublimate is the *sublimed white lead.* It has a good covering power and is not so readily darkened by hydrogen sulphide.

Red Lead, Pb_3O_4. It is prepared by heating lead monoxide to 473–480°C in air for a long time.

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$

Red lead is a brilliant red powder. On heating it becomes violet and finally black. However, on cooling, the original red colour is restored.

Organometallic Compounds of Group 14 Elements. These have been discussed in Chapter 34 on Organometallic Compounds.

QUESTIONS

1. (*a*) Name the elements of Group 14 of the periodic table.
   (*b*) Discuss the variation in properties of Group 14 elements with reference to
   (*i*) Oxidation state (*ii*) Catenation (*iii*) Electronegativity (*iv*) Metallic character.
2. (*a*) What is catenation ? Explain the uniqueness of carbon to catenate. How does the catenation tendency vary in Group 14 elements and why ?
   (*b*) Why is CO_2 a gas and SiO_2 a highly stable solid ?
   (*c*) Describe the structures of CO and CO_2 molecules.

3. (*a*) What are carbides ? How do we classify them ?
   (*b*) Discuss the structure of silicon carbide. Give its important uses in industry.
4. Explain the following :
   (*a*) Acidic character of dioxides of Group 14 elements decreases as we move down the group.
   (*b*) Diamond is a non-conductor while graphite is a good conductor of electricity.
   (*c*) CCl_4 resists hydrolysis while $SiCl_4$ gets readily hydrolysed.
   (*d*) Pb^{4+} compounds are oxidising agents.
5. Discuss the preparation, properties and uses of permono and perdicarbonates.
6. How are perdicarbonates of sodium and potassium prepared ? Illustrate the oxidising character of these compounds.
7. (*a*) What are silicates ? Draw the structures of four different types of silicates and give the name and formula of one example of each type.
   (*b*) Write a short note on silicones.
   (*c*) Why does silicon have less tendency to get bonded to itself than does carbon ?
8. (*a*) Discuss the structure of $(SiO_4)^{4-}$ ion. "All silicates contain the $(SiO_4)^{4-}$ units. They differ only in the manner in which these units are linked together." Justify this statement.
   (*b*) Compare and contrast one significant feature of : (*i*) CO_2 and SiO_2 (*ii*) CCl_4 and $SiCl_4$
9. What are metal cyanides ? How are they classified ? Give the preparation, properties and structures of ionic cyanides, covalent cyanides and complex cyanides.
10. What are metal carbonyls ? Discuss the methods of preparation, properties and structures of some typical metal carbonyls.
11. Discuss the methods of preparation, properties and uses of carbon disulphide.
12. What are intercalation compounds ? Describe in details the intercalation compounds of graphite
    (*i*) with alkali metals (*ii*) with oxoacids (*iii*) with metal halides and (*iv*) with halogens
    What are the typical characteristics of these compounds ?
13. Discuss in details the structure of intercalation compounds of graphte with potassuim metal.
14. What are silicones ? Describe their structures. Give a brief account of their applications in technology.
15. How is calcium carbide manufactured. Discuss its important reactions and structure.
16. How is white lead prepared ? Describe the reactions involved in its preparation from lead.

17 THE ELEMENTS OF GROUP 15

Group 15 contains five elements, namely, **nitrogen, phosphorus, arsenic, antimony** and **bismuth**, and after the first element of the group, they are known as the **nitrogen family.** These elements, except phosphorus, do not occur very abundantly in nature. Nitrogen constitutes only about 0·0045 per cent, phosphorus 0·116 per cent, arsenic 5×10^{-4} per cent, antimony 1×10^{-4} per cent and bismuth $1{\cdot}8\times10^{-5}$ per cent, of the igneous rocks of the earth. Phosphorus is the only abundant element of the group which, in fact, ranks tenth in abundance amongst all the elements. Nitrogen is a very well known element. It constitutes nearly 78 per cent by volume of the atmosphere and is an essential constituent of fertilizers, explosives and food stuffs (proteins). Phosphorus is important because of its occurrence in phosphate rocks which can be converted into phosphatic fertilizers and also because it can form a number of alloys and finds many other uses. Arsenic, antimony and bismuth occur mostly as sulphide ores.

Electronic Configurations. The electronic configurations of these elements are presented in Table 1.

TABLE 1

Electronic Configurations of Elements of Group 15

Element	Atomic number	Electronic Configuration
Nitrogen, N	7	[He] $2s^2p^3$
Phosphorus, P	15	[Ne] $3s^2p^3$
Arsenic, As	33	[Ar] $3d^{10}\,4s^2p^3$
Antimony, Sb	51	[Kr] $4d^{10}\,5s^2p^3$
Bismuth, Bi	83	[Xe] $4f^{14}\,5d^{10}\,6s^2p^3$

As can be seen, the general outer electronic configuration of the elements of Group 15 may be written as $\mathbf{ns^2p^3}$. The three *p* electrons are equally distributed, in each case, among the three *p* orbitals as p_x^1, p_y^1 and p_z^1, in accordance with the Hund's rule. In other words, the *p* orbitals in the outer shells are only half-filled. Since electronic configurations involving fully filled or exactly half-filled orbitals are the most stable, the elements of Group 15, having exactly half-filled *p* orbitals, are also fairly stable and not so reactive (*e.g.*, nitrogen behaves as an almost inert element).

GENERAL CHARACTERISTICS OF GROUP 15 ELEMENTS

Some important physical properties of Group 15 elements are summed up in Table 2.

TABLE 2

Important Physical Properties of Elements of Group 15.

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic number	7	15	33	51	83
Atomic mass (a.m.u.)	14·007	30·97	74·92	121·75	208·98
Density in solid state (g cm^{-3})	1·03	1·82	5·73	6·62	9·78
Atomic volume (cm^3)	17·3	17·0	13·1	18·4	21·3
Atomic radius (Å)	0·75	1·06	1·19	1·38	1·46
Ionic radius of trivalent ion (Å)	1·71	2·12	2·22	2·45	1·20
Ionisation energy (kJ mol^{-1})	1402	1012	944	831	703
Oxidation states	−3, +1, +2, +3, +4, +5	−3, +3, +4, +5	−3, +3, +5	−3, +3, +5	+3, +5
Electronegativity (Pauling's values)	3·0	2·2	2·2	2·0	2·0
Melting point (°C)	−210 (white)	44·1 (at 30 atm)	817	630·5	271·3
Boiling point (°C)	−195·8	280 Sublimes	713	1380	1470
Heat of fusion (kJ mol^{-1})	0·36	0·63	27·7	19·9	10·9

1. Metallic and non-metallic character. The change from non-metallic to metallic character with increase in atomic number in the same group, which was exhibited by elements of Group 14, is also exhibited equally well by the elements of Group 15. The first two elements, nitrogen and phosphorus, are distinctly non-metals, the succeeding two elements, arsenic and antimony, are partly non-metals and partly metals while the last element, bismuth, is a metal.

2. Variation in physical state. There is also a gradual transition in physical state of the elements under ordinary conditions. The first element, nitrogen, is a gas which can be converted into a liquid only at a very low temperature. The next element, phosphorus, though a solid, can pass readily into vapour state. The succeeding elements, arsenic, antimony and bismuth, are solids of varying melting and boiling points, the boiling points rising with increase in atomic masses.

3. Atomic volume and atomic radius. Atomic volumes and atomic radii, as expected, increase with increase in atomic number. Arsenic, however, shows an exceptionally low value of atomic volume.

4. Ionisation energy. The ionisation energy of nitrogen, the first element, is very high, being 1402 kJ mol^{-1}. The values for the succeeding elements decrease systematically from 1012 to 703 kJ mol^{-1} on moving down the group, as is the case in Groups 1 and 2.

5. Melting points and boiling points. The melting points (except for antimony and bismuth) and boiling points increase with increase in atomic number, *i.e.*, as we move down the group from nitrogen to bismuth. The melting point of bismuth is unusually low.

6. Electronegativity. Electronegativity decreases gradually as we move down the group indicating a gradual change from non-metallic to metallic character.

7. Chemical bonding. It is evident from the electronic configurations given in Table 1, that the outer shell is short of three electrons in each element. Since it is not easy, from energy considerations, to gain three electrons to achieve stable configuration, the formation of tri-negative ion (Z^{3-}) is rare. Such an ion is formed only by nitrogen which is the smallest and the most electronegative element of the family. However, covalent compounds of nitrogen are more common. The electronegativities of other elements are so low that they would generally form covalent bonds even with highly electropositive elements. Bismuth compounds, although covalent, do give ionic species in polar solvents like water. This tendency decreases in moving up the group from bismuth through antimony to phosphorus.

8. Positive oxidation states. Since electronegativities decrease as we move down the group towards heavier elements, positive oxidation states are expected to become more frequent on moving down the group. The electronic configuration ns^2p^3 for the outer shell suggests that these elements can have two positive oxidation states, namely, + 3 and + 5. For example, the elements of this group form two types of oxides, M_2O_3 and M_2O_5. The + 3 state becomes more and more common on moving down the group from P to Bi. Nitrogen does not form compounds in +5 state such as NF_5, NCl_5, etc., because it does not have vacant *d* orbitals in its outermost shell which can enable it to extend its octet. Covalency of nitrogen generally is restricted to only three while other members of the group exhibit covalency of five, as in PF_5 and SbF_5. Nitrogen and phosphorus also show oxidation state of +4 because of the ability of one lone pair in NH_3 and PH_3 to form dative bond with Lewis acids. Nitrogen can exist in other oxidation states as well. In combination with oxygen, for example, it is found in +1(N_2O), +2 (NO) and +4(NO_2) oxidation states also.

9. Negative oxidation states. The oxidation state of nitrogen in ammonia (NH_3) is −3. As is evident from the decreasing electronegativities and decreasing ionisation energies, the tendency of the elements to pass into −3 oxidation state decreases on moving down from phosphorus to bismuth. In fact, bismuth, the last member of the group, hardly exhibits negative oxidation state. This shows why the stability of hydrides of these elements decreases as we move down the group.

10. Reluctance of heavier elements to show higher oxidation states. As stated above, the +5 oxidation state becomes less and less common as we move from nitrogen to bismuth. This is due to the fact that heavier elements are reluctant to show higher oxidation states, the reasons for which have already been explained in Chapter 12.

11. Electron-donor properties. All the elements in the tri-positive state (*i.e.*, +3 oxidation state) have a tendency to act as electron pair donors. Nitrogen shows this tendency to the maximum extent.

12. Electron-acceptor properties. Nitrogen does not have *d* orbitals and hence it cannot act as electron-acceptor. Other elements, having vacant *d* orbitals in their valency shells, do act as electron-acceptors.

13. Catenation or self-linkage. Catenation, although, considered to be a property peculiar to carbon, is shown, to some extent, by the elements which lie close to carbon in the periodic table. All the elements of Group 15 show this property but to a much smaller extent than carbon. The decrease in tendency to form chains is mostly due to a decrease in the element-to-element bond energies. The bond energies of C – C, N – N, P – P and As – As bonds are 353·9, 163·1, 200·8 and 146·8 kJ mol^{-1}. It is clear that there is a big drop of bond energy as we move from carbon to the next element nitrogen. The catenation in stable nitrogen compounds is, thus, restricted generally to two or three N atoms as, for example, in N_2H_4, N_3^-, etc. (although very unstable compounds containing chains of upto eight nitrogen atoms have also been synthesised.) Also, as is evident from single bond energies of N – N, P – P and As – As bonds, phosphorus has maximum tendency to catenate amongst Group 15 elements. The extent of catenation in the compounds of Group 15 elements is much less than in the compounds of carbon.

14. Allotropy. All the elements (except bismuth) show allotropy. Thus, two *solid* forms of nitrogen known as α-*nitrogen* with cubic crystalline structure and β-*nitrogen* with hexagonal crystalline structure have been reported. The transition temperature is – 238·5°C. Phosphorus exists in a number of allotropic forms such as *white* phosphorus, *red* phosphorus, *scarlet* phosphorus, metallic or α-*black* phosphorus, β-*black* phosphorus and *violet* phosphorus. Arsenic exists in three allotropic forms, *viz.*,

grey, yellow and *black*. Similarly, antimony exists in three different forms. These are *metallic form, yellow* or *α-antimony* and *black* or *β-antimony*.

15. Chemical reactivity. The various elements differ from one another appreciably in their chemical reactivity. Nitrogen because of its very high dissociation energy (945 kJ mol^{-1}) is practically inert. It combines with oxygen only when heated in an electric arc to a temperature of the order of 2500°C and above to form nitric oxide.

Phosphorus, in one of its allotropic forms known as white phosphorus, on the other hand, is extremely reactive. It burns readily in oxygen forming oxides of phosphorus.

The heavier elements (As, Sb and Bi) burn only when heated in air or oxygen, to form oxides. The difference can be attributed largely to difference in the electronegativities of the five elements. Nitrogen (electronegativity 3) is the most electronegative, the others have values smaller than that of nitrogen, *viz.*, phosphorus 2·2, arsenic 2·2, antimony 2·0 and bismuth 2·0.

16. Combination with metals. All the five elements combine with metals forming compounds in which the elements show normal valency of 3. For example, nitrogen forms **nitrides** (Mg_3N_2), phosphorus forms **phosphides** (Ca_3P_2), arsenic gives **arsenides** (Na_3As), antimony gives **antimonides** (Zn_3Sb_2) and bismuth gives **bismuthides** (Mg_3Bi_2).

Difference between Nitrogen and the rest of the Family Members

As usual, nitrogen, the first element of Group 15, differs considerably from the rest of the family members. These differences can be attributed largely to the following characteristics of nitrogen :

1. Small size 2. High electronegativity and 3. Non-availability of *d* orbitals in valency shell.

The main points of difference are as follows :

1. Nitrogen is a gas while the other members are solids.

2. Nitrogen is diatomic. The two nitrogen atoms are bonded together strongly by sharing of three electron pairs, as shown below :

$$:N\vdots\vdots N: \quad \text{or} \quad N\equiv N$$

Other elements form tetra-atomic molecules such as P_4, As_4 and Sb_4, involving the sharing of only one electron pair between any two atoms of the element concerned.

3. Because of its high electronegativity, nitrogen is distinctly non-metallic while the other two members (As, Sb) are metalloids and bismuth is distinctly a metal.

4. Nitrogen exhibits a large number of oxidation states, such as + 1, + 2, + 3, + 4, +5, – 1, – 2 and – 3 as in N_2O, NO, N_2O_3, N_2O_4, N_2O_5, NH_2OH, N_2H_4 and NH_3, respectively. Other elements do not exhibit such a variety of oxidation states.

5. Except for NF_3, the trihalides of nitrogen (NCl_3, NBr_3, NI_3) are unstable and highly explosive. The trihalides of other elements of this group, on the other hand, are fairly stable. This behaviour of nitrogen can be attributed to its high electronegativity.

6. Hydride of nitrogen (NH_3) is stable. The hydrides of other elements are not stable.

7. The trioxide and pentoxide of nitrogen, N_2O_3 and N_2O_5, are monomeric. The trioxides and pentoxides of other elements, on the other hand, are dimeric (cf. P_2O_6, P_4O_{10}).

8. Nitrogen forms oxides such as N_2O, NO, N_2O_4. No such oxides are formed by other elements.

9. Nitrogen differs markedly from the rest of the elements in its electronic configuration. Its valency shell contains only *s* and *p* orbitals and no *d* orbitals. All other elements of Group 15, on the other hand, have vacant *d* orbitals in their valency shells. Thus, while nitrogen cannot accept any electron pairs, all other elements do. For instance, phosphorus readily forms PCl_5 by accommodating two pairs of electrons from two chlorine atoms in its vacant *d* orbitals. But the corresponding compound of nitrogen, NCl_5, is unknown.

10. Since nitrogen is one of the most electronegative elements (next only to fluorine and oxygen), it extensively enters into hydrogen bond formation in its hydrogen compounds. Other elements, having comparatively low electronegativities, do not form hydrogen bonds.

EXTRACTION OF ELEMENTS OF GROUP 15

Preparation of Nitrogen. Nitrogen is fairly widely distributed in nature both in the free as well as in the combined state. About four-fifths of air is free nitrogen. In the combined state, it occurs mostly as nitrates, *viz.*, $NaNO_3$ (chile saltpeter) and KNO_3 (saltpeter). Coal contains compounds which on distillation yield ammonia which is an important compound of nitrogen. Nitrogen is also an essential constituent of all living cells of animal or vegetable origin where it is present in the form of proteins which contain about 16 per cent of combined nitrogen.

Nitrogen, on laboratory scale, can be obtained by heating ammonium nitrite or ammonium dichromate. It can also be obtained by the action of HNO_2 ($NaNO_2 + H_2SO_4$) or alkali metal hypochlorite (NaOBr) on urea. *Pure nitrogen*, in small amounts, can be obtained by heating sodium or barium azide.

On a **commercial scale**, nitrogen is invariably obtained by liquefying *air* and then carrying out its fractional evaporation. Nitrogen, having a lower boiling point (77·2 K), boils off more readily than the less volatile oxygen (b.p. 90·0 K).

Extraction of Phosphorus. Since phosphorus is an extremely active element, it does not occur free in nature. In the combined form, however, it is widely distributed in nature. It occurs as phosphates in the rocks and in the soil and as phosphoproteins in all living things. The principal minerals containing phosphorus are *phosphorite*, $Ca_3(PO_4)_2$, *apatite*, $3Ca_3(PO_4)_2.CaF_2$ and *chlorapatite*, $3Ca_3(PO_4)_2.CaCl_2$.

Phosphorus is an essential constituent of bones and is also present in the blood, brain and other parts of the body. It is also necessary for the growth of plants. Bone ash (animal charcoal) contains about 80 per cent calcium phosphate.

Phosphorus is manufactured by heating *bone ash* or phosphorite rock [$Ca_3(PO_4)_2$], with sand (SiO_2) and coke (C), in an electric furnace.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4$$

Extraction of Arsenic. Arsenic occurs rarely in free state. It is found largely in combination with sulphur, oxygen and iron. The important ores are *realgar* (As_2S_2) ; *orpiment* (As_3S_3) and *arseno-pyrites* (FeAsS).

The metal is generally extracted from *arsenopyrites*.

Arsenopyrites on roasting yield the volatile arsenious oxide, As_2O_3, which condenses as a white solid.

$$4FeAsS + 3O_2 \longrightarrow 4FeS + 2As_2O_3$$

Arsenic is obtained by heating arsenious oxide and charcoal together in a crucible.

$$As_2O_3 + 3C \longrightarrow 2As + 3CO$$

Arsenic collects as a sublimate while carbon monoxide escapes.

Extraction of Antimony. Antimony occurs in free state in small amounts only. Its chief source is the sulphide ore, *stibnite*, Sb_2S_3.

The metal can be obtained by heating the sulphide ore with iron.

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$

FeS, being lighter, floats over the layer of antimony and can thus be easily separated.

Alternatively, the sulphide ore is first roasted in a free supply of air to convert Sb_2S_3 into Sb_2O_3. The roasted ore is then heated with charcoal in a crucible to reduce it to antimony.

$$2Sb_2S_3 + 9O_2 \longrightarrow 2Sb_2O_3 + 6SO_2$$

$$Sb_2O_3 + 3C \longrightarrow 2Sb + 3CO$$

Extraction of Bismuth. Bismuth occurs in the free state as well as in the combined form. The important sources of the element are *bismuth glance*, Bi_2S_3, *bismuth telluride*, Bi_2Te_3 and the oxide, Bi_2O_3, known as *bismuth ochore*.

Bismuth is isolated by roasting the sulphide ore in a current of air when sulphur burns away as sulphur dioxide and bismuth oxide is formed.

$$2Bi_2S_3 + 9O_2 \longrightarrow 2Bi_2O_3 + 6SO_2$$

The oxide is reduced by heating with carbon.

$$Bi_2O_3 + 3C \longrightarrow 2Bi + 3CO$$

PROPERTIES OF ELEMENTS OF GROUP 15

Properties of Nitrogen. Physical Properties. Nitrogen is a colourless gas without any taste or odour. It does not support combustion or respiration but, unlike carbon dioxide, it is not poisonous. It is only sparingly soluble in water, 1 litre of water dissolving only 23 ml of the gas at N.T.P. Liquid nitrogen is colourless and boils at –195·8°C. On rapid evaporation, the liquid nitrogen changes into an ice-like solid melting at –209·9°C. At –238·5°C, it changes into another solid form.

Naturally occurring nitrogen consists of two isotopes ^{14}N and ^{15}N with an approximate ratio $^{14}N : {}^{15}N = 272{\cdot}0$. The isotope ^{15}N is often used as a radioactive tracer.

Chemical Properties. Nitrogen is an inert diatomic gas having a triple bond electronic structure, *viz.*,

$$:N\vdots\vdots N: \quad \text{or} \quad N{\equiv}N$$

The internuclear distance is 1·095 Å.

The heat of dissociation of nitrogen is extremely large, being 945 kJ per mole.

$$N_2\,(g) \rightleftharpoons 2N\,(g)\ ; \qquad \Delta H = +945 \text{ kJ}$$

The dissociation constant is extremely small and even at 3000°C there is no appreciable dissociation. This speaks for a very great strength of the N ≡ N bond which is principally responsible for the chemical inactivity of free nitrogen.

Important reactions of nitrogen are given below.

1. Combination with highly electropositive metals. Nitrogen readily combines with highly electropositive metals (metals of Group 1), even at room temperature, to give nitrides. For example,

$$6Li + N_2 \longrightarrow 2Li_3N$$

These nitrides are *ionic compounds* in which nitrogen is present as a trinegative anion, N^{3-}. Thus, lithium nitride may be represented as $Li_3^+N^{3-}$.

These nitrides are crystalline compounds and have high melting points.

2. Combination with less electropositive metals. Nitrogen combines with less electropositive metals like magnesium, calcium, strontium and barium at *red heat* ; with boron and aluminium at *bright red heat* and with silicon at *white heat*, to form the corresponding nitrides.

The nitrides formed with metals of Group 2 are generally *ionic* while those formed with elements of Groups 13 and 14 are *covalent* in character.

The nitrides formed with transition metals, such as iron, manganese, molybdenum, tungsten, are true *interstitial compounds* with nitrogen atoms occupying the interstices in the metal structures. These nitrides are extremely hard, have high melting points, possess metallic lustre and metallic conductivity.

3. Combination with hydrogen. Nitrogen combines with hydrogen to give ammonia (Haber process).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3\ ; \qquad \Delta H = -92{\cdot}0 \text{ kJ}$$

The reaction is carried out in the catalytic presence of finely divided iron containing a little molybdenum, at a pressure of 100—1000 atm and temperature of 400 – 550°C.

4. Combination with oxygen. Nitrogen combines with oxygen to give nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO\ ; \qquad \Delta H = +180{\cdot}7 \text{ kJ}$$

The reaction is highly endothermic and takes place at elevated temperatures (about 3000°C) ; even then the yield of nitric oxide is not more than 5 per cent by volume.

5. Combination with calcium carbide. Nitrogen combines with calcium carbide to form calcium cyanamide.

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

The reaction takes place by heating calcium carbide to about 1000°C in a current of nitrogen.

6. Catenation. As already mentioned, nitrogen shows some tendency for catenation, although this tendency is very weak as compared to carbon. Thus, the following compounds of nitrogen containing chains of three or more nitrogen atoms have been reported :

$$R-N=N-NR_2,\ R_2N-N=N-NR_2,\ RN=N-N(R)-N=NR$$

$$RN=N-N(R)-N=N(R)-N=NR$$

R represents some organic alkyl or aryl radical. In some compounds, R may also stand for H. Some cyclic compounds containing rings with upto five consecutive nitrogen atoms have also been reported.

However, these compounds are not very stable. This is because the bond energies of N– N and N = N bonds are quite low.

7. Hydrogen bonding. Since nitrogen is one of the most electronegative elements, next only to fluorine and oxygen, it readily enters into hydrogen bond formation in its hydrogen compounds.

Active Nitrogen. Active nitrogen is produced by the action of an electric discharge upon nitrogen gas at low pressures. The process is accompanied by a yellow glow which persists for several hours and indicates *slow release of energy* in the process.

Active nitrogen, as the name implies, is *highly reactive* chemically. It reacts with liquid mercury and with vapours of sodium, arsenic, phosphorus, etc., giving nitrides.

The exact nature of active nitrogen has not been fully understood. There is some evidence to show that it contains some nitrogen in the atomic state.

The active nitrogen gets deactivated on collision with the walls of the vessel. This process is accompanied by release of energy and accounts for the yellow after-glow.

Properties of Phosphorus. Allotropy. Phosphorus exhibits allotropy. It exists in a number of allotropic forms such as white phosphorus, red phosphorus, scarlet phosphorus, metallic or α-black phosphorus, β-black phosphorus, violet phosphorus, etc. The main allotropic forms, however, are white, red and black phosphorus.

White Phosphorus. *White phosphorus is obtained by rapidly cooling the vapours of phosphorus.* When pure, it is a transluscent waxy solid. *White phosphorus is readily soluble in carbon disulphide* and evaporation of the solution yields octahedral crystals of phosphorus. Below 800°C, the vapour density corresponds to the formula P_4. Above 800°C, P_4 dissociates into P_2. At 1700°C, its formula is P_2. White phosphorus melts at 44·1°C and boils at 280°C.

Its ignition temperature is very low (~ 30°C). When exposed to air it undergoes oxidation which

gradually raises its temperature and ultimately it catches fire when the temperature exceeds 30°C. For this reason it is always kept under water.

It glows in the dark on account of its slow oxidation. This phenomenon is known as *phosphorescence*. During oxidation, it gives a smell like that of garlic.

White phosphorus is extremely poisonous. A dose of 0·15 g or even less, proves fatal. The vapours of phosphorus, if continuously inhaled, cause *necrosis* of the bones particularly those of the jaws and nose. In *very small doses, however, phosphorus acts as a stimulent.*

White phosphorus is readily soluble in turpentine oil and ether.

Phosphorus molecule is now known to have the formula P_4. The four phosphorus atoms lie at the corners of a regular tetrahedron, as shown in Fig. 1. Each phosphorus atom is linked to each of the other three atoms by covalent bonds so that each atom completes its valency shell.

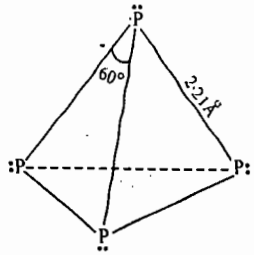


Fig. 1. Tetrahedral phosphorus molecule.

Red Phosphorus. It is a violet red powder consisting, in part, of small crystals and some amorphous variety. It is prepared by heating white phosphorus at 253°C in a cast iron egg-shaped vessel in which *air is replaced* by carbon dioxide gas or coal gas. The red phosphorus obtained may contain some white phosphorus which must be eliminated for obvious reasons. This is done by boiling it with sodium hydroxide solution when any unconverted white phosphorus goes off as phosphine.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3\uparrow + 3NaH_2PO_2$$

Red phosphorus is not attacked by sodium hydroxide. It is then washed repeatedly with hot water and dried.

Red phosphorus differs markedly from white phosphorus. It is stable under ordinary conditions. It does not ignite spontaneously in air and is not poisonous. It sublimes on heating giving vapours which are the same as given by white phosphorus. When the vapours are condensed, white phosphorus results. This gives an easy method of reconverting red phosphorus into white phosphorus.

Red phosphorus, which was once thought to be amorphous, is now known to have minute crystalline structure. It has an iron-grey lustre. It does not show phosphorescence.

Red phosphorus melts at about 610°C under pressure giving a yellow liquid which on cooling gives white phosphorus. It dissolves in alcoholic potash giving a deep red solution from which red phosphorus can be reprecipitated by acidifying the solution. It is insoluble in carbon disulphide and other organic solvents.

Red phosphorus does not melt at a definite temperature. Its density is also variable. Because of this reason, red phosphorus is not regarded as a definite allotropic form of phosphorus. It is thought to be a solid solution of scarlet phosphorus in metallic (α-black) phosphorus. The exact nature of red phosphorus, however, is uncertain.

Metallic or α-Black Phosphorus. This variety is obtained by dissolving red phosphorus in molten lead at 400°C in a sealed tube for sufficiently long time. On cooling, crystals of black phosphorus are obtained. Lead is dissolved out by treatment with dilute nitric acid.

It is a very stable allotrope of phosphorus and does not oxidise in air unless heated very strongly. It does not conduct electricity.

β-Black Phosphorus. It is obtained by heating white phosphorus at 2000°C under a very high pressure of about 4000 atm. It may also be obtained by heating white phosphorus at 220 – 370°C for 8 days in the presence of mercury which acts as a catalyst.

This is the only form of phosphorus whose structure is definitely known. It is crystalline in nature and consists of corrugated sheets, each phosphorus atom being covalently bonded to the three neighbouring

phosphorus atoms, as shown in Fig. 2. The P – P – P angles are of 99°. The P – P distance between two nearest phosphorus atoms is 2·18 Å.

The adjacent layers are 3·68 Å apart. The atoms within a layer are more strongly bound than the atoms in adjacent layers. This gives rise to flaky crystals resembling those of graphite.

It has a definite sharp melting point of 587°C. Its specific gravity is 2·69.

It is also a stable form of phosphorus and does not burn in air even up to 400°C. Like graphite, it is also a fairly good conductor of electricity.

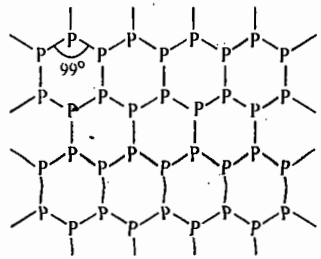


Fig. 2. Layer structure of β-black phosphorus.

Scarlet Phosphorus. This allotrope is obtained in the form of an amorphous scarlet powder by boiling a 10 per cent solution of phosphorus in phosphorus tribromide for about 10 hours. Pure scarlet phosphorus may be prepared by heating phosphorus tribromide with mercury at 240°C.

$$2PBr_3 + 3Hg \longrightarrow 3HgBr_2 + \underset{\text{Scarlet phosphorus}}{2P}$$

Scarlet phosphorus resembles the red variety in its physical properties and the white phosphorus in its chemical properties. It is, however, only slowly oxidised in air.

Violet Phosphorus. This variety is obtained by heating white phosphorus with a trace of sodium at 230°C under high pressure. It is crystalline in structure.

Chemical Properties. Phosphorus is an active element and combines directly with oxygen, sulphur, the halogens, etc. It also combines with a number of metallic elements. White phosphorus is more reactive than the other varieties. This is in accordance with the general principle that the unstable form of any compound or element is more reactive than the stable form. White phosphorus, as expected, has also a higher vapour pressure and is more soluble in various solvents.

Chemical Properties. Some important chemical properties of phosphorus are discussed below.

1. Combustion. Phosphorus burns in air forming phosphorus trioxide and pentoxide.

2. Phosphorescence. White phosphorus undergoes *spontaneous* slow oxidation in air giving a greenish glow which is visible in the dark. This phenomenon is known as *phosphorescence*. The main product of this slow oxidation is phosphorus trioxide.

3. Reaction with caustic alkalies. White phosphorus reacts with hot solution of caustic soda or caustic potash giving phosphine.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

Red phosphorus does not react with caustic alkalies. This property is made use of in separating red phosphorus from the white variety.

4. Reaction with the halogens. Phosphorus reacts with the halogens forming first the trihalides and then the pentahalides. White phosphorus reacts more vigorously than the red phosphorus. For instance, white phosphorus *spontaneously* catches fire in chlorine forming phosphorus trichloride and pentachloride while the red phosphorus catches fire in chlorine only on heating.

5. Reaction with sulphur. Phosphorus combines with sulphur with explosive violence forming a number of sulphides such as P_2S_3, P_2S_5, P_4S_3 and P_4S_7.

6. Reaction with metals. Phosphorus combines with a number of metals forming phosphides. For example,

$$6Mg + P_4 \longrightarrow 2Mg_3P_2$$

$$6Ca + P_4 \longrightarrow 2Ca_3P_2$$

Sodium and potassium react vigorously accompanying a bright flash.

7. Reducing properties. Since white phosphorus can be easily oxidised, it acts as a strong reducing agent. It reduces nitric acid to nitrogen dioxide and sulphuric acid to sulphur dioxide. It reduces solutions of copper, silver and gold salts to the corresponding metals. For example,

$$P_4 + 8CuSO_4 + 14H_2O \longrightarrow 8Cu + 8H_2SO_4 + 2H_3PO_4 + 2H_3PO_3$$

Thus, a colloidal solution of gold may be prepared by reducing a solution of gold chloride with phosphorus dissolved in ether.

Uses of Phosphorus. 1. It is mostly used in the manufacture of matches. Red variety is preferred to yellow variety owing to its non-poisonous nature. 2. It is used as a rat poison. 3. It is used in making *phosphorus bronze* which is hard, tenacious and not corroded by water. 4. It is used in the manufacture of tracer bullets, incendiary bombs and for producing smoke screens. 5. It is also employed in the preparation of compounds like phosphorus chlorides, phosphoric acids and hypophosphites used in industry and in medicine.

Properties of Arsenic. Physical Properties. Arsenic exists in three allotropic forms ; *grey, yellow* and *black.*

Grey Arsenic. It is a metallic looking brittle solid of density 5·73 g cm^{-3}. It is a feeble conductor of electricity though a good conductor of heat. It sublimes, without melting, at 613°C under atmospheric pressure giving yellow vapours. If heated under pressure it melts at about 500°C.

Yellow Arsenic. It is obtained by rapid cooling of arsenic vapour in carbon disulphide. It is a wax-like solid of much lower density (3·98 g cm^{-3}) than grey arsenic. It is soluble in carbon disulphide. It is readily oxidised causing luminescence, like white phosphorus. On warming gently it reverts to grey arsenic which is the most stable variety. It is non-metallic in nature, has no metallic lustre, is a very poor conductor of electricity and is readily volatile. It is poisonous.

Black Arsenic. Sometimes, during the conversion of yellow into grey arsenic by warming, as mentioned above, black arsenic is formed as an intermediate product. It is also obtained as a deposit when arsine, AsH_3, is passed through a heated tube. It has a density of 4·6 g cm^{-3}. It is a poor conductor of electricity.

Metalloidal Character of Arsenic. *Elements which resemble metals as well as non-metals are called* ***metalloids.*** Like most non-metals, arsenic is non-malleable and exists in three allotropic forms. It forms the hybride AsH_3, which is similar to ammonia, NH_3 and phosphine, PH_3. It gives chlorides which are easily hydrolysed. It reacts with nitric acid to form oxo-acids, as does phosphorus.

Its oxides are amphoteric being soluble in strong acids as well as in strong alkalies. This again shows its dual character because typical non-metals form only acidic oxides while typical metals form only basic oxides.

Arsenic also resembles metals in certain respects. For example, it is a conductor (though feeble) of electricity, forms a number of important alloys with metals and the stable allotropic form (grey arsenic) has a characteristic metallic luster. It is also brittle and has a fairly high density like most metals.

Chemical Properties. Arsenic is comparatively an inert substance at ordinary temperatures. It burns in air with a bluish flame forming white clouds of arsenious oxide, As_2O_3.

It combines readily with chlorine and sulphur forming arsenic chloride and arsenic sulphide, respectively.

It is not attacked by dilute hydrochloric acid or dilute sulphuric acid. Dilute nitric acid has no action at ordinary temperatures but on heating, it oxidises arsenic into arsenious acid.

$$As + HNO_3 + H_2O \longrightarrow H_3AsO_3 + NO$$

Hot concentrated sulphuric acid also oxidises arsenic to arsenious acid.

$$2As + 3H_2SO_4 \longrightarrow 2H_3AsO_3 + 3SO_2$$

Concentrated nitric acid oxidises arsenic to arsenic acid, H_3AsO_4.

$$2As + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$$

When fused with alkalies, arsenic forms arsenites.

$$2As + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2$$

Uses. Arsenic forms alloys with many metals. The addition of 0·5 per cent of arsenic to lead lowers the melting point of the latter. The alloy is harder than lead and is used in making lead shots which are more spherical than shots made with other materials. Compounds of arsenic are used for killing weeds and also in medicine.

Tests for Arsenic when Present in Traces. On account of toxic nature of arsenic, it is often necessary to detect its presence even in very small quantities, in a number of compounds. Further, arsenic is fatal even when administered in extremely small doses. Therefore, in cases of deaths under suspicious circumstances, it becomes necessary to test for compounds of arsenic, generally arsenic oxide, in the tissues of the human body. Any of the following tests may be applied for the purpose.

1. Marsh Test. A flask for the production of pure hydrogen is set up. It contains zinc and dilute sulphuric acid (or hydrochloric acid) both of which must be free from arsenic. The gas is made to pass through a horizontal side tube containing lead acetate to remove hydrogen sulphide, if any, and fused calcium chloride to remove moisture. When all the air has been completely expelled from the apparatus, the horizontal tube is heated at its middle for about 20 minutes. If no black stain is produced, the absence of As_2O_3 in the material used for the generation of hydrogen is proved.

The substance to be tested is suitably brought into solution which is introduced into the flask through a thistle tube. The horizontal tube is heated again as before. If As_2O_3 is present, a black mirror, just a little beyond the heated portion, will deposit. Further, if a flame is brought near the exit, hydrogen, resulting from the decomposition of arsine, will burn.

The reactions involved may be represented as follows :

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

$$As_2O_3 + 12H \longrightarrow 2AsH_3 + 3H_2O$$

$$2AsH_3 \longrightarrow 2As + 3H_2$$

The concentration of arsenic may be estimated by comparing the intensity of the black stain with a standard stain produced from a known amount of arsenic.

Antimony also gives a similar black deposit under these conditions. However, the two deposits can be distinguished from one another since, while arsenic mirror is soluble in sodium hypochlorite, antimony mirror is not.

2. Gutzeit test. In Gutzeit test, arsenic oxide is converted into arsine by bringing it in contact with zinc and dilute sulphuric acid, as in Marsh test. The gas is then allowed to come into contact with a filter paper moistened with a solution of silver nitrate when metallic silver deposits as a black stain.

$$AsH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3AsO_3$$

This test is not given by antimony compounds and, therefore, serves to distinguish between arsenic and antimony compounds.

Properties of Antimony. Physical Properties. Like phosphorus and arsenic, antimony exists in different allotropic forms. These are *metallic form, yellow* or *α-antimony and black or β-antimony.*

Metallic Form. This is the common variety of antimony. It has a silvery-white lustre. It is brittle and has specific gravity 6·7. It deposits large rhombohedral crystals when the fused metal is allowed to cool gradually. It shows stronger metallic character than arsenic. However, it is a poor conductor of heat and electricity, like arsenic. It melts at 630·5°C in an atmosphere of carbon monoxide and boils at 1380°C.

Yellow or α-Antimony. This is obtained by the action of ozonised oxygen on liquid stibine at – 90°C.

$$4SbH_3 + 3O_2 \longrightarrow 4Sb + 6H_2O$$

It is unstable and changes readily into the black or β-antimony. It can exist only at low temperatures. It is slightly soluble in carbon disulphide.

Black or β-Antimony. It is an amorphous black powder and is quite stable and reverts only gradually to the metallic form. It is regarded as an intermediate form between the α and metallic forms. It is formed directly by rapidly cooling antimony vapour. On warming, it reverts rapidly to metallic form.

Chemical Properties. 1. Antimony is not attacked by air if it is dry but gets slowly oxidised and tarnished in moist air. When heated in air or oxygen, it burns with a blue flame and forms antimony trioxide, Sb_2O_3 and antimony tetroxide, Sb_2O_4.

2. It is not attacked by water but it decomposes steam at red heat.

$$2Sb + 3H_2O \xrightarrow[\text{(Steam)}]{\text{Red heat}} Sb_2O_3 + 3H_2$$

3. It burns in chlorine forming antimony trichloride, $SbCl_3$. Prolonged treatment gives $SbCl_5$.

With bromine and iodine, only trihalides $SbBr_3$ and SbI_3 are formed.

4. It also combines readily with sulphur and phosphorus forming sulphide and phosphide, respectively.

5. It is not attacked by dilute acids. It is, however, attacked by concentrated hydrochloric acid liberating hydrogen. It is attacked by hot concentrated sulphuric acid giving sulphur dioxide.

With concentrated nitric acid it gets oxidised to meta antimonic acid, $HSbO_3$.

$$2Sb + 10HNO_3 \longrightarrow 2HSbO_3 + 10NO_2 + 4H_2O$$

Uses of Antimony. The main use of antimony is in the making of different alloys. About half of the world's production of antimony is used in the manufacture of lead storage batteries because lead containing a small amount of antimony is harder and more resistant to the action of acids than ordinary lead. It is used for colouring pottery, cloth and paper. Its oxochlorides are used as modrants. Oxides of antimony are used in glass-making. Antimony sulphide is used in the vulcanisation of rubber.

The important alloys of antimony are *type metal, pewter, britannia metal* and *babbit's metal*. Type metal, containing 82 per cent lead and 15 per cent antimony, has low melting point and expands on solidification and, therefore, is highly useful in casting.

Properties of Bismuth. Physical Properties. Bismuth, unlike arsenic and antimony, does not exist in allotropic forms. It has distinct metallic lustre (silvery white with a reddish tinge). It is brittle and has density equal to 9·8 g cm^{-3}. It has a low melting point (271·3°C). It boils at 1470°C. The molten metal expands slightly on passing into solid state. It conducts electricity fairly well, like metals.

Chemical Properties. 1. Bismuth, like antimony, is not attacked by air at ordinary temperatures and does not tarnish. When heated it burns in air to form bismuth trioxide, Bi_2O_3.

2. It combines with chlorine forming bismuth trichloride, $BiCl_3$.

3. Bismuth, like antimony, is not attacked by dilute hydrochloric acid. However, it dissolves in dilute nitric acid forming bismuth nitrate, $Bi(NO_3)_3$. It is not attacked by dilute sulphuric acid. But hot concentrated sulphuric acid attacks the metal giving sulphur dioxide.

Uses. Bismuth is used largely for making alloys having low melting points. Some of these alloys melt even below 100°C and are called **fusible alloys.** The examples of these alloys are :

1. *Woods metal* which melts at 60·4°C and consists of Bi 50%, Pb 25%, Sn 12·5% and Cd 12·5%.
2. *Rose metal* which melts at 93·75°C and consists of Bi 50%, Pb 27%, and Sn 23%.
3. *Lipowitz* which melts at 60°C and consists of Bi 50%, Pb 27%, Sn 13% and Cd 10%.

These alloys are used mainly in making automatic electrical fuses, automatic fire alarms, automatic sprinklers, automatic safety plugs of boilers, etc.

COMPOUNDS OF GROUP 15 ELEMENTS

I. A Comparative Study

1. Hydrides

All the elements of this group form volatile trihydrides of the formula MH_3, *viz.*, NH_3 (ammonia), PH_3 (phosphine), AsH_3 (arsine), SbH_3 (stibine) and BiH_3 (bismuthine). The lighter elements also form hydrides of the formula M_2H_4, *viz.*, N_2H_4 (hydrazine), P_2H_4 (diphosphine) and As_2H_4 (diarsine). Nitrogen forms hydride of the formula HN_3 as well. This is called hydrazoic acid.

The most important hydrides of elements of Group 15 are the trihydrides. A comparative study of trihydrides of Group 15 elements is given below.

Trihydrides of Group 15 Elements. Preparation. The trihydrides of Group 15 elements are prepared from binary metal compounds such as Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2, Mg_3Bi_2, by the action of water or dilute acids. For example,

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$
$$Mg_3N_2 + 6HCl \longrightarrow 3MgCl_2 + 2NH_3$$
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
$$Zn_3As_2 + 6HCl \longrightarrow 3ZnCl_2 + 2AsH_3$$

They can also be prepared by the reduction of trichlorides of these elements, MCl_3, with $LiAlH_4$.

$$MCl_3 + 3LiAlH_4 \longrightarrow MH_3 + 3LiCl + 2AlH_3$$
(M = N, P, As, Sb)

The most important trihydride, *viz.*, **ammonia,** NH_3, which is extensively used in the manufacture of HNO_3 and important chemical fertilizers such as ammonium sulphate, urea, calcium ammonium nitrate, ammonium-calcium phosphate, is prepared on an *industrial scale* by the **Haber process.** It involves the direct combination of nitrogen and hydrogen according to the equation

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 ; \qquad \Delta H = -92{\cdot}0 \text{ kJ}$$

The reaction is reversible, exothermic and proceeds forward with a tremendous decrease in volume. Hence, according to Le Chatelier's principle, *low temperature* and *high pressure* will be favourable for a better yield of ammonia. In actual practice, the reaction is allowed to take place at 450 – 550°C under a pressure of 100 – 1000 atm.

In order to accelerate the reaction at this low range of temperature, a catalyst is required. The best catalyst known is *highly porous finely divided iron* containing small amounts of *promoters* usually molybdenum or oxides of potassium and aluminium. The yield of ammonia varies from about 10 to 40 per cent depending upon the pressure. A mixture of N_2 and H_2 is now-a-days obtained by *partial oxidation* of hydrocarbons (derived from naphtha, natural gas or coal gas) by oxygen-enriched air in the

presence of a catalyst (nickel supported on magnesite).

$$\text{Hydrocarbon} + O_2 + \underbrace{O_2 + N_2}_{\text{Air}} \xrightarrow{\text{Catalyst}} xCO + \underbrace{yH_2 + N_2}$$

Carbon monoxide is eliminated by the usual methods.

The trihydride **PH_3** is generally prepared by boiling white phosphorus with a concentrated solution of sodium hydroxide in an inert atmosphere of carbon dioxide, oil gas or hydrogen.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

The trihydrides **AsH_3** and **SbH_3** are prepared by the reduction of compounds of arsenic and antimony by nascent hydrogen generated by the action of sulphuric acid on zinc. Thus,

$$As_2O_3 + 12H \longrightarrow 2AsH_3 + 3H_2O$$

$$AsCl_3 + 6H \longrightarrow AsH_3 + 3HCl$$

$$SbCl_3 + 6H \longrightarrow SbH_3 + 3HCl$$

The trihydride **BiH_3** is extremely unstable and decomposes readily even at ordinary temperatures into Bi and H_2. The hydride BiH_3, therefore, is difficult to prepare.

Structure. The trihydrides have **pyramidal structure**, as illustrated in the case of ammonia in Fig. 3. In this case, nitrogen orbitals undergo sp^3 hybridisation.

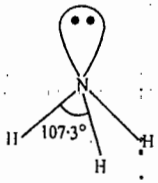


Fig. 3. Pyramidal structure of NH_3 molecule.

Three of the four sp^3 hybrid orbitals are used in forming three N – H bonds while the fourth is occupied by a lone pair of electrons. Due to larger lone pair–bond pair repulsion than bond pair–bond pair repulsion, the molecule gets a little distorted and the bond angle H – N – H decreases from 109·5° (normal tetrahedral angle) to 107·3°. The other hydrides also have pyramidal structure but the bond angle decreases as we go down the group, as shown below.

NH_3	PH_3	AsH_3	SbH_3
107·3°	93·6°	91·8°	91·3°

The variation in bond angle may be explained on the basis of the size and electronegativity of the central atom. As we move down the group, the size of the central atom goes on increasing and its electronegativity goes on decreasing. As a result, the location of the bond pairs of electrons shifts more and more away from the central atom as we go from NH_3 to SbH_3. Consequently, the bonded pairs of electrons will move away from each other to greatest extent in NH_3 and least extent in SbH_3. Therefore, the bond angle is maximum in NH_3 and minimum in SbH_3.

Properties. 1. Boiling points. The boiling points of the trihydrides of Group 15 elements are given below.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
–34·5°C	–87·5°C	–62·4°C	–18·4°C	+16·8°C

Except for ammonia, the boiling point increases as we move down the group. The abnormally high boiling point of ammonia is due to the association of its molecules through hydrogen bonding.

2. Basic character. All the trihydrides have one lone pair of electrons on the central atom and, therefore, they behave as Lewis bases. On going down the group, the basic character of these hydrides decreases. For example, NH_3 is distinctly basic and forms salts with acids both weak and strong [*e.g.*, NH_4Cl, $(NH_4)_2CO_3$]. PH_3 is also a base but very much weaker than NH_3 The hydrides of As, Sb and Bi have no basic character at all. The decrease in basic character of the hydrides is due to the decrease in the availability of the lone pair of electrons as we go down the group. The size of the central atom

increases as move from N to Bi. As a result, the electron charge cloud of the lone pair diffuses over larger volume and, therefore, the electron charge donor capacity (*i.e.*, basic strength) of the elements decreases as we go down the group.

3. Thermal stability. The thermal stability of the trihydrides of Group 15 elements decreases as we move from NH_3 to BiH_3. Thus, while ammonia (NH_3) is most stable, phosphine (PH_3), arsine (AsH_3), stibine (SbH_3) and bismuthine (BiH_3) are progressively less stable. Bismuthine, the last hydride, is extremely unstable and has a fleeting existence with a half-life period of only 20 minutes under ordinary conditions.

As we go down the group, the size of the central atom increases and, therefore, its tendency to form stable covalent bond with comparatively small hydrogen atom decreases. Consequently, the strength of M – H bond and hence the thermal stability goes on decreasing as we move from NH_3 to BiH_3. The largest atom, bismuth, forms least stable bond with hydrogen so that the hydride formed (BiH_3) is so unstable that it cannot be kept above – 45°C.

4. Reducing character. With progressive decrease in stability, the reducing character of the trihydrides increases as we move down the group. Thus, while ammonia, being stable, is not a good reducing agent, the other hydrides, being unstable, act as good reducing agents.

5. Formation of complexes. Aqueous ammonia forms stable complex ions with many cations notably of transition metals, *e.g.*, Ag^+, Cu^{2+}, Cd^{2+}.

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

This property is made use of in the separation of silver, copper and cadmium from other cations in qualitative analysis.

Compared with ammonia, PH_3, AsH_3, SbH_3, BiH_3 have lesser tendency to form complexes with cations of transition metals.

6. Precipitation of metals from their aqueous salt solutions. Ammonia precipitates heavy metals as *hydroxides* from their aqueous salt solutions. For example,

$$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{Ppt.}}{Fe(OH)_3} + 3NH_4Cl$$

Phosphine, arsine, stibine and bismuthine precipitate metals such as silver, copper, etc., as *phosphides, arsenides, antimonides* and *bismuthides*, respectively, when these gases are passed through aqueous solutions of salts of these metals. Thus,

$$3CuSO_4 + 2PH_3 \longrightarrow \underset{\text{Ppt.}}{Cu_3P_2} + 3H_2SO_4$$

$$3AgNO_3 + AsH_3 \longrightarrow \underset{\text{Ppt.}}{Ag_3As} + 3HNO_3$$

$$3AgNO_3 + SbH_3 \longrightarrow \underset{\text{Ppt.}}{Ag_3Sb} + 3HNO_3$$

$$3CuSO_4 + 2BiH_3 \longrightarrow \underset{\text{Ppt.}}{Cu_3Bi_2} + 3H_2SO_4$$

7. Hydrogen bonding. As already discussed under reactions of nitrogen, ammonia molecules are bonded together through hydrogen bonding. This is because nitrogen is much more electronegative than hydrogen and also because ammonia molecule is not symmetrical but is *pyramidal* in structure.

Electronegativities of P, As, Sb and Bi (2·2, 2·2, 2·0 and 2·0, respectively) are quite close to that of hydrogen (2·1). Hence, PH_3, AsH_3, SbH_3 and BiH_3 do not show hydrogen bonding.

Some of the physical constants of the hydrides of Group 15 elements are summed up in Table 3.

TABLE 3

Some Physical Constants of Hydrides of Elements of Group 15

Physical Constants	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point (°C)	– 77·8	– 133·5	– 116·3	– 88·0	–
Boiling point (°C)	– 34·5	– 87·5	62·4	– 18·4	16·8
Bond angle H – X – H	107·3°	93·6°	91·8°	91·3°	–
Bond length H – X (Å)	1·02	1·42	1·52	1·71	–
Heat of formation (kJ mol^{-1})	– 46·1	– 9·6	66·4	145·1	277·8

2. Halides

Trihalides. All the elements of this group form trihalides of the general formula MX_3. These are mostly covalent and only partly ionic. The ionic character, however, increases as we go down the group. Thus, $BiCl_3$ and BiF_3 are predominantly ionic. The trihalides, particularly the chlorides, are readily hydrolysed, the products of hydrolysis are, however, different in different cases. Thus, while nitrogen trichloride (NCl_3) hydrolyses giving hypochlorous acid and ammonia,

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HClO$$

the trichlorides of phosphorus and arsenic are completely and irreversibly hydrolysed into hydrochloric acid and the oxoacid or the oxide of the element.

$$PCl_3 + 3H_2O \longrightarrow 3HCl + H_3PO_3$$

$$2AsCl_3 + 3H_2O \longrightarrow 6HCl + As_2O_3$$

Antimony and bismuth trichlorides are only partly and reversibly hydrolysed to hydrochloric acid and oxochlorides of the metal. Thus,

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The addition of excess of hydrochloric acid suppresses the hydrolysis by shifting the equilibrium towards the left.

The trihalides of P and As (especially the fluorides and chlorides) show electron-acceptor properties and, therefore, act as Lewis acids.

$$PF_3 + F_2 \longrightarrow PF_5$$

$$SbF_3 + 2F^- \longrightarrow [SbF_5]^{2-}$$

$$SbCl_3 + 2Cl^- \longrightarrow [SbCl_5]^{2-}$$

All the trihalides have **pyramidal structure.**

The most important trihalide is the trichloride of phosphorus. This has been described below in some details.

Phosphorus Trichloride. Phosphorus trichloride is a low boiling liquid (b.p. 74°C) having a pungent odour. It fumes in moist air.

Chemical Properties. 1. As mentioned above, PCl_3 is violently hydrolysed by water giving phosphorous acid and hydrochloric acid gas.

$$PCl_3 + 3H_2O \longrightarrow 3HCl + H_3PO_3$$

2. It reacts with chlorine or sulphur chloride forming phosphorus pentachloride.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

$$3PCl_3 + SCl_2 \longrightarrow PCl_5 + 2PSCl_3$$

3. It readily combines with oxygen or sulphur trioxide forming phosphorus oxotrichloride.

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

$$3PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$$

4. Phosphorus trichloride undergoes many substitution reactions. Some of these are given below :

$$\left.\begin{array}{l} PCl_3 \xrightarrow{ROH} P(OR)_3 \\ PCl_3 \xrightarrow{NH_3} P(NH_2)_3 \\ PCl_3 \xrightarrow{RSH} P(SR)_3 \\ PCl_3 \xrightarrow{R_2NH} P(NR_2)_3 \end{array}\right\} \text{R = alkyl radical}$$

$$PCl_3 \xrightarrow{AgCN} P(CN)_3$$

$$PCl_3 \xrightarrow{AgCNO} P(NOC)_3$$

$$PCl_3 \xrightarrow{PF_3} PCl_2F + PClF_3$$

5. PCl_3 forms an adduct with BBr_3.

$$PCl_3 + BBr_3 \longrightarrow [BBr_3(PCl_3)]$$

6. PCl_3 replaces CO from carbonyl complexes.

$$PCl_3 + Ni(CO)_4 \longrightarrow Ni(PCl_3)_4 + 4CO$$

Pentahalides. While phosphorus, arsenic and antimony form pentahalides, nitrogen and bismuth do not. Nitrogen cannot form pentahalide because nitrogen does not have vacant *d* orbitals in its valence shell and, therefore, cannot expand its octet. Phosphorus, arsenic and antimony form pentahalides because of the availability of vacant *d* orbitals in their outer shells. Bismuth does not form pentahalides because its lower +3 oxidation state is more stable than +5 state, the reason for which has been discussed in Chapter 12.

The pentahalides have a **trigonal bipyramidal structure.**

They are thermally less stable than the trihalides. PCl_5 exists as $[PCl_4]^+[PCl_6]^-$ in the crystalline state. PBr_5 and PI_5 also exist in ionic forms as $[PBr_4]^+[Br]^-$ and $[PI_4]^+I^-$, respectively, in solid state.

Amongst the pentahides, the most important is phosphorus pentachloride which has been described below.

Phosphorus Pentachloride. Phosphorus pentachloride is a yellowish white crystalline compound having a sharp odour. It sublimes on heating at 160°C and melts at 45°C under pressure.

Chemical Properties. 1. Phosphorus pentachloride dissociates on heating into phosphorus trichloride and chlorine.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

2. It is violently hydrolysed by water giving phosphorus oxochloride or phosphoric acid depending upon the quantity of water.

$$PCl_5 + H_2O \xrightarrow{\text{Insufficient water}} POCl_3 + 2HCl$$

$$PCl_5 + 4H_2O \xrightarrow{\text{Excess of water}} H_3PO_4 + 5HCl$$

3. It reacts with compounds containing hydroxyl groups forming chloro derivatives. In all these cases, the hydroxyl group is replaced by chlorine. For example,

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$

$$\underset{\text{Sulphuric acid}}{HO.SO_2.OH} + 2PCl_5 \longrightarrow \underset{\text{Sulphuryl chloride}}{Cl.SO_2.Cl} + 2POCl_3 + 2HCl$$

4. It reacts with P_4O_{10} to form phosphorus oxotrichloride.

$$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$$

5. When heated with ammonium chloride, polymeric phosphonitrilic chloride is formed.

$$nPCl_5 + nNH_4Cl \longrightarrow (NPCl_2)_n + 4nHCl$$

6. Phosphorus pentachloride combines with Cl^- acceptors to form tetrahedral $[PCl_4]^+$ ion.

$$PCl_5 + BCl_3 \longrightarrow [PCl_4]^+[BCl_4]^-$$

7. It is reduced to phosphorus trichloride by hydrogen.

$$PCl_5 + H_2 \longrightarrow PCl_3 + 2HCl$$

8. It combines with potassium fluoride as follows :

$$PCl_5 + 6KF \longrightarrow KPF_6 + 5KCl$$

Other Halides. In addition to trihalides and pentahalides, some other halides are also known. Nitrogen forms fluorides such as N_2F_4 (dinitrogen tetrafluoride), N_2F_2 (dinitrogen difluoride) and N_3F (trinitrogen fluoride). Several mixed halides and hydrohalides of nitrogen such as NCl_2F, $NClF_2$, $NBrF_2$, NF_2H, NCl_2H, etc., are also known. However, these are unstable and difficult to isolate. Phosphorus also forms P_2Br_4 (dinitrogen tetrabromide) and several mixed halides such as PCl_4F, $PClF_4$, PCl_2F_3. Arsenic and antimony also form mixed halides such as AsF_2Cl, $AsFCl_2$, $AsClBr_2$, $AsCl_2Br$, $SbCl_4F$, etc.

Pseudohalides of phosphorus are also known. Examples are $P(NCS)_3$, $PF_2(NCS)$, $P(CN)_3$ and $P(NCO)_3$.

3. Oxohalides

Nitrogen forms two types of oxohalides. These are nitrosyl halides, XNO and nitryl halides, XNO_2. The **nitrosyl halides** are covalent gases and can be prepared by direct combination of NO with the halogen X_2.

$$2NO + X_2 \longrightarrow 2XNO$$

Nitrosyl halides are powerful oxidising agents. They are thermally unstable. They are readily hydrolysed by water to form a mixture of oxides and oxoacids of nitrogen.

$$3XNO + 2H_2O \longrightarrow HNO_2 + 2NO + 3HX$$

The **nitryl halides** are prepared by the following reactions :

$$HNO_3 + ClSO_3H \longrightarrow ClNO_2 + H_2SO_4$$

$$NaNO_2 + F_2 \longrightarrow FNO_2 + NaF$$

$$N_2O_4 + 2CoF_3 \longrightarrow 2FNO_2 + 2CoF_2$$

These are colourless reactive gases, the reactions being similar to those of XNO. Their hydrolysis yields nitric acid and HX, *e.g.*,

$$ClNO_2 + H_2O \longrightarrow HNO_3 + HCl$$

The most important oxohalides of phosphorus are phosphoryl halides, POX_3. These are prepared by (*i*) the controlled hydrolysis of PX_5 (*ii*) by the oxidation of PX_3 or (*iii*) by the action of P_4O_{10} on PX_5.

4. Oxides

All the elements of Group 15 are capable of forming trioxides and pentoxides of the general formulae R_2O_3 and R_2O_5.

Trioxides. Nitrogen trioxide, N_2O_3, exists pure only in the solid state at low temperatures. In the liquid state, it is dissociated into NO and NO_2.

$$N_2O_3\,(g) \rightleftharpoons NO\,(g) + NO_2\,(g)$$

In the vapour state, it is almost entirely present as an equimolar mixture of NO and NO_2.

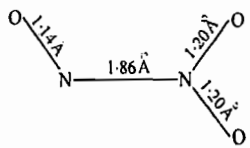
It is best obtained by interaction of stoichiometric quantities of NO and NO_2. On cooling such a mixture below $-20°C$, a blue liquid corresponding to the composition N_2O_3 is obtained. The oxide N_2O_3 is formally referred to as the anhydride of nitrous acid since with water it gives nitrous acid, HNO_2. When dissolved in alkalies it produces nitrites.

Phosphorus trioxide exists as a dimer and is formulated as P_4O_6. It is prepared by the combustion of white phosphorus in a limited supply of air when both P_4O_6 and P_4O_{10} are formed. The vapour of the mixture of oxides are passed through a condenser in which water at 50 – 60°C is circulated. P_4O_{10} being solid at 60°C separates out easily. The oxide P_4O_6 is considered as an anhydride of phosphorous acid since it dissolves in water to give phosphorous acid, H_3PO_3.

The **trioxides of arsenic, antimony** and **bismuth** are obtained by the direct reaction of metals with oxygen.

The trioxides of nitrogen, phosphorus and arsenic are *acidic*. The trioxide of antimony is *amphoteric* while that of bismuth is *basic* in character.

Structures. The structure of N_2O_3 is not definitely known. The spectroscopic studies, however, reveal that its structure is as shown below. It may be noted that lines between the atoms do not show exact bond order.



Based on the tetrahedral structure of phosphorus molecule, the **tetrahedral** structure assigned to P_4O_6 is as shown in Fig. 4.

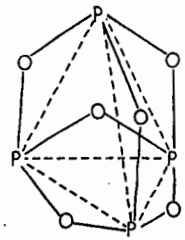


Fig. 4. Structure of phosphorus trioxide.

It is evident that in P_4O_6, the phosphorus atoms lie at the corners of a tetrahedron and the six oxygen atoms are present along the edges in between the phosphorus atoms. Each phosphorus atom is covalently bonded to three oxygen atoms each of which is bonded to two phosphorus atoms (Fig. 4). In this manner all the phosphorus and oxygen atoms have 8 electrons in each of their valency shells.

This structure has been confirmed by X-ray diffraction data.

The oxides **As_4O_6 and Sb_4O_6** also have **tetrahedral structures.**

At higher temperatures, As_4O_6 and Sb_4O_6 partially transform into As_2O_3 and Sb_2O_3. Both the latter compounds have sheet-like structures consisting of pyramidal AsO_3 and SbO_3 units.

Another mixed oxide $Sb^{III}Sb^{V}O_4$ is known in two crystallographic forms α and β and can be obtained by heating Sb_2O_3 in dry air upto 500°C.

Pentoxides. Nitrogen pentoxide, N_2O_5 is prepared by the dehydration of HNO_3 with phosphorus pentoxide. The mixture of HNO_3 and P_2O_5 is distilled in an all-glass apparatus in the presence of ozonised oxygen. The latter is essential to avoid decomposition of N_2O_5.

Phosphorus pentoxide, P_4O_{10}, is obtained by burning phosphorus in a free supply of air or oxygen. The pentoxide formed is purified further by sublimation at 360°C.

Arsenic pentoxide and antimony pentoxide are obtained by the oxidation of the metals with concentrated HNO_3.

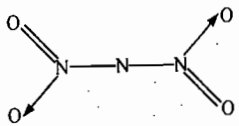
The structure of As_2O_5 consists of strands of AsO_6 octahedra and AsO_4 tetrahedra. Sb_2O_5 can also be obtained by the hydrolysis of $SbCl_5$ followed by dehydration.

Bismuth pentoxide is obtained by the action of strong oxidising agents on Bi_2O_3. The pentoxide, however, is extremely unstable and rapidly loses oxygen to form the trioxide.

All the pentoxides are *acidic* in nature but the acidity decreases as we move down the group. Thus, N_2O_5 is the strongest acidic oxide while Bi_2O_5 is the weakest. All the pentoxides can readily lose oxygen to form lower oxides. Hence they act as strong oxidising agents.

Amongst the various pentoxides, P_2O_5 has the strongest affinity for water. It can extract water from several inorganic and organic compounds and thus acts as a *strong dehydrating agent*. It dehydrates H_2SO_4 to SO_3, HNO_3 to N_2O_5, cellulose to carbon and amides to nitriles.

Structures. N_2O_5 has a simple structure which may be represented as shown.



All the terminal NO bond distances are equal due to resonance between N = O and N → O bonds in the molecule.

The structure assigned to P_4O_{10} molecule is shown in Fig. 5. In this structure, the phosphorus atoms lie at the corners of a tetrahedron with six oxygen atoms lying along the edges and the remaining four occupying positions along the extended three-fold axes of the tetrahedron. The twelve P – O distances between the P atoms and shared O atoms are 1·62 Å each while the other four apical P – O distances are 1·39 Å each. Thus, while the former P – O bonds are single bonds, the latter are double bonds with considerable $p\pi - d\pi$ bonding.

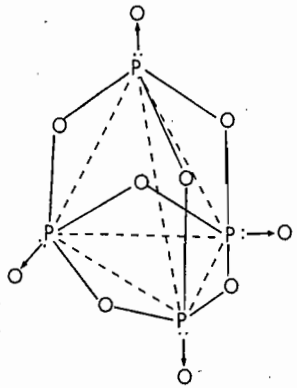


Fig. 5. Structure of phosphorus pentoxide molecule.

The structures of pentoxides of other elements of the group have not been fully established.

Other Oxides. Nitrogen, phosphorus, antimony and bismuth also form **dioxides** of the general formula RO_2. Amongst these, the most thoroughly studied and best understood is the dioxide of nitrogen, **NO_2.**

Nitrogen dioxide, NO_2. This oxide also exists as a dimer N_2O_4, known as **dinitrogen tetroxide.** The two oxides are in a temperature-dependent equilibrium :

$$N_2O_4 \rightleftharpoons 2NO_2$$

In the solid state, the oxide consists only of N_2O_4 molecules and is colourless. At – 11·2°C, the solid melts. Even in the liquid state, partial dissociation occurs and the liquid may be considered as a dilute solution of NO_2 in N_2O_4. The colour of the liquid gradually changes from yellow to orange with rise in temperature indicating an increase in the percentage of NO_2. At 22°C, the liquid boils giving brown vapours. At 100°C, the composition of the mixture has been found to be 90 per cent NO_2 and 10 per cent N_2O_4. Above 140°C, the dissociation is complete and the oxide consists only of NO_2 molecules. Beyond this temperature, the nitrogen dioxide starts dissociating into nitric oxide and oxygen, both of

which are colourless.

$$\underset{\text{Brown}}{2NO_2} \rightleftharpoons \underset{\text{Coloureless}}{2NO + O_2}$$

Above 620°C, the gas becomes colourless indicating complete dissociation into NO and O_2. All these changes are reversed on cooling. At some intermediate temperature (found to be 300°C experimentally), the equilibrium mixture contains equimolar quantities of NO_2 and NO. Thus, if the gas at 300°C is treated with an alkali, it produces pure nitrite.

$$NO + NO_2 + 2NaOH \longrightarrow 2NaNO_2 + H_2O$$

This fact is utilised in the commercial preparation of sodium nitrite.

Nitrogen dioxide, when dissolved in water, gives a mixture of nitrous acid and nitric acid.

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3$$

Hence, it is formally known as the 'mixed anhydride' of these two acids.

The hot aqueous solution of NO_2 gives NO because of the disproportionation of HNO_2 ($3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$). The overall reaction is

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

In aqueous solution, it oxidises sulphur dioxide to sulphuric acid.

$$SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$$

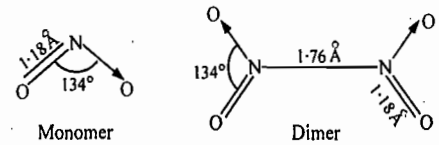
The manufacture of sulphuric acid by Lead Chamber Process is based on the oxidation of sulphur dioxide by nitrogen dioxide in the presence of steam.

Structure. Nitrogen dioxide is known to have the electronic structure, $:\ddot{O}::\dot{N}:\ddot{O}:$ or O=N→O. Obviously, nitrogen dioxide *has an unpaired electron* and, therefore, it behaves as a typical odd molecule. It is coloured and has a tendency to polymerise to give a colourless **dimer,** N_2O_4, with even number of electrons, as shown :

$$\begin{array}{ccccccc} O & = & N & - & N & = & O \\ & & \downarrow & & \downarrow & & \\ & & O & & O & & \end{array}$$

The monomer, NO_2, is known to have an angular structure with ONO bond angle = 134° and NO distance = 1·18 Å.

The planar structures of the monomer and the dimer are shown below.



Monomer Dimer

All the terminal NO bond distances in the dimeric N_2O_4 molecule are equal due to resonance between N = O and N_2 → O bonds.

Nitrogen also forms two additional oxides, *viz.*, nitrous oxide and nitric oxide, which are very important and are described below in some details.

Nitrous Oxide, N_2O. Nitrous oxide is prepared in the laboratory as well as on a commercial scale by carefully heating ammonium nitrate to about 250°C.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

In the laboratory, the gas is collected over *hot* water (as the gas is fairly soluble in *cold* water) and on a commercial scale it is stored in steel cylinders under a pressure of about 100 atm.

Physical Properties. Nitrous oxide is a colourless gas fairly soluble in cold water but practically insoluble in hot water. It can be easily liquefied at room temperature by applying pressure as its critical temperature is 35°C. It has a faint odour. When inhaled in moderate quantities, it produces hysterical laughter, hence the name *laughing gas*. In small amounts, it acts as an anaesthetic.

Chemical Properties. Chemically nitrous oxide is relatively inert. It does not react with halogens, alkali metals and even ozone at room temperature.

At high temperatures, it decomposes into nitrogen and oxygen.

$$2N_2O \xrightarrow{600°C} 2N_2 + O_2$$

Nitrous oxide reacts with molten alkali metal amides to form azides.

$$NaNH_2 + N_2O \xrightarrow{200°C} NaN_3 + H_2O$$

Uses. Commercially, it is used as the propellant gas in 'whipped' cream bombs. It is also used as an anaesthetic.

Structure. Nitrous oxide is known to be a *resonance hybrid* of two highly polar and linear structures with *opposing* dipole moments, as represented below :

$$:N\equiv N-\overset{+}{\underset{..}{O}}: \longleftrightarrow :\overset{..}{N}=\overset{+}{N}=\ddot{O}:$$

This structure readily accounts for a very low dipole moment (0·1 D) of N_2O. Thus, N_2O has linear structure. The N – N and N – O bond lengths are 1·12 Å and 1·19 Å, respectively, as shown :

$$N \overset{1\cdot12\,Å}{—} N \overset{1\cdot19\,Å}{—} O$$

Nitric Oxide, NO. Nitric oxide is usually prepared by the action of cold dilute nitric acid on copper turnings.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

On a commercial scale, nitric oxide is obtained by the catalytic oxidation of ammonia.

$$4NH_3 + 5O_2 \xrightarrow[750-900°C]{Pt} 4NO + 6H_2O$$

Physical Properties. Nitric oxide is a colourless gas which readily combines with atmospheric oxygen giving brown nitrogen dioxide. Hence, the gas must be handled out of contact with air. Since its critical temperature is very low (– 93°C), it can be liquefied with some difficulty. The liquid has a blue colour which boils at – 142·8°C and freezes at – 150°C. It is neutral in character.

Chemical Properties. The most important reactions of nitric oxide are oxidation and reduction reactions.

1. It readily combines with oxygen giving brown nitrogen dioxide.

2. It is easily oxidised to nitric acid by strong oxidising agents such as potassium permanganate, potassium dichromate, halogens, etc. Thus, acidified potassium permanganate is decolourised when nitric oxide is passed into it.

$$6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$$

The reaction with $KMnO_4$ is quantitative and is, therefore, used for the estimation of nitric oxide.

3. *Nitric oxide is oxidised to nitrogen dioxide with concentrated nitric acid.*

$$2HNO_3 + NO \rightleftharpoons 3NO_2 + H_2O$$

This reaction is of particular interest because it explains why metals like copper, mercury, etc., give nitric oxide with dilute nitric acid but nitrogen dioxide with concentrated nitric acid. In the case of dilute nitric acid, that is, when sufficient water is present, the reaction is pushed backwards giving nitric oxide but with concentrated nitric acid, the reaction proceeds in the forward direction giving nitrogen dioxide. It follows from this that *at some intermediate concentration of nitric acid, both* NO *and* NO_2 *should be formed. It is actually so.* A 5 M solution of nitric acid on reaction with copper gives an almost equimolar mixture of NO and NO_2

4. Nitric oxide is reduced also equally easily. With sulphurous acid it is reduced to nitrous oxide while with chromous or stannous ions, it yields hydroxyl amine.

$$2NO + H_2SO_3 \longrightarrow N_2O + H_2SO_4$$

$$2NO + 6H \xrightarrow[\text{or } Cr^{2+}]{Sn^{2+}} 2NH_2OH$$

5. Nitric oxide directly combines with halogens (fluorine, chlorine, bromine but not iodine) to give the corresponding nitrosyl halides.

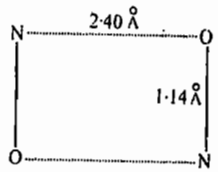
$$\underset{\text{Halogen}}{2NO + X_2} \longrightarrow \underset{\text{Nitrosyl halide}}{2NOX}$$

These halides are highly reactive and are used as powerful oxidising agents.

6. Nitric oxide is absorbed in ferrous sulphate solution giving a dark brown coloration (*a test for nitric oxide and nitrates*). The brown colour is due to the formation of a hydrated nitrosyl complex of iron, having the formula $[Fe(H_2O)_5NO]^{2+}$. This compound is responsible for the formation of brown ring in the 'ring test' for nitrates.

This complex is stable only at low temperatures. On heating, it decomposes to set free nitric oxide. The reaction, therefore, provides a method for the purification of the gas as well as for its separation from other gases.

Structure of nitric oxide. Nitric oxide molecule has 11 valency electrons. Evidently, all of these cannot be paired. The molecule, therefore, contains an *odd electron*. Nitric oxide, therefore, is *paramagnetic* in the gaseous state. But it is *diamagnetic* in the solid state. The reason is that in the latter state, loose dimers are formed in which the unpaired electrons of the two NO monomeric units get paired up. The structure of the dimer is as shown.



The electronic structure of nitric oxide is conventionally represented as a resonance hybrid of two structures, as shown below :

$$:N=\ddot{O}: \longleftrightarrow :\overset{..}{N}=\overset{+}{O}:$$

The bond length in nitric oxide (1·14 Å) is in between that of a double bond and a triple bond.

The electronic structure of NO is best explained on the basis of molecular orbital theory (Chapter 4). The molecular orbital structure of NO is

$$NO : KK'\sigma(2s)^2\sigma^*(2s)^2\sigma(2p_z)^2\pi(2p_x)^2\pi(2p_y)^2\pi^*(2p_x)^1$$

or

$$KK'\sigma_1^2\sigma_2^{*2}\sigma_3^2\pi_1^2\pi_2^2\pi_3^{*1}$$

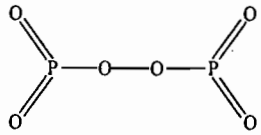
The bond order in this case is given by

$$\text{Bond order} = \tfrac{1}{2}\,(\text{Number of electrons in BMOs} - \text{Number of electrons in ABMOs})$$

$$= \tfrac{1}{2}\,[8 - 3] = 2\tfrac{1}{2}$$

Thus, the molecular orbital theory predicts $2\frac{1}{2}$ bonds in nitric oxide.

The lesser known oxides of phosphorus are phosphorus peroxide P_2O_6 and phosphorus suboxide P_2O_2. The structure of suboxide is not well known. The structure of P_2O_6 is as shown.



5. Oxoacids

All the elements of Group 15 form **oxoacids.**

Nitrogen forms a large number of oxoacids such as $H_2N_2O_2$, H_2NO_2, HNO_2, HNO_3, HOONO and HNO_4.

Phosphorus forms much larger number of oxoacids such as H_3PO_2, H_3PO_3, $H_4P_2O_6$, H_3PO_4, $H_4P_2O_7$, HPO_3, H_4PO_5 and $H_4PO_5P_8$.

Arsenic forms two oxoacids, H_3AsO_3 and H_3AsO_4.

Antimony forms only one oxoacid, H_2SbO_3, which, however, is unstable and exists only in solution.

Bismuth gives one stable oxoacid, namely, meta bismuthic acid, $HiBO_3$, which is obtained as a scarlet red solid.

A brief description of the various oxoacids is given below.

Oxoacids of Nitrogen

Hyponitrous Acid, $H_2N_2O_2$. For preparing hyponitrous acid, its sodium salt is first obtained by the reduction of sodium nitrite with sodium amalgam.

$$2NaNO_2 + 4H_2 \xrightarrow{Na-Hg} Na_2N_2O_2 + 2H_2O$$

The solution of sodium hyponitrite is then neutralised with acetic acid and treated with silver nitrate when a yellow precipitate of silver hyponitrite, $Ag_2N_2O_2$, is obtained.

$$Na_2N_2O_2 + 2AgNO_3 \longrightarrow Ag_2N_2O_2 + 2NaNO_3$$

The precipitate is separated, washed and treated with a solution of HCl in ether.

$$Ag_2N_2O_2 + 2HCl \longrightarrow H_2N_2O_2 + 2AgCl$$

Silver chloride gets precipitated and is filtered off. The filtrate containing hyponitrous acid in ether is evaporated to dryness in vacuum when hygroscopic crystals of the acid are obtained.

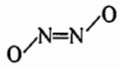
Properties. Pure hyponitrous acid forms white leaflets which decompose on rubbing.

In aqueous solution, the acid decomposes on warming to give nitrous oxide and water, the reaction being irreversible.

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$

Hyponitrous acid is a very weak dibasic acid ($K_1 = 1{\cdot}26\times10^{-7}$, $K_2 = 10^{-11}$). It behaves as a strong reducing agent.

From a study of the infrared spectra of sodium, mercury and silver salts of hyponitrous acid, it has been found to have the structure as shown.



This structure readily accounts for a zero dipole moment of the acid as the moment of one part of the molecule is internally balanced by the moment of the other part.

Nitroxylic Acid, $H_4N_2O_4$. This acid is also called **hydronitrous acid.** It is highly explosive and has not been obtained as such. Only the salts of the acid have been isolated. The sodium salt, for example, can be prepared by the electrolysis of sodium nitrite in liquid ammonia or by the reduction of sodium nitrite with sodium metal in liquid ammonia.

$$2NaNO_2 + 2Na \xrightarrow{Liq.\ NH_3} Na_4N_2O_4$$

The sodium salt, which is obtained as a fine yellow powder, must be handled in complete absence of oxygen and moisture. It readily gets oxidised when exposed to atmospheric oxygen.

$$Na_4N_2O_4 + O_4 \longrightarrow (NaO)_2N - O - O - N(ONa)_2$$
$$\longrightarrow 2NaNO_2 + Na_2O_2$$

It decomposes in the presence of water.

Nitrous Acid, HNO_2. The free acid is unknown. It exists only in solution and there, too, it is unstable. Solutions of nitrous acid can be easily obtained by acidifying solutions of nitrites with mineral acids.

An aqueous solution of the acid, free of salts, can be obtained by acidifying barium nitrite with a calculated amount of dilute sulphuric acid. The reaction is carried out in the cold and the precipitated barium sulphate is removed by filtration.

Properties. 1. Nitrous acid is a weak acid with a dissociation constant of $6{\cdot}0\times10^{-6}$ at 25°C. As mentioned earlier, the free liquid acid does not exist although it can be obtained in the vapour phase when the following equilibrium is established :

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O$$

Even in aqueous solution, the acid is unstable and changes slowly at room temperature and rapidly on heating, into nitric acid.

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

Thus, in aqueous solution, nitrous acid undergoes what is known as *autoxidation.*

On account of its unstable nature, nitrous acid is prepared *in situ* by the action of dilute mineral acids on sodium or potassium nitrite.

2. Nitrous acid behaves both as a *reducing* as well as an *oxidising agent.* It reduces potassium permanganate, potassium dichromate, hydrogen peroxide and other strong oxidising agents. It oxidises strong reducing agents, such as hydriodic acid, sulphurous acid, etc.

It oxidises iron (II) and titanium (III) to higher valency states, in acid medium.

$$Fe^{2+} + HNO_2 + H^+ \longrightarrow Fe^{3+} + NO + H_2O$$
$$Ti^{3+} + HNO_2 + H^+ \longrightarrow Ti^{4+} + NO + H_2O$$

3. Nitrous acid decomposes urea and other aliphatic amino compounds giving nitrogen.

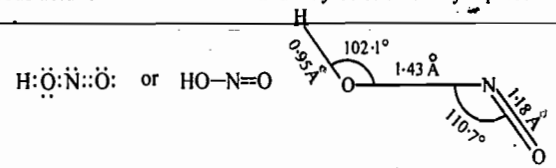
$$\underset{\text{Urea}}{NH_2CONH_2} + 2HNO_2 \longrightarrow CO_2 + 2N_2 + 3H_2O$$

$$\underset{\text{Ethyl amine}}{C_2H_5NH_2} + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$$

4. With aromatic amines and at low temperatures, the well known *diazo reaction* takes place, yielding diazonium salts.

$$\underset{\text{Aniline hydrochloride}}{C_6H_5NH_2.HCl} + HNO_2 \longrightarrow \underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + 2H_2O$$

Structure. Nitrous acid is a monobasic acid and may be structurally represented as follows:



Microwave spectroscopic studies have shown that nitrous acid in the gaseous state has the trans configuration, as shown above.

Nitric Acid, HNO_3. Nitric acid can be conveniently prepared in the **laboratory** by heating a mixture of sodium nitrate and concentrated sulphuric acid in a glass retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

The vapours of nitric acid are condensed in a water-cooled receiver.

On a **commercial scale,** the acid is now almost invariably prepared by the catalytic oxidation of ammonia (**Ostwald's process**). The ammonia obtained by the Haber process is mixed with about 10 volumes of air and passed over a platinum or platinum-rhodium gauze at 750 – 900°C when ammonia is oxidised to nitric oxide.

$$4NH_3 + 5O_2 \xrightarrow[750\text{–}900°C]{Pt} 4NO + 6H_2O\,; \qquad \Delta H = -90{\cdot}0 \text{ kJ}$$

Since the reaction is exothermic, the heat of the reaction maintains the temperature of the catalyst. The yield varies from 90 to 95 per cent.

The nitric oxide is then oxidised by air to nitrogen dioxide which is cooled to about 50°C and absorbed in water (in the presence of air) to give nitric acid.

$$2NO + O_2 \rightleftharpoons 2NO_2$$
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Properties. 1. Anhydrous nitric acid is a colourless liquid boiling at 84·1°C and freezing at –41·55°C to a crystalline solid. The pure acid undergoes autoionization giving nitrate ion and nitronium ion.

$$2HNO_3 \rightleftharpoons \underset{\text{Nitronium ion}}{NO_2^+} + NO_3^- + H_2O$$

2. The aqueous solution containing about 70 per cent of nitric acid by mass forms a constant boiling mixture, boiling at 120·5°C. This is the usual concentrated nitric acid and has a density of 1·4048 g cm^{-3} at 20°C. It is colourless but often develops a yellow colour on account of its photochemical decomposition to nitrogen dioxide.

$$2HNO_3 \xrightarrow{h\nu} 2NO_2 + H_2O + 1/2\,O_2$$

Pure nitric acid can be obtained by distilling the less concentrated acid with concentrated sulphuric acid. The *fuming nitric acid* is obtained by dissolving an excess of nitrogen dioxide in concentrated nitric acid. It is brown in colour.

3. Oxidising Properties of Concentrated Nitric Acid. Since concentrated nitric acid can easily lose its oxygen according to the equation

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O,$$

it acts as a powerful **oxidising agent.**

The oxidising action of nitric acid has been shown to be more due to NO_2 produced than due to oxygen. Thus colourless nitric acid has practically no action on sulphur, phosphorus, metals, etc. But the oxidation starts instantaneously on introducing a small amount of NO_2 (nitric acid itself decomposes at high temperatures to give NO_2). During the course of oxidation, more and more of NO_2 is formed and the reaction, therefore, becomes faster and faster. Because of this reason, the fuming nitric acid, containing dissolved NO_2, is much stronger in its oxidising action. If the NO_2 formed during the reduction of nitric acid is constantly removed, for instance by adding urea, the oxidising action ceases.

It readily oxidises solid non-metals and metalloids to their respective oxoacids. Thus, phosphorus, sulphur, iodine, arsenic, antimony and tin are oxidised to phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), iodic acid (HIO_3), arsenic acid (H_3AsO_4), antimonic acid (H_3SbO_4) and meta stannic acid (H_2SnO_3), respectively.

Carbon is oxidised first to *mellitic acid*, $C_6(COOH)$ and then to carbon dioxide. Graphite gives a greenish yellow insoluble acid, named as *graphitic acid*, $C_{11}H_4O_5$.

4. Oxidising Reactions of Dilute Nitric Acid. Dilute nitric acid can also give oxygen easily according to the equation

$$2HNO_3 \longrightarrow 2NO + H_2O + 3O$$

Hence, reducing agents such as hydrogen sulphide, hydrogen iodide, ferrous sulphate, etc., are oxidised *even* by dilute nitric acid.

5. Action on Metals. a. Metals lying below hydrogen in the electrochemical series. Metals such as Na, K, Ca, Mg, Al, Zn, etc., lying below hydrogen in the electrochemical series normally displace hydrogen from dilute acids. Nitric acid also *primarily* behaves in the same manner. But, since it is a strong oxidising agent and hydrogen is a reducing agent, *secondary reactions* take place resulting in the reduction of nitric acid to give NO, N_2O, N_2 or NH_3, depending upon the nature of the metal, the temperature and the concentration of the acid. Thus, *dilute* nitric acid reacts with zinc in the *cold* giving N_2O or N_2 according to the following equations :

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$
$$5Zn + 12HNO_3 \longrightarrow 5Zn(NO_3)_2 + N_2 + 6H_2O$$

Very dilute nitric acid gives NH_3 which, of course, is neutralised by nitric acid to form NH_4NO_3.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$$

Similarly, iron and tin also give NH_4NO_3 with *dilute* nitric acid.

Lead gives nitric oxide with dilute nitric acid in cold.

Magnesium and manganese give hydrogen.

Concentrated nitric acid essentially behaves as an oxidising agent and metals like aluminium, iron, chromium, etc., are rendered **'passive'** probably due to *surface oxidation.*

b. Metals lying above hydrogen in the electrochemical series. Metals such as Cu, Hg, Ag, lying above hydrogen in the electrochemical series, *do not* liberate hydrogen from acids. In the case of these metals, the action of nitric acid involves only the oxidation of the metals into the metallic oxides which dissolve in the acid to form nitrates accompanied by evolution of NO or NO_2 according as the acid is dilute or concentrated. For instance, *concentrated* acid attacks copper giving NO_2.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Dilute nitric acid gas gives NO.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

c. Noble metals like Au, Pt, Rh and Ir are not attacked by nitric acid. Gold and platinum, however, are attacked by *aqua regia* (3 parts conc. HCl and 1 part conc. HNO_3) which contains free atomic chlorine.

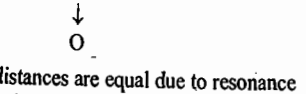
$$HNO_3 + 3HCl \longrightarrow 2H_2O + 2Cl + NOCl$$

The atomic chlorine attacks gold and platinum forming soluble chlorides which form complexes with HCl, *e.g.*,

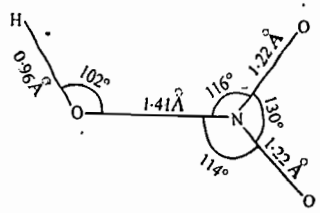
$$Au + 3Cl \longrightarrow AuCl_3$$
$$AuCl_3 + HCl \longrightarrow HAuCl_4$$

6. Action on Proteins. Nitric acid attacks proteins giving a yellow nitro compound called **xanthoprotein.** Hence, nitric acid stains the skin and renders wool yellow. This is used as a delicate test for proteins.

Structure. Nitric acid is a monobasic acid and may be structurally represented as shown :



Both the terminal NO bond distances are equal due to resonance between $N = O$ and $N \rightarrow O$ bonds in the molecule.



Gaseous nitric acid is a *planar* molecule. The bond lengths and bond angles are as shown.

Peroxonitrous Acid, HOONO. Peroxonitrous acid is isomeric with nitric acid. It is unstable though some of its salts are stable.

It is formed as an unstable intermediate during the oxidation of acidified aqueous solutions of nitrates and nitrites using hydrogen peroxide. These solutions are orange-red and are more oxidising than either H_2O_2 or HNO_3. These are found to contain peroxonitrites of the formula M(OONO).

Peroxonitric Acid, HNO_4. Peroxonitric acid is obtained by dissolving nitrogen pentoxide in anhydrous hydrogen peroxide.

$$N_2O_5 + H_2O_2 \longrightarrow HNO_3 + HNO_4$$

Peroxonitric acid is unstable and explosive. It smells like bleaching powder.

It is a strong oxidising agent. It oxidises aniline to nitrobenzene and liberates bromine from a solution of potassium bromide.

Oxoacids of Phosphorus

Hypophosphorous Acid (Phosphinic Acid), H_3PO_2. This acid is prepared by heating white phosphorus with alkalies like barium hydroxide when barium hypophosphite (precipitate) is formed which is separated and treated with a calculated quantity of sulphuric acid to recover the acid itself.

$$3Ba(OH)_2 + 2P_4 + 6H_2O \longrightarrow 2PH_3 + 3Ba(H_2PO_2)_2$$

$$3Ba(H_2PO_2)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 6H_3PO_2$$

Barium sulphate is separated by filtration and the solution concentrated when hypophosphorous acid separates out in the form of well defined crystals.

Properties. 1. It is a colourless crystalline solid (m.p. 26·3°C) soluble in water.

2. It is a monobasic acid, ionising as

$$H_3PO_2 \longrightarrow H^+ + H_2PO_2^-$$

The other two hydrogen atoms are not ionisable.

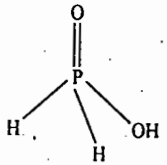
3. The acid as well as its salts are **strong reducing agents.** Thus, mercuric chloride is reduced to mercurous chloride and mercury. The acid itself is oxidised to orthophosphoric acid.

4. The acid is reduced to phosphine when treated with zinc and dilute hydrochloric acid.

5. When a concentrated solution of the acid is heated to 40°C or above, it decomposes giving phosphine and phosphorous acid.

$$3H_3PO_2 \longrightarrow PH_3 + 2H_3PO_3$$

Structure. Hypophosphorous acid, as already mentioned, is a fairly strong acid, its ionisation constant being 1×10^{-2}. It has only one ionisable hydrogen atom, *i.e.*, the acid is monobasic. This suggests the presence of only one OH group in its molecule. X-ray analysis and Raman spectra of salts have suggested the structure as shown.



Phosphorous Acid (Phosphonic Acid), H_3PO_3. As already explained, phosphorous acid is obtained by the hydrolysis of phosphorus trichloride and phosphorus trioxide.

Properties. 1. It is a colourless deliquescent crystalline solid (m.p. 70·1°C), extremely soluble in water.

2. It is a strong acid. Although it contains three hydrogen atoms, only two are ionisable. Hence, it is a dibasic acid ionising as

$$H_3PO_3 \longrightarrow H^+ + H_2PO_3^- \;; \quad K_1 = 1\times10^{-2}$$

$$H_2PO_3^- \longrightarrow H^+ + HPO_3^{2-} \;; \quad K_2 = 2\times10^{-7}$$

It gives two series of salts, such as NaH_2PO_3 and Na_2HPO_3, known as primary phosphites and secondary phosphites, respectively. The third series (*e.g.*, Na_3PO_3) is unknown.

3. Phosphorous acid and its salts (phosphites) are **strong reducing agents** as they are readily oxidisable to phosphoric acid and phosphates, respectively.

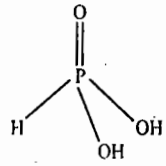
$$HPO_3^{2-} + 3OH^- \longrightarrow PO_4^{3-} + 2H_2O + 2e^-$$

Thus, phosphorous acid reduces salts of copper, silver, gold, etc., to the respective metals.

4. On heating, phosphorous acid decomposes into phosphine and phosphoric acid.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

Structure. It is a dibasic acid which suggests the presence of two OH groups. The third hydrogen is not ionised. The structure for this acid is as shown.



Hypophosphoric Acid, $H_4P_2O_6$. This acid is prepared by controlled oxidation of red phosphorus with sodium chlorite solution at room temperature when disodium salt of hypophosphoric acid crystallises at *p*H 5·2.

$$2P + 2NaClO_2 + 8H_2O \longrightarrow Na_2H_2P_2O_6.6H_2O + 2HCl$$

The free acid is obtained by passing the solution of sodium salt through a column of a cation exchanger in its H^+ form.

$$2H\text{-(Resin)} + Na_2P_2O_6 \longrightarrow 2Na\text{-(Resin)} + H_4P_2O_6$$

Properties. 1. It is a solid, melting at 70°C. It forms well defined crystals having composition $H_4P_2O_6.2H_2O$ which melt at 62°C.

2. It is stable towards alkalies and does not decompose even when heated with 80% NaOH at 200°C. However, in the presence of acids, it is readily hydrolysed giving a mixture of phosphorous and phosphoric acids.

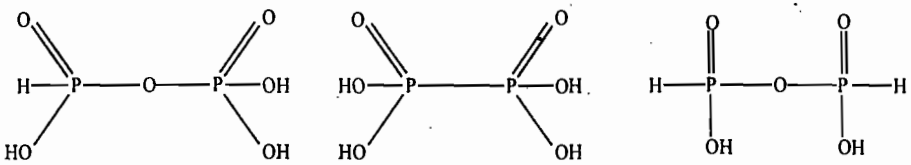
$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

3. It slowly undergoes rearrangement and disproportionation above room temperature to give a mixture of isohypophosphoric acid, pyrophosphoric acid and pyrophosphorous acid.

Structure. Hypophosphoric acid is a tetrabasic acid, the dissociation constants for the four stages of ionisation being

$$K_1 = 6{\cdot}4\times10^{-3} \quad K_2 = 1{\cdot}5\times10^{-5} \quad K_3 = 5{\cdot}4\times10^{-8} \quad K_4 = 9{\cdot}4\times10^{-11}$$

Accordingly, the structure of the acid is given below. The structures of isohypophosphoric acid (which is a tribasic acid) and pyrophosphorous acid (which is a dibasic acid) are also given below.



iso hypophosphoric acid hypophosphoric acid pyrophosphoric acid

Orthophosphoric Acid, H_3PO_4. This is the best known oxoacid of phosphorus and is commonly known as **phosphoric acid.** It is prepared by the following methods.

1. By adding phosphorus pentoxide to water and boiling the solution.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

A small amount of metaphosphoric acid that may be formed, changes readily into orthophosphoric acid in the boiling solution.

2. In the laboratory, the best method for its preparation is to react pure white phosphorus with a solution of nitric acid of specific gravity 1·2 (obtained by adding an equal volume of water to concentrated nitric acid of density 1·4); when the following reaction takes place :

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

The solution is concentrated by heating and when it becomes syrupy at about 166 – 170°C, it is allowed to cool over concentrated sulphuric acid in a vacuum desiccator. The phosphoric acid separates out in a crystalline form.

Manufacture. There are two methods of its manufacture.

1. By the action of concentrated sulphuric acid with rock phosphate or bone ash each of which contains calcium phosphate.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

The mixture is allowed to stand after reaction when calcium sulphate settles down. The clear supernatant syrupy liquid is separated. It contains about 85 per cent phosphoric acid (*syrupy* phosphoric acid) and this is the form in which it is generally used.

2. Phosphorus pentoxide is first prepared commercially by the combustion of phosphorus vapour in air or by heating calcium phosphate and sand in electric furnace.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

$$2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$$

Phosphorus pentoxide in either case is then dissolved in water giving phosphoric acid.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Properties. 1. The concentrated phosphoric acid (85%) is a clear 'syrupy' liquid which on the removal of water at a low temperature in vacuum yields six-sided prismatic crystals melting at 42·3°C.

2. It combines with water giving the semi-hydrate of the formula $2H_3PO_4.H_2O$ which melts at about 29°C.

3. It decomposes on heating, giving pyrophosphoric acid at 250°C,

$$2H_3PO_4 \xrightarrow{250°C} H_4P_2O_7 + H_2O$$

and metaphosphoric acid at higher temperatures.

$$H_4P_2O_7 \xrightarrow{600°C} 2HPO_3 + H_2O$$

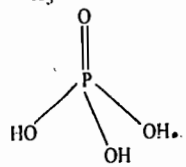
4. It is a tribasic acid, ionising in three stages, as represented below :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- ; \qquad K_1 = 7{\cdot}5\times10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} ; \qquad K_2 = 6{\cdot}2\times10^{-8}$$

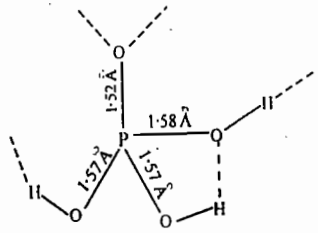
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} ; \qquad K_3 = 1{\cdot}0\times10^{-13}$$

As is evident from the ionisation constants given above, the first ionisation takes place to a considerable extent, the second ionisation takes place only slightly while the third ionisation is extremely small. It forms three series of salts.



Being a tribasic acid, the structure of the acid is as shown.

The crystalline phosphoric acid has a hydrogen bonded layer structure in which tetrahedral PO_4 groups are bonded by hydrogen bonds, as shown in the figure. The hydrogen bonding is responsible for the **syrupy** nature of the acid.



Pyrophosphoric Acid, $H_4P_2O_7$. This acid is also called diphosphoric acid. It is obtained by heating orthophosphoric acid to 250°C.

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

It is a obtained in pure form by heating orthophosphoric acid with $POCl_3$.

$$5H_3PO_4 + POCl_3 \longrightarrow 3H_4P_2O_7 + 3HCl$$

Properties. 1. It is a colourless crystalline solid melting at 61°C.

2. It is reconverted into orthophosphoric acid on boiling with water. It is a slightly stronger acid than phosphoric acid.

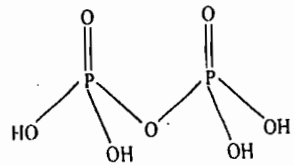
$$H_4P_2O_7 + H_2O \longrightarrow 2H_3PO_4$$

Th dissociation constants for the four stages of dissociation are : $K_1 = 1\times10^{-1}$; $K_2 = 3{\cdot}2\times10^{-2}$; $K_3 = 1{\cdot}7\times10^{-6}$; $K_4 = 6{\cdot}0\times10^{-9}$

3. It is a tetrabasic acid. However, only two series of salts, *e.g.*, $Na_2H_2P_2O_7$, and $Na_4P_2O_7$, are readily obtained. Tetraethyl ester, $(C_2H_5)_4P_2O_7$, has also been obtained.

4. When heated strongly, it yields metaphosphoric acid.

$$H_4P_2O_7 \xrightarrow{600°C} 2HPO_3 + H_2O$$



Structure. Pyrophosphoric acid has been assigned the structure as shown :

Metaphosphoric Acid, HPO_3. This acid is obtained on treating phosphorus pentoxide with a small amount of water,

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3$$

or on heating orthophosphoric acid or pyrophosphoric acid strongly.

$$H_3PO_4 \xrightarrow{600°C} HPO_3 + H_2O$$

$$H_4P_2O_7 \xrightarrow{600°C} 2HPO_3 + H_2O$$

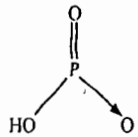
Properties. 1. It is a transparent glassy solid and is, therefore, also known as **glacial phosphoric acid.** It melts at 38·4°C within a range. It is soluble in water.

2. The solution of the acid in water changes into orthophosphoric acid on boiling.

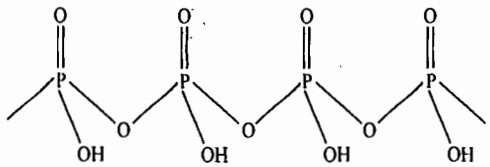
$$HPO_3 + H_2O \longrightarrow H_3PO_4$$

3. *It is a monobasic acid forming salts known as metaphosphates, e.g.,* $NaPO_3$.

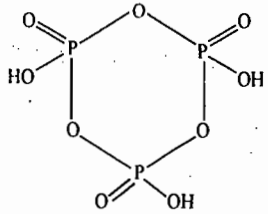
Structure. Metaphosphoric acid is monobasic. The structure of the monomer, based on its formation from orthophosphoric acid by the elimination of water molecule, may be represented as shown.



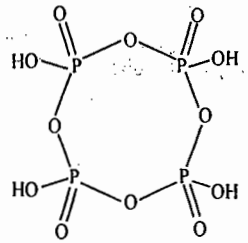
However, it does not exist as a simple monomer, rather it exists as a polymer. The acid is, therefore, represented as $(HPO_3)_n$ and has the structure given below :



Trimetaphosphoric acid $(HPO_3)_3$ and tetrametaphosporic acid $(HPO_3)_4$, are known to have cyclic structures, as shown below :



$(HPO_3)_3$
Trimetaphosphoric acid



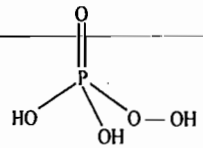
$(HPO_3)_4$
Tetrametaphosphoric acid

Peroxophosphoric Acids. Two peroxophosphoric acids are known. They are **peroxomonophosphoric acid, H_3PO_5** and **peroxodiphosphoric acid, $H_4P_2O_8$.** Both are strong oxidising agents.

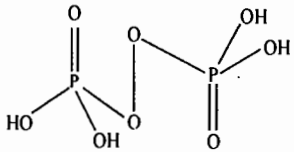
Peroxomonophosphoric acid is obtained in solution by treating phosphorus pentoxide with 30% hydrogen peroxide.

Peroxodiphosphoric acid is obtained by electrolysis of a concentrated solution of secondary potassium phosphate and potassium fluoride.

Structures. The structures of the two peroxophosphoric acids are represented below :

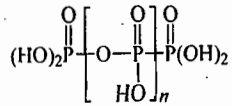


Peroxomonophosphoric acid



Peroxodiphosphoric acid

Apart from these, a number of polyphosphoric acids and their salts are known. Their general structure is as given below.



(n = 1 to 18)

Oxoacids of Arsenic, Antimony and Bismuth

Oxoacids of Arsenic. The nature of the lower oxoacid of arsenic, *viz.*, arsenious acid, H_3AsO_3 is not fully established. It is, therefore, safely represented as $As_2O_3.xH_2O$. It is readily oxidised even on exposure to air. The higher oxoacid, *viz.*, *arsenic acid,* H_3AsO_4, is well known. It is obtained by reacting arsenic metal with concentrated HNO_3 when white crystals of $H_3AsO_4.1/2H_2O$ are obtained. Unlike H_3PO_4, it is a moderately strong oxidising agent in acid solution. H_3AsO_4 is tribasic but it is somewhat weaker than H_3PO_4.

Oxoacids of Antimony. No lower oxoacid of antimony is known. The higher acid, too, exists only in solution. It has the formula H_3SbO_3. It is formed by the oxidation of antimony metal with concentrated HNO_3.

Oxoacids of Bismuth. Bismuth gives one well defined oxoacid, *viz.*, metabismuthic acid, $HBiO_3$, which exists as a scarlet red solid. The compound H_3BiO_3 is basic in character and can be better represented as $Bi(OH)_3$

6. Sulphides

With the exception of nitrogen, all the elements of Group 15 form sulphides. Phosphorus directly combines with sulphur above 100°C to form a number of sulphides, the most important of which are P_4S_3, P_4S_5, P_4S_7 and P_4S_{10}. The sulphide P_4S_3 is used commercially in match industry. The structures of all the four sulphides are known. The sulphide P_4S_{10} has the same structure as P_4O_{10}. The structures of other sulphides are as shown in Fig. 6. It may be noted that the lines between the atoms do not indicate the exact bond order.

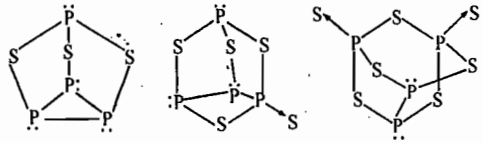


Fig. 6. Structures of P_4S_3, P_4S_5 and P_4S_7

Arsenic directly combines with sulphur to form the sulphides As_4S_3, As_4S_4, As_2S_3 and As_2S_5. The last two sulphides can also be precipitated by passing H_2S gas through solutions of As (III) and As (V) salts acidified with HCl.

Antimony forms the sulphides Sb_2S_3, Sb_2S_4 and Sb_2S_5 by direct interaction of antimony and sulphur. The sulphides Sb_2S_3 and Sb_2S_5 can also be obtained by precipitation with H_2S from Sb (III) and Sb (V) salt solutions.

Bismuth gives dark brown Bi_2S_3 on precipitation of Bi(III) salt solutions by H_2S. A sulphide BiS_2 is obtained as grey needles by direct interaction of Bi and sulphur at 1250°C under high pressure.

The stability of sulphides increases with increase in atomic mass of the element. Their acidic character decreases on moving down the group. The sulphides of arsenic and antimony are soluble in yellow ammonium sulphide while bismuth sulphide is not. The solubility is due to the formation of anionic complexes.

II. Important Compounds of Elements of Group 15

NITRIDES

Nitrides can be prepared either by the direct reaction of nitrogen or ammonia with the metal or by

thermal decomposition of metal amides.

$$Ca + N_2 \longrightarrow Ca_3N_2$$

$$3Mg + 2NH_3 \longrightarrow Mg_3N_2 + 3H_2$$

$$3Ba(NH_2)_2 \longrightarrow Ba_3N_2 + 4NH_3$$

The nitrides can be classified into the following groups :

1. Salt-like Nitrides. Lithium and alkaline earth metals form nitrides in which the bonding is essentially ionic. Hence, their formulae can be represented as $(Li^+)_3N^{3-}$ and $(M^{2+})_3N_2^{3-}$ (M = Ca, Ba, Sr, Be, Mg). Thermodynamic stability of alkaline earth metal nitrides depends upon the type of the metal ion in the nitride. Thus, whereas Be_3N_2 melts without decomposition at 2200°C, Mg_3N_2 decomposes readily even at about 300°C.

2. Covalent Nitrides. Some common examples of covalent nitrides are BN (graphite-like polymorphs), C_2N_2, P_3N_5, S_2N_2, S_4N_4, etc. The properties of covalent nitrides depend upon the element bonded with nitrogen. These nitrides have, therefore, been described at appropriate places in the book while discussing the compounds of these elements.

3. Diamond-like Nitrides. Group 13 elements (B, Al, Ga, In and Tl) form nitrides with the formula MN. Of these, BN exists in two polymorphic forms analogous to graphite and diamond. The rest of the nitrides of the elements of Group 13 have diamond or SiC structure. The metal – nitrogen bond varies from covalent to partly ionic to essentially metallic as we move down the group, *i.e.*, as we move from lighter to heavier elements. These nitrides are quite hard and stable.

4. Interstitial Nitrides. Interstitial nitrides are formed by transition and innner transition metals. Examples are : ScN, LaN, CeN, TiN, ZrN, HfN, VN, TaN, NbN, CrN, MoN, WN, Ti_2N, etc. The nitorgen atoms in these nitrides occupy the interstitial sites in cubic or hexagonal close packed metal lattices. Some of the nitrides have variable composition and are similar in properties to the interstitial carbides and borides. These nitrides are very hard and chemically inert refractory materials. Their hardness approaches that of diamond. They are highly conducting like metals and have metallic lustre. They are used for making crucibles and high temperature reaction vessels. They have also been tried as heterogeneous catalysts.

5. Nitrido Complexes. The nitrido complexes are prepared by thermal decomposition of azides or by deprotonation of coordinated ammonia. Most of the nitrido complexes have a terminal $[\equiv N]^{3-}$ group as in $[VCl_3N]^-$, $[MoO_3N]^-$, $[WCl_5N]^{2-}$, $[RuN(OH)_2X_4]^-$. The metal to nitrogen distance is much shorter than the normal sigma M – N distance. The nitgrogen in nitrido complexes can also act as a bridge as in $[(H_2O)Cl_4Ru - N - RuCl_4(OH)_2]^{3-}$ complex.

PHOSPHIDES

Stable binary phosphides are formed by almost all elements. They exist in a large number of stoichiometries such as M_2P, M_3P_2, MP_2, MP, M_4P_3, MP_5, M_4P_3, M_6P_5, etc.

Preparation. Binary phosphides are prepared

1. By direct combination of the elements at elevated temperature :

$$nM + mP \xrightarrow{\text{Heat}} M_nP_m$$

2. By the electrolysis of fused metal phosphates to which appropriate metal oxides and halides are added. Thus,

$$\underbrace{(NaPO_3)_n + NaCl + WO_3}_{\text{Fused}} \xrightarrow{\text{Electrolysis}} W_3P$$

3. Reduction of phosphate of the metal with carbon at high temperature.

$$Ca_3(PO_4)_2 + 8C \xrightarrow{1200°C} Ca_3P_2 + 8CO$$

4. Interaction of a metal with phosphine :

$$2PH_3 + 4Ti \longrightarrow 2Ti_2P + 3H_2$$

5. Stoichiometries of phosphides can be changed by heating a given metal phosphide with the metal or phosphorus. Thus,

$$Th_3P_4 + Th \xrightarrow{900°C} 4ThP$$

$$4RuP + P_4 \xrightarrow{650°C} 4RuP_2$$

Classification of Phosphides. Phosphides can be classified into the following categories :

1. Metal-rich phosphides. They are hard, brittle and refractory materials with a metallic lusture. They have high thermal and electrical conductivity. The P atom in crystals of such phosphides is surrounded by 6, 7, 8, and 9 metal atoms. (The exact type of crystal structure depends upon the M/P size ratio). Their structures have more M atoms than P atoms.

2. Monophosphides (MP). These can adopt a variety of crystalline structures depending on their M/P size ratios. Phosphides of elements of Group 13 have zinc blende type of structure ; SnP has NaCl type of crystal structure, VP has hexagonal NiAs type of crystal structure whereas MoP has WC type of structure. More complicated crystal structures also exist for these monophosphides.

3. Phosphorus-rich Phosphides. (M_nP_m, m > n). Such phosphides have lower melting points and lower thermal stabilities compared to metal-rich or monophosphides. They are semiconductors and contain catenated P atoms in their crystal structures, *i.e.*, such phosphides may contain chains, double chains, and layers of P atoms in their crystal structure, as in PdP_2, $ZnPbP_{14}$ and CuP_2, respectively.

4. Phosphides with Ionic-Covalent Bonding. Examples are phosphides of Li, Be, Mg and lanthanides. These phosphides have appreciable ionic–covalent and metal–metal bonding character.

Uses. Ferrophosphorus is used for blasting rocks when mixed with dynamite. It is also used in the manufacture of steel. Monophosphides are valuable semiconductors. Ca_3P is used by navy to generate flares in the sea. Nb, Ta and W give phosphides which are resistant to attack by oxygen even at very high temperatures.

ARSENIDES, ANTIMONIDES AND BISMUTHIDES

Alkali metals form arsenides, antimonides and bismuthides of general formula M_3A (A = As, Sb, Bi). Similarly, alkaline earth metals form compounds of the formula M_3A_2 with arsenic, antimony and bismuth. Some of the alkali metals form compounds with As, Sb and Bi having formula MA. Of these, LiBi and NaBi have alloy structures and are superconductors below 2·47 K and 2·22 K, respectively. Some others such as LiAs, NaSb and KSb have parallel spirals of long length containing As and Sb atoms. They have metallic lusture and conduct electricity. Sc, Y, La, lanthanides and actinides form compounds with As, Sb, Bi which have the stoichiometries MA, M_3A_4 and MA_2. These compounds are crystalline and are metallic in nature.

Transition metals form a large number of compounds with As, Sb, Bi of which the important ones are $CoAs_3$ and NiAs. Their crystal structure is similar to that of FeS_2 (pyrites).

Group 13 metals (Al, Ga, In, Tl) form a number of compounds with As, Sb and Bi which are commercially used as semiconductors.

Group 14 elements also form compounds like GeAs, $GeAs_2$, SnAs (a superconductor below 3·5 K) and Sn_4As_3 (a superconductor below 1·2 K), Sn and Pb also form a number of industrially important compounds with As, Sb and Bi.

HYDRAZINE, N_2H_4

Preparation. 1. Raschig's method. Hydrazine is prepared on a **commercial** as well as **laboratory scale** by boiling aqueous ammonia with an alkaline solution of sodium hypochlorite in the presence of a small amount of glue or gelatin. The over-all reaction is as follows :

$$2NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$$

Actually, the reaction proceeds in two steps. In the first step, hypochlorite reacts with ammonia giving chloramine, NH_2Cl.

(*a*) $$NH_3 + NaOCl \longrightarrow NaOH + NH_2Cl$$

The chloramine then reacts with ammonia producing hydrazine.

(*b*) $$NH_3 + NaOH + NH_2Cl \longrightarrow N_2H_4 + NaCl + H_2O$$

The hydrazine produced may react with chloramine giving nitrogen.

(*c*) $$2NH_2Cl + N_2H_4 \longrightarrow 2NH_4Cl + N_2$$

This decreases the yield of hydrazine.

The presence of a small amount of glue or gelatin has been found to be very useful for suppressing the undesirable reaction (*c*) and also for catalyzing the reaction (*b*). The resulting solution contains 60 – 70 per cent of hydrazine which is distilled to get a dilute aqueous solution of hydrazine that may be concentrated to about 85 per cent by further distillation. Anhydrous hydrazine may be obtained by further distillation over barium oxide, sodium hydroxide or potassium hydroxide.

Alternatively, the hydrazine present in the resulting solution is precipitated as sparingly soluble crystalline hydrazine sulphate, on treatment with sulphuric acid.

$$N_2H_4 + H_2SO_4 \longrightarrow \underset{\text{Hydrazine sulphate}}{N_2H_4.H_2SO_4}$$

The precipitate is removed and treated with an alkali when hydrazine hydroxide $H_2N.NH_3OH$ is obtained. This is distilled under reduced pressure over an alkaline dehydrating agent, such as barium oxide or solid sodium hydroxide, to liberate free hydrazine.

$$N_2H_5OH + BaO \longrightarrow \underset{\text{Hydrazine}}{N_2H_4} + Ba(OH)_2$$

Physical Properties. Anhydrous hydrazine is a colourless fuming liquid (m.p. 2°C and b.p. 113·5°C), soluble in water in all proportions. It is also soluble in alcohol. It is strongly hygroscopic.

Chemical Properties. 1. Hydrazine may be regarded as derived from NH_3 by the replacement of one H atom by the NH_2 group. It behaves as a diacid base.

$$N_2H_4\,(aq) + H_2O \rightleftharpoons N_2H_5^+ + OH^- ; \qquad K_b = 8{\cdot}5\times10^{-7}$$

$$N_2H_5^+\,(aq) + H_2O \rightleftharpoons N_2H_6^{2+} + OH^- ; \qquad K_b = 8{\cdot}9\times10^{-16}$$

Thus, it forms two series of hydrazinium salts containing $N_2H_5^+$ and $N_2H_6^{2+}$ ions. For example, with hydrochloric acid it forms hydrazine monochloride $N_2H_5^+Cl^-$ and hydrazine dichloride $(N_2H_6)^{2+}Cl_2^-$.

2. Hydrazine burns rapidly and completely in air with a considerable evolution of heat.

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O ; \qquad \Delta H = -622 \text{ kJ}$$

This has created lot of interest in this compound and some of its alkyl derivatives are used as potential **rocket fuels.**

3. It reacts with sodium in an inert atmosphere giving sodium hydrazide and evolving hydrogen.

$$2N_2H_4 + 2Na \longrightarrow 2N_2H_3Na + H_2$$

4. It reacts with nitrous acid giving hydrazoic acid.

$$N_2H_4 + HNO_2 \longrightarrow 2H_2O + \underset{\text{Hydrazoic acid}}{HN_3}$$

5. Since hydrazine and its salts can be readily oxidised to nitrogen, they are used as powerful reducing agents. Thus, hydrazine reduces salts of platinum, gold and silver to the metallic state.

$$PtCl_4 + N_2H_4 \longrightarrow Pt + N_2 + 4HCl$$

$$4AuCl_3 + 3N_2H_4 \longrightarrow 4Au + 3N_2 + 12HCl$$

$$4AgNO_3 + N_2H_4 \longrightarrow 4Ag + N_2 + 4HNO_3$$

Similarly, it reduces Fehling solution to red cuprous oxide, ferric chloride to ferrous chloride and iodates to iodides.

$$4Cu(OH)_2 + N_2H_4 \longrightarrow 2Cu_2O + 6H_2O + N_2$$

$$4FeCl_3 + N_2H_4 \longrightarrow 4FeCl_2 + N_2 + 4HCl$$

$$2IO_3^- + 3N_2H_4 \longrightarrow 2I^- + 6H_2O + 3N_2$$

Uses. Hydrazine is used as rocket fuel. It is also used as a reagent in organic chemistry.

Structure of hydrazine. Structurally, hydrazine resembles hydrogen peroxide in that both H_2O_2 and N_2H_4 exist in gauche forms at room temperature. The plane containing N – N bond and one of the N – H bonds of one N is at an angle of 95° to the plane containing the N – N bond and one of the N – H bonds of the other N. Thus, the lone pairs of electrons on the two nitrogens are not cis to each other but are at an angle of 95° to each other (Fig. 7).

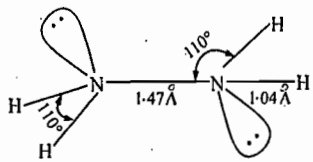


Fig. 7. Structure of hydrazine.

The N – N distance is 1·47 + 0·02 Å, the N – H distance is 1·04 Å and HNH and HNN angles are about 110°C each.

HYDRAZOIC ACID, HN_3

Hydrazoic acid, although formally referred to as a hydride of nitrogen, bears no resemblance to NH_3 and N_2H_4. While ammonia and hydrazine are basic, HN_3 is acidic in character.

Preparation. It is prepared by treating an aqueous solution of hydrazine hydrochloride with nitrous acid ($NaNO_2$ and HCl).

$$N_2H_4.HCl + N_2O \longrightarrow HN_3 + HCl + 2H_2O$$

An alternative method is to first prepare sodium azide (NaN_3) by the oxidation of sodamide by nitrous oxide or sodium nitrate.

$$NaNH_2 + N_2O \xrightarrow{190°C} NaN_3 + H_2O$$

$$3NaNH_2 + NaNO_3 \xrightarrow{175°C} NaN_3 + 3NaOH + NH_3$$

Sodium azide is then distilled with dilute sulphuric acid under reduced pressure.

$$2NaN_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HN_3$$

The distillate is an aqueous solution of hydrazoic acid which is concentrated to about 91 per cent by simple heating and dehydrated further with fused calcium chloride.

Properties. Free hydrazoic acid is a colourless liquid, boiling at 37°C. It is dangerously explosive and dissociates into its constituents with the evolution of a large amount of heat.

$$2HN_3 \longrightarrow 3N_2 + H_2\,; \qquad \Delta H = -51{\cdot}5\ \text{kJ}$$

It is a weak acid, its strength being equal to that of acetic acid ($K_a = 1{\cdot}8\times10^{-5}$). Thus,

$$HN_3\,(aq) \rightleftharpoons H^+\,(aq) + N_3^-\,(aq)\,; \qquad K_a = 1{\cdot}8\times10^{-5}$$

It forms salts with alkalies and active metals (Zn, Mg, etc.).

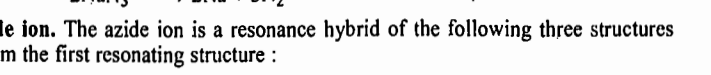
$$HN_3 + NaOH \longrightarrow NaN_3 + H_2O$$

$$2HN_3 + Mg \longrightarrow Mg(N_3)_2 + H_2$$

Salts of heavy metals are highly explosive. Thus, azides of lead, mercury and barium are used in detonation caps because these azides explode on being struck sharply. The azides of alkali metals are not explosive and decompose smoothly and quantitatively when heated to 300°C or above. Thus, sodium azide decomposes to give sodium and nitrogen.

$$2NaN_3 \longrightarrow 2Na + 3N_2$$

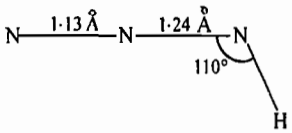
Structure of the azide ion. The azide ion is a resonance hybrid of the following three structures with major contribution from the first resonating structure :



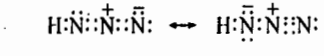
Thus, **the azide ion** has a linear, symmetrical structure, as shown below. The lines between the atoms do not show exact bond order.

$$[N \overset{1{\cdot}16\,\text{Å}}{—} N \overset{1{\cdot}16\,\text{Å}}{—} N]^-$$

In **hydrazoic acid, HN_3,** however, the symmetry is lost and the molecule has a bent structure, as shown. The lines between the atoms do not show the exact bond order.



The electronic structure of the acid is a resonance hybrid of the following two structures :



HYDROXYLAMINE, NH_2OH

It may be regarded as derived from ammonia by the replacement of one H atom by an OH group.

It is prepared by the reduction of nitrites with sulphur dioxide under carefully controlled conditions. A concentrated solution of sodium nitrite is mixed with a solution of sodium carbonate and sulphur dioxide at a temperature below 3°C is passed till the solution becomes just acidic. The following reactions are supposed to take place :

$$Na_2CO_3 + SO_2 + H_2O \longrightarrow NaHSO_3 + NaHCO_3$$

$$NaNO_2 + 3NaHSO_3 \longrightarrow \underset{\substack{\textit{Hydroxlamine}\\ \textit{sodium sulphonate}}}{HON(SO_3Na)_2} + Na_2SO_3 + H_2O$$

The sulphonate can be easily hydrolysed to hydroxylamine.

$$HON(SO_3Na)_2 + 2H_2O \longrightarrow NH_2OH + 2NaHSO_4$$

Alternatively, it is prepared by the electrolytic reduction of nitric acid in 50% H_2SO_4 using amalgamated lead cathode.

$$NO_2 - OH + 6H^+ + 6e^- \longrightarrow NH_2OH + 2H_2O$$

It is a colourless solid melting at 33°C. It is freely soluble in water and lower alcohols. It is unstable and decomposes violently even at 20°C.

$$3NH_2OH \longrightarrow NH_3 + N_2 + 3H_2O$$

The aqueous solution of hydroxylamine is less basic than ammonia ($K_b = 1{\cdot}8\times10^{-5}$). Thus,

$$NH_2OH\,(aq) + H_2O \longrightarrow NH_3OH^+ + OH^-\,; \qquad K_b = 6{\cdot}6\times10^{-9}$$

Like H_2O_2, it acts as an oxidising as well as a reducing agent depending upon circumstances.

NITROGEN TRIFLUORIDE, NF_3

It is conveniently prepared by fluorinating ammonia in the catalytic presence of Cu.

$$4NH_3 + 3F_2 \xrightarrow{Cu} NF_3 + 3NH_4F$$

It can also be prepared by the electrolysis of NH_4F.

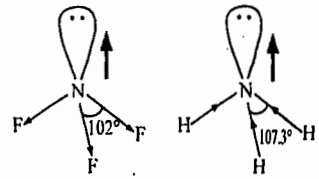
It is a colourless gas (m.p. – 207°C ; b.p. – 129°C) which is quite stable thermodynamically.

The gas acts as a fluorinating agent. It thus converts Cu into CuF.

$$2NF_3 + 2Cu \longrightarrow N_2F_4 + 2CuF$$

As, Sb and Bi also get fluorinated by interaction with NF_3.

NF_3 has a pyramidal structure with FNF angle = ~ 102° and dipole moment = 0·24 D, compared with HNH angle = ~ 107° and dipole moment = 1·48 D in the case of NH_3. The difference in the dipole moments of NF_3 and NH_3 (both of which have pyramidal structure though) is due to the fact that while the dipole moments due to N – F bonds in NF_3 are in *opposite direction* to the direction of the dipole moment of the lone pair on N atom, the dipole moments of N – H bonds in NH_3 are in the *same direction* as the direction of the dipole moment of the lone pair on N atom, an shown.



Because of its lower dipole moment, NF_3 is a weaker ligand than NH_3.

NF_3 is known to form complexes such as $[NF_4]^+$ and $F_3N \rightarrow O$. Thus,

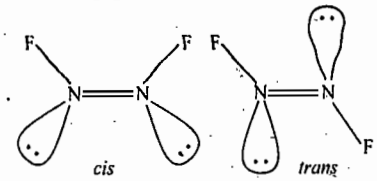
$$NF_3 + 2F_2 + SbF_5 \xrightarrow[\text{High pressure}]{200°C} [NF_4^+][SbF_6]^-$$

DINITROGEN DIFLUORIDE, N_2F_2

Dinitrogen difluoride is best prepared by reacting NHF_2 with KF.

$$2KF + 2HNF_2 \xrightarrow[\text{temperature}]{\text{low}} 2KF.HNF_2 \xrightarrow{\text{Room temperature}} N_2F_2 + 2KHF_2$$

The reaction yields both cis and trans isomers whose structures are as shown.



Both the isomeric forms are gases at room temperature, the cis form boiling at – 106°C and the trans form boiling at –112°C. The cis form is thermodynamically more stable than the trans form.

Above 70°C, nearly 90% of N_2F_2 is present in the cis form :

$$\text{trans } N_2F_2 \overset{>70^\circ C}{\rightleftharpoons} \underset{(\sim 90\%)}{\text{cis } N_2F_2}$$

If, however, the isomeric mixture is treated with $AlCl_3$ or the chlorides of bivalent Mn, Co, Ni and Fe, at low temperature, the major product is trans N_2F_2.

The cis form reacts *selectively* with AsF_5 to form $[N_2F]^+[AsF_6]^-$ which when reacted with NaF – HF, regenerates the original compounds. The trans form does not react with AsF_5.

$$\underset{\text{Mixture of } cis \text{ and trans isomers}}{N_2F_2} + AsF_5 \longrightarrow \underset{\text{Formed by cis } N_2F_2}{[N_2F]^+[AsF_6]^-} + \underset{trans}{N_2F_2}$$

$$[N_2F]^+[AsF_6]^- \xrightarrow{NaF-HF} \underset{cis}{N_2F_2} + AsF_5$$

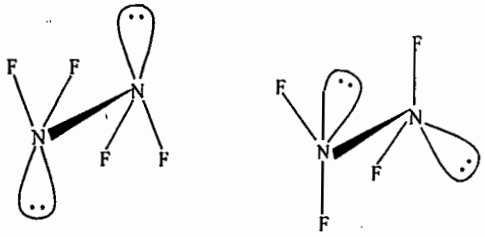
DINITROGEN TETRAFLUORIDE, N_2F_4

N_2F_4 is prepared by reacting HNF_2 with NaClO.

$$2HNF_2 \xrightarrow{NaClO} N_2F_4 + H_2O$$

HNF_2, in turn, is obtained by first fluorinating urea and then treating the fluorinated product with concentrated sulphuric acid.

N_2F_4 exists both in the staggered and the gauche conformations as shown below :



Staggered Form (Side View) Gauche Form

It is a colourless gas (b.p. – 73°C ; m.p. – 164°C).

It is a strong fluorinating agent. Thus,

$$SiH_4 + N_2F_4 \longrightarrow SiF_4 + N_2 + 2H_2$$

$$10Li + N_2F_4 \longrightarrow 4LiF + 2Li_3N$$

$$AsF_5 + N_2F_4 \longrightarrow [N_2F_3]^+[AsF_6]^-$$

N_2F_4 easily yields, at room temperature, the free radical $\cdot NF_2$ which reacts readily with a number of compounds. For example,

$$N_2F_4 \rightleftharpoons 2(\cdot NF_2) \xrightarrow{Cl_2} 2ClNF_2$$

$$N_2F_4 \rightleftharpoons 2(\cdot NF_2) \xrightarrow{2NO} 2ONNF_2$$

TRISILYLAMINE, $N(SiH_3)_3$

Trisilylamine is prepared by reacting monochlorosilane with ammonia.

$$3SiH_3Cl + 4NH_3 \longrightarrow N(SiH_3)_3 + 3NH_4Cl$$

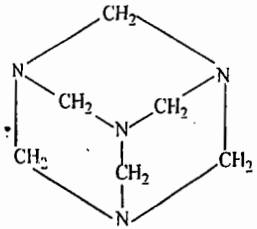
Trisilylamine is a trigonal planar compound with N orbitals in sp^2 hybrid state, unlike trimethyl or triethylamine which is pyramidal and has N orbitals in sp^3 hybrid state. There is considerable $d\pi$ overlap between the *p* orbital (containing the lone pair) of N atom and the vacant $d\pi$ orbitals of Si atoms. The trigonal planar structure of $N(SiH_3)_3$ is, thus, strengthened due to $p\pi - d\pi$ bonding.

Since the lone pairs of electrons of N atom are engaged in $p\pi - p\pi$ bonding between N and Si, they are no longer available for donation to Lewis acids. Trisilylamine, therefore, behaves as a much weaker base compared to trimethylamine or triethylamine. Hence, trisiylamine does not form adducts with BH_3 even at low temperature whereas trimethylamine or triethylamine does so readily. Due to the same reason, $N(SiH_3)_3$ acts as a much weaker ligand compared to $N(CH_3)_3$ and $N(C_2H_5)_3$.

HEXAMETHYLENE TETRAMINE, HEXAMINE, UROTROPINE, $(CH_2)_6N_4$

Hexamethylene tetramine is prepared by reacting formaldehyde with concentrated ammonia solution.

$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$

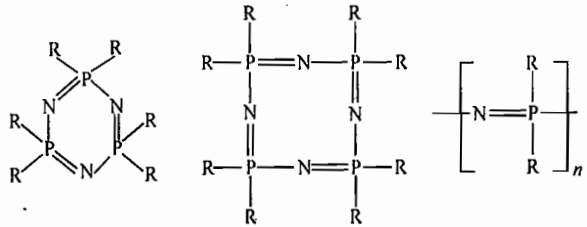


Hexamine has a complicated ring structure. The bonding (but not the exact orientations of the rings) in the compound is roughly as shown.

It is a white crystalline compound soluble in water. It is basic in nature and is used for adjusting the *p*H of aqueous solutions during *p*H-sensitive complexometric titrations. Hexamine is used for the treatment of gout and rheumatism.

PHOSPHAZINES, $(NPR_2)_n$

Phosphazines are cyclic or chain polymers which contain $-N=\underset{R}{\overset{R}{P}}-$ as the repeating unit. Common phosphazines exist as cyclic trimers, cyclic tetramers and also as linear polymers, as shown below.



Cyclic Trimer Cyclic Tetramer Linear Polymer

Chlorophosphazines. Two important chlorophosphazines are described here.

Hexachlorocyclotriphosphazine, $(NPCl_2)_3$. It is prepared by the reaction of PCl_5 with NH_4Cl in the presence of $C_2H_4Cl_2$ or C_6H_5Cl under controlled conditions.

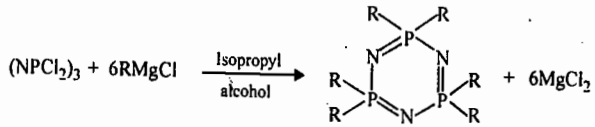
$$3PCl_5 + 3NH_4Cl \xrightarrow[\text{or } C_6H_5Cl]{C_2H_4Cl_2} (NPCl_2)_3 + 12HCl$$

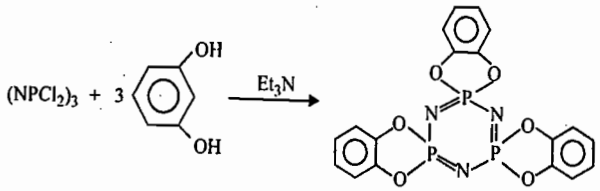
The above reaction produces a mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$. Any tetramer produced along with the trimer can be easily separated since the trimer sublimes in vacuum at 50°C as a white crystalline solid whereas the tetramer does not do so under these conditions.

Hexachlorocyclotriphosphazine is the key material for the synthesis of a number of linear polymers. Thus,

$$(NPCl_2)_3 + 6NaF \longrightarrow (NPF_2)_3 + 6NaCl$$

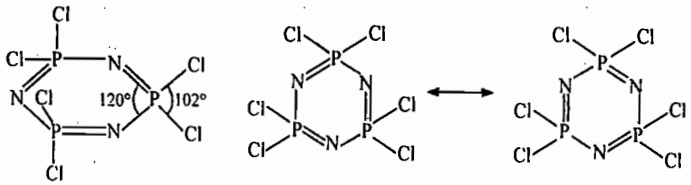
$$(NPCl_2)_3 + 6NaOR \longrightarrow [NP(OR)_2]_3 + 6NaCl$$



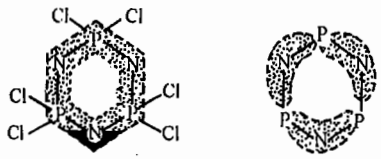


The mechanism of replacement of Cl by other nucleophiles is not well understood. However, it appears to involve S_N2 attack on P atom.

Structure of Hexachlorocyclotriphosphazine. The trimer is known to be a planar six-membered ring (structure I) in which the bond angles are consistent with sp^2 hybridisation of N orbitals and an approximate sp^3 hybridisation of P orbitals of the ring. Resonance structures II and III can also be drawn, as in the case of benzene, indicating aromaticity in the ring.



But unlike benzene which involves extensive $p\pi$–$p\pi$ bonding, phosphazine involves $p\pi$–$d\pi$ bonding. The extent of π bonding in phosphazine appears to be quite appreciable as the N – P distance (1·6 Å) is considerably shorter than the normal N – P single bond distance (1·75 – 1·8Å). The main question about the π bonding is whether the π electron charge cloud is *delocalised on all the ring atoms*, as shown in (I) or *there are more intensely localised islands within the NPN segments*, as shown in (II).

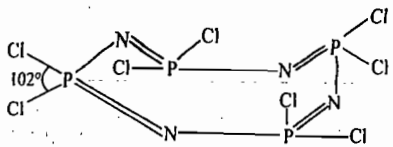


Complete delocalisation of π electron charge cloud. (I)

Localised islands of π electron charge cloud over NPN segments. (II)

This question remains unanswered. However, considering the difference in the electronegativities of N and P and the location of a lone pair of electrons on each N atom of the ring, structure (II) appears to be more probable than structure (I).

Structure of Octachlorocyclotetraphosphazine. $(NPCl_2)_4$ has a 'tub-like' structure, as shown.



This structure is, evidently, non-planar.

Phosphazines of high molar masses have been discussed in details in Chapter 35 on 'Inorganic Polymers'.

Another polymeric nitrogen compound of phosphorus is $P_4(NR)_6$, the structure of this compound is analogous to P_4O_6 in which the bridging oxygens are replaced by bridging NR groups. Another polymeric nitrogen compound is $P(N(CH_3)_2)_3$ which is analogous to $P(OR)_3$ in which OR groups are replaced by $N(CH)_3$ groups.

Organometallic Compounds of Grop 15 Elements

These have been discussed in details in Chapter 34 on Organometallic Compounds.

FERTILIZERS

Essential Nutrients for Plants. Plants require phosphorus, potassium, nitrogen, sulphur, calcium, iron and magnesium, besides traces of a few other elements such as copper, boron, zinc, manganese, molybednum and cobalt for their growth and health. These elements are generally present in the soil to more or less extent in the form of minerals or otherwise. However, after a few years of continuous cropping, the soil becomes poorer and poorer in these materials and there is need to put back what has been taken out from the soil by successive crops. If the soil is not replenished by what it has lost, in time, it would become less productive and, in extreme cases, may become even infertile. In order to keep up soil fertility and to get good yields of various crops, it is necessary to add materials containing nitrogen, phosphorus and potassium in the form of *manures* which may be natural or artificial. The artificial manures are called **chemical fertilizers.** Nitrogen, phosphorus and potassium are regarded as essential plant nutrients.

Functions of Essential Nutrients

1. **Nitrogen.** Nitrogen is highly essential for rapid growth of plants and hence it improves the yields of crops. It also raises protein content of the crops and thus adds to their food value.

2. **Phosphorus.** Phosphates, the potential source of phosphorus for plants, are highly valuable fertilizers. Experiments have shown that phosphates promote early growth as well as early maturity of plants. The addition of phosphates also increases resistance of plants to frost and disease and helps in formation of high yielding seeds.

3. **Potassium.** Potassium develops a healthy root system which helps the plants to get regular supply of nutrients from the soil. As a result, we get a healthy plant which develops sufficient resistance towards various diseases. It also helps in the formation of albuminoids and carbohydrates in the various plants.

Potassium compounds are generally used in mixed fertilizers containing nitrogen and phosphorus. Such materials are commonly referred to as **N.P.K. fertilizers.**

Types of Manures. There are two types of manures :

1. *Natural* and 2. *Artificial Manures* (*i.e., Chemical Fertilizers*)

Natural Manures. Natural manures generally added to soil include animal dung, blood, bones, horns, hair stock, leather waste, fish scrap, night soil, animal excreta, guano, sewage, sludge, etc. Manures prepared out of vegetable growth such as leaves, barks, seeds, ashes, etc., are also included in this category. Leguminous plants grown in the soil are also ploughed back into the soil for replenishing nitrogen content of the soil.

Artificial Manures or Fertilizers. Artificial manures are generally called **fertilizers.** These are chemical compounds containing nitrogen, phosphorus or potassium.

Every compound of nitrogen, phosphorus or potassium *cannot* be used as a fertilizer. A good fertilizer must be *soluble in water* and nitrogen, phosphorus or potassium contained in it should be in such a form that it can *readily be made available* to the plants. The common **nitrogenous fertilizers** are ammonium sulphate, ammonium nitrate, urea and nitrates of potassium and calcium. The most important **phosphatic manure** is calcium superphosphate. The most widely used compound of **potassium** is

potassium nitrate. Potassium chloride and potassium sulphate are also used in fertilizers.

Sometimes it is necessary to add certain chemicals which are not plant nutrients themselves but they help the nutrients already present in the soil to be more readily available to the plants. These are called **stimulant fertilizers.** Examples are lime and gypsum.

NITROGENOUS FERTILIZERS

Although sufficient amount of nitrogen is available in the atmosphere, it is of no use as such for the plants because excepting *leguminous plants, algae, fungi* and *mosses*, no other plant can assimilate free nitrogen for its growth. This nitrogen, therefore, has to be converted into those forms of chemical compounds which can easily be assimilated by plants.

The important nitrogenous compounds used as fertilizers are described below.

1. Ammonium sulphate. There are two important sources of ammonium sulphate.

a. Ammonia liquor obtained from dry distillation of coal. The bituminous coal which is used for this purpose contains about 1·5 per cent of nitrogen in combined state. During the process of distillation, this nitrogen gets converted into ammonium salts and collects along with other volatile matter as *ammonia liquor*. The ammonium salts present in the liquor are ammonium carbonate, $(NH_4)_2CO_3$, ammonium sulphide, $(NH_4)_2S$, ammonium chloride, NH_4Cl and ammonium sulphate, $(NH_4)_2SO_4$.

In order to recover ammonia, the liquor is mixed with lime and heated in stills by steam when the salts decompose evolving ammonia.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3$$

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O + 2NH_3$$

Ammonia coming off from the salts along with steam is passed through 60 per cent sulphuric acid when crystals of ammonium sulphate, $(NH_4)_2SO_4$, separate out.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

b. Ammonia obtained from Haber process. As is well known, ammonia is prepared commercially by direct combination of nitrogen and hydrogen at a temperature of about 500°C and under a pressure of 100–1000 atm in the presence of a catalyst (finely divided iron with a little molybdenum).

$$N_2 + 3H_2 \overset{100-1000\text{ atm, }500°C}{\rightleftharpoons} 2NH_3$$

Ammonia obtained as above is converted into ammonium sulphate by treatment with sulphuric acid as mentioned above or with gypsum in the presence of CO_2.

$$2NH_3 + CO_2 + CaSO_4.2H_2O \longrightarrow (NH_4)_2SO_4 + CaCO_3 + H_2O$$

Calcium carbonate is removed by filtration. It is an important by-product. The solution is concentrated and crystallised. Ammonium sulphate contains theoretically over 25 per cent ammonia. The compound, as obtained commercially, however, contains only about 20 per cent of ammonia. This ammonia cannot be easily utilized by plants. It is first converted into nitrite and nitrate ions through the action of *nitrifying bacteria* present in the soil. The nitrite and nitrate can be taken up easily by plants from the soil.

Ammonium sulphate should not be used too frequently as this renders the soil *acidic*. This is particularly so when the soil is poor in lime which, if present, can neutralise acidity to some extent. It should be used after the seeds have germinated.

2. Calcium Ammonium Nitrate (CAN). It is also known as **nitro limestone**. Ammonia synthesised by Haber process is partly converted into nitric acid by Ostwald's process using platinum or platinum-rhodium as the catalyst. Nitric acid and ammonia are then made to react with each other to give ammonium nitrate.

The solution is concentrated and treated with powdered limestone. The slurry so obtained is converted into small *pellets* in specially designed evaporators and sold under the name **calcium ammonium nitrate.**

Ammonium nitrate is explosive. The function of limestone is to prevent it from exploding.

Calcium ammonium nitrate is *hygroscopic*. The pellets are, therefore, coated with soap stone to protect them from moisture.

Calcium ammonium nitrate is considered to be superior to ammonium sulphate in some respects. Firstly, it is *more soluble in water* and secondly, the presence of calcium *prevents development of acidity in the soil.*

3. Urea. Urea is a better manure than either ammonium sulphate or calcium ammonium nitrate. This is because the ammonia liberated by hydrolysis

$$O{=}C(NH_2)_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

is assimilated by the soil through the interaction of *nitrifying bacteria* as in the case of ammonium sulphate or calcium ammonium nitrate. The only thing that it leaves behind is carbon dioxide which, unlike sulphate or nitrate ion, does no harm to the soil. The sulphate and nitrate ions render the soil acidic.

Another advantage lies in the fact that it contains much higher percentage of nitrogen than either ammonium sulphate or ammonium nitrate. There is also no risk in storage of urea as it is not subject to explosion hazards.

However, there is one disadvantage. Urea is not so stable as other nitrogenous fertilizers. It decomposes even at lower temperatures particularly in humid atmosphere releasing ammonia and carbon dioxide.

Urea is prepared on a large scale by reacting ammonia (obtained from Haber process) with carbon dioxide at 135°C and about 220 atm pressure to yield ammonium carbamate, some of which decomposes simultaneously to give urea.

(*i*) $$2NH_3 + CO_2 \longrightarrow \underset{\text{Amm. carbamate}}{NH_2COONH_4}$$

(*ii*) $$NH_2COONH_4 \longrightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

The undecomposed ammonium carbamate is processed separately under reduced pressure to give urea.

In the modern manufacturing plants, the production of urea has been made highly economical. Hydrogen required for the manufacture of ammonia and carbon dioxide required for reacting with ammonia, are both obtained from *naphtha*. For this purpose, crude naphtha from oil refineries is subjected to *partial combustion* in specially designed burners to give a mixture of hydrogen and carbon monoxide. The mixture is made to react with *steam* in the presence of a *catalyst* (usually a mixture of Fe, Cr and Co) when carbon monoxide is oxidised to carbon dioxide.

$$\underbrace{CO + H_2}_{\text{From naphtha}} + \underset{\text{(steam)}}{H_2O} \longrightarrow CO_2 + 2H_2$$

Carbon dioxide is separated by washing with water under pressure or by treatment with $KHCO_3$ solution.

The hydrogen, obtained as above, is converted into ammonia by Haber process. The carbon dioxide, recovered easily from the aqueous or the alkali carbonate solution, is compressed and reacted with ammonia to give urea, as indicated by chemical equations (*i*) and (*ii*) given above.

PHOSPHATIC FERTILIZERS

The *phosphate rock*, which is primarily tricalcium phosphate, $Ca_3(PO_4)_2$ and *apatite*, $CaF_2.3Ca_3(PO_4)_2$, are too little soluble in water to serve as a source of phosphorus for plants. These are, therefore, converted into calcium dihydrogen phosphate which is commonly known as *calcium superphosphate*. This is the most important phosphatic fertilizer. Other such fertilizers are : *triple phosphate, phosphatic slag and nitrophosphate.*

Calcium Superphosphate. This is manufactured by treating the insoluble phosphate rock with a calculated quantity of sulphuric acid (commercial) when we get the more soluble calcium dihydrogen phosphate (superphosphate) and calcium sulphate.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \longrightarrow 2CaSO_4 + Ca(H_2PO_4)_2$$

A sufficient amount of water is then added to convert calcium sulphate into its dihydrate, $CaSO_4.2H_2O$ (gypsum).

The mixture of calcium dihydrogen phosphate and gypsum is marketed under the name of superphosphate of lime and is used as a fertilizer.

Being soluble in water and containing about 18 per cent of P_2O_5, it is considered a good phosphatic fertilizer. However, care should be taken in its storage as it has a tendency to set in the form of hard lumps.

Phosphatic Slag. Phosphatic slag is a by-product of steel industry. This results from the presence of small amounts of phosphorus in iron ores.

When during smelting the iron ore is heated with lime stone in the presence of air, calcium phosphate and calcium silicate appear as slag. The following reactions are probably involved :

$$4P + 5O_2 \longrightarrow 2P_2O_5$$

$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The slag being lighter rises on the top of the molten iron and is easily separated. It contains 14 – 18 per cent of P_2O_5 and 40 per cent of lime which is useful in lowering soil acidity.

Phosphatic slag is also known as **Thomas slag.** It is well ground and used as a valuable fertilizer.

Nitrophosphate. Nitrophosphate is prepared in the same way as superphosphate from phosphatic rock, using nitric acid instead of sulphuric acid. The advantage of this fertilizer is that in addition to phosphorus, it contains nitrogen as well.

POTASH FERTILIZERS

Potassium Nitrate, KNO_3. Potassium nitrate is the chief potash fertilizer. This occurs as an efflorescent on the soil at a number of places in India and other tropical countries. The presence of nitrogen as nitrate ion adds to the value of this fertilizer.

Potassium chloride and **potassium sulphate** are also used as fertilizers.

Mixed Fertilizers. A fertilizer which contains more than one of the major plant nutrients, is called a *mixed fertilizer*. In most cases, mixed fertilizers contain nitrogenous, phosphatic and potash fertilizers. Ammonium sulphate, ammonium nitrate or calcium ammonium nitrate is used as a source of nitrogen. Calcium superphosphate is used as a source of phosphorus while potassium chloride or potassium sulphate is used as source of potassium. These are referred to as **N.P.K. fertilizers.**

QUESTIONS

1. (*a*) Name the elements of Group 15 of the periodic table. How do the following properties vary in this group :
   (*i*) Ionisation energy (*ii*) Catenation (*iii*) Metallic character (*iv*) Electronegativity ?
2. (*a*) Why is nitrogen anomalous in its behaviour as compared to the other members of its group ? Discuss with examples.
   (*b*) Explain with reasons : (*i*) NF_5 is not known while PF_5 is so well known. (*ii*) NH_3 has higher boiling point than PH_3. (*iii*) Nitrogen is a gas while phosphorus is a solid at room temperature. (*iv*) Nitrogen molecule is diatomic but phosphorus molecule is tetratomic.
3. Name the hydrides of Group 15 elements. Discuss the variation in their properties with reference to (*a*) basic character (*b*) thermal stability (*c*) reducing character (*d*) bond angle (*e*) covalent nature.
4. Give a brief account of the halides of Group 15 elements with special reference to the properties of PCl_3 and PCl_5.
5. Give a detailed description of the oxides of the elements of Group 15 with special reference to the oxides of nitrogen and phosphorus. Give the structures of these oxides.
6. Give a detailed description of the oxoacids of nitrogen. Give their important characteristics and structures.
7. Give a detailed description of oxoacids of phosphorus. Give their important characteristics and strcutures.
8. Give a brief description of the sulphides of Group 15 elements. Give the structure of the well known sulphides of phosphorus.
9. (*a*) How are hydrazine and hydrazoic acid prepared ? Give their properties and structures.
   (*b*) Give the preparation, properties and uses of hydroxyl amine.
10. Write short notes on :
    Nitrogen trifluoride, Dinitrogen difluoride, Dinitrogen tetrafluoride, Tri silylamine, Urotropine.
11. What are phosphazines ? How are they prepared ? Discuss the structures of important chlorophosphazines.
12. What are artificial manures ? Give the preparation of artificial manures which are in common use. Discuss their relative merits and demerits.

18 THE ELEMENTS OF GROUP 16

Group 16 contains five elements, namely, **oxygen, sulphur, selenium, tellurium** and **polonium** and after the first element of the group, they are also named as **oxygen family.** The first four elements of the group are non-metals. These are also collectively known as **chalcogens** (meaning *ore forming*) because many metal ores occur as oxides, sulphides, etc. Oxygen is the most abundant element and constitutes 46·5 per cent of earth's crust. As water, it comprises 89 per cent of the ocean. It also occurs free and constitutes about 21 per cent by volume of the atmosphere. Sulphur occurs less abundantly and forms nearly 0·052 per cent of the earth's crust. It also occurs in the free state. The other members of the family, *viz.*, selenium, tellurium and polonium, are comparatively rare and constitute, respectively, only 10^{-7}, 10^{-7} and 10^{-14} per cent of the earth's crust.

Electronic Configurations. The electronic configurations of these elements are given in Table 1.

As can be seen, the general outer electronic configuration of the elements of Group 16 may be written as ns^2p^4.

TABLE 1
Electronic Configurations of Elements of Group 16

Element	Atomic Number	Electronic Configuration
Oxygen, O	8	[He] $2s^2p^4$
Sulphur, S	16	[Ne] $3s^2p^4$
Selenium, Se	34	[Ar] $3d^{10}\ 4s^2p^4$
Tellurium, Te	52	[Kr] $4d^{10}\ 5s^2p^4$
Polonium, Po	84	[Xe] $4f^{14}\ 5d^{10}\ 6s^2p^4$

GENERAL CHARACTERISTICS OF GROUP 16 ELEMENTS

Some important properties of elements of Group 16 are summed up in Table 2.

TABLE 2
Important Properties of Elements of Group 16

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Atomic number	8	16	34	52	84
Atomic mass (a.m.u.)	15·999	32·064	78·96	127·60	(210)
Density in solid state (g cm^{-3})	1·14	2·07	4·79	6·23	(9·2)
Atomic radius (Å)	0·73	1·09	1·16	1·35	–
Ionic radius (Å) of divalent ion	1·40	1·84	1·98	2·21	–
Atomic volume (c.c.)	14·0	15·5	16·5	20·5	22·7
Ionisation energy (kJ mol^{-1})	1313·7	999·4	940·9	869·5	813·5
Oxidation states	–2, –1	–2, +2, +4, +6	–2, +2, +4, +6	–2, +2, +4, +6	+2, +4
Electronegativity (Pauling's values)	3·5	2·6	2·5	2·1	2·0
Melting point (°C)	–218·8	114·00	217·0	449·5	254·0
Boiling point (°C)	–183·0	444·6	685·0	989·8	962
Heat of fusion (kJ mol^{-1})	0·22	1·42	5·3	17·7	11·0
Heat of atomisation (kJ mol^{-1})	250	280	207	197	145

1. Atomic volume, atomic radius and **density,** as expected, increase gradually with increase in atomic number.

2. Melting points and boiling points. The melting points and boiling points increase regularly with increase in atomic number, *i.e.,* as we move down the group. The melting point of polonium, however, is rather low.

3. Ionisation energy. The ionisation energy of the first element, oxygen, is very high being 1313·7 kJ per mole. The values for the succeeding elements decrease systematically from 999·4 to 813·5 kJ per mole on moving down the group.

4. Metallic and non-metallic character. The first four elements are non-metals but the non-metallic character is stronger in oxygen and sulphur and weaker in selenium and tellurium. The last element, polonium, is distinctly a metal. However, it is radioactive and is only short-lived.

5. Electronegativity. Electronegativity decreases gradually as we move down the group which also indicates a change from non-metallic to metallic character.

6. Oxidation states. As is evident from Table 2, all the elements have s^2p^4 configuration in their outer shells. These elements, therefore, tend to gain or share two electrons in order to attain a noble gas configuration. Since oxygen has a very high electronegativity, it tends to complete its valency shell preferably by gaining electrons. Even if the octet is completed by sharing of electrons, these electrons, for the purpose of determining the oxidation state, are counted towards oxygen because, excepting F_2O, oxygen forms the electronegative atom in all its compounds. Oxygen, thus, exhibits oxidation state of –2 only. Thus, most of the metal oxides are ionic and contain oxygen as di-negative anion, O^{2-}. However, there are a few exceptions in which the oxidation state of oxygen is not –2. For example, the oxidation state of oxygen in H_2O_2 is –1 and in F_2O it is + 2.

The electronegativities of other elements are, however, low. Their compounds, even with most electropositive elements, are rarely more than 50% ionic. Hence, there is much less probability of the formation of di-negative ions in the case of S, Se and Te. Since the electronegativities and ionisation energies decrease as we move down the group, the tendency of the elements to pass into –2 oxidation state decreases on moving from sulphur to polonium. The least electronegative element, polonium, in fact, does not exhibit negative oxidation state at all. Rather it shows +2 oxidation state.

Excepting oxygen, all the elements have vacant *d* orbitals in their valency shells. In the ground state, they have only two unpaired electrons which permit formation of two bonds. In the excited state, however, one of the *p* electrons goes to the vacant *d* orbital of the same shell, thus, making 4 unpaired electrons available for chemical bonding. This accounts for +4 oxidation state. Thus, S, Se and Te are tetravalent in their typical compounds with oxygen.

On further excitation, the *s* electrons also get unpaired thereby making *6 unpaired electrons available* for bond formation. This explains +6 oxidation state. Thus, in their compounds with fluorine these elements exhibit an oxidation state of +6.

In the case of oxygen, the 2*p* electrons on excitation have to go to 3*s* orbital, there being no *d* orbitals in *L* shell. But, since too much energy is required to excite an electron into a higher shell (in this case from *L* to *M* shell), the electrons in oxygen do not get unpaired. Therefore, oxygen, behaves as a divalent and only as a divalent element.

7. Molecular structure. Oxygen exists in the form of a stable diatomic molecule, O_2. This accounts for its being a gas. The succeeding elements, however, have more complex molecules and exist in solid state. For example, sulphur and selenium occur as S_8 und Se_8 molecules at room temperature and have a puckered ring structure, as shown for sulphur in Fig. 1.

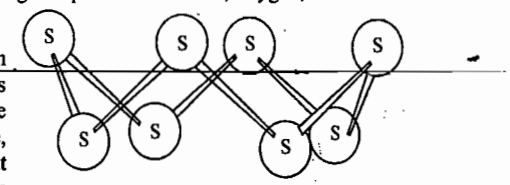


Fig. 1. Puckered ring structure of sulphur, S_8, molecule.

A question arises as to why oxygen forms only O_2 molecule and is, therefore, a gas while sulphur forms S_8 molecule and, therefore, is a solid.

The answer lies in the tendency of oxygen atom to form multiple bonds with itself, a tendency which is missing in the case of sulphur atom. The bond energy of oxygen–oxygen double bond (O = O) is quite large being about three times that of oxygen–oxygen single bond (O – O). On the other hand, sulphur–sulphur double bond (S = S) is not very strong, its bond energy being less than twice the value for sulphur–sulphur single bond (S – S). As a result, the catenated – O – O – O – chains are less stable as compared to O = O bond while catenated – S – S – S – chains are more stable as compared to S = S bond. Therefore, at room temperature, while oxygen exists as a diatomic gas, sulphur exists as S_8 solid.

Tellurium exists in two forms one of which is metallic and the other non-metallic. Polonium also exists in two forms known as α-form and β-form, both of which are metallic.

8. Catenation. The first two elements, oxygen and sulphur, show the property of catenation, the latter showing it to a larger extent. Thus, fairly stable polyoxides and polysulphides are known, *e.g.*,

H – O – O – H H – S – S – H H – S – S – S – H H – S – S – S – S – H

9. Allotropy. Like the elements of Groups 14 and 15, all the elements of Group 16 show allotropy. Thus, oxygen exists in two allotropic forms, O_2 and O_3 (ozone). Sulphur occurs in a number of allotropic forms such as *rhombic* (or α) sulphur, *monoclinic* (or β) sulphur, *plastic* (or γ) sulphur, *colloidal* (or δ) sulphur, λ *sulphur* and μ *sulphur*. These are all non-metallic in character. Selenium exists in two forms : the *red form* which is non-metallic and *grey form* which is metallic in nature.

EXTRACTION OF THE ELEMENTS OF GROUP 16

Preparation of Oxygen. Oxygen occurs in the free state in the atmosphere, being about one-fifth of the air by volume. It also occurs in abundance in the combined state being about 46·5 per cent of the earth's crust in the form of numerous compounds. It is present to the extent of 89 per cent by mass in pure water.

Oxygen can be prepared by thermal decomposition of some unstable oxides (*e.g.*, HgO, Ag_2O) as well as salts rich in oxygen (*e.g.*, KNO_3, $KClO_3$, $K_2Cr_2O_7$, etc.). Oxygen is set free on heating some of the higher oxides such as $KMnO_4$, $K_2Cr_2O_7$ with sulphuric acid.

In the laboratory, oxygen is usually prepared by heating a 5:1 mixture of $KClO_3$ and MnO_2 (catalyst).

A more convenient laboratory method of preparing oxygen is by the action of water on sodium peroxide :

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

The most important source of **commercial oxygen** is air. For this purpose, air is liquefied and then fractionated to get oxygen (as well as nitrogen). Oxygen is also obtained commercially by the electrolysis of water.

Extraction of Sulphur. Sulphur is one of the widely occurring elements and constitutes nearly 0·1 per cent of the earth's crust. In the free state, it occurs in volcanic regions of Sicily, Iceland, Mexico and Louisiana and Texas states of U.S.A. In smaller quantities, it occurs in Newzealand, Russia, Japan and Baluchistan (Pakistan). However, it occurs more abundantly in the combined state as *galena* (PbS), *copper pyrites* ($CuFeS_2$), *cinnabar* (HgS), *zinc blende* (ZnS), *iron pyrites* (FeS_2), *gypsum* ($CaSO_4.2H_2O$), *celestite* ($SrSO_4$) and *heavy spar* ($BaSO_4$). It also occurs as hydrogen sulphide in spring waters, coal gas, sewage gas, etc. Sulphur forms an essential constituent of many natural products of plant and animal origin, *e.g.*, garlic, mustard, eggs, hair, etc.

There are two main sources of world supply of sulphur. One is from deposits in Louisiana and Texas States of U.S.A. and the other is from deposits in Sicily. Each source has a special method of its own for the extraction of the element.

1. Frasch Process. Sulphur in American deposits occurs at a depth of about 250 – 400 metres and is covered by sand, clay and rocks. Therefore, it is not possible to carry out ordinary mining operations. It was in 1901 that Frasch developed a very ingenious process for bringing sulphur to the surface. Three concentric pipes are sunk from the surface down to the sulphur deposit. Superheated water at 170–180°C is admitted through the outermost pipe, while hot, compressed air is forced down the innermost pipe. The hot water melts the sulphur and a foam of water, sulphur and air is produced. This foam is brought up to the surface through the middle pipe by the action of the air blast. The process is continuous. The sulphur obtained is about 99·5 per cent pure and is marketed as such.

2. Sicillian Process. Sulphur deposits in Sicily are associated with nearly 75 per cent of clay and gypsum. In order to recover sulphur, the sulphur-bearing rock is stacked on a sloping floor of a circular kiln called **calcroni** and ignited. A part of the sulphur is burnt and acts as a fuel. The rest of the sulphur melts and collects at the lowest point of the inclined bottom of the kiln. The method is wasteful since nearly one-third of the sulphur is lost.

The calcroni kilns have now been replaced by more economical kilns called **Gill's kilns.** These kilns, consisting of a series of chambers connected with one another, are arranged in a circle and have a common chimney at the centre. Each chamber has an inlet of air. Air enters the first chamber containing the hot residue of a former operation while other chambers contain crude sulphur. Air is thus heated up and then it passes to the next chamber where some of the sulphur gets burnt and the heat produced melts the rest. The hot gases then pass to the other chambers, in turn, heating the crude sulphur present there. In this way, the loss of heat is reduced to a minimum. The recovery of sulphur is about 80 per cent. The melted sulphur is collected in wooden moulds and is called *block sulphur*. This contains nearly 95 per cent sulphur. It may be purified further by sublimation.

Extraction of Selenium. Selenium occurs in small amounts in sulphide ores, particularly in copper pyrites and iron pyrites. It constitutes nearly 10^{-8} per cent of the earth's crust.

Selenium is recovered from the *fine dust* formed during the treatment of sulphide ores of copper and iron, in the form of a solution in potassium cyanide.

$$KCN + Se \longrightarrow KCNSe$$

Selenium gets precipitated on the addition of hydrochloric acid to the solution.

$$KCNSe + HCl \longrightarrow Se + HCN + KCl$$

Selenium is also recovered from anode mud during the electrorefining of copper. The anode mud containing traces of selenium in the form of selenides of Cu, Ag, etc., is heated with Na_2CO_3 in free supply of air. The resulting compound Na_2SeO_3 is then heated with H_2SO_4 and H_2SeO_3 thus formed is treated with SO_2 to give Se.

$$Ag_2Se + Na_2CO_3 + O_2 \xrightarrow{\Delta} Na_2SeO_3 + CO_2 + 2Ag$$

$$Cu_2Se + Na_2CO_3 + 2O_2 \xrightarrow{\Delta} Na_2SeO_3 + CO_2 + 2CuO$$

$$Na_2SeO_3 + H_2SO_4 \longrightarrow H_2SeO_3 + Na_2SO_4$$

$$H_2SeO_3 + 2SO_2 + H_2O \longrightarrow Se + 2H_2SO_4$$

Extraction of Tellurium. It occurs, like selenium, in sulphide ores, particularly in copper pyrites. It also occurs as tellurides of silver and gold. It constitutes nearly 2×10^{-7} per cent of the lithosphere.

Tellurium is extracted from the anode-mud resulting from the electrolytic refining of copper. The mud is fused with a mixture of sodium nitrate and sodium hydroxide when the soluble sodium tellurite is formed. Tellurium is precipitated as oxide from the solution on the addition of an acid.

$$Te + 2NaOH + O_2 \text{ (from } NaNO_3) \longrightarrow Na_2TeO_3 + H_2O$$

$$Na_2TeO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + TeO_2 \downarrow$$

The oxide is then reduced to elementary tellurium on heating with carbon.

Extraction of Polonium. Polonium is a radioactive element and has been known since 1898. It occurs in nature in radium minerals such as *pitch blende* to the extent of 5×10^{-9} per cent.

It can be obtained in small (milligram) quantities by the bombardment of ^{209}Bi with neutrons.

$$^{209}_{83}Bi + ^{1}_{0}n \longrightarrow ^{210}_{83}Bi + \gamma \text{ rays}$$

$$^{210}_{83}Bi \longrightarrow ^{210}_{84}Po + \beta \text{ rays}$$

PROPERTIES OF ELEMENTS OF GROUP 16

Properties of Oxygen. Physical Properties. Oxygen is colourless, odourless and tasteless gas. It is slightly soluble in water and is slightly heavier than air. It can be liquefied by application of pressure when cooled below its critical temperature (–118·7°C). The liquid is pale blue in colour and is strongly magnetic. It boils at –183°C and freezes to a bluish white solid at –219°C. The O–O bond distance in O_2 is 1·21 Å.

Chemical Properties. 1. Oxygen is highly reactive. It forms stable compounds (oxides) with all elements except the noble gases. Most of these oxides are formed by direct combination of oxygen with the element concerned. However, oxides of the halogens and of gold, silver and platinum are formed indirectly.

Oxygen is a vigorous supporter of combustion.

Oxygen brings about oxidation of several organic and inorganic compounds on heating in the presence of a catalyst.

Uses. 1. The chief importance of oxygen lies in its supporting vital processes such as combustion and respiration. It is also used for artificial respiration. For this purpose, it is mixed with carbon dioxide or helium. It is also used in providing suitable atmosphere for breathing in submarines or aeroplanes flying at high altitudes.

2. In industry, its important application is in producing oxy-hydrogen and oxy-acetylene flames used in welding and cutting of metals.

3. Liquid oxygen mixed with finely divided carbon is used as a substitute for dynamite in coal mining. Liquid oxygen mixed with liquid fuels (alcohol or petrol) is used in the propulsion of rockets.

Structure of Oxygen Molecule. The electronic structure $:\underset{\cdot\cdot}{O}::\underset{\cdot\cdot}{O}:$ with no unpaired electron fails to account for the paramagnetic behaviour of oxygen although it accounts for the high dissociation energy of oxygen molecule.

Suitable explanation for the existence of two unpaired electrons and consequent paramagnetic behaviour, alongwith a very high dissociation energy of O_2 molecule, has been offered by the **molecular orbital theory** according to which the structure of O_2 molecule is as follows :

$$O_2 : KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \sigma(2p_z)^2 \pi(2p_x)^2\ \pi(2p_y)^2\ \overset{*}{\pi}(2p_x)^1\ \overset{*}{\pi}(2p_y)^1$$

or $$KK\ \sigma_1^2\ \overset{*}{\sigma}{}_2^2\ \sigma_3^2\ \pi_1^2\ \pi_2^2\ \overset{*}{\pi}{}_3^1\ \overset{*}{\pi}{}_4^1$$

Bond order in this case is evidently 2. Oxygen molecule thus contains a double bond which accounts for its high bond dissociation energy. This structure also accounts for two unpaired electrons and hence its paramagnetic character.

Anomalous Behaviour of Oxygen. Oxygen differs considerably from the rest of the family members. The differences can be attributed largely to the following characteristics of oxygen.

(*i*) Small size (*ii*) High electronegativity and (*iii*) Non-availability of *d orbitals* in the valency shell.

The main **points of difference** are as follows.

1. Oxygen is a *gas* while the other members are solids.

2. Oxygen is *diatomic*, O_2, while the rest of the members have complex molecular structures. For example, sulphur and selenium occur as S_8 and Se_8 molecules which have puckered ring structures.

3. Because of very high electronegativity, oxygen is distinctly *non-metallic* while the other two members (Se, Te) show weak non-metallic character and the last element (Po) is distinctly a metal.

4. Because of its high electronegativity, oxygen is *more ionic in its compounds* than the rest of the members. Thus, the dinegative anion, O^{2-}, is quite common but the dinegative anions of other elements, *viz.*, S^{2-}, Se^{2-} and Te^{2-} are much less common.

5. Because of high electronegativity, oxygen exhibits an oxidation state of only –2. It does not show any positive oxidation state except in OF_2 in which oxygen exhibits an oxidation state of +2. Other members, however, show both negative and positive oxidation states. Positive oxidation states are more frequent.

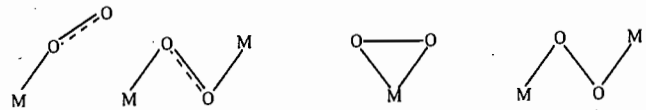
6. Again, on account of high electronegativity, oxygen extensively enters into *hydrogen bond formation*. Other elements because of low electronegativities do not form hydrogen bonds. It is because of hydrogen bonding that the hydride of oxygen (H_2O) is a liquid with a high boiling point and the hydrides of other elements (*e.g.*, H_2S, H_2Se, etc.) are gases with very low boiling points.

7. Maximum covalency of oxygen is two because it cannot expand its valency shell beyond the octet (there being no vacant *d* orbitals). Other elements, because of vacant *d* orbitals, can exercise covalency of 4 and 6.

8. Another striking feature which distinguishes oxygen from the rest of the family members is its paramagnetic behaviour in the gaseous, liquid and solid states.

9. Oxygen molecule is highly stable. Its bond dissociation energy is 494·6 kJ per mole. As a result oxygen combines with other elements (metals or non-metals) only at high temperatures. The reaction requires high energy of activation. It is for this reason that in nature oxide ores are fewer than sulphide ores.

10. There are several oxygen-carrying metalloproteins like haemoglobin, myoglobin, etc., present in biological systems in which O_2 is coordinated to the metal ion. Apart from this, a number of transition metal peroxo and superoxo compounds have been synthesised in which O_2 is ligated to the metal ion in the following manner :



Bonding in superoxo compounds Bonding in peroxo compounds

The O – O distance in superoxo compounds is shorter (1·25 – 1·30Å) than in peroxo compounds (1·45 – 1·50 Å).

Atomic Oxygen. Oxygen molecule is very stable. It dissociates only to a small extent when heated to a very high temperature, the reaction being highly endothermic.

$$O_2 \longrightarrow 2(O)\ ; \qquad \Delta H = +494{\cdot}6 \text{ kJ}$$

However, when an electric discharge is passed through oxygen at a very low pressure, it dissociates to the extent of about 20 per cent.

Atomic oxygen oxidises chlorine to Cl_2O and ClO_2, bromine to BrO_2 and hydrogen bromide to bromine and water.

It reacts vigorously with aliphatic alcohols like methanol and ethanol and with hydrocarbons like methane, acetylene and benzene. It reacts with nitric oxide giving a characteristic greenish white luminescence which serves to detect the presence of atomic oxygen.

$$NO + O \longrightarrow NO_2^*$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$

NO_2^* stands for an excited NO_2 molecule which changes to normal NO_2 molecule after emitting an energy $h\nu$ in the form of electromagnetic radiation.

Atomic oxygen reacts slowly with hydrogen, molecular oxygen and carbon monoxide, as shown below :

$$H_2 + O \longrightarrow \cdot OH + H\cdot$$

$$O_2 + O \longrightarrow O_3$$

$$CO + O \longrightarrow CO_2$$

OZONE, O_3

Ozone is an unstable triatomic allotropic form of oxygen. It is a constituent of the upper atmosphere.

Preparation. Ozone is generally prepared by passing silent electric discharge through oxygen. The concentration of ozone approaches upto 10 per cent by this method. It is believed that some of the oxygen molecules get dissociated in the process and then atomic oxygen combines with oxygen molecules to give ozone.

Another method of preparing ozone with a higher yield consists in electrolysing a concentrated solution of perchloric acid at –50°C between a lead cathode and a platinum anode. It is believed that oxidation of water occurs at the anode giving ozone.

Properties. It is a light blue gas which condenses at –120°C as a dark blue liquid. The liquid freezes at –193°C.

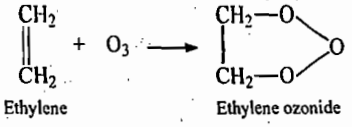
It is one of the strongest oxidising agents. The reduction potential in acid solutions is +2·07 V. This is represented as

$$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O\,; \qquad E^\circ = 2{\cdot}07\ V$$

There are only three other substances having reduction potentials higher than +2·07 V. These are fluorine, atomic oxygen and F_2O.

It oxidises moist sulphur to sulphuric acid, lead sulphide to lead sulphate, Fe^{2+} to Fe^{3+} state and liberates iodine from aqueous potassium iodide. It is seen that one oxygen atom per molecule of ozone is used up in all such reactions.

However, a few reactions in which all the three atoms of oxygen are used up are also known. Thus, all the three atoms are added up at unsaturated sites when reacted with ethylene.



Structure of Ozone. It is known from electron diffraction and microwave spectroscopy that ozone molecule is angular, the angle between the three oxygen atoms being 116·8° and the O – O distance being 1·28 Å.

Nature of bonding involved in the formation of ozone molecule is best illustrated on the basis of valence bond theory as well as the molecular orbital theory.

Valence Bond Concept. Since the angle O – O – O is close to 120°, the $2s$, $2p_x$ and $2p_y$ orbitals of the central oxygen atom are assumed to hybridise to give three sp^2 hybrid orbitals. Two of the three sp^2 hybrid orbitals are used up for sigma bonding with the terminal oxygens and the third one accommodates a lone pair of electrons. The p_z orbital of the central oxygen atom, which is left out of hybridisation, overlaps with the p_z orbital of either of the terminal oxygen atoms leading to structures a and b, as shown in Fig. 2. Since both the O – O bonds in ozone molecule are of equal length, it leads to the conclusion that the structures a and b are in resonance with each other as shown.

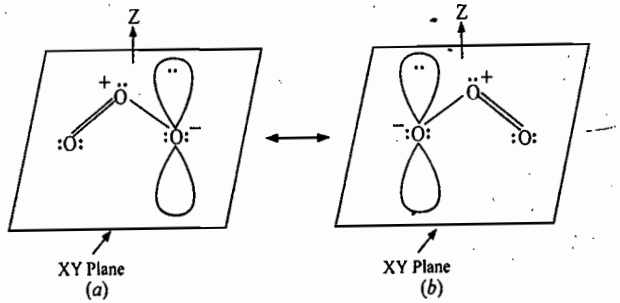


Fig. 2. Resonance structure of O_3 molecule.

Molecular Orbital Concept. As mentioned above, two of the three sp^2 hybrid orbitals of the central oxygen atom are utilised for sigma bonding with the terminal oxygen atoms and the third one accommodates a lone pair of electrons. The remaining p_z orbital of the central oxygen atom can linearly combine with the p_z orbital of the terminal oxygen atom to yield three pi molecular orbitals designated as ψ_1, ψ_2 and ψ_3. These molecular orbitals are represented in Fig. 3.

All the lobes of p_z orbitals of the three O atoms above the plane as well as below the plane of ozone molecule produce a positive overlap in ψ_1. Therefore, it is a *bonding molecular orbital and has lowest energy*. The BMO is thus written as :

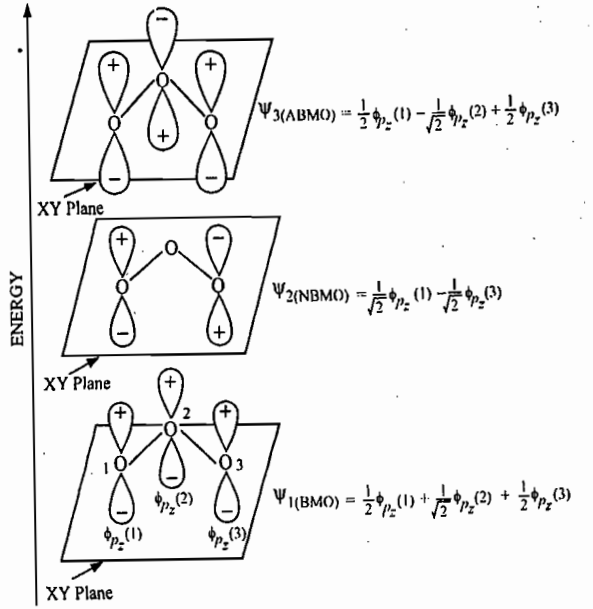


Fig. 3. The pi molecular orbitals of O_3

$$\psi_{1(BMO)} = \frac{1}{2}\phi_{p_z}(1) + \frac{1}{\sqrt{2}}\phi_{p_z}(2) + \frac{1}{2}\phi_{p_z}(3)$$

The $\phi_{p_z}(2)$ orbital does not participate in the formation of ψ_2. Also, $\phi_{p_z}(1)$ and $\phi_{p_z}(3)$ orbitals are too far away and figure in the representation of $\psi_{2(NBMO)}$ with opposite signs (Fig.3), Hence, their lobes cannot overlap. That is why $\psi_{2(NBMO)}$ is a *non-bonding molecular orbital*. The NBMO is thus written as :

$$\psi_{2(NBMO)} = \frac{1}{2}\phi_{p_z}(1) - \frac{1}{\sqrt{2}}\phi_{p_z}(3)$$

In ψ_3, the overlap amongst the lobes above the plane as well as below the plane of the ozone molecule is negative. This type of overlap opposes bonding and hence ψ_3 is an *antibonding molecular*

orbital and has highest energy. The ABMO is written as

$$\Psi_{3(ABMO)} = \frac{1}{2}\phi_{p_z}(1) - \frac{1}{\sqrt{2}}\phi_{p_z}(2) + \frac{1}{2}\phi_{p_z}(3)$$

The relative energies of the three molecular orbitals are shown in Fig. 4.

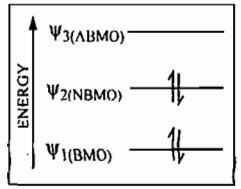


Fig. 4. Relative energies of the three MOs involved in the structure of ozone.

Out of the 18 valence electrons of the oxygen atoms, 14 electrons are either used up in sigma bonding or are present as lone pairs. The remaining 4 valence electrons are accommodated in the bonding and non-bonding molecular orbitals as shown above. Since only two electrons are present in the bonding molecular orbitals, the bond order of the pi bond which is delocalised over all the three oxygen atoms is *one*.

Allotropes of Sulphur. Sulphur exists in several allotropic forms, the more important of which are discussed below

1. Rhombic, octahedral or α-sulphur. This is the common form of sulphur and is stable at temperatures below 95·6°C. In order to get good crystals of rhombic sulphur, a solution of roll sulphur in carbon disulphide is allowed to evaporate slowly. Its specific gravity is 2·06. It melts at 114°C when heated *rapidly* (so as to avoid its transformation into monoclinic sulphur, which is a slow process). It is soluble in carbon disulphide. Its crystal structure contains cyclic S_8 rings packed in a manner which leads to the formation of rhombic crystals.

2. Monoclinic, prismatic or β-sulphur. It is stable above 95·6°C. It is prepared by melting rhombic sulphur in a dish and allowing it to cool until a crust is formed at the surface. Two holes are then pierced into the crust. The liquid sulphur lying below the crust (which has not yet solidified) is poured out through one of the holes. On removing the crust, small needle-like crystals of monoclinic sulphur become visible. Its specific gravity is 1·96. It melts at 120°C. It is soluble in carbon disulphide like α-sulphur. Its crystal structure also contains cyclic S_8 rings but the mode of packing is different than that in α-sulphur. The packing in this case is such that it leads to the formation of monoclinic crystals.

3. γ-Sulphur. This allotrope of sulphur is best obtained by decomposing ethylene xanthate of copper (I) in pyridine or by chilling hot solution of sulphur in carbon disulphide. It exists in the form of pale yellow needles. Its crystal structure also consists of cyclic S_8 rings which are packed in lattice in a more compact manner than in the crystals of α or β-sulphur. Its specific gravity is 2·18. γ-sulphur slowly changes into α and β-forms of sulphur.

4. Colloidal or δ-Sulphur. When hydrogen sulphide is passed through an oxidising solution such as nitric acid, potassium permanganate, etc., sulphur separates out in the colloidal state.

$$2HNO_3 + H_2S \longrightarrow \underset{\text{Colloidal sulphur}}{S} + 2NO_2 + 2H_2O$$

Colloidal sulphur is also obtained by passing hydrogen sulphide through water containing dissolved sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + \underset{\text{Colloidal sulphur}}{3S}$$

5. Plastic or χ-sulphur. When molten sulphur heated to about 350°C is poured into cold water, a soft rubber-like mass, called plastic sulphur, is obtained. It hardens on standing and changes gradually into rhombic sulphur. It is dark in colour and has specific gravity of 1·95. It is soluble in carbon disulphide and has no sharp melting point. This form is a mixture of allotropes of sulphur containing cyclic S_8 rings and long helical chains of a large number of S atoms. Plastic sulphur can be converted into *fibres* when it is heated in an atmosphere of nitrogen at 300°C for a few minutes and then quenched in water. The fibres, while kept in water, can be stretched. Their structure contains open polymeric helical chains of S atoms.

Plastic sulphur is considered to be a supercooled liquid, *i.e.*, a liquid which due to rapid cooling below its freezing point had no time to settle into a cystalline form.

6. Sulphur Allotropes Containing Cyclic S_6, S_7, S_{10}, S_{12}, S_{18} and S_{20} Rings. Cyclohexasulphur (Engel's sulphur or ε sulphur) containing cyclic S_6 rings can be prepared by the following reaction :

$$S_2Cl_2 + H_2S_4 \longrightarrow S_6 + 2HCl$$

It can also be prepared by adding concentrated HCl to a cold $Na_2S_2O_3$ solution between −10°C to 0°C. The structure of cyclohexasulphur consists of closely packed, cyclic S_6 rings in chair form. As a result of this close packing the specific gravity (2·2 at −10°C) of this form of sulphur is higher than specific gravities of all the other forms. This form of sulphur is highly reactive.

Other forms of sulphur containing cyclic S_7, S_{10}, S_{12}, S_{18} and S_{20} rings in their structures are also known. These are prepared by reacting sulphur chlorides with hydrogen polysulphide, as, for example,

$$S_2Cl_2 + H_2S_8 \longrightarrow 2HCl + S_{10}$$

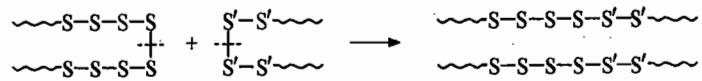
$$S_4Cl_2 + H_2S_8 \longrightarrow 2HCl + S_{12}$$

These cyclosulphurs are quite unstable with the exception of S_{18} and S_{20}.

Uncommon Features of Liquid Sulphur. When rhombic sulphur is gradually heated, it melts to give a thin, pale-yellow liquid between 113°C and 115°C. On continuing the gradual heating, the liquid becomes darker and increasingly viscous. At about 200°C the liquid becomes dark brown and so viscous that it scarcely flows even when the vessel is inverted. On further heating, the viscosity decreases rapidly till the liquid begins to flow at 444·5°C.

The above uncommon features of liquid sulphur may be accounted for as follows :

The yellow coloured liquid sulphur at 113–115°C, called **λ-sulphur**, mainly consists of *mobile* S_8 rings. Because of the mobility of S_8 rings, the viscosity of λ-sulphur is sufficiently low as a result of which it can flow easily. On further heating, the S – S bonds of the cyclic S_8 rings start breaking. The resulting linear S_8 chains then start joining together to give linear polymeric chains containing a large number of S atoms. The sulphur melt thus obtained at about 200°C is called **μ-sulphur**. Since the mobility of linear polymeric chains of μ-sulphur is much less than the mobility of cyclic S_8 chains of λ-sulphur, the viscosity of μ-sulphur becomes very high so much so that the liquid scarcely flows. The packing per unit volume of polymeric chains of μ-sulphur is much higher than that of cyclic S_8 units of λ-sulphur. Therefore, the density of μ-sulphur is much higher than that of λ-sulphur. At higher temperatures, some old polymeric chains of μ-sulphur start breaking, while some new polymeric chains start forming, as illustrated below (sulphur atoms of the second polymeric chain are labelled as S′).



At higher temperatures, the linear polymeric chains start breaking. In the initial stage, some of the fragmented linear chains reunite to form bigger linear chains. With further increase in temperature, however, there is greater fragmentation of long linear chains and lesser reunion of the smaller linear chains with the result that at about 444°C, almost all the long linear chains get broken into smaller chains. Since the mobility of smaller chains is greater than that of the longer chains, the viscosity of μ-sulphur decreases and at about 444°C it becomes so low that the melt starts flowing again.

λ-sulphur on solidification gives crystalline (α or β) sulphur soluble in carbon disulphide while μ-sulphur on solidification gives amorphous plastic sulphur insoluble in carbon disulphide.

Polyatomic Sulphide Ions. A number of polysulphide ions are known to be present in the salts of alkali and alkaline earth metals. Their melting points are lower than the melting points of corresponding salts of mono-atomic S^{2-} ions. The polyatomic ions known are S_3^{2-}, S_4^{2-}, S_5^{2-}, S_6^{2-}, etc. The S_3^{2-} ion is bent but planar. Other anions have bent but non-planar structure.

The salts of polysulphide ions can be prepared by heating stoichiometric amounts of sulphur with the element in a sealed tube or by reacting sulphur with MSH (M = alkali or alkaline earth metal) in ethanol.

Properties of Sulphur

Sulphur is a yellow solid with no taste and odour. It is freely soluble in carbon disulphide but insoluble in water and only sparingly soluble in alcohol and ether. Its vapours are poisonous for bacteria and fungi but not for animals or human beings.

Chemical Properties. 1. It burns in oxygen or air with a blue flame giving sulphur dioxide mixed with a small amount of sulphur trioxide.

2. It combines directly with carbon, phosphorus, arsenic and many of the metals at high temperatures, giving the corresponding sulphides.

3. It also combines with hydrogen and chlorine when the gases are led through boiling sulphur to form H_2S and S_2Cl_2, respectively.

4. Sulphur does not react with water in the cold but reacts with ste am when the latter is made to pass through boiling sulphur.

$$3S + 2H_2O \longrightarrow 2H_2S + SO_2$$

5. It gets oxidised by concentrated sulphuric acid and nitric acid yielding sulphur dioxide and sulphuric acid, respectively.

6. It is also attacked by concentrated alkalies forming sulphides and thiosulphates.

$$4S + 6KOH \longrightarrow K_2S_2O_3 + 2K_2S + 3H_2O$$

If sulphur is present in excess, potassium sulphide combines with it yielding potassium pentasulphide.

Uses of Sulphur. Sulphur is put to the following uses, amongst many others : 1. As a disinfectant for houses and for destroying bacteria, fungi, insects, etc. 2. For vulcanising rubber. 3. In medicine, for internal as well as external applications. 4. In dyes. 5. For the manufacture of sulphur dioxide, sulphuric acid, carbon disulphide, matches, gun powder, fire works, etc. 6. For the manufacture of bisulphites of calcium and magnesium which are required as bleaching agents.

Properties of Selenium. Selenium obtained from KCNSe is a *red amorphous powder*. On dissolving it in carbon disulphide and evaporating the solution *slowly* at a temperature around 72°C it is possible to get red α monoclinic cystalline form of selenium. If, however, the same solution is evaporated rapidly, β monoclinic form of selenium results. These forms are non-metallic and have puckered Se_8 ring structure. On keeping any of the forms at 200 – 220°C for sometime, the stable allotropic form of *grey metallic selenium*, having hexagonal crystals, is obtained. The *vitreous black selenium* is the commercial form of selenium which does not have a sharp melting point. It transforms readily into grey form when heated to 180°C.

Selenium is a poor conductor of heat and electricity. Its main use lies in emission of electrons when exposed to light. It is, therefore, used in photoelectric cells. It is also used for decolorising glass, in semiconductor devices and in pharmaceuticals.

The most important application of selenium is in the process of xeroxing.

Role of Selenium in Xerography

The word xerography in Greek means dry writing. The process of xeroxing is based on the *photoconducting* nature of selenium, *i.e.*, selenium is non-conducting in dark but becomes conducting in the presence of light. The commercial xeroxing machines make use of reusable *photoreceptor* for producing xerox copies of documents. The basic steps involved in the process of xeroxing are as follows :

1. Fabrication of Photoreceptor and its Sensitisation. The photoreceptor is prepared by vacuum-depositing a thin film of amorphous selenium, about 50 μm thick, on an aluminium sheet. The selenium layer is then sensitised in the dark by an electrostatic charge produced from a device which utilises a

field of the order of 10^5 V cm^{-1}, as shown in Fig. 5.

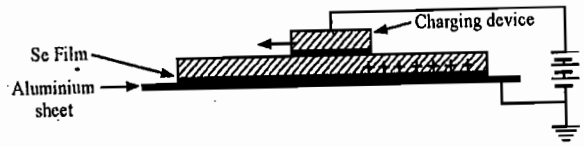


Fig. 5. Sensitisation of Photoreceptor.

2. Formation of Latent Image. The image of the document to be xeroxed, which consists of light and dark patterns, is then allowed to fall on the sensitised photoreceptor. The surface potential of the receptor gets reduced in the light regions because selenium in such regions becomes photoconducting leading to a reduction of electrostatic charge from such regions. The surface potential in the dark regions remains unaltered because Se is non-conducting in the absence of light. In this way, a latent or hidden electrostatic image of the document is formed. This is illustrated in Fig. 6.

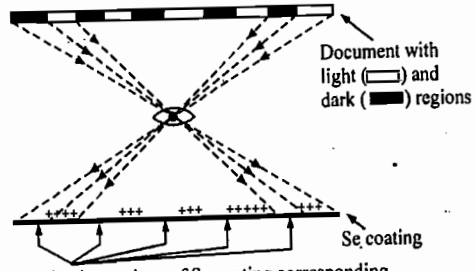


Fig. 6. Formation of latent image

3. Development of Latent Image. Coloured (usually black) *toner particles* (~ 10 μm in size) mixed with spherical *carrier beads* (~ 100 μm in size) are allowed to run over the photoreceptor. The toner particles become negatively charged due to friction and are attracted by the electrostatically charged patterns on the photoreceptor. The toner particles are not attracted by the uncharged patterns on the receptor. The adherence of the toner particles on selective parts of the photoreceptor thus leads to the formation of a visible image from the latent electrostatic image (Fig. 7).

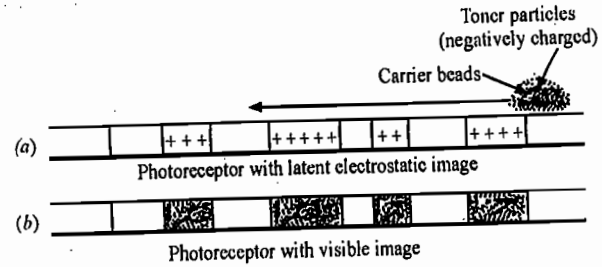


Fig. 7. Formation of visible image from latent image.

4. Transfer of the Image on Print Paper. The print paper which is kept parallel to the photoreceptor is then electrostatically charged. This process transfers the toner particles from the photoreceptor to the print paper (Fig. 8).

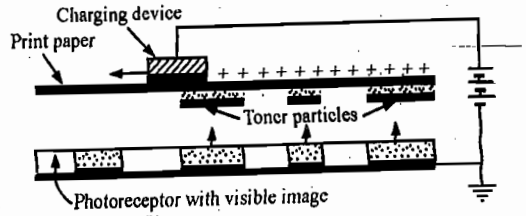


Fig. 8. Transfer of the image on print paper.

5. Fixing. The toner particles are then fixed permanently on the print paper by melting them on the surface of the print paper by electric heating.

6. Cleaning. After the image has been transferred from the photoreceptor to the print paper, any toner particles left on the photoreceptor are removed either by mechanical means or by a combination of elecrostatic and mechanical means.

7. Erasing of the Image. The photoreceptor is then exposed to bright light so that the whole of the Se layer becomes equally conducting. As a result, the surface potential on the photoreceptor attains a *uniformly low value*. The pattern of the electrostatic charge on the surface of the photoreceptor, *i.e.*, latent electrostatic image, therefore, *vanishes* and the photoreceptor is ready to be used again.

Properties of Tellurium. Tellurium obtained from anode mud resulting from electrolytic refining of copper is in *metallic form*. It consists of grey crystals. It has low electrical conductance. It is stable and is not affected by light.

The *non-metallic amorphous form* is precipitated from telluric acid by passing sulphur dioxide gas. It is less stable than the metallic form. Both the forms consist of network of spiral chains of Te atoms.

The element is added to lead to improve its resistance to heat and corrosion.

Properties of Polonium. Polonium is alpha-emitter. Its half-life period is 138·4 days. Its high activity (4·5 curies per milligram) renders it a dangerous substance.

It is a soft metal resembling lead in appearance. It exists in two crystalline forms : *cubic* and *rhombohedral*, both of which are metallic. The most common oxidation state of the metal is +4.

Polonium, intimately mixed with beryllium, serves as a useful source of neutrons.

COMPOUNDS OF GROUP 16 ELEMENTS

I. A Comparative Study

1. HYDRIDES

Hydrides of Formula H_2R. All the members of oxygen family form hydrides of the same type, *viz.*, H_2R (H_2O, H_2S, H_2Se, H_2Te and H_2Po).

Preparation. The hydride of oxygen, *viz.*, water is available in abundance in nature. The hydrides of S, Se and Te are readily obtained by the action of acids on metal sulphides, selenides and tellurides, *e.g.*,

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
$$K_2Se + H_2SO_4 \longrightarrow K_2SO_4 + H_2Se$$

H_2Po, on the other hand, has been prepared only in traces by dissolving magnesium foil plated with Po in 0·2 M HCl.

The hydrides of sulphur, selenium, tellurium and polonium, at ordinary temperatures, are offensive smelling gases. The hydride of oxygen (water) is an odourless and colourless liquid. The trends in their properties are discussed below.

1. Volatility. The volatility increases markedly from H_2O to H_2S and then decreases. This is evident from their boiling points given below :

H_2O	H_2S	H_2Se	H_2Te	H_2Po
100·0°C	– 60·75°C	– 41·5°C	– 1·8°C	–

The abnormally high boiling point of water is due to the association of molecules through hydrogen bonding.

2. Acid character. The hydrides are all weak acids and dissociate to varying degrees to give H^+ ions. For example, H_2S behaves as a weak diprotic acid ionising as

$$H_2S \rightleftharpoons HS^- + H^+$$
$$HS^- \rightleftharpoons S^{2-} + H^+$$

The acidic strength *increases* from H_2O to H_2Te. This is evident from the values of the dissociation constants of these hydrides as acids, given in Table 3. Evidently, this behaviour cannot be explained on the basis of the electronegativity of the central atom. However, it can be easily explained on the basis of the size of the central atom. As shown in Chapter 2, the atomic size increases gradually as we move from O to Te. As a result, the length of the X – H bond also increases gradually as we move down the group (Table 3). Since the strength of a bond is inversely proportional to its length, the strength of the X – H bond decreases as we move from O to Te. Consequently, the tendency of the hydrides to dissociate to yield H^+ ions increases as we move from H_2O through H_2S and H_2Se to He_2Te.

3. Thermal stability. The thermal stability of the hydrides decreases with rise in molar mass. Thus, while water dissociates only at 2000°C, tellurium hydride, H_2Te, decomposes even at ordinary temperatures.

4. Reducing character. All the hydrides, except water, are reducing agents. The reducing character *increases* on moving from H_2S to H_2Te. This is, evidently, due to decrease in stability in moving from H_2S to H_2Te.

5. Complex forming capability. H_2S is a much poorer ligand than H_2O. Some rare examples of species containing complexed H_2S are $[AlBr_3(SH_2)]$, $[W(CO)_5(SH_2)]$, $[Ru_3(CO)_9(SH_2)]$, $[Ru(NH_3)_5(SH_2)]^{2+}$, etc.

6. Bond angles. The bond angles H – X – H, in H_2O, H_2S, H_2Se and H_2Te are 104·5°, 92·5°, 90·0° and 89·0°, respectively. The reason for this gradation has already been discussed in Chapter 5 on the basis of electronegativities of the central atoms.

The various properties of these hydrides are summed up in Table 3.

TABLE 3

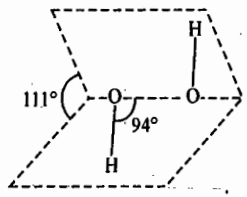
Important Properties of Hydrides of Elements of Group 16

Property	H_2O	H_2S	H_2Se	H_2Te
Melting point (°C)	0	–85·5	–65·7	–51·1
Boiling point (°C)	100·0	–60·75	–41·5	–1·8
Bond angle H – X – H	104·5°	92·5°	90°	89°
Bond length H – X (Å)	0·95	1·30	1·45	1·72
Dissociation constant as an acid at 25°C	$1·0\times10^{-14}$	$1·0\times10^{-7}$	$1·7\times10^{-4}$	$2·3\times10^{-3}$

Hydrides of Formula H_2R_2. The first two members of the family also form hydrides of the formula H_2R_2 (*viz.*, H_2O_2, H_2S_2). However, these two hydrides differ considerably from each other. Whereas H_2O_2 is fairly stable (except in the presence of certain impurities such as finely divided Cu, Pt, etc.), H_2S_2 is unstable and decomposes readily to give sulphur and hydrogen sulphide. The decomposition is accelerated by hydroxyl ions.

$$H_2S_2 \xrightarrow{OH^-} H_2S + S$$

Also, whereas H_2O_2 acts as a strong oxidising agent, H_2S_2 does not. H_2O_2, on account of hydrogen bonding, is highly associated whereas H_2S_2 forms discrete molecules. Both the hydrides have similar nonplanar skew *structures*.



The structure of H_2O_2 in gaseous phase is as shown.

For H_2O_2 in solid phase, the dihedral angles between the two planes and the lengths of OH bonds are different. This is because of the hydrogen bonding which occurs in H_2O_2 in solid phase.

The structure of H_2S_2 is similar to that of H_2O_2.

Other Hydrides. Hydrides with the formulae varying from H_2S_4 to H_2S_{18} have also been reported in literature.

2. HALIDES

The elements of Group 16 form several halides. These are given in Table 4.

TABLE 4
Halides of Group 16 Elements

Elements	Fluorides	Chlorides	Bromides	Iodides
Oxygen	F_2O_2, F_2O	Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7	Br_2O, BrO_2, BrO_3	I_2O, I_2O_4, I_2O_5
Sulphur	S_2F_2, SF_4, SF_6, S_2F_{10}	S_2Cl_2, SCl_2, SCl_4	S_2Br	–
Selenium	Se_2F_2, SeF_4, SeF_6	Se_2Cl_2, $SeCl_4$	Se_2Br_2, $SeBr_4$	–
Tellurium	TeF_4, Te_2F_{10}, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Polonium	–	$PoCl_2$, $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

Since fluorine is more electronegative than oxygen, its compounds with oxygen are called fluorides. Thus, F_2O should be written as OF_2 and named as oxygen difluoride. But since oxygen is more electronegative than chlorine, bromine and iodine, the compounds of these halogens with oxygen are called oxides. Thus, Cl_2O_7 is called chlorine heptoxide. The compounds of oxygen with halogens are discussed in details in the next chapter dealing with the halogens.

A brief general discussion of the rest of the important halides is given below.

Hexahalides. Amongst hexahalides, hexafluorides are the only stable compounds. Fluorine directly combines with S, Se and Te to form hexafluorides SF_6, SeF_6, and TeF_6, respectively.

They are formed by sp^3d^2 hybridisation and have, therefore, an **octahedral** structure.

SF_6 is extremely stable and chemically inert ; SeF_6 is slightly more reactive and TeF_6 is still more reactive. TeF_6 is completely hydrolysed in contact with water.

$$TeF_6 + 6H_2O \longrightarrow 6HF + H_6TeO_6$$

All these hexafluorides are colourless gases. Their high volatility indicates high degree of covalency. No other halogen forms the hexahalides.

Hexahalides are not formed by chlorine, bromine and iodine. As the size of the halogen atom increases, the coordination number of the elements of this group decreases. As a result, hexachlorides, hexabromides and hexaiodides are unknown. For the same reason, the number of tetrabromides is only three, all of which are unstable and the number of tetraiodides is only two.

Pentahalides. Only one pentahalide, *viz.*, pentafluoride of sulphur is known and it is a dimer S_2F_{10}. The two SF_5 units are linked through S – S bonds. The orbitals of each sulphur atom in SF_5 unit are sp^3d^2 hybridised.

Tetrahalides. Tetrafluorides cannot be obtained by direct combination of the elements with fluorine because the reaction cannot be arrested at the tetrafluoride stage. On account of the reactivity of fluorine, the end product is always the hexafluoride. The tetrafluorides can, however, be obtained indirectly. For example,

$$S + 4CoF_3 \longrightarrow SF_4 + 4CoF_2$$

$$3SCl_2 + 4NaF \xrightarrow{75°C} SF_4 + S_2Cl_2 + 4NaCl$$

$$SeCl_4 + 4AgF \longrightarrow SeF_4 + 4AgCl$$

$$SF_4 + SeO_2 \xrightarrow{100°C} SeF_4 + SO_2$$

$$Te + 2F_2 \xrightarrow{0°C} TeF_4$$

$$TeO_2 + 2SeF_4 \longrightarrow TeF_4 + 2SeOF_2$$

Out of these, SF_4 is gaseous, SeF_4 is liquid and TeF_4 is solid. They are all highly reactive fluorinating agents. Amongst the tetrachlorides, OCl_4 does not exist, SCl_4 is an unstable liquid while the other tetrachlorides are solids.

All the tetrachlorides can be easily prepared by direct combination of the elements with chlorine.

$$M + 2Cl_2 \longrightarrow MCl_4 \ (M = S, Se, Te)$$

Amongst the tetrabromides, the tetrabromide of oxygen, OBr_4, is not known. $SeBr_4$ is unstable and dissociates into diselenium dibromide and bromine as follows.

$$2SeBr_4 \longrightarrow Se_2Br_2 + 3Br_2$$

It is also readily hydrolysed as shown below.

$$SeBr_4 + 4H_2O \longrightarrow \underset{\text{unstable}}{Se(OH)_4} + 4HBr$$

$$Se(OH)_4 \longrightarrow H_2SeO_3 + H_2O$$

Tetrabromides of Te and Po are fairly stable.

O, Te and Po are the only elements which are known to form the tetraiodides. The tetraiodides of oxygen, however, are not so common.

Tetrafluorides have Lewis acid character since they readily accept electrons and change over to hexafluorides.

$$SF_4 + F_2 \longrightarrow SF_6$$

The central atom in these tetrahalides utilises five sp^3d hybrid orbitals for bonding. The fifth hybrid orbital accommodates a lone pair of electrons. This is illustrated in Fig. 9 with reference to the structure of $TeCl_4$.

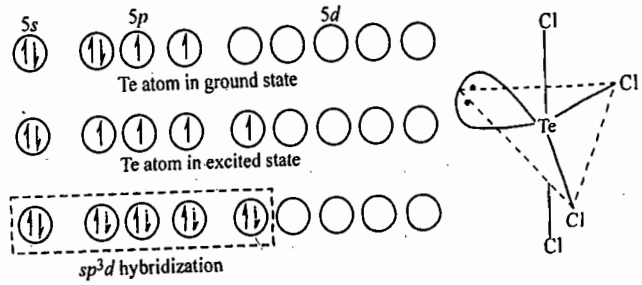


Fig. 9. Structure of $TeCl_4$ molecule formed by sp^3d hybridisation of Te orbitals.

Other tetrahalides, *viz.*, the fluorides, bromides and iodides are supposed to have similar structure.

Dihalides. All the elements except selenium form stable dichlorides and dibromides. Di-iodides are not formed. Dihalides of selenium are not stable. Amongst the dihalides, the best known is SCl_2. It is

formed by saturating S_2Cl_2 with chlorine at ordinary temperatures. $TeBr_2$ is formed by direct combination of the elements. They form bent molecules in which the central atom utilises sp^3 hybrid orbitals for bonding and for accommodating lone pair of electrons.

Since two of the four hybrid orbitals are occupied by lone pairs of electrons and since the repulsion between two lone pairs is more than the repulsion between two bond pairs or that between a lone pair and a bond pair, the tetrahedral angle of 109·5° gets distorted. Thus, the bond angle is 103° in SCl_2, 101·5° in OF_2 and 98° in $TeBr_2$.

The formation of SCl_2 molecule is illustrated in Fig. 10.

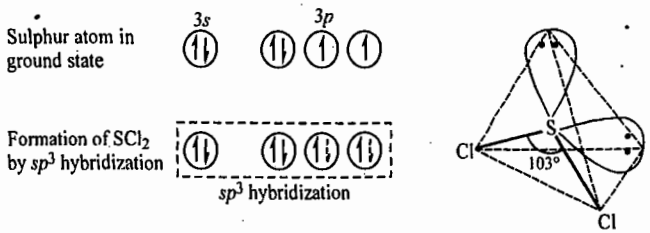


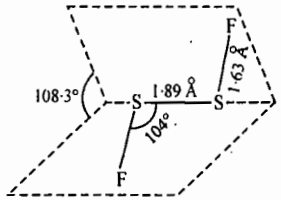
Fig. 10. Bent structure of SCl_2 molecule formed by sp^3 hybridisation of S orbitals.

Monohalides. Amongst the monohalides, the dimeric monohalides, such as S_2F_2, Se_2Br_2 are well known. These are hydrolysed slowly and also undergo disproportionation, *e.g.*,

$$2S_2F_2 + 2H_2O \longrightarrow 4HF + SO_2 + 3S$$

$$2SeCl_2 \longrightarrow SeCl_4 + Se$$

The electron diffraction studies have shown that the structure of S_2F_2 is nonplanar and is similar to that of H_2O_2, as shown.



3. OXIDES

The elements of Group 16 form several oxides as shown in Table 5.

TABLE 5
Oxides of Sulphur, Selenium, Tellurium and Polonium

Names	Sulphur	Selenium	Tellurium	Polonium
Lower oxides	SO, S_2O, S_2O_2 S_6O, S_7O, S_8O		TeO	PoO
Dioxides	SO_2	SeO_2	TeO_2	PoO_2
Trioxides	SO_3	SeO_3	TeO_3	–
Heptoxides	S_2O_7	–	–	–

Oxides of sulphur are more stable than the corresponding oxides of other elements. Thus, SO_2 and SO_3 are more stable than the corresponding dioxides and trioxides of the other elements. Heptoxide is formed only by sulphur.

Lower Oxides. All elements, except selenium, form monoxides. Sulphur monoxide is formed by passing electric discharge through sulphur dioxide. S_2O_2, which has a life time of several seconds, is prepared by microwave irradiation of SO_2 in vacuum when a mixture of oxides containing SO, S_2O, S_2O_2 is obtained.

Other lower oxides known are S_6O, S_7O and S_8O. Tellurium monoxide and polonium monoxide are formed by heating the corresponding trioxides.

Dioxides. All the members of oxygen family (excepting, of course, oxygen) form dioxides of the formula MO_2 (SO_2, SeO_2, TeO_2 and PoO_2). These, however, differ from one another considerably in their properties and structures. SO_2 is a gas (b.p. –10°C) and forms *discrete molecules* even in the solid state. SO_2 and SeO_2 are acidic oxides and are soluble in water. TeO_2 and PoO_2 are insoluble in water. These are amphoteric oxides as they dissolve in both acids and bases. Thus, acidic character of the dioxide decreases as we go down the group. Sulphur dioxide molecule has a bent structure in which S atom utilises sp^2 hybrid orbitals for sigma bonding, as illustrated in Fig. 11.

Out of the three sp^2 hybrid orbitals of sulphur, one is occupied by a lone pair of electrons. The remaining two half-filled hybrid orbitals overlap with one of the p orbitals of each of the two oxygen atoms forming sigma bonds. This gives rise to bent structure.

Since one of the three sp^3 hybrid orbitals of S atom is occupied by a lone pair of electrons and since the repulsion between a lone pair and a bond pair is more than that between two bond pairs, the bond angle OSO is slightly reduced from 120° to 119·5°. Sulphur atom has still two half-filled orbitals (one p and one d orbital). Each oxygen atom has also one half-filled p orbital. So, p orbital of one of the oxygen atoms overlaps with p orbital of the sulphur atom forming $p\pi - p\pi$ bond. Similarly, p orbital of the second oxygen atom overlaps with d orbital of sulphur atom forming a $p\pi - d\pi$ bond. In this manner, both sulphur and oxygen atoms get all their electrons fully paired.

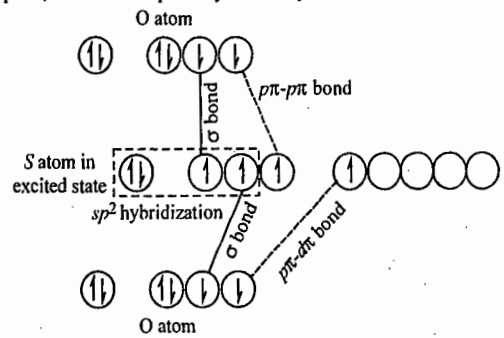


Fig. 11. Bent structure of SO_2 molecule formed by sp^2 hybridisation of S orbitals.

It is evident from the above discussion that one of the oxygen atoms is bonded to sulphur atom by $\sigma\ sp^2 - p$ and $p\pi - p\pi$ bonds while the other oxygen atom is bonded by $\sigma\ sp^2 - p$ and $p\pi - d\pi$ bonds. This would point towards two different bond lengths. But actually both the S – O bonds have exactly the same length. This is because of resonance which may be represented as below :

$$O\frac{p-sp^2}{p\pi-p\pi}S\frac{sp^2-p}{p\pi-d\pi}O \longleftrightarrow O\frac{p-sp^2}{p\pi-d\pi}S\frac{sp^2-p}{p\pi-p\pi}O$$

The multiple bonding also explains the shorter length of the S – O bond. The $p\pi - d\pi$ overlap is illustrated in Fig. 12. There is a sidewise overlap of a p orbital of oxygen atom with a d orbital of the sulphur atom. This $p\pi - d\pi$ interaction results in bringing the two atoms closer and thus accounts for the shorter length of S – O bond.

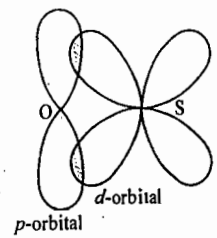


Fig. 12. Lateral overlapping of p and d orbitals.

SeO_2 is a white volatile solid (normal sublimation temperature 315°C). In the gaseous state, SeO_2 exists in the form of discrete monomeric molecules, just like SO_2, but in the solid state it has polymeric structure comprising of infinite chains, as shown in Fig. 13.

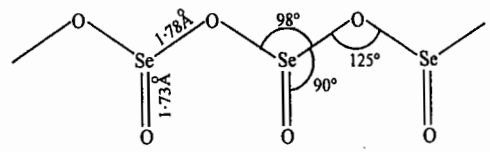


Fig. 13. Polymeric structure of SeO_2 in solid state.

TeO_2 and PoO_2 are also non-volatile crystalline ionic solids and occur in two crystalline forms each.

The dioxides also differ from one another

in their reaction with water. SO_2 dissolves giving H_2SO_3, which, however, exists only in solution and cannot be isolated.

SeO_2 dissolves giving selenious acid which can be isolated in a crystalline state. TeO_2 is almost insoluble in water. It, however, dissolves in alkalies to form tellurites and in acids to form basic salts, showing that it is amphoteric in character. PoO_2 behaves similarly.

Trioxides. Amongst the trioxides, SO_3 is the most important. SeO_3 and TeO_3 are also known. They are all acidic in nature and dissolve in water to give acids.

$$SO_3 + H_2O \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$SeO_3 + H_2O \longrightarrow \underset{\text{Selenic acid}}{H_2SeO_4}$$

The strength of the acid decreases on moving down the group. Thus, H_2SO_4 is the strongest acid of the family.

The trioxides, in gaseous state, are known to have planar trigonal structure being formed by sp^2 hybridisation of S orbitals, as illustrated in Fig. 14 for the formation of **SO_3 molecule.**

The three half-filled sp^2 hybrid orbitals of sulphur overlap with one of the p orbitals of each of the three oxygen atoms forming sp^2–p sigma bonds.

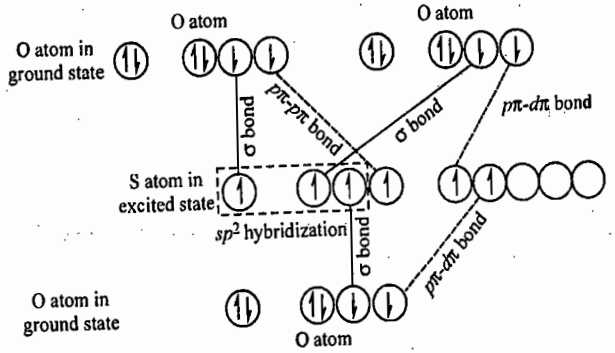


Fig. 14. Bent structure of SO_3 molecule formed by sp^2 hybridisation of S orbitals.

Sulphur atom has still three half-filled orbitals (one p and two d orbitals). Each oxygen atom has one half-filled p orbital. Therefore, p orbital of one of the oxygen atoms overlaps with p orbital of the sulphur atom forming $p\pi - p\pi$ bond. The p orbitals of the other two oxygen atoms overlap with d orbitals of sulphur atom forming the $p\pi - d\pi$ bonds, as shown in the figure.

Due to the formation of three sigma bonds, SO_3 has a planar trigonal structure.

The bond angles in SO_3 are exactly 120° each and S = O bond lengths are 1·42 Å.

In solid state, sulphur trioxide polymerises and has either a ring structure or a linear layer structure, as shown in Fig. 15.

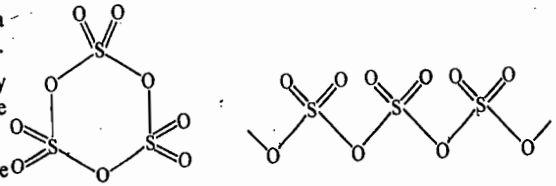


Fig. 15. Cyclic and linear layer structures of sulphur trioxide in solid state.

Sulphur trioxide exists in three forms :

1. **α-Sulphur trioxide.** This is a colourless liquid which solidifies in the form of prismatic needle-like crystals. It melts at 17°C and boils at 45°C. Its specific gravity is 1·923 at 25°C.

This form is obtained by repeated fractionation of sulphur trioxide. The molar mass of this substance, as determined by freezing point depression, is about 80.

2. **β-Sulphur trioxide.** The α form, if allowed to stand at 16°C for some time, changes gradually into the β form. This form solidifies giving asbestos-like needles at 32·5°C. Its molar mass is close to

160 which corresponds to the formula S_2O_6. When kept at a temperature between 50 and 100°C, it changes into α variety.

3. **γ-Sulphur trioxide.** It is obtained from β form on complete drying. It sublimes without melting under ordinary pressure.

SeO_3 is prepared by the direct oxidation of Se or SeO_2. It is a white hygroscopic solid (m.p.118°C). It exists as a monomer in vapour phase but as a cyclic tetramer, Se_4O_{12}, in crystalline state. The structure of the tetramer is shown in Fig. 16.

TeO_3 also exists. It is unattacked by water. At high temperatures it acts as a powerful oxidising agent.

PoO_3 has been detected on a tracer scale but has not been well characterised.

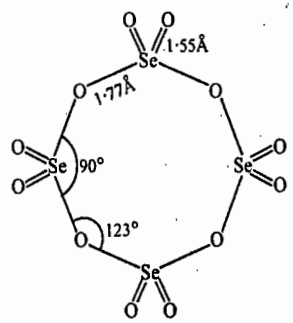


Fig. 16. The cyclic structure of tetrameric Se_4O_{12}.

Higher Oxides of Sulphur. The reaction of SO_2 or SO_3 with O_2 in silent electric discharge gives a polymer with the formula SO_{3+x} ($0 < x < 1$). It has the structure $-O-\overset{O}{\overset{\|}{S}}-O-O-S-$. Hydrolysis of this polymer yields H_2SO_4 and H_2SO_5.

4. OXOACIDS

Sulphur, selenium and tellurium form a variety of oxoacids. The more important of these are listed in Table 6.

TABLE 6

Important Oxoacids of Sulphur, Selenium and Tellurium

Sulphur	Selenium	Tellurium
Sulphurous acid, H_2SO_3	Selenous acid, H_2SeO_3	Tellurous acid, H_2TeO_3
Sulphuric acid, H_2SO_4	Selenic acid, H_2SeO_4	Telluric acid, H_6TeO_6
Permonosulphuric acid, H_2SO_5		
Perdisulphuric acid, $H_2S_2O_8$		
Thiosulphuric acid, $H_2S_2O_3$		
Dithionic acid, $H_2S_2O_5$		
Pyrosulphuric acid, $H_2S_2O_7$		

Description of some of the important oxoacids is given below.

Sulphurous Acid. This acid is obtained by dissolving SO_2 gas in water, the reaction being represented as

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

The acid is known only in solution. It is a fairly strong acid and, being diprotic, it ionises in two stages as

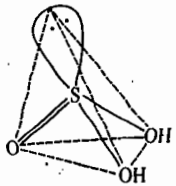
$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

$$HSO_3^- \rightleftharpoons H^+ + HSO_3^{2-}$$

The acid acts as a strong reducing agent on account of the ease with which it gets oxidised to H_2SO_4 even by atmospheric oxygen. Thus, it reduces halogens to their hydracids, ferric salts to ferrous salts, acidified permanganates to Mn (II) salts, dichromates to Cr (III) salts and iodates to iodine.

Sulphurous acid (or sulphur dioxide in the presence of water) acts as a bleaching agent. The bleaching action is due to its reducing properties. Thus, the red rose leaves or fibres dyed with 'magenta'

become colourless when moistened with water and exposed to sulphur dioxide. The bleaching is believed to be due to the reduction of the coloured compounds to colourless *leuco bases*. The colour is very often restored on exposure to air for a long time due to reoxidation of the leuco bases.



Structure of Sulphurous Acid. The structure of the unionised acid is in much doubt. *It has been suggested that the molecule has pyramidal structure as shown. In this case sulphur utilises three of the four* sp^3 hybrid orbitals for *sigma bonding* and one of the sp^3 hybrid orbitals is occupied by a lone pair of electrons. In addition to this, there is a $d\pi - p\pi$ bond between S and O atoms, as shown.

Sulphuric Acid, H_2SO_4. Sulphuric acid, probably the most important 'heavy chemical,' finds extensive use in the manufacture of fertilisers, explosives, dyestuffs, plastics and lacquers, paints and pigments and a host of other valuable products. It is used in coal tar and petroleum refining, leather tanning, electroplating, textile and paper industry and in many metallurgical processes. In fact, the industrialisation of a country is judged from the amount of sulphuric acid it consumes.

The acid is manufactured these days mostly by the **contact process**. This process involves the oxidation of sulphur dioxide by air in the presence of a catalyst, to give sulphur trioxide,

$$2SO_2 + O_2 \overset{\text{catayst}}{\rightleftharpoons} 2SO_3$$

which is dissolved in 98% sulphuric acid to give oleum.

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7}$$

Sulphuric acid of any desired concentration can then be obtained by diluting oleum with water.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The maximum yield of sulphur trioxide is obtained when sulphur dioxide and oxygen present in molecular proportions of 2 : 3 are passed over a suitable catalyst (platinised asbestos or V_2O_5) at a temperature of 400–500°C under atmospheric pressure.

Properties. Pure sulphuric acid is a colourless, viscous heavy liquid (density 1·84 at 15°C). It freezes at 10·38°C and boils at 340°C with some decomposition ($H_2SO_4 \longrightarrow SO_3 + H_2O$). It forms a constant boiling mixture with water containing 98 per cent sulphuric acid boiling at 330°C. This is the common concentrated sulphuric acid. At 444°C, the vapour of sulphuric acid dissociate completely into steam and sulphur trioxide.

Concentrated sulphuric acid has strong affinity for water and a large amount of heat is produced on mixing the acid with water. The temperature may rise as high as 120°C, hence the acid is always diluted by adding the acid to water (and *not by adding water to acid*) slowly with constant stirring. The evolution of heat is due to the formation of definite hydrates such as $H_2SO_4.H_2O$ (m.p. 8·5°C) and $H_2SO_4.2H_2O$ (m.p. 38°C).

Since sulphuric acid has great affinity for water, it readily removes water not only from materials which contain it but also frequently eliminates oxygen and hydrogen from other compounds in the proportions required to form water (H_2O). Thus, paper and wood [which are largely cellulose, $(C_6H_{10}O_5)_x$ and sugar ($C_{12}H_{22}O_{11}$)] get charred by concentrated sulphuric acid as carbon is formed by their dehydration.

Similarly, oxalic acid is dehydrated to CO and CO_2 and formic acid to CO.

Dehydration of certain organic compounds yields industrially important compounds. For example, diethyl ether is obtained by the dehydration of ethyl alcohol.

Similarly, dehydration of a mixture of chlorobenzene and trichloroacetaldehyde (chloral) gives D.D.T.,

$$\underset{\text{Chlorobenzene}}{2C_6H_5Cl} + \underset{\text{Chloral}}{CCl_3CHO} \xrightarrow[-H_2O]{H_2SO_4} \underset{\text{D.D.T}}{ClC_6H_4 - CH(CCl_3) - C_6H_4Cl}$$

The dehyrating action of sulphuric acid is made use of in drying gases which do not react with the acid (*e.g.*, SO_2, Cl_2, HCl, etc.) and in eliminating water in many reactions such as esterification and nitration and in the manufacture of dyes and explosives.

Dilute sulphuric acid has no oxidising action but the hot concentrated acid acts as a strong oxidising agent. It accepts electrons provided by a reducing agent so that the general reaction may be represented as

$$6H^+ + H_2SO_4 + 6e^- \longrightarrow S + 4H_2O$$
$$6H^+ + H_2SO_4 + 8e^- \longrightarrow S^{2-} + 4H_2O$$
$$8H^+ + H_2SO_4 + 8e^- \longrightarrow H_2S + 4H_2O$$

Most of the common metals, but not the noble metals, are oxidised by sulphuric acid. The main products are the sulphate of the metal, sulphur dioxide and water.

Sulphuric acid also oxidises certain non-metals, *e.g.*, carbon and sulphur, to their oxides.

The oxidising effect of sulphuric acid is also noticeable in its reactions with bromides and iodides. The HBr formed is oxidised to Br_2 and HI formed is oxidised to iodine.

$$H_2SO_4 + KBr \longrightarrow KHSO_4 + HBr$$
$$2HBr + H_2SO_4 \longrightarrow 2H_2O + Br_2 + SO_2$$
$$H_2SO_4 + KI \longrightarrow KHSO_4 + HI$$
$$6HI + H_2SO_4 \longrightarrow 4H_2O + S + 3I_2$$
$$8HI + H_2SO_4 \longrightarrow 4H_2O + H_2S + 4I_2$$

Aromatic compounds react with sulphuric acid forming sulphonic acids. For example,

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} + H_2O$$

Since sulphuric acid is a dihydroxy compound ($HO-SO_2-OH$), it reacts with phosphorus pentachloride giving chlorosulphonic acid and sulphuryl chloride.

$$HO - SO_2 - OH + PCl_5 \longrightarrow \underset{\text{Chlorosulphonic acid}}{Cl - SO_2 - OH} + POCl_3 + HCl$$

$$HO - SO_2 - OH + 2PCl_5 \longrightarrow \underset{\text{Sulphuryl chloride}}{Cl - SO_2 - Cl} + 2POCl_3 + 2HCl$$

On heating crystals of potassium ferrocyanide with concentrated sulphuric acid, carbon monoxide is evolved.

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

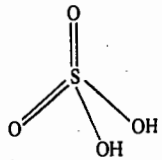
On heating potassium chlorate with concentrated sulphuric acid, chlorine dioxide is evolved with explosion.

$$2KClO_3 + 3H_2SO_4 \longrightarrow 2KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

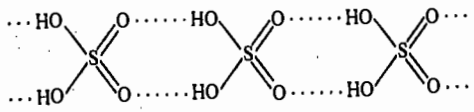
Dilute sulphuric acid gives all the reactions typical of a dibasic acid.

Uses. As already mentioned, sulphuric acid is perhaps the most important heavy chemical and finds extensive use in industry and laboratory. It is used : 1. For the preparation of fertilizers (ammonium sulphate and superphosphate). 2. In petroleum refining to remove unsaturated compounds (which darken by air oxidation of crude oil). 3. In the manufacture of other important chemicals such as hydrochloric acid, nitric acid, sulphates of metals, alums, ethers, etc. 4. In the preparation of dyes, drugs and disinfectants 5. In the 'pickling' of steel before coating it with enamel, tin or zinc. 6. In metallurgical processes for the purification of metals by electrolysis where sulphuric acid is commonly used as bath 7. In preparing paints and pigments. Many of the pigments used in paints are sulphates, *e.g.*, barium and lead sulphates. 8. In the manufacture of explosives such as nitroglycerine, gun cotton, T.N.T., etc. Sulphuric acid is used to eliminate the water formed during the organic reactions. 9. In textile and paper industry. 10. In leather industry for tanning 11. As a dehyrating agent. 12. As a laboratory reagent.

Structure of Sulphuric Acid. Sulphuric acid is a dibasic acid and has been assigned tetrahedral structure as shown.



The high boiling point and viscosity of sulphuric acid indicate association of sulphuric acid molecules due to hydrogen bonding, as shown below :



Pyrosulphuric Acid, $H_2S_2O_7$, Oleum. Pyrosulphuric acid is obtained by dissolving sulphur trioxide in concentrated sulphuric acid.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

This can also be obtained by distilling ferrous sulphate monohydrate crystals. The receiver should contain preferably some sulphuric acid.

$$6FeSO_4.H_2O \longrightarrow Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2 + 6H_2O$$

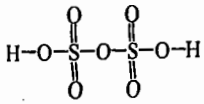
$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$$

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

It is a viscous brownish liquid and is believed to be a solution of sulphur trioxide in conc. sulphuric acid. It fumes in air and hence the name *fuming sulphuric acid*. This is due to the escape of sulphur trioxide. It changes into ordinary sulphuric acid on warming as the dissolved sulphur trioxide escapes into the air. It solidifies on cooling below 0°C. It is used in the manufacture of dyes and explosives and in refining of petroleum.

If forms salts, known as **pyrosulphates**. Sodium pyrosulphate, $Na_2S_2O_7$, is definitely known. This shows that the acid is a definite compound of the composition $H_2S_2O_7$.

Structure of Pyrosulphuric Acid. The structure of the acid is as shown below :

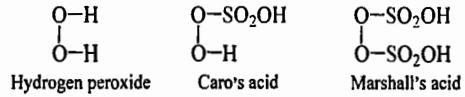


Peroxosulphuric Acids

Two peroxosulphuric acids are known. These are

1. *Peroxomonosulphuric acid*, H_2SO_5 (Caro's acid)
2. *Peroxodisulphuric acid*, $H_2S_2O_8$ (Marshall's acid)

These acids may be considered as derived from hydrogen peroxide by the replacement of one or both atoms of hydrogen by sulphonic groups :



Caro's acid, Peroxomonosulphuric acid, H_2SO_5. This is obtained

1. By the low conversion of peroxodisulphuric acid in aqueous solution or by grinding potassium peroxodisulphate crystals with conc. sulphuric acid in a freezing mixture.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$

$$K_2S_2O_8 + H_2SO_4 \longrightarrow H_2SO_5 + K_2S_2O_7$$

2. By the reaction of chlorosulphonic acid with anhydrous hydrogen peroxide.

$$HOOH + ClSO_2OH \longrightarrow HOOSO_2(OH) + HCl$$

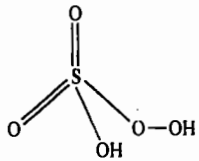
It is a white crystalline mass (m.p. 45°C). It is fairly stable. It has strong oxidising properties, as such it is stronger than peroxodisulphuric acid. Thus, it liberates iodine from potassium iodide much more readily than peroxodisulphuric acid does. This serves to distinguish between the two acids.

It also oxidises sulphur dioxide to sulphur trioxide, ferrous salts to ferric state, hydrogen chloride to chlorine, aniline to nitrosobenzene and nitrobenzene.

It precipitates peroxides from salts of copper, silver, manganese, etc.

No solid salts of Caro's acid are known. However, a solution of $KHSO_5$ is believed to be formed by the action of hydrogen peroxide on $KHSO_3$. The acid, therefore, is considered to be monobasic.

Structure. Peroxomonosulphuric acid has been assigned a tetrahedral structure as shown.



Marshall's acid, Peroxodisulphuric acid, $H_2S_2O_8$. This acid is prepared

1. By anodic oxidation of sulphuric acid. Peroxodisulphuric acid is obtained by the electrolysis of 50 per cent sulphuric acid in cold.

The reaction is represented as below :

Cathode : $H^+ + e^- \longrightarrow H$

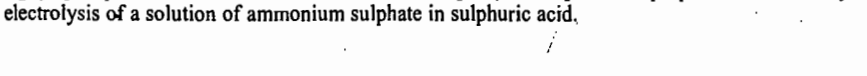
$H + H \longrightarrow H_2$

Anode : $HSO_4^- + HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

Another explanation for the formation of peroxodisulphuric acid at the anode is that the bisulphate ions are oxidised by the nascent oxygen that appears at the anode as a result of electrolysis.

$$2HSO_4^- + H_2O + O \longrightarrow H_2S_2O_8 + 2OH^-$$

2. By sulphonation of hydrogen peroxide. Treatment of hydrogen peroxide with chlorosulphonic acid (in the molar ratio of 1 : 2), yields peroxodisulphuric acid.



Preparation of Peroxodisulphates. By the electrolysis of a saturated aqueous solution of potassium hydrogen sulphate (or that of potassium sulphate in sulphuric acid), crystals of **potassium peroxodisulphate, $K_2S_2O_8$**, separate out at the anode. **Ammonium peroxodisulphate** is prepared conveniently by the electrolysis of a solution of ammonium sulphate in sulphuric acid.

Potassium and ammonium peroxodisulphates are also prepared by the action of fluorine on potassium hydrogen sulphate or ammonium hydrogen sulphate, as the case may be.

$$2KHSO_4 + F_2 \longrightarrow K_2S_2O_8 + 2HF$$

Properties of Peroxodisulphuric acid and Peroxodisulphates. Peroxodisulphuric acid is a stable compound. It is a crystalline solid (m.p. 65°C) and is fairly soluble in water. Its salts, the peroxodisulphates, decompose on heating evolving sulphur dioxide and oxygen.

$$K_2S_2O_8 \longrightarrow K_2SO_4 + SO_2 + O_2$$

The solutions of peroxodisulphates give oxygen slowly in cold and rapidly on heating.

$$2K_2S_2O_8 + 2H_2O \longrightarrow 4KHSO_4 + O_2$$

The peroxodisulphates are powerful oxidising agents. They liberate iodine from potassium iodide solution.

$$K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$$

Similarly, they oxidise ferrous salts to ferric state, manganous salts to permanganates and chromic salts to dichromates in the catalytic presence of silver nitrate.

Barium peroxodisulphate is soluble in water. This fact helps in distinguishing between a peroxodisulphate and a sulphate by the addition of barium chloride when a soluble sulphate gives a precipitate of barium sulphate while a peroxodisulphate does not give any precipitate.

Some metals, *e.g.*, zinc, dissolve in an aqueous solution of peroxodisulphates giving sulphates.

$$K_2S_2O_8 + Zn \longrightarrow K_2SO_4 + ZnSO_4$$

Ammonium peroxodisulphate is used as bleaching and reducing agent.

Peroxodisulphuric acid, in aqueous solution, changes gradually into Caro's acid.

$$H_2S_2O_8 + H_2O \longrightarrow \underset{\text{Caro's acid}}{H_2SO_5} + H_2SO_4$$

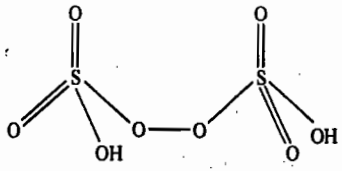
Caro's acid is further hydrolysed to give H_2O_2 and H_2SO_4.

$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4$$

Distinction between Caro's acid, Marshall's acid and Hydrogen peroxide. Caro's acid, Marshall's acid and Hydrogen peroxide can be distinguished from one another by the following tests.

1. Caro's acid liberates iodine almost instantaneously from potassium iodide.
2. Marshall's acid liberates iodine slowly from potassium iodide.
3. Hydrogen peroxide decolorises (reduces) potassium permanganate which is not done by either of the two peroxodisulphuric acids.

Structure. The peroxodisulphuric acid is assigned the structure, as shown.



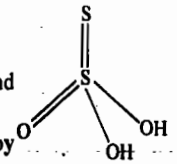
This structure accounts for its dibasic character.

Thiosulphuric acid, $H_2S_2O_3$. Thiosulphuric acid is highly unstable. It exists only in solution and there, too, it changes rapidly into sulphurous acid depositing free sulphur.

$$H_2S_2O_3 \longrightarrow H_2SO_3 + S$$

The salts, known as **thiosulphates**, as, for example, $Na_2S_2O_3$ are fairly stable and important.

Structure. Thiosulphuric acid may be regarded as derived from sulphuric acid by the replacement of one of the oxygen atoms by a sulphur atom as shown.



Dithionous acid, $H_2S_2O_4$. The acid $H_2S_2O_4$ is not known but its salts in anhydrous form (known as dithionites) are known.

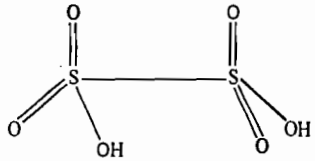
The dithionites are unstable compounds and hydrolyse rapidly.

Dithionic acid, $H_2S_2O_6$. The free acid has not been prepared. It is known only in solution. The concentrated aqueous solution of dithionic acid can be prepared by treatment of the barium salt with sulphuric acid.

$$BaS_2O_6\,(aq) + H_2SO_4\,(aq) \longrightarrow H_2S_2O_6\,(aq) + BaSO_4$$

The salts of dithionic acid, *viz.*, dithionates, are thermally stable above room temperature and are readily soluble in water.

Structure. Dithionic acid has been assigned the structure, as shown, in which the bond angles are approximately equal to normal tetrahedral angles.



Polythionic Acids and Polythionates. The free acids are not stable ; they rapidly decompose to give sulphur and sulphur dioxide. Polythionic acids and polythionates are named according to the total number of sulphur atoms present. Thus, polythionates $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ are named as trithionate, tetrathionate, pentathionate and hexathionate, respectively.

Mixtures of thionates are obtained by the reduction of a thiosulphate solution with SO_2 in the presence of As_2O_3. Individual members can, however, be prepared by selective methods.

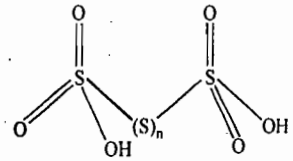
Trithionate, for example, can be prepared by the action of H_2O_2 on cold saturated solution of a thiosulphate.

$$2S_2O_3^{2-} + 4H_2O_2 \longrightarrow S_3O_6^{2-} + SO_4^{2-} + 4H_2O$$

Tetrathionates are obtained by the oxidation of a thiosulphate with iodine solution.

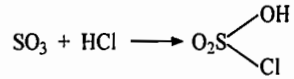
$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Structure. Polythionic acids have – S –S – linkages and their general structure may be represented as shown.



Chlorosulphonic Acid, $HOSO_2Cl$. It may be considered as a derivative of sulphuric acid in which one of the hydroxyl groups present in the acid ($HO - SO_2 - OH$) is replaced by chlorine. It can be prepared

1. By passing dry hydrogen chloride gas into fuming sulphuric acid, *i.e.*, sulphuric acid containing dissolved sulphur trioxide. Hydrogen chloride directly unites with sulphur trioxide giving chlorosulphonic acid.



The resulting product is recovered and purified by distillation.

2. By distilling a mixture of sulphuric acid and phosphorus pentachloride or phosphorus oxochloride.

$$H_2SO_4 + PCl_5 \longrightarrow ClSO_2OH + POCl_3 + HCl$$

$$2H_2SO_4 + POCl_3 \longrightarrow 2ClSO_2OH + HPO_3 + HCl$$

Properties. Chlorosulphonic acid is a colourless liquid boiling at 151°C. It strongly fumes in air.

It is rapidly hydrolysed by water with explosive violence.

$$ClSO_2OH + H_2O \longrightarrow HCl + HOSO_2OH$$

When heated at 170–180°C, its vapours decompose into sulphuryl chloride and sulphuric acid.

$$2ClSO_2OH \longrightarrow SO_2Cl_2 + H_2SO_4$$

At still higher temperatures, it breaks into Cl_2, SO_2 and H_2SO_4.

It reacts with aromatic hydrocarbons giving sulphonic derivatives. For example,

$$\underset{\text{Benzene}}{C_6H_6} + ClSO_2OH \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} + HCl$$

It is used in organic chemistry as a sulphonating agent.

Oxoacids of Selenium and Tellurium

Selenium forms only two oxoacids, namely, selenous acid, H_2SeO_3 and selenic acid, H_2SeO_4.

Selenous acid is prepared by dissolving selenium dioxide in water and then slowly crystallising the solution. It can also be prepared by the oxidation of powdered selenium with dilute HNO_3.

$$3Se + 4HNO_3 + H_2O \longrightarrow 3H_2SeO_3 + 4NO$$

Selenous acid is a white stable solid. It can be dehydrated to selenium dioxide in a stream of dry air. It is converted to selenic acid by refluxing with hydrogen peroxide. With alkalies, selenous acid forms two types of salts, $MHSeO_3$ and M_2SeO_3 (M = alkali metal).

Selenic acid can be prepared by the following methods :

1. Oxidation of selenium with chlorine or bromine water.

$$Se + 3Cl_2 + 4H_2O \longrightarrow H_2SeO_4 + 6HCl$$

2. Oxidation of selenous acid by hydrogen peroxide or potassium permanganate :

$$H_2SeO_3 + H_2O_2 \longrightarrow H_2SeO_4 + H_2O$$

$$8H_2SeO_3 + 2KMnO_4 \longrightarrow 5H_2SeO_4 + K_2SeO_3 + 2MnSeO_3 + 3H_2O$$

Anhydrous selenic acid is a viscous liquid and crystallises to a white solid (m.p. 62°C). It resembles sulphuric acid in its chemical properties but is a much stronger oxidising agent. It can dissolve Au, Pd and even Pt in the presence of chloride ion. Like H_2SO_4, it forms several hydrates such as $H_2SeO_4.H_2O$, $H_2SeO_4.4H_2O$, etc. It forms selenates which resemble sulphates.

Tellurous acid, H_2TeO_3, was not known earlier because it could not be prepared by dissolving TeO_2 in water as TeO_2 is almost insoluble in water. These days it is obtained by the hydrolysis of a tetrahalide of tellurium. Its structure has not been established. It has also been found to form two types of salts, *viz.*, $MHTeO_3$ and M_2TeO_3 with aqueous alkalies.

Telluric acid, H_6TeO_6, on the other hand, is quite stable and is well known. It can be prepared by the oxidation of powdered tellurium with chloric acid or by the oxidation of Te or TeO_2 with a mixture of nitric acid and chromic acid.

$$5Te + 6HClO_3 + 12H_2O \longrightarrow 5H_6TeO_6 + 3Cl_2$$

It is a white solid (m.p. 136°C). It is quite different from sulphuric and selenic acids and exists as octahedral $Te(OH)_6$ molecules. It is a fairly strong oxidising agent but unlike H_2SO_4 and H_2SeO_4, it is a weak dibasic acid. The anhydrous telluric acid is stable in air upto 100°C but above 120°C, it loses water to form polymetatelluric acid.

OXOHALIDES OF SULPHUR

The two important oxohalides of sulphur are thionyl dihalides (SOX_2) and sulphuryl dihalides (SO_2X_2). Although a number of thionyl dihalides like SOF_2, SOFCl, $SOCl_2$ and $SOBr_2$ are known, the most important of these is thionyl dichloride $SOCl_2$. It is readily prepared by chlorination of SO_2 with

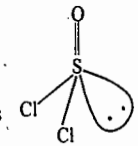
PCl_5 or by reacting SO_3 with SCl_2.

$$SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$$

$$SO_3 + SCl_2 \longrightarrow SOCl_2 + SO_2$$

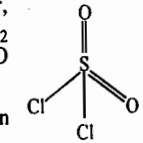
Thionyl chloride vigorously reacts with water and is used for drying some inorganic halides.

$$MX_m.nH_2O + nSOCl_2 \longrightarrow MX_m + nSO_2 + 2nHCl$$



It is widely used as a nonaqueous solvent. S in $SOCl_2$ is sp^3 hybridised. It forms one S = O bond and two S – Cl bonds and has a lone pair, as shown.

Amongst the known sulphuryl dihalides, *viz.*, SO_2F_2, SO_2FCl, SO_2Cl_2 and SO_2FBr, the most important is **sulphuryl dichloride** which is prepared by reacting SO_2 with Cl_2 using activated charcoal as catalyst. S in SO_2Cl_2 is sp^3 hybridised and forms two S = O and two S – Cl bonds, as shown.



It is a useful chlorinating agent. It is also used for introducing – SO_2Cl group in organic compounds.

NITRIDES OF SULPHUR

Tetrasulphur Tetranitride, S_4N_4. This is the most important nitride of sulphur which can be prepared by any of the following reactions :

1. $$16NH_3 + 6S_2Cl_2 \xrightarrow[CCl_4]{50°C} S_4N_4 + 8S + 12NH_4Cl$$

2. $$4NH_4Cl + 6S_2Cl_2 \xrightarrow{160°C} S_4N_4 + 8S + 16HCl$$

3. $$10S + 4NH_3 \longrightarrow S_4N_4 + 6H_2S$$

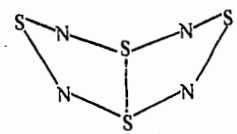
$$H_2S + 2NH_3 \longrightarrow (NH_4)_2S$$

S_4N_4 is an orange compound with a melting point of 178°C. It explodes to give S and N_2 when struck or heated. It forms adducts $S_4N_4.BF_3$ and $S_4N_4.SbCl_5$ with BF_3 and $SbCl_5$, respectively.

S_4N_4 gets hydrolysed by dilute and concentrated alkali solutions.

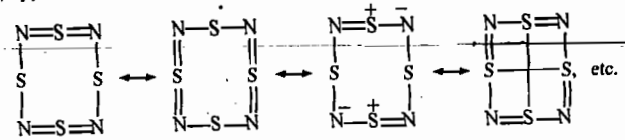
$$2S_4N_4 + 6OH^- \text{ (dilute)} + 9H_2O \longrightarrow S_2O_3^{2-} + 2S_3O_6^{2-} + 8NH_3$$

$$S_4N_4 + 6OH^- \text{ (concentrated)} + 3H_2O \longrightarrow S_2O_3^{2-} + 2S_3O_3^{2-} + 4NH_3$$



Structure of S_4N_4. Tetrasulphur tetra-nitride has a cradle-like skeletal structure as shown.

All the S–N bond distances are equal (*i.e.*, 1·60 Å) which are shorter than the calculated S – N single bond distance of 1·75 Å. This indicates some double bond character in S – N bonds. The trans annular S – S distances are shorter than twice the van der Waals radius for S atom indicating that there may be a weak association between the trans annular S atoms. The actual structure of S_4N_4 appears to be a resonance hybrid of a number of the following types of structures :

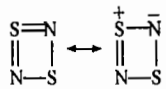


Disulphur Dinitride, S_2N_2. This compound is prepared by pumping vapours of S_4N_4 through silver wool.

$$S_4N_4 + 8Ag \longrightarrow 4Ag_2S + 2N_2$$

$$S_4N_4 \xrightarrow{Ag_2S} 2S_2N_2$$

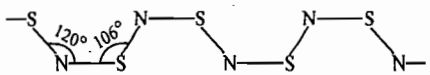
S_2N_2 is a colourless crystalline compound which explodes on heating. On slow heating, it polymerises to $(SN)_x$. It has a square planar cyclic structure, as shown :



Polythiazyl, $(SN)_x$. It is prepared by heating pure S_4N_4 at 70°C and condensing the vapour produced on glass surface at 10–30°C. It is also produced by slow heating of S_2N_2, as mentioned above.

Polythiazyl shows optical anisotropy and electrical anisotropy. It is superconducting at 0·26 K. $(SN)_x$ is a rare example of a superconducting compound obtained from a non-metal.

Its structure contains a zig-zag chain having SNS angle of 120° and NSN angle of 106°, as shown



Other sulphur-nitrogen compounds known are S_4N_2, $S_{11}N_2$ and S_5N_6. A number of cationic and anionic species such as S_2N^+, $S_3N_2^+$, $S_4N_3^+$, $S_4N_4^{2+}$, $S_4N_5^+$, $S_5N_5^+$, $S_4N_5^-$, $S_3N_3^-$, etc., are also known.

ORGANOMETALLIC COMPOUNDS

Amongst the elements of Group 16, only selenium and tellurium are known to form organometallic compounds. A detailed discussion of these compounds is beyond the scope of the book. Only a brief description is given below.

Organometallic Compounds of Selenium and Tellurium. The common organoselenium compounds are RSeX, R_2SeX_2, R_2Se and RSeH. These are prepared by the following reactions :

$$2RBr + Na_2Se \longrightarrow R_2Se + 2NaBr$$

$$R_2Se + X_2 \longrightarrow R_2SeX_2$$

$$RBr + Na_2Se_2 \xrightarrow{\text{liq. } NH_3} R_2Se_2 + 2NaBr$$

$$R_2Se_2 \xrightarrow{Zn, X_2} 2RSeX$$

$$R_2Se_2 \xrightarrow{2H} 2RSeH$$

(R is alkyl or aryl group ; X is the halogen)

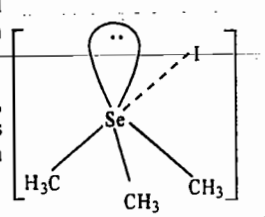
Selenium and tellurium also form compounds which are analogous to carbonyl compounds and the amides.

The structures of derivatives of seleno and tellurocarbonyls and amides are given below :

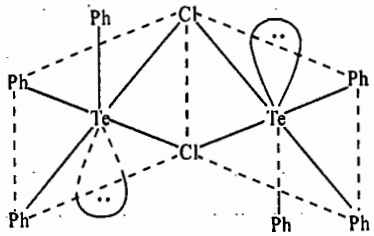
$$R-\underset{\underset{Se\ (or\ Te)}{\|}}{C}-OR \qquad Rh-\underset{\underset{Se\ (or\ Te)}{\|}}{C}-N(Me)_2$$

Telluro derivatives are more reactive than the corresponding seleno derivatives.

Both Se and Te have a tendency to increase their coordination numbers in the presence of suitable ions. Thus, the compound $[Se(CH_3)_3]^+I^-$ has I^- ion associated with Se as shown.



Similarly, the compound, commonly written as $[Ph_3Te]^+Cl^-$, is a dimer with the structure as shown.



QUESTIONS

1. Name the elements of Group 16. Discuss the gradation in the properties of the elements of Group 16 with reference to
   (*i*) ionisation energy (*ii*) catenation (*iii*) electronegativity and (*iv*) oxidation state
2. (*a*) The first member of a group differs from the remaining members. Justify the statement by taking the example of oxygen.
   (*b*) Explain the following :
   (*i*) Water is a weaker acid that H_2S.
   (*ii*) Water has a higher boiling point than H_2S.
   (*iii*) Water is weaker reducing agent than H_2S.
   (*c*) Discuss the structure of oxygen molecule.
3. (*a*) Discuss one method of preparation and structure of principal fluorides of sulphur.
   (*b*) Why is oxygen a gas while sulphur is a solid ?
   (*c*) How and why does the acid strength vary among hydrides of the elements of Group 16 ?
   (*d*) Oxygen exhibits –2 oxidation state but other members of the group show in addition to –2, other oxidation states of +2, +4 and +6 also. Why is it so ?
4. (*a*) Give one method of preparation, two important properties and structures of
   (*i*) SO_2 (*ii*) SO_3 (*iii*) H_2SO_3 (*iv*) H_2SO_4 .
   (*b*) The formula for telluric acid is H_6TeO_6 or $Te(OH)_6$. Explain as to why the analogous sulphuric acid, $S(OH)_6$ does not exist.
   (*c*) Give examples to illustrate the Lewis acid character of SF_4 and $TeCl_4$.
5. (*a*) Arrange H_2X (X = O, S, Se, Te, Po) compounds in order of increasing (*i*) acidity (*ii*) stability (*iii*) boiling point (*iv*) reducing character.
   (*b*) Why is the bond angle in H_2O more than that in H_2S ?
   (*c*) Give the structures of SO_2 and SO_3 molecules.
6. (*a*) Out of the elements of Group 16, select one with (*i*) highest ionisation energy (*ii*) highest ability to catenate (*iii*) smallest atomic radius (*iv*) highest electronegativity.
   (*b*) Name two peroxoacids of sulphur. Give their structures.
7. List the various oxoacids of sulphur. Discuss their structures.
8. What do you know about Caro's acid and Marshall's acid ? Discuss their preparation and properties.
9. How does selenium occur in nature ? How is the metal prepared ? Discuss its important properties and uses.
10. What is meant by photoconductivity ? Discuss in deails how selenium is used in xerography.
11. (*a*) How does tellurium occur in nature ? How is the metal obtained ? Describe its properties and uses.
    (*b*) Write a short note on the preparation, properties and uses of polonium.
12. Explain the following :
    (*a*) O_2 molecule is paramagnetic.
    (*b*) SF_6 is known but SCl_6 is not known.
    (*c*) H_2Te is stronger acid than H_2S.
    (*d*) The O – O bond energy in O_2 is much larger than the S – S bond energy in S_8.
    (*e*) Maximum covalency of oxygen is two.

19 THE ELEMENTS OF GROUP 17

Group 17 comprises of five elements, namely, **fluorine, chlorine, bromine, iodine** and **astatine.** They do not occur free but in the combined state they occur fairly abundantly in nature. Fluorine, chlorine, bromine and iodine constitute, respectively, 0·06 to 0·09, 0·031, 0·00016 and 0·00003 per cent of earth's crust. Astatine is radioactive and occurs very sparsely.

Fluorine, chorine, bromine and iodine have closely related properties and are known collectively as the **halogens** (Greek, *halos* = sea salts, *genes* = born) since the salts of the first three occur in sea water. On account of their close resemblance and gradual transition of physical and chemical properties, the halogens constitute a well-marked group.

Electronic Configurations. The electronic configurations of the halogens are given in Table 1.

TABLE 1
Electronic Configurations of the Halogens

Element	Atomic Number	Electronic Configuration
Fluorine, F	9	[He] $2s^2p^5$
Chlorine, Cl	17	[Ne] $3s^2p^5$
Bromine, Br	35	[Ar] $3d^{10}4s^2p^5$
Iodine, I	53	[Kr] $4d^{10}5s^2p^5$
Astatine, At	85	[Xe] $4f^{14}5d^{10}6s^2p^5$

As is evident, the halogens have the general outer electronic configurations $\mathbf{ns^2p^5}$.

GENERAL CHARACTERISTICS OF GROUP 17 ELEMENTS

Some important **physical properties** of the halogens are given in Table 2.

1. Atomic volume, atomic radius and **density** increase regularly with increase in atomic number, as expected.

2. Ionisation energy. Ionisation energies of the halogens are very high indicating that they have very small tendency to lose electrons. The values, however, decrease on moving down the group, as expected. In the case of iodine, the value is comparatively low. This enables the iodine atom to lose an electron and form I^+ ion.

3. Electronegativity. The halogens have very high electronegativities. Fluorine is the most electronegative with electronegativity = 4. The values decrease as we move down the group from fluorine to iodine indicating a gradual decline in the non-metallic character, so much so that the last element iodine, with an electronegativity of 2·6, shows some metallic character also. For instance, it forms in a few cases a positive ion and has a metallic lustre.

TABLE 2
Physical Properties of the Halogens

Property	Fluorine	Chlorine	Bromine	Iodine
Atomic Number	9	17	35	53
Atomic mass (a.m.u.)	18·998	35·453	79·909	126·904
Physical state	Gas	Gas	Liquid	Solid
M.P. (°C)	−218·6	−101·0	−7·2	113·9
B.P. (°C)	−188·1	−34·6	59·5	185·2
Density in liquid state (g cm^{-3})	1·108	1·1557	2·948	3·76 (in solid state)
Colour of vapour	Pale yellow	Greenish yellow	Orange red	Violet
Colour of liquid	Clear yellow	Amber yellow	Reddish brown	Shining dark solid
Atomic radius (Å)	0·72	0·99	1·14	1·33
Ionic radius of X^- ion (Å)	1·33	1·84	1·96	2·20
Atomic volume (c.c.)	17·1	18·7	23·5	25·7
Electronegativity (Pauling's values)	4·0	3·1	2·9	2·6
Electron affinity (kJ mol^{-1})	332·6	348·5	324·7	295·5
Ionisation energy (kJ mol^{-1})	1680·8	1255·5	1140·1	1008·8
Oxidation states	−1	−1, +1, +3 +4, +5, +6, +7	−1, +1, +3 +4, +5, +6	−1, +1, +3, +4, +5, +6, +7
Bond energy (kJ mol^{-1})	158·8	242·6	192·8	151·1
Standard electrode potential (volts)	+2·87	+1·36	+1·06	+0·53

4. Non-metallic character. On account of high electronegativities, all the halogens are non-metallic in character. The non-metallic character, however, decreases as we move down the group. The last element, iodine, has comparatively very small electronegativity and exhibits metalloidal character. It has a metallic lustre and has a tendency to lose an electron to form a positive ion (*cf.* alkali metals), as mentioned above.

5. Colour. All the halogens are coloured. This is because of the absorption of visible light by their molecules resulting in the excitation of electrons from the highest filled molecular orbitals to the lowest unoccupied molecular orbitals. The excitation energy, evidently, depends upon the size of the halogen atom. The smaller the atom, the greater is the force of attraction between the nucleus and the outer electrons and hence greater is the amount of the energy required to raise the electrons to higher levels. Consequently, the excitation energy is very large in the case of fluorine and comparatively very small in the case of iodine. Hence, fluorine absorbs violet portion of the light which is associated with higher energy and thus appears *yellow*. Iodine, on the other extreme, absorbs yellow and green radiations which are associated with lower energy and thus appears *violet*. Similarly, we can account for the *greenish yellow* colour of chlorine and *orange red* colour of bromine.

6. Electron affinity. All the elements have high electron affinities. Therefore, they have a strong tendency to gain an electron to acquire noble gas configuration, *viz.*, s^2p^6. Chlorine has the highest electron affinity which decreases gradually as we move down the group from Cl to I. The electron affinity of fluorine is lower than that of chlorine. The unexpectedly lower value is due to the small size of the atom. The addition of an extra electron in fluorine atom produces a high electron density in a relatively compact 2*p* subshell and, therefore, there is a strong electron–electron repulsion. Consequently, fluorine has lesser tendency to accept extra electron, that is, its electron affinity is low.

7. Oxidation states. It is evident from Table 1 that all the halogens have the configuration s^2p^5 in the outer shell in the ground state. These elements, therefore, tend to gain or share one electron to acquire noble gas configuration. Hence they show an oxidation state of −1 or +1, depending upon whether the element with which they combine is less electronegative or more electronegative than the halogen.

Since fluorine is the most electronegative element, it *always exhibits an oxidation state of* −1. It does not exhibit any positive oxidation state. Also, fluorine has no *d* orbitals in its valency shell and hence it cannot have any excited states. Consequently, it does not exhibit any higher oxidation state.

The other halogens exhibit higher positive oxidation states of +3, +4, +5, +6 and +7 as well because they have vacant *d* orbitals in their valency shells which allow for easy excitation of *p* as well as *p* and *s* electrons, *as* illustrated in Fig. 1.

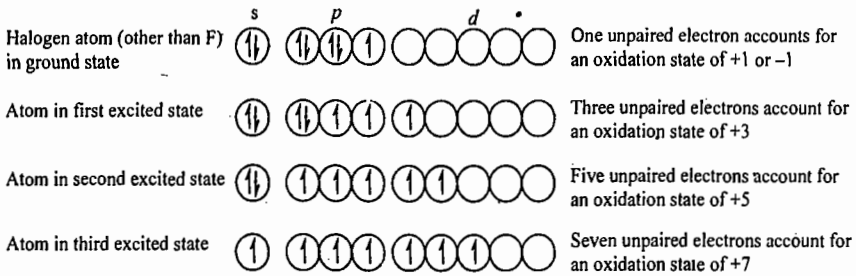


Fig. 1. Various oxidation states exhibited by the halogens other than fluorine.

In the first excited state, one pair of *p* electrons gets unpaired providing three unpaired electrons. This accounts for an oxidation state of +3. Thus, in the interhalogen compounds, ClF_3, BrF_3 and IF_3, chlorine, bromine and iodine are in +3 oxidation state.

In the second excited state, both the pairs of *p* electrons get unpaired providing five unpaired electrons which account for an oxidation state of +5. Thus, in $HClO_3$, $HBrO_3$ and HIO_3, the halogens are in +5 oxidation state.

Similarly, in BrF_5 and IF_5, bromine and iodine are in +5 oxidation states. Iodine is also in +5 oxidation state in I_2O_5.

In the third excited state, the pairs of *p* as well as *s* electrons get unpaired, providing seven unpaired electrons which account for an oxidation state of +7. Thus, in $HClO_4$ and Cl_2O_7, chlorine is in an oxidation state of +7 and in HIO_4, iodine is also in an oxidation state of +7. *Bromine does not exhibit +7 oxidation state.* Thus, compounds such as $HBrO_4$, Br_2O_7 are not known.

Chlorine and bromine exhibit oxidation states of +4 and +6 as well in their oxygen compounds, *e.g.*, ClO_2, BrO_2 and Cl_2O_6 and Br_2O_6, respectively. Iodine exhibits an oxidation state of +4 in I_2O_4.

8. Oxidising power. Since the halogens, on account of high electron affinities, have a strong tendency to pick up electrons, they act as strong oxidising agents. The oxidising character, however, decreases on moving down the group. This can be explained with the help of the **Born-Haber cycle.** The reaction

$$\frac{1}{2}X_2(s, l \text{ or } g) + e^- + aq \xrightarrow{\Delta E} X^-(aq)$$

representing the oxidising action of the halogen is actually a complicated process. It involves the following steps if we assume the halogen to be solid (*e.g.*, I_2)

1. The solid halogen (*e.g.*, I_2) changes into the liquid state. The energy required in this process is known as the heat of fusion, ΔH_f. Thus,

$$X_2(s) \xrightarrow{\Delta H_f} X_2(l)$$

2. The liquid halogen changes into the gaseous state. The energy required in this process is known as the heat of vaporisation, ΔH_v. Thus,

$$X_2(l) \xrightarrow{\Delta H_v} X_2(g)$$

3. The gaseous molecular halogen changes into the atomic state. The energy required in this case is known as the heat of dissociation, ΔH_d. Thus,

$$X_2(g) \xrightarrow{\Delta H_d} X(g)$$

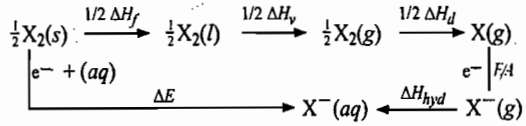
4. The gaseous atom changes into the gaseous ion. The energy involved in this process is known as electron affinity (*EA*). Thus,

$$X(g) + e^- \xrightarrow{EA} X^-(g)$$

5. The gaseous ion finally changes into the hydrated ion. The energy involved in this process is known as the heat of hydration of the ion, ΔH_{hyd}. Thus,

$$X^-(g) + aq \xrightarrow{\Delta H_{hyd}} X^-(aq)$$

In order to work out the value of ΔE for the halogen which, in fact, is a measure of its oxidising strength, the various changes are represented as follows :



(ΔH_f and ΔH_v are not involved if the halogen is a gas. ΔH_f is not involved if the halogen is liquid).

Since energy is invariably *absorbed* in converting a solid into liquid and a liquid into gaseous state and also in converting molecular halogen into the atomic state, ΔH_f, ΔH_v and ΔH_d have *positive* values. However, energy is *released* in the formation of a negative ion as well as in the process of its hydration. Hence, the numerical values of electron affinity and ΔH_{hyd} are *negative*. Consequently, from Hess's law, the net energy (ΔE) required for the reaction

$$\frac{1}{2}X_2(s) + e^- + aq \longrightarrow X^-(aq)$$

is given by the expression

$$\Delta E = \frac{1}{2}\Delta H_f + \frac{1}{2}\Delta H_v + \frac{1}{2}\Delta H_d - EA - \Delta H_{hyd}$$

ΔE is a measure of the oxidising potential, *i.e.*, the tendency of the halogen to act as an oxidising agent.

The values of ΔE calculated as above for the various halogens are given below.

Halogen	$\frac{1}{2}$ Heat of fusion (kJ)	$\frac{1}{2}$ Heat of vaporisation (kJ)	$\frac{1}{2}$ Heat of dissociation (kJ)	Electron affinity (kJ)	Heat of hydration (kJ)	ΔE (kJ)
F_2	–	–	+79	–332	–515	–768
Cl_2	–	–	+122	–348	–381	–607
Br_2	–	+15	+96	–324	–347	–575
I_2	+8	+22	+76	–295	–305	–524

Since fluorine and chlorine are gaseous at room temperature, the heats of fusion and vaporisation are not involved. Similarly, in the case of bromine, which is liquid at ordinary temperatures, the heat of fusion has been omitted.

The magnitude of ΔE is maximum in the case of fluorine and gradually decreases as we move down the group. Thus, fluorine is the strongest oxidising agent and iodine is the weakest oxidising agent. These results also explain why chlorine, which has the maximum electron affinity, is not the strongest oxidising agent. Inspection of the above table shows that the stronger oxidising character of F_2 in comparison to Cl_2 is mainly due to its relatively lower bond dissociation energy and higher heat of hydration. It is the *oxidising potential* and not the electron affinity alone *which controls the strength of the halogen to act as an oxidising agent in aqueous medium.*

9. Combination with metals and non-metals. All the halogens react with metals and also with many non-metals to form halides. Fluorine is the most reactive. The reactivity decreases as we move down the group. For instance, with sulphur, fluorine forms the hexafluoride (SF_6), chlorine forms the tetrachloride (SCl_4), bromine forms the dibromide (SBr_2) whereas iodine does not react at all.

10. Reaction with water. The interaction of halogens with water provides another illustration of gradation in properties with increase in atomic number. For example, fluorine decomposes water very energetically ; chlorine and bromine do so much less readily according to the equation

$$X_2 + H_2O \longrightarrow HOX + HX$$

while iodine scarcely reacts with water.

11. Reaction with hydrocarbons. All the halogens react with hydrocarbons but the reactivity decreases with increase in atomic number. Fluorine is the most reactive and brings about decomposition of the hydrocarbon.

$$CH_4 + 2F_2 \longrightarrow C + 4HF$$

Chlorine brings about the substitution of hydrogen atoms.

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

Bromine also brings about substitution but at a slow rate. Iodine has little or no action.

PREPARATION OF ELEMENTS OF GROUP 17

Preparation of Fluorine. Because of its extremely reactive nature, fluorine does not occur free in nature. In combined state, it is fairly and widely distributed. It constitutes nearly 0·08 per cent of lithosphere. It occurs in *fluorspar* (CaF_2), *cryolite* ($AlF_3.3NaF$) and *apatite* [$CaF_2.3Ca_3(PO_4)_2$]. In small quantities, it occurs in some of the micas. Traces of fluorine occur in sea water, some mineral springs, bones, teeth, blood, milk, plants, etc. As a matter of fact, small quantities of fluorides present in soil find their way into river water, sea and plants and from plants into bones, blood and teeth of animals and human beings. The total abundance of fluorine on the earth has been estimated to be comparable with that of carbon, nitrogen and chlorine.

Isolation of fluorine presented a tough problem to chemists for about a century. All the difficulties inherent in its production arose from its extraordinary reactivity. It attacked water giving oxygen so that its production by the electrolysis of aqueous solution of fluorides was negated. It attacked glass, carbon and almost all metals including platinum and hence the apparatus could not be made of these materials. The problem was, however, finally solved by Moissan, in 1886, who prepared fluorine by the electrolysis of a solution of potassium hydrogen fluoride (KHF_2) in anhydrous hydrogen fluoride using an apparatus made of platinum-iridium alloy using electrodes also of the same alloy.

In later years, Moissan found that platinum-iridium alloy could be safely replaced by copper. This metal, though attacked by fluorine, gets covered with a thin impervious layer of copper fluoride which resists further attack.

For laboratory preparation of fluorine, **Dennis, Veeder** and **Rochow** electrolysed perfectly dry and fused potassium hydrogen fluoride in a heavy V-shaped tube (about 5 cm in diameter) made of copper, using graphite electrodes (Fig. 2). The ends of the tube are closed by copper caps through which pass the graphite electrodes. The latter are sealed and insulated by bakelite cement which is found to resist the attack of fluorine. The tube is heated in an electric resistance furnace to fuse the potassium hydrogen fluoride.

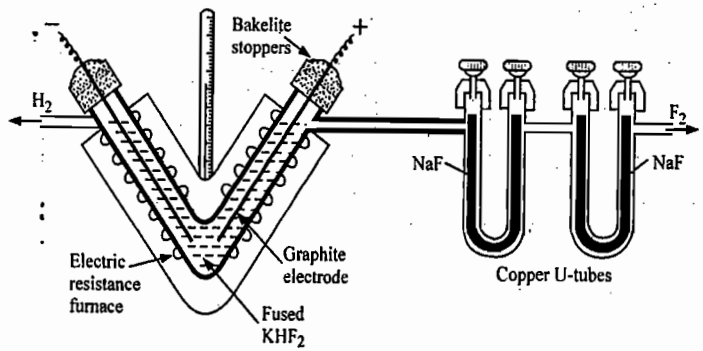


Fig. 2. Dennis apparatus for the preparation of fluorine.

For electrolysis, a current of 5 amperes at 12 volts is passed when hydrogen is liberated at the cathode and fluorine is liberated at the anode. The fluorine liberated at the anode is passed through copper U-tubes containing sodium fluoride to free it from hydrogen fluoride ($NaF + HF \longrightarrow NaHF_2$).

Commercial Preparation. Today even the commercial preparation of fluorine is no problem. Fluorine gas stored in steel tanks under pressure is offered for sale in America and other countries

The essentials of the electrolytic cell used for the industrial preparation of fluorine are shown in Fig. 3. It consists of a rectangular steel tank surrounded by a steam jacket. The tank is fitted with air-tight removable cover which carries a carbon anode, two 'slitted' copper or steel cathodes and a steel gas barrier, as shown. The cathode is 'slitted' to permit circulation of the electrolyte. The anode and the barrier are insulated from each other and also from the cathode with a special material, teflon or P.T.F.E. [polytetrafluoroethylene, $(C_2F_4)_n$] which is not attacked by fluorine. The gas barrier surrounds the anode and extends below the surface of the eletrolyte with a view to separating the products of electrolysis.

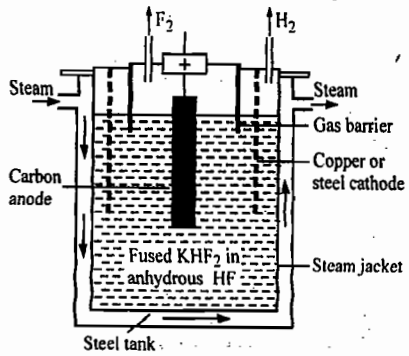


Fig. 3. Modern method for the manufacture of fluorine.

The electrolyte in this case is a 90 per cent solution of KHF_2 in anhydrous hydrogen fluoride. This is kept in the molten state by heating it to about 95°C with the help of steam passing through the steam jacket. But once the electrolysis starts, heating is no longer necessary because sufficient heat is produced during the process of electrolysis itself. On the other hand, cooling may sometimes be needed to maintain the electrolyte at about 95°C. The loss of hydrogen fluoride from the electrolyte is made good by passing in hydrogen fluoride periodically.

The fluorine obtained in this process is almost pure and is compressed into steel cylinders at a pressure of about 25 atm. If required, the small contamination of hydrogen fluoride is removed as usual by passing the gas over sodium fluoride.

Preparation of Chlorine. Chlorine constitutes nearly 0·19 per cent of lithosphere. It occurs mostly as chlorides of sodium and other alkali and alkaline earth metals. It is prepared mainly from sodium chloride which is crystallised from brine. In the **laboratory**, it is obtained by the oxidation of chloride ion in acid medium by using MnO_2 or permanganate ion as the oxidising agent.

$$2Cl^- + 4H^+ + MnO_2 \longrightarrow Mn^{2+} + 2H_2O + Cl_2$$

Bulk of chlorine required for **commercial purposes** is prepared by electrolysis of brine solution. The electrolysis is carried out primarily for the purpose of manufacturing caustic soda and chlorine is an important by-product of this process.

It is also a by-product of the manufacture of sodium (by electrolysis of fused sodium chloride) as well as of magnesium and calcium (by electrolyses of their fused chlorides)

Preparation of Bromine. Bromine, which constitutes nearly 0·01 per cent of lithosphere, occurs in combined state in sea water.

In laboratory, it can be prepared by oxidation of Br^- ion in the same way as that of Cl^- ion for the preparation of chlorine.

On a large scale, it is obtained from sea water by passing chlorine into sea water which contains bromides in sufficient amounts.

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$

The free bromine thus liberated is blown out with air and dissolved in sodium carbonate solution to get sodium bromide and sodium bromate.

$$3CO_3^{2-} + 3Br_2 \longrightarrow 5Br^- + BrO_3^- + 3CO_2$$

Bromine is recovered from this solution by acidification.

$$6H^+ + 5Br^- + BrO_3^- \longrightarrow 3H_2O + 3Br_2$$

Preparation of Iodine. Iodine is the rarest of all the halogens. It constitutes merely 10^{-4} per cent of lithosphere. Its main source is *'kelp', viz.,* the ash obtained on burning sea-weeds in which it occurs as iodides and *chile saltpetre* in which it occurs as iodates.

The kelp containing about 0·1 percent of iodine as iodides is extracted with water. The extract is concentrated when sulphates and chlorides which are less soluble separate out while the iodides remain in solution (mother liquor). Iodine is recovered by passing chlorine through the mother liquor.

$$2I^- + Cl_2 \longrightarrow 2Cl^- + I_2$$

It is purified by sublimation.

Isolation of iodine from iodates (recovered from *chile saltpetre*) is affected by its reduction with sodium bisulphite.

$$2IO_3^- + 5HSO_3^- \longrightarrow 3HSO_4^- + 2SO_4^{2-} + H_2O + I_2$$

Preparation of Astatine. Astatine has not been found amongst the products of natural radioactive decay. Astatine of mass number 211 is the longest lived isotope. But even this has a half-life period of 7·5 hours. Astatine of mass number 211 can be made by bombarding bismuth with alpha particles.

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{211}_{85}At + 2^{1}_{0}n$$

It is isolated from bismuth by vacuum sublimation.

PROPERTIES OF ELEMENTS OF GROUP 17

Properties of Fluorine. Physical Properties. Fluorine is a pale greenish yellow gas, somewhat paler than chlorine. It possesses characteristic strong pungent odour resembling that of a mixture of ozone and chlorine. It can be condensed to a yellow liquid boiling at −188°C and a pale yellow solid melting at −223°C. The relative vapour density indicates a diatomic molecule, F_2.

Chemical Properties. Chemically, fluorine is the most reactive of all the elements. It combines directly with almost all other elements (except nitrogen and oxygen) with extreme vigour forming fluorides. It also attacks many other compounds, particularly organic compounds, breaking them down to fluorides. Organic compounds generally burn in the gas.

The more important reactions of fluorine are given below.

1. Combination with hydrogen. Fluorine directly combines with hydrogen with explosive violence even in the dark, forming hydrogen fluoride.

The fluoro-hydrogen flame has a very high temperature of about 4000°C.

2. Combination with metals. Fluorine attacks *all metals* forming fluorides, the intensity of attack depending upon the nature of the metals. Thus,

1. Alkali metals and alkaline earth metals burn spontaneously in the presence of fluorine gas to produce the corrosponding flourides.

2. Metals like magnesium, aluminium, nickel and silver require a little warming to start the reaction.

3. Metals like gold and platinum are a little resistant and are attacked on heating to about 300°C.

4. Metals like copper, steel and nickel get covered with a superficial impervious layer of fluoride which resists further attack. Hence, vessels of these metals are quite suitable for preparing and storing the gas.

5. Metals such as palladium and iridium are attacked at about 500°C.

3. Combination with non-metals. Non-metals such as carbon, sulphur, phosphorus, boron, silicon burn in fluorine forming the highest fluorides (*e.g.,* CF_4, PF_5, SiF_4, SF_6, etc.). **Metalloids** such as arsenic and antimony burn in the gas forming lower fluorides, *e.g.,*

$$2Sb + 3F_2 \longrightarrow 2SbF_3$$

4. Action of water. Fluorine reacts vigorously with water giving oxygen and ozone.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

At the same time, some oxygen fluoride (OF_2) is also formed.

A jet of steam burns in an atmosphere of fluorine like an illuminating gas.

5. Oxidising action. Since fluorine readily attacks water giving oxygen and ozone, it acts as a powerful oxidising agent. In fact, fluorine is the strongest chemical oxidising agent. It oxidises chlorates

to perchlorates, chromic salts to dichromates and a warm solution of potassium bisulphate to potassium peroxodisulphate.

$$2KHSO_4 + F_2 \longrightarrow 2HF + K_2S_2O_8$$

It oxidises vigorously all the common reducing agents.

6. Action on glass and quartz. Fluorine readily attacks glass and quartz forming silicon fluoride, SiF_4. But the reaction is extremely slow when the reactants are thoroughly freed from adsorbed water. Hence, *dry fluorine* can be easily manipulated in *dry* glass apparatus.

7. Action on hydrocarbons. As already mentioned, most of the organic compounds burn or explode when brought in contact with fluorine. The reaction of fluorine with hydrocarbons is also explosive. The initial reaction in the case of methane, for example, is

$$CH_4 + 2F_2 \longrightarrow C + 4HF$$

However, by diluting fluorine with nitrogen, **fluorination of hydrocarbons** has been successfully carried out. For this purpose, a mixture of the hydrocarbon, fluorine and nitrogen is passed through a metal tube packed with copper gauze, at a temperature of 160–350°C. Fluorine attacks copper forming copper fluoride which acts as a catalyst. The resulting product is a complex mixture. For example, methane yields a mixture of CH_3F, CH_2F_2, CHF_3, CF_4, C_2F_6 and C_3F_8. These **fluoro compounds** have acquired great industrial importance as refrigerants and for use in air conditioning.

9. Action on other compounds. Fluorine also reacts with ammonia giving nitrogen and a small amount of NF_3 along with some other products. Sulphur dioxide and hydrogen sulphide are also decomposed by fluorine. It does not react with nitrogen even at a very high temperature.

10. Combination with halogens. Fluorine reacts with halogens forming a number of compounds known as *inter-halogen compounds*. For example,

1. It reacts with chlorine at 250°C forming chlorine monofluoride, ClF. With excess of fluorine, chlorine trifluoride, ClF_3, results. Both ClF and ClF_3 are colourless gases.

2. Fluorine reacts with bromine forming bromine trifluoride. BrF_3 which is a colourless liquid. With excess of fluorine, a colourless solid, bromine pentafluoride, BrF_5, is obtained.

3. Fluorine also attacks iodine forming iodine pentafluoride, IF_5, which is a colourless solid. With excess of fluorine and at 300°C, iodine heptafluoride, IF_7, is formed.

Uses. Fluorine is now extensively used for the preparation of fluorine compounds on large scale. Difluorodichloromethane, CF_2Cl_2, sold under the commercial name, **freon-12**, is a valuable fluorine compound. It is used in refrigeration and air conditioning in place of ammonia and sulphur dioxide. It has an advantage in being non-toxic and non- flammable. Freon is also used as a solvent for D.D.T. and other insecticides. A new plastic, **teflon**, which is resistant to the action of acids, alkalies and oxidising agents, is polymerised tetrafluoroethylene, $(F_2C = CF_2)_n$.

Fluroine compounds, such as sodium fluoride and cryolite, are used as insecticides. Small amounts of fluorides in drinking water are believed to be useful in preventing tooth decay. D.D.F.T., which is similar to D.D.T., is an extremely active fungicide and fumigant.

Uranium hexafluoride (UF_6) is used in the separation of isotopes of uranium. Sulphur hexafluoride (SF_6), because of its high dielectric constant and insulating properties, is used in X-ray and high voltage machines.

Peculiarities of Fluorine, the First Element of the Group

The first element, fluorine, differs considerably from the other members of the halogen family as is generally the case with the first members of other groups of *s* and *p* block elements. This difference is

due to the following characteristics of fluorine :

(*i*) *Small size*

(*ii*) *Very high electronegativity* (fluorine, in fact, is the most electronegative of all the elements).

(*iii*) *Non-availability of d orbitals* in the valency shell.

The **main points of difference** are as follows.

1. Since fluorine is the most electronegative element, it exhibits *only a negative oxidation state* of –1. *It does not show any positive oxidation state.* The remaining members, on the other hand, show negative as well as positive oxidation states. Thus, oxidation states of +1, +3, 4, +5, +6 and +7 are quite frequent amongst halogens other than fluorine.

2. Flourine is most reactive amongst the halogens. This is due to the low energy of the F – F bond, the value for which is 158·8 kJ per mole. The bond is weak because of the repulsion between the non-bonding electrons in the molecule.

The X – X bond is much stronger in Cl_2, Br_2 and I_2. This is due to the hybridisation of *p* and *d* orbitals.

3. Again, on account of high electronegativity, fluorine extensively enters into hydrogen bond formation in its hydrides. Other elements, on account of comparatively small electronegativities, do not form hydrogen bonds. Thus, while HCl, HBr and HI are gaseous under ordinary conditions, HF is a liquid (b.p. 19·5°C). This is because HF exists as associated molecule $(HF)_n$ because of hydrogen bonding.

4. Maximum covalency of fluorine is *one* because it cannot expand its valency shell beyond the octet as there are no *d* orbitals in the valency shell. Other elements, on the other hand, can exercise covalencies upto 7 because of the availability of vacant *d* orbitals.

5. The hydride of fluorine (HF) in aqueous solution behaves only as a very weak acid whereas the other hydrides under similar circumstances behave as strong acids. The cause of this behaviour has been explained in a subsequent section.

6. The salts of hydrofluoric acid (fluorides) also differ from the corresponding salts (halides) of the other hydracids. Thus, while silver fluoride (AgF) is soluble, the other silver halides are insoluble. Similarly, while calcium fluoride (CaF_2) is insoluble, the other calcium halides are soluble.

7. Most of the fluorides are ionic ; these contain the F^- ion. This is due to small size of F^- ion, its radius being 1·36 Å. Chlorides, bromides and iodides have mostly molecular lattices.

8. The fluoride ion, by a process of hydrogen bonding, forms the anion, HF_2^-. This tendency is almost absent with the other halides. Thus, the compound KHF_2, written as $K^+(F\cdots\cdots H–F)^-$, is well known but the corresponding compounds of other halogens (*e.g.*, $KHCl_2$ and $KHBr_2$) are unknown.

9. The fluoride ion has great tendency to form complex ions, *e.g.*, $[AlF_6]^{3-}$, $[FeF_6]^{3-}$, in which the metal atom exhibits a higher covalency. Aluminium and iron exhibit coordination number 6 in these complexes. The other halide ions show this tendency to a much smaller extent.

10. Fluorine, on account of its high electronegativity, readily transforms sulphur into +6 oxidation state, forming thereby a stable hexafluoride SF_6. No other halogen forms the hexahalide.

11. Fluorine, because of the absence of *d* orbitals in its valency shell, does not form any polyhalides. *Other halogens frequently associate with the halide ions forming polyhalide ions because of the vacant d orbitals in their valency shell. Thus, we have* I_3^-, Br_3^-, Cl_3^- *ions but no* F_3^- *ion.*

Properties of Chlorine, Bromine and Iodine. Some important properties of chlorine, bromine and iodine are summed up in Table 3. Properties of fluorine are also included in the table for the sake of comparison.

TABLE 3

Chemical Properties of the Halogens

Property	Fluorine	Chlorine	Bromine	Iodine
1. Combination with hydrogen	Combines most readily with explosive violence even in the dark	Combines readily with explosion in sunlight but slowly in the dark	Combines only on heating	Combines on heating and in the presence of a catalyst
2. Combination with non-metals	Combines directly with all non-metals except nitrogen	Combines directly with all non-metals except N_2, O_2 and C	Combines directly with all non-metals except N_2, O_2, C and Si	Combines only with H_2, P, As and other halogens
3. Combination with metals	Most of the metals burn to form fluorides	Many metals burn to form chlorides	Most of the metals are attacked giving bromides	Combines with metals giving iodides
4. Reaction with water	Decomposes readily giving HF, O_2 and ozone	Decomposes slowly to give HCl and O_2	Decomposes very slowly but only in sunlight giving HBr and O_2	Little or no reaction
5. Oxidising property	Oxidises energetically	Oxidises readily	Oxidises slowly	Little or no oxidising action
6. Reaction with oxidising agents	No reaction	No reaction	Reacts with ozone to a small extent	Is oxidised by ozone as well as by HNO_3 to give I_2O_5 which with water gives HIO_3
7. Reaction with alkalies	Reacts briskly giving flourides, oxygen and water	Reacts readily giving chlorides and hypochlorites in cold and chlorides and chlorates in hot solutions	Reacts less readily giving bromides and hypobromites in cold and bromides and bromates in hot solutions	Reacts slowly forming iodides and hypoiodous acid and finally an iodate.
8. Bleaching action	No reaction	Moist chlorine is a good bleaching agent	Moist bromine shows a slow beaching action	No bleaching action
9. Reaction with hydrocarbons	Hydrocarbons are decomposed	Substitution of hydrogen takes place	Substitution of hydrogentakes place slowly	Very little action

Properties of Astatine. On account of its radioactive nature and short half-life period, the chemistry of astatine has been studied chiefly by tracer techniques. It resembles iodine in being soluble in organic solvents and in forming At^- and AtO_3^- ions similar to I^- and IO_3^- ions.

COMPOUNDS OF GROUP 17 ELEMENTS

I. A Comparative Study

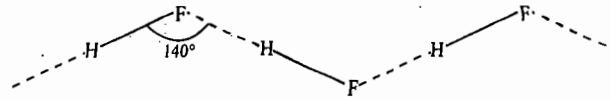
1. HYDRIDES OF THE HALOGENS (HYDROGEN HALIDES)

Formation. All the halogens combine with hydrogen to form hydrides (hydrogen halides) :

$$X_2 + H_2 \longrightarrow 2HX$$

But, the readiness with which the halogens combine with hydrogen decreases from fluorine to iodine. Thus, hydrogen combines explosively with fluorine even in the dark ; also explosively with chlorine but in the presence of light ; non-explosively with bromine and that too on heating to about 500°C and only slowly with iodine on heating in the presence of platinum as a catalyst. The reaction with iodine is reversible and incomplete.

Properties 1. Physical state. While, under ordinary conditions, HCl, HBr and HI are gases, HF is a liquid (b.p. 19·5°C). The unexpectedly high boiling point of HF is due to hydrogen bonding as a result of the high electronegativity of fluorine. Consequently, hydrogen fluoride exists as an associated species and may be described as $(HF)_n$. The crystalline HF has been found to have the following zig-zig structure :



2. Stability. The stability of the hydrides also decreases as we go down the group. Thus, hydrogen fluoride is most stable whereas hydrogen iodide is least stable. For example, while HF and HCl are not dissociated even at 1200°C, HBr is dissociated to the extent of 1 per cent and HI is dissociated to the extent of 20 per cent even at 400°C.

3. Reducing character. Since stability of hydrides decreases on moving from HF to HI, the reducing property increases in the same order. Thus, HF is not a reducing agent at all. HCl is a mild reducing agent, HBr is a stronger reducing agent while HI is the strongest reducing agent of all the hydrides.

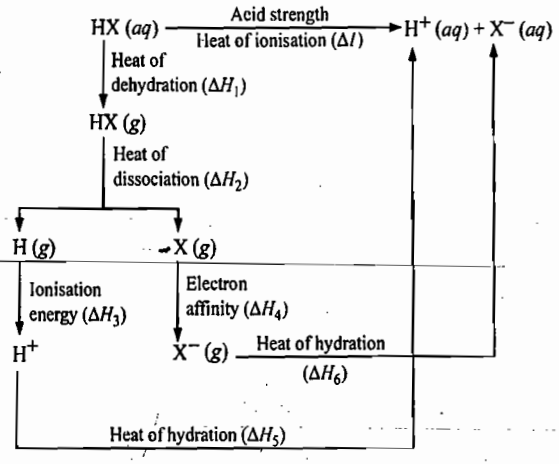
4. Nature of bonds. All the halides are essentially covalent compounds with some ionic character. The ionic character, which depends upon electronegativity difference between H and the halogen atom, decreases in the order :

$$HF > HCl > HBr > HI$$

The predominant covalent nature is indicated by their low melting and boiling points and also by the fact that the compounds in pure state are bad conductors of electricity.

5. Relative strengths as acids. Hydrogen halides in the gaseous state are essentially covalent. In aqueous solutions, however, they ionise and act as acids. HF is only slightly ionised but HCl, HBr and HI are almost completely ionised. In aqueous medium, the relative strengths of the acids have been found to follow the sequence HI > HBr > HCl > HF. In other words, of all the halogen hydracids, HF is the weakest and HI is the strongest acid .

At first sight, the above sequence appears to be rather surprising. Since fluorine is the most electronegative halogen, the electronegativity difference should be the maximum in HF and should gradually decrease as we move towards iodine through chlorine and bromine. Thus, the hydride HF should be more ionic in character than any other hydride and consequently, it should be the strongest acid. Actually, it is just the reverse. This has been explained with the help of the **Born-Haber cycle,** taking into consideration the various factors which determine the strengths of the acids in aqueous medium.



The ionisation reaction

$$HX(aq) \longrightarrow H^+(aq) + X^-(aq)$$

the extent of which determines the strength of the acid, involves different stages which can be represented in the form of **Born-Haber cycle,** as shown.

Evidently, the stages involving dehydration of HX(*aq*), dissociation of HX(*g*) into H(*g*) and X(*g*), conversion

of H(g) to $H^+(g)$ will be accompanied by the *absorption* of heat. The other stages involving conversion of X(g) into $X^-(g)$ and hydration of $H^+(g)$ and $X^-(g)$ will be accompanied by the *evolution* of heat. Hence, the heat of ionisation (ΔI) is equal to the sum of all the energy terms and will be given by the expression :

$$\Delta I = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - (\Delta H_5 + \Delta H_6)$$

These values in kJ per mole for the various halogen acids are given below :

Acid	ΔH_1	ΔH_2	ΔH_3	ΔH_4	$\Delta H_5 + \Delta H_6$	ΔI
HF	48	566	1312	−322	−1606	−12
HCl	18	431	1312	−384	−1472	−59
HBr	21	366	1312	−324	−1438	−63
HI	23	299	1312	−295	−1396	−57

The values of ΔI can easily explain the feasibility of the ionisation reaction. *The larger the negative value of ΔI, the greater is the feasibility of the ionization reaction and hence the greater is the strength of the halogen acid.* It is clear from the above table that the ΔI values for all the halogen acids are negative indicating that all of them can easily ionise. However, the value for HF is small compared with the values for other acids. Hence, HF is the weakest acid. The values also explain the gradually increasing strengths of HCl and HBr but they fail to explain the relative strength of HI. According to these values, the sequence of increasing strengths should be HF, HI, HCl and HBr. The discrepancy has been explained on the basis of *entropy change* ΔS accompanying the process of ionisation, the discussion of which, however, is beyond the scope of the book.

A close perusal of the data given in the above table reveals that the lower acid strength of HF in comparison to HCl, HBr and HI is largely due to its higher bond dissociation energy ΔH_2.

These compounds have been discussed further under the heading Important Compounds of Group 17 Elements.

2. OXIDES OF THE HALOGENS

All the halogens form oxides. Twelve such oxides are positively known. These are listed in Table 4 along with some of their physical characteristics. The oxides of fluorine are considered as oxygen fluorides since fluorine is more electronegative than oxygen.

TABLE 4
Oxides of the Halogens

Fluorine	Chlorine	Bromine	Iodine
OF_2 (Pale yellow gas, b.p. −145°C)	Cl_2O (orange liquid, b.p. 2°C)	Br_2O (dark-brown liquid, fr.p. − 10°C)	
O_2F_2 (yellowish orange solid, stable below − 95°C)	ClO_2 (yellowish-green liquid, b.p. 11°C)	BrO_2 (yellow solid, stable below − 40°C)	
O_3F_2 (blood-red viscous liquid, stable below −163°C)	Cl_2O_6 (dark red liquid, fr. p. 4°C)	BrO_3 (white crystalline solid, stable below − 70°C)	I_2O_5 (white solid, m.p. 300°C) decomposes to I_2 and O_2 above 300°C
O_4F_2 (reddish-brown solid, stable below −183°C)	Cl_2O_7 (colourless oily liquid, stable)		

Most of these oxides are unstable and are liable to explode. All the oxides of halogens are powerful oxidising agents.

Structures. The structures of only the monoxides would be discussed here. All the three monoxides, *viz.*, OF_2, Cl_2O and Br_2O have **angular structure** being formed by sp^3 hybridisation of oxygen orbitals.

The bonds will, evidently, be distorted because two of the four orbitals are occupied by lone pairs of electrons. The bond angle, therefore, will be different from 109·5°, the angle of regular tetrahedron. It is interesting to note that, while the bond angle FOF is less than 109·5°, being 103°, the bond angle ClOCl is more than 109·5°, being 110·9° (Fig. 4). This can be explained as follows :

In F_2O, since fluorine is more electronegative than oxygen, the bonding electrons lie nearer to the fluorine atom. Consequently, the repulsion between the bond pairs is less than the repulsion between the lone pairs and hence the bond angle is less then 109·5°.

In Cl_2O, since oxygen is more electronegative than chlorine, the bonding electrons lie closer to the oxygen atom. Consequently, the repulsion between the bond pairs is more than the repulsion between lone pairs and hence the bond angle is greater than 109·5°.

Since bromine is less electronegative than chlorine, the bonding electrons in Br_2O will be drawn all the more towards oxygen and hence the repulsion between the bond pairs will be even greater. Thus, the angle BrOBr is even greater than 110·9°.

The bond angles in various halogen monoxides are as follows :

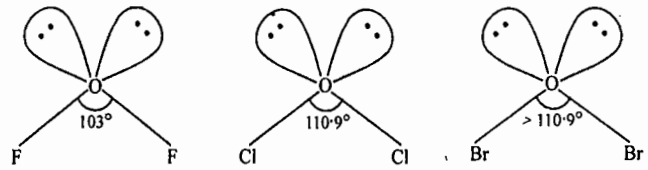


Fig. 4. Bond angles in various halogen monoxides.

3. OXOACIDS OF THE HALOGENS

Fluorine does not form oxoacids. This is because fluorine is more electronegative than oxygen. The oxoacids of chlorine and iodine, particularly containing more oxygen (*e.g.*, perchloric acid, $HClO_4$, iodic acid, HIO_3 and periodic acids HIO_4 and H_5IO_6) are fairly stable and are known in pure state. This is consistent with the observation that increase in the oxidation state of the halogen atom from +1 to +7 leads to increased stability of its oxides.

Oxoacids of bromine are known only in solution or in the form of their salts. For example, $HBrO_3$ is known only in solution and $HBrO_2$ only in the form of its salts. Perbromic acid, $HBrO_4$, is unknown.

The strength of oxoacids in which the halogens are in the same oxidation state, generally, decreases with rise in atomic number of the halogen. Thus, $HClO_3$ is the strongest while HIO_3 is the weakest of all the oxoacids in which oxidation state of the halogen is 5.

The halate ion (ClO_3^-, BrO_3^- or IO_3^-) is formed by sp^3 hybridisation and has a **pyramidal structure.**

The names, formulae, structures, stability and strengths as acids of important oxoacids of the halogens are given in Table 5.

TABLE 5
Important Oxoacids of the Halogens

Names of the acids and their salts	Oxidation state of the halogen in the acid	Oxoacids of : Cl	Br	I	Stability	Acid strength
Hypohalous, Hypohalites	+1	HClO	HBrO	HIO	Stability *decreases* on moving down	Acidity *increases* on moving down
Halous, Halites	+3	$HClO_2$				
Halic, Halates	+5	$HClO_3$	$HBrO_3$	HIO_3		
Perhalic, Perhalates	+7	$HClO_4$	$HBrO_4$	HIO_4		

Oxides and oxoacids of the halogens have been discussed further under the heading Important Compounds of Group 17 Elements.

II. Some Important Compounds of Group 17 Elements

HYDROGEN HALIDES

All the halogens give hydrogen halides, a brief discussion of which is given below.

Hydrogen Fluoride. On a small scale, hydrogen fluoride (*anhydrous*) is obtained by heating dry potassium hydrogen fluoride in a copper retort connected with a copper condenser.

$$KHF_2 \longrightarrow KF + HF$$

Industrially, hydrogen fluoride is obtained by heating *fluorspar* (CaF_2) with concentrated sulphuric acid in a lead vessel.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Hydrogen fluoride distils over and the vapours are condensed in water taken in lead receivers. Aqueous hydrogen fluoride (or hydrofluoric acid) thus obtained is stored in *gutta parcha* or wax bottles. It cannot be stored in glass or silica bottles as it attacks silicates as well as silica :

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

$$CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

This action of hydrofluoric acid on silica and silicates is used for *etching glass*.

Hydrogen Chloride. In laboratory, hydrogen chloride is prepared by heating sodium chloride with concentrated sulphuric acid. The gas is dried by passing through concentrated sulphuric acid.

Hydrogen chloride is manufactured by reacting chlorine with an excess of hydrogen.

It is highly soluble in water. It forms a constant boiling mixture having 20·4 per cent of HCl, boiling at 110°C.

Hydrogen Bromide and Hydrogen Iodide. Unlike hydrogen chloride, hydrogen bromide and hydrogen iodide cannot be prepared by heating a bromide or an iodide with concentrated sulphuric acid. The reason is that HBr and HI evolved are strong reducing agents. They reduce sulphuric acid to sulphur dioxide and get themselves oxidised to bromine or iodine, as the case may be.

This can be avoided by heating bromide or iodide with phosphoric acid instead of sulphuric acid. Since phosphoric acid is not an oxidising agent, it is not attacked by HBr or HI formed during the reaction.

Properties. All the hydrogen halides are colourless gases with pungent odour. They fume in air and are extremely soluble in water. The important physical properties of the anhydrous and aqueous hydrogen halides are given in Table 6.

TABLE 6
Properties of Anhydrous and Aqueous Hydrogen Halides

Property	Hydrogen fluoride, HF	Hydrogen chloride, HCl	Hydrogen bromide, HBr	Hydrogen iodide, HI
Physical state (15°C)	Liquid	Gas	Gas	Gas
Boiling point (°C)	19·4	–85	–67	–35·5
Melting point (°C)	–83	–111	–86	50·8
Solubility in water at 0°C (g/litre)	85·3	42·0	49·0	57·1
B.P. (°C) of constant boiling mixture	120	110	126	127
Composition of constant boiling mixture	36% HF	20·4% HCl	47% HBr	57% HI

Property	Hydrogen fluoride, HF	Hydrogen chloride, HCl	Hydrogen bromide, HBr	Hydrogen iodide, HI
Heat of formation (kJ mol^{-1})	–271·1 (gas)	–92·3 (gas)	–36·4 (gas)	+ 24·5 (gas)
Reducing action	Not a reducing agent	Has slight reducing properties	Strong reducing agent	Stronger reducing agent
Hydrogen bonding	Maximum	Little	Very little	Very little
Bond energy (kJ mol^{-1})	574·0	428·1	362·5	294·6
Stength as an acid in aqueous solution	Weak acid	Very strong acid	Very strong acid	Very strong acid
Apparent degree of dissociation in 0·1 M solution at room temperature	0·08	0·93	0·94	0·95
Solubility of silver salt (g/100 g)	172	0·00154	0·000084	0·000028
Solubility of calcium salt (g/100 g)	0·0016	42·7	58·8	67·6
Heating with a mixture of MnO_2 and H_2SO_4	—	Chlorine gas evolved by the oxidation of HCl.	Bromine (reddish-brown vapour) is evolved. Turns starch paper yellow.	Iodine (violet vapour) is evolved. Turns starch paper violet.
Addition of silver nitrate solution	No precipitate AgCl, insoluble in	White precipitate of tate of AgBr insolu- dilute nitric acid but soluble in ammonia.	Pale yellow precipi- of AgI, insoluble in ble in dilute nitric acid but partly soluble in ammonia	Yellow precipitate dilute HNO_3 as well as in ammonia.
Addition of calcium chloride solution	White precipitate of calcium fluoridesoluble in concentrated HCl (distinction from sulphate)	No. ppt.	No ppt.	No ppt.
Addition of lead acetate solution	No ppt.	White ppt. of $PbCl_2$	White ppt. of $PbBr_2$	Yellow ppt. of PbI_2
Addition of chlorine water	–	–	Bromine liberated. Add carbon disulphide, orange solution.	Iodine liberated. Add carbon disulphide, violet solution.
Confirmatory tests	Heat with conc. H_2SO_4. Hold a glass rod moistened with water in the mouth of the tube, a white film of silicic acid is formed.	Heat with $K_2Cr_2O_7 + H_2SO_4$. Chromyl chloride fumes. When passed into lead acetate solution, a yellow ppt. of lead chromate is formed	Action of chlorine water given above serves as the confirmatory test.	Action of chlorine water given above serves as the confirmatory test.

OXIDES OF FLOURINE

Only two oxides of fluorine are well known. These are described below.

Difluorine Oxide, F_2O. This is prepared by passing fluorine gas through sodium hydroxide solution.

$$2NaOH + 2F_2 \longrightarrow F_2O + 2NaF + H_2O$$

It is a pale yellow gas which is highly poisonous.

It decomposes in the presence of water to yield hydrogen fluoride.

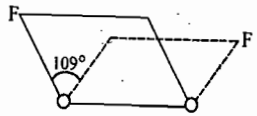
$$H_2O + F_2O \longrightarrow 2HF + O_2$$

F_2O is used as a rocket fuel.

Structure. The structure of F_2O has already been described.

The orbitals of central oxygen atom are sp^3 hybridised. Two of the sp^3 hybrid orbitals are occupied by lone pairs of electrons and the other two are involved in sigma bonding with the two fluorine atoms. The FOF angle is 103°. The reason for the angle being considerably less than the tetrahedral angle of 109·5° has already been discussed.

Difluorine Dioxide, F_2O_2. This compound is prepared by passing an electric discharge through a mixture of fluorine and oxygen at a very low temperature. It is an unstable yellowish orange solid. It is a very good fluorinating and oxidising agent.



Structure. The two planes, each containing the O – O bond and one of the two O – F bonds, are at an angle of 109° to each other, as shown.

OXIDES OF CHLORINE

Chlorine forms a number of oxides such as Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7. All of them are unstable and highly reactive. All the four oxides are discussed below in some details.

Dichlorine Oxide, Cl_2O. This is prepared by passing chlorine over freshly precipitated mercuric oxide.

$$2Cl_2 + 2HgO \longrightarrow HgO.HgCl_2 + Cl_2O$$

It is an orange liquid below 2°C. It boils at 2°C to give yellowish brown gas. At higher temperatures, the gas explodes.

It undergoes photochemical decomposition giving oxygen and chlorine.

$$2Cl_2O + h\nu \longrightarrow 2Cl_2 + O_2$$

It dissolves in water to form hypochlorous acid with which it exists in equilibrium in aqueous solution.

$$Cl_2O + H_2O \rightleftharpoons 2HOCl$$

Cl_2O is, therefore, regarded as the anhydride of hypochlorous acid.

Its gaseous mixture with ammonia explodes violently. The overall reaction may be represented as

$$3Cl_2O + 10NH_3 \longrightarrow 2N_2 + 6NH_4Cl + 3H_2O$$

Structure. As already discussed, Cl_2O has an angular structure, as shown in Fig. 5. The Cl – O – Cl bond angle is 110·9° and O – Cl bond lengths are 1·70 Å each. The oxygen orbitals are sp^3 hybridised. Two of the four sp^3 hybrid orbitals are occupied by lone pairs of electrons and the remaining two are used in forming sigma bonds with the two chlorine atoms.

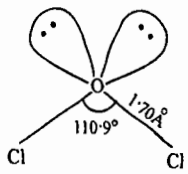


Fig. 5. Structure of Cl_2O.

Chlorine Dioxide, ClO_2. It is prepared by treating silver chlorate with dry chlorine at 90°C.

$$2AgClO_3 + Cl_2 \xrightarrow{90°} 2AgCl + 2ClO_2 + O_2$$

It can also be prepared by the action of chlorine on sodium chlorite.

$$2NaClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2NaCl$$

ClO_2 is evolved as a paramagnetic yellowish-green gas which is condensed by cooling to give a coloured liquid (b.p. 11°C). It is a powerful oxidising and chlorinating agent. It dissolves in water exothermically.

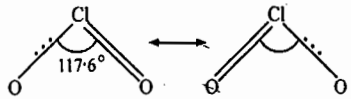
It reacts with alkalies to form chlorites and chlorates and thus can be regarded as a mixed anhydride of chlorous acid ($HClO_2$) and chloric acid ($HClO_3$).

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

The aqueous solution of ClO_2 undergoes photochemical decomposition to give a mixture of chloric acid and hydrochloric acid.

$$ClO_2 + H_2O \xrightarrow{h\nu} HCl + HClO_3$$

Structure. It has an angular structure with O – Cl – O bond angle of 117·6° and Cl – O bond length of 1·47Å. Since it contains odd number of electrons, the molecule may be considered to be having a three-electron bond in addition to a normal electron pair bond. Since both the ClO bond distances are equal, its structure is believed to be a resonance hybrid of the two structures :



The three-electron bond accounts for the shorter bond length and its paramagnetic character.

Dichlorine Hexoxide, Cl_2O_6. It is obtained by mixing chlorine dioxide with ozonised air at 0°C.

$$2ClO_2 + 2O_3 \longrightarrow 2Cl_2O_6 + 2O_2$$

It is a dark red liquid which freezes at 6°C. It is a strong oxidising agent. It reacts with alkalies to give chlorates and perchlorates.

$$Cl_2O_6 + 2NaOH \longrightarrow NaClO_3 + NaClO_4 + H_2O$$

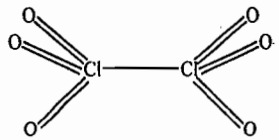
Hydrolysis of Cl_2O_6 yields a mixture of chloric and perchloric acids.

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

Liquid Cl_2O_6 is diamagnetic and gives diamagnetic solution in CCl_4. However, its vapours are paramagnetic due to its partial dissociation to chlorine trioxide having an unpaired electron.

$$Cl_2O_6 \rightleftharpoons 2ClO_3$$

The structure of Cl_2O_6 has not been known with certainty. However, its dissociation to ClO_3 supports the structure as shown containing Cl – Cl linkage. Each Cl in Cl_2O_6 molecule appears to be sp^3 hybridised.



Dichlorine Heptoxide, Cl_2O_7. It is obtained by dehydrating perchloric acid with phosphorus pentoxide.

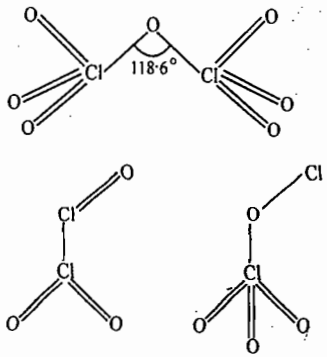
$$2HClO_4 \xrightarrow{P_2O_5} Cl_2O_7 + H_2O$$

It is a colourless oily liquid and dissolves in water giving perchloric acid.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

It is thus an anhydride of perchloric acid. Cl_2O_7 is the only exothermic oxide of chlorine and is thermodynamically more stable than any of the other oxides of chlorine. It is not so strong an oxidising agent as the other oxides of chlorine. It is less reactive than the lower oxides of chlorine.

Structure. Chlorine heptoxide has the structure, as shown, in which Cl – O – Cl angle is 118·6°.



Dichlorine trioxide and Dichlorine tetraoxide. Recently, the oxides Cl_2O_3 and Cl_2O_4 have also been synthesised. The former is a dark brown solid and decomposes into Cl_2 and O_2 at 0°C and the latter is a pale yellow liquid which decomposes at room temperature into Cl_2, O_2, ClO_2 and Cl_2O_6. The structures of Cl_2O_3 and Cl_2O_4 are as shown.

OXIDES OF BROMINE

Bromine forms a number of oxides, the most well known amongst which are Br_2O, BrO_2 and BrO_3.

Dibromine Oxide, Br_2O. It can be prepared by dropping bromine over dry HgO at 50 – 70°C.

$$2Br_2 + 2HgO \longrightarrow HgBr_2.HgO + Br_2O$$

It is a dark brown liquid which freezes at – 17·5°C. It is the anhydride of hypobromous acid, HBrO. It forms hypobromite with cold alkalies. It oxidises iodine to iodine pentoxide. Its structure is similar to that of Cl_2O.

Bromine Dioxide, BrO_2. It is obtained by passing an electric discharge through an oxygen-bromine mixture, at low pressure, at a temperature below –100°C.

It can also be prepared by low temperature ozonolysis of bromine.

$$Br_2 + 4O_3 \xrightarrow[CF_3Cl]{-78°C} 2BrO_2 + 4O_2$$

It is stable below – 40°C when it exists as a yellow solid. It dissolves in alkalies giving bromides and bromates.

$$6BrO_2 + 6NaOH \longrightarrow NaBr + 5NaBrO_3 + 3H_2O$$

Bromine Trioxide, BrO_3. It is prepared by the action of slow electric discharge on a mixture of bromine and oxygen between – 10°C and 20°C.

BrO_3 is a white crystalline solid which is stable only below – 70°C. It is a strong oxidising agent. It gives acidic solution in water.

OXIDES OF IODINE

Iodine forms oxides such as I_2O_4, I_4O_9 and I_2O_5. Among these, I_2O_5 is the most stable and is described below.

Iodine Pentoxide, I_2O_5. It is prepared by heating iodic acid to about 240°C.

$$2HIO_3 \xrightarrow{240°C} I_2O_5 + H_2O$$

It can also be prepared by heating iodine with conc. HNO_3.

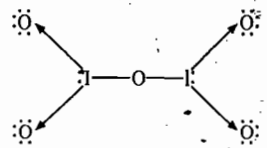
$$I_2 + 10HNO_3 \longrightarrow I_2O_5 + 10NO_2 + 5H_2O$$

It is a white solid which decomposes to iodine and oxygen above 300°C. With water, it forms iodic acid, HIO_3. It has such a strong affinity for water that the commercial I_2O_5 exists as $I_2O_5.HIO_3$. It is a strong oxidising agent. It oxidises CO to CO_2 quantitatively liberating iodine which can be titrated against sodium thiosulphate.

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

Hence, I_2O_5 is used for the detection and estimation of carbon monoxide. This forms the basis of analytical method for determining CO in atmosphere or in other gaseous mixtures.

Structure. The structure of I_2O_5 has been determined with a fair degree of reliability from IR spectrum data. It has two pyramidal IO_3 units joined through a common oxygen atom. Each I atom in I_2O_5 has a lone pair of electrons as well.



OXOACIDS OF THE HALOGENS AND THEIR SALTS

A few of the oxaocids of the halogens and their salts are discussed below.

Hypohalous acid (HOX) and Hypohalites. Hypohalous acids (HOCl, HOBr and HOI) are unstable and are known only in solution. These are obtained in aqueous solution by mixing suspension of mercuric oxide with the halogen concerned. Thus, **hypochlorous acid (HOCl)** is obtained by shaking precipitated mercuric oxide in water with chlorine.

$$2Cl_2 + 2HgO + H_2O \longrightarrow HgO.HgCl_2 + 2HOCl$$

The halogen in these acids is present in +1 oxidation state. These are weak acids, the acid strength decreasing with increase in size of the halogen. The dissociation constants of the acids are as follows :

Acid	HOCl	HOBr	HOI
K_a	$2·9\times10^{-8}$	5×10^{-9}	$\sim 10^{-11}$

Thermal stability also decreases in the same order. Thus, HOCl is not only a stronger acid but also more stable than HOBr and HOI. HOI is not only weakest of these weak acids but is also least stable. Their salts are known as **hypohalites.** The most stable hypohalites are those of Li, Ca, Sr and Ba. NaOCl is less stable and cannot be isolated in pure form. KOCl is known only in solution.

Sodium hypochlorite, NaClO is one of the important salts of hypochlorous acid. This is used in bleaching. It is prepared by the electrolysis of brine. The following reactions take place at the cathode and anode.

At cathode : $2H^+ + 2e^- \longrightarrow H_2\,(g)$

At anode : $2Cl^- \longrightarrow Cl_2\,(g) + 2e^-$

With the discharge of H^+ ions, the concentration of OH^- ions rises at the cathode while chlorine is released at the anode. The electrolyte is kept agitated so that the OH^- ions and chlorine gas come into intimate contact and react as follows :

$$2OH^- + Cl_2 \longrightarrow ClO^- + Cl^- + H_2O$$

In this way, the solution becomes progressively richer in NaOCl and there is very little evolution (loss) of chlorine.

Hypohalite ions, XO^-, are all unstable. They disproportionate in basic solution as follows :

$$3XO^- \longrightarrow XO_3^- + 2X^-$$

The hypochlorite ion OCl^- changes to chlorate ion, ClO_3^- by the above mechanism only in *hot* solution. The conversion of hypobromite ion, BrO^- to bromate ion, BrO_3^- takes place rapidly at 50°C while that of hypoiodite ion, IO^- to iodate ion, IO_3^- takes place even at room temperature.

Structure. The hypochlorite ion, ClO^-, has a structure in which a half-filled *p* orbital of chlorine atom overlaps with a half-filled *p* orbital of oxygen atom to form the Cl – O sigma bond.

Bleaching Powder. It is obtained by passing chlorine over slaked lime.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaCl(OCl) + H_2O$$

When treated with even such a weak acid as CO_2, most of the chlorine gets evolved.

$$CaCl(OCl) + H_2O + CO_2 \longrightarrow CaCO_3 + H_2O + Cl_2$$

Bleaching powder is a mixed salt of HCl and HOCl, *viz.*, Cl – Ca – OCl and is used as a convenient source of chlorine.

Halous acids (HXO_2) and Halites. Only chlorous acid, $HClO_2$, is known and that, too, in solution. It contains chlorine in +3 oxidation state. It is a stronger acid ($K_a = 1{\cdot}1\times10^{-2}$) than hypochlorous acid, ($K_a = 2{\cdot}9\times10^{-8}$).

It is obtained in aqueous solution by the action of sulphuric acid on barium chlorite.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_2$$

The decomposition of $HClO_2$ depends upon the concentration of the acid and the concentrations of H^+ and Cl^- ions in the solution. The various decomposition reactions of $HClO_2$ are given below :

$$5HClO_2 \longrightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O$$

$$3HClO_2 \longrightarrow 2ClO_3^- + Cl^- + 3H^+$$

$$HClO_2 \longrightarrow Cl^- + O_2 + H^+$$

Sodium chlorite, $NaClO_2$, which is an important salt of the acid, is obtained by the reaction of ClO_2 with sodium peroxide.

$$Na_2O_2 + 2ClO_2 \longrightarrow 2NaClO_2 + O_2$$

When heated, it changes to sodium chlorate and sodium chloride.

$$3NaClO_2 \longrightarrow 2NaClO_3 + NaCl$$

The aqueous solution of $NaClO_2$ also decomposes on boiling to $NaClO_3$ and NaCl.

Photochemical decomposition of aqueous solution of $NaClO_2$ is *p*H-dependent. Thus, at *p*H 8·4, the solution is photolysed to $NaClO_3$, NaCl and O_2.

$$6NaClO_2 \xrightarrow{h\nu} 2NaClO_3 + 4NaCl + 3O_2,$$

whereas at *p*H 4·0, it is photolysed to $NaClO_3$, $NaClO_4$, NaCl and O_2.

$$10NaClO_2 \xrightarrow{h\nu} 2NaClO_3 + 2NaClO_4 + 6NaCl + 3O_2$$

Structure. The ClO_2^- ion involving sp^3 hybridisation of Cl orbitals has an angular structure as illustrated in Fig. 6.

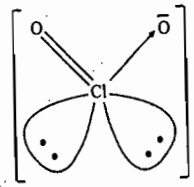


Fig. 6. Angular structure of ClO_2^- ion.

Halic acids (HXO_3) and Halates. Chloric, bromic and iodic acids ($HClO_3$, $HBrO_3$ and HIO_3) are known. The first two are known only in solution while HIO_3 is stable and is known in free state. The halogen in these acids exists in +5 oxidation state. Their salts, known as **halates** (chlorates, bromates and iodates), are quite stable at ordinary temperature.

Chloric and bromic acids are obtained in solution by the action of sulphuric acid on their barium salts. For example,

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$$

Iodic acid, however, separates out as a white crystalline solid on treating iodine with fuming nitric acid.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 4H_2O + 10NO_2$$

These acids are fairly strong ($K_a \approx 10^{-2}$) and are good oxidising agents.

Amongst the halates, chlorates are much more soluble than bromates and iodates. These are obtained conveniently by the electrolysis of *hot* alkali chloride solutions. Thus, **potassium chlorate, $KClO_3$,** is obtained by the electrolysis of hot (70 – 75°C) solution of potassium chloride. The solution is kept

agitated so that the OH^- ions present in the cathodic solution and the chlorine gas liberated at the anode react as follows :

$$6OH^- + 3Cl_2 \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$$

The halates decompose on heating. The chlorates of alkali metals decompose to give either chloride and oxygen,

$$6KClO_3 \longrightarrow 2KCl + 3O_2,$$

or chloride and perchlorates, if the temperature is high.

$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

The bromates of alkali metals decompose to give bromide and oxygen.

$$2KBrO_3 \longrightarrow 2KBr + 3O_2$$

They do not decompose to give perbromates.

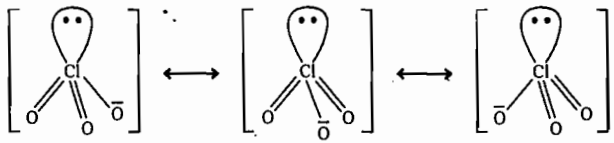
The iodates of alkali metals give iodides and periodates.

$$4KIO_3 \longrightarrow 3KIO_4 + KI$$

Chlorates are used as strong oxidising agents. They are also used in making crackers and matches.

Structure of ClO_3^- ion. The structure of chlorate ion has already been discussed in Chapter 5. It should, therefore, have a bond angle of 109·5°. But since one orbital is occupied by a lone pair of electrons, there is slight distortion and the ion has actually a **pyramidal structure.**

There are two Cl = O bonds and one Cl – O bond in the instant structure of ClO_3^- ion. However, all the three Cl – O bonds are of equal length. This is due to the fact that the actual structure of the ClO_3^- ion is a resonance hybrid of three structures, as shown below :



Perhalic Acids and Perhalates. Perchloric and periodic acids as well as their salts (perchlorates and periodates) exist. Perbromic acid and perbromates are much less stable and are not important. Perbromic acid $HBrO_4$ is isomorphous with $HClO_4$.

Perchloric acid, $HClO_4$. Preparation. 1. It is obtained by heating potassium perchlorate with sulphuric acid at a low pressure of 10 – 20 torr. The acid distils over as a colourless oily liquid.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

2. It can also be prepared by distilling chloric acid under reduced pressure.

$$3HClO_3 \longrightarrow HClO_4 + 2O_2 + Cl_2 + H_2O$$

Properties. 1. It is a colourless liquid which turns dark on keeping. It decomposes at its boiling point (90°C). It strongly fumes in moist air.

2. It is a very strong acid, the dissociation constant being of the order of 10^{-1}. The cold aqueous acid attacks iron, zinc, etc., liberating hydrogen :

$$Zn + 2HClO_4 \longrightarrow Zn(ClO_4)_2 + H_2$$

3. It is a strong oxidising agent and may explode in the presence of a reducing agent, carbon in particular.

4. It forms a number of hydrates, such as mono, di and trihydrates $HClO_4.H_2O$, $HClO_4.2H_2O$ and $HClO_4.3H_2O$.

Perchlorates. Perchlorates are obtained by heating chlorates under controlled conditions :

$$4KClO_3 \xrightarrow[\text{Silica flask}]{480°C} 3KClO_4 + KCl$$

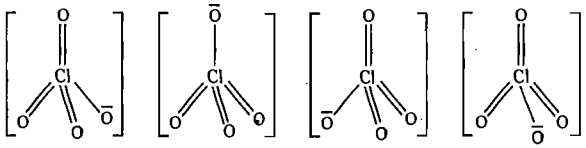
Potassium perchlorate is also obtained by electrolytic oxidation of cooled solution of potassium chlorate using high current density.

Perchlorates are strong oxidising agents. They are used in safety matches and explosives. Almost all perchlorates are highly soluble in water.

Perchlorates are isomorphous with permanganates.

Structure. The prechlorate ion has **tetrahedral** structure involving sp^3 hybridisation of chlorine orbitals, as already illustrated in Chapter 5.

Actually, the structure of ClO_4^- ion is a resonance hybrid of four structures, as shown below :



This accounts for the fact that the length of all the four ClO bonds in ClO_4^- ion is exactly the same.

Periodic acids and Periodates. Four periodic acids and their salts (periodates) are known. The periodic acids are : HIO_4, meta periodic acid, $H_4I_2O_9$, dimeso periodic acid, H_3IO_5, meso periodic acid and H_5IO_6, para periodic acid.

Examples of the corresponding periodates are KIO_4, $Na_4I_2O_9$, $Pb_3(IO_5)_2$, Ag_5IO_6

The acids as well as their salts are powerful oxidising agents.

Meta periodic acid, HIO_4 and para periodic acid, H_5IO_6, are the most stable. The oxidation state of iodine in each of these compounds is +7. Their preparation and properties are given below.

Meta periodic acid, HIO_4 is obtained by heating para periodic acid in vacuum at 130°C.

$$H_5IO_6 \longrightarrow HIO_4 + 2H_2O$$

It is a weak acid, dissociating as

$$HIO_4 \rightleftharpoons H^+ + IO_4^-$$

HIO_4 is a strong oxidising agent.

When dissolved in water, it changes back to H_5IO_6.

$$HIO_4 + 2H_2O \longrightarrow H_5IO_6$$

Its salts, meta periodates, are prepared by thermal decomposition of iodates :

$$4KIO_3 \longrightarrow 3KIO_4 + KI$$

They are strong oxidising agents in acidic medium.

$$2IO_4^- + 16H^+ + 14e^- \longrightarrow I_2 + 8H_2O$$

Structure. There is evidence from X-ray data that in meta periodate ion, iodine lies at the centre of a **regular tetrahedron** and the four oxygen atoms are arranged symmetically around it.

Para periodic acid, H_5IO_6. The first step in its preparation consists in passing a stream of chlorine gas in a boiling solution of iodine in the presence of excess of sodium hydroxide, when the following reaction takes place.

$$7Cl_2 + I_2 + 18NaOH \longrightarrow \underset{\text{White ppt.}}{2Na_2H_3IO_6} + 14NaCl + 6H_2O$$

The precipitate is treated with silver nitrate solution when a black precipitate of silver para periodate is obtained.

$$Na_2H_3IO_6 + 5AgNO_3 \longrightarrow \underset{\text{Silver para periodate}}{Ag_5IO_6} + 2NaNO_3 + 3HNO_3$$

Chlorine is then passed into the suspension of silver para periodate when para periodic acid is obtained.

$$4Ag_5IO_6 + 10Cl_2 + 10H_2O \longrightarrow 4H_5IO_6 + 20AgCl + 5O_2$$

Para periodic acid is obtained as colourless crystals on evaporating this solution.

Properties. 1. It is a white crystalline solid, soluble in water and alcohol. It melts at 146°C.

2. It starts decomposing when heated above its melting point.

$$2H_5IO_6 \longrightarrow 2HIO_3 + 4H_2O + O_2$$

3. If heated in vacuum, however, it decomposes in a different manner yielding a series of periodic acids at increasing temperatures, as represented below.

$$\underset{\text{Para periodic acid}}{2H_5IO_6} \xrightarrow[-3H_2O]{80°C} \underset{\text{Dimeso periodic acid}}{H_4I_2O_9} \xrightarrow[-H_2O]{100°C} \underset{\text{Meta periodic acid}}{2HIO_4} \xrightarrow[-O_2]{140°C} \underset{\text{Iodic acid}}{2HIO_3}$$

4. It is a strong oxidising agent and oxidises organic matter readily.

5. As an acid, it is weaker than iodic acid.

Structure. There is evidence from X-ray data that the acid as well as para periodate ion have an **octahedral structure** with iodine atom lying at the centre of the octahedron, as shown in Fig. 7.

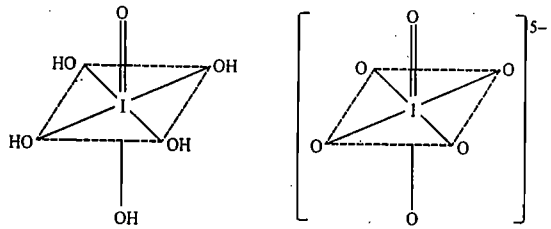


Fig. 7. Octahedral structure of para periodic acid, H_5IO_6 and para periodate ion, IO_6^{5-}.

Relative Strengths of Oxoacids of the Halogens. As already mentioned,

1. The acid strength of oxoacids of any halogen increases with increase in the number of oxygen atoms attached to the central halogen atom.

2. For a particular series of oxoacids with the same general formula, the acid strength decreases with increase in the size of the halogen atom.

Explanation of observation 1. The observation 1 mentioned above may be explained as follows : We know that oxoacids are generally formed by halogens other than fluorine whose electronegativities are lower than that of oxygen. Let us consider the series of oxoacids of chlorine, *viz.*, HClO, $HClO_2$, $HClO_3$ and $HClO_4$. The dissociation of HClO may be represented as follows :

$$HClO \rightleftharpoons H^+ + ClO^- \qquad ...(1)$$

The unit negative charge of the anion ClO^- will naturally be localised on the more electronegative oxygen atom rather than the chlorine atom. The oxygen atom in ClO^- would, therefore, attract the H^+ ion with a considerable force with the result that the two ions on the right hand side of Eq. 1 would recombine to form HClO. This implies that only a small fraction of HClO would remain ionized at equilibrium which means that HClO behaves as a *weak acid*.

Now, consider the ionization of $HClO_2$, *viz.*,

$$HClO_2 \rightleftharpoons H^+ + ClO_2^- \quad ...(2)$$

The unit negative charge now remains distributed mainly on the two oxygen atoms. This means that the charge localised on each oxygen atom is only half of that localised in the case of HClO. As a result, the force of attraction exerted by oxygen atom of ClO_2^- anion on H^+ ion is only half of that exerted by the oxygen atom of ClO^- anion on H^+ ion. This implies that the recombination of ClO_2^- and H^+ ions in Eq. 2 is less favourable which means that greater extent of $HClO_2$ remains in the ionized form. Hence, $HClO_2$ behaves as a stronger acid than HClO.

$HClO_3$ ionizes as

$$HClO_3 \rightleftharpoons H^+ + ClO_3^- \quad ...(3)$$

In this case, the unit negative charge is mainly distributed on the three oxygen atoms so that the charge on each oxygen atom is only about one-third in magnitude. As a result, the oxygen atom of ClO_3^- anion attracts the H^+ ion with still lesser force and the back reaction (3) becomes still less favourable. This implies that $HClO_3$ remains largely in ionised form and thus behaves as a stronger acid than both $HClO_2$ and HClO.

$HClO_4$ ionises as

$$HClO_4 \rightleftharpoons H^+ + ClO_4^- \quad ...(4)$$

The unit negative charge is now distributed on four oxygen atoms of ClO_4^- anion. Arguing as before it can be concluded that the back reaction (4) is least favourable out of all the back reactions (1–4). $HClO_4$ thus ionizes to the greatest extent and hence behaves as the strongest acid.

To sum up, the acidic strength of the four oxoacids varies in the order :

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

Relative acidity in terms of stability of oxoanions. The relative acidity may also be interpreted in terms of the relative stability of the anions of these acids.

We know that *any mechanism which involves distribution or delocalisation of the negative charge on an anion, would stabilise that anion.* In the case of oxoacids of chlorine, a unit negative charge is localised on one O atom in ClO^- ion whereas it is distributed over two O atoms in ClO_2^- ion, three O atoms in ClO_3^- ion and over four O atoms in ClO_4^- ion. Therefore, ClO_4^- ion involving maximum distribution or spreading of charge is most stable whereas ClO^- ion involving minimum distribution of charge is least stable.

Representing the dissociation of the oxoacid as

$$HZ \rightleftharpoons H^+ + Z^- \quad ...(5)$$

where Z^- is ClO^-, ClO_2^-, ClO_3^- or ClO_4^-, we can easily visualise that if the anion Z^- is stable, it would be capable of independent existence and would have very little tendency to combine with the proton to form the unionised acid HZ. This means that reaction (5) would be favoured in the forward direction and that the acid HZ would behave as a strong acid. If, on the other hand, the anion Z^- is unstable, it would be less capable of independent existence and would readily combine with the proton to form the unionised acid HZ. This means that reaction (5) would now be favoured in the reverse direction and that HZ would behave as a weak acid. Since, as discussed above, the stability of the oxo-anion increases with increase in the number of oxygen atoms, hence the stability of the anions of the oxoacids varies in the order

$$ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$$

and, consequently, the acidity of the oxoacids varies in the order :

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

Similar trends in acidity are shown by oxoacids of bromine and iodine.

Explanation for observation 2. The observation 2 may be explained as follows : We know that atomic size increases and, therefore, electronegativity decreases as we move from chlorine to bromine to iodine. For a particular series of oxoacids with the same general formula, the strength of the acid depends directly on the electronegativity of the central halogen atom. The greater the electronegativity of the halogen atom, the easier it would be for the H atom to be released as H^+ ion and hence the greater would be the strength of its oxoacid. Accordingly, out of $HClO_3$, $HBrO_3$ and HIO_3, $HClO_3$ is the strongest and HIO_3 is the weakest acid.

INTERHALOGEN COMPOUNDS OR INTERHALOGENS

Each halogen combines with every other halogen to form compounds amongst themselves. These are known as **interhalogens** or **interhalogen compounds**. The less electronegative halogen is written first. In naming the compounds also, the less electronegative element is mentioned first.

Interhalogens may be divided into two categories :

(*i*) *Neutral molecules* containing two or more halogen atoms such as ICl, ClF_3, IF_5, IF_7, etc.

(*ii*) Negatively charged interhalogen *anions* such as ICl_2^- and ICl_4^- and positively charged interhalogen *cations* such as ICl_2^+ and IF_4^+.

The formulae and names of stable interhalogen compounds, which are definitely known, are presented in Table 7.

TABLE 7
Some Well Known Interhalogen Compounds

	Interhalogens of the Type :		
XY	**XY_3**	**XY_5**	**XY_7**
ClF Chlorine fluoride BrF Bromine fluoride IF Iodine fluoride BrCl Bromine chloride ICl Iodine chloride IBr Iodine bromide	ClF_3 Chlorine trifluoride BrF_3 Bromine trifluoride ICl_3 Iodine trichloride	BrF_5 Bromine pentafluoride IF_5 Iodine pentafluoride	IF_7 Iodine hepta fluoride

Interhalogens of the Type XY (Diatomic Interhalogens)

In this type, one atom of each halogen is present. The compounds are ClF, BrF, IF, BrCl, ICl and IBr. They are generally prepared by the direct combination of the halogens. For example,

$$Cl_2 + F_2 \xrightarrow{250°C} 2ClF$$

$$I_2 + F_2 \xrightarrow{-45°C} 2IF$$

$$I_2 + X_2 \longrightarrow 2IX \qquad (X = Cl, Br).$$

Some of these interhalogens can also be prepared by other methods. For example,

$$Cl_2 + ClF_3 \xrightarrow{300°C} 3ClF$$

$$I_2 + AgF \xrightarrow{0°C} IF + AgI$$

Interhalogens of the type XY are essentially covalent compounds because of small difference in electronegativities of the two halogen atoms involved. They differ in thermal stabilities. For example, ClF is extremely stable. ICl and IBr are moderately stable while BrCl is unstable and readily dissociates reversibly into its constituents.

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

BrF and IF are also unstable and undergo disproportionation rapidly and irreversibly as shown below.

$$3BrF \longrightarrow Br_2 + BrF_3$$

$$5IF \longrightarrow 2I_2 + IF_5$$

The properties of interhalogens lie in between those of the parent halogens. However, they are more reactive than the halogens concerned. The reason is that the bond energy of X – Y bond is less than the bond energy of X – X or Y – Y bond. Thus, these compounds readily convert metals into mixed metal halides.

$$XY + 2M \longrightarrow MX + MY$$

e.g., $ICl + 2Na \longrightarrow NaI + NaCl$

On hydrolysis, they give oxo-halides and the hydrides of the more electronegative halogen.

$$XY + H_2O \longrightarrow HOX + HY \text{ (Y is more electronegative)}$$

e.g., $BrCl + H_2O \longrightarrow HOBr + HCl$

$$ICl + H_2O \longrightarrow HOI + HCl$$

They add themselves at olefinic double bond sites.

$$-CH=CH- + XY \longrightarrow -\underset{X}{\underset{|}{CH}}-\underset{Y}{\underset{|}{CH}}-$$

e.g., $CH_2=CH_2 + BrCl \longrightarrow \underset{Br}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH_2}}$

They also give addition products with halides of alkali metals, as for example,

$$NaBr + IBr \longrightarrow NaIBr_2$$

All the six interhalogens of the type XY are individually discussed below.

1. Chlorine Fluoride, ClF. It is formed either by the action of chlorine on fluorine at 250°C or by heating chlorine and chlorine trifluoride at 300°C as mentioned above.

$$Cl_2 + F_2 \xrightarrow{250°C} 2ClF$$

$$Cl_2 + ClF_3 \xrightarrow{300°C} 3ClF$$

It is a colourless gas and dissociates when heated strongly.

$$2ClF \longrightarrow Cl_2 + F_2$$

It acts as a fluorinating agent and reacts with a number of metals and non-metals more vigorously than fluorine.

$$Se + 4ClF \longrightarrow SeF_4 + 2Cl_2$$

$$W + 6ClF \longrightarrow WF_6 + 3Cl_2$$

It can also act as a chlorofluorinating agent.

$$CO + ClF \longrightarrow COFCl$$

$$SF_4 + ClF \longrightarrow SF_5Cl$$

$$SO_2 + ClF \longrightarrow SO_2FCl$$

2. Bromine Fluoride, BrF. *It is formed either by the direct combination of bromine and fluorine in gaseous phase or by the action of bromine trifluoride on bromine.*

$$Br_2 + F_2 \longrightarrow 2BrF$$

$$Br_2 + BrF_3 \longrightarrow 3BrF$$

It is a reddish brown liquid (b.p. 23°C). It is unstable and readily disproportionates to Br_2 and BrF_3.

3. Iodine Fluoride, IF. It is formed by the direct combination of iodine and fluorine at – 45°C.

$$I_2 + F_2 \xrightarrow{-45°C} 2IF$$

It can also be prepared by the action of iodine on silver fluoride at 0°C.

$$I_2 + AgF \longrightarrow IF + AgI$$

It is unstable and readily disproportionates into I_2 and IF_5 at room temperature.

4. Bromine Chloride, BrCl. It is obtained by passing chlorine gas into liquid bromine cooled below 10°C.

$$Br_2 + Cl_2 \longrightarrow 2BrCl$$

It is a reddish brown liquid which decomposes at 10°C into chlorine and bromine. It is insoluble in water, ether and carbon disulphide.

5. Iodine Chloride, ICl. It is formed by passing chlorine over solid iodine at temperatures below 0°C.

$$I_2 + Cl_2 \longrightarrow 2ICl$$

It is also prepared by heating iodine with potassium chlorate.

$$KClO_3 + I_2 \longrightarrow KIO_3 + ICl$$

It is a dark red liquid which solidifies on standing. The solid is capable of existing in two forms :

1. A *stable form* which is obtained as red needle-like crystals on cooling the liquid rapidly. It melts at 27°C.

2. A *metastable form* which is obtained as a black solid by cooling the liquid slowly at – 10°C. It melts at 13·9°C.

ICl is hydrolysed with disproportionation as shown below.

$$5ICl + 3H_2O \longrightarrow 2I_2 + HIO_3 + 5HCl$$

ICl, in the fused state, dissociates as

$$3ICl \rightleftharpoons I_2Cl^+ + ICl_2^-$$

Therefore, it can be used as a non-aqueous solvent.

ICl reacts with alkali metal chlorides as shown below :

$$ICl + MCl \rightleftharpoons M^+(ICl_2)^- \quad (M = \text{alkali metal})$$

Thus, alkali metal chlorides act as bases in this solvent.

ICl reacts with $AlCl_3$ as shown below :

$$2ICl + AlCl_3 \rightleftharpoons [I_2Cl]^+[AlCl_4]^-$$

Thus, $AlCl_3$ acts as an acid in this solvent.

ICl is used for the estimation of iodine number of oils and fats. Iodine number, in fact, is a measure of the unsaturation of oils and fats.

6. Iodine Bromide, IBr. It is formed by the direct combination of the elements. It is a crystalline solid, resembling iodine in colour and shape. Its vapours dissociate to a small extent on heating.

$$2IBr \longrightarrow I_2 + Br_2$$

Both ICl and IBr partially dissociate into ions and have appreciable conductivity in the molten state. Their dissociation may be represented as

$$2ICl \rightleftharpoons I^+ + [ICl_2]^-$$
$$IBr \rightleftharpoons I^+ + Br^-$$

Thus, in these compounds, iodine exists as a cation. These interhalogens can be used as non-aqueous ionizing solvents.

Interhalogens of the Type XY_3 (Tetraatomic Interhalogens)

In this type, three atoms of one halogen combine with one atom of another halogen. The known compounds of this type are ClF_3, BrF_3 and ICl_3.

These compounds are generally prepared by the direct combination of the elements under suitable conditions. Among these. ClF_3 is most reactive. All the three interhalogens of the type XY_3 are described below individually.

1. Chlorine Trifluoride, ClF_3. It is formed by direct fluorination of chlorine or chlorine fluoride in gaseous phase at 200°– 300°C in copper, nickel or monel metal vessel.

$$Cl_2 + 3F_2 \xrightarrow{200-300°C} 2ClF_3$$
$$ClF + F_2 \xrightarrow{200-300°C} ClF_3$$

It is a colourless gas which condenses to give a pale green liquid (b.p. –12°C). It is one of the most reactive interhalogens and reacts violently with many substances which otherwise are thought to be inert. It readily ignites materials such as wood, asbestos, etc.

It reacts with water giving a red liquid which crystallises at – 70°C. The compound formed has been characterised to be ClFO.

It acts as a strong fluorinating agent. It converts most of the chlorides to fluorides.

$$2AgCl + ClF_3 \longrightarrow 2AgF + Cl_2 + ClF$$

It also reacts with oxides such as MgO, NiO, CaO, Al_2O_3, Co_3O_4, MnO_2, etc., to form fluorides, *e.g.*,

$$6NiO + 4ClF_3 \longrightarrow 6NiF_2 + 2Cl_2 + 3O_2$$
$$2Co_3O_4 + 6ClF_3 \longrightarrow 6CoF_3 + 3Cl_2 + 4O_2$$

It reacts violently with NH_3 and N_2H_4 to give HF. The reaction, however, can be controlled by suitable dilution with inert gases such as nitrogen.

$$2NH_3 + 2ClF_3 \longrightarrow 6HF + N_2 + Cl_2$$
$$3N_2H_4 + 4ClF_3 \longrightarrow 12HF + 3N_2 + 2Cl_2$$

It also reacts with uranium to give UF_6.

$$U(s) + 3ClF_3 \xrightarrow{50-90°C} UF_6(l) + 3ClF(g)$$

Liquid ClF_3 shows electrical conductance which is explained on the basis of the following self-dissociation.

$$2ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$$

ClF_3 is used as a fluorinating agent, as an incendiary and in cutting oil well tubes. It is used as an oxidiser for propellants. It is also used in the production of UF_6.

2. Bromine Trifluoride, BrF_3. It is prepared by mixing bromine vapour and fluorine in a stream of nitrogen.

$$Br_2 + 3F_2 \longrightarrow 2BrF_3$$

It is also obtained by the action of ClF_3 on bromine at 10°C.

$$ClF_3 + Br_2 \longrightarrow BrF_3 + BrCl$$

BrF_3 also results when BrF undergoes disproportionation.

$$3BrF \longrightarrow BrF_3 + Br_2$$

Bromine trifluoride, BrF_3, is a straw-coloured liquid (b.p. 125·8°C and m.p. 8·8°C). It has high electrical conductivity due to its self-ionization :

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

This compound is also a useful fluorinating agent. It converts several metals, their oxides and chlorides into fluorides.

$$6M + 2BrF_3 \longrightarrow 6MF + Br_2$$
$$3MCl + BrF_3 \longrightarrow 3MF + BrCl_3$$

It dissolves in certain metal fluorides such as KF to yield tetra fluorobromates

$$KF + BrF_3 \longrightarrow KBrF_4$$

Similarly, it dissolves in SbF_3 to give hexafluorobromates.

$$SbF_3 + BrF_3 \longrightarrow SbBrF_6$$

It is decomposed violently by water. It is very reactive and displaces oxygen from oxides such as SiO_2, B_2O_3, As_2O_3, SeO_3, I_2O_5, CuO.

$$3SiO_2 + 4BrF_3 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$$
$$2B_2O_3 + 4BrF_3 \longrightarrow 4BF_3 + 2Br_2 + 3O_2$$

It is used as a fluorinating agent. It is also used as a non-aqueous ionizing solvent.

3. Iodine Trichloride, ICl_3.. It is formed by the action of excess of chlorine on iodine or iodine monochloride at 100°C.

$$I_2 + 3Cl_2 \longrightarrow 2ICl_3$$
$$ICl + Cl_2 \longrightarrow ICl_3$$

It is also formed when I_2O_5 is heated with hydrochloric acid.

$$I_2O_5 + 10HCl \longrightarrow 2ICl_3 + 5H_2O + 2Cl_2$$

It is a bright yellow solid which fumes readily. In crystalline state, it is believed to exist as I_2Cl_6. It dissociates on heating at 68°C giving iodine monochloride and chlorine.

$$ICl_3 \longrightarrow ICl + Cl_2$$

It has appreciable electrical conductivity in the molten state. This is explained on the basis of the following self-dissociation :

$$2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

It is used in medicine.

Interhalogens of the Type XY_5 (Hexaatomic Interhalogens)

In this type, five atoms of one halogen combine with one atom of another halogen. The stable compounds are ClF_5, IF_5 and BrF_5. These are generally prepared by the direct fluorination of the element or the lower fluorides. These are briefly discussed below.

1. Chlorine Pentafluoride, ClF_5. It is prepared by the fluorination of Cl_2 or ClF_3.

$$Cl_2 + 5F_2 \xrightarrow[250\ atm]{350°C} 2ClF_5$$

$$ClF_3 + F_2 \xrightarrow{h\nu} ClF_5$$

It is a gas (m.p. – 103°C, b.p. – 13·1°C). It is an extremely vigorous fluorinating agent. It reacts with water to liberate HF and $FClO_2$.

$$ClF_5 + 2H_2O \longrightarrow FClO_2 + 4HF$$

AsF_5 and SbF_5 form 1:1 adducts with ClF_5, *viz.*, $[ClF_4]^+[AsF_6]^-$ and $[ClF_4]^+[SbF_6]^-$ which are ionic.

2. Bromine Pentafluoride, BrF_5. It is formed by the action of fluorine on bromine using excess of fluorine.

$$Br_2 + 5F_2 \xrightarrow[\text{above}150°C]{\text{excess } F_2} 2BrF_5$$

It can also be prepared by the action of fluorine on KBr.

$$KBr + 3F_2 \xrightarrow{25°C} KF + BrF_5$$

Bromine pentafluoride is much more reactive than iodine pentafluoride. It reacts very violently. It is, therefore, generally diluted with nitrogen whenever required for the preparation of fluorides.

It is used in organic synthesis. It is also recommended as an oxidiser for propellants.

3. Iodine Pentafluoride, IF_5. It is formed by the direct combination of the elements (using excess of fluorine),

$$I_2 + 5F_2 \longrightarrow 2IF_5$$

or by the action of fluorine on iodine pentoxide.

$$2I_2O_5 + 10F_2 \longrightarrow 4IF_5 + 5O_2$$

It is also formed by heating iodine with silver fluoride.

$$I_2 + 10AgF \longrightarrow 2IF_5 + 10Ag$$

IF_5 is a colourless liquid boiling at 104·5°C. It is a good conductor of electricity as it ionises as

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

It reacts with iodine pentoxide to give iodine oxofluoride.

$$3IF_5 + I_2O_5 \longrightarrow 5IOF_3$$

IOF_3 is a white solid. It decomposes when heated at 110°C giving back IF_5.

$$2IOF_3 \longrightarrow IF_5 + IO_2F$$

Interhalogens of the Type XY_7 (Octaatomic Interhalogens)

In this type, seven atoms of one halogen combine with one atom of another halogen. Only one compound, IF_7, of this type is known to be formed. The reason for the formation of this compound lies in the large size of iodine atom and very small size of fluorine atom. A brief description of this compound is given below.

Iodine Heptafluoride, IF_7. It is formed by heating iodine pentafluoride with fluorine at 250°– 300°C.

$$IF_5 + F_2 \xrightarrow{250°-300°C} IF_7$$

It can also be prepared by the action of fluorine on KI or PbI_2.

$$KI + 4F_2 \xrightarrow{250°C} KF + IF_7$$

$$PbI_2 + 8F_2 \longrightarrow PbF_2 + 2IF_7$$

It is a gas at ordinary temperatures. It resembles ClF_3 and BrF_5 in being highly reactive. It reacts with silica and pyrex glass.

$$2IF_7 + SiO_2 \xrightarrow{100°C} 2IOF_5 + SiF_4$$

IF_7 vapours are hydrolysed by water yielding HF and iodine oxopentafluoride.

$$IF_7 + H_2O \longrightarrow IOF_5 + 2HF$$

It forms adducts with AsF_5 and SbF_5 such as $[IF_6]^+[AsF_6]^-$ and $[IF_6]^+[SbF_6]^-$ which are ionic.

Structures of Interhalogen Compounds

Interhalogen compounds are generally covalent compounds in which the larger halogen forms the central atom.

1. Type XY. As expected, the compounds of the type XY are linear. Thus, ClF, BrF, IF, BrCl, IBr and ICl are all **linear in structure.**

Electronic configuration of valency shell of chlorine atom, for example, is as represented in Fig. 8 (*a*). The unpaired electron forms a covalent bond with an atom of the second halogen (F, Br or I), as shown in Fig. 8 (*b*). The resulting molecule, XY, is, therefore, *linear*.

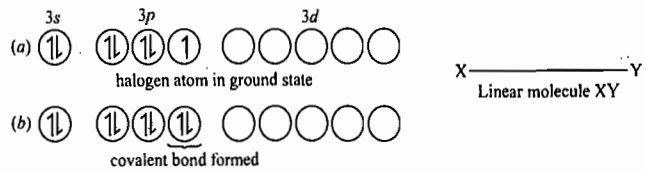


Fig. 8. Linear structure of the interhalogen compounds of the type XY.

2. Type XY_3. Compounds of the type XY_3 have T-shaped structure, as shown in Fig. 9 for ClF_3 molecule. The orbitals of the central halogen atom are involved in sp^3d hybridisation.

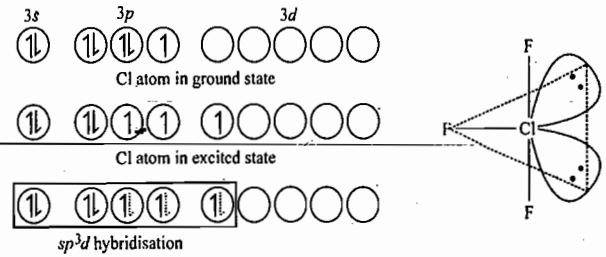


Fig. 9. sp^3d hybridisation of Cl orbitals involved in the formation of ClF_3 molecule.

3. Type XY_5 (IF_5, BrF_5, etc.). These compounds are formed by sp^3d^2 hybridisation of the orbitals of the central atom X and have **square pyramidal structure**, as shown in Fig. 10 for IF_5 molecule.

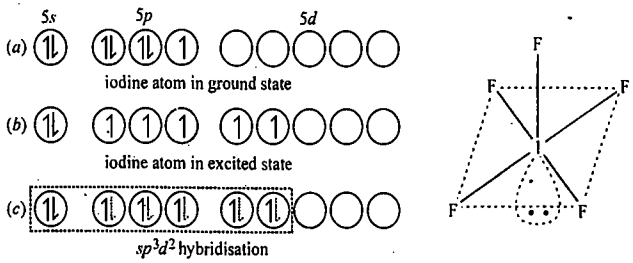


Fig. 10. Square pyramidal structure of IF_5 molecule involving sp^3d^2 hybridisation of the orbitals of iodine atom.

4. Type XY_7 (IF_7). This compound has a **pentagonal pyramidal** structure since this is formed by sp^3d^3 hybridisation of the orbitals of the central atom, as shown in Fig. 11.

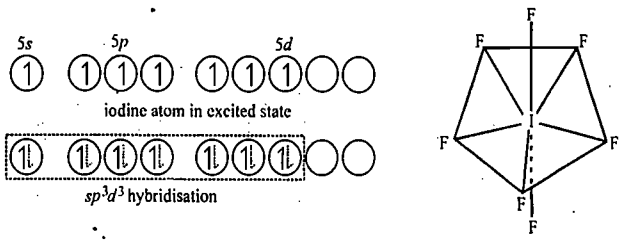


Fig. 11. Pentagonal bipyramidal structure of IF_7 molecule involving sp^3d^3 hybridisation of the orbitals of iodine atom.

INTERHALOGEN AND POLYHALOGEN ANIONS AND CATIONS

In addition to neutral interhalogens, a large number of interhalogen and polyhalogen anions and cations are also known. These are listed in Table 8.

TABLE 8

Interhalogen and Polyhalogen Anions and Cations

	Anions
Triatomic anion	ICl_2^-, IBr_2^-, $BrCl_2^-$, ClF_2^-, $IBrCl^-$, BrF_2^-, I_3^-, Cl_3^-, Br_3^-
Pentaatomic anion	ICl_4^-, BrF_4^-, I_5^-
Heptaatomic anion	IF_6^-, BrF_6^-
Diatomic cation	I_2^+, Br_2^+
Triatomic cation	ICl_2^+, IBr_2^+, BrF_2^+, ClF_2^+, IF_2^+, I_2^+, Br_2^+
Pentaatomic cation	IF_4^+, ClF_4^+, BrF_4^+
Heptaatomic cation	IF_6^+, BrF_6^+, ClF_6^+

Interhalogen Anions

In general, for a given cation, symmetrical interhalogen anions are more stable than the unsymmetrical ones. Stability also increases with increasing size of the central atom.

The structures of interhalogen anions have been well established by X-ray measurements. The structures of triatomic and pentaatomic anions are discussed below.

1. Structures of triatomic interhalogen anions. As an example, we may consider the structure of ICl_2^- anion.

The electronic configuration of I^- ion in ground state is as shown in Fig. 12. The formation of ICl_2^- anion will involve sp^3d hybridisation of the orbitals of I^- ion. The two half-filled hybrid orbitals of I^- ion overlap with the half-filled $2p$ orbitals of the chlorine atoms to form the anion $(Cl–I–Cl)^-$. The remaining three hybrid orbitals of I^- ion are occupied by lone pairs of electrons. Due to the symmetrical arrangement of the three lone pairs around the central I atom,the net bond pair-lone pair repulsion is the same along the axial directions. The anion $(Cl–I–Cl)^-$, therefore, has a **linear structure**, as shown. The dotted arrows indicate electrons contributed by Cl atoms.

Similarly, the interhalogen anion ClF_2^- has a linear geometry.

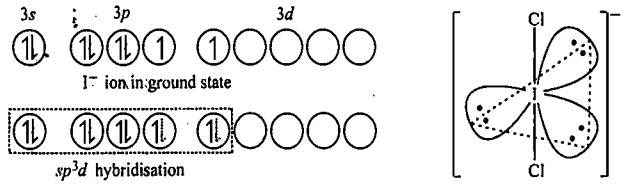


Fig. 12. Linear structure of ICl_2^- ion involving sp^3d hybridisation of I^- orbitals.

2. Structures of penta atomic interhalogen anions. As an example, we may consider the structure of ICl_4^- anion.

The electronic configuration of I^- ion in excited state is as shown in Fig. 13. The formation of ICl_4^- anion will, evidently, involve sp^3d^2 hybridisation of the orbitals of I^- ion. The four half-filled hybrid orbitals of I^- ion overlap with the half-filled $3p$ orbitals of chlorine atom to form the anion ICl_4^-. The remaining two hybrid orbitals of the I^- ion are occupied by lone pairs so as to minimise electron pair repulsion (VSEPR theory). As a result, the anion ICl_4^- acquires a square planar geometry, as shown in the figure. The dotted arrows represent electrons contributed by chlorine atoms.

The interhalogen anion BrF_4^- has similar geometry.

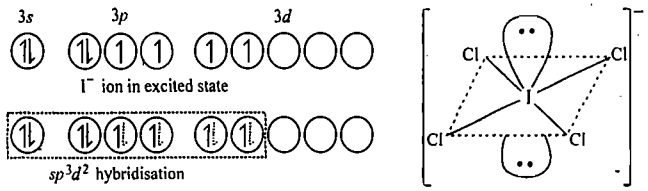


Fig. 13. Square planar structure of ICl_4^- ion involving sp^3d^2 hybridisation of I orbitals.

Interhalogen Cations

These are generally prepared by the addition of appropriate interhalogen and halide ion acceptor. For example, gold dissolves in BrF_3 to form $[BrF_2]^+[AuF_4]^-$. ClF_3 combines with $AsCl_3$ to form $[ClF_2]^+[AsF_4]^-$. ICl_2^+ is prepared by mixing stoichiometric amounts of I_2, Cl_2 and $SbCl_5$ which form $[ICl_2]^+[SbCl_6]^-$. The compounds of pentaatomic cations such as ClF_4^+, BrF_4^+, IF_4^+ and of heptaatomic cations such as IF_6^+ and ClF_6^+ have also been synthesised and characterised.

PSEUDOHALIDES AND PSEUDOHALOGENS

Pseudohalides. There are several uni-negative groups which show certain characteristics of halide ions. These are called **pseudohalides** or **pseudohalide ions.** The more important ones are given in Table 9.

Pseudohalogens. As each halide ion has a corresponding halogen, (chloride ion, for example, has chlorine as the corresponding halogen), attempts have been made to isolate **pseudohalogens** corresponding to pseudohalides. So far, only four pseudohalogens which are covalent dimers of the pseudohalide ions, have been isolated. These are also included in Table 9.

TABLE 9
Pseudohalide ions and Pseudohalogens

Pseudohalide ions	Formulae	Pseudohalogens	Formulae
Cyanide	CN^-	Cyanogen	$(CN)_2$
Cyanate	OCN^-		
Thiocyanate	SCN^-	Thiocyanogen	$(SCN)_2$
Selenocyanate	$SeCN^-$	Selenocyanogen	$(SeCN)_2$
Azide	N_3^-		
Azidothiocarbonate	$SCSN_3^-$	Azidocarbon disulphide	$(SCSN_3)_2$
Isocyanate	ONC^-		

Characteristic Reactions of Pseudohalides and Pseudohalogens. The important characteristic reactions of pseudohalide ions and the pseudohalogens are given below. The points of resemblance or contrast with halogens and halide ions are also mentioned where necessary.

1. Pseudohalogens are volatile like the halogens.

2. With hydrogen, the pseudohalide ions, like the halide ions, give acids which, however, are very weak. Thus, azide ion gives hydrazoic acid, HN_3, the pK_a value of which is 4·4, while cyanide ion gives hydrocyanic acid, HCN, the pK_a value of which is 8·9. The halide ions, on the other hand, give very strong acids like HCl and HBr.

3. Pseudohalides of silver, lead and mercury(I) [*e.g.*, AgCN, $Pb(CNS)_2$), HgCNS] are insoluble like the corresponding halides (*e.g.*, AgCl, $PbCl_2$, Hg_2Cl_2).

4. Pseudohalogens, like the halogens, add at ethylenic double bond linkage. Thus,

$$H_2C = CH_2 + (SCN)_2 \longrightarrow \underset{NCS}{H_2C} - \underset{SCN}{CH_2}$$

5. Pseudohalogens, like the halogens, react with alkalies.

$$(SCN)_2 + 2KOH \longrightarrow KSCN + KSCNO + H_2O$$

$$3(SCN)_2 + 6KOH \longrightarrow 5KSCN + K(SCN)O_3 + 3H_2O$$

6. Pseudohalogens form covalent pseudohalides, *e.g.*, ICN, $Si(SCN)_4$, $Co(N_3)_2$. The corresponding covalent halides are ICl, $SiCl_4$ and $CoCl_2$.

7. Pseudohalides form several complexes which are similar to halide complexes. The examples are : $[Co(SCN)_4]^{2-}$ and $[Hg(CN)_4]^{2-}$. The corresponding halide complexes are : $[CoCl_4]^-$ and $[HgI_4]^{2-}$.

8. Certain pseudohalides of lead(IV) decompose on heating to give lead(II) salt and free pseudohalogen.

$$Pb(SCN)_4 \longrightarrow Pb(SCN)_2 + (SCN)_2$$

$$Pb(SeCN)_4 \longrightarrow Pb(SeCN)_2 + (SeCN)_2$$

This reaction is similar to the decomposition of lead (IV) halides. For example,

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

We shall now consider a few details about each individual member of the pseudohalogens.

Cyanogen, $(CN)_2$. It is obtained by heating silver cyanide alone or a mixture of mercuric cyanide and mercuric chloride.

$$2AgCN \longrightarrow 2Ag + (CN)_2$$

$$Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2$$

It is also obtained by heating a mixture of aqueous solutions of $CuSO_4$ and KCN.

$$CuSO_4 + 4KCN \xrightarrow{60°C} (CN)_2 + 2CuCN + K_2SO_4$$

It is a colourless gas, soluble in water and poisonous in nature. On cooling, it condenses to a liquid at – 21·2°C and freezes at – 27·9°C. When heated, it polymerises to give insoluble paracyanogen, $(CN)_n$.

Cyanogen is fairly stable in water but its alkaline solution decomposes to give CN^- and OCN^- ions.

Thiocyanogen, $(SCN)_2$. It can be prepared by the action of bromine on silver sulphocyanide suspended in ether.

$$2AgSCN + Br_2 \longrightarrow 2AgBr + (SCN)_2$$

It is a yellow solid. It polymerises irreversibly at room temperature to give a brick-red material, insoluble in water. It oxidises iodides to iodine, Cu^+ to Cu^{2+} ions and H_2S to sulphur.

$$(SCN)_2 + 2KI \longrightarrow 2KSCN + I_2$$

$$(SNC)_2 + 2CuSCN \longrightarrow 2Cu^{2+} + 4(SCN)^-$$

$$(SCN)_2 + H_2S \longrightarrow 2H^+ + S + 2(SCN)^-$$

Selenocyanogen, $(SeCN)_2$. This can be prepared by heating the corresponding lead (IV) salt.

$$Pb(SeCN)_4 \longrightarrow Pb(SeCN)_2 + (SeCN)_2$$

This can also be prepared by the action of iodine on silver selenocyanate.

$$2AgSeCN + I_2 \longrightarrow 2AgI + (SeCN)_2$$

It is a yellow crystalline substance which turns red on standing. It is quite stable when dry but reacts with water as below.

$$2(SeCN)_2 + 3H_2O \longrightarrow H_2SeO_3 + 3HSeCN + HCN$$

Azidocarbondisulphide, $(SCSN_3)_2$. It is obtained in the form of white crystals when potassium azidothiocarbonate (obtained by the action of CS_2 on potassium azide) is oxidised with hydrogen peroxide.

$$CS_2 + KN_3 \xrightarrow{40°C} KSCSN_3 \xrightarrow{H_2O_2} (SCSN_3)_2$$

It is not a stable compound as it decomposes even at room temperature in accordance with the equation :

$$(SCSN_3)_2 \longrightarrow 2N_2 + 2S + (SCN)_2$$

Pseudohalogen-Halogen Compounds. Pseudohalogen–halogen compounds, as for example, CNCl and CNBr, can be prepared by the action of chlorine and bromine on HCN.

$$Cl_2 + 2HCN \longrightarrow 2CNCl + H_2$$

$$Br_2 + 2HCN \longrightarrow 2CNBr + H_2$$

Amongst other such compounds are chloroazide, ClN_3, bromoazide, BrN_3 and iodoazide, IN_3.

Thiocyanogen, $(SCN)_2$, in chloroform solution, combines with chlorine to yield white crystals of SCNCl.

Inter-Pseudo Halogen Compounds. Inter–psedudo halogen compounds are also known. Thus, $CN.N_3$ can be obtained by reacting cyanogen bromide with sodium azide.

$$CNBr + NaN_3 \longrightarrow NaBr + CN.N_3$$

Compounds like CN(SCN) and CN(SeCN) have also been obtained.

Electropositive Character of Iodine

Due to their high electronegativities and high ionisation energies, all the halogens are non-metallic. However, the ionization energy and hence, the non-metallic character decreases as we go down the group. The last element iodine has comparatively very low ionisation energy and exhibits metalloidal character. It has a metallic lustre and has a tendency to lose electrons to form cations I^+ and I^{3+}. The evidence for the existence of these cations is given below.

Evidence for the existence of I^+ ion. 1. Molten ICl is a good conductor of electricity. On electrolysis, a mixture of iodine and chlorine is liberated at the anode while only iodine is liberated at the cathode. This suggests that ICl ionises as

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

2. When ICl is dissolved in nitrobenzene or anhydrous acetic acid, the transport number measurements support the above mode of ionisation of ICl.

Similar studies on IBr suggest that this compound ionises as

$$IBr \rightleftharpoons I^+ + Br^-$$

3. On electrolysis of ICN in pyridine, only I_2 is liberated at the cathode. This suggests that ICN ionises as

$$ICN \rightleftharpoons I^+ + CN^-$$

4. A large number of compounds have been prepared which contain unipositive iodine. For example, when silver nitrate and iodine are mixed in chloroform in the presence of pyridine (py), the complex compound $[I(py)_2]NO_3$ is formed.

$$AgNO_3 + I_2 + 2py \longrightarrow [I(py)_2]NO_3 + AgI$$

Electrolysis of the complex compound in anhydrous chloroform gives iodine at the cathode which suggests the presence of I^+ in the complex compound.

5. Hypoiodous acid (HIO) is amphoteric and is known to ionise as :

$$HOI \rightleftharpoons H^+ + IO^-$$

$$HOI \rightleftharpoons OH^- + I^+$$

This also supports the existence of I^+ ion.

Evidence for the existence of I^{3+} ion. Molten ICl_3 conducts electricity. On electrolysis, it gives a mixture of iodine and chlorine at both the electrodes. This suggests the ionisation of ICl_3 as :

$$2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

As is evident, the ICl_2^+ and ICl_4^- ions contain iodine in the form of I^{3+} ions.

Iodine can be oxidised by fuming nitric acid in the presence of acetic anhydride to give iodine triacetate, $I(acetate)_3$. When this compound is electrolysed, using silver electrodes, one equivalent of silver iodide is formed at the cathode for every 3 faradays of electricity passed. This is in accordance with the ionisation

$$I(CH_3COO)_3 \rightleftharpoons I^{3+} + 3CH_3COO^-$$

Similarly, I_2 is oxidised by O_3 in the presence of $HClO_4$ to form $I(ClO_4)_3$ and by fuming HNO_3 in the presence of H_3PO_4 to form $I(PO_4)$.

$$I_2 \xrightarrow{O_3,\ HClO_4} \underset{\text{Iodine triperchlorate}}{I(ClO_4)_3}$$

$$I_2 \xrightarrow{HNO_3,\ H_3PO_4} \underset{\text{Iodine phosphate}}{IPO_4}$$

Both these compounds contain I^{3+} ion.

FLUOROCARBONS

Fluorocarbons are hydrocarbons or other organic molecules in which most of the hydrogen atoms are replaced by fluorine atoms. These compounds have very valuable properties and wide industrial applications.

Preparation. Fluorocarbons can be prepared by the following methods.

1. By heating metal fluorides (MF_x) such as LiF, NaF, CsF, HgF_2, ZnF_2, SbF_3, etc., with organic halides. Thus,

$$RCl + MF \longrightarrow \underset{\text{Fluoro carbon}}{RF} + MCl$$

The difference in the lattice energies of MF and RCl is the main driving force for this reaction. Within a group, the above difference increases with increase in the size of the metal M. Hence, within a group, the fluorides with bigger metal ions make the reaction more facile. Accordingly, CsF is a better fluorinating agent than NaF.

2. By electrolysing organic compounds in liquid HF in steel cells with Ni anodes and steel cathodes. For example,

$$C_8H_{18} \xrightarrow[\text{in liquid HF}]{\text{Electrolysis}} C_8F_{18}$$

$$(C_4H_9)_3N \xrightarrow[\text{in liquid HF}]{\text{Electrolysis}} (C_4F_9)_3N$$

3. By heating organic halides with anhydrous HF in the presence of SbF_5 at 50–100°C temperature and 50 – 500 atm pressure.

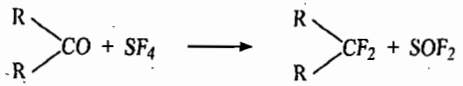
$$2CCl_4 + 3HF \xrightarrow{SbF_5} CCl_2F_2 + CCl_3F + 3HCl$$

4. By reacting organic compounds directly with fluorine in the presence of a suitable catalyst such as copper gauze. The reaction is carried out in the presence of an inert gas such as helium or nitrogen.

For example,

$$C_6H_6 + 9F_2 \xrightarrow[N_2 \text{ or He}]{\text{Cu at 265°C}} C_6F_{12} + 6HF$$

5. By fluorinating oxygen-containing organic compounds with SF_4. For example,



Properties. 1. Since bond energy of C – F bond (486 kJ mol^{-1}) is very high compared to the bond energies of C – H bond (415 kJ mol^{-1}) and C – Cl bond (332 kJ mol^{-1}), fluorocarbons are highly stable compounds.

2. Fluorocarbons are stable towards hydrolysis. This is because carbon does not have the *d* orbitals which could permit the formation of the 5-coordinated intermediate by necleophilic attack of H_2O molecule (cf. hydrolysis of silicon halides).

3. Fluorine atom has a small size so that the replacement of H atoms by F atoms does not produce any appreciable strain in the molecule. Replacement of H atoms by other halogens causes appreciable strain in the resulting molecules because of larger differences in the sizes of H and halogen atoms. As a result, the fluoro compounds are more stable than the other halogen compounds.

4. The fluorine atoms in fluorocarbons shield the carbon atoms very effectively thereby making them less vulnerable to attack by other reagents. The fluoro compounds are thus not very reactive.

5. Fluorine being more electronegative than carbon, pulls the electronic charge of the bond pair of electrons in C – F bond towards itself. Carbon atom in C – F bond thus develops a partial positive charge and can be considered as *oxidised*. Hydrogen, on the other hand, is less electronegative than carbon and hence the electronic charge of the bond pair of electrons in C – H bond is pulled a little more towards carbon. Carbon atom in C – H bond thus develops a partial negative charge and is considered as *reduced*. Thus, when exposed to atmospheric oxygen, hydrocarbons are readily oxidised. The fluorocarbons, on the other hand, are not oxidised at all because the partial positive charge on the carbon atom of fluorocarbons makes further loss of electrons from it extremely difficult.

6. Fluorocarbons are not attacked by acids, alkalies and most other chemicals. They are attacked only by hot metals such as molten sodium.

7. Completely fluorinated compounds have very low boiling points. The intermolecular forces in these compounds are also very low as a result of which these compounds have very low coefficients of friction.

Uses. 1. Fluorocarbons are used as lubricants because of their very low coefficients of friction.

2. Chlorofluorocarbons such as CCl_3F, $CClF_3$ and CF_2Cl_2 are used as refrigerants.

3. $CF_3CHBrCl$ and some similar other compounds are used as anaesthetics.

4. $CHClF_2$ is used for preparing tetrafluoro ethylene which is further converted into teflon by polymerisation.

$$2CHClF_2 \xrightarrow{500 - 1000°C} CF_2 = CF_2 + 2HCl$$

$$n\,CF_2 = CF_2 \xrightarrow{\text{Polymerisation}} \underset{\text{Teflon}}{-(CF_2 - CF_2)_n -}$$

5. Certain perfluoro organics are used as 'synthetic blood' for small mammals. These perfluoro compounds are non-toxic and have the capacity to dissolve, transport and release oxygen by simple solubility.

CHLORINE OXOFLUORIDES

Chlorine oxofluorides are very good fluorinating and oxidising agents and are of great industrial importance. Five well characterised chlorine oxofluorides are now known. These are FClO, F_3ClO, $FClO_2$, F_3ClO_2 and $FClO_3$. The preparation, properties and structures of these compounds are described below.

Chlorine Oxofluoride, FClO. FClO is prepared by any one of the following methods :

1. $$ClF + O_3 \xrightarrow[\text{low temperature}]{\text{Argon}} FClO + O_2$$

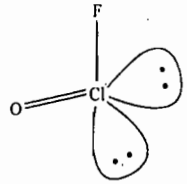
2. $$ClF_3 + H_2O \xrightarrow{\text{low temperature}} FClO + 2HF$$

3. $$Cl_2O + F_2 \longrightarrow FClO + ClF$$

FClO is a colourless gas which is highly unstable. Its half-life period is less than half a minute. It decomposes as follows :

$$2FClO \longrightarrow FClO_2 + ClF$$

Structure. FClO has a V-shaped structure with two lone pairs of electrons on the chlorine atom. Chlorine atom is sigma-bonded to fluorine atom and sigma and pi-bonded to oxygen atom. The chlorine atom, thus, needs four sp^3 hybrid orbitals to accommodate 7 + 2 – 1 = 8 electrons (*i.e.*, valency electrons of central atom + number of sigma bonds – number of π bonds formed with central atom). Because of the presence of two lone pairs of electrons, the geometry of FClO is **V-shaped**, as shown.



Chlorine Oxotrifluoride, F_3ClO. F_3ClO can be prepared by any one of the following methods.

(*i*) $$Cl_2O + 2F_2 \xrightarrow[-80°C]{NaF} F_3ClO + ClF$$

(*ii*) $$Cl_2O + N_2O_5 \xrightarrow{0°C} 2ClONO_2$$

$$ClONO_2 + 2F_2 \xrightarrow{-40°C} F_3ClO + FNO_2$$

Properties. 1. F_3ClO is a colourless gas boiling at – 28°C and freezing at – 43°C. It is more stable than FClO and is stored in teflon containers since it is a very strong fluorinating agent.

2. It decomposes slowly above 300°C to give ClF_3.

$$F_3ClO \xrightarrow[>300°C]{\text{heat}} ClF_3 + 1/2\,O_2$$

3. It is a strong fluorinating agent. It fluorinates several compounds :

$$Cl_2 + F_3ClO \xrightarrow{200°C} 3ClF + 1/2\,O_2$$

$$Cl_2O + F_3ClO \xrightarrow[\text{temperature}]{\text{room}} 2ClF + FClO_2$$

$$ClOSO_2F + F_3ClO \longrightarrow ClF + FClO_2 + SO_2F_3$$

4. F_3ClO is a strong oxidising agent. It oxidises SF_4, N_2F_4 and HNF_2 to SF_6, NF_3 and NF_3O, respectively.

5. F_3ClO also acts as a reducing agent in converting PtF_6 to $[PtF_6]^-$.

$$PtF_6 + F_3ClO \longrightarrow [F_2ClO]^+[PtF_6]^- + 1/2\,F_2$$

6. It is hydrolysed by water to $FClO_2$.

$$F_3ClO + H_2O \longrightarrow FClO_2 + 2HF$$

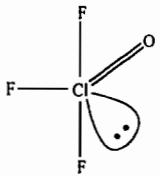
7. F_3ClO acts as Lewis base by donating a fluoride ion to PF_5, AsF_5, SbF_5, etc.

$$F_3ClO + MF_5 \longrightarrow [F_2ClO]^+[MF_6]^- \qquad (M = P, As, Sb, etc.)$$

8. It can also accept fluoride ion from alkali metal fluorides and thus acts as a Lewis acid as well.

$$F_3ClO + KF \longrightarrow K^+[F_4ClO]^-$$

Structure. In the structure of F_3ClO, the three fluorine atoms are sigma bonded and the solitary oxygen atom is sigma and π bonded to the central chlorine atom. The chlorine atom thus needs five sp^3d hybrid orbitals to accommodate $7 + 4 - 1 = 10$ electrons (*i.e.*, valency electrons of central atom + number of sigma bonds – number of π bonds formed with the central atom). The geometry of F_3ClO is, therefore, as shown, with a lone pair of electrons occupying an equatorial position (why ?).



Chlorine Dioxofluoride, $FClO_2$. $FClO_2$ is prepared by reacting $NaClO_3$ with ClF_3.

$$6NaClO_3 + 4ClF_3 \xrightarrow[\text{temperature}]{\text{room}} 6FClO_2 + 6NaF + 2Cl_2 + 3O_2$$

It is also prepared by reacting ClF_5 with water.

$$ClF_5 + 2H_2O \longrightarrow FClO_2 + 4HF$$

Properties. 1. $FClO_2$ is a colourless gas boiling at –50°C and freezing at –115°C.

2. It is thermally stable at room temperature but is chemically more reactive than $FClO_3$. Some of its reactions with protonic solvents are given below.

(*i*) $2FClO_2 + H_2O \longrightarrow 2HF + 2ClO_2 + 1/2\ O_2$

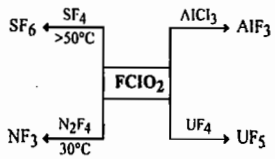
(*ii*) $2FClO_2 + 2HONO_2 \longrightarrow 2HF + 2ClO_2 + N_2O_5 + 1/2\ O_2$

(*iii*) $FClO_2 + HCl \longrightarrow HF + ClO_2 + 1/2\ Cl_2$

3. It reacts with NaOH as follows :

$$FClO_2 + 2NaOH \longrightarrow NaClO_3 + NaF + H_2O$$

4. $FClO_2$ is a good fluorinating and oxidising agent. Thus, it gives a number of reactions as shown.



5. It acts as a Lewis base due to its tendency to donate F^- ion. Thus,

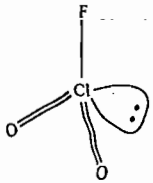
$$FClO_2 + AsF_5 \longrightarrow [ClO_2]^+[AsF_6]^-$$

$$FClO_2 + SbF_5 \longrightarrow [ClO_2]^+[SBF_6]^-$$

6. It can also act as F^- ion acceptor. Thus,

$$CsF + FClO_2 \longrightarrow Cs^+[F_2ClO_3]^-$$

Structure. The central chlorine atom in $FClO_2$ is sigma bonded to fluorine atom and (sigma + pi) bonded to two oxygen atoms. It, therefore, needs four sp^3 hybrid orbitals to accommodate $7 + 1 + 2 - 2 = 8$ electrons. The geometry of $FClO_2$ is, thus, **pyramidal** with one lone pair of electrons on the central atom.



Chlorine Dioxotrifluoride, F_3ClO_2. F_3ClO_2 is prepared by reacting $FClO_2$ with PtF_6 and FNO_2.

$$2FClO_2 + 2PtF_6 \longrightarrow [F_2ClO_2]^+[PtF_6]^- + [ClO_2]^+[PtF_6]^-$$

$$[ClO_2]^+[PtF_6]^- + [F_2ClO_2]^+[PtF_6]^- + 2FNO_2 \longrightarrow F_3ClO_2 + 2[NO_2]^+[PtF_6]^- + FClO_2$$

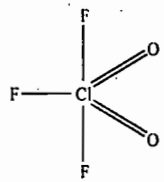
Properties. F_3ClO_2 is a colourless gas, boiling at –22°C and freezing at –81°C. It is highly reactive and is hence stored in teflon containers.

It acts as a strong oxidising agent. It donates F^- ion to compounds such as BF_3, AsF_6 and thus, behaves as a Lewis base.

$$F_3ClO_2 + BF_3 \longrightarrow [F_2ClO_2]^+[BF_4]^-$$

$$F_3ClO_2 + AsF_5 \longrightarrow [F_2ClO_2]^+[AsF_6]^-$$

Structure. There are three F – Cl sigma bonds and two (sigma and π) Cl = O bonds in F_3ClO_2. The chlorine atom thus needs five sp^3d hybrid orbitals to accommodate $7 + 5 - 2 = 10$ electrons. The geometry of the molecule is, therefore, **trigonal bipyramidal** with the two Cl = O bonds in equatorial positions.



Chlorine Trioxofluoride, $FClO_3$. A convenient method for the large scale preparation of $FClO_3$ involves the fluorination of $KClO_4$ with $HOSO_2F - SbF_5$.

$$KClO_4 \xrightarrow[\text{room temperature}]{HOSO_2F\text{–}SbF_5} FClO_3$$

It can also be prepared by passing fluorine gas through an aqueous solution of $NaClO_3$.

$$NaClO_3 + F_2 \longrightarrow NaF + FClO_3$$

Properties. 1. $FClO_3$ is a colourless gas, boiling at – 47°C and freezing at – 148°C. The gas has high thermal and kinetic stability. It, however, decomposes at elevated temperatures.

2. $FClO_3$ undergoes slow hydrolysis in alkaline medium.

$$FClO_3 + 2NaOH \longrightarrow NaF + NaClO_4 + H_2O$$

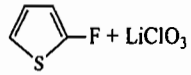
3. It reacts with liquid ammonia in the following manner :

$$FClO_3 + 3NH_3 \longrightarrow [NH_4]^+[HNClO_3]^- + NH_4F$$

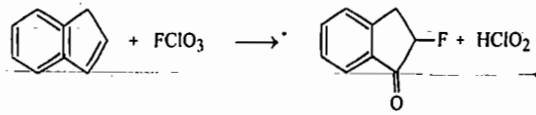
4. $FClO_3$, in sharp contrast with other chlorine oxofluorides, does not form adducts either with Lewis acids or with Lewis bases.

5. $FClO_3$ acts as a very good electrophile and hence has great utility in organic synthesis. For example,

$$FClO_3 + Li^+Ph^- \longrightarrow PhClO_3 + LiF$$

$$FClO_3 + Li^+[C_4H_3S]^- \longrightarrow$$  $$+ LiClO_3$$

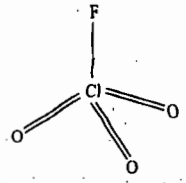
6. $FClO_3$ also acts as a two-centre electrophile, as in the following reaction :



7. It fluorinates reactive CH_2 groups in organic compounds. For example,

$$CH_2(COOR)_2 + 2FClO_3 \longrightarrow CF_2(COOR)_2 + 2HClO_3$$

Structure. $FClO_3$ contains one Cl – F sigma bond and three (sigma and π) Cl = O bonds. The central chlorine atom, therefore, utilises four sp^3 hybrid orbitals to accommodate $7 + 4 - 3 = 8$ electrons. The geometry of the molecule is, thus, **tetrahedral**, as shown.



BROMINE OXOFLUORIDES

These compounds are less studied than the chlorine oxofluorides. Some of the important bromine oxofluorides are discussed below.

Bromine Dioxofluoride, $FBrO_2$. This compound is prepared by any of the following reactions :

1. $$BrF_5 + 2KBrO_3 + 2HF \longrightarrow 3FBrO_2 + 2KHF_2$$
2. $$FIO_2 + BrF_5 \longrightarrow FBrO_2 + IF_5$$

Properties. 1. It is a colourless liquid freezing at – 10°C.

2. It decomposes rapidly above 65°C as follows :

$$3FBrO_2 \xrightarrow{>65°C} BrF_3 + Br_2 + 3O_2$$

3. It reacts with aqueous NaOH as follows :

$$FBrO_2 + 2NaOH \longrightarrow NaBrO_3 + NaF + H_2O$$

4. It can transfer F^- to Lewis acids such as AsF_5, SbF_5, etc.

$$FBrO_2 + AsF_5 \longrightarrow [BrO_2]^+[AsF_6]^-$$

Structure. $FBrO_2$ has a **pyramidal** structure similar to that of $FClO_2$.

Bromine Oxotrifluoride, F_3BrO. This compound is prepared by the following reactions

1. $$K[F_4BrO] + O_2^+[AsF_6]^- \longrightarrow F_3BrO + KAsF_6 + O_2 + 1/2\ F_2$$
2. $$K[F_4BrO] + HF \longrightarrow F_3BrO + KHF_2$$

Properties. 1. It is a white solid at low temperatures and melts at –5°C.

2. It slowly decomposes at room temperature to BrF_3 and O_2.

$$2F_3BrO \longrightarrow 2BrF_3 + O_2$$

3. It can donate as well as accept a F^- ion.

$$F_3BrO + BF_3 \longrightarrow [F_2BrO_2]^+[BF_4]^-$$
$$F_3BrO + KF \longrightarrow K[F_4BrO]$$

Structure. F_3BrO has structure similar to that of F_3ClO.

Bromine Trioxofluoride, $FBrO_3$. This compound can be prepared by reacting $KBrO_4$ with AsF_5 and BrF_5 in the presence of HF as follows :

$$KBrO_4 + 2AsF_5 + 3HF \longrightarrow FBrO_3 + [H_3O]^+[AsF_6]^- + KAsF_6$$
$$2KBrO_4 + BrF_5 + 2HF \longrightarrow 2FBrO_3 + FBrO_2 + 2KHF_2$$

Properties. 1. It is a reactive gas at room temperature.

2. It reacts with moisture very rapidly as follows :

$$FBrO_3 + H_2O \longrightarrow BrO_4^- + HF + H^+$$

3. It reacts with NaOH in aqueous solution to give $NaBrO_4$ and NaF.

$$FBrO_3 + 2OH^- \longrightarrow BrO_4^- + F^- + H_2O$$

IODINE OXOFLUORIDES

Several iodine oxofluorides have been synthesised and studied. Some of the important iodine oxofluorides are discussed below.

Iodine Dioxofluoride, FIO_2. This compound can be prepared by the action of fluorine on I_2O_5.

$$I_2O_5 + F_2 \xrightarrow[20°C]{HF\ at} 2FIO_2 + 1/2\ O_2$$

Properties. 1. It is a colourless molecular solid.

2. It reacts with NaOH in aqueous solution to give iodates.

$$FIO_2 + 2NaOH\ (aq) \longrightarrow NaIO_3 + NaF + H_2O$$

3. It captures a F^- ion from KF to give $K^+[F_2IO_2]^-$.

$$FIO_2 + KF \xrightarrow{HF} K^+[F_2IO_2]^-$$

Structure. The structure of the compound is similar to that of $FClO_2$.

Iodine Oxotrifluoride, F_3IO. This compound can be prepared by the action of IF_5 on I_2O_5.

$$I_2O_5 + 3IF_5 \xrightarrow{105°C} 5F_3IO$$

Properties. It is a colourless solid which decomposes above 110°C to give IF_5 and FIO_2.

$$2F_3IO \xrightarrow[>110°C]{\Delta} IF_5 + FIO_2$$

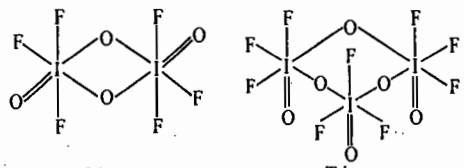
Structure. The structure of F_3IO is similar to that of F_3ClO.

Iodine Dioxotrifluoride, F_3IO_2. This compound can be prepared by first reacting $Ba_3H_4(IO_6)_2$ with HSO_3F and then treating the product formed with SO_3.

$$Ba_3H_4(IO_6)_2 \xrightarrow{HSO_3F} [HIO_2F_4] \xrightarrow{SO_3} F_3IO_2$$

It is a yellow solid melting at 41°C. Since the compound is quite unstable, its properties have not been studied.

Structure. Unlike monomeric F_3ClO_2, the structure of F_3IO_2 is polymeric as shown below.



Dimer Trimer

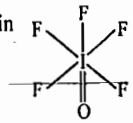
In both the polymeric forms of F_3IO_2, iodine has a coordination number 6.

Iodine Oxopentafluoride, F_5IO. This compound can be prepared by reacting IF_5 with I_2O_5 or H_2O.

$$5IF_5 + I_2O_5 \longrightarrow F_5IO + I_2$$
$$IF_5 + H_2O \longrightarrow F_5IO + H_2$$

It is a colourless solid, melting at 45°C. Its properties have not been investigated in detail since it is unstable.

Structure. The compound has an octahedral structure, as shown :



QUESTIONS

1. (*a*) Name the halogens and give their electronic configurations.

(*b*) Discuss the trends in the properties of halogens with respect to the following ?

(*i*) Oxidation states (*ii*) Electronegativity (*iii*) Ionisation energy

(*iv*) Oxidising power (*v*) Nature of bonds with other elements.

(c) While fluorine always exhibits an oxidation state of −1, other halogens exhibit additional oxidation states of +3, +5 and +7. Why is it so ?

2. (a) Write a brief note on the oxides of halogens.
   (b) Why is the bond angle FOF in F_2O smaller than the bond angle ClOCl in Cl_2O ?
   (c) Why is HF a weak acid as compared to HI in water ?
   (d) HF is a liquid while HCl is a gas. Explain.
3. (a) Give a detailed account of the interhalogen compounds with special reference to the compounds involving iodine. What structures have been assigned to the following interhalogen compounds: IF_3, IF_5, ICl, IF_7
   (b) Write a brief note on the cationic compounds of iodine.
   (c) "While fluorine is a non-metal, iodine exhibits some metallic character as well." Comment on this statement.
4. (a) Although the electronegativity difference is maximum in the case of HF and minimum in the case of HI, yet HF is the weakest and HI is the strongest halogen hydracid. How would you explain this anomaly ?
   (b) Why does fluorine differ from the rest of the family members ? Bring out the main points of difference.
   (c) Discuss the geometry of the following :
   (i) ClF_3 (ii) ICl_4^- (iii) I_3^-
5. Explain giving reasons why
   (a) HF is a liquid whereas HCl, HBr and HI are gases.
   (b) Compound of formula KHF_2 is well known but compounds of formulae $KHCl_2$ and $KHBr_2$ do not exist.
   (c) Complex ions, I_3^-, Br_3^-, I_5^-, etc., are known but the complex ion F_3^- is not.
   (d) Fluorine exists only in oxidation state of −1 whereas other halogens exhibit negative as well as positive oxidation states.
   (e) HF is polymeric.
   (f) Iodine shows metallic character.
   (g) Dissociation energy of F_2 is less than that of Cl_2.
   (h) Iodine is more soluble in KI solution than in water.
6. (a) Describe the modern method for the preparation of fluorine. Mention some of its compounds which are of industrial importance.
   (b) Explain with the help of Born-Haber cycle, the relative strengths of the various halogen hydracids. Explain clearly why HF is such a weak acid.
7. (a) Compare and contrast the properties of fluorine, chlorine, bromine and iodine.
   (b) Compare and contrast the properties of HF, HCl, HBr and HI.
8. Describe in details the preparation, properties and uses of the interhalogens belonging to XY, XY_3, XY_5 and XY_7 types.
9. (a) What are pseudohalogens ? Why are they so called ? Describe the important characteristics of pseudohalogens.
   (b) How would you account for the following order in the acid strengths of the oxoacids of halogens :
   (i) HOCl > HOBr > HOI (ii) $HClO_4 > HClO_3 > HClO_2 > HClO$
10. (a) Give one method for the preparation and structure of the following :
   (i) Para periodic acid (ii) Iodine pentafluoride (iii) Diiodine pentoxide (v) Chloric acid.
   (b) In what order the oxidising power of oxoacids of chlorine increase and why ?
   (c) Discuss the structures of ICl_2^-, IF_5, ClF_3 ClO_3^-.
11. What happens when (give equations)
   (a) Molten ICl_3 is electrolysed.
   (b) Potassium chlorate is heated with iodine.
   (c) Bromine trifluoride reacts with silica.
   (d) Periodic acid is heated in vacuum at 130°C.
   (e) Chloric acid is distilled under reduced pressure.
   (f) Bromine dioxide dissolves in sodium trifluoride.
   (g) Ammonia reacts with dilute chlorine trifluoride.
12. (a) Give one method of preparation and structure of the following :
   (i) ClF_3 (ii) $HClO_4$ (iii) I_2O_5 (iv) OF_2 (v) IF_5
   (b) Why is fluorine more reactive than other halogens ?
13. Describe the methods of preparation, properties and uses of the following :
   (1) Fluorocarbons (2) Chlorine oxofluorides (3) Bromine oxofluorides (4) Iodine oxofluorides

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THE ELEMENTS OF GROUP 18
THE NOBLE GASES

The noble gases comprise of **helium, neon, argon, krypton, xenon** and **radon.** All these gases, except radon, are present in the atmosphere. Radon results from the disintegration of radium and is radioactive itself. These gases have highly stable s^2p^6 electronic configurations in their outer (valency) shells and, therefore, they have *very little tendency to form chemical compounds with other elements.* In fact, till comparatively recently, no chemical reaction of these elements was known and they were referred to as **inert gases.** However, recent researches have shown that they do enter into chemical reactions with some specific elements under certain specific conditions forming chemical compounds. The word 'inert', therefore, is no longer considered appropriate. It is more usual now to refer to them as **noble gases**, the word 'noble' signifying that they enter into very few chemical reactions.

Occurrence. The noble gases occur only as minor constituents in the atmosphere. They are, therefore, also called *rare gases* of the atmosphere. The percentage by volume of the various gases is given below.

Gas	He	Ne	Ar	Kr	Xe
Percentage by volume	$5{\cdot}24\times10^{-4}$	$1{\cdot}82\times10^{-3}$	$9{\cdot}34\times10^{-1}$	$1{\cdot}45\times10^{-3}$	$8{\cdot}70\times10^{-6}$

Radon, as already mentioned, is evolved as radioactive emanation from the disintegration of radium which is going on spontaneously in nature.

The first element, **helium,** also occurs in natural gas, some minerals and in sun's atmosphere.

Helium occurs up to 7 per cent in certain natural hydrocarbon gases coming out from wells in Kansas (U.S.A.) and other surrounding areas. These gases, at present, constitute the most important source of helium.

In small quantities helium occurs in a variety of minerals such as *clevite, monazite* and *pitchblende.* The gas is actually *occluded, i.e.,* enclosed in the pores of the minerals and is released on heating the minerals to about 1000°C in vacuum.

Helium was first observed spectroscopically to be present in sun's atmosphere. It is now known that helium is being constantly produced there by nuclear fusion involving the formation of helium from 4 hydrogen atoms.

History of Discovery of Noble Gases. The history of discovery of noble gases shows *importance of paying utmost attention to even minutest discrepancies in laboratory experiments.* Cavendish, in 1785, performed a number of experiments to determine the composition of air. He passed repeated electric sparks in a mixture of dry air freed of carbon dioxide, with excess of oxygen. His idea was to cause complete conversion of nitrogen of the air into nitrogen dioxide by the reaction,

$N_2 + 2O_2 \longrightarrow 2NO_2$. He absorbed the resulting nitrogen dioxide and the unused oxygen in potassium pentasulphide, K_2S_5. There should have been no residual gas left. But, to his surprise, he observed that about 1/120th of the original volume of air remained undissolved. Cavendish, however, could not characterize this component of air which was identified as argon about 100 years later.

In 1868, Lockyer observed a bright yellow line near sodium D lines in the solar spectrum during a total eclipse. This line could not be attributed to any element known at that time. Lockyer concluded that the new spectral line is due to the presence of a new element in the sun. He called this element **helium** (Greek : *helios*, the sun). Twenty one years later, Hillebrand observed that uranium minerals like *clevite* and *monazite* gave off, on heating, a gas which he supposed to be nitrogen. Ramsay, however, on examining the spectrum of the gas, in 1895, found that it was *not* nitrogen but helium, the element which had been located by Lockyer in the spectrum of the sun. Ramsay was thus the first to find helium on the earth. Kayser, in the same year, detected helium in traces in the atmosphere.

In 1894, *i.e.*, 109 years after the experiments of Cavendish, Lord Rayleigh found the density of nitrogen isolated from the atmosphere to be about 0·47 per cent higher than that of the nitrogen prepared in the laboratory by the thermal decomposition of ammonium nitrite ($NH_4NO_2 \longrightarrow N_2 + 2H_2O$). The actual values were found to be 1·2572 and 1·2505, respectively. This minor discrepancy would have been ignored by many investigators. Rayleigh, however, persevered in his pursuits and repeated his experiments several times and each time he found the same discrepancy. He, therefore, concluded that *the nitrogen that was obtained from the atmosphere must contain some constituent or constituents which are heavier than nitrogen.*

Rayleigh then worked in collaboration with Ramsay. They improved upon the earlier experiments of Cavendish and showed that the residual gas left behind after complete conversion of nitrogen into nitrogen dioxide through electric sparking was heavier than nitrogen. Its vapour density was found to be 20 with respect to hydrogen taken as 1 whereas the vapour density of nitrogen on the same scale is about 14. It was examined spectroscopically and found to be an unknown gas. This gas was found to be chemically inert. The name **argon** (Greek : *argos*, inert or idle) was given to it.

Ramsay and Travers suspected argon to be, in reality, a mixture of a number of similar constituent gases. Spectroscopic evidence convinced them that this was actually so. They continued their work for several years during which they carefully and repeatedly distilled the liquefied gas. The first fraction was found to contain a new element which they named **neon** (*neon* means new). Its spectrum established its identity as a new element. Its vapour density was found to be 10·1 with respect to hydrogen taken as 1.

Once again, starting with a large volume of liquefied gas and refractionating the various fractions, Ramsay and Travers isolated another element and named it **krypton** (meaning *hidden*). Shortly afterwards they were successful in isolating another new element which they called **xenon** (meaning *stranger*). The vapour densities of krypton and xenon were found to be 40 and 64, respectively. The last member of the family, **radon**, was discovered in 1902 amongst the radioactive disintegration products of radium, thorium and actinium. This discovery, which completed the family of noble gases, was announced by Dorn but Ramsay and some other scientists had also made similar observations simultaneously.

Isolation of Noble Gases from the Atmosphere. Two principal methods are used for the separation of noble gases from the atmosphere. These are : 1. *Chemico-physical Method* 2. *Physical Method based on Fractionation of Liquid Air.*

1. Chemico-physical Method. The first step in this method is to isolate the noble gases mixed together, from the atmosphere by passing repeated electric sparks in air so as to remove nitrogen and oxygen as nitrogen dioxide ($N_2 + 2O_2 \longrightarrow 2NO_2$). The second step is to separate the various constituents from one another taking advantage of the fact that they can be *adsorbed* on activated charcoal at *different temperatures*. Both the steps are described below.

Step 1. Removal of oxygen and nitrogen of the atmosphere as nitrogen dioxide. Rayleigh's method. The basis of this method was laid down by Cavendish in his famous sparking experiments mentioned above.

The technique was much improved by Rayleigh and Ramsay. Their apparatus is shown in Fig. 1. It consists of a large flask of 50 – 60 litre capacity provided with (*i*) two large platinum electrodes for passing an electric discharge (*ii*) two tubes for the circulation of concentrated caustic soda solution, one bringing and discharging the solution in the form of a fountain at the base of the flask and the other carrying it back for recirculation and (*iii*) a tube for the introduction of dried and CO_2-free air mixed with excess of oxygen (9 parts of air mixed with 11 parts of oxygen).

An electric discharge of about 6000 – 8000 volts from an induction coil, is passed between the platinum electrodes. As a result, the nitrogen is removed from the air by combination with oxygen to form nitric oxide and then nitrogen dioxide which is absorbed in concentrated sodium hydroxide solution.

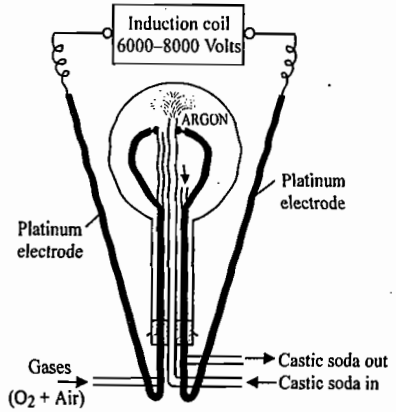


Fig. 1. Separation of noble gases from the atmosphere. Rayleigh's method.

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

The noble gases, of which argon is the major constituent, together with traces of oxygen, accumulate in the flask. The oxygen is absorbed by pyrogallol. Thus, a mixture consisting of noble gases only is left behind.

Step 2. Separation of the gases from one another by Dewar's method. This method is based on *differential adsorption of these gases by charcoal.* In this method, the mixture is introduced into a bulb filled with coconut charcoal and placed in a cold bath (– 100°C), in a Dewar flask (Fig 2). It is allowed to remain there for about an hour. Argon, krypton and xenon get adsorbed. The unadsorbed gases (helium and neon) are pumped out of the bulb and brought into contact with another charcoal maintained at – 180°C when neon is adsorbed and helium is obtained in free condition. Neon can be recovered from this charcoal on warming.

The first charcoal containing argon, krypton and xenon is now placed in contact with a third charcoal cooled to the liquid air temperature. Argon diffuses into this charcoal and can be recovered by heating this charcoal. The first charcoal would now contain krypton and xenon. Its temperature is

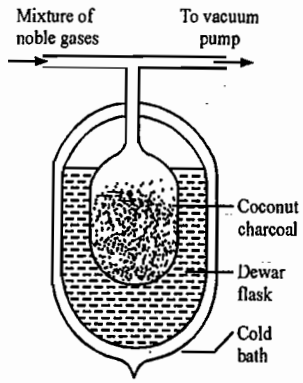
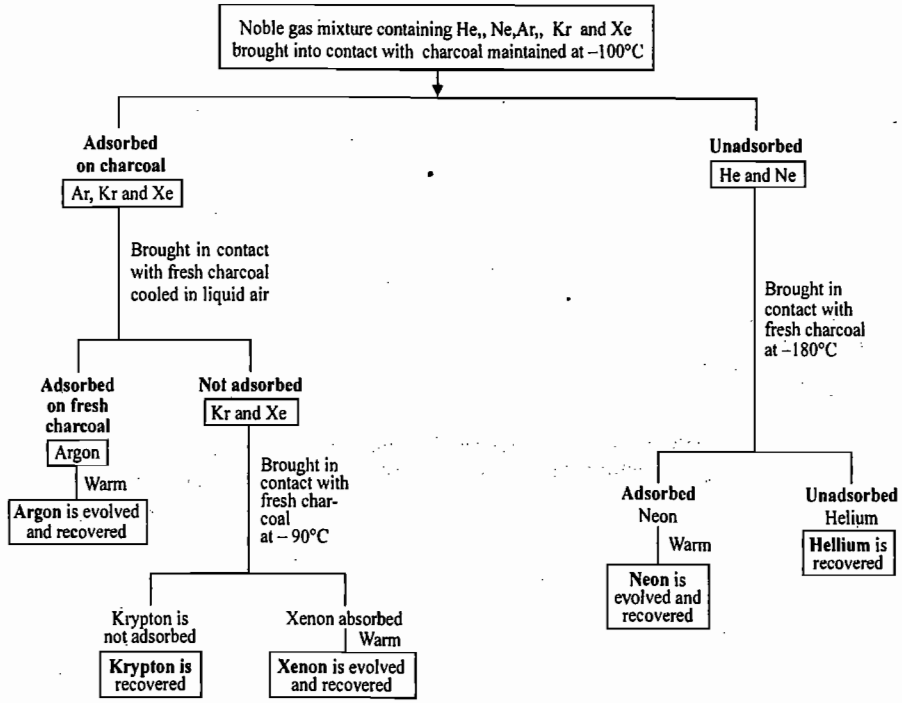


Fig. 2. Dewar's charcoal method for the separation of noble gases.

raised to – 90°C when krypton which remains unadsorbed separates out and is collected. Xenon which remains adsorbed is evolved by warming the charcoal.

The above procedure is illustrated with the help of a **flow sheet chart**, as shown below.



2. The Method Based on Fractionation of Liquid Air. When required on a large scale, the noble gases are isolated by the fractionation of liquid air. The method was developed by Rayleigh and Ramsay after a few years of the discovery of these elements.

The boiling points of the various constituents of air at 760 mm pressure are given below :

Gas	He	Ne	N_2	Ar	O_2	Kr	Xe
Boiling point (K)	4·2	27·2	77·2	87·3	90·3	119·7	165·0

It is evident from the above table that

1. Helium and neon being *most volatile* will pass along with nitrogen as the first fraction during the fractionation of the liquid air.

2. Argon is almost *as volatile as oxygen* and, therefore, it will remain mixed with oxygen.

3. Krypton and xenon are the *least volatile* components and, therefore, will remain behind when all other components distil off.

Separation of helium and neon. The most volatile fraction containing nitrogen, helium and neon is passed through a spiral column lying in a bath of liquid nitrogen. Most of the nitrogen gas present in the said fraction gets liquefied while helium and neon, being more volatile, escape. Any residual nitrogen

which may escape alongwith helium and neon can be removed by passing the mixture over heated calcium carbide :

$$CaC_2 + N_2 \rightleftharpoons CaNCN + C$$

The gas now consists of neon (about 3 parts) and helium (about 1 part) only. Their separation can be affected by cooling the mixture in *liquid hydrogen* when neon gets solidified while helium passes out still as a gas. Another way to separate them from each other is to pass them over activated charcoal cooled to – 180°C when neon is adsorbed by the charcoal while helium passes over as such.

Separation of argon. The second fraction consisting mainly of oxygen mixed with argon, krypton and xenon and some residual nitrogen, is fed at *A* into the middle of a rectifying column shown in Fig. 3. The upper part of this column has a series of tubes (*B*) kept cooled in a bath of liquid nitrogen. Oxygen, which is less volatile, gets liquefied and passes down the column alongwith krypton and xenon. Argon and nitrogen, being more volatile, rise above the column, alongwith some oxygen, as shown in the figure. This gaseous mixture consisting, roughly, of 47 per cent of nitrogen, 47 per cent of argon and 6 per cent of oxygen, is led at *C* into the middle of another column, as shown. The upper part of this column also has a series of tubes (*D*) which are kept cooled in a bath of liquid nitrogen. The nitrogen gas present in the gaseous mixture cannot liquefy under these conditions and, therefore, passes out from above the column as shown, while argon, mixed with residual oxygen, passes down the column and is collected as liquid at the bottom. This liquid is evaporated by the heat of compressed air passing through a coil and the gas consisting of argon and oxygen escapes at *F*, as shown. The oxygen, which is present now only in very small amounts, is removed by passing the mixture over heated copper. Argon passes out in *pure* state.

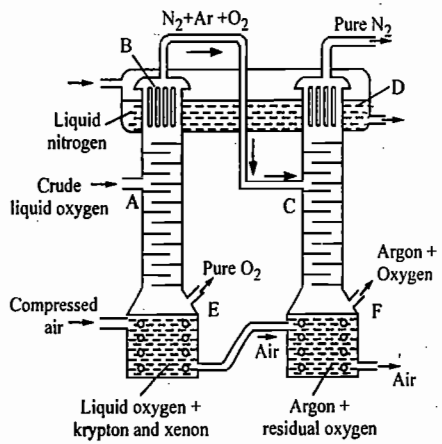


Fig. 3. Isolation of argon from liquid oxygen.

Separation of krypton and xenon. As krypton and xenon are the least volatile constituents, they accumulate in liquid oxygen at the bottom of the column shown on the left of Fig. 3. The oxygen present in this liquid is evaporated off by the heat of compressed air while krypton and xenon still remain in the liquid state. Some of the residual oxygen may still be present in the liquid state. This liquid is then made to flow through another rectifier column having at the bottom a coil or pipe through which compressed air is circulated. This causes evaporation of the oxygen. The liquid mixture of krypton and xenon then flows down at the base of the column.

The separation of krypton and xenon may be affected by treatment in another rectifier or by Dewar's charcoal method. Quite often the mixture of the two gases is used as such and their separation is not considered necessary.

Special methods of obtaining helium. In addition to its isolation from air by the chemical or fractionation methods discussed above, helium can also be obtained from natural gas on an industrial scale. The natural gas contains hydrocarbons (methane, etc.), carbon dioxide, nitrogen and helium as the main constituents. The carbon dioxide is removed first by absorption through concentrated potassium hydroxide and the residual gas is passed through a rectifying column. Nitrogen, helium and a little methane pass over while the rest of the gases are liquefied. The gaseous mixture is then subjected to compression (100 atm) and cooling (to – 200°C) repeatedly when nearly 99 per cent pure helium passes over while nitrogen and methane get liquefied.

If required, it can be further purified by cooling it to – 180°C in the presence of charcoal when all other gases except helium are adsorbed and thus got rid of.

Electronic Configurations of Noble Gases. The atomic numbers of Group 18 elements are 2, 10, 18, 36, 54 and 86, respectively. Their electronic configurations are given in Table 1. All of the these, except helium, have the *highly stable* **ns^2p^6 configuration** in the outer (valency) shell. Helium has the *stable* **s^2 configuration.**

TABLE 1
Electronic Configurations of Noble Gases

Noble gas	Atomic number	Electronic Configuration	Configuration of outer shell
He	2	$1s^2$	$1s^2$
Ne	10	$1s^2 2s^2p^6$	$2s^2p^6$
Ar	18	$1s^2 2s^2p^6 3s^2p^6$	$3s^2p^6$
Kr	36	$1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^6$	$4s^2p^6$
Xe	54	$1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^6d^{10} 5s^2p^6$	$5s^2p^6$
Rn	86	$1s^2 2s^2p^6 3s^2p^6d^{10} 4s^2p^6d^{10} 5s^2p^6d^{10} f^{14} 6s^2p^6$	$6s^2p^6$

General Physical Properties. Some of the important physical properties of noble gases, including atomic numbers and molar masses are given in Table 2.

TABLE 2
Some Physical Properties of Noble Gases

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
Atomic number	2	10	18	36	54	86
Molar mass (a.m.u.)	4·003	20·183	39·948	83·30	131·30	222
Boiling point (°C)	– 268·93	– 246·06	– 185·86	– 153·35	– 108·1	– 62
Melting point (°C)	– 272·1	– 246·61	– 189·37	– 157·2	– 111·8	– 71
Ionisation energy (kJ mol^{-1})	2372·1	2080·4	1520·3	1350·6	1170·2	1037
Heat of vaporisation (kJ mol^{-1})	0·08	1·74	6·52	9·05	12·65	18·1
Van der Waals radius (Å)	0·93	1·31	1·74	2·09	2·14	–
Critical temperature (°C)	– 267·9	– 228·7	– 122·4	– 62·5	16·6	14·5
Critical pressure (atm)	2·26	26·9	50·0	54·3	58·2	62·4
$\gamma = C_p/C_v$	1·653	1·643	1·60	1·67	1·60	–
Absorption coefficient in water at 25°C	0·0097	0·0114	0·0053	0·1105	0·2420	0·5100

1. Melting points and boiling points. It is seen that boiling as well as melting points of noble gases are very low. This is due to very weak intermolecular (van der Waals) forces of attraction in these gases. The melting and boiling points of helium are the lowest of any known element. Further, it is seen that the boiling points and melting points, in most gases, increase regularly when we move down the group. This is due to increase in the magnitude of the van der Waals forces with increase in the size of the noble gas atoms.

All the gases, except radon, solidify at 2 to 9°K below their normal boiling points. Helium is most difficult to be solidified. It solidifies only when it is cooled to about 1 K under a pressure of 25 atm. Liquid helium is, therefore, used as an ideal cooling agent for research at low temperatures.

2. Liquefaction. The noble gases are liquefied with great difficulty. This is indicated by their very low critical temperatures. This is again because of weak van der Waals or intermolecular forces existing in these gases. Heat of vaporisation is also low. However, van der Waals forces seem to increase with increase in atomic size, as is evident from increase in critical temperatures on moving from helium to xenon. The heat of vaporisation also increases in the same order.

3. Solubility in water. These gases are only slightly soluble in water (8 to 40 ml per litre at 25°C). The solubility, in general, increases with increasing molar mass.

4. Ionisation energies and electron affinities. The ionisation energies of these elements are quite high, as shown in Table 2. The values, however, decrease with increasing molar mass, as shown. The electron affinities are close to zero.

5. Mono-atomicity. The gases exist as monoatomic molecules since their atoms are not capable of combining even amongst themselves. The monoatomic nature is confirmed by the value of γ being close to 1·66 (Table 2).

6. Characteristic spectra. These gases give *characteristic spectra* by means of which they can be identified. Thus, helium gives characteristic spectrum containing conspicuous green and yellow lines while neon gives a characteristic spectrum with orange and red lines and so on.

Uses of Noble Gases. The noble gases are put to a variety of uses, as described below.

Uses of helium. 1. Helium is used chiefly in filling lighter-than-air crafts such as air ships, weather balloons, etc. Although it is twice as heavy as hydrogen, its lifting power (which is determined by the difference between the density of air and the density of the balloon) is 92 per cent of that of hydrogen. This small difference in buoyancy (*i.e.*, lifting power) is not a serious disadvantage in view of reasons of safety because, unlike hydrogen, helium is non-flammable.

2. Since helium, unlike nitrogen, is not soluble in blood even under pressure, a mixture of 80 per cent helium and 20 per cent oxygen is used, instead of ordinary air, in modern diving apparatus. If air is used as such in the diving apparatus, the nitrogen dissolves in the blood of the diver due to high pressure when he is down in the deep sea. As soon as he comes to the surface, the pressure is released and the dissolved nitrogen escapes. This gives rise to **coisson disease** or the 'bends'. A similar helium-oxygen mixture is used to assist breathing in asthma and other respiratory diseases.

3. Helium has also a number of scientific uses, *e.g.*, liquid helium (b.p. 4·2 K) is used as a cryogenic fluid to provide low temperatures for studying a number of phenomena which occur near absolute zero. It is also used in gas thermometers required for low temperature measurements.

4. Helium is also used in providing an inert atmosphere for a number of metallurgical processes, *e.g.*, in the preparation of reactive metals such as titanium, as well as during the welding of magnesium, aluminium, titanium and stainless steel. These metals get attacked by both oxygen and nitrogen at red heat. Therefore, the operation is carried out in an atmosphere of helium or any other noble gas.

Uses of neon. 1. Neon has a characteristic property of giving an orange-red glow in a discharge tube at low pressure (2 mm) at 1000 volts. It is, therefore, extensively used in neon glow lamps (commonly known as **neon tubes**) for advertising purposes. If mercury vapours are mixed with neon, a glow of blue or green colour is obtained. Various different colours can be obtained according to the composition of the gas mixture and the type of glass used.

2. Neon has a remarkable property of carrying exceedingly high electric currents even under high voltage. It is, therefore, used in safety devices for protecting electrical instruments such as voltmeters, relays and rectifiers, from high voltages.

Uses of argon. 1. Argon is used for filling incandescent metal filament electric bulbs. Its action there is to prevent the volatilisation of the tungsten filament at the high temperature of the lamp.

2. It is also used to some extent in discharge tubes for illumination purposes instead of neon. Thus a mixture of argon and mercury vapour in discharge tubes produces a glow of blue or green colour.

3. It is chiefly employed in welding and other operations which require absence of nitrogen as well as a non-oxidising atmosphere.

Uses of krypton and xenon. Krypton and xenon are also used in filling incandescent metal filament electric bulbs. Recent knowledge has shown that these gases are superior to argon for this purpose. They are also used to a small extent in discharge tubes.

Radon has not found any important industrial application so far. However, it has been used in the treatment of cancer. It is also gaining some importance in radioactive research.

Importance of noble gases in theoretical chemistry. Noble gases have played an important role in the development and elucidation of various subjects of theoretical chemistry. With their discovery and their subsequent introduction between strongly electronegative halogens and strongly electropositive alkali metals, the anomaly in Mendeleeff's table has been removed. The 'inertness' of these gases has helped the scientists to a very great extent in formulating the *electronic theory of valency*. Kossel and Lewis assumed that noble gases have stable electronic configurations and every other element tends to acquire the structure of noble gases either by transfer of electrons (electrovalency) or by sharing of electrons (covalency). Further, the identification of alpha particle as doubly ionized helium atom (He^{2+}), was of great assistance in formulating the theory of radioactive disintegration and group displacement law.

COMPOUNDS OF NOBLE GASES

The noble gases have most stable electronic configurations, as already mentioned (Table 1). Till comparatively recently, their compounds were almost unknown. In fact, on account of their high ionisation energy and almost zero electron affinity, they were not expected to be reactive at all. However, recent researches have shown that *under certain conditions* some of these elements are in a position to form a few chemical compounds. This has been a highly exciting field and has yielded results which, at one time, were considered to be most improbable.

Compounds Known Before 1962. The only compounds known before 1962 were the hydrates and the clathrates of noble gases.

Hydrates of Noble Gases. The **hydrates** of noble gases are formed by compressing the gases in water. **Deuterates** are also formed by compressing the gases in heavy water. The hydrates and deuterates of the heavier noble gases are known to be more stable. Thus, **$Xe.6H_2O$** is the most stable hydrate of a noble gas. It is believed that under the influence of molecules with strong dipoles (such as water), the atoms of noble gases *get polarised, i.e.,* acquire a weak induced dipole of their own. This causes dipole–dipole interaction between the noble gas and water, yielding the hydrate. Noble gases with larger atoms are influenced more than those with smaller atoms. Thus, xenon and krypton are influenced much more than argon and helium. Hence, the hydrate of xenon, $Xe.6H_2O$, is the most stable. This is also the reason why the solubility of noble gases in water generally increases on moving down the group from helium to xenon.

Clathrates of Noble Gases. Noble gases form a number of compounds in which *the gases are trapped within cavities of crystal lattices of certain organic and inorganic substances.* Such compounds are known as **clathrates** (Latin : *clathrate* meaning enclosed or protected by cross bars). These are also referred to as **cage compounds.**

Thus, when β-quinol (*o*-dihydroxy benzene) is allowed to crystallise from its solution in water in the presence of a heavier noble gas (argon, krypton or xenon) under a pressure of 10 – 40 atm, the atoms of the noble gas get trapped within the lattice of quinol crystals. In other words, *the crystals obtained are not of quinol but of a clathrate compound of the noble gas with quinol.* The crystals are quite stable and can persist for several years. However, when heated or dissolved in water, the gas escapes and quinol remains behind as such.

X-ray examination shows that a crystal of β-quinol is a three-dimensional network containing several cavities of 4 Å diameter, the quinol molecules being bound together with hydrogen bonds. When

β-quinol is allowed to crystallise from its solution in the presence of any foreign atom or molecule of *suitable size which can fit in the cavities tightly*, a clathrate compound results. The trapped atoms or molecules are unable to escape. If the molecules are too small, as those of helium and neon, they are able to escape easily from the cavities. Thus, *helium and neon do not form clathrate compounds with quinol.* Argon, krypton and xenon molecules, on the other hand, are of suitable sizes and form these compounds.

Since three molecules of quinol can form one cavity of 4 Å diameter, the composition of these clathrate compounds corresponds to 3 molecules of quinol for every one molecule of argon, krypton or xenon.

Similarly, when water is allowed to freeze in the presence of argon, krypton or xenon, under pressure, the atoms of the noble gas get trapped in the crystal structure of ice yielding clathrate of composition approximating to 5·75 molecules of water for every 1 molecule of the noble gas.

It may be of interest to know that any molecule of a suitable size can form clathrate compound in quinol. Thus, oxygen, sulphur dioxide, hydrogen sulphide and methanol are examples of other molecules which form clathrates with quinol. The crystal structure with cavities is called the *'host'* while the atom entrapped in it is called the *'guest'*.

The essential conditions for clathrate formation, evidently, are that the crystal lattice of the *'host'* should be such as to have cavities of appropriate size and the *'guest'* molecules or atoms, as the case may be, should be of appropriate size to fit in tightly into these cavities.

Uses of clathrates of noble gases. Helium and neon can be separated from argon, krypton and xenon when quinol is crystallised from its solution in the presence of a mixture of these gases. Helium and neon which do not form clathrates escape while argon, krypton and xenon are caught in the crystals as clathrates.

Clathrates of argon, krypton and xenon provide convenient means of handling and transporting of isotopes of these gases.

$Krypton^{85}$ clathrate provides a safe source for β radiations while $xenon^{133}$ clathrate provides a useful source for γ radiations.

Compounds discovered from 1962 onwards. During the investigation of the chemistry of PtF_6, Bartlett, in 1962, found that oxygen gas reacts with PtF_6 to give a solid compound of the formula O_2PtF_6. The X-ray examination showed that the compound actually consisted of O_2^+ and PtF_6^- ions and could be represented as $O_2^+PtF_6^-$. *Since the ionisation energy of xenon* (1170 kJ mol^{-1}) *is fairly close to that of molecular oxygen* (1180 kJ mol^{-1} for $O_2 \longrightarrow O_2^+ + e^-$), *it occurred to Bartlett that the reaction between xenon and* PtF_6 *should also be tried.* When he mixed deep red vapours of PtF_6 with excess of xenon, he found that the reaction occurred fairly readily even at room temperature yielding an orange-yellow solid compound which was identified as $Xe^+PtF_6^-$.

$$Xe(g) + PtF_6(g) \longrightarrow \underset{\text{(orange-yellow)}}{Xe^+PtF_6^-}$$

This was the first real compound of any of the noble gases.

The occurrence of the reaction of xenon with PtF_6 demonstrated for the first time that xenon is *not* a totally inert gas. This led to other investigations in the same direction.

Looking at the ionisation energies of these elements given in Table 2, it is seen that leaving aside radon, which is unstable, only xenon and krypton, have ionisation energy comparable with common elements like carbon, nitrogen and oxygen. Xenon, therefore, forms the largest number of compounds. Krypton comes next. Neon, argon and helium, which have much higher ionisation energies, hardly form any compound. Further, since reactivity of xenon and krypton is due to their tendency to part with their electrons, it is evident that the combining atom should have *strong affinity for electrons, i.e.,* should be

strongly electronegative. It is for this reason that xenon and krypton form compounds mostly with strong electron-acceptors, *viz.*, fluorine and oxygen. The most stable of these compounds are *fluorides*; *oxofluorides* and *oxides*.

Xenon combines directly with fluorine. Its compounds with oxygen are obtained from its fluorides. Xenon chloride is known but it is not stable. Only one compound with nitrogen is known but it is highly unstable.

Some of the stable compounds of xenon are given in Table 3.

TABLE 3

Some Stable Compounds of Xenon with Fluorine and Oxygen in Different Oxidation States of Xenon

Oxidation State of Xenon	Compounds of Xenon
2	XeF_2
4	XeF_4, $XeOF_2$
6	XeF_6, $XeOF_4$, XeO_2F_2, XeO_3
8	XeF_8, XeO_4, XeO_3F_2, XeO_2F_4

Fluorides are amongst the most important compounds of xenon. A series of stable fluorides of xenon with compositions XeF_2, XeF_4, XeF_6 and XeF_8 have been prepared and identified. The first two fluorides, namely, XeF_2 and XeF_4, are more stable than the rest.

FLUORIDES, OXOFLUORIDES AND OXIDES OF XENON

We shall now give a descriptive account of preparation, properties and structures of fluorides, oxofluorides and oxides of xenon in its different oxidation states.

Xenon (II) Compounds

Xenon Difluoride, XeF_2. Preparation. 1. Xenon difluoride is best prepared by heating a mixture of xenon and fluorine in molecular ratio of 2:1 at 400°C in a sealed nickel tube. On cooling quickly, a colourless solid XeF_2 results.

$$Xe + F_2 \xrightarrow[400°C]{Ni} XeF_2$$

Alternatively, the 1:1 mixture of xenon and fluorine may be subjected to electric discharge to get xenon difluoride.

2. It is also formed by photochemical combination of xenon and fluorine under the influence of mercury vapour.

$$Xe + F_2 \xrightarrow{\text{Hg vapour}} XeF_2$$

3. It can also be prepared by fluorination of xenon by oxygen monofluoride (O_2F_2) at – 178°C.

$$Xe + O_2F_2 \xrightarrow{-178°C} XeF_2 + O_2$$

Properties. 1. Xenon difluoride is a colourless, crystalline solid which melts at 140°C.

2. It dissolves in hydrogen fluoride without reacting with it.

3. It reacts with hydrogen to give xenon and hydrogen fluoride.

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$

4. It reacts with water evolving oxygen.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

5. It oxidises iodine in the presence of BF_3 to give IF.

$$XeF_2 + I_2 \xrightarrow{BF_3} 2IF + Xe$$

6. It reacts with sulphur trioxide to give xenon.

$$XeF_2 + 2SO_3 \longrightarrow Xe + S_2O_6F_2$$

7. It is a mild fluorinating agent. Thus, it reacts with benzene to give fluorobenzene, C_6H_5F.

8. It is also a strong oxidising agent. It oxidises HCl to Cl_2 and Ce (III) to Ce (IV).

9. In BrF_3 solution, xenon difluoride donates F^- to MF_5 (where M = P, As, Sb, etc.).

$$XeF_2 + SbF_5 \longrightarrow [XeF]^+[SbF_6]^-$$

$$2XeF_2 + AsF_5 \longrightarrow [Xe_2F_3]^+[AsF_6]^-$$

10. It reacts with anhydrous HSO_3F, $HClO_4$, CF_3COOH to give mixed fluoro-oxy compounds $FXeOSO_2F$, $FXeOClO_3$, $FXeOOCCF_3$, respectively.

11. It reacts with $\bullet CF_3$ in vapour phase to give $Xe(CF_3)_2$ which contains Xe – C bond.

$$C_2F_6 \xrightarrow{\text{plasma}} 2\bullet CF_3$$

$$2\bullet CF_3 + XeF_2 \longrightarrow Xe(CF_3)_2 + F_2$$

12. It reacts with $HN(SO_2F)_2$ in CF_2Cl_2 to give $F - Xe - N(SO_2F)_2$

$$XeF_2 + HN(SO_2F)_2 \longrightarrow F\text{–}Xe\text{–}N(SO_2F)_2 + HF$$

Structure of XeF_2 molecule. Spectroscopic analysis has shown that XeF_2 molecule has linear geometry. This is explained on the basis of VSEPR theory as follows.

In the formation of XeF_2 molecule, one of the 5*p* electrons in xenon is assumed to shift to the 5*d* orbital so that there are two unpaired electrons (one in 5*p* and one in 5*d* orbital) in the excited state of xenon. One 5*s*, three 5*p* and one 5*d* orbitals hybridise to give five sp^3d hybrid orbitals. The two sp^3d hybrid orbitals of xenon containing single electrons overlap with the half-filled *p* orbitals of the two fluorine atoms forming two Xe – F sigma bonds. The xenon and the two fluorine atoms lie in a straight line (*i.e.*, are linear) while the three equatorial positions are occupied by the three lone pairs of electrons to minimise electron pair repulsions (VSEPR theory). The molecule has thus a **linear geometry**, as shown in Fig. 4.

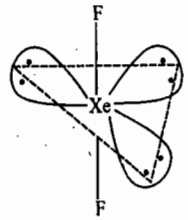


Fig. 4. The structure of XeF_2 molecule.

Xenon (IV) Compounds

1. Xenon Tetrafluoride, XeF_4. Preparation. 1. It is prepared by passing a mixture of xenon and fluorine, in the molecular ratio of 1:5, through a nickel tube, at 400°C under a pressure of 5–6 atm.

$$Xe + 2F_2 \xrightarrow[5\text{–}6\,atm]{400°C} XeF_4$$

2. It is also synthesised by passing an electric discharge through a mixture of xenon and fluorine in the molecular ratio of 1:2 at –80°C.

Properties. 1. It is a colourless, crystalline solid which melts at 117·1°C. It sublimes readily.

2. It dissolves in hydrogen fluoride without reacting.

3. It is reduced by hydrogen at 117°C to give xenon.

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

4. It reacts with boron trichloride to form boron trifluoride.

5. It undergoes disproportionation in water giving a highly explosive solid compound, XeO_3.

$$2XeF_4 + 3H_2O \longrightarrow Xe\,(g) + XeO_3\,(s) + 6HF\,(aq) + F_2(g)$$

But, if the reaction is carried out at – 80°C, it forms xenon oxofluoride.

$$XeF_4 + H_2O \xrightarrow{-80°C} XeOF_2 + 2HF$$

6. It combines with molten TaF_5 to form a straw-coloured compound, $Xe(TaF_6)_2$.

$$XeF_4 + 2TaF_5 \longrightarrow Xe(TaF_6)_2 + F_2$$

7. It is a stronger fluorinating agent than XeF_2. It converts Hg to HgF_2, Pt to PtF_4, NO and NO_2 to NOF and NO_2F, SF_4 to SF_6, etc. Thus,

$$2Hg + XeF_4 \longrightarrow Xe + 2HgF_2$$

$$Pt + XeF_4 \longrightarrow Xe + PtF_4$$

$$2SF_4 + XeF_4 \longrightarrow Xe + 2SF_6$$

8. It forms an addition compound with antimony pentafluoride.

$$XeF_4 + SbF_5 \longrightarrow XeF_4.SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$$

Structure of XeF_4 molecule. The structure of XeF_4 molecule can be explained as follows.

Since no double bonds are formed in the structure of XeF_4, the number of valence electron pairs around Xe atom would be $\frac{1}{2}(8+4)$ (four electrons come from the four covalently bonded fluorine atoms).

In the formation of xenon tetrafluoride, two of the *5p* electrons go to the *5d* orbitals so that there are now four unpaired electrons (two in *5p* and two in *5d* orbitals). The six orbitals (one *5s*, three *5p* and two *5d*) of Xe hybridise to form six sp^3d^2 hybrid orbitals. The covalent bonds are formed by overlapping of four of these hybrid orbitals (each contain- ing a single electron) of xenon with half-filled *p* orbitals of fluorine atoms. The molecule has a **square planar** structure as shown in Fig. 5. The two lone pairs occupy axial positions so as to minimise electron pair repulsion (VSEPR theory). The xenon and the four fluorine atoms are coplanar.

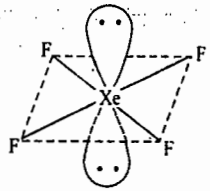


Fig. 5. The structure of XeF_4 molecule.

2. Xenon Oxodifluoride, $XeOF_2$. It is prepared by slow and partial hydrolysis of XeF_4 at a low temperature (– 80°C).

$$XeF_4 + H_2O \xrightarrow{80°C} XeOF_2 + 2HF$$

It is not a very stable compound.

Structure of $XeOF_2$ molecule. In arriving at the structure of this compound, two of the *5p* electrons of Xe are assumed to go to the *5d* orbitals when Xe atom is in excited state. The five orbitals (one *s*, three *p* and one *d*) of Xe atom hybridise to form five sp^3d hybrid orbitals. Three of the five hybrid orbitals which are *singly filled* are used in forming sigma bonds with two fluorine atoms and one oxygen atom. One *5d* orbital which is not involved in hybridisation and is singly filled is used in forming an additional bond, which is a pi bond, with the oxygen atom. There is thus a double bond (one sigma bond and one pi bond) between xenon and oxygen atoms. The two lone pairs of electrons occupy two equatorial positions in this structure to minimise electron pair repulsions. The compound, therefore, has a **T-shaped structure**, as shown in Fig. 6.

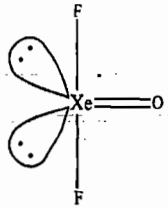


Fig. 6. The T-shaped structure of $XeOF_2$ molecule.

In the case of $XeOF_2$ molecule, the number of Xe orbitals involved in hybridisation is calculated by ignoring the contribution of doubly bonded oxygen and taking into consideration the contribution of only the fluorine atoms bonded to the central atom by sigma bonds. Accordingly, the number of orbitals involved in hybridisation = $\frac{1}{2}(8+2) = 5$. Thus, this molecule involves sp^3d hybridisation of Xe orbitals.

Xenon (VI) Compounds

1. Xenon Hexafluoride, XeF_6. Preparation. 1. It is prepared by heating xenon with excess of fluorine (in the ratio of 1:20) in a nickel vessel at 250 – 300°C under a pressure of 50–60 atm.

$$Xe + 3F_2 \longrightarrow XeF_6$$

2. It can be obtained by interaction of XeF_4 and F_2 under pressure.

$$XeF_4 + F_2 \longrightarrow XeF_6$$

3. It is also prepared by passing electric discharge through a mixture of xenon and fluorine in the ratio of 1 : 3 at a low temperature.

Properties. 1. It is a crystalline solid substance which melts at 49·5°C.

2. It is most volatile of all the fluorides of xenon. Its vapours have a greenish yellow colour.

3. It dissolves in hydrogen fluoride giving a solution which is a good conductor of electricity. This is attributed to the formation of ions, as shown below.

$$HF + XeF_6 \longrightarrow XeF_5^+ + F_2^-$$

4. It is extremely reactive. It cannot be stored in glass or quartz vessels due to the following reactions which finally give the dangerously explosive xenon trioxide.

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

(explosive)

5. It is reduced to xenon by the action of H_2, NH_3 or HCl.

$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$

$$XeF_6 + 8NH_3 \longrightarrow Xe + 6NH_4F + N_2$$

$$XeF_6 + 6HCl \longrightarrow Xe + 3Cl_2 + 6HF$$

6. It undergoes *slow hydrolysis* with atmospheric moisture producing *highly explosive* XeO_3.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

7. It reacts with fluoride ion acceptors to form adducts.

$$XeF_6 + SbF_5 \longrightarrow XeF_6.SbF_5 \longrightarrow [XeF_5]^+[SbF_6]^-$$

$$XeF_6 + AsF_5 \longrightarrow XeF_6.AsF_5 \longrightarrow [XeF_5]^+[AsF_6]^-$$

With alkali metal fluorides, it forms compounds containing XeF_7^- and XeF_8^{2-} ions, thus behaving as F^- ion acceptor.

$$2RbF + 2XeF_6 \xrightarrow{20°C} 2RbXeF_7 \xrightarrow{50°C} (Rb^+)_2 XeF_8^{2-} + XeF_6$$

8. It reacts with alkalies to give perxenates.

$$2XeF_6 + 16NaOH \longrightarrow Na_4XeO_6 + Xe + O_2 + 12NaF + 8H_2O$$

Structure of XeF_6 molecule. In this case, the number of orbitals around the Xe atom would be $\frac{1}{2}(8+6) = 7$. In the formation of XeF_6 molecule, three of the $5p$ electrons of Xe move into the $5d$ orbitals so that 6 unpaired electrons (three in $5p$ orbitals and three in $5d$ orbitals) become available for chemical bonding. Thus, seven orbitals (one s, three p and three d) hybridise to give seven sp^3d^3 hybrid orbitals [Structure (*a*)]. Six of these orbitals containing a single electron each are used in bonding with six atoms of fluorine. The seventh hybrid orbital accommodates a lone pair of electrons.

Due to sp^3d^3 hybridisation, the molecule should have structure based on **pentagonal bipyramidal geometry**, with a lone pair of electrons at one position, as shown in Fig. 7 (*a*). However, this structure has not yet been confirmed. There has been controversy regarding its structure since its discovery. It has been suggested that the molecule has a **distorted octahedral structure** in which all the six positions are occupied by fluorine atoms and the lone pair is present at the centre of one of the triangular faces [Structure (*b*)].

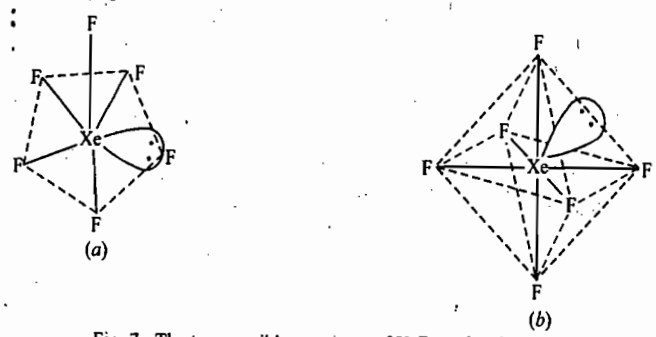


Fig. 7. The two possible structures of XeF_6 molecule.

2. Xenon Oxotetrafluoride, $XeOF_4$. Preparation. 1. Xenon oxotetrafluoride is formed to a small extent by partial hydrolysis of xenon hexafluoride.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

2. It is prepared in appreciable quantities by heating a mixture of xenon and fluorine in the molecular ratio of 1: 4 in the presence of a large excess of oxygen at about 230°C. It can be purified by vacuum distillation.

Properties. 1. It is a colourless compound melting at – 46°C.

2. On treatment with hydrogen it is reduced to xenon.

$$XeOF_4 + 3H_2 \longrightarrow Xe + H_2O + 4HF$$

3. It reacts with water to form another oxofluoride, XeO_2F_2, in which xenon remains in the same oxidation state. This compound is named xenon dioxodifluoride.

$$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$$

4. It also reacts with silica to yield xenon dioxodifluoride.

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

Structure of $XeOF_4$ molecule. *In considering the structure of $XeOF_4$, three of the $5p$ electrons are supposed to move to $5d$ orbitals when excited.*

The formation of the compound involves hybridisation of six Xe orbitals. These are $5s$, all the three $5p$ and two of the $5d$ orbitals. This is thus a case of sp^3d^2 hybridisation of Xe orbitals.

Five of the singly occupied hybrid orbitals are involved in sigma bond formation with four fluorine atoms and one oxygen atom. The $5d$ orbital which does not take part in hybridisation, forms a pi bond with the oxygen atom. Thus oxygen is combined to xenon by a double bond, one of which is a sigma bond and the other is a pi bond. It may be noted that one of the hybridised orbitals contains a lone pair of electrons. The molecule has a **square pyramidal** structure as shown in Fig. 8. The fluorine atoms are coplanar, *i.e.*, lie in the same plane. The lone pair of electrons lies opposite to the oxygen atom which is bonded to xenon atom by a double bond. This is to minimise electron pair repulsion.

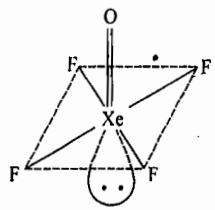


Fig. 8. The square pyramidal structure of $XeOF_4$ molecule.

The molecule contains an Xe=O bond. The number of orbitals involved in hybridisation in this case would be $\frac{1}{2}(8+4) = 6$. (The contribution due to doubly bonded oxygen atom is to be ignored as per rule). The molecule, therefore, involves sp^3d^2 hybridisation of Xe orbitals.

3. Xenon dioxodifluoride, XeO_2F_2. Preparation. 1. It is obtained by mixing XeO_4 and $XeOF_4$ at a low temperature close to – 78°C.

It is also formed when $XeOF_4$ is hydrolysed or reacted with silica (see properties of $XeOF_4$).

Properties. 1. It is a colourless solid and melts at 30·8°C.

2. It is easily hydrolysed to give xenon trioxide.

Structure of XeO_2F_2. In order to understand the structure of this compound, three of the $5p$ electrons of Xe are supposed to move into $5d$ orbitals when excited. The formation of the compound involves hybridisation of five orbitals of Xe. These are $5s$, all the three $5p$ orbitals and one of the $5d$ orbitals, as shown. This is evidently a case of sp^3d hybridisation. There are six half-filled orbitals, including the four hybrid orbitals. The four hybrid orbitals are involved in sigma bond formation with two fluorine atoms and two oxygen atoms. The remaining two singly filled orbitals which do not take part in hybridisation, form pi bonds with the same two oxygen atoms. Each oxygen atom is thus bonded to xenon atom by a double bond, one of which is a sigma bond and the other a pi bond. It may be noted that one of the hybrid orbitals contains a lone pair of electrons. The lone pair of electrons is present in one of the equatorial positions. The actual geometry of the molecule is, therefore, as shown in Fig. 9.

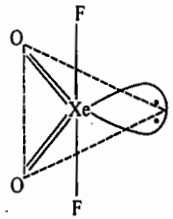


Fig. 9. The distorted trigonal bipyramidal structure of XeO_2F_2 molecule.

According to the empirical rule also, the number of electrons around Xe atom to be accommodated in hybrid orbtials is $\frac{1}{2}(8+2) = 5$ (contribution due to doubly bonded O atoms is to be ignored as per rule). Therefore, the hybridisation of Xe orbitals is sp^3d.

4. Xenon Trioxide, XeO_3. Preparation. Xenon trioxide is formed in small amounts when xenon tetrafluoride undergoes disproportionation on hydrolysis with water,

$$2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 6HF + F_2$$

or when xenon hexafluoride reacts slowly with atmospheric moisture.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Properties. 1. Xenon trioxide is a white non-volatile compound which is soluble in water.

2. It is quite stable when present in aqueous solution. However, it explodes violently when dry. It can be detonated by simple rubbing or pressing and produces about the same effect as T.N.T. This has created lot of interest in the preparation of this compound.

3. It is a powerful oxidising agent and is often used for this purpose. For instance, it oxidises Pu^{3+} to Pu^{4+} in the presence of H^+ ions.

$$6Pu^{3+} + XeO_3 + 6H^+ \longrightarrow 6Pu^{4+} + Xe + 3H_2O$$

4. When dissolved in aqueous sodium hydroxide, it undergoes disproportionation. Xenon gas is evolved and sodium perxenate, $Na_4XeO_6.8H_2O$, formed in the reaction can be recovered from the solution.

$$2XeO_3 + 4NaOH + 6H_2O \longrightarrow Xe + O_2 + Na_4XeO_6.8H_2O$$

The X-ray analysis of sodium perxenate reveals the existence of octahedral perxenate ion, XeO_6^{4-}, in the substance.

Sodium perxenate when dissolved in an acid solution decomposes slowly to give XeO_3 and oxygen. The acid solution of sodium perxenate, therefore, has strong oxidising properties. It can convert, for instance, manganous ion into permanganate ion.

Structure of XeO_3 molecule. In the formation of XeO_3, three of the *5p* electrons of Xe are supposed to move to *5d* orbitals when excited. The formation of XeO_3 molecule thus involves sp^3 hybridisation of the orbitals of Xe.

Three of the four hybrid orbitals which are singly filled, form three sigma bonds with three oxygen atoms. The three *5d* orbitals which are excluded from hybridisation, form three pi bonds with the same three oxygen atoms. Thus, each oxygen atom is bonded to xenon by a double bond. One of the hybrid orbitals of Xe contains a lone pair of electrons. The molecule has a **pyramidal structure**, as shown in Fig. 10.

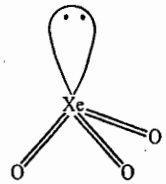


Fig. 10. The pyramidal structure of XeO_3 molecule.

The empirical rule also suggests sp^3 hybridisation since the number of orbitals involved in hybridisation would be $\frac{1}{2}(8+0) = 4$ (the contribution due to doubly bonded oxygen atoms is to be ignored).

Xenon (VIII) Compounds

1. Xenon Octafluoride, XeF_8. This compound is believed to be formed, to a small extent, by reacting xenon with a large excess of fluorine under high pressure.

$$Xe + 4F_2 \longrightarrow XeF_8$$

The structure of this compound has not yet been established.

2. Xenon Tetroxide, XeO_4. Xenon tetroxide can be prepared from barium perxenate on treatment with anhydrous sulphuric acid.

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

It is not as stable as the trioxide. It decomposes to give xenon and oxygen.

The molecule has **tetrahedral structure** as shown in Fig. 11 (*a*).

3. Xenon Oxohexafluoride, $XeOF_6$. This compound of Xe (VIII) is also known. It is formed in small amounts alongwith XeF_4 when xenon and fluorine are heated together in air. The oxygen comes from the atmosphere.

The properties of this compound are still under investigation.

4. XeO_3F_2 and XeO_2F_4. These compounds of xenon (VIII) have not yet been well characterised. However, their structures have been adequately confirmed. The structure of XeO_3F_2 has been found to be **trigonal bipyramidal** (Fig. 11*b*) in which three doubly bonded oxygen atoms are present in equatorial positions whereas the structure of XeO_2F_4 has been found to be **octahedral** in which two doubly bonded oxygen atoms occupy trans positions, as shown in Fig. 11 (*c*).

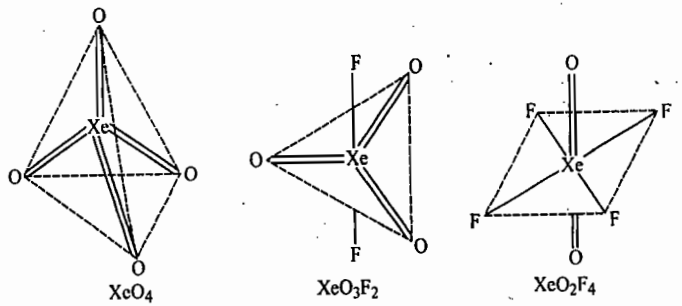


Fig. 11. Structures of (*a*) XeO_4 (*b*) XeO_3F_2 and (*c*) XeO_2F_4

FLUORIDES OF KRYPTON AND RADON

Fluorides of Krypton. Recent experiments have shown that krypton can also combine with fluorine under suitable conditions yielding krypton difluoride, KrF_2 and krypton tetrafluroide, KrF_4.

Krypton difluoride, KrF_2. It can be prepared by irradiating a mixture of krypton and fluorine with γ radiation at very low temperature (– 153°C).

Properties. 1. KrF_2 is a colourless solid.

2. It is much less stable than the corresponding compound of xenon. Therefore, it gets hydrolysed easily.

$$2KrF_2 + 2H_2O \longrightarrow 2Kr + O_2 + 4HF\ (aq)$$

3. It is a powerful oxidising and fluorinating agent.

4. It forms adducts with SbF_5 and AsF_5. Thus,

$$KrF_2 + 2SbF_5 \longrightarrow KrF_2.2SbF_5 \longrightarrow [KrF_2]^+ [Sb_2F_{11}]^-$$

5. When KrF_2 is γ irradiated, it produces $\cdot KrF$.

$$KrF_2 \xrightarrow{\gamma\ \text{irradiation}} \cdot KrF + \cdot F$$

The structure of KrF_2 is similar to that of XeF_2 (Fig. 4) in which Kr orbitals are involved in sp^3d hybridisation. The molecule has a linear structure, as shown in Fig. 12.

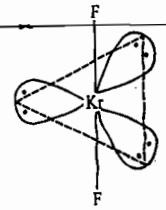


Fig. 12. Structure of KrF_2.

Krypton tetrafluoride, KrF_4. It is prepared by passing an electric discharge through a mixture of krypton and fluorine at the temperature of liquid nitrogen.

KrF_4 is highly unstable and is thus easily hydrolysed by water giving krypton, oxygen and aqueous hydrogen fluoride.

$$KrF_4 + 2H_2O \longrightarrow Kr + O_2 + 4HF\ (aq)$$

Radon fluoride, RaF_2, *has also been prepared by similar methods. It is, however, highly unstable.*

Oxocompound of Krypton. Krypton trioxide (hydrated), $KrO_3.xH_2O$. It is obtained in very small quantities by the hydrolysis of krypton tetrafluoride, KrF_4, using ice at a temperature below −30°C. The value of x may be 1, 2 or 3 when compound of the formula H_2KrO_4, H_4KrO_5 or H_4KrO_6 is produced. Krypton trioxide resembles xenon trioxide in its properties. It is also a strong oxidising agent.

Are Compounds of Helium and Neon Possible ? It may be noted that in normal state, all the *s* and *p* orbitals of xenon, krypton and radon atoms are fully filled. However, there are vacant *d* orbitals in their valency shells which allow for the promotion of electrons and formation of hybrid bonds. Accordingly, *it seems unlikely that compounds of this type will ever be formed in the case of helium and neon which have no d orbitals at all.*

It may also be mentioned that ionisation energies of helium and neon are considerably higher that those of fluorine and oxygen. This fact also *rules out the possibility of the formation of compounds of helium and neon even with fluorine and oxygen.*

QUESTIONS

1. What are noble gases ? Comment on the statement : "Periodic table was incomplete before the discovery of noble gases." Give a brief history of the discovery of noble gases.
2. (*a*) Discuss the position of noble gases in the periodic table.
   (*b*) Why is it more appropriate to call elements of Group 18 as noble gases instead of inert gases ?
3. (*a*) Give an account of the discovery of noble gases. How can they be separated from one another ?
   (*b*) Compare the buoyancy of helium with that of hydrogen.
4. Describe the methods employed, indicating the physico-chemical principles involved in them, for the separation of rare gases of the atmosphere. Indicate their importance in industry.
5. (*a*) Give an account of the discovery of helium. How does it occur in nature ?
   (*b*) How is helium obtained on large scale ? What are the important properties and uses of this gas ?
6. (*a*) How was argon discovered ? How is it obtained on a large scale ? What are the important uses of noble gases?
   (*b*) What are clathrate compounds of noble gases ? Describe the clathrate compounds of noble gases with quinol.
7. What prompted Bartlett to conjecture that it is possible to prepare the fluorides of xenon. Give the preparation and properties of one fluoride of xenon. Discuss its structure.
8. (*a*) Give methods of preparation, properties and structures of the following :
   (*i*) XeF_2 (*ii*) $XeOF_4$ (*iii*) XeF_6 (*iv*) XeO_3 (*v*) XeF_4 (*vi*) KrF_2 (*vii*) XeO_2F_2
   (*b*) Complete the following reactions :
   (*i*) $XeF_4 + H_2O \longrightarrow$ (*ii*) $XeF_2 + H_2 \longrightarrow$ (*iii*) $XeF_6 + SiO_2 \longrightarrow$
   (*iv*) $XeF_6 + NH_3 \longrightarrow$ (*v*) $XeF_6 + 3H_2O \longrightarrow$
9. (*a*) How is XeF_4 prepared ? Describe its reactions with (*i*) Hg (*ii*) F_2 (*iii*) BCl_3 (*iv*) SF_4.
10. Discuss the structures of fluorides and oxofluorides of xenon in various oxidation states.
11. Give a brief description of fluorides of krypton and radon.
12. Comment on the statement that there is no likelihood of the formation of compounds of helium and neon.

THE *d* BLOCK ELEMENTS. GENERAL CHARACTERISTICS

21

The Transition Elements. The **transition elements** may be broadly defined *as those which as elements or as ions have partly filled d or f subshells.* If the *d* subshell is partly filled, the elements are known as ***d*-block or transition elements.** If the *f* subshell is partly filled, the elements are known as ***f* block or inner transition elements.** Both transition and inner transition elements have been discussed at an appropriate level in this book.

THE TRANSITION ELEMENTS. THE *d* BLOCK ELEMENTS

Electronic Configurations. The *d* block elements consist of three rows called **first, second** and **third transition series.** The electronic configurations of these elements are discussed below.

Elements of First Transition Series. The elements from scandium (Z = 21) to zinc (Z = 30) constitute the First transition series. In the first element, scandium, the 3*d* subshell starts filling up. Its electronic configuration is $1s^2 2s^2 p^6 3s^2 p^6 d^1 4s^2$.

For reasons of space, we shall describe configurations of outer shells only, leaving aside the configuration upto 3*p* level (argon configuration) which remains the same throughout the period. The outer electronic configuration of scandium may, thus, be written as $3d^1 4s^2$.

The next element, titanium (Z = 22), has one more *d* electron added to it. Its outer electronic configuration is $3d^2 4s^2$. This procedure continues and the *d* orbitals get filled up more and more, step by step, on moving towards the right along this period. Accordingly, the outer electronic configurations of the succeeding elements, *viz.*, vanadium (Z = 23), chromium (Z = 24), manganese (Z = 25), iron (Z = 26), cobalt (Z = 27), nickel (Z = 28), copper (Z = 29) and zinc (Z = 30), are as given below :

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3*d*	1	2	3	5	5	6	7	8	10	10
4*s*	2	2	2	1	2	2	2	2	1	2

The last element, zinc, has the maximum permissible number of electrons in the *d* orbitals. Its outer electronic configuration is $3d^{10} 4s^2$, as shown. But, the definition of *d* block elements based on the number of electrons in the *d* subshell excludes zinc from the first transition series of *d* block since neither zinc nor any of its common ions has a *partly filled d subshell.*

The atoms of chromium and copper, unlike the others, have a single electron in the 4*s* orbital. This is due to the *additional stability* gained by the atom when the *d* subshell is *exactly half-filled* (*i.e.*, it contains 5 electrons) or *completely filled* (*i.e.*, it contains 10 electrons). Accordingly, one of the 4*s* electrons moves to the 3*d* level in the atoms of chromium and copper. The 3*d* level in the case of chromium gets *exactly half-filled* and that in the case of copper gets *completely filled.*

Elements of Second Transition Series. The ten elements from yttrium to cadmium (Z = 39 to 48) constitute the Second transition series. In yttrium, 4*d* subshell begins filling up and its outer electronic

configuration is $4d^1\ 5s^2$. The filling up of the $4d$ orbitals continues as we keep moving in this period towards the next nine elements, namely, zirconium (Z = 40), niobium (Z = 41), molybdenum (Z = 42), technetium (Z = 43), ruthenium (Z = 44), rhodium (Z = 45), palladium (Z = 46), silver (Z = 47) and cadmium (Z = 48). In cadmium (Z = 48), the $4d$ subshell has now the maximum permissible number of 10 electrons, the configuration of the outer shell being $4d^{10}\ 5s^2$. The outer electronic configurations of these elements are given below.

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$4d$	1	2	4	5	5	7	8	9	10	10
$5s$	2	2	1	1	2	1	1	1	1	2

The number of $4d$ electrons varies from 1 to 10 as we move from yttrium to cadmium.

According to the definition of *d* block elements already given, the nine elements from Y to Ag, may be taken as constituting the second series of *d* block elements. The definition, based on the number of electrons in the $4d$ subshell, excludes Cd from the Second transition series.

There are evidently some pronounced irregularities in the configurations of these elements. The configurations of Mo ($4d^5\ 5s^1$) and Ag ($4d^{10}\ 5s^1$) can be easily understood on the basis of higher stability of exactly half-filled and completely filled subshells as is noticed in the case of Cr and Cu in the First transition series. This concept, however, cannot explain the anomalous configurations of Nb, Ru, Rh and Pd. As a matter of fact, no simple explanation for such anomalies can be offered. Suffice to say that nuclear–electron and electron–electron interactions play significant role in determining these configurations about which much cannot be said in the present volume.

Elements of Third Transition Series. The Third transition series starts from hafnium (Z = 72) in which the filling of $5d$ subshell begins*. The outer electronic configuration of hafnium is $4f^{14}\ 5d^2\ 6s^2$. This process continues thereafter in tantalum (Z = 73), tungsten (Z = 74), rhenium (Z = 75), osmium (Z = 76), iridium (Z = 77), platinum (Z = 78), gold (Z = 79) and mercury (Z = 80). The $5d$ subshell gets enlarged by the addition of one electron at each step and gets completed when mercury (Z = 80) is reached, its outer electronic configuration being $5d^{10}\ 6s^2$. The outer electronic configurations of these elements are given below :

	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
$5d$	2	3	4	5	6	7	8	10	10
$6s$	2	2	2	2	2	2	2	1	2

Since mercury and its common ions have their *d* orbitals completely filled, it should, by definition, be excluded from the *d* block elements.

GENERAL CHARACTERISTICS OF *d* BLOCK ELEMENTS

Some of the important characteristics of the *d* block elements are given in Table 1.

1. Metallic Character. All the transition elements are metals. This is to be expected since the number of electrons in the outermost shell is very small being only 1 or 2 which can be readily lost. They are good conductors of heat and electricity. They are also malleable and ductile and form alloys with several other metals. They differ from non-transition metals, however, in being hard and brittle. Mercury is an exception. Although hardness and brittleness are associated with covalent bonding between

*Lanthanum (Z = 57) with outer electronic configuration $5d^1\ 6s^2$ is , by definition, a *d* block element of Third transition series. However, in its physical and chemical properties, it closely resembles the series of 14 elements, *viz.*, cerium (Z = 58) to lutetium (Z = 71) which follows it. These elements are called lanthanides. Therefore, lanthanum is considered as a member of the lanthanide series and is studied along with them.

TABLE 1
Important Characteristics of *d* Block Elements

Elements	Atomic number	Outer electronic configuration	Molar volume ($cm^3\ mol^{-1}$)	Density ($g\ cm^{-3}$)	Atomic radius (Å)	Melting point (°C)	Boiling point (°C)
First Transition Series							
Sc	21	$3d^1\ 4s^1$	15·0	3·01	1·62	1539	2730
Ti	22	$3d^2\ 4s^2$	10·6	4·51	1·47	1668	3260
V	23	$3d^3\ 4s^2$	8·3	6·10	1·34	1900	3450
Cr	24	$3d^5\ 4s^1$	7·2	7·19	1·27	1875	2665
Mn	25	$3d^5\ 4s^2$	7·4	7·43	1·26	1245	2150
Fe	26	$3d^6\ 4s^2$	7·1	7·86	1·26	1536	3000
Co	27	$3d^7\ 4s^2$	6·7	8·90	1·25	1495	2900
Ni	28	$3d^8\ 4s^2$	6·6	8·90	1·24	1453	2730
Cu	29	$3d^{10}\ 4s^1$	7·1	8·96	1·28	1083	2595
Zn	30	$3d^{10}\ 4s^2$	9·2	7·14	1·38	419·5	906
Second Transition Series							
Y	39	$4d^1\ 5s^2$	19·8	4·47	1·80	1509	2927
Zr	40	$4d^2\ 5s^2$	14·1	6·49	1·60	1852	1500
Nb	41	$4d^4\ 5s^1$	10·8	8·40	1·46	2415	3300
Mo	42	$4d^5\ 5s^1$	9·4	10·21	1·39	2610	5560
Tc	43	$4d^5\ 5s^2$	–	11·50	1·36	2200	–
Ru	44	$4d^7\ 5s^1$	8·3	12·20	1·34	2500	4900
Rh	45	$4d^8\ 5s^1$	8·3	12·40	1·34	1966	4500
Pd	46	$4d^9\ 5s^1$	8·9	12·00	1·37	1552	3980
Ag	47	$4d^{10}\ 5s^1$	10·4	10·51	1·44	960·8	2210
Cd	48	$4d^{10}\ 5s^2$	13·1	8·65	1·54	320·9	765
Third Transition Series							
La	57	$5d^1\ 6s^2$	22·5	6·17	1·87	920	3470
Hf	72	$5d^2\ 6s^2$	13·6	13·10	1·58	2222	5400
Ta	73	$5d^3\ 6s^2$	10·9	16·60	1·46	2996	5425
W	74	$5d^4\ 6s^2$	9·5	19·30	1·39	3410	5930
Re	75	$5d^5\ 6s^2$	8·8	21·00	1·37	3180	5900
Os	76	$5d^6\ 6s^2$	8·4	22·60	1·35	2700	5500
Ir	77	$5d^7\ 6s^2$	8·5	22·50	1·36	2454	5300
Pt	78	$5d^8\ 6s^2$	9·1	21·40	1·38	1769	4530
Au	79	$5d^{10}\ 6s^1$	10·2	19·30	1·44	1063	2920
Hg	80	$5d^{10}\ 6s^2$	14·8	13·60	1·57	– 38·4	357

the metal atoms, the existence of metallic bonding cannot be denied because the transition metals are good conductors of heat and electricity. It appears that covalent and metallic bonding both exist amongst the atoms of the transition elements. While the overlapping of unfilled *d* orbitals of metal atoms causes covalent bonding, the valence *s* electrons cause metallic bonding. Copper, silver and gold are particularly outstanding in their thermal and electrical conductivities.

2. Molar Volumes and Densities. The molar volumes of transition elements are shown in Table 1. These are much lower than those of the *s* and *p* block elements of the neighbouring groups. The reason is obvious. As the inner orbitals get filled, the increased nuclear charge pulls the electrons inward. The molar volume, therefore, decreases.

As a result of decrease in molar volume, there is corresponding increase in density. Accordingly, the densities of the transition elements are quite high. Most of these elements have densities greater than 5 g cm^{-3}. Scandium, titanium and yttrium, with density 3·01, 4·51 and 4·47 g cm^{-3}, respectively, are the only exceptions.

3. Atomic Radii. The atomic radii of the transition elements of a given series are seen to decrease, generally, with increase in the atomic number as expected from the fact that increase in the nuclear charge would tend to attract the electron charge cloud inward. There are, however, a few exceptions.

The radii of the elements, from chromium to copper, however, are very close to one another. This is due to the fact that the successive addition of *d* electrons screens the outer electrons (4*s* electrons) from the inward pull of the nucleus. As a result of this, the size of the atom does not alter much in moving from chromium to copper.

4. Ionic Radii. The ionic radii follow the same trend as the atomic radii. This is evident from the values given in Table 2 for the ionic radii of elements of the First transition series. It is seen that for ions of the given charge (valency), the radius decreases slowly with increase in atomic number. The radii of the doubly charged ions, although small, are comparable with the radius of Ca^{2+} ion. Their oxides, therefore, are similar to calcium oxide, although somewhat less basic and less soluble in water.

TABLE 2

Ionic Radii (Å) of the Elements of the First Transition Series

Element	Ion	Radius (Å)	Element	Ion	Radius (Å)
Sc	Sc^{2+}	0·81	Fe	Fe^{2+}	0·76
				Fe^{3+}	0·64
Ti	Ti^{2+}	0·91	Co	Co^{2+}	0·74
	Ti^{3+}	0·76		Co^{3+}	0·63
V	V^{2+}	0·88			
	V^{3+}	0·74	Ni	Ni^{2+}	0·72
Cr	Cr^{2+}	0·84	Cu	Cu^{2+}	0·72
	Cr^{3+}	0·69			
Mn	Mn^{2+}	0·80	Zn	Zn^{2+}	0·74
	Mn^{3+}	0·66			

5. Melting Points and Boiling Points. The melting and boiling points of the transition elements are, generally, very high. The melting points of most of the transition elements (except Cd and Hg) are above 900°C. This seems to be a very high temperature when compared with the melting points of *s* block elements. For example, lithium melts at 108·5°C and cesium at 28·7°C.

Zinc, cadmium and mercury which, by definition based on the number of *d* electrons, are *excluded* from the *d* block elements, have relatively low melting points, being 419·5°C, 320·9°C and –38·4°C, respectively. These are, therefore, the notable exceptions. These elements, like the other *d* block elements, are moderately volatile. The reason for such exceptional behaviour is that the atoms of these elements have completely filled sets of *d* orbitals, *i.e.*, the *d* orbitals in each case contain the maximum of 10 electrons. There can, therefore, be *no covalent bonding* amongst the atoms of these elements. The covalent bonding, which is responsible for high melting and boiling points, can occur in the rest of the *d* block elements on account of vacant *d* orbitals.

6. Ionisation Energies. The ionisation energy of an element gives an idea of the ease with which an electron can be removed from its isolated gaseous atom. The ionisation energies of elements of the

First transition series are given in Table 3.

TABLE 3

Ionisation Energies of the Elements of the First Transition Series

Element	Ionisation Energies (kJ mol^{-1}) :		
	First	*Second*	*Third*
Sc	632·6	1245·1	2450·6
Ti	659·0	1320·5	2721·3
V	650·2	1376·1	2873·6
Cr	652·3	1635·1	2994·9
Mn	716·3	1513·3	3258·1
Fe	762·3	1564·0	2963·9
Co	758·1	1647·6	3237·6
Ni	736·0	1756·9	3400·7
Cu	744·7	1961·9	3560·6
Zn	906·7	1736·3	3838·8

Since the atoms are small in size, their ionisation energies are fairly high. The values, in most cases, lie in between those of *s* and *p* block elements. This indicates that the transition elements are less electropositive than the elements of Groups 1 and 2 (*s* block). Thus, although transition elements do form ionic compounds, yet they do not do so as readily as alkali and alkaline earth metals do. Also, unlike the alkali and alkaline earth metals, the transition elements have a tendency to form covalent compounds as well under certain conditions. Generally, the compounds in which a smaller valency is exercised are ionic compounds while those in which a higher valency is exercised are covalent compounds.

The ionisation energy along a given period is generally expected to increase with increase in the atomic number. This is due to the effect of increasing nuclear charge which would tend to pull the outer electron charge cloud inward with increasing force. In the case of transition elements, however, the addition of increasing number of *d* electrons increases the screening effect and hence shields the outer *s* electrons from the inward pull of the positive nucleus. For instance, the nuclear charge which pulls the electron towards the nucleus increases from 21 to 22 units in going from Sc to Ti. But, at the same time, the screening constant for 4*s* electrons which gives a measure of the shielding of the electrons from the pull of the nucleus, also increases from 18·00 (in the case of Sc) to 18·85 units (in the case of Ti). The screening constants have been calculated with the help of the Slater's rules as illustrated in Chapter 1. Thus, the effects of increasing nuclear charge and expansion of *d* subshell tend to oppose each other. On account of these counter effects, the ionisation energies increase rather slowly on moving along the period. Accordingly, in the First transition series, the values for the first four elements (Sc, Ti, V and Cr) differ only slightly from one another. Similarly, the values for Fe, Co, Ni and Cu are fairly close to one another. The value for zinc, however, is appreciably higher. This is due to the additional stability conferred on the atom on account of complete filling of the 3*d* subshell.

The second ionisation energies are seen to increase, more or less regularly, with increase in atomic number. The values for Cr and Cu, however, are notably higher than those of their neighbours. The reason for this lies in the outer electronic configurations of the singly charged chromium and copper ions. The outer electronic configuration of singly charged chromium ion is $3d^5$ and that of singly charged copper ion is $3d^{10}$. Thus, the second ionisation of chromium involves the removal of one of the five *d* electrons constituting *exactly half-filled* 3*d* subshell which is *highly stable*. Similarly, the second ionisation of copper involves the removal of one of the ten *d* electrons constituting the *fully filled* 3*d* subshell which is also *highly stable*.

7. Reactivity. The atoms of transition elements are rather small and, therefore, their ionisation energies are fairly high as pointed out above. Due to the existence of covalent bonding they have high

heats of sublimation, *i.e.*, they require a large amount of energy to change them from solid to vapour state. The metal ions, because of their low positive charge density, do not get hydrated easily. Thus, on account of their high heats of sublimation, high ionisation energies and low heats of hydration of their ions, the transition elements have a small tendency to react. They have rather a tendency to remain unreative or 'noble'. This tendency is very well pronounced in platinum and gold (of the Third transition series).

8. Oxidation States. While discussing the chemistry of transition elements, it is more covenient to use the term **oxidation state** instead of valency. The transition elements show a large number of oxidation states which are related to their electronic configurations. This is illustrated below by taking into consideration the oxidation states of the elements of the First transition series.

TABLE 4

Oxidation States of the Elements of the First Transition Series

Elements	Outer Electronic Configuration	Oxidation States
Sc	$3d^1\,4s^2$	+2, +3
Ti	$3d^2\,4s^2$	+2, +3, +4
V	$3d^3\,4s^2$	+2, +3, +4, +5
Cr	$3d^5\,4s^1$	+1, +2, +3, +4, +5, +6
Mn	$3d^5\,4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6\,4s^2$	+2, +3, +4, +5, +6
Co	$3d^7\,4s^2$	+2, +3, +4
Ni	$3d^{10}\,4s^2$	+2, +3, +4
Cu	$3d^{10}\,4s^1$	+1, +2
Zn	$3d^{10}\,4s^2$	+2

The outer electronic configuration of scandium (Sc), the first element of the First transition series, is $3d^1\,4s^2$ (Table 4). It exhibits an oxidation state of +2 in those compounds in which it uses both of its 4*s* electrons. It can also exhibit an oxidation state of +3 when it uses its two 4*s* electrons as well as one 3*d* electron in chemical bonding.

The outer electronic configuration of titanium (Ti) is $3d^2\,4s^2$. It shows an oxidation state equal to +2 when it uses both the 4*s* electrons, equal to +3 when both the *s* electrons and one *d* electron is used and +4 when both the *s* and both the *d* electrons are used in chemical bonding.

Similarly, vanadium (V), with electronic configuration $3d^3\,4s^2$, shows oxidation states equal to +2, +3, +4, +5, depending on whether it uses the two *s* electrons only or also in addition to that, it uses one, two or three of its *d* electrons as well.

Chromium (Cr), the next element with outer electronic configuration $3d^5\,4s^1$, has only one *s* electron. Accordingly, it can have an oxidation state of +1 when it uses only this electron in chemical bonding. In addition, it may have oxidation states equal to +2, +3, +4, +5 and +6 when it uses one, two, three, four or all the five of its *d* electrons as well. Similarly, manganese (Mn), having the outer electronic configuration $3d^5\,4s^2$, may have oxidation states from 2 to 7.

It is clear from the above discussion that the first five elements of the First transition series upto Mn in which the 3*d* subshell is no more than half-filled, the minimum oxidation state is given by the number of electrons in the outer *s* subshell and the maximum oxidation state is given by the sum of the outer *s* and *d* electrons.

In the next elements, *viz.*, iron ($3d^5\,4s^1$), cobalt ($3d^7\,4s^2$), nickel ($3d^8\,4s^2$), copper ($3d^{10}\,4s^1$) and zinc ($3d^{10}\,4s^2$), in which the number of 3*d* electrons is more than five, the minimum oxidation state is still equal to the number of the outer *s* electrons. The maximum oxidation state, however, is not related at all with the electronic configuration. In fact, the maximum oxidation state is rarely higher than +2 or +3. For example, the oxidation state of iron, which has outer electronic configuration as $3d^6\,4s^2$, is largely confined to +2 or +3. The +4, +5 and +6 oxidation states are known but are rare and +8 oxidation state is unknown. The +8 oxidation state, however, is important in the chemistry of the other members of the iron family, namely, ruthenium and osmium.

9. Standard Electrode Potentials. The standard electrode potential of a transition element is generally negative compared to the potential of the standard hydrogen electrode (taken as zero). For instance, the standard potentials of the elements of the First transition series, excepting copper, given in

Table 5, are appreciably more negative than the potential of the standard hydrogen electrode. It is expected, therefore, that these metals, excepting copper, would evolve hydrogen gas when reacted with acid solution :

$$M + 2H^+(aq) \longrightarrow M^{2+}(aq) + H_2(g)$$

However, in actual practice, the rate at which most of these metals react with acids is very low. Some of the metals, in fact, get protected from the attack of acids by a thin impervious layer of an inert oxide. Chromium, for instance, in spite of its considerable high negative electrode potential, is so unreactive that it can be used as a protective non-oxidising metal. The reason is that it gets coated with a non-reactive oxide, Cr_2O_3.

TABLE 5

Standard Electrode Potentials of the Elements of the First Transition Series

Elements	Electrode Reactions	Standard Electrode Potentials (volts)
Sc	$Sc^{3+} + 3e^- \longrightarrow Sc$	−2·10
Ti	$Ti^{2+} + 2e^- \longrightarrow Ti$	−1·60
V	$V^{2+} + 2e^- \longrightarrow V$	−1·20
Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0·74
Mn	$Mn^{2+} + 2e^- \longrightarrow Mn$	−1·18
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0·44
Co,	$Co^{2+} + 2e^- \longrightarrow Co$	−0·27
Ni	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0·24
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0·34
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0·76

10. Reducing Properties. All *d* block elements, except copper, have standard potentials considerably more negative than that of the standard hydrogen electrode (taken as zero), as shown in Table 5 above. Hence, these metals, excepting copper, are oxidised easily to their ions in aqueous solutions.

$$M \longrightarrow M^{2+}(aq) + 2e^-$$

They should, therefore, be good reducing agents. However, they are not as good reducing agents as the metals of Groups 1, 2 and 13. The reducing capacity of a metal depends on its tendency to change into aquated ions. On account of their high heats of vaporisation and high ionisation energies and low heats of hydration of their ions, the transition metals do not get converted into their aquated ions as easily as the metals of Groups 1, 2 and 13 and, therefore, are not as good reducing agents as the metals of Groups 1, 2 and 13.

Copper has a positive electrode potential. This means that copper is not able to displace H^+ ions from acid solutions. The reaction

$$Cu + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2$$

simply does *not* occur. The tendency of copper to change into cupric ion

$$Cu \longrightarrow Cu^{2+}(aq) + 2e^-$$

is extremely small since E°(oxidation) for this reaction is negative (−0·34V). Hence, copper is a particularly poor reductant.

11. Colour. Most of the compounds of transition metals are coloured in the solid or in solution states. This is unlike the compounds of *s* and *p* block elements which are usually colourless or in any case not strongly coloured.

Colour of a substance arises invariably from the property of the substance to absorb light of certain wave lengths in the region of visible light ($\lambda = 3800 - 7600$ Å). If a substance absorbs wave length corresponding to, say, red light, the transmitted light will consist of wave lenghts corresponding to other colours, of blue colour in particular. The substance will, therefore, appear blue. The transmitted light has complementary colour to that of the absorbed light. Hydrated copper (II) ion, for example, absorbs radiations corresponding to red light. The ion, therefore, transmits radiations of wave lengths corresponding to blue colour (which is complementary to red colour). Anhydrous cobalt (II) compounds also absorb red light and, therefore, appear blue. The hydrated cobalt (II) compounds, however, absorb radiations of wave lengths corresponding to blue colour and, therefore, appear red.

As discussed in Chapter 27, the energies of *d* orbitals of metal ions in their complexes are split into two sets of energy levels because of crystal field effects. The colour of transition metal ions arises from the excitation of electrons from the *d* orbitals of lower energy to the *d* orbitals of higher energy. Light radiations corresponding to such small amounts of energy which are required for the above mentioned *d – d* electron excitations, are available in the visible range. It is for this reason that transition metal ions have the property to absorb certain radiations from the visible region and exhibit the complementary *colours*.

The transition metal ions which have completely filled *d* orbitals are colourless. There are no vacant *d* orbitals to permit the above type of excitation of electrons. Thus, $Zn^{2+}(3d^{10})$, $Cd^{2+}(4d^{10})$ and $Hg^{2+}(5d^{10})$ ions are *colourless*. The transition metal ions which have *completely empty d* orbitals are also *colourless*. Thus, Sc^{3+} and Ti^{4+} ions are colourless.

Colours and outer electronic configurations of important ions of the elements of the First transition series are given in Table 6.

TABLE 6

Colour of Ions of the Elements of The First Transition Series

Ion	Outer Electronic Configuration	Number of Unpaired Electrons	Colour of the Ion
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^0$	0	Colourless
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
Mn^{2+}	$3d^5$	5	Light Pink
Mn^{3+}	$3d^4$	4	Violet
Fe^{2+}	$3d^6$	4	Light green
Fe^{3+}	$3d^5$	5	Yellow
Co^{3+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Cu^{+}	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

The ions of *s* and *p* block elements are colourless because the excitation of electrons from the lower *s* or *p* orbital to the higher *s*, *p* or *d* orbitals can only be carried out by the absorption of a very high amount of energy which is associated only with the radiation in the ultraviolet region. There is, therefore, no absorption of light from the visible region. As a result, the *s* and *p* block elements are colourless.

12. Magnetic Properties. Matter, in general, is associated with magnetic properties. Majority of substances are either *paramagnetic* or *diamagnetic*. A **paramagnetic substance** is one which is attracted into a magnetic field and a **diamagnetic substance** is one which is repelled by a magnetic field. The diamagnetic behaviour is due to the fact that small magnetic moments are induced into a substance when a magnetic field is brought in the vicinity of the substance. These magnetic moments are not normally present in the substance. The magnetic moments induced, however, are in **opposition** to the inducing field. This causes *repulsion* of the substance by the magnetic field.

Paramagnetism *arises from the presence of unpaired electrons in atoms, ions, complex ions or molecules*. We may recall from our knowledge of elementary physics that the motion of an electric charge creates a magnetic field. Thus, *the motion (spin motion and orbital motion) of an electron, a charged particle, creates a magnetic field*. Each electron may, in fact, be regarded as a *micromagnet* having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.

In substances in which electrons in their atoms are completely paired, the effects of individual electrons are mutually compensated. These substances, therefore, do not show paramagnetic behaviour. In fact, they show diamagnetic behaviour when placed in a magnetic field.

But if the atoms of a substance contain one or more unpaired electrons, the effects are not mutually compensated. The magnetic moments due to spin and orbital motion of such electrons get aligned parallel to the direction of external magnetic field applied. The magnetic moments due to unpaired electrons are of sufficiently high magnitude to overcome the small magnetic moments induced due to the paired electrons in the atoms by external magnetic field. Such a substance, therefore, instead of experiencing repulsion, experiences attraction in a magnetic field, *i.e.*, it shows **paramagnetic behaviour**.

As mentioned above, paramagnetism is shown by ions and molecules containing odd numbers of electrons. It is also shown by molecules containing even numbers of electrons provided there is one or more unpaired electrons in their structures (as, for example, the O_2 molecule).

The magnetic moment of an electron, as discussed above, is partly due to its *spin motion* and partly due to its *orbital motion*. The total or **effective magnetic moment** μ_{eff} of a substance containing an unpaired electron, is thus made up of *two components* :

(*i*) The component due to the orbital angular momentum of the electron, $\mu_{orbital}$, which is related to orbital angular momentum quantum number *l* and

(*ii*) The component due to the spin angular momentum of the electron, μ_{spin}, which is related to spin quantum number *s*.

In transition metal ions, the unpaired electrons are generally present in the outer orbitals. The orbital motion of such unpaired electrons is severely disturbed by the electrons of the surrounding ligands thereby 'quenching' the orbital angular momentum in the transition metal compounds. Therefore, in such cases, the μ_{spin} contribution becomes much more significant than the $\mu_{orbital}$ contribution so that the latter may be neglected in many cases. The effective magnetic moment, μ_{eff}, in such cases may thus be given by the expression

$$\mu_{eff} = \mu_{spin} = \sqrt{n(n+2)}$$

where *n* is the number of unpaired electrons.

The magnetic moment is expressed in *Bohr magneton*. A Bohr magneton (B.M.) is given by the expression

$$\text{B.M.} = eh/(4\pi mc)$$

where *h* is the Planck's constant, *e* is the electronic charge, *c* is the velocity of light and *m* is the mass of electron.

The effective magnetic moment of a substance thus depends mainly on the number of unpaired electrons present in it. If there is only one unpaired electron, the magnetic moment, evidently, will be approximately $\sqrt{3}$ or 1·732 B.M. If there are two unpaired electrons, the magnetic moment will be approximately $\sqrt{8}$ or 2·84 B.M. For 3, 4, 5 and 6 unpaired electrons, the values, as can be easily calculated from the above expression, will be approximately 3·87, 4·90, 5·92 and 6·93 B.M. respectively.

TABLE 7

Magnetic Moments of the Ions of the Elements of the First Transition Series

Ion	Outer Electronic Configuration	Number of Unpaired Electrons	Calculated Magnetic Moment (μ_{spin}) (B.M.)
Sc^{3+}	$3d^0$	0	0
Ti^{3+}	$3d^1$	1	1·73
Ti^{2+}	$3d^2$	2	2·84
V^{2+}	$3d^3$	3	3·87
Cr^{2+}	$3d^4$	4	4·90
Mn^{2+}	$3d^5$	5	5·92
Fe^{2+}	$3d^6$	4	4·90
Co^{2+}	$3d^7$	3	3·87
Ni^{2+}	$3d^8$	2	2·84
Cu^{2+}	$3d^9$	1	1·73
Zn^{2+}	$3d^{10}$	0	0

The calculated magnetic moments (μ_{spin} values) of some of the ions of the elements of the First transition series are given in Table 7. The actual magnetic moments may differ slightly from these values depending upon the extent of quenching of orbital angular momentum of the electrons in the ions. This, in turn, depends upon the type of arrangement of the anions (or ligands) around the transition metal ions in their compounds (or complexes) and the extent of spin-orbit coupling.

In the case of iron, cobalt and nickel, the magnetic moment due to unpaired electron spins are aligned parallel to the

external magnetic field more efficiently resulting in an exceptionally strong reinforcement of paramagnetism. These substances are, therefore, much more paramagnetic than the rest of the elements and are said to be **ferromagnetic**.

13. Catalytic Properties. Most of the transition metals and their compounds have good catalytic properties. Platinum, iron, vanadium pentoxide, nickel, etc., are important examples. Platinum is a general catalyst and is used particularly in the Contact process involving combination of sulphur dioxide and oxygen to yield sulphur trioxide. Vanadium pentoxide is also a good catalyst for the same reaction. Iron catalyses the combination of nitrogen and hydrogen in the Haber process for the manufacture of ammonia. Nickel is a good catalyst in hydrogenation processes.

According to the modern theory of catalysis, a catalytic substance is capable of forming an unstable intermediate compound which readily decomposes yielding the product and regenerating the catalyst :

$$\underset{\text{Reactants}}{A + B + \text{catalyst}} \longrightarrow \underset{\text{Intermediate unstable compound}}{A.B.\text{catalyst}} \longrightarrow \underset{\text{Product}}{C + \text{catalyst}}$$

The transition elements, on account of their variable valency, are able to form unstable intermediate compounds very readily.

14. Tendency to form Complexes. The transition metals are almost unique in their tendency to form coordination complexes. The tendency of cations of transition elements to form complexes is due to *two factors*. Firstly, these ions are very small in size and, therefore, have high positive charge density. This facilitates acceptance of lone pairs of electrons from other molecules. Secondly, they have vacant orbitals and these orbitals have the right type of energy to accept lone pairs of electrons. The formation and structures of the complex compounds have been discussed in details in Chapters 26 and 27.

QUESTIONS

1. What are *d* block elements ? Give their electronic configurations. How are they subdivided in the various series ?
2. What is meant by *d* block elements ? How do they differ from *s* and *p* block elements? Discuss their general characteristics.
3. How do the atomic radii of transition elements vary with increase in atomic number in any series ? Why are the atomic radii of Cr, Mn, Fe, Co, Ni and Cu so close to one another ?
4. What is meant by the term ionisation energy ? Discuss the variation of ionisation energies of transition elements with increase in atomic number. Why do the ionisation energies in a given series increase very slowly on moving along a period ?
5. "Although the number of electrons in the outermost level in transition elements is the same (*viz.*, 1 or 2) as in alkali or alkaline earth metals, yet the transition elements are much less reactive." How would you account for it ?
6. The electrode potentials of the transition metals are generally higher than that of hydrogen, still these metals do not displace hydrogen from acid solutions. How would you explain this anomaly ?
7. "Since the electrode potentials of transition metals are very high, they should be good reducing agents. But actually they are not." How would you explain ?
8. "Compounds of *s* and *p* block elements are generally colourless (*i.e.*, white) but those of transition metals are generally coloured." How would you explain this behaviour?
9. Explain giving reasons why :
   (*i*) Most of the transition metals are paramagnetic (*ii*) Iron, cobalt and nickel are ferromagnetic (*iii*) Compounds of transition metals are generally coloured. (*iv*) All transition metals exhibit variable valency.

22 THE ELEMENTS OF THE FIRST TRANSITION SERIES

The First Transition Series comprises of ten elements, namely, **scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper** and **zinc**. The general characteristics of these elements alongwith those of Second and Third Transition Series have already been discussed in the previous chapter. Their important physical properties are reproduced in Table 1 for convenience of reference. The purpose of this chapter is to describe the chemistry of the individual elements, from scandium to zinc, of the First Transition Series.

TABLE 1

Important Physical Properties of the Elements of the First Transition Series

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Outer electronic configuration	$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^5\ 4s^1$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^7\ 4s^2$	$3d^8\ 4s^2$	$3d^{10}\ 4s^1$	$3d^{10}\ 4s^2$
Atomic mass (a.m.u.)	44·96	47·90	50·95	52·01	54·94	55·85	58·94	58·71	63·54	65·38
Atomic radius (Å)	1·44	1·32	1·22	1·17	1·17	1·16	1·16	1·15	1·17	1·25
Stable oxidation states	+3	+4	+3, +4, +5	+2, +3 +6	+2, +3 +4, +7	+2, +3	+2, +3	+2	+1, +2	+2
Atomic volume (c.c.)	15·02	10·60	8·35	7·23	7·30	7·10	6·70	6·60	7·10	9·20
Density (g/c.c.)	3·01	4·51	6·10	7·19	7·43	7·86	8·90	8·90	8·96	7·14
Melting point (°C)	1539	1668	1900	1875	1245	1536	1495	1453	1083	419·5
Boiling point (°C)	2730	3260	3450	2665	2150	3000	2900	2730	2595	906
First ionization energy (kJ mol^{-1})	632·6	659·0	650·2	652·3	716·3	762·3	758·1	736·0	744·7	906·7
Ionic radius (Å) :										
Divalent ion	–	0·91	0·88	0·84	0·80	0·76	0·74	0·72	0·72	0·74
Trivalent ion	0·81	0·76	0·74	0·69	0·66	0·64	0·63	0·63	–	–
Heat of fusion (kJ mol^{-1})	15·9	15·5	17·6	13·8	14·6	15·3	15·2	17·6	13·0	7·4
Heat of vaporisation (kJ mol^{-1})	338·9	445·6	443·5	305·4	224·7	353·9	389·1	380·7	338·9	114·6

SCANDIUM

Occurrence. Scandium occurs in nature only in the combined state. It is present in minerals such as *monazite* which is a complex phosphate. It is not particularly a rare element. It is, in fact, as common as arsenic and twice as abundant as boron. However, due to low concentration of scandium in its ores, it is difficult to obtain it in a pure state.

Extraction. The extraction of scandium from its compounds is not an easy matter. The oxide is highly stable being more so even than alumina. Hence, even the thermite process cannot be used for its extraction. The element is also highly electropositive and liberates hydrogen from water. The electrolysis of aqueous solutions of its compounds, therefore, cannot be used for its preparation. The metal can be obtained, however, by electrolysis of its fused chloride. A small amount of sodium chloride is added to lower the melting point. Zinc is used as the cathode. Scandium deposited on it forms Zn–Sc alloy. Zinc is volatilised off at low pressures. Scandium remains behind in a reasonably pure state.

Properties. 1. Scandium has a silvery-white lustre but gets tarnished in air due to formation of its oxide, Sc_2O_3.

2. It has a melting point of about 1539°C and a boiling point of about 2730°C.

3. The outer electronic configuration of scandium is $3d^1\,4s^2$. It forms trivalent ion, Sc^{3+}, in solution. This is brought about through the loss of two *s* and one *d* electron. Compounds with higher oxidation states are unknown. The +2 state is also not stable.

4. All the scandium compounds in +3 state are colourless and diamagnetic because the 3*d* subshell in these compounds is empty.

COMPOUNDS OF SCANDIUM

Scandium forms compounds *only* in the +3 oxidation state. Thus, the oxides, halides and oxohalides have the formulae Sc_2O_3, ScX_3 and ScOX, respectively.

Scandium oxide, Sc_2O_3. It is formed readily by heating the salts like scandium carbonate and scandium nitrate.

$$Sc_2(CO_3)_3 \xrightarrow{\text{Heat}} Sc_2O_3 + 3CO_2$$

$$4Sc(NO_3)_3 \xrightarrow{\text{Heat}} 2Sc_2O_3 + 12NO_2 + 3O_2$$

It can also be obtained by the interaction of scandium with water.

$$2Sc + 3H_2O \xrightarrow{\text{Heat}} Sc_2O_3 + 3H_2$$

It is a weak base.

Scandium halides. All scandium halides are soluble in water with the exception of ScF_3. When flouride ions are added to the solution of a Sc(III) compound, the precipitate of ScF_3 is formed first which, in the presence of excess flouride ions, redissolves to give the complex ion $[ScF_6]^{3-}$

Scandium halides are best prepared by heating the element in a current of the halogen.

Scandium hydroxide. This compound does not have a definite formula $Sc(OH)_3$. It is considered to be a *hydrous oxide*, $Sc_2O_3.nH_2O$. It is less basic than $Ca(OH)_2$ but more basic than $Al(OH)_3$ which, in fact, is amphoteric.

Scandium hydride. Scandium forms a hydride which is not quite stoichiometric, the number of hydrogen atoms per atom of scandium being nearer to 2. Its formula may be written as ScH_2. This compound contains hydrogen in the form of hydride ion, H^-. The compound probably contains one Sc^{3+} ion per two H^- ions. The third electron of Sc is present in the conduction band. That is why solid ScH_2 is a conductor of electricity. Nevertheless, there is still lot of controversy with regard to the type of bonding involved in ScH_2. It reacts with water liberating hydrogen.

Scandium carbide, ScC_2. It is obtained by heating the oxide with carbon at a high temperature of about 1000° C.

$$Sc_2O_3 + 7C \longrightarrow 2ScC_2 + 3CO$$

It is an *acetylide* as it reacts with water liberating acetylene. It has been shown by conductivity and magnetic measurements that scandium carbide is an ionic compound having Sc^+ and C_2^- ions.

Complexes. The tendency of an ion to form complexes depends upon its size ; the smaller the size of an ion, the greater is its tendency to form complexes.

The size of Sc^{3+} ion is smaller than that of other ions of this group (*cf.* Table 1). It, therefore, readily forms complex ions, as for example, $[ScF_6]^{3-}$, $[Sc(bipy)_3]^{3+}$, $[Sc(DMSO)_3]^{3+}$, etc., where bipy is bipyridyl and DMSO is dimethylsulphoxide. Some bidentate chelating agents such as $C_2O_4^{2-}$ and acac (acetyl acetonate anion) are also known to form chelates with Sc^{3+}. Examples are : $[Sc(C_2O_4)_2]^-$, $[Sc(acac)_3]$, etc.

TITANIUM

Occurence. Titanium constitutes about 0·58 per cent by mass of the earth's crust. It is the tenth most abundantly occurring element in the earth's crust. However, its deposits are not very rich in the element. The commercially useful deposits for the extraction of the element are scarce. The important ores are *rutile*, TiO_2 and *ilmenite*, $FeTiO_3$.

Extraction. 1. By Reduction Process. Reduction of TiO_2 in *rutile* ore on heating with carbon is not satisfactory as it leads to the formation of the stable titanium carbide. Heating in air also leads to the formation of titanium nitride. Production of titanium on a large scale is, therefore, possible by converting the oxide in *rutile* (TiO_2) ore into titanium tetrachloride, $TiCl_4$ and then reducing the latter with magnesium. This process of extraction is known as **Kroll process.**

In actual process, chlorine is passed over rutile heated to about 900° C with carbon :

$$TiO_2 + C + 2Cl_2 \longrightarrow TiCl_4 + CO_2$$

The vapours of $TiCl_4$ are condensed to get it in liquid state (b.p. 136° C). It is purified by fractional distillation and then reduced by passing it in vapour state over magnesium heated to 800° C.

$$TiCl_4 + 2Mg \xrightarrow{800^\circ\,C} Ti + 2MgCl_2$$

The $TiCl_4$ vapours continue attacking magnesium till nearly 85 per cent of the metal has reacted. Titanium formed is chipped off from the reactor mechanically. The residual magnesium and magnesium chloride are removed from the metal chips by leaching with dilute hydrochloric acid.

2. By Electrolysis in an Inert Atmosphere. Titanium can also be prepared by the electrolysis of the ionic compound, $TiCl_2$, in the fused state. Sodium chloride and potassium chloride are added to lower the melting point.

Physical Properties. Titanium has a high melting point (1668° C) and a high boiling point (3260°C). It is a shining white metal, having rather a low density of 4·5 g per c.c.

Chemical Properties. 1. Action of air. On exposure to air at ordinary temperatures, titanium reacts with oxygen and nitrogen to form a thin protective surface coating of oxide and nitride. This coating protects the metal from corrosion. It remains stable in air even at 400° C.

2. Combination with non-metals. At high temperatures the metal is quite reactive. It combines with non-metals like oxygen, nitrogen, halogens, carbon, boron and silicon. The compounds like TiN, TiC, TiB are **interstitial compounds.** These are *hard* and have *refractory properties.*

3. Action of acids. Titanium is passive and resists attack by acids. The passivity is due to formation of a protective surface coating of oxide and nitride.

The metal dissolves slowly in hot concentrated hydrochloric and nitric acids. It explodes with fuming nitric acid. It dissolves in hydrofluoric acid giving hexafluoro complex compound.

$$Ti + 4HF \longrightarrow TiF_4 + 2H_2$$

$$TiF_4 + 2HF \longrightarrow H_2[TiF_6]$$

4. Action of alkalies. The metal is not attacked by alkalies even at elevated temperatures.

Technical Applications. Pure titanium is an extremely strong metal even stronger than iron. Due to formation of a protective surface coating of oxide and nitride, it is resistant to corrosion. Its mechanical properties are better than those of steel. Due to its mechanical strength, lightness and resistance to

corrosion, the metal is of great technical importance. It is used as a structural material in the fabrication of supersonic aircrafts, jet engines, turbine engines and marine equipment. It is also used for hardening of steel.

Amongst its compounds, its carbide is used as a refractory material, its nitride in the fabrication of high speed tools and its oxide as a white pigment.

Electronic Configuration and Oxidation States. The outer electronic configuration of titanium is $3d^2\,4s^2$. It shows oxidation states of +2, +3 and +4. The +4 state is the most common, the most stable and also the most important oxidation state of the element. It also exercises, though rarely, 0 and +1 oxidation states in the formation of some of its complexes.

COMPOUNDS OF TITANIUM

Compounds of Titanium(II). The +2 oxidation state of titanium is not very stable. It has no aqueous chemistry because it is readily oxidised by water liberating hydrogen. The two important compounds formed by Ti(II) are TiO and $TiCl_2$. $TiBr_2$ and TiI_2 are also known.

Titanium(II) oxide, TiO. It is obtained by heating TiO_2 with Ti. It is a non-stoichiometric compound with composition $TiO_{0.75}$. It changes readily to TiO_2. Due to this reaction, it acts as a *strong reducing agent*. For instance, it readily reduces water to hydrogen.

$$TiO + H_2O \longrightarrow TiO_2 + H_2$$

It is basic and ionic in character.

Titanium(II) chloride, $TiCl_2$. It can be prepared by the reduction of titanium tetrachloride with titanium metal.

$$TiCl_4 + Ti \longrightarrow 2TiCl_2$$

It can also be obtained by the disproportionation of Ti(III) chloride.

$$2TiCl_3 \longrightarrow TiCl_2 + TiCl_4$$

Titanium tetrachloride is volatile and can be easily removed by distillation.

It also undergoes disproportionation giving titanium(IV) chloride and titanium.

$$2TiCl_2 \longrightarrow TiCl_4 + Ti$$

Compounds of Titanium(III). Ti(III) ion is, evidently, a d^1 system. Ti(III) compounds are prepared from the corresponding Ti(IV) compounds on reduction with zinc and dilute hydrochloric acid. The reduction can also be carried out electrolytically.

Anhydrous $TiCl_3$ is prepared by passing vapours of $TiCl_4$ mixed with excess of hydrogen through a tube heated to about 650°C.

$$2TiCl_4 + H_2 \longrightarrow 2TiCl_3 + 2HCl$$

$TiCl_3$(anhydrous) is a violet powder.

The hydrated titanium chloride exists in two forms having different colours. These two forms have the formulae $[Ti(H_2O)_6]Cl_3$ and $[Ti(H_2O_5)Cl]Cl_2$.

The **anhydrous oxide, Ti_2O_3**, can be obtained by heating TiO_2 to 1000°C in a stream of hydrogen.

$$2TiO_2 + H_2 \longrightarrow Ti_2O_3 + H_2O$$

It has the *corundum* structure. It is highly stable and is attacked only by nitric acid.

The **hydroxide, $Ti(OH)_3$**, is more basic than $Ti(OH)_4$. In general, Ti(III) compounds are more ionic than Ti(IV) compounds.

Titanium(III) exists in aqueous solution as the blue-violet $[Ti(H_2O)_6]^{3+}$ complex ion.

Ti(III) compounds have *strong reducing properties* as they have a tendency to change to Ti(IV) compounds.

$$Ti_2O_3 + O \longrightarrow 2TiO_2$$

Thus, they reduce permanganates to Mn^{2+} ions.

$$5Ti^{3+} + MnO_4^- + H_2O \longrightarrow 5TiO^{2+} + Mn^{2+} + 2H^+$$

Ti^{3+} salts are used for the volumetric estimation of Fe^{3+} where NH_4SCN is used as an indicator. It gives red colour as long as Fe^{3+} is present in the solution.

$$FeCl_3 + TiCl_3 + H_2O \longrightarrow FeCl_2 + TiOCl_2 + 2HCl$$

Ti^{3+} salts are also used for the estimation of organic nitrites where methylene blue is used as an indicator. When even a slight excess of Ti^{3+} is generated, methylene blue is reduced and is rendered colourless.

$$RNO_2 + 6Ti^{3+} + 4H_2O \longrightarrow RNH_2 + 6TiO_2^{2+} + 6H^+$$

Complexes of Ti(III). Ti(III) forms a number of complexes which have been frequently referred to in Chapters 26 and 27 on Coordination Compounds. The *colour* and *magnetic properties* of these complexes have also been discussed in these chapters.

Compounds of Titanium(IV). Titanium(IV) oxide, TiO_2 is the most important oxide of titanium. It occurs in nature as *rutile* which is an important ore of titanium.

It is a white powder, insoluble in water.

It is *amphoteric* in character but is more acidic than alkaline in nature. It dissolves in alkalies yielding titanates.

$$TiO_2 + 2NaOH \longrightarrow Na_2TiO_3 + H_2O$$

When heated with carbon in a stream of chlorine, it gives titanium tetrachloride

$$TiO_2 + 2C + 2Cl_2 \longrightarrow TiCl_4 + 2CO$$

It exists in three crystalline forms, namely, *rutile, brookite* and *anatase*. The rutile structure has already been described in Chapter 6 on Structure of Solids. Brookite and anatase have distorted octahedral arrangement of O atoms around Ti atom in their crystal lattices.

It is used in large quantities as a *white* pigment in paint as well as cosmetic industry. It is quite inert and has good covering power.

Titanates. When Na_2O is fused with TiO_2, Na_2TiO_3 is formed. When Na_2TiO_3 is heated in an atmosphere of hydrogen, non-stoichiometric compounds of the formulae approximating to $Na_{0.2-0.25}TiO_2$ are formed. These compounds are known as 'titanium bronzes' which have high electrical conductivity and a metallic bluish lustre.

Calcium titanate, $CaTiO_3$, occurs naturally as *perovskite*. **Iron titanate, $FeTiO_3$,** also occurs naturally as *ilmenite*. Other titanates also acquire either perovskite structure when the two cations of the titanate are of considerably different sizes or ilmenite structure when the two cations are of similar sizes.

The crystal structure of ilmenite comprises of hcp arrangement of O^{2-} ions with 1/3rd of octahedral sites occupied by Ti^{4+} ions and another 1/3rd of octahedral sites occupied by Fe^{3+} ions.

The structure of perovskite comprises of ccp arrangement of O^{2-} ions and Ca^{2+} ions in which Ti^{4+} ions occupy 1/4th of octahedral sites formed by O^{2-} ions *only*.

Some titanates such as $MgTi_2O_4$ have a spinel structure in which O^{2-} ions form *ccp* arrangement, Mg^{2+} ions occupy the octahedral sites and Ti^{4+} ions occupy the tetrahedral sites.

It has a high refractive index and, therefore, its crystals show great brilliance, even greater than diamond. However, being soft, it is not so well suited for use in jewellery. Nevertheless, it is used as a semiprecious artificial gem.

Titanium(IV) chloride, $TiCl_4$. It can be prepared in the laboratory by passing chlorine over a hot mixture of titanium dioxide and carbon.

$$TiO_2 + C + Cl_2 \longrightarrow TiCl_4 + CO_2$$

1. It is a colourless, fuming liquid at ordinary temperatures and boils at 137°C.

2. It gets readily hydrolysed by water yielding titanium dioxide.

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$$

If water is not present in excess, hydrolysis takes place only to a limited extent yielding titanium oxochloride, $TiOCl_2$

3. It is reduced to metallic titanium on treatment with Mg or Na.

4. It dissolves in concentrated hydrochloric acid yielding chloro complexes having formulae $[TiCl_5(H_2O)]^-$ and $[TiCl_6]^{2-}$.

5. Titanium chloride is a strong Lewis acid and accepts electrons from strong oxygen-donors like ethers, alcohols and esters yielding addition compounds of the type $(R_2O)TiCl_4$ and $(R_2O)_2TiCl_4$.

Uses. $TiCl_4$ is used for producing dense white smoke screens and for making writings in the sky in army operations. This is because the spraying of liquid $TiCl_4$ into moist air results in its hydrolysis forming dense white smoke of TiO_2.

It is also used as a catalyst in the manufacture of polyethylene.

Titanium(IV) in solution. Ti^{4+} ion does not exist in aqueous solution but titanyl ion, TiO^{2+}, does exist in aqueous solution and forms a number of salts such as $TiOSO_4$ which can be crystallised out from the aqueous solution containing TiO^{2+} and SO_4^{2-} ions.

Complexes of Ti(IV). The colorimetric estimation of TiO^{2+} or $[Ti(OH)_2]^{2+}$ in aqueous solution is carried out by the addition of H_2O_2 to the solution when an orange colour is developed due to the formation of a peroxo complex of Ti^{4+} whose probable formula is $[Ti(O_2)OH.(H_2O)_n]^+$. The O_2^{2-} ion is attached with Ti as peroxo group.

Ti(IV) halides, $TiCl_4$ and TiF_4 react with HCl and HF, respectively, to give hexa coordinate complex ions :

$$TiCl_4 + 2HCl \longrightarrow H_2[TiCl_6]$$
$$TiF_4 + 2HF \longrightarrow H_2[TiF_6]$$

The tetrahalides also react with amines, phosphines and arsines to give hexa coordinate complexes, as, for example, $[TiF_4.2PPh_3]$.

Tetraalkylammonium chloride reacts with $TiCl_4$ to give $[Et_4N]^+[TiCl_5]^-$ which contains five-coordinated Ti^{4+} in its anion.

In the complex $[Ti(NO_3)_4]$, the coordination number of Ti^{4+} is 8 since NO_3 group is bidentate in this complex.

VANADIUM

Occurrence. Vanadium is widely distributed but its concentration in the deposits is very small. Its abundance is about 0·02 per cent by mass of the earth's crust. Nearly ninety minerals containing vanadium are known but, since concentrated deposits are very few, its extraction is not very economical.

The most important minerals are *patronite* (V_2S_5), *vanidinite* ($Pb_5(VO_4)_3Cl$) and *carnotite* ($K(UO_2)VO_4.3/2H_2O$). The last ore is most important because of its uranium content.

Extraction. The extraction of vanadium in pure state from its ores is very difficult. This is on account of its high melting point and reactivity at high temperatures. Pure metal can be prepared only by reduction of its compounds such as vanadium pentoxide (V_2O_5), vanadium tetrachloride (VCl_4) and vanadium pentachloride (VCl_5). The chlorides are prepared more easily by working with *ferro-vanadium*, an alloy of iron and vanadium. The first step, therefore, is to prepare vanadium pentoxide or ferro-vanadium alloy.

Preparation of Vanadium Pentoxide. The vanadium ore, generally the sulphide ore (*patronite*), is roasted in air and then fused with a mixture of sodium carbonate and sodium nitrate when sodium vanadate, $NaVO_3$, is formed. It is extracted with water and the solution treated with ammonium chloride when ammonium vanadate, NH_4VO_3, separates out as an orange-coloured precipitate. This on heating yields vanadium pentoxide.

$$2NH_4VO_3 \xrightarrow{600^\circ C} V_2O_5 + 2NH_3 + H_2O$$

Preparation of Ferro-Vanadium Alloy. The alloy contains 35–45 percent of vanadium. It is obtained by heating a mixture of vanadium pentoxide and iron oxide with carbon in an electric furnace using carbon electrodes. Some lime or fluorspar is added as a flux.

(The ferro-vanadium alloy is used in steel industry where it acts as a scavenger for oxygen and nitrogen and as a strengthening agent. When added to molten steel, vanadium takes up oxygen and nitrogen and at the same time dissolves in the molten iron to improve its ductility, tensile strength and shock-resistance).

Preparation of Vanadium Metal. A fairly satisfactory process, known as the **Jantesh process,** for preparing vanadium metal, consists in heating ferro-vanadium alloy in a current of chlorine when vanadium tetrachloride, VCl_4, is obtained as a dark red liquid. This is separated from ferric chloride, also formed in the reaction, by disitillation and then reduced by heating the vapour with hydrogen at 600° C.

$$2VCl_4 + 4H_2 \xrightarrow{600^\circ C} 2V + 8HCl$$

An alternate process known as the **Beard and Crook's process,** consists in reduction of vanadium pentoxide with metallic calcium in an inert atmosphere of helium or argon. Some iodine is also added. V_2O_5 reacts with calcium and the reaction being exothermic produces a high temperature.

$$V_2O_5 + 5Ca \longrightarrow 2V + 5CaO$$

The name vanadium is derived from *vanadis*, the Scandinavian goddess of beauty. This is due to the beautiful colours of vanadium compounds.

Physical Properties. The pure metal is silvery-grey in colour. It melts at 1900° C. The melting point rises appreciably on the addition of carbon. It is hard and corrosion-resistant.

Chemical Properties. 1. Action of acids. Vanadium is unreactive towards mineral acids at ordinary temperatures. It, however, dissolves in hot nitric acid, concentrated sulphuric acid and aqua regia to form meta vanadic acid, HVO_3. The reaction with HNO_3 is

$$V + 5HNO_3 \longrightarrow 2H_2O + 5NO_2 + HVO_3$$

It is also attacked by hydrofluoric acid.

2. Action of alkalies. When fused with alkalies, it gives the corresponding vanadate evolving hydrogen.

$$2V + 6NaOH + 2H_2O \longrightarrow 2Na_3VO_4 + 5H_2$$

3. Combination with non-metals. When heated, it combines with oxygen forming vanadium pentoxide, mixed with lower oxides.

$$4V + 5O_2 \longrightarrow 2V_2O_5$$

It combines with nitrogen at high temperature yielding vanadium nitride, VN, which is an interstitial compound. It also forms a sulphide V_2S_3 by passing CS_2 over V_2O_5.

It combines with halogens on heating giving compounds like VF_5, VCl_4, VBr_3 and VI_3. These are covalent volatile compounds and get easily hydrolysed by water.

It reacts with carbon at high temperature to form carbides, VC and VC_2. The first one is an *interstitial* compound, white and hard. The second one is an ionic compound and reacts with water

liberating acetylene. Vanadium also forms a carbide V_4C_3 which has 'defect structure' as carbon atoms are missing from some of the lattice positions.

It also forms a non-stoichiometric hydride of the formula $VH_{0.71}$

Uses. The chief application of vanadium is in steel industry where it is used in the form of *ferro-vanadium* alloy for making special steels. Only 0·1 to 0·2 percent of this alloy is needed. It improves the quality of steel in several ways : (1) It acts as a scavenger for oxygen and nitrogen and makes the steel stronger, tougher and shock resistant. (2) It also makes the steel more ductile and raises its tensile strength. Steel containing chromium and vanadium is used in making parts for motor vehicles. Vanadium is used as a catalyst in the oxidation reactions of certain organic compounds. V_2O_5 is used as a catalyst in Contact process for with the manufacture of sulphuric acid.

Alloys of vanadium with titanium, copper and aluminium are used in industry for various purposes, in particular for standing high temperatures.

Electronic Configuration and Oxidation States. The outer electronic configuration of vanadium is $3d^3\ 4s^2$. It shows oxidation states of +2, +3, +4 and +5 in its compounds. The compounds in the lower oxidation states are good reducing agents. They are also ionic in character and on account of incomplete electron shells, they are also coloured.

In +5 oxidation state, the *d* subshell is completely empty. The compounds of vanadium corresponding to this state, therefore, are generally colourless.

When a colourless compound in which vanadium is in +5 state is reduced with zinc, it first turns *blue*, then *green* and finally *violet*, corresponding to stepwise reduction to +4, +3 and +2 oxidation states. Thus, oxidation state of vanadium can be determined by noting the colour of its compounds. This, however, may not be the case always.

COMPOUNDS OF VANADIUM

Compounds of Vanadium(II). Vanadium forms fairly stable compounds in which its oxidation state is +2. This state, however, is least stable compared to other oxidation states of vanadium.

Vanadium(II) oxide, VO is prepared by reducing V_2O_5 with H_2 at about 2000°C.

$$V_2O_5 + 3H_2 \xrightarrow{\sim 2000^\circ C} 2VO + 3H_2O$$

It is a blackish solid with metallic lustre. It has NaCl–type structure with considerable degree of lattice defects. Because of these defects, VO conducts electricity.

It is soluble in water. The addition of alkalies to its aqueous solution yields precipitate of $V(OH)_2$ whereas the addition of acids yields a water– soluble violet coloured complex $[V(H_2O)_6]^{2+}$.

Vandium(II) chloride, VCl_2, is obtained by reducing VCl_4 vapours with hydrogen in a red hot tube.

$$VCl_4 + H_2 \longrightarrow VCl_2 + 2HCl$$

It forms bright green lustrous leaflet crystals. It is soluble in water. The vanadous ion V^{2+} is a *strong reducing agent*. Thus, the violet solution of VCl_2 soon turns green because of its oxidation to trivalent state with evolution of hydrogen (reduction of water).

$$2VCl_2 + 2H_2O \longrightarrow 2VOCl + 2HCl + H_2$$

Vanadium(II) sulphate, $VSO_4.7H_2O$, is prepared by the electrolytic reduction of vanadium pentoxide dissolved in sulphuric acid in the presence of sulphur trioxide till the solution turns violet.

It is soluble in water and forms red-violet monoclinic crystals which are isomorphous with $FeSO_4.7H_2O$. The double salt, $VSO_4.(NH_4)_2SO_4.6H_2O$ is isomorphous with Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$.

It is a *strong reducing agent*. As such the violet coloured aqueous solution containing V^{2+} ion in the form of $[V(H_2O)_6]^{2+}$ complex ion becomes green due to oxidation of $[V(H_2O)_6]^{2+}$ ion to $[V(H_2O)_6]^{3+}$ ion

with the liberation of hydrogen (reduction of water).

$$\underset{\text{violet}}{[V(H_2O)_6]^{2+}} + H^+ \longrightarrow \underset{\text{green}}{[V(H_2O)_6]^{3+}} + \tfrac{1}{2}H_2$$

Complexes of Vanadium (II). Apart from the already mentioned $[V(H_2O)_6]^{2+}$ complex ion, some other V(II) complexes are also known. Examples are $K_4[V(CN)_6]$ and $[V(en)_3]Cl_2$. The V(II) complexes, in general, are not very stable.

Compounds of Vanadium (III). Compounds of vanadium (III) are prepared by the reduction of compounds of vanadium with higher oxidation states. Thus, **vanadium trichloride, VCl_3,** is obtained by the reduction of VCl_4.

$$2VCl_4 + H_2 \longrightarrow 2VCl_3 + 2HCl$$

Vanadium trichloride forms beautiful peach-blossom coloured crystal leaflets. It is non-volatile. It is readily hydrolysed by water.

Vanadium trichloride is easily oxidised by atmospheric air and is, therefore, *reducing in character*.

VCl_3 is polymeric in nature. Each V atom is surrounded octahedrally by six Cl atoms. These Cl atoms form bridges between V atoms.

VCl_3 dissolves in water giving $[V(H_2O)_6]^{3+}$ and Cl^- ions. With amines, it forms complexes which have trigonal bipyramidal structure. Well known example is $[VCl_3(NR_3)_2]$.

The trihalide **VI_3** is also obtained by reducing VI_4 with hydrogen. It is thermally less stable than VCl_3 and readily disproportionates as follows :

$$2VI_3 \longrightarrow VI_2 + VI_4$$

Vanadium(III) oxide, V_2O_3, is obtained by the reduction of V_2O_5 with carbon or hydrogen at high temperatures.

$$V_2O_5 + 2H_2 \longrightarrow V_2O_3 + 2H_2O$$

It is readily oxidised and thus acts as a strong *reducing agent*.

V_2O_3 is *basic* in nature and dissolves in acids to give solutions of complex hexaaqua ion, $[V(H_2O)_6]^{3+}$.

V_2O_3 is actually a non-stoichiometric compound with composition varying from $V_2O_{2.75}$ to V_2O_3.

Vanadium(III) sulphate, $V_2(SO_4)_3$, is obtained by the electrolytic reduction of a solution of V_2O_5 in H_2SO_4 till a green solution results.

The green solution, on evaporation, deposits green lustrous needles having the composition $V_2(SO_4)_3.H_2SO_4.12H_2O$. This compound, on heating at 180° C, loses water and SO_3, leaving a *yellow powder* of the composition $V_2(SO_4)_3$, which is insoluble in water.

Aqueous solutions containing V^{3+} ions are remarkably stable in the presence of sulphuric acid. They get oxidised slowly when exposed to atmosphere.

Vanadium(III) sulphate is a powerful reducing agent.

Vanadium(III) Complexes. Vanadium(III) forms a large number of complexes, most of them being anionic. ~~Examples are $[V(C_2O_4)_3]^{3-}$, $[V(CN)_6]^{3-}$ and $[V(NCS)_6]^{3-}$. A well known example of cationic~~ complex is $[V(H_2O)_6]^{3+}$.

Compounds of Vanadium(IV). The +4 is the most stable oxidation state of vanadium. It forms a number of compounds in which its oxidation state is +4. Important amongst these are *vanadium dioxide*, VO_2, *halides e.g.*, VCl_4 and *oxohalides. e.g.*, $VOCl_2$. The oxide and the halides are *covalent* while oxohalides are *ionic* in character containing the blue VO^{2+} ion.

A brief description of these compounds is given below.

Vanadium(IV) oxide, VO_2. It is formed by the reduction of vanadium pentoxide by hydrogen sulphide, sulphur dioxide or oxalic acid.

It is a blue amphoteric solid with *rutile structure*. It reacts with non-oxidising acids to form vanadyl and vanadium salts.

$$VO_2 + 2HCl \longrightarrow \underset{\text{Vanadyl chloride}}{VOCl_2} + H_2O$$

$$VO_2 + 4HCl \longrightarrow \underset{\text{Vanadium chloride}}{VCl_4} + 2H_2O$$

It reacts with alkalies to form vanadites.

$$VO_2 + 2NaOH \longrightarrow \underset{\text{Sodium vanadite}}{Na_2VO_3} + H_2O$$

Vanadium(IV) halides. Vanadium tetrachloride can be readily prepared by passing chlorine over powdered vanadium metal at 180° C.

$$V + 2Cl_2 \xrightarrow{180^\circ C} VCl_4$$

It is a dark, reddish-brown oily *liquid* boiling at 154° C. It is unstable and slowly decomposes into trichloride and chlorine. The decomposition becomes very rapid above the boiling point.

$$2VCl_4 \longrightarrow 2VCl_3 + Cl_2$$

Vanadium tetrachloride fumes in moist air and is hydrolysed by water giving *vanadyl chloride*.

$$VCl_4 + H_2O \rightleftharpoons VOCl_2 + 2HCl$$

VCl_4 is tetrahedral in gaseous phase and dimeric in the liquid phase.

Vanadium(IV) oxodichloride (Vanadyl chloride), $VOCl_2$, is obtained by the hydrolysis of VCl_4.

$$VCl_4 + H_2O \longrightarrow VOCl_2 + 2HCl$$

It can also be prepared by the action of HCl on V_2O_5.

$$V_2O_5 + 6HCl \longrightarrow 2VOCl_2 + 3H_2O + Cl_2$$

Pure compound is prepared by heating $VOCl_3$ with metallic zinc in a sealed tube.

$$2VOCl_3 + Zn \longrightarrow 2VOCl_2 + ZnCl_2$$

The compound, so prepared, is obtained as grassy green crystals.

Vanadyl chloride is used commercially in dyeing. It is a strong reducing agent.

Vanadium(IV) oxosulphate (Vanadyl sulphate), $VOSO_4$. This is prepared by the reduction of a solution of vanadium pentoxide in concentrated sulphuric acid by sulphur dioxide. The resulting blue solution deposits, on evaporation, bright blue crystals of the hydrated acid vanadyl sulphate, $2VOSO_4.H_2SO_4.xH_2O$, the exact composition depending upon the temperature.

When acid vanadyl sulphate is heated with concentrated sulphuric acid at 260° C, a grey-green crystalline powder of *anhydrous vanadyl sulphate*, $VOSO_4$, separates out.

Vanadyl sulphate is used for potentiometric titrations of weak oxidising agents. Its acidic solution is used for removing traces of oxygen from gases.

Vanadium(IV) Complexes. Vanadium tetrachloride and tetrafluoride form complexes of the types VCl_4L and VCl_4L_2, where L stands for a unidentate ligand. These complexes are readily hydrolysed by water.

Several other complexes of V(IV) are also known. Some of these complexes are of the type $[VOX_4]^{2-}$, $[VO(acac)_2]$ and $[VO(bipy)_2Cl]^+$ where X is the halogen anion, bipy is bipyridyl and acac is acetyl acetonate anion. These complexes have square pyramidal structures in which O atom occupies the apical position.

Compounds of Vanadium(V). Vanadium forms only a few stable compounds in which the oxidation state is +5.

Vanadium(V) oxide, V_2O_5. This is perhaps the most important compound of vanadium(V). This is obtained as a red or orange solid on thermal decomposition of ammonium metavanadate, NH_4VO_3.

$$2NH_4VO_3 \longrightarrow V_2O_5 + 2NH_3 + H_2O$$

Vanadium pentoxide is also formed as a brick red precipitate when ammonium vanadate solutions are treated with dilute sulphuric acid.

It is also prepared by heating the metal in oxygen.

It melts at about 650° C and is insoluble in water.

Vanadium(V) oxide has all its outer electrons fully paired in covalent bonds. There is no incomplete electron shell. The compound, therefore, should be colourless. But actually it is orange-red in colour. The reason of this anomaly lies in *defects in the solid state* due to which charge transfer transitions in the visible region are possible (exact explanation is beyond the scope of the book).

It is *amphoteric* in character. It dissolves in acid solutions to give salts such as $VOCl_2$, **vanadyl chloride** or **VCl_5, vanadium pentachloride.**

$$V_2O_5 + 6HCl \longrightarrow 2VOCl_2 + 3H_2O + Cl_2$$

$$V_2O_5 + 10HCl \longrightarrow 2VCl_5 + 5H_2O$$

Liberation of chlorine on dissolving V_2O_5 in hydrochloric acid shows that V_2O_5 can act as a moderately strong oxidising agent.

It dissolves in alkalies giving vanadates.

$$V_2O_5 + 6NaOH \longrightarrow \underset{\text{Sod. vanadate}}{2Na_3VO_4} + 3H_2O$$

The vanadate ion, VO_4^{3-}, is stable only in strongly alkaline solutions. On lowering the *p*H, the VO_4^{3-} ion polymerises. The products formed are known as *isopolyvanadates*.

$$\begin{array}{ccccccccc}
VO_4^{3-} & \xrightarrow{pH\ 12} & [VO_3.OH]^{2-} & \xrightarrow{pH\ 10} & [V_2O_6.OH]^{3-} & \xrightarrow{pH\ 7} & [V_3O_9]^{3-} & & \\
 & & & & & & \downarrow pH\ 7 & & \\
[VO_2]^+ & \xleftarrow{pH<1} & [V_{10}O_{28}]^{6-} & \xleftarrow{pH\ 2} & [V_2O_5(H_2O)_9] & \xleftarrow{pH\ 6\cdot5} & [V_5O_{14}]^{3-} & &
\end{array}$$

Vanadate ion also polymerises with the anions of other acids such as molybdate and tungstate anions. The polymeric ions thus obtained are known as *heteropoly acids*.

The pentoxide on reduction yields lower oxides :

$$VO_2 \underset{\text{Heat}}{\xleftarrow{SO_2}} V_2O_5 \underset{\text{Heat}}{\xrightarrow{H_2}} V_2O_3 \xrightarrow[\text{at low pressure}]{\text{Heat with V}} VO$$

Vanadium pentoxide is used as a *catalyst* in various oxidation reactions involving the use of oxygen as the oxidising agent. The well known example is the conversion of sulphur dioxide to sulphur trioxide,

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

in the manufacture of sulphuric acid by Contact process.

The other catalytic reactions are oxidation of alcohol and hydrogenation of olefins.

The structure of V_2O_5 consists of distorted trigonal bipyramidal VO_5 units sharing edges with similar other units to form zig-zag chains.

Vanadium(V) fluoride. Vanadium combines with fluorine at high temperature to yield VF_5.

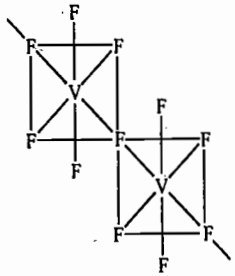
$$2V + 5F_2 \xrightarrow{300^\circ C} 2VF_5$$

It may also be prepared by heating VF_4 at 600°C in an atmosphere of nitrogen.

$$2VF_4 \xrightarrow[\text{nitrogen}]{600^\circ C} VF_5 + VF_3$$

Vanadium(V) chloride is a volatile white solid melting at 19·5° C. When heated in air it changes into oxofluoride.

$$2VF_5 \xrightarrow[\text{(air)}]{O_2} 2VOF_3 + 2F_2$$



VF_5 is polymeric in solid and liquid phases consisting of VF_6 octahedral units joined together through V–F–V bridges, as shown.

In gaseous phase, VF_5 is monomeric and probably has trigonal bipyramidal structure.

Some other compounds in which vanadium is in +5 oxidation state are oxohalides described below.

Vanadium(V) oxohalides. Vanadium oxotrichloride, $VOCl_3$, as well as **oxotribromide, $VOBr_3$,** can be prepared by halogenating V_2O_3.

$$V_2O_3 + 3X_2 \longrightarrow 2VOX_3 + O_2$$

Vanadium oxotrichloride, however, can be prepared more readily by passing chlorine over a mixture of vanadium pentoxide and carbon at red heat.

$$V_2O_5 + 3C + 3Cl_2 \longrightarrow 2VOCl_3 + 3CO$$

Vanadium oxotrifluoride, VOF_3, is also known. It can be prepared by treating oxotrichloride with hydrofluoric acid in the cold.

$$VOCl_3 + 3HF \longrightarrow VOF_3 + 3HCl$$

The oxohalides are simple covalent compounds and are readily hydrolysed.

$$VOCl_3 + 2H_2O \longrightarrow HVO_3 + 3HCl$$

Vanadium(V) Complexes. Vanadium fluoride and vanadium oxofluoride form complexes with other metal fluorides.

$$VF_5 + 2KF \longrightarrow K_2[VF_7]$$

$$VOF_3 + 3NaF \longrightarrow Na_3[VOF_6]$$

Anionic complexes containing fluorovanadate complex ion are formed by interaction of V_2O_5 with alkali metal fluorides in hydrofluoric acid solution. These complexes are of the type $M[VOF_4]$, $M_2[VOF_5]$ and $M_2[VO_2F_3]$, where M stands for an alkali metal such as Na, K, etc.

CHROMIUM

Occurrence. Chromium does not occur free in nature. In combined state, it occurs as *chromite ore*, $FeCr_2O_4$ or $FeO.Cr_2O_3$. It also occurs as *crocoisite* which is lead chromate, $PbCrO_4$. Chromium forms nearly 0·037 per cent of the earth's crust.

Extraction. The most important source for the extraction of chromium is the *chromite ore*, $FeO.Cr_2O_3$. The concentrated ore is mixed with excess of sodium carbonate and roasted in a reverberatory furnace in a free supply of air. The chromium oxide (Cr_2O_3) present in the chromite ore is converted into sodium chromate (Na_2CrO_4).

$$\underset{\text{Chromite ore}}{4FeO.Cr_2O_3} + \underset{\text{(from air)}}{8Na_2CO_3 + 7O_2} \longrightarrow \underset{\text{soluble}}{8Na_2CrO_4} + \underset{\text{insoluble}}{2Fe_2O_3} + 8CO_2$$

The roasted mass is extracted with water when Na_2CrO_4 goes in solution leaving behind the insoluble Fe_2O_3. The sodium chromate solution is treated with a calculated amount of sulphuric acid to convert the

chromate into dichromate.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The solution is concentrated when the less soluble Na_2SO_4 crystallises out leaving behind the more soluble $Na_2Cr_2O_7$ in solution. The solution is further concentrated to get solid $Na_2Cr_2O_7$ which is heated with carbon to yield sodium chromite.

$$Na_2Cr_2O_7 + 3C \longrightarrow \underset{\text{Sod. chromite}}{Na_2Cr_2O_4} + 3CO$$

Sodium chromite is treated with water to give a precipitate of chromium oxide, Cr_2O_3.

$$Na_2Cr_2O_4 + H_2O \longrightarrow \underset{\text{ppt.}}{Cr_2O_3} + 2NaOH$$

Chromic oxide is finally reduced to chromium by the *aluminothermic process*. The large amount of heat evolved in the highly exothermic reaction,

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr\,; \qquad \Delta H = -468{\cdot}6\ kJ$$

melts the chromium which collects as a liquid at the bottom of the crucible under the alumina. This process yields chromium of about 92 per cent purity.

The metal is refined electrolytically using chromium chloride as the electrolyte. Mercury is used as the cathode while impure chromium acts as the anode. Chromium-amalgam formed at the cathode is finally heated in vacuum when mercury volatilises off leaving behind the metal in pure state (99·7% purity).

Ferrochrome. Ferrochrome containing nearly 75 per cent chromium and the rest iron is prepared by reducing chromite ore with carbon in an electric furnace. The reduction is carried out in the presence of lime and fluorspar.

$$FeO.Cr_2O_3 + 4C \longrightarrow \underbrace{Fe + 2Cr}_{\text{Ferrochrome}} + 4CO$$

Ferrochrome is extensively used for alloying with iron to make special steels.

Physical Properties. Chromium is a bluish-white lustrous metal (m.p. 1875° C). It takes a good polish which lasts long because of the formation of an invisible, self-protective oxide coating. Pure metal is soft and malleable but, as usually obtained, chromium is among the hardest of the common metals. It is resistant to corrosive agents. The compounds of chromium are all coloured.

Chemical Properties. 1. Action of air. Chromium is not affected by air at ordinary temperatures and, therefore, does not tarnish in air. However, on heating in air or oxygen, it is oxidised superficially to green chromic oxide, Cr_2O_3. It burns with brilliance in oxygen at about 2000° C forming chromic oxide. It reacts with nitrogen also, at elevated temperatures, giving chromium nitride.

2. Action of water. Chromium is not at all attacked by water under ordinary conditions. It, however, decomposes steam at red heat to give chromic oxide and hydrogen.

$$2Cr + 3H_2O \longrightarrow Cr_2O_3 + 3H_2$$

3. Action of acids. The metal dissolves in dilute acids, slowly in cold but more rapidly on heating, evolving hydrogen and giving blue solutions of chromium(II) salts which change into green chromium(III) salts due to oxidation in air.

With hot concentrated sulphuric acid, chromium gives chromium(III) sulphate and sulphur dioxide.

Concentrated nitric acid renders the metal 'passive' due to the formation of an insoluble surface layer of chromium(III) oxide as a result of surface oxidation.

The metal is not attacked by **alkalies** under ordinary conditions.

4. Action of halogens. Heated chromium combines directly with fluorine or dry chlorine giving chromium(III) fluoride or chloride.

5. Reducing properties. In the finely divided state, chromium acts as good reducing agent. This is due to the fact that in this form chromium readily reacts with oxygen.

In the massive state, however, it gets protected by a thin coating of the oxide Cr_2O_3 and is, therefore, extremely resistant to corrosion.

Industrial Applications of Chromium. The most important use of chromium is in the production of special steels. For this purpose, it is added to steel in the form of an alloy with iron known as *ferrochrome*, obtained from chromite ore, as described earlier.

Chromium is now-a-days extensively used for plating metals (**chrome plating**) because it is very resistant to corrosion. Alloys of nickel and chromium containing about 20 per cent of chromium are used in making electrical resistances for heaters, electric furnaces, etc., since they resist oxidation effectively even at red heat. Chromium is also a constituent of acid resistant alloys. The most important of these alloys are the **stainless steels.**

Electronic Configuration and Oxidation States. The outer electronic configuration of chromium is $3d^5\ 4s^1$. It exhibits a large number of oxidation states, *viz.*, from 0 to 6. The zero oxidation state occurs in the carbonyl compounds, *e.g.*, $Cr(CO)_6$. The oxidation state of +1 is not so common and exists only when chromium is present in certain complex compounds, *e.g.*, $[Cr(diphenyl)_3]^+ClO_4^-$.

The stable and important oxidation states of Cr are +2, +3 and +6. These arise from the transference or sharing of one or more of the *d* electrons as well.

The various oxidation states of chromium with examples of common compounds in each state are summed up in Table 2.

TABLE 2

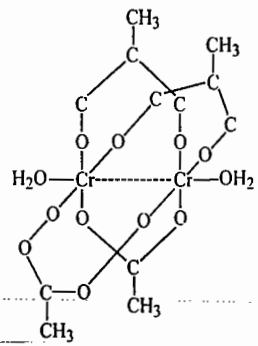
Oxidation States of Chromium

Oxidation State	Compounds
0	$Cr(CO)_6$
1	$[Cr(dipyridyl)_3]^+ClO_4^-$
2	CrO, $Cr(OH)_2$, $CrCl_2$, $(CH_3COO)_2Cr$, $CrSO_4$
3	$CrCl_3$, $Cr_2(SO_4)_3$, Cr_2O_3, $Cr(OH)_3$
6	CrO_3, K_2CrO_4, $K_2Cr_2O_7$, Na_2CrO_4, $Na_2Cr_2O_7$

IMPORTANT COMPOUNDS OF CHROMIUM

Chromium forms a number of compounds in which its oxidation state is +2, +3 and +6.

Compounds of Chromium(II). Cr(II) state is not very stable. Some of the hydrated salts are, however, relatively more stable. The examples are: $CrCl_2.4H_2O$ and $CrSO_4.7H_2O$. Chromium(II) acetate hydrate is known to exist in the form of a dimer, $[(CH_3COO)_2Cr.H_2O]_2$ whose structure is as shown.



Some complexes of Cr(II) such as $[Cr(NH_3)_6]^{2+}$ are relatively more stable than Cr(II) compounds.

Compounds of Chromium(III). As already mentioned, the +3 oxidation state is the most important and the most stable state of chromium. This state also forms a large number of complexes.

The +3 oxidation state is highly stable in acid solutions but it gets oxidised readily to +6 oxidation state in alkali solutions. Thus, Cr_2O_3 is oxidised to Na_2CrO_4 in alkaline medium.

$$2Cr_2O_3 + 8NaOH + 3O_2 \longrightarrow 4Na_2CrO_4 + 4H_2O$$

Compounds in +3 state are prepared by the reduction of Cr(VI) compounds such as chromates and dichromates.

Chromium(III) salts dissolve in water to give violet solution. The violet colour is due to the hydrated chromium(III) ion, $[Cr(H_2O)_6]^{3+}$. This is a highly stable ion and can be exposed to air without undergoing

any oxidation or reduction. It is now well established that six water molecules surrounding the Cr(III) ion are located at the apices of a regular octahedron.

The solution of Cr(III) ion is *slightly acidic* on account of the following reaction :

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H^+$$

When a base is added to an aqueous solution containing chromium (III) ions, a dirty green precipitate of hydrated chromium(III) hydroxide, $Cr(OH)_3.xH_2O$, results. The percipitate dissolves when excess of the base is added giving a deep green solution which is characteristic of chromite ion.

$$Cr(OH)_3 + 3OH^- \longrightarrow [Cr(OH)_6]^{3-}$$

Chromium(III) chloride, $CrCl_3$. It is obtained in anhydrous state by passing chlorine either over heated chromium or over a mixture of chromium (III) oxide and carbon heated strongly.

$$Cr_2O_3 + 3C + 3Cl_2 \longrightarrow 2CrCl_3 + 3CO$$

It is a pinkish violet solid almost insoluble in water. It volatilises at 1065° C and dissociates when heated above 1300° C.

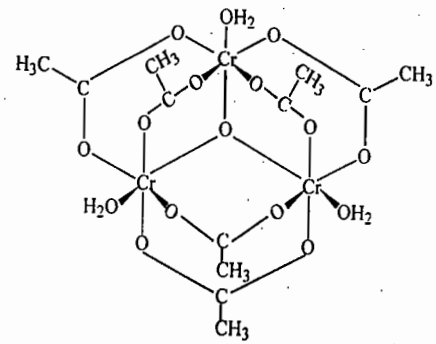
$$2CrCl_3 \rightleftharpoons 2CrCl_2 + Cl_2$$

It forms three crystalline hexahydrates all having the molecular formula $CrCl_3.6H_2O$. Two of these are green (light green and dark green) in colour and the third is greyish blue. Their structural formulae are :

Dark green (α) *variety*	$[Cr(H_2O)_4Cl_2]Cl.2H_2O$
Light green (γ) *variety*	$[Cr(H_2O)_5Cl]Cl_2.H_2O$
Greyish blue (β) *variety*	$[Cr(H_2O)_6]Cl_3$

Complexes of Cr(III). Apart from the above mentioned complexes containing Cl and H_2O as ligands, many other complexes of Cr(III) are also known. Some of the common examples are $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5Cl]^{2+}$, $[Cr(NH_3)_3Cl_3]$, $[Cr(oxalate)_3]^{3-}$, etc. The last complex shows optical isomerism. There are many other complexes of Cr(III) which have been synthesised and studied.

Chromium (III) Basic Acetate Complex $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$. The structure of this complex cation comprises of three Cr atoms in a *triangular plane.* These are bonded to an O atom placed in the middle of the plane. There are two acetato bridges across each edge of the triangular plane, *i.e.*, between any two Cr atoms. The three H_2O molecules occupy the remaining three octahedral sites on the Cr atoms, as shown.



Compounds of Chromium(IV). The **oxide CrO_2**, a stable compound of Cr(IV), is prepared in the following manner :

$$CrO_3 + H_2 \longrightarrow CrO_2 + H_2O$$

It is a ferromagnetic black coloured material which is extensively used in making recording tapes.

The fluoride CrF_4 can be prepared from its elements at elevated temperature.

Compounds of Chromium(V). The compounds of Cr(V) are rare and generally dissociate to give more stable Cr(III) or Cr(IV) compounds. The best known examples of compounds of Cr(V) are CrF_5 and $[Cr(O_2)_4]^{3-}$ which contains O_2^{2-} groups.

Compounds of Chromium(VI). There are only a few compounds of chromium in which its oxidation state is +6. The important ones are the oxide, CrO_3, oxochloride, CrO_2Cl_2. chromates, CrO_4^{2-} and dichromates, $Cr_2O_7^{2-}$.

Chromium(VI) oxide, CrO_3. It is obtained by the action of concentrated sulphuric acid on a concentrated solution of potassium dichromate.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + H_2O + 2CrO_3$$

The mixture is allowed to cool when scarlet needle-like crystals of CrO_3 separate out. On heating at 250° C, CrO_3 decomposes readily evolving oxygen and Cr_2O_3. The decomposition is complete at 450° C.

It is readily soluble in water giving a red solution which is highly acidic and contains a number of chromic acids.

It is a powerful oxidising agent. It oxidises alcohols, glycerine, oxalic acid, sugar, etc. In acidic medium, it oxidises sulphur dioxide, hydrogen sulphide, stannous salts, ferrous salts, iodine, etc. Chromium(VI) oxide itself is reduced to a chromium(III) salt in every case. Some of the oxidising reactions are represented below.

$$2CrO_3 + 3H_2S + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3S + 6H_2O$$

$$2CrO_3 + 6FeSO_4 + 6H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O$$

$$2CrO_3 + 3SnCl_2 + 12HCl \longrightarrow 2CrCl_3 + 3SnCl_4 + 6H_2O$$

It reacts with gaseous hydrogen chloride to give **chromyl chloride.**

$$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O$$

It dissolves in alkalies to give chromates. For example,

$$CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$$

Chromate ion, CrO_4^{2-}, is *yellow* in colour. The above solution is, therefore, yellow. But when acidified, the solution turns orange due to the formation of dichromate ion, $Cr_2O_7^{2-}$.

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O$$

The reaction is reversed on the addition of an alkali.

Chromic Acids. As already pointed out, the solution of CrO_3 in water is strongly acidic. It contains several chromic acids, the simplest of which called *monochromic acid* (or simply *chromic acid*) is known only in solution.

$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$

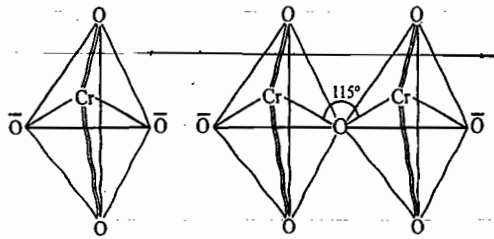
The higher chromic acids are supposed to be formed through condensation of 2, 3 or more molecules of chromic acid with the elimination of water. For example,

$$2H_2CrO_4 \longrightarrow \underset{\text{Dichromic acid}}{H_2Cr_2O_7} + H_2O$$

$$3H_2CrO_4 \longrightarrow \underset{\text{Trichromic acid}}{H_2Cr_3O_{10}} + 2H_2O$$

The salts of H_2CrO_4 and $H_2Cr_2O_7$ are known as chromates and dichromates, respectively.

Chromate ion has a **tetrahedral structure** with Cr atom lying at the centre. Dichromate ion consists of two such tetrahedra, as shown.



Structure of chromate ion Structure of dichromate ion

The oxygen atom commonly linked to the two chromium atoms subtends Cr—O—Cr angle equal to 115°, as shown.

Potassium Dichromate, $K_2Cr_2O_7$. It is prepared by mixing hot saturated solution of sodium dichromate (*obtained from chromite ore as explained earlier*) and potassium chloride.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow 2NaCl + K_2Cr_2O_7$$

Sodium chloride precipitates out from the hot solution and is removed by filtration. On cooling the mother liquor, crystals of potassium dichromate separate out.

Physical Properties. Potassium dichromate forms orange-red crystals melting at 398° C. It is moderately soluble in cold water but freely soluble in hot water.

Chemical Properties. 1. On strong heating, it decomposes to give chromic oxide and oxygen.

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

2. Potassium dichromate, when heated with concentrated sulphuric acid and a soluble chloride, such as sodium chloride, gives red vapours of chromyl chloride.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

3. It reacts with hydrochloric acid evolving chlorine.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

4. Potassium dichromate is a *powerful oxidising agent.* In acidic solution, as for example, in the presence of dilute sulphuric acid, it readily *takes up electrons* from a reducing agent and gets reduced to Cr^{3+} ion.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Typical **oxidation reactions** are given below.

(*i*) *Liberation of iodine from potassium iodide solution.*

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

(*ii*) *Oxidation of* Fe^{2+} to Fe^{3+}.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

(*iii*) *Oxidation of sulphite ion* (SO_3^{2-}) *to sulphate ion* (SO_4^{2-})

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

(*iv*) *Oxidation of* H_2S *to* S *and* SO_2 *to sulphuric acid* (SO_4^{2-} ion)

$$Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$$

5. On the addition of an alkali, the orange colour of potassium dichromate solution changes to yellow due to the formation of potassium chromate.

$$\underset{\text{Orange red}}{K_2Cr_2O_7} + 2KOH \longrightarrow \underset{\text{Yellow}}{2K_2CrO_4} + H_2O$$

On acidifying with H_2SO_4, the colour again changes to orange-red owing to the formation of dichromate.

$$2K_2CrO_4 + 2H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

Actually, in dichromate solution, the $Cr_2O_7^{2-}$ ions are in equilibrium with CrO_4^{2-} ions.

$$\underset{\text{Orange red}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\text{Yellow}}{2Cr_2O_4^{2-}} + 2H^+$$

Uses. Potassium dichromate is used 1. As a volumetric reagent in laboratory for the estimation of ferrous ions, iodide ions, etc.

2. For the preparation of several chromium compounds such as chrome alum, chrome red ($PbCrO_4$,PbO), zinc yellow ($ZnCrO_4$), chrome yellow ($PbCrO_4$), etc.

3. In dyeing, chrome tanning and calico printing.

4. *In photography*

5. A mixture of $K_2Cr_2O_7$ and concentrated H_2SO_4 is used as a cleansing agent for glass-ware, etc.

Perchromic acid and Chromium peroxide. When solutions of chromates or dichromates are shaken with dilute sulphuric acid and hydrogen peroxide, an intense blue colour is formed which disappears very quickly. However, if a small amount of ether is present, the blue colour formed persists in the ethereal layer. This is used as a *test for chromium* in the third group of qualitative analysis of basic radicals.

The blue colour was formerly thought to be due to formation of *perchromic acid*, H_3CrO_8 but recent work has shown that the compound formed is *chromic peroxide*, $CrO(O_2)_2$.

$$\underset{\text{Yellow}}{CrO_4^{2-}} + 2H^+ + 2H_2O_2 \longrightarrow \underset{\text{Blue}}{CrO(O_2)_2} + 3H_2O$$

But, when the solution of K_2CrO_4 is shaken with aqueous KOH in the presence of H_2O_2, a reddish brown compound K_3CrO_8 is obtained which contains four peroxo ligands and can, therefore, be written as $K_3[Cr(O_2)_4]$.

Compounds of Chromium with Unusual Oxidation States. The compounds of Cr(I) are very uncommon but one compound of Cr(I) is well characterised. It is $[Cr(dipyridyl)_3]^+ClO_4^-$.

In $Cr(CO)_6$, the metal is present in zero oxidation state. Similarly, in dibenzene chromium, $Cr(C_6H_6)_2$, the metal is present in zero oxidation state. This compound is prepared as follows :

$$3CrCl_3 + 6C_6H_6 + 2Al + AlCl_3 \longrightarrow 3[Cr(\eta^6\text{-}C_6H_6)_2]^+[AlCl_4]^-$$

$$2[Cr(\eta^6\text{-}C_6H_6)_2]^+[AlCl_4]^- + Na_2S_2O_4 + 4NaOH \longrightarrow 2[Cr(\eta^6\text{-}C_6H_6)_2] + 2Na_2SO_3 + 2NaCl + 2AlCl_3 + 2H_2O$$

The metal atom in this compound is 'sandwitched' between the two benzene rings. A similar η^5-C_5H_5 complex of Cr(0) is also known.

In $[Cr_2(CO)_{10}]^{2-}$ and $[Cr(CO)_5]^{2-}$ complex anions, chromium is in –1 and –2 state, respectively.

Biological Importance of Chromium. Trace amounts of chromium are necessary in the diet of mammals. Cr(III) and insulin both maintain the correct level of glucose in the blood. If Cr(III) is totally absent in the body, the removal of glucose from the blood would occur at lesser rates than normal.

MANGANESE

Occurrence. Manganese occurs relatively abundantly as it constitutes about 0·085 per cent of the earth's crust. The most important ores of manganese are *pyrolusite*, (MnO_2), *braunite* (Mn_2O_3) and *hausmannite* (Mn_3O_4).

Extraction. Manganese is generally obtained from pyrolusite by reduction with aluminium (*aluminothermic process*).

Since manganese dioxide gives an explosive reaction with finely divided aluminium, it is first converted into manganomanganic oxide, Mn_3O_4, by heating it to redness. This is then reduced on heating with aluminium powder in a fire-clay crucible embedded in sand.

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$$

It is purified by distillation under reduced pressure.

Refining. The metal is purified further by an electrolytic process using $MnCl_2$ or $MnSO_4$ solution as the bath. The impure metal is made the anode while an iron rod in contact with flowing mercury is made the cathode. The amalgam of manganese thus obtained is distilled in vacuum at 250° C to remove the mercury.

Physical Properties. Manganese is a grey metal and exists in three allotropic forms which are stable over various temperature ranges. It is hard and brittle with a specific gravity of 7·43. It melts at a fairly high temperature of 1245° C and boils at 2150° C. It is paramagnetic.

***Chemical Properties.* 1. Reactions with non-metals.** Manganese is not so reactive towards non-metals at ordinary temperatures. However, when heated, it reacts vigorously. Thus, it combines with fluorine yielding the fluorides MnF_2 and MnF_3. It burns in chlorine to give the chloride $MnCl_2$ and combines with nitrogen to give the nitride Mn_3N_2. It combines with oxygen to give various oxides ; with sulphur, it forms manganese sulphide, MnS. It also combines with carbon at the temperature of carbon arc forming manganese carbide, Mn_2C.

2. Reaction with acids. The oxidation potential of the reaction

$$Mn \longrightarrow Mn^{2+} + 2e^-$$

is 1·05 volt. Manganese is, therefore, fairly electropositive. It dissolves readily in dilute acids evolving hydrogen.

$$Mn + 2H^+ \longrightarrow Mn^{2+} + H_2$$

3. Action of water. Manganese decomposes water even in cold, though slowly, with the evolution of hydrogen. The reaction becomes quicker on heating.

$$Mn + 2H_2O \longrightarrow Mn(OH)_2 + H_2$$

Pure manganese, however, does not decompose water at ordinary temperatures. Steam attacks it slightly.

Uses. About 80 per cent of manganese produced is used in the manufacture of *manganese steel.* Manganese when added to steel performs two functions. If added in small amounts, it acts as a scavenger (cleansing agent) in removing oxygen and sulphur forminsg manganese oxide and manganese sulphide, which can be easily eliminated. This improves the strength of the final product. When added in large amounts upto 14 per cent, it imparts special hardness and toughness to the steel. Ordinary steel contains from 0·6–1·5 per cent of manganese, the toughness increases with increase in the manganese content.

The steel containing about 14 per cent manganese, known as *manganese steel,* is very hard and tough and is used for making rock crushers, steel helmets, etc. Some other alloys of manganese with iron and carbon are *spiegeleisen* and *ferromanganese* which are used in the Bessemer process for the manufacture of steel. Amongst the other useful alloys of manganese, mention may be made of *manganin* (Cu = 83–85%, Ni = 3–4%, Iron = 0·4%, Mn = 10–14%) which has a very low temperature coefficient of resistance. *Manganese bronze* is an alloy of manganese, with copper and zinc. Its approximate composition is Cu = 60–65%, Zn = 30–40%, Iron = 0·5–1%, Mn = 0·5–3%. It is resistant towards water and is, therefore, used in making parts connected with shipping, etc.

Electronic Configuration and Oxidation States. The outer electronic configuration of manganese is $3d^5 4s^2$. It exhibits a large number of oxidation states varying from 0 to 7.

The important oxidation states of manganese with examples of common compounds in each state are summed up in Table 3.

TABLE 3

Various Oxidation States of Manganese

Oxidation state	Common compounds
0	$Mn(CO)_5$
+1	$[Mn(CO)_5]Cl$
+2	MnO, $Mn(OH)_2$, MnS, $MnSO_4$, $MnCl_2$
+3	MnF_3, Mn_2O_3, $MnPO_4$, $[Mn(CN)_6]^{3-}$
+4	MnO_2, MnF_4
+6	K_2MnO_4, MnO_3
+7	$KMnO_4$, Mn_2O_7

Aqueous Chemistry of Manganese in Different Oxidation States

Chemistry of Mn(II). Manganese changes readily into Mn^{2+} ion in acid solution on account of its fairly high oxidation potential of 1·05 V. Unlike Cr^{2+} ion, Mn^{2+} ion is fairly stable and does not change into

higher oxidation state easily. In fact, its potential for the reaction

$$Mn^{2+} \longrightarrow Mn^{3+} + e^-$$

is negative being −1·51 volts. This suggests that it is very difficult to oxidise Mn(II) to Mn(III). The reverse of it, on the contrary, is easy under standard conditions. The solutions of Mn(II) ions, in neutral or acidic medium, can remain unaffected even on prolonged exposure to oxygen. Mn(II) ion, therefore, is not a reducing agent.

The reason for high stability of Mn(II) ion lies in its electronic configuration. Mn(II) ion is formed by the loss of both the 4*s* electrons. Its configuration is, therefore, $3d^5$. This corresponds to exactly half-filled *d* subshell which adds to the stability of the structure. Thus, Mn(II) ion is much more stable than Cr(II) or Fe(II) ion.

The aqueous solutions of Mn(II) ion, contain complex cation $[Mn(H_2O)_6]^{2+}$ and are more or less colourless. However, manganese(II) salts like $MnCl_2$ or $MnSO_4$ have faint pink coloration.

Complexes of Mn(II). Complexes of Mn(II) are most well known. Some of the hydrated salts, such as $Mn(ClO_4)_2.6H_2O$ contain the complex ion, $[Mn(H_2O)_6]^{2+}$ in which manganese is in +2 oxidation state. The formation of hexammine ion $[Mn(NH_3)_6]^{2+}$ is also reported by the direct action of ammonia on anhydrous salts of Mn(II). These complexes are *octahedral* and have pink colour. They have five unpaired electrons in 3*d* subshell. Their mangetic moments, therefore, lie in the range of 5·8–6·1 BM. They are highly stable and resist attack by oxidising as well as reducing agents.

A few octahedral complexes with low magnetic moment (*i.e., low spin complexes*) are also known. The examples are $[Mn(CN)_6]^{4-}$ and $[Mn(CN)_5NO]^{3-}$. They have only one unpaired electron and their magnetic moment lies in the range of 1·8 – 2·1 BM. These complexes, however, are not so stable and get oxidised readily as, for example,

$$[Mn(CN)_6]^{4-} \longrightarrow [Mn(CN)_6]^{3-} + e^-$$

Several tetrahedral complexes of Mn(II) are also known. These, however, are not stable in aqueous solution and exist in solvents of low dipole moments such as chloroform, nitrobenzene, etc. The examples are tetrahalo anions, $[MnX_4]^{2-}$, in compounds with large cations (*e.g.*, R_4N^+, R_4P^+). The tetrahedral complexes show green-yellow colour. They have five unpaired electrons in the 3*d* subshell and are, therefore, high spin complexes with magnetic moment falling in the range of 5·8 – 6·1 BM.

Chemistry of Manganese(III). Manganese(III) ion is not stable in aqueous solution because, as mentioned above, it gets reduced easily to Mn(II) ion.

Since Mn(III) ion can be easily reduced, it acts as a strong oxidising agent. It is so strong that it can evolve oxygen even from water.

In the +3 oxidation state, therefore, manganese can exist only in solids and complex ions. There is, accordingly, no solution chemistry of Mn(III) ion.

In aqueous solution, Mn(III) ion undergoes disproportionation to give manganese in +2 and +4 oxidation states.

$$2Mn^{3+} + 2H_2O \longrightarrow Mn^{2+} + MnO_2(s) + 4H^+$$

In this reaction, evidently, while one of the Mn(III) ion is reduced to Mn(II) ion, the other is oxidised to MnO_2 in which manganese is in +4 oxidation state.

The only way to stabilize the Mn(III) ion is to prevent the above disproportionation reaction. This can be done by allowing formation of a complex of Mn(III) ion with cyanide ion when $[Mn(CN)_6]^{3-}$ complex is obtained. The complexing can be done with oxalate ion as well when $[Mn(C_2O_4)_3]^{3-}$ is obtained. Thus,

$$Mn^{3+} + 6CN^- \longrightarrow [Mn(CN)_6]^{3-} \quad \text{(low spin complex)}$$

$$Mn^{3+} + 3(C_2O_4)^{2-} \longrightarrow [Mn(C_2O_4)_3]^{3-} \quad \text{(high spin complex)}$$

During the titration of oxalate anion with $KMnO_4$, it is possible that some $[Mn(C_2O_4)_2]^{3-}$ may be formed. But, since this complex is unstable at 65°C, these titrations are carried out at this temperature so that the whole of Mn(VII) is reduced exclusively to Mn(II).

An unusual basic acetate of Mn(III), *viz.*, $[Mn_3O(CH_3COO)_6(H_2O)_3]^+$ is also known. It is used industrially for the oxidation of toluene to phenol. The structure of the complex cation of basic acetate of Mn(III) is similar to the structure of the complex cation of basic acetate of Cr(III), *viz.*, $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$ discussed earlier.

The Mn(III) ion, as stated above, is stable only in the solid state. Thus, Mn(III) ion is quite stable in insoluble compounds like $MnPO_4$. The oxide Mn_2O_3 in which also manganese is in +3 state, is insoluble.

Complexes of Mn(III). The complexes of Mn(III) are fairly stable. In fact, Mn(III) ion is stabilized only through formation of complexes. Two well known complexs of Mn(III) are $[Mn(CN)_6]^{3-}$ and $[Mn(C_2O_4)_3]^{3-}$ which have already been referred to above. These complexes are *octahedral* in structure.

Chemistry of Mn(IV). Manganese in +4 state exists primarily as its oxide, MnO_2 which is commonly prepared by heating Mn in oxygen. The oxide is insoluble in water and reacts with hot concentrated hydrochloric acid and concentrated sulphuric acid to release Cl_2 and O_2, respectively.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

$$2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + 2H_2O + O_2$$

When fused with NaOH, it gives Na_2MnO_4 which is a green solid.

MnO_2 is a strong oxidising agent and is commonly used in the oxidation of organic compounds. A large quantity of pure MnO_2 is used in dry batteries. It is also used in glass industry to produce purple glass. One of its major uses in industry is in the manufacture of potassium permanganate, as shown below:

$$MnO_2 \xrightarrow[\text{NaOH and } KNO_2]{\text{fuse with}} K_2MnO_4$$

$$2K_2MnO_4 + 2H_2O \xrightarrow[\text{oxidation}]{\text{Electrolytic}} 2KMnO_4 + 2KOH + H_2$$

MnO_2 is also used as a catalyst in the laboratory preparation of oxygen from $KClO_3$.

Since, as mentioned above, Mn(IV) exists primarily as water-insoluble MnO_2, there is very little aqueous chemistry of Mn(IV).

However, some complexes of Mn (IV) are well known. These include $K_2[MnF_6]$, $K_2[MnCl_6]$, $K_2[Mn(CN)_6]$, etc.

Chemistry of Manganese(V). Mn(V) is a very unstable state of manganese. So far, only one compound of this state is known ; this is K_3MnO_4. It is obtained by reacting an aqueous solution of $KMnO_4$ with potassium sulphite.

$$KMnO_4 + K_2SO_3 + H_2O \longrightarrow K_3MnO_4 + H_2SO_4$$

K_3MnO_4 is bright blue compound which, however, is quite unstable.

Chemistry of Manganese(VI). Manganese in +6 oxidation state exists in manganate ion, MnO_4^{2-}. The ion, however, is stable only in highly alkaline solutions. In acidic solutions, it changes readily into permanganate ion in which manganese exists in the highest oxidation state (+7).

$$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2(s) + 2MnO_4^- + 2H_2O$$

Manganate ion changes into permanganate ion even by passing carbon dioxide in its solution.

$$3MnO_4^{2-} + 2H_2O + 4CO_2 \longrightarrow MnO_2 + 2MnO_4^- + 4HCO_3^-$$

In view of extreme instability of manganate ion in dilute alkali, water and acid solution, there is not much of aqueous chemistry of Mn(VI).

Chemistry of Manganese(VII). Manganese(VII) is best known as permanganate, MnO_4^-, ion. It is one of the *strongest oxidising agents.* The aqueous chemistry of Mn(VII) is, in fact, the chemistry of MnO_4^- ion.

Potassium Permanganate, $KMnO_4$. Potassium permanganate is the most important compound of Mn(VII). Its preparation from potassium manganate may be represented as

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2\downarrow + 2H_2O$$

Manganese dioxide is removed by filtration. Potassium permanganate, being less soluble than potassium sulphate, crystallises out first.

When required on a large scale, potassium permanganate is prepared from manganese(IV) oxide. The solid manganese(IV) oxide is fused with potassium hydroxide and the melt is well stirred in contact with air when the following reaction takes place :

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

The mass is extracted with water when a green solution of potassium manganate is obtained. Chlorine gas is then passed to oxidise potassium manganate into potassium permanganate.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

The solution is concentrated when the less soluble potassium permanganate separates out leaving the more soluble potassium chloride in solution.

Alternatively and preferably, the oxidation is carried out electrolytically (anodic oxidation) using nickel anode and iron cathode. The anodic compartment contains the manganate solution under oxidation while the cathodic compartment is filled with dilute alkali solution.

During electrolysis, the manganate ion is oxidised to the permanganate ion in the anodic compartment,

$$MnO_4^{2-} \longrightarrow MnO_4^- + e^-$$

while hydrogen is evolved in the cathodic compartment.

$$\underset{\text{From ionisation of water}}{2H^+} + 2e^- \longrightarrow 2H \longrightarrow H_2$$

Physical Properties. Potassium permanganate, like all other permanganates, possesses purple colour which is the characteristic colour of the permanganate ion, MnO_4^-. It forms deep purple rhombic prisms. It is isomorphous with potassium perchlorate, $KClO_4$. It is fairly soluble in water, about 5 g dissolving in 100 g of water at 15° C.

Chemical Properties. 1. When heated alone or in alkaline solution, it decomposes evolving oxygen.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

$$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

2. On treatment with concentrated sulphuric acid, it gives manganese (VII) oxide which decomposes explosively on heating.

$$2KMnO_4 + H_2SO_4 \longrightarrow Mn_2O_7 + K_2SO_4 + H_2O$$

3. Potassium permanganate is a powerful *oxidising agent.* A well powdered mixture of sulphur, charcoal and potassium permanganate burns when heated and explodes when rubbed, like gun powder. Similarly, a well powdered mixture of potassium permanganate and oxalic acid catches fire spontaneously after a few seconds. The same thing happens when a drop of glycerine is poured over powdered potassium permanganate.

4. The permanganate ion is a typical example of a *strong oxidising agent* in solution. The course of the reaction depends whether it is carried out in *alkaline, neutral* or *acidic solution.*

a. **In alkaline solution.** In alkaline solution, the permanganate ion is first reduced to manganate ion and then to insoluble manganese (IV) oxide. The solution changes first from purple to green and finally

becomes colourless. The chemical changes may be represented by the following equations :

$$2MnO_4^- + 2OH^- \longrightarrow 2MnO_4^{2-} + H_2O + O$$

$$2MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_2 + 4OH^- + 2(O)$$

$$2MnO_4^- + H_2O \xrightarrow{\text{Alkali}} 2MnO_2 + 2OH^- + 3(O)$$

Thus, 2 molecules of potassium permanganate in alkaline solution give three atoms (or 6 equivalents) of available oxygen. Therefore, the equivalent mass of potassium permanganate as an oxidising agent in alkaline solution is one-third of its molar mass.

Iodides are oxidised to iodates by alkaline potassium permanganate.

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

Alkaline potassium permanganate also oxidises ethylene to glycol and toluene to benzoic acid.

$$C_2H_4 + H_2O + (O) \longrightarrow HOCH_2\text{–}CH_2OH$$

$$C_6H_5CH_3 + 3(O) \longrightarrow C_6H_5COOH + H_2O$$

b. **In neutral solution.** In neutral solution, potassium permanganate is reduced directly to manganese dioxide.

$$2MnO_4^- + H_2O \longrightarrow 2OH^- + 2MnO_2 + 3(O)$$

Evidently, the equivalent mass of potassium permanganate in neutral solution is one-third of its molar mass.

Hydrogen sulphide is oxidised to sulphur and sodium thiosulphate is oxidised to sodium sulphate and sulphur by the action of neutral potassium permanganate.

$$2MnO_4^- + 3H_2S \longrightarrow 2MnO_2 + 3S + 2H_2O + 2OH^-$$

$$2MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 2MnO_2 + 3SO_4^{2-} + 3S + 2OH^-$$

c. **In acidic solution.** In acidic solution, potassium permanganate is reduced to manganese(II) ion and five atoms of oxygen are rendered available from two molecules of the permanganate.

$$2MnO_4^- + 6H^+ \longrightarrow Mn^{2+} + 3H_2O + 5(O)$$

The best acid to be used is dilute sulphuric acid.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$$

This reaction is used extensively in volumetric estimations. At the end point, the colour changes from purple (due to MnO_4^- ion) to almost colourless (due to Mn(II) ion). The equivalent mass of potassium permanganate in this case, evidently, is one-fifth of its molar mass. The oxidation reactions of acidified potassium permanganate are catalysed by the Mn(II) ion.

A few examples of the oxidation reactions falling in this category are given below :

1. *Ferrous salts are oxidized to ferric salts.*

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

Similarly, stannous salts are oxidised to stannic salts.

2. *Oxalic acid is oxidised to carbon dioxide.*

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

3. *Sulphites are oxidised to sulphates.*

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Similarly, nitrites are oxidised to nitrates, arsenites to arsenates and thiosulphates to sulphates and sulphur.

4. *Potassium iodide is oxidised to iodine.*

$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

5. *Halogen hydracids are oxidised to the corresponding halogens.*

$$2MnO_4^- + 16H^+ + 10X^- \longrightarrow 2Mn^{2+} + 8H_2O + 5X_2$$

(X = Cl, Br, I)

6. *Hydrogen sulphide is oxidised to sulphur.*

$$2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

7. *Sulphur dioxide is oxidised to sulphuric acid.*

$$2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

8. Acidified potassium permanganate is also used as an oxidising agent for organic compounds. For example, it oxidises ethyl alcohol to acetaldehyde.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

Uses. Potassium permanganate is used mainly as an oxidising agent in laboratory as well as in industry. It is used in qualitative analysis for detecting halides, sulphites, oxalates, etc. For volumetric estimations, potassium permanganate is generally used in acid solution. In this way, iron (ferrous), oxalic acid and oxalates, nitrous acid and nitrites, sulphites, potassium iodide and hydrogen peroxide are estimated.

Potassium permanganate is employed in the manufacture of saccharin, benzoic acid, acetaldehyde, etc. It also finds extensive applications as a disinfectant. Alkaline potassium permanganate is used in organic chemistry under the name *Baeyer reagent.*

Unusual Oxidation States of Manganese. Manganese is present in –1 oxidation state in $[Mn(CO)_5]^-$ complex anion which is quite stable. The oxidation state of the metal is zero in complexes $[Mn_2(CO)_{10}]$ and $K_6[Mn(CN)_6].2NH_3$. The latter is highly reducing. The +1 oxidation state is found in the complex $K_5[Mn(CN)_6]$ which is rather unstable. This complex can be prepared by the reduction of $K_3[Mn(CN)_6]$ with liquid ammonia.

Biological Importance of Manganese. Mn(II) is an important constitutent of animal as well as plant enzymes. The Mn(II) enzymes produced in the liver, convert nitrogenous waste products into urea which is carried by the blood to the kidneys which excrete it into the urine.

Maganese is an essential element for plant growth. It, along with fertilisers, enriches the soil.

IRON

Occurrence. Iron occurs seldom in native (uncombined) form. In combined state, it occurs as *magnetite* (Fe_3O_4), *haematite* (Fe_2O_3), *lymonite* ($Fe_2O_3.3H_2O$), *siderite* (FeO_3) and *iron pyrites* (FeS_2).

Varieties of Iron. There are three commercial varieties of iron which are put to different industrial uses. They are : *cast iron, wrought iron* and *steel.* The differences in their properties lie in their carbon and phosphorus contents.

Cast iron is the least pure form of iron. It contains from 2·5 to 4·5 per cent of carbon together with some sulphur, phosphorus, silicon and manganese.

Wrought iron is the purest form of iron containing not more than 0·5 per cent of carbon and other impurities.

Steel comes in between cast iron and wrought iron. Its carbon content varies between 0·4 and 1·5 per cent. It usually contains some manganese as well.

CAST IRON (PIG IRON)

Extraction. Cast iron is extracted chiefly from its oxide ore (haematite) by heating in the presence of coke and limestone in a blast furnace. At first, the coke lying at the bottom of the furnace burns in air to

form CO_2. As this gas rises upward, it reacts with more of carbon to give carbon monoxide.

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393{\cdot}3 \text{ kJ}$$

$$CO_2(g) + C(s) \longrightarrow 2CO(g); \quad \Delta H = +242{\cdot}7 \text{ kJ}$$

The carbon monoxide then reacts with oxides of iron contained in the ore giving iron and carbon dioxide.

$$3CO(g) + Fe_2O_3(s) \longrightarrow \underset{\text{Cast iron}}{2Fe(l)} + 3CO_2(g)$$

$$CO(g) + Fe_3O_4(s) \longrightarrow 3FeO(s) + CO_2(g)$$

$$CO(g) + FeO(s) \longrightarrow \underset{\text{Cast iron}}{Fe(l)} + CO_2(g)$$

Silica present in the ore is removed as calcium silicate (slag) on reacting with calcium oxide which results from the heating of limestone.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + SiO_2(s) \longrightarrow \underset{\text{Slag}}{CaSiO_3(l)}$$

The slag being lighter floats above the molten iron and can easily be skimmed off.

Cast iron contains from 2·6 to 4·3 per cent carbon, 0·7 to 3 per cent silicon and small quantities of phosphorus, sulphur and manganese. The carbon is present partly as free carbon in the form of graphite and partly in combination with iron as *cementite,* Fe_3C. When it is melted and then rapidly cooled, it becomes very hard and brittle and is known as *white cast iron.* This contains most of the carbon as cementite only. If the molten iron is cooled slowly, on the other hand, most of the carbon separates out as graphite and a softer and less brittle variety, known as *grey iron,* is obtained.

Cast iron, on account of impurities, melts at a much lower temperature of 1150 to 1250°C whereas pure iron melts at 1536°C.

It is hard but too brittle to be used in making machinery. It *expands on solidifying* and, therefore, finds extensive application in casting variously-shaped articles such as stoves, radiators, toys, tools, cooking ranges, pipes, agricultural implements, etc. A large quantity of cast iron is used in making wrought iron.

WROUGHT IRON

Wrought iron is comparatively pure form of iron. It contains not more than 0·5 per cent of impurities of which carbon amounts to about 0·2 percent. The other impurities are sulphur, phosphorus, silicon and manganese.

Manufacture. It is obtained by purifying cast iron by the process known as **'puddling'** (meaning stirring). The cast iron is heated on the hearth of a reverberatory furnace (known as puddling furnace) lined with haematite (Fe_2O_3). Heat supplied by reflection from the roof of the furnace falls upon the charge placed on the hearth. The cast iron is melted and stirred. The haematite supplies the oxygen required to oxidise the carbon, silicon, manganese and phosphorus present in the cast iron to carbon monoxide, silica, manganous oxide and phosphorus pentoxide, respectively.

Manganous oxide and silica combine to form manganous silicate (slag). Phosphorus pentoxide combines with haematite to form ferric phosphate slag.

The melting point of iron rises with the loss of impurities. Iron, therefore, attains a semi-solid state. At this state, it is taken out in the form of balls and the slag squeezed out by hammering.

Wrought iron retains about 0·2 per cent of carbon, besides traces of phosphorus, silicon, etc., in the form of slag. It is soft, ductile and malleable and can be welded. The presence of slag gives strength and toughness to the metal and makes it resistant towards rusting and corrosion. It is used in the manufacture of articles which are to be subjected to sudden stresses, such as chains, wires, anchors, bolts and nails. It is also used in making cores of electromagnets.

STEEL

The carbon content of steel is intermediate between that of cast iron and wrought iron. It varies between 0·1 and 1·5 per cent. The hardness of steel increases with increase in carbon content. Steel usually contains manganese as well. Sometimes, other elements such as chromium, silicon, nickel, tungsten, vanadium and molybdenum are added for making **special steels.**

Manufacture. There are three methods in common use for the production of steel on a large scale. These are : *1. The Bessemer Process 2. The Open Hearth Process* and *3. The Electric Furnace Process.* These methods are based on removing impurities from pig iron and then adding calculated amounts of carbon, manganese, chromium and other elements.

1. The Bessemer Process. In this process, molten pig iron, taken directly from the blast furnace, is run into Bessemer converter which is a pear-shaped furnace about 6 metres high and 3 metres in diameter (Fig. 1). It is made of steel plates and is lined inside with heat-resisting fire clay bricks. At the base, there are a number of holes, callled *tuyeres,* through which air can be admitted. The converter can be rotated on a horizontal central axis, as shown.

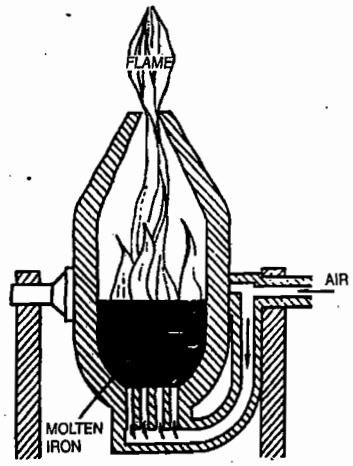


Fig. 1. The Bessemer converter.

To start with, the converter is turned into the horizontal position and molten pig iron introduced into it. A blast of hot air is admitted through the tuyeres. The converter is then rotated so as to bring its mouth vertically upwards. The blowing of air is continued. As the air passes upwards through the molten metal, it oxidises the impurities (manganese, silicon, carbon, phosphorus, sulphur, etc.) present in the pig iron. During the first five to ten minutes, oxidation of only manganese and silicon takes place. The manganese oxide and silica thus formed combine together to form manganous silicate slag.

Later on, carbon is oxidised to carbon monoxide which burns with a blue flame at the mouth of the converter.

When the whole of carbon is oxidised, the blue flame suddenly dies out. The requisite amount of carbon is then added (to convert iron into steel) usually in the form of an alloy of iron, manganese and carbon, called *spiegeleisen.* The blast is continued just for a moment to ensure complete mixing. The resulting product is manganese steel which is much harder and possesses much greater tensile strength than ordinary steel. Sometimes, a little aluminium or silicon-iron alloy is also added to the molten steel. This takes up any dissolved carbon monoxide or nitrogen from the molten metal so as to avoid any subsequent defects, such as 'blow holes', in the castings.

At the end, the converter is tilted to pour out the molten steel.

2. The Open Hearth Process. In this process, a mixture of cast iron, scrap iron, iron ore (haematite) and lime is melted in an Open Hearth furnace. The hearth is lined with silica (SiO_2) or calcined dolomite ($CaO.MgO$) depending upon the nature of the impurities present in cast iron. Silica lining is used if the impurities are manganese, silicon, etc., and calcined dolomite lining is used if much of phosphorus is present. Heating to about 1500°C is done by burning producer gas. *A regenerative system of heat economy* is employed to save the fuel.

Heating is continued for about 8 to 10 hours. During this period, the impurities (C, Si, S, P) get oxidised by haematite. Carbon is removed as carbon monoxide. Sulphur is eliminated as sulphur dioxide. Silicon and phosphorus are oxidised to silica (SiO_2) and phosphorus pentoxide, respectively. These react with lime forming slag.

Samples are withdrawn from the hearth from time to time and analysed. The carbon content is adjusted to the proper value. Requisite quantities of other metals may also be added if special steels are to be obtained. After setting up the desired composition, the finished batch of molten steel is removed from the furnace by tilting the hearth.

3. The Electric Furnace Process. This process involves the setting up of a carbon arc. The electrodes are held vertically and the charge consisting of cast iron, scrap iron and iron ore (haematite), mixed with requisite quantities of lime, is held in between.

The furnace is usually lined with dolomite. The chemical reactions start almost instantaneously. Silicon is oxidised to silica. This helps in forming silicate slags of calcium and manganese. The excessive carbon in the iron ore is oxidised off as carbon monoxide while phosphorus is oxidised as phosphorus pentoxide which, as in the Bessemer process, combines with lime forming calcium phosphate. This passes into slag, as in the Bessemer process. The furnace is then tilted carefully so as to pour off the phosphate and other slags (which being lighter remain above the metallic portion). After this, a charge consisting of coke, lime and sand is added. The iron sulphide, still present as impurity, reacts with lime producing calcium sulphide and ferrous oxide.

Calcium sulphide passes into the slag while iron oxide is reduced to the metallic state by the coke (carbon). As phosphorus and sulphur are almost completely removed, the steel obtained by this process is very much superior.

This method is also used in making high quality **alloy steels** which are obtained by incorporating one or more of the metals like chromium, manganese, nickel, tungsten, molybdenum, silicon, etc.

Some special alloy steels are given in Table 4.

TABLE 4

Some Special Alloy Steels

Name	Composition	Properties	Uses
1. Chrome steel	2–4% Chromium	High tensile strength	Ball bearings, cutting tools such as files
2. Tungsten steel	10–20% Tungsten	Retains hardness even at high temp.	Cutting tools for high speed lathes.
3. Stainless steel	18% Chromium and nickel	Resists corrosion	Utensils, ornamental pieces
4. Manganese steel	10–18% Manganese	Very hard and resistant to wear	Grinding machinery, safes.
5. Nickel steel	2·5–5% Nickel	Resists corrosion, hard and elastic	Wire cables, gears, drive shafts
6. Molybdenum steel	0·3–3% Molybdenum	Resists corrosion even at high temperatures.	Cutting tools and axles
7. Invar	36% Nickel	Practically no coefficient of expansion	Meter scales and pendulum rods
8. Silicon steel	15% Silicon	Extremely hard and resistant to acids	Pumps and pipes for carrying acids

Case-hardening. The process of hardening of surface of wrought iron by the presence of carbon *at the surface* is known as **case-hardening.** This is produced by heating wrought iron in contact with potassium ferrocyanide when due to the decomposition of the ferrocyanide ultimately into carbon, a surface layer of steel results. In other words, a surface layer of steel is formed on the wrought iron. The inner portions still remain as wrought iron and, therefore, retain the toughness associated with the wrought iron. Case hardened wrought iron is used for making **armour plates** and several parts of machinery which are subjected to constant wear and tear.

A steel with very hard surface, frequently used for cylinder bores, is prepared by what is known as **nitriding process** which consists in heating steel containing about 1 percent aluminium in an atmosphere of ammonia at 550–600°C. It is believed that the nitrogen formed by the dissociation of ammonia reacts with iron and aluminium to form on the surface, iron and aluminium nitrides which settle in the interstices of the iron crystals producing a compact and hard surface.

Properties of Steel. The carbon content of steel, as already mentioned, varies between 0·5 and 1·5 per cent. The properties depend upon the carbon content as well as upon the heat treatment. If the carbon content is low, the steel is soft and ductile and is termed as **mild steel.** As the carbon content rises, the ductility decreases but the tensile strength increases up to 1·5 per cent of carbon content. Thereafter, it begins to decrease. The tensile strength of cast iron is of the order of 10 tons per square inch, that of wrought iron is 29 tons per square inch while that of steel varies from 30–100 tons per square inch depending upon the carbon content.

Steel, on account of impurities (carbon, etc.), melts at a lower temperature than wrought iron. Addition of elements other than carbon imparts special features. Thus, a little of manganese produces elasticity apart from adding to the tensile strength. The presence of 10 per cent manganese makes steel extremely hard which is used in making mechnical crushers. The addition of chromium imparts resistance to chemical attack and gives the popularly known **stainless steel** used in cutlery, etc. These and some other varieties of steel, their approximate compositions and uses have been summed upon in Table 4.

Annealing and Tempering. Steel has a highly characteristic property that its hardness and elasticity can be controlled by proper heat treatment. For example, when it is heated to red heat and then allowed to cool slowly, it becomes soft. This process is known as **annealing**. On the other hand, if it is cooled (quenched) suddenly on plunging into ice-cold water, it becomes very hard and brittle. This process is known as **tempering**. On reheating this product to 250–300° C, the brittleness disappears but hardness remains. The degree of hardness can be controlled by heating the product once again to a suitable temperature varying from 200° to 350° C (depending upon the hardness required) and then allowing it to cool slowly. The temperature to which steel is heated is judged from the colour of the oxide film formed on the surface, *e.g.*, a pale yellow colour indicates 230° C, brown 260°C, purple 280° C and blue 300° C.

Properties of Iron. Physical Properties. Pure iron is grey-white lustrous metal melting at 1536° C. It boils at about 3000° C. Its specific gravity is 7·86 and specific heat 0·11. It possesses *strong ferromagnetic properties* which it loses when heated above 766° C (the *curie point*). It is malleable and ductile but has a very high tensile strength.

The metal exhibits **allotropy**. It exists in three forms which differ from one another in crystalline shape only. The names and transition temperatures are as shown below :

$$\alpha\text{-iron} \underset{}{\overset{906^\circ\,C}{\rightleftharpoons}} \gamma\text{-iron} \overset{1410^\circ\,C}{\rightleftharpoons} \delta\text{-iron}$$

The name β-iron is given to the non-magnetic form produced at 766° C. However, it has the same crystalline form as α-iron and is, therefore, not considered as a distinct allotropic form.

Chemical Properties. Iron is a chemically reactive element. It reacts with air, water and acids. It also combines with other elements and displaces metals from their compounds.

1. Action of Air. The Rusting of Iron. When exposed to air and moisture, iron gets rapidly oxidised to a *hydrous oxide*, known as **rust of iron**. Although the composition of the rust varies somewhat, it consists mainly of hydrated iron oxide, $2F_2O_3.3H_2O$, together with a small quantity of iron (II) carbonate.

Several workers have carefully investigated the conditions which promote rusting. It has been observed that

(*i*) *Pure iron* if kept in contact with *pure water* (redistilled, CO_2-free) does not rust.

(*ii*) The rust appears if iron is impure or if water contains some dissolved impurities.

(*iii*) The presence of carbon dioxide or acidity in water is also necessary.

(*iv*) The presence of even traces of other metals such as zinc or copper in iron promotes formation of the rust.

(*v*) The presence of certain other metals like chromium and nickel which can form solid solutions with iron, on the other hand, slows down or even prevents rusting.

(*vi*) The presence of alkalies also retards rusting.

Electrochemical Theory of Rusting. According to one of the current views, *rusting is an electrochemical phenomenon* and takes place due to local action. When impure iron comes in contact with water containing carbon dioxide, *an internal voltaic cell is set up.* The iron and the other metals present as impurities, constitute the electrodes while water charged with carbon dioxide acts as an electrolyte. As iron is more electropositive than many other metals, it passes into solution as iron (II) ion more readily than the rest of the metals.

$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$$

The ferrous ions in aqueous solution get oxidised in the presence of air to Fe^{3+} ions also generating hydroxyl ions and precipitating out ferric hydroxide.

$$4Fe^{2+} + O_2 + 2H_2O \longrightarrow 4Fe^{3+} + 4OH^-$$

$$Fe^{3+} + 3OH^- \longrightarrow \underset{\text{(Rust)}}{Fe(OH)_3}$$

Protection of iron from rusting. Iron is protected from rusting by coating it with zinc or by painting or white-washing it with lime. The idea is to prevent the iron surface from coming in contact with air and moisture. Iron pipes are protected by heating and then dipping in a solution of coal tar. An impervious coating results. Another method, known as *Barf process,* consists in heating the iron to redness in steam when a protective coating of iron(II)-iron(III) oxide (Fe_3O_4), also known as ferrosoferric oxide, is formed. The oxide layer is very firm and coherent. A good method consists in electroplating iron with metals like nickel or chromium. An alternative method more frequently employed is **galvanising** iron rods or sheets or wires by coating them with a thin film of zinc.

2. Action of Water. Iron displaces hydrogen from steam at high temperatures.

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

3. Displacement of Other Metals. Iron displaces less electropositive metals such as copper, silver, etc., from their salts.

$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$

4. Action of Acids. Since oxidation potential of the reaction

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

is positive, being +0·44 volt, iron dissolves in dilute hydrochloric acid or sulphuric acid liberating hydrogen

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

It also dissolves in *dilute nitric acid* forming ammonium nitrate.

$$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

When placed in *highly concentrated nitric acid,* it becomes *'passive' i.e.*, it loses it normal reactivity (see below).

5. Combination with Other Elements. Iron combines directly with chlorine and other halogens on heating. It also combines with other non-metals like S, P, B, C and Si at high temperature.

Passive Iron. When a piece of iron is lowered in concentrated nitric acid, a slight reaction takes place which then ceases completely. The iron does not appear to undergo any change in its appearance but it does not react with dilute nitric acid nor does it precipitate copper from copper sulphate solution although ordinary iron undergoes these reactions very readily. The iron in this form is said to be **'passive'**.

Passive iron returns to the normal state when scratched or heated in a reducing atmosphere of hydrogen or carbon monoxide or immersed in a concentrated solution of an alkali.

Passivity of iron is believed to be due to the formation of an extremely thin (almost imperceptible) and impervious film of ferroso-ferric oxide, Fe_3O_4, on the surface of iron. The reaction of nitric acid, therefore, slows down to such an extent that it cannot be detected. This view receives support from the fact that passivity is removed by scratching or by dissolving out the iron oxide in an alkali solution or in iodine solution. The passivity of iron is important in preventing corrosion of iron.

Electronic Configuration and Oxidation States. The outer electronic configuration of iron is $3d^6\,4s^2$. It shows oxidation states of 0, +2, +3, +4, +5 and +6 but only +2 and +3 states are common. The zero oxidation state occurs in the case of carbonyls where the bonding electrons are contributed by CO molecules.

Oxides of Iron. The oxide **FeO** is non-stoichiometric, the approximate composition being $Fe_{0.95}O$. It is a basic oxide and dissolves readily in acids. It has a NaCl type structure with some crystal lattice defects. The oxide $\mathbf{Fe_2O_3}$ is also non-stoichiometric, the approximate composition being $Fe_{1.95}O_3$. This oxide reacts with Na_2CO_3 to give sodium ferrite.

$$Fe_2O_3 + Na_2CO_3 \longrightarrow 2NaFeO_2 + CO_2$$

Fe_2O_3 is known in a number of modifications of which α-Fe_2O_3 and γ-Fe_2O_3 are more important. The oxide ions in α-Fe_2O_3 structure have hcp arrangement. The metal ions occupy the octahedral sites. The mineral haematite is also α form of Fe_2O_3. The γ form of Fe_2O_3 is obtained by careful oxidation of Fe_3O_4. The structure of γ-Fe_2O_3 contains ccp arrangement of oxide ions with metal ions occupying octabedral and tetrahedral sites at random. It is used as magnetic material in the production of recording tapes.

The oxide $\mathbf{Fe_3O_4}$ is a mixed oxide which can be written as $FeO.Fe_2O_3$. It has an *inverse spinel structure* in which the oxide ions have a *ccp* arrangement. All the Fe^{2+} ions are present in octahedral sites whereas the Fe^{3+} ions are half in tetrahedral and half in octahedral sites created by the arrangement of oxide ions.

Aqueous Chemistry of Iron in Different Oxidation States. As already mentioned, the common oxidation states of iron are +2 (ferrous) and +3 (ferric). Almost all the aqueous chemistry of iron is confined to the +2 and +3 oxidation states.

Chemistry of Iron(II). Iron(II) in aqueous solution exists as $[Fe(H_2O)_6]^{2+}$. This ion is pale-green in colour. All the iron(II) salts, therefore, have this colour.

$[Fe(H_2O)_6]^{2+}$ ion in aqueous medium can be readily oxidised even on exposure to air to Fe^{3+} ion, as shown below.

$$2Fe^{2+}(aq) + \tfrac{1}{2}O_2 + 2H^+(aq) \longrightarrow 2Fe^{3+}(aq) + H_2O\,; \qquad E^\circ = +0{\cdot}44 \text{ volt}$$

When a solution of Fe^{2+} ion is treated with an alkali, it precipitates out as $Fe(OH)_2$. Although this substance is white, it immediately turns dark brown due to its oxidation to iron(III) state in the presence of air, in alkaline medium.

$$4Fe(OH)_2(s) + \underset{\text{(air)}}{O_2(g)} + 2H_2O \longrightarrow 4Fe(OH)_3(s)$$

Since Fe^{2+} ion is readily oxidised to Fe^{3+} ion, it is a fairly strong reducing agent. It reduces Hg^{2+} to Hg^+, Sn^{4+} to Sn^{2+} and MnO_4^- to Mn^{2+} and so on.

$$Hg^{2+} + Fe^{2+} \longrightarrow Fe^{3+} + Hg^+$$
$$Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$$
$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Iron(II) forms a number of complexes in which the coordination number of Fe^{2+} ion is *six*. Most of the complexes have octahedral structure (cf. Chapter 26).

Iron(II) chloride combines with ammonia gas yielding the hexaammine complex which contains the complex hexaammine ion, $[Fe(NH_3)_6]^{2+}$. The compound has the formula $[Fe(NH_3)_6]Cl_2$.

The famous ring test for nitrate and nitrite ions is based on the fact that NO gas is first generated by the action of H_2SO_4 on nitrate or nitrite ion. This gas then combines with Fe^{2+} ion to yield a brown complex $[Fe(H_2O)_5NO]^{2+}$. This is the theory of **ring test.**

Another complex of the same type is $Na_2[Fe(CN)_5(NO)]$ in which NO is present as NO^+. It is known as sodium nitroprusside.

Sodium nitroprusside or sodium nitrosopentacyanoferrate(II), $Na_2[Fe(NO)(CN)_5].2H_2O$. This compound is obtained on boiling potassium ferrocyanide with dilute nitric acid and neutralising with sodium carbonate. The solution is filtered and evaporated when red crystals of the compound separate

out. The following reactions are involved :

$$3K_4[Fe(CN)_6] + 4HNO_3 \longrightarrow 3K_3[Fe(CN)_6] + NO + 2H_2O + 3KNO_3$$
$$2K_3[Fe(CN)_6] + 3Na_2CO_3 \longrightarrow 2Na_3[Fe(CN)_6] + 3K_2CO_3$$
$$Na_3[Fe(CN)_6] + NO \longrightarrow Na_2[Fe(CN)_5(NO)] + NaCN$$

It is used in qualitative analysis in the detection of soluble sulphides with which it gives deep purple coloration.

$$Na_2S + \underset{\text{Sod. nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Violet or purple colour}}{Na_4[Fe(CN)_5(NOS)]}$$

Potassium ferrocyanide or Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$. It is obtained on a large scale from coal gas which contains about 0·2 percent of hydrogen cyanide as an impurity. The gas is passed through a washer containing iron(II) sulphate and potassium hydroxide. The following reactions take place.

$$HCN + KOH \longrightarrow KCN + H_2O$$
$$6KCN + FeSO_4 \longrightarrow K_4[Fe(CN)_6] + K_2SO_4$$

Another commercial method, which also makes use of coal gas as the source, consists in passing the gas through hydrated iron oxide which contains ferrous hydroxide as well as some ferric hydroxide. The oxide purifies the gas by absorbing hydrogen cyanide and forms ferric ferrocyanide, also known as *prussian blue*, $Fe_7C_{18}N_{18}$. The course of the reaction is represented as follows :

$$Fe(OH)_2 + 2HCN \longrightarrow Fe(CN)_2 + 2H_2O$$
$$Fe(OH)_3 + 3HCN \longrightarrow Fe(CN)_3 + 3H_2O$$
$$3Fe(CN)_2 + 4Fe(CN)_3 \longrightarrow \underset{\substack{\text{Ferric ferrocyanide}\\ \text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3}$$

The prussian blue formed is boiled with lime when it yields calcium ferrocyanide.

$$Fe_7C_{18}N_{18} + 6Ca(OH)_2 \longrightarrow 3Ca_2[Fe(CN)_6] + 4Fe(OH)_3$$

Calcium ferrocyanide passes into solution to which some potassium carbonate is added when potassium ferrocyanide is formed.

$$Ca_2[Fe(CN)_6] + 2K_2CO_3 \longrightarrow 2CaCO_3 + K_4[Fe(CN)_6]$$

Calcium carbonate is removed by filtration and the solution evaporated to obtain the crystals of potassium ferrocyanide.

In the laboratory, it is obtained by mixing a solution of iron(II) sulphate with that of potassium cyanide until a small amount of the precipitated iron(II) cyanide remains undissolved.

$$FeSO_4 + 2KCN \longrightarrow Fe(CN)_2 + K_2SO_4$$
$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6]$$

The solution is evaporated to crystallisation as usual.

Properties. 1. Potassium ferrocyanide exists as lemon-yellow crystals associated with three molecules of water of crystallisation, the formula being $K_4[Fe(CN)_6].3H_2O$. The trihydrate loses its water of crystallisation when heated to 140° C.

2. It is a very stable compound which in solution ionises as

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

3. When heated, it decomposes to give iron carbide, potassium cyanide and nitrogen.

$$K_4[Fe(CN)_6] \longrightarrow 4KCN + FeC_2 + N_2$$

4. When boiled with dilute sulphuric acid, hydrogen cyanide is evolved.

$$2K_4[Fe(CN)_6] + 3H_2SO_4 \longrightarrow \underset{\text{Potassium iron(II) hexacyanoferrate}}{K_2Fe[Fe(CN)_6]} + 3K_2SO_4 + 6HCN$$

On treatment with hot concentrated sulphuric acid, carbon monoxide is evolved.

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + 3(NH_4)_2SO_4 + 6CO + FeSO_4$$

5. It combines with cupric salts to form reddish brown precipitate of cupric ferrocyanide.

$$2Cu^{2+} + K_4[Fe(CN)_6] \longrightarrow 4K^+ + \underset{\text{(Reddish brown)}}{Cu_2[Fe(CN)_6]}$$

6. It reacts with ferric salts to give a blue precipitate of ferric ferrocyanide, called prussian blue.

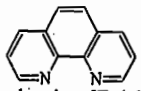
$$4Fe^{3+} + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + 12K^+$$

7. The ferrocyanide ion evidently contains iron in +2 oxidation state. It can, thus, be oxidised on treatment with chlorine, etc., to the ferricyanide ion, $[Fe(CN)_6]^{3-}$, which contains iron in +3 oxidation state.

$$2[Fe(CN)_6]^{4-} + Cl_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2Cl^-$$

Uses. Potassium ferrocyanide is used as a reagent in the laboratory for qualitative analysis. It gives, for example, blue, red and white precipitates with iron(II), copper(II) and zinc(II) ions, respectively. It is also used for the manufacture of *prussian blue.*

Several bidentate ligands such as ethylenediamine (en), 1,10 phenanthrolin (phen) and 2,2' bipyridyl (bipy) form stable complexes with Fe(II). The complexes $[Fe(en)_3]^{2+}$, $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ are octahedral in structure.

The ligand 1,10 phenanthrolin  is used in colorimetric estimation of Fe(II) since it produces intense red coloured complex ion $[Fe(phen)_3]^{2+}$ quantitatively. This ligand is also used as 'ferroin' indicator in the redox titration of Fe(II) which gets converted to Fe(III) by an oxidising agent. The complex ion $[Fe(phen)_3]^{2+}$ is highly stable and does not oxidise until an excess of oxidising agent is present. In other words, the red colour given by 'ferroin' with Fe(II) does not fade unless the whole of Fe(II) is oxidised to Fe(III).

Chemistry of Iron(III). Iron(III) salts are obtained through the oxidation of corresponding iron(II) salts. Iron(III) ion, on account of its small size and high charge density, readily gets hydrolysed yielding hydrogen ions. It, therefore, behaves as an acid in aqueous solution. Since the ion is present as $[Fe(H_2O)_6]^{3+}$ in aqueous solution, its hydrolysis may be represented as

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H^+$$

The equilibrium constant of the above reaction at ordinary temperatures is 9×10^{-4}.

The yellow-brown colour which is characteristic of iron(III) salts is largely due to $[Fe(H_2O)_5(OH)]^{2+}$ ion. By adding an acid, such as nitric acid, the colour disappears on account of the reversibility of the above reaction.

By adding an alkali, on the other hand, the colour deepens due to the shifting of the equilibrium towards the left. Ultimately, reddish brown hydrated iron(III) oxide, $Fe_2O_3.xH_2O$, precipitates out from the solution.

Iron(III) compounds are much less ionised than the iron(II) compounds. For instance, iron(III) fluoride, FeF_3, is so little ionised that its solution in water does not give any test for Fe^{3+} ion or for F^- ion. For the same reason, $Fe(OH)_3$ is much less basic than $Fe(OH)_2$.

Fe^{3+} ion can be reduced to Fe^{2+} ion by reducing agents such as nascent hydrogen, H_2S, Sn^{2+} ions, etc,

$$Fe^{3+} + H \longrightarrow Fe^{2+} + H^+$$

$$2Fe^{3+} + H_2S \longrightarrow 2Fe^{2+} + 2H^+ + S$$

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

It is used as an indicator in volumetric estimation of dichromate.

Fe^{3+} ion forms even larger number of complexes than Fe^{2+} ion. In most of these, the coordination number of Fe^{3+} ion is *six* and the complexes formed are *octahedral* (*cf.* Chapters 26 and 27). However, a few complexes in which the coordination number is *four* and the structure is *tetrahedral* are also known: $[FeCl_4]^-$ is the most important tetrahedral complex. The tetrahalo complexes of Fe(III) are particularly stable if the cation is bigger in size. Examples are $[(t\text{-}Bu)_4N]^+[FeX_4]^-$ where X is Cl^-, Br^- and I^-

A variety of octahedral complexes are known. Fe^{3+} ion has a strong tendency to form complexes with ligands which coordinate via oxygen, *e.g.*, the monophosphate and the oxalate ions. The trioxalato complex, $[Fe(C_2O_4)_3]^{3-}$ is highly stable (That is why oxalic acid is used for removing iron stains from clothes). The hexaaqua ion, $[Fe(H_2O)_6]^{3+}$, is stable only in strongly acidic solution. However, the hexachloro and hexacyanoferrate(III) complexes, *i.e.*, $[FeCl_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ are known to be highly stable. This complex ion contains only one unpaired electron and is, therefore, of *low spin.*

Potassium ferricyanide, or potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$. It can be prepared by the oxidation of potassium ferrocyanide by chlorine or hydrogen peroxide.

$$2K_4[Fe(CN)_6] + Cl_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KCl$$

$$2K_4[Fe(CN)_6] + H_2O_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KOH$$

Properties. The salt separates out from solution as dark red crystals. It is comparatively less stable than potassium ferrocyanide.

Since it can be readily reduced to potassium ferrocyanide in alkaline solution,

$$2K_3[Fe(CN)_6] + 2KOH \longrightarrow 2K_4[Fe(CN)_6] + H_2O + (O)$$

it is used as a good oxidising agent. Thus, in alkaline solution, it oxidises lead monoxide to lead dioxide, hydrogen sulphide to sulphur, sulphur dioxide to sulphuric acid, chromic salts to chromates, etc.

(*i*) $2K_3[Fe(CN)_6] + 2KOH + PbO \longrightarrow 2K_4[Fe(CN)_6] + H_2O + PbO_2$

(*ii*) $2K_3[Fe(CN)_6] + 2KOH + H_2S \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + S$

(*iii*) $2K_3[Fe(CN)_6] + 2KOH + SO_2 \longrightarrow 2K_4[Fe(CN)_6] + H_2SO_4$

(*iv*) $3K_3[Fe(CN)_6] + CrCl_3 + 8KOH \longrightarrow 3K_4[Fe(CN)_6] + K_2CrO_4 + 4H_2O + 3KCl$

Prussian blue. Turnbull's blue. On adding an iron(III) salt to potassium ferrocyanide, a dark blue precipitate of **prussian blue** is obtained. The reaction is represented as

$$Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow \{[Fe[Fe(CN)_6]\}^-$$

e.g., $$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Pot. ferricferrocyanide}}{K\{Fe[Fe(CN)_6]\}} + 3KCl$$

A colloidal solution of prussian blue is formed when the amount of iron(III) salt added to potassium ferrocyanide is less than the equivalent amount.

A similar compound, known as **Turnbull's blue,** is formed on the addition of an iron(II) salt to potassium ferricyanide. In this case, the iron(II) ion is first oxidised to iron(III) ion by the ferricyanide ion which is reduced to ferrocyanide ion.

$$Fe^{2+} + \underset{\text{Ferricyanide}}{[Fe(CN)_6]^{3-}} \longrightarrow Fe^{3+} + \underset{\text{Ferrocyanide}}{[Fe(CN)_6]^{4-}}$$

The iron(III) ion then reacts with ferrocyanide ion as in the formation of prussian blue described above, *i.e.*,

$$Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow \{Fe[Fe(CN)_6)\}^{-}$$

The compound formed is, evidently, $K\{Fe[Fe(CN)_6]\}$, *i.e.*, potassium ferric ferrocyanide.

Thus, it will be seen that the composition of Turnbull's blue is the same as that of prussian blue. However, the colour of Turnbull's blue is less intense. This is due to the presence in it of a white compound of the formula $K_2\{Fe[Fe(CN)_6]\}$ named as potassium ferrousferrocynide. This compound is formed by the reaction between some of the iron (II) salt added initially with potassium ferrocyanide solution.

$$FeSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Pot. ferrous ferrocyanide}}{K_2\{Fe[Fe(CN)_6]\}} + K_2SO_4$$

Although most of this compound is readily oxidised to potassium ferric ferrocyanide, some of it remains as such and is responsible for the dilution of the colour of the Turnbull's blue.

Unusual Oxidation States of Iron. Iron is present in –2 oxidation state in the complex $[Fe(CO)_4]^{2-}$ and in zero oxidation state in complexes $[Fe(CO)_5]$, $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$. It has recently been confirmed that the complex $[Fe(H_2O)_5NO]^{2+}$ which is responsible for the brown ring test for nitrate, contains iron in +1 oxidation state, NO being present as NO^+. The magnetic moment of the complex is 3·9 B.M. which indicates the presence of three unpaired electrons.

Biological Importance of Iron. Iron is the most important transition metal in biological systems. It functions as oxygen carrier in the blood of animals in the form of haemoglobin, a complex compound of iron.

Iron is an essential constituent of myglobin which stores oxygen in muscles. Iron is also present in plants and bacteria in the form of cytochromes and ferredoxin which are responsible for electron transfer reactions in biological systems. Apart from this, iron is an important constituent of *nitrogenase* (a nitrogen-fixing enzyme) and a number of other important enzymes in biological systems.

COBALT

Occurrence. Cobalt occurs in nature much less abundantly than iron. It constitutes about 0·002 per cent of the earth's crust.

Cobalt occurs in combination with sulphur and arsenic. The chief ores are : *(i) Speiss cobalt or smaltite,* $CoAs_2$ *(ii) Cobalt glance or cobaltite,* CoAsS *(iii) Cobalt bloom,* $Co_2(AsO_4).8H_2O$ and *(iv) Linnacite,* Co_3S_4.

These ores are invariably associated with nickel, iron, copper and sometimes also with traces of silver.

Extraction. Th e extraction of cobalt from its ores involves the following steps.

1. Roasting and Smelting of the Ore. The ore is finely powdered and then roasted when most of the sulphur and arsenic are volatilised off. It is then mixed with limestone and sand and smelted in a small blast furnace. The iron present in the ore rises above as ferrous silicate slag. The rest of the metals separate into two layers ; the upper layer known as *speiss* consisting mainly of arsenites of nickel, cobalt, iron and copper and the lower layer consisting of impure silver.

2. Roasting the Speiss with Sodium Chloride. The speiss is separated, ground and roasted with sodium chloride in a reverberatory furnace. Most of the arsenic and sulphur are driven off while the metals are converted into their chlorides.

3. Separation of Iron and Copper. The roasted mass is extracted with water and lime is added to precipitate iron, arsenic and antimony. Copper that goes into the filtrate is removed by adding sodium carbonate while cobalt and nickel remain in solution as *chlorides*. Silver, if present, is extracted by cyanide process.

4. Separation of Nickel from Cobalt. Cobalt is precipitated out as cobalt(III) hydroxide, almost *free from nickel*, from the solution of chlorides of cobalt and nickel on the addition of lime and bleaching powder.

$$CoCl_2 + Ca(OH)_2 \longrightarrow Co(OH)_2 + CaCl_2$$
$$2Co(OH)_2 + H_2O + CaOCl_2 \longrightarrow 2Co(OH)_3 + CaCl_2$$

Nickel that remains in solution can be precipitated as basic carbonate on the addition of sodium carbonate.

The cobalt(III) hydroxide is ignited to give cobalt(II)-cobalt(III) oxide, Co_3O_4.

$$12Co(OH)_3 \longrightarrow 4Co_3O_4 + 18H_2O + O_2$$

5. Reduction of the Cobalt(II)-*Cobalt*(III) *Oxide.* The cobalt(II)-cobalt(III) oxide is reduced to the metal cobalt either by heating with carbon and lime-stone in an electric furnace or by means of aluminium (Goldschmidt process).

$$Co_3O_4 + 4C \longrightarrow 3Co + 4CO$$
$$3Co_3O_4 + 8Al \longrightarrow 9Co + 4Al_2O_3$$

6. Refining. The metal is refined electrolytically using solution of cobalt ammonium sulphate as the electrolyte. Impure metal is made the anode while pure cobalt acts as the cathode.

Properties. Cobalt is a hard metal, white in colour and is malleable and ductile. It is *ferromagnetic* but much less so than iron. It has a density of 8·9 g per c.c. and melts at 1495° C. It is not attacked by air but is oxidised on heating.

Reaction with acids. Cobalt is slightly electropositive, the standard oxidation potential of the reaction,

$$Co \rightleftharpoons Co^{2+} + 2e^-$$

being 0·28 volt. It is, therefore, slowly attacked by dilute hydrochloric acid and sulphuric acid evolving hydrogen and forming cobalt(II) salts. Thus,

$$Co + H_2SO_4 \longrightarrow CoSO_4 + H_2$$

It is attacked rapidly by dilute nitric acid.

$$3Co + 8HNO_3 \longrightarrow 3Co(NO_3)_2 + 2NO + 4H_2O$$

It is rendered passive on treatment with concentrated nitric acid.

Uses. Compounds of cobalt are used as pigments in glass and porcelain. When CoO is fused with silica and K_2CO_3, a blue coloured mass, known as **smalt,** is obtained. It imparts blue colour to the glass to which it is added in the fused state. Cobalt is also used in making some useful alloys such as *cobalt steel* (35% cobalt) used in making permanent magnets and *stellite* (cobalt : 55%, tungsten : 25%, chromium : 15%, molybdenum : 5%) used for making cutting tools and surgical instruments and *cochrome* (containing cobalt, iron and chromium) which is used in making electrical goods. Cobalt is also used for electroplating iron and other base metals, using cobalt(II) ammonium sulphate, $CoSO_4.(NH_4)_2SO_4.6H_2O$, as the bath.

Electronic Configuration and Oxidation States. The outer electronic configuration of cobalt is $3d^7 4s^2$. Its two important oxidation states are +2 and +3, as in the case of iron. Cobalt also shows oxidation state of zero, like iron, in the formation of carbonyls.

Aqueous Chemistry of Cobalt in Different Oxidation States. Like iron, cobalt has two important oxidation states of +2 and +3.

Chemistry of Cobalt(II). Cobalt(II) ion, Co^{2+}, is more stable than Fe^{2+} ion as it cannot be oxidised easily to cobalt(III) state which is far less stable. All cobalt(II) salts are, therefore, stable. However, in basic solutions, oxidation of Co^{2+} to Co^{3+} takes place relatively easily. It can be kept exposed to air for an indefinite period. Co^{2+} ion, in water, exists in the hydrated state as $[Co(H_2O)_6]^{2+}$ and is pink in colour. It

turns blue when heated due to dehydration. Thus, the *anhydrous* Co(II) salts are blue in colour. Cobalt chloride, $CoCl_2$, is blue when anhydrous. It turns pink when hydrated. Anhydrous $CoCl_2$ added to silica gel, is, therefore, used for *testing moisture*. Most of the cobalt(II) compounds are soluble in water.

When a base is added to a solution containing Co^{2+} ion, cobalt(II) hydroxide separates out as a blue precipitate.

When cobalt(II) hydroxide is heated in the *presence of air*, cobalt(II)-cobalt(III) oxide, Co_3O_4, is obtained. This oxide has a normal spinel structure with Co^{2+} ions in tetrahedral and Co^{3+} ions in octahedral sites created due to *ccp* arrangement of oxide ions.

Co(II) forms a number of complexes which are not as stable as the corresponding complexes of Co(III). It forms tetrahedral complex ions $[CoX_4]^{2-}$ where X is Cl^-, Br^-, I^-, OH^-, etc. When a solution of NH_4SCN is added to an aqueous solution containing Hg^{2+} and Co^{2+} ions, the tetrahedral complex $Hg[Co(NCS)_4]$ is obtained. This blue coloured complex is used for calibrating magnetic balance.

Chemistry of Cobalt(III). The cobalt(III) ion, Co^{3+}, is a strong oxidising agent and, therefore, gets itself reduced to cobalt(II) state easily. The potential of the reduction half reaction,

$$Co^{3+} + e^- \longrightarrow Co^{2+}$$

is quite high, being about 1·84 volts. Such a high value shows that Co^{3+} *can oxidise water to oxygen rapidly.* Consequently, there is no aqueous chemistry of Co(III) as it gets reduced readily to Co(II) state.

$$4Co^{3+} + 2H_2O \longrightarrow 4Co^{2+} + O_2(g) + 4H^+$$

Only a few simple cobalt(III) salts are known. The important ones are cobalt(III) fluoride, CoF_3 and cobalt(III) sulphate, $Co_2(SO_4)_3.18H_2O$. These, too, contain the complex ion $[Co(H_2O)_6]^{3+}$ and decompose in aqueous solution evolving oxygen and producing cobalt(II) ion.

The Co^{3+} ion can exist in stable state only if it is complexed. It is then not easily reduced.

Sodium hexanitritocobaltate(III) or Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$. Although cobalt(III) nitrite is not known, the complex cobaltinitrites [hexanitritocobaltates(III)] of alkali metals are readily formed. For example, when sodium nitrite (in excess) dissolved in acetic acid is added to a cobalt(II) salt, sodium cobaltinitrite is formed. First of all, the nitrite ions bring about the oxidation of cobalt(II) to cobalt(III) ions which then combine with the excess of nitrite ions to form the complex hexanitritocobaltate(III) ion.

$$Co^{2+} \longrightarrow Co^{3+} + e^-$$
$$NO_2^- + 2H^+ + e^- \longrightarrow NO + H_2O$$
$$Co^{3+} + 6NO_2^- \longrightarrow [Co(NO_2)_6]^{3-}$$

Sodium cobaltinitrite is fairly soluble in water.

Potassium hexanitritocobaltate(III) or Potassium cobaltinitrite, $K_3[Co(NO_2)_6]$. It is a yellow solid which is only sparingly soluble in water. It is used as a yellow pigment. The addition of a solution of sodium cobaltinitrite to a potassium salt, therefore, gives a yellow precipitate of potassium cobaltinitrite. This provides a test for potassium ion. Sodium cobaltinitrite, therefore, is used as a laboratory reagent for detecting and estimating potassium salts.

~~In addition to the complexes described above, Co(III) forms a large number of complexes such as~~ $K_3[Co(CN)_6]$, $K_3[Co(en)_3]$, $[Co(NH_3)_6]Cl_3$, etc. These are known to be highly stable.

Unusual Oxidation States of Cobalt. Cobalt is present in –1 oxidation state in its complexes formed by pi acid ligands. Well known examples are $K[Co(CO)_4]$ and $[Co(CO)_3NO]$. Another complex, $[Co(H)N_2(PPH_3)_3]$, which is known to have a trigonal bipyramidal geometry, also contains cobalt in –1 oxidation state. Cobalt is present in zero oxidation state in complexes such as $[Co_2(CO)_8]$, $K_4[Co(CN)_4]$ and $[Co(PMe_3)_4]$.

Biological Importance of Cobalt. Co(III) is an important constituent of vitamin B_{12}. Cobalt in traces is essential for the healthy growth of animals.

NICKEL

Occurrence. Nickel occurs even less abundantly than cobalt. It is found in nature mainly in combination with arsenic, antimony and sulphur. The chief ores of nickel are : *Pentlandite,* a copper, iron and nickel sulphide, *Garnierite*, a double silicate of nickel and magnesium, $NiMgSiO_3.H_2O$, *Kupfer nickel*, NiAs and *Nickel glance*, NiAsS. The *pentlandite* ore constitutes the principal source of nickel.

Extraction. The extraction of nickel from the sulphide ore involves the following steps :

1. Roasting. The concentrated ore is roasted in a tall furnace about 9 metres high and 6·5 metres wide. Roasting is continued for 8–10 weeks when most of the iron(II) sulphide is converted into iron(II) oxide and sulphur dioxide.

$$2FeS_2 + 5O_2 \longrightarrow 2FeO + 4SO_2$$

Copper(II) and nickel(II) sulphides present in the ore remain almost unaffected.

2. Smelting. The roasted material is mixed with coke and quartz and then smelted in a blast furnace. Most of the iron(II) sulphide, which escaped oxidation during roasting, is now converted into iron(II) oxide. Any iron(III) oxide that might have been produced during roasting is also reduced by coke to iron(II) oxide. The entire amount of iron(II) oxide is converted into iron(II) silicate slag on interaction with quartz (silica).

$$FeO + SiO_2 \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

The slag being lighter floats above the heavier impure sulphides of nickel and cobalt together with a little bit of iron. This heavier mass is known as **matte.**

3. Bessemerisation. The *matte* is heated in a Bessemer converter having a basic lining and fitted with tuyeres to admit hot air under pressure. A silicious flux is added and the hot blast of air is blown through. The remaining iron(II) sulphide is oxidised to iron(II) oxide which combines with silica to form iron(II) silicate slag and is easily skimmed off. The *bessemerised matte,* thus obtained, contains about 56 per cent of nickel, a small amount of cobalt, 25–30 per cent of copper and 0·2–0·4 per cent of iron all in the form of their sulphides.

4. Conversion of Bessemerised Matte into Pure Nickel. Pure nickel can be extracted from bessemerised nickel-copper matte by either the *Mond Precess* or the *Electrolytic Process.*

1. The Mond Process. The *matte* is first roasted in order to convert nickel(II) and copper(II) sulphides to the respective oxides. The oxide mixture is digested with dilute sulphuric acid at 80° C. Copper(II) oxide dissolves giving copper(II) sulphate,

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

while nickel(II) oxide remains as such. It is dried and introduced at the top of a **reducing tower** maintained at a temperature of 200° C. A current of water gas ($CO + H_2$) is led up the tower which reduces the oxide to the metallic state.

$$NiO + H_2 \longrightarrow Ni + H_2O$$
$$NiO + CO \longrightarrow Ni + CO_2$$

The crude nickel containing copper and iron as impurities is led into another tower called the **volatilising tower**, maintained at 50° C. A current of carbon monoxide is passed up through the tower when only nickel forms the volatile nickel carbonyl, $Ni(CO)_4$. The carbonyl vapours are then led through another tower, called a **decomposer,** filled with nickel shots and heated to 150–180° C where the carbonyl decomposes to give pure nickel (which deposits on the nickel shots) and carbon monoxide.

$$Ni(CO)_4 \longrightarrow Ni + 4CO$$

The carbon monoxide can be used again.

Nickel obtained by this process is about 98 per cent pure. It may be further **refined** electrolytically using nickel(II) ammonium sulphate as the electrolyte. Impure nickel is made the anode while pure nickel is used as the cathode.

2. The Electrolytic Process. The electrolytic process has now replaced the Mond process at a number of places, particularly in U.S.A. The *matte* is first roasted and treated with dilute sulphuric acid at 80° C to remove copper as in the Mond process. The residue consisting mostly of nickel(II) compounds is made the anode in a solution of nickel(II) ammonium sulphate. Iron plates are made the cathode. On electrolysis, pure nickel deposits on these plates.

Properties. Nickel is a greyish-white metal with a density of 8·9 g per c.c. It is hard and malleable and melts at 1453° C. It is ferromagnetic though much less than iron. It has high electrical and thermal conductivities. Both these are nearly 15% of those of silver.

Chemical Properties. 1. Action of Air and Water. In bulk state, nickel is quite resistant to attack by air or water at ordinary temperatures. This is due to the formation of a thin protective film of oxide on the surface of the metal. Nickel is particularly resistant to attack in alkaline media. In powder state, however, it is fairly reactive towards air. It may be pyrophoric under certain conditions.

It reacts with **steam** at a high temperature giving hydrogen.

$$Ni + \underset{\text{Steam}}{H_2O} \longrightarrow NiO + H_2$$

2. Oxidation. Nickel is more inert to chemical oxidation than iron and cobalt. The standard oxidation potential of the change.

$$Ni\,(s) \rightleftharpoons Ni^{2+}\,(aq) + 2e^-$$

is +0·25 volt which is lowest of all the three metals.

3. Action of Acids and Alkalies. Due to positive value (+0·25 volt) of oxidation potential, nickel is able to evolve hydrogen from dilute mineral acids. Thus,

$$Ni + 2H^+ \longrightarrow Ni^{2+} + H_2$$

When added to concentrated nitric acid, the metal becomes *passive* like iron and cobalt.

It readily dissolves in aqua regia. It resists the attack of alkalies.

4. Action of Halogens. It is attacked by halogens forming metal halides. For example,

$$Ni + Cl_2 \longrightarrow NiCl_2$$

Uses. 1. Nickel, in a finely divided state, is used as a hydrogenating catalyst for *hardening of oils*. It is also used in *electroplating*.

2. Nickel is used in making laboratory ware such as spatulas, crucibles and tongs for alkali fusion purposes since it is not attacked by fused alkalies.

3. Nickel forms a number of **useful alloys** with other metals. It imparts hardness to steel. Thus, *nickel steel*, an alloy containing 2·5–5 per cent nickel, is extremely hard, tough and yet elastic. It is also rust proof and is, therefore, used in laying underground cables, making armour plates, aeroplane and automobile parts.

Invar is another alloy of nickel and steel containing about 36 percent nickel. It has extremely low coefficient of expansion and is, therefore, used in making pendulums for clocks and other precision instruments.

Monel metal, containing about 60 per cent nickel and the rest copper is acid-proof and is used in boilers, turbine blades, propellers, etc. It has a shining surface and is, therefore, used for making decoration pieces.

Another alloy of copper and nickel, *cupronickel* (20% Ni) is used in making bullet sheaths.

German silver, an alloy of copper (60%), nickel (20%) and zinc (20%), is used for making domestic utensils.

Nichrome (Ni = 60%, Cr = 15%, Fe = 25%) is used for making electrical resistances.

Constantan (Ni = 40%, Cu = 60%) is used in electrical work.

Nickel alloys are also used for coinage purposes. One such alloy, known as *nickel coinage*, contains 25% nickel and 75% copper. *Silver coinage* contains 5% nickel.

Electronic Configuration and Oxidation States. The outer electronic configuration of Ni is $3d^8\,4s^2$. It shows oxidation states of 0, −1, +1, +2, +3 and +4. The anion $[Ni_2(CO)_6]^{2-}$ contains nickel in −1 oxidation state whereas $[Ni(CO)_4]$, $[Ni(PF_3)_4]$, $[Ni(PF_3)_2(CO)_2]$ and $K_4[Ni(CN)_4]$ contain nickel in zero oxidation state. The +1 oxidation state of nickel is very rare. Nickel in +1 state is present in $K_4[Ni_2(CN)_6]$.

The +2 state ($3d^8$) is the only stable state. A few compounds of trivalent nickel ($3d^7$) which are known, are very strong oxidising agents since nickel(III) has a strong tendency to change into nickel(II). Nickel(IV) occurs in certain oxide systems and in a few complexes.

Aqueous Chemistry of Nickel(II). In keeping with the general tendency of *decreased stability of higher oxidation states with increase in atomic number*, nickel shows stable oxidation state of +2 only. It may be noted that in the case of iron, both +2 and +3 states are stable. In the case of cobalt, both states are known but +3 state is much less stable. In aqueous solutions, Co(III) can exist only as a part of complex ions. When we come to nickel, the +3 state becomes still less stable.

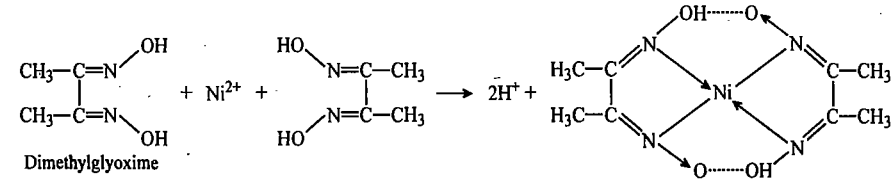
Nickel(II) ion, Ni^{2+}, is generally hydrated and exists as $[Ni(H_2O)_6]^{2+}$. It is green in colour. The salts of Ni^{2+} are green or blue.

Nickel(II) ion gets precipitated from aqueous solutions as a voluminous green gel on the addition of sodium or potassium hydroxide.

$$Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2$$

The precipitate dissolves in aqueous ammonia due to formation of the complex ion $[Ni(NH_3)_6]^{2+}$. When treated with a mild oxidising agent like bromine in an alkaline medium, a black impure oxide with composition close to $Ni_2O_3.2H_2O$ is precipitated. When treated with strong oxidising agents like chlorine, an impure oxide with composition close to NiO_2 is precipitated. Thus, it is possible to prepare oxides in which nickel is in +3 and +4 oxidation states. The oxides, however, are not pure. Nevertheless these are used as strong oxidising agents.

Ni^{2+} forms an interesting complex with dimethyl glyoxime known as *bis(dimethyl glyoxime)nickel(II)*. It is electrically neutral and is red in colour. It is quantitatively precipitated from ammoniacal solution of nickel(II) salt on the addition of dimethylglyoxime. This reaction serves as a *confirmatory test of nickel(II) in qualitative analysis and is used also in the estimation of nickel.* The formation of this neutral complex may be represented as follows :



The complex, bis(dimethylglyoximato)nickel (II) is square planar and diamagnetic. The complex ion $[Ni(CN)_4]^{2-}$ is also square planar and diamagnetic.

Apart from $[Ni(H_2O)_6]^{2+}$, some other octahedral complexes of Ni(II) are $[Ni(NH_3)_6]^{2+}$, $[Ni(NH_3)_4(H_2O)_2]^{2+}$, $[Ni(\text{ethylenediamine})_3]^{2+}$, etc. The octahedral Ni(II) complexes are generally paramagnetic.

Some paramagnetic tetrahedral Ni(II) complexes such as $[Ph_4As]_2[NiCl_4]$ are also known.

The +3 and +4 Oxidation States of Nickel. As described above, when $Ni(OH)_2$ is oxidised with Br_2 in alkaline medium, $Ni_2O_3.2H_2O$ is precipitated which contains nickel in +3 oxidation state. A number of complexes of Ni(III) are known. Well known examples are $[Ni(en)_2Cl_2]Cl$ and $[Ni(PEt_3)_2Br_2]Br$. While the

former complex is octahedral, the latter is trigonal bipyramidal.

Compounds containing Ni(IV) are very rare. One such compound is $K_2[NiF_6]$ which is prepared by reacting a mixture of $NiCl_2$ and KCl with fluorine. The complex is strongly oxidising and liberates oxygen from water.

COPPER

Occurrence. Native copper which is 99·9 per cent pure, is found in large quantities in Michigan state (U.S.A.). In combined state, it occurs as *copper glance* (Cu_2S), *copper pyrites* ($CuFeS_2$), *cuprite* (Cu_2O) and *malachite* [$Cu(OH)_2.CuCO_3$].

Extraction. Copper is extracted mostly from copper pyrites. The concentrated ore is *roasted* in a current of air in a reverberatory furnace when a part of the sulphur is removed as sulphur dioxide and impurities of arsenic and antimony are removed as volatile oxides. A mixture chiefly consisting of copper(I) and iron(II) sulphides is left behind.

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

The roasted ore is then mixed with some coke and sand and heated strongly, that is, *smelted*, in a blast furnace. Most of the iron sulphide is converted into the oxide which is removed as a slag.

$$2FeS + 3O_2 \longrightarrow 2FeO + SO_2$$
$$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

The molten mixture of Cu_2S and the remaining FeS obtained above is transferred to a *Bessemer converter* and a blast of air mixed with sand is blown through the molten mass. The following reactions take place :

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \longrightarrow FeSiO_3$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

The molten copper thus obtained is cast into ingots. It is about 99 per cent pure copper. If need be, it is refined by the usual electrolytic method.

Uses. World production of copper is of the order of 3 million tons per year. Except for iron and aluminium, it is probably the most importasnt technical metal. It finds application in many ways.

1. The chief use lies in its high electrical conductivity. Enormous quantities of copper are used for making electric cables and other electric goods.
2. As it is not attacked by water or air, it is used in making utensils, containers, kettles, evaporating pans, coins, etc.
3. It is used for making a large number of **alloys** like *brass, bronze, bell metal,* etc. It is also used for alloying with gold and silver to make them hard for the purpose of making *ornaments* and *coins.*
4. It is also used in electroplating and electotyping, etc.

Alloys of Copper. Copper forms a number of alloys with other metals like zinc, tin, nickel, aluminium, etc. Some of the most important alloys of copper are given in Table 5.

TABLE 5
Important Alloys of Copper

Alloys	Composition	Uses
Brass	Cu 80% Zn 20%	Wires, parts of machinery, utensils
Bronze	Cu 80% Zn 10% Sn10%	Statues, coins, cooking utensils
Gun metal	Cu 90% Sn 10%	Gun barrels
Bell metal	Cu 80% Sn 20%	Bells, gongs.
German silver	Cu 60% Zn 20% Ni 20%	Silverware, plating.

Physical Properties. Copper is a reddish brown metal which melts at 1083°C. It is malleable and ductile and can be drawn into wires of as small a diameter as 0·03 mm. It is an excellent conductor of heat and electricity, the best conductor next to silver. The presence of other metals even in small quantities lowers the conductivity appreciably. Thus the presence of even 0·03 per cent of arsenic lowers the conductivity by about 15 per cent.

Chemical Properties. Copper, being weakly electropositive, is not very reactive. It resists the action of most of the common chemical reagents like air, water, non-oxidising acids and alkalies. Its important chemical reactions are detailed below.

1. Action with Air or Oxygen. It is not attacked by dry air at ordinary temperatures. But when heated to redness in air or oxygen, it first forms copper(I) oxide, Cu_2O and finally copper(II) oxide, CuO. If the temperature is too high, copper(II) oxide changes back to copper(I) oxide, Cu_2O.

$$CuO + Cu \longrightarrow Cu_2O$$

In the presence of atmospheric carbon dioxide and moisture it is covered with a green layer of basic carbonate, $CuCO_3.Cu(OH)_2$. This layer protects the rest of the metal from further action.

2. Action with Water. Copper does not decompose water or steam at normal tempertatures. However, at white heat, steam acts upon it to give the oxide.

3. Action with Acids. Non-oxidizing acids (*e.g.*, hydrochloric acid and dilute sulphuric acid) are without any effect in the absence of air or oxygen. In the presence of air, these acids dissolve the metal forming the corresponding salt and water.

$$Cu + 2HCl + \tfrac{1}{2}O_2\,(air) \longrightarrow CuCl_2 + H_2O$$
$$Cu + H_2SO_4 + \tfrac{1}{2}O_2\,(air) \longrightarrow CuSO_4 + H_2O$$

Acids possessing oxidizing properties (*e.g.*, nitric acid and concentrated (H_2SO_4) readily attack copper, yielding in each case the copper (II) salts, water and a reduction product of the acid.

$$Cu + 2H_2SO_4\,(conc.) \longrightarrow CuSO_4 + 2H_2O + SO_2$$
$$3Cu + 8HNO_3\,(dilute) \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$Cu + 4HNO_3\,(conc.) \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

4. Action with Non metals. Copper combines with chlorine and other halogens to form halides.

$$Cu + Cl_2 \longrightarrow CuCl_2$$

It combines with sulphur when heated giving a non-stoichiometric compound of the composition $Cu_{1.87}S$.

5. Action with Aqueous Ammonia. Copper is dissolved by aqueous ammonia in the presence of air or oxygen, owing to formation of the complex ion, $[Cu(NH_3)_4]^{2+}$.

$$2Cu + 2H_2O + O_2 + 8NH_3 \longrightarrow 2[Cu(NH_3)_4]^{2+} + 4OH^-$$

6. Action with Cyanides. Copper also dissolves in aqueous solution of potassium cyanide yielding the complex, $[Cu(CN)_4]^{2-}$

7. Displacement of Silver and other less Electropositive Metals. Copper displaces silver and mercury from solutions of their salts.

$$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$$

or

$$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

Electronic Configuration and Oxidation States. The outer electronic configuration of copper is $3d^{10}\,4s^1$. It shows oxidation states of +1 ($3d^{10}$) and +2 ($3d^9$) in its compounds, known commonly as *cuprous* and *cupric* compounds. The +1 oxidation state is not stable. It undergoes almost complete disproportionation as

$$2Cu^+ \rightleftharpoons Cu^{2+} + Cu$$

The +2 oxidation state, therefore, is much more stable. The +1 oxidation state is stable only in insoluble and complex compounds.

Aqueous Chemistry of Copper(I). Copper(I) ion, Cu^+, has the electronic structure $3d^{10}$. All the *d* orbitals are completely filled and the electrons are fully paired. The copper(I) compounds are, therefore, diamagnetic. Copper(I) ion in solution changes readily to copper(II) ion. Actually it is a case of disproportionation.

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$$

The oxidation potentials for the half-cell reactions involved are given below:

(*i*) $Cu(s) \longrightarrow Cu^+ + e^-$; $E^\circ = -0{\cdot}52$ volt

(*ii*) $Cu^+ \longrightarrow Cu^{2+} + e^-$; $E^\circ = -0{\cdot}18$ volt

Evidently, the reaction (*ii*) has a greater tendency to occur. Hence, even if some Cu^+ ions are produced by reaction (*i*), these are consumed in reaction (*ii*).

This also explains the fact that when the insoluble copper(I) oxide, Cu_2O, is dissolved in dilute sulphuric acid, the product is copper(II) sulphate and *not* copper (I) sulphate.

$$Cu_2O(s) + 2H^+ \longrightarrow Cu^{2+} + Cu(s) + H_2O$$

This is again a case of disproportionation ; copper(I) ion disproportionates into copper(II) ion and copper as soon as produced. The above reaction is considered to take place in two steps.

$$Cu_2O(s) + 2H^+ \longrightarrow 2Cu^+ + H_2O$$
$$2Cu^+ \longrightarrow Cu^{2+} + Cu(s)$$

The Cu^+ ion can be stabilised by formation of insoluble substances or complex ions. For example, copper(I) ion can form the insoluble copper (I) chloride when brought in contact with chloride ions.

$$2Cu^+ + 2Cl^- \longrightarrow 2CuCl(s)$$

The solubility product of CuCl is sufficiently low ($K_{sp} = 3{\cdot}2\times10^{-7}$) and, therefore, there can only be traces of copper (I) ions in solution.

The precipitated copper(I) chloride dissolves in excess of chloride ions yielding the complex ion $[CuCl_2]^-$.

$$\underset{\text{(Ppt.)}}{CuCl} + Cl^- \longrightarrow \underset{\text{(Soluble)}}{[CuCl_2]^-}$$

Cuprous chloride also dissolves in aqueous ammonia. The ammoniacal solution can readily absorb carbon monoxide.

$$CuCl + CO \longrightarrow Cu(CO)Cl.$$

The ammoniacal solution of cuprous chloride is thus used for eliminating traces of CO from gases.

The insoluble copper(I) salts can also be prepared by the reduction of copper (II) salts by iodide ions.

$$2Cu^{2+} + 4I^- \longrightarrow \underset{\text{(Insoluble)}}{2CuI} + I_2$$

Thus, when potassium iodide is added to a solution of copper sulphate, a precipitate of copper(I) iodide mixed with free iodine is obtained. The reaction involves two steps : Iodide ion first reduces copper(II) to copper(I) state.

$$2Cu^{2+} + 2I^- \longrightarrow 2Cu^+ + I_2$$

This is followed by the precipitation of copper (I) iodide.

$$2Cu^+ + 2I^- \longrightarrow \underset{\text{(Ppt.)}}{2CuI}$$

This reaction is used for *estimating copper* volumetrically. All that is to be done is to estimate molecular iodine formed in the process by titrating against sodium thiosulphate.

It may be noted that chloride ion cannot bring about this reaction since it is not a reducing agent.

Cyanide ions also act as reducing agents like iodide ions but they also act, in addition, as complexing agents. Thus, when potassium cyanide is added to a solution of copper(II) sulphate, first the insoluble copper(I) cyanide is obtained which dissolves in excess of potassium cyanide to give the complex compound potassium tetracyanocuperate (I), $K_3[Cu(CN)_4]$.

$$2Cu^{2+} + 2CN^- \longrightarrow 2Cu^+ + C_2N_2$$
$$2Cu^+ + 2CN^- \longrightarrow \underset{\text{(Ppt).}}{2CuCN}$$
$$CuCN + 3CN^- \longrightarrow \underset{\text{(Soluble)}}{[Cu(CN)_4]^{3-}}$$

Aqueous Chemistry of Copper(II). The aqueous chemistry of copper in +2 oxidation state is similar to that of +2 ions of other transition elements. Although most of the *anhydrous* copper(II) salts are colourless, they are blue when hydrated. This is due to the presence of the hydrated ion $[Cu(H_2O)_4]^{2+}$ which is *blue*. Solutions of copper(II) salts are acidic due to hydrolysis.

$$Cu^{2+} + H_2O \rightleftharpoons [Cu(OH)]^+ + H^+$$

The degree of hydrolysis, however, is quite small.

The outer electronic configuration of copper(II) is $3d^9$. It has thus an unpaired electron. The copper(II) compounds are, therefore, paramagnetic. They are blue or green in colour.

When a base is added to a solution containing Cu^{2+} ions, copper(II) hydroxide, a light blue precipitate, is obtained.

$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$$

If some aqueous ammonia is added, copper(II) hydroxide dissolves giving an intense blue solution due to formation of a complex.

$$Cu(OH)_2(s) + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$$

The copper-ammonia complex decomposes on the addition of acids.

$$[Cu(NH_3)_4]^{2+} + 4H^+ \longrightarrow Cu^{2+} + 4NH_4^+$$

The complex also decomposes on heating to liberate ammonia gas.

$$[Cu(NH_3)_4]^{2+} \longrightarrow Cu^{2+} + 4NH_3$$

Copper(II) hydroxide, $Cu(OH)_2$, is basic in character and dissolves in acids to give copper(II) salts. Copper(II) oxide which is black in colour is also basic in character.

An interesting compound of copper(II) is $Cu(CH_3COO)_2.H_2O$. The bonding between Cu^{2+} ion and CH_3COO^- ion is partly covalent. The compound is actually dimeric in which each Cu^{2+} is present in octahedral environment. The structure of the compound is similar to that of chromium(II) acetate discussed earlier.

Compounds of Copper(III). Although +3 oxidation state of copper is quite uncommon, yet some compounds such as $KCuO_2$, $K_3[CuF_6]$, etc., are known in which copper is present in +3 oxidation state.

Biological Importance of Copper. Copper is an essential constituent of many metallo proteins and enzymes. The copper-containing enzymes play an important role in the pigmentation of skin, functioning of brain and in iron metabolism in the human body. The deficiency of copper in the human system results in inability to utilise the iron stored in the liver. The approximate quantity of iron in human body is around 100 mg.

The excess of copper in human body is, however, harmful. A disease, known as Wilson disease, upsets the copper metabolism of the human system in such a way that it gets deposited in excess in the liver, kidneys and brain. The patient suffering from such a disease is treated with controlled does of EDTA which forms a water-soluble complex with Cu^{2+} ion and gets excreted through urine.

Haemocyanin is a copper-containing protein which is present in the blood of snails, lobsters, etc., and acts as oxygen-carrier.

Plastocyanin, containing copper, is present in chloroplasts of green plants and plays an important role in the process of photosynthesis as an electron carrier.

A copper-containing protein, azurin, is found in certain bacteria.

ZINC

Occurrence. Zinc occurs mainly in combined state, the most important ore being *zinc blende*, ZnS. The other ores are *calamine*, $ZnCO_3$, *zincite*, ZnO and *silicious zinc*, $Zn_2SiO_4.H_2O$.

Extraction. Zinc blende (ZnS) and calamine ($ZnCO_3$) are the only ores of commercial interest.

1. Roasting. The concentrated ore is roasted in a current of air in a rotary shaft furnace at 900° C to convert the sulphide into the oxide.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

High temperature calcination of zinc blende is necessary to decompose any zinc sulphate which may be formed during roasting.

$$2ZnSO_4 \longrightarrow 2ZnO + 2SO_2 + O_2$$

Roasting in the case of calamine is not necessary. Simple heating converts the ore into ZnO and eliminates moisture.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

2. Reduction. The oxide obtained above is mixed with crushed coke and heated to 1400–1450° C in fire-clay retorts when the oxide is reduced to the metal.

$$ZnO + C \longrightarrow Zn + CO$$

$$ZnO + CO \longrightarrow Zn + CO_2$$

Zinc being volatile distils over and is condensed.

3. Refining. Zinc obtained in the above process is usually contaminated with cadmium which occurs along with it in its ores. Advantage is taken of the fact that cadmium is more volatile (b.p.775° C) than zinc (b.p. 906° C). Pure zinc, therefore, can be obtained by fractional distillation.

The metal can also be refined by electrolysis. In electrolytic refining, impure zinc is made the anode and pure zinc plates are made the cathode in an electrolytic cell. Zinc sulphate solution mixed with a little sulphuric acid is used as the electrolyte. When electric current is passed, pure zinc is deposited on the cathode.

Electrolytic Process for the Extraction of Zinc. Zinc can also be extracted from its ores by an electerolytic process. The ore is first crushed and concentrated in the usual manner and then roasted at moderate temperature. Zinc sulphide gets oxidised mainly to zinc sulphate and to some extent to zinc oxide as well. The roasted ore is leached with dilute sulphuric acid so as to change zinc oxide also to zinc sulphate.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

The solution obtained is treated with milk of lime when salts of iron, aluminium, arsenic and antimony present as impurity get precipitated. The purified zinc sulphate solution is electrolysed using high current density employing thin sheets of pure aluminium as the cathode. As zinc melts at lower temperature (421° C) than aluminium (660° C), it can be scrapped off from aluminium sheets on heating.

Elecrolytic method has a number of advantages. It can be applied to ores with low zinc content and gives the metal of a high degree of purity e en to the extent of 99·9 per cent. It also permits the recovery of other useful metals often present in zinc o

Physical Properties. Pure and polished zinc has a bluish white metallic lustre but it soon gets tarnished in moist air due to the formation of basic carbonate. It melts at 421° C. At ordinary temperatures

it is brittle. On heating at about 155° C it becomes malleable and ductile. At 220° C the metal becomes brittle and can be easily powdered. The change is due to the formation of different allotropic forms, the exact transition temperatures of which are not exactly known.

Chemical Properties. 1. Action of Air. When heated in air to about 500°C, it burns to form a white cloud of zinc oxide which settles to form a woolly flock generally called 'philosophers wool'.

$$2Zn + O_2 \longrightarrow 2ZnO$$

2. Action of Water. Pure zinc does not react with water but impure zinc decomposes steam quite readily with the evolution of hydrogen.

$$Zn + H_2O \longrightarrow ZnO + H_2$$

It forms basic carbonate in moist air which dulls its lustre and forms a bluish grey film on its surface.

$$4Zn + 3H_2O + 2O_2 + CO_2 \longrightarrow ZnCO_3.3Zn(OH)_2$$

3. Action of Mineral Acids. Pure zinc does not react with dilute mineral acids but impure metal reacts differently with different acids. The non-reactivity of pure zinc is due to the very large overvoltage of hydrogen at the zinc surface. But when mixed or connected with metals like copper, silver and platinum, on the surface of which hydrogen gas has a low overvoltage, zinc reacts readily evolving hydrogen on the surface of the other metal, with the simultaneous dissolution of zinc.

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

The amalgamation of impure zinc stops such reactions as it gives uniformity to the surface.

If pure zinc is coated with copper, over which hydrogen has very low overvoltage, it reacts readily with dilute acids evolving hydrogen. *Zinc-copper couple* is , therefore, used as a reducing agent in a number of organic reactions.

The reaction with sulphuric acid depends upon the concentration of the acid and the temperature of the reaction. If the acid is dilute and cold, zinc sulphate and hydrogen are formed.

Concentrated sulphuric acid when heated with zinc gives sulphur dioxide.

The reaction with nitric acid is also complicated. If the acid is very dilute, ammonium nitrate results.

$$Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

If the acid is moderately strong, nitric oxide is formed.

$$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 4H_2O + 2NO$$

If the acid is concentrated and hot, nitrogen dioxide is the chief product.

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

4. Action of Alkalies. It reacts with moderately strong alkalies on heating and forms soluble zincates.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

5. Action with Alkyl Halides. Zinc, like magnesium, forms addition compounds with alkyl halides.

$$Zn + C_2H_5I \longrightarrow ZnC_2H_5I$$

The compound decomposes on heating.

$$2ZnC_2H_5I \longrightarrow \underset{\text{Zinc diethyl}}{Zn(C_2H_5)_2} + ZnI_2$$

Uses of Zinc. 1. Zinc is used in the preparation of alloys such as *brass, delta metal* and *German silver*. 2. On account of its resistance to rusting and corrosion, zinc is used to coat iron. This is done by dipping the clean metal in molten zinc or by spraying molten zinc on the iron sheets. This process is known as **galvanizing**. An alternate method is to heat the iron articles with zinc dust. The process is known as **sherardising**. The galvanised iron sheets are used for roofs, gutters, etc. 3. Amalgamated zinc

rods are used as electrodes in Leclanche and Daniell cells. 4. Zinc dust is used as a reducing agent in the laboratory as well as in commerce in the manufacture of drugs, dyestuffs and chemicals. 5. Zinc is used in the Parke's process for the extraction of silver from lead. 6. Zinc dust is used as a precipitating agent in the cyanide process for precipitating gold and silver. 7. Zinc oxide (*white zinc*) is used in paints. It is superior to white lead as it does not blacken. Lithopone, a mixture of zinc sulphide and barium sulphate, is superior to both on account of greater covering power. Zinc chromate is used as a yellow pigment.

Aqueous Chemistry of Zn(II). Zinc shows +2 oxidation state in all its compounds.

Zinc ion is colourless. It undergoes slight hydrolysis in water giving acidic solution.

$$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$$

The degree of hydrolysis is very small, even smallar than that of Cu^{2+} ion. Thus, a solution of Zn^{2+} ions is much less acidic than that of Cu^{2+} ions of the same concentration.

When a base is added to a solution of Zn^{2+} ions, a precipitate of zinc hydroxide is obtained.

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$

Zinc hydroxide is amphoteric. It dissolves in dilute acids forming salts.

$$Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$$

It dissolves in alkalies forming the complex ion, $[Zn(OH)_4]^{2-}$.

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2[Zn(OH)_4]$$

The formation of the complex ions from zinc in alkaline solutions may be represented by the following reaction :

$$Zn(s) + 4OH^- \longrightarrow [Zn(OH)_4]^{2-} + 2e^-$$

The oxidation potential for this half reaction is 1·22 volts, while that in acid solution it is only 0·76 volt. This shows that zinc metal acts as a stronger reducing agent in alkaline solution than in acid solution.

As already mentioned, Zn^{2+} ion forms a number of complexes, like ions of other transition elements.

Zn^{2+} ion is hydrated in solution, yielding the complex ion $[Zn(H_2O)_4]^{2+}$. Thus, a solution of zinc chloride in water may be written as $[Zn(H_2O)_4]Cl_2$.

A precipitate of zinc hydroxide dissolves in ammonia due to formation of the complex ion $[Zn(NH_3)_4]^{2+}$.

$$Zn(OH)_2 + 4NH_3 \longrightarrow [Zn(NH_3)_4](OH)_2.$$

Zinc hydroxide also dissolves in cyanide solution giving the complex $[Zn(CN)_4]^{2-}$.

$$Zn(OH)_2 + 4KCN \longrightarrow K_2[Zn(CN)_4] + 2KOH$$

The tetracyano complex is more stable than the tetraammine complex. This is shown by the values of the equilibrium constants of the decomposition reactions of these complexes.

$$[Zn(CN)_4]^{2-} \rightleftharpoons Zn^{2+} + 4CN^-; \qquad K = 1{\cdot}2 \times 10^{-18}$$

$$[Zn(NH_3)_4]^{2+} \rightleftharpoons Zn^{2+} + 4NH_3; \qquad K = 3{\cdot}4 \times 10^{-10}$$

All the above complexes have *tetrahedral* structure.

The complex ion $[Zn(NH_3)_6]^{2+}$ is known in crystals only. It has *octahedral* structure.

Biological Importance of Zinc. Zinc is very important for proper functioning of the enzyme system of animals. Human body contains about 2g of zinc which is next only to iron (about 4 g). There are more than twenty zinc-containing enzymes in the body which are responsible for proper absorption of CO_2 by red blood cells in muscles and other tissues and for maintaining proper *p*H in the muscles and tissues.

Some of the zinc-containing enzymes play an important role in the digestion of proteins by animals. Besides this, zinc enzymes are also involved in the energy release processes, sugar metabolism and metabolism of alcohol in the human body.

QUESTIONS

1. Name the elements included in the First Transition Series. Give their electronic configurations. Why do these elements exhibit predominantly an oxidation state of +2 ?
2. How does scandium occur in nature ? How is it extracted from its ores ? Discuss its general chemical behaviour. Why does this element exhibit a stable oxidation state of +3 only ?
3. (*a*) How does titanium occur in nature ? How is it extracted from its ores ? Discuss its general chemical behaviour.
   (*b*) How would you account for +2, +3 and +4 oxidation states of titanium ? Which of these states is most stable and why ?
   (*c*) Account for the industrial importance of titanium.
4. (*a*) How is $TiCl_4$ prepared ? Give its important properties and uses.
   (*b*) List some important resemblances of titanium and tin of Group IV.
5. (*a*) What are the important ores of vanadium ? How is vanadium extracted (*i*) in pure form (*ii*) in the form of ferro-vanadium alloy ?
   (*b*) What are the various oxidation states of vanadium ? How would you account for them ?
   (*c*) How does vanadium react with strong oxidising acids, molten alkalies and non-metals at elevated temperatures ?
6. Discuss the general chemical behaviour of vanadium.
   Give the preparation, properties and uses of vanadium pentoxide, vanadyl chloride, and vanadium trichloride.
7. Describe the extraction of chromium from one of its important ores. Describe its properties and uses.
8. Name the important oxidation states of chromium. Discuss the aqueous chemistry of chromium in the various oxidation states. Give the structures of the complexes formed by Cr^{2+} ion.
9. (*a*) How is manganese extracted from its ores ?
   (*b*) Discuss the aqueous chemistry of manganese in different oxidation states.
   (*c*) Desribe the preparation of potassium permanganate from pyrolusite. When reduced in alkaline solution, it yields, either a colourless solution or a dark brown precipitate or a green solution. Explain these results.
10. (*a*) What is the difference between cast iron, wrought iron and steel ? Describe the important properties of iron.
    (*b*) Explain the rusting of iron. How may rust proofing be accomplished ?
    (*c*) Name the important oxidation states of iron. Why is Fe(III) more stable than Co(III) and Ni(III) ?
11. (*a*) Give an account of the aqueous chemistry of iron in different oxidation states. Why are compounds of Fe(III) so deeply coloured ?
    (*b*) Give an account of the complexes formed by Fe^{2+} and Fe^{3+} ions. Discuss their structures.
12. Give an account of the metallurgy of either cobalt or nickel together with methods of preparation of the important compounds of the metal selected.
13. (*a*) Describe Mond's process for extracting nickel. Discuss the various uses of the metal.
    (*b*) Name the important oxidation states of nickel. Discuss the aqueous chemistry of nickel in various oxidation states.
14. (*a*) Give an account of the metallurgy of copper.
    (*b*) Discuss the chemistry of copper in +1 and +2 oxidation states.
    (*c*) Iodine is liberated when KI is added to a solution of Cu^{2+} ions but chlorine is not liberated when KCl is added. How would you explain this ?
15. (*a*) How is zinc extracted from its ores ? Discuss its important properties and uses. Why does zinc show only +2 oxidation state ?
    (*b*) Discuss briefly the aqueous chemistry of zinc(II). ~~Describe the important complexes of Zn^{2+} ion.~~

23 THE ELEMENTS OF THE SECOND TRANSITION SERIES

The Second transition series comprises of ten elements, namely, **yttrium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver** and **cadmium.** The general characteristics of these elements have already been discussed in Chapter 21. Some of the important physical constants of these elements are given in Table 1. The aim of the present chapter is to discuss the chemistry of the individual members of the series in some details.

YTTRIUM

Extraction. Yttrium occurs in the lanthanide minerals and can be extracted by digesting the mineral with an acid or an alkali. The salts thus obtained are then subjected to ion-exchange treatment, selective complexation and solvent extraction. This results in the separation of the various salts of lanthanum, yttrium and other lanthanides. The yttrium salt, YF_3, thus separated, is then reduced with Ca metal to get yttrium metal.

Properties. Yttrium is a silvery-white metal. Some of its properties are listed in Table 1.

COMPOUNDS OF YTTRIUM

Oxides and Hydroxides. Yttrium forms the oxide Y_2O_3. $Y(OH)_3$ is obtained as gelatinous precipitate when alkali is added to an aqueous solution of Y^{3+} salt. $Y(OH)_3$ is basic in character.

Halides. With the exception of YF_3, all halides are soluble in water. These are prepared by heating the metal with the halogens.

Hydrides. Yttrium forms a non-stoichiometric hydride with the formula approaching YH_3.

Complexes. Yttrium forms a number of complexes with EDTA, acac, NCS^- with formulae, [Y(EDTA)], $[Y(acac)_3.H_2O]$, $[Y(NCS)_6]^{3-}$, respectively. Complexes of Y^{3+} with coordination numbers 8 and 10 are also known.

Organometallic Compounds. Yttrium forms $Y(C_5H_5)_3$ when YCl_3 reacts with NaC_5H_5. The bonding in $Y(C_5H_5)_3$ is predominately ionic. The compound $Y(CH_2C(CH_3)_3)_3$ has also been isolated.

ZIRCONIUM

Extraction. The important minerals containing zirconium are *baddeleyite*, containing ZrO_2 and *zircon*, $ZrSiO_4$. The ores are treated with carbon and chlorine at red heat to get crude $ZrCl_4$. This compound, after purification, is reduced with magnesium to yield zirconium.

Properties and Uses. Zirconium is much more soft than titanium, its analogue of the First transition series. It resembles titanium in most of its properties including its passivity and resistance to corrosion. It resembles stainless steel in appearance. Like titanium, it forms interstitial borides, carbides, nitrides, etc. Due to increased atomic size, its oxides are more basic. Like titanium, this metal is also resistant to the action of acids. It dissolves in HF, however, resulting in formation of anionic fluoro complexes. Its important difference from titanium is that its lower oxidation states +3 and +2 are not so stable and important. The most important and stable oxidation state, as in Ti, is +4.

The property of zirconium to react with oxygen and nitrogen is made use of in removing traces of these gases from thermionic valves. It is also used in making bullet-proof alloy steels.

TABLE 1

Important Physical Constants of Elements of the Second Transition Series

Elements and their atomic numbers	Outer electronic configuration	Atomic mass (a.m.u.)	Atomic volume (ml)	Density (g ml^{-1})	Melting point (°C)	Boiling point (°C)	Atomic radius (Å)	Stable oxidation state	Ionic radius (Å) for stable oxid. state	First ionization energy (kJ mol^{-1})	Heat of fusion (kJ mol^{-1})	Heat of vaporisation (kJ mol^{-1})
Y (39)	$4d^1\,5s^2$	88·90	19·8	4·47	1509	2927	1·80	+3	0·93	635·9	11·3	389·1
Zr (40)	$4d^2\,5s^2$	91·22	14·1	6·49	1852	3580	1·58	+4	0·80	669·4	16·7	502·0
Nb (41)	$4d^4\,5s^1$	92·91	10·8	8·40	2415	3300	1·46	+5	0·70	652·7	26·7	—
Mo (42)	$4d^5\,5s^1$	95·94	9·4	10·21	2610	5560	1·39	+6	0·62	694·5	27·6	535·5
Tc (43)	$4d^5\,5s^2$	(99)	—	11·50	2200	—	1·36	+4	—	698·7	23·0	502·5
Ru (44)	$4d^7\,5s^1$	101·70	8·3	12·20	2500	4900	1·34	+3	0·69	723·8	25·5	602·6
Rh (45)	$4d^8\,5s^1$	102·90	8·3	12·40	1966	4500	1·34	+3	0·86	744·7	21·7	577·4
Pd (46)	$4d^{10}\,5s^0$	106·40	8·9	12·00	1552	3980	1·37	+2	0·50	803·3	16·7	380·7
Ag (47)	$4d^{10}\,5s^1$	07·87	10·3	10·51	960·8	2210	1·44	+1	1·26	732·2	11·3	286·2
Cd (48)	$4d^{10}\,5s^2$	200·57	13·1	8·65	320·9	765	1·54	+2	0·97	866·1	6·1	99·9

COMPOUNDS OF ZIRCONIUM

Oxides and Hydroxides. Hydrous oxide, $ZrO_2.nH_2O$ is obtained as a gelatinous precipitate on adding an alkali to zirconium (IV) solutions. On strong heating, the hydrous oxide gives ZrO_2. The hydrous oxide is also obtained by vapour phase oxidation of $ZrCl_4$. This is done by passing the vapour of $ZrCl_4$ mixed with air through a special flame produced by burning a hydrocarbon in excess of oxygen.

It is a hard and white pigment like TiO_2 and is used as such. It is insoluble in water. It has an extremely high melting point, *viz.*, 2700° C. It resists attack by both acids and alkalies. It has good mechanical properties and is used in making crucibles and furnaces. ZrO_2 is more basic than TiO_2.

Halides. $ZrCl_4$ is made in the same way as $TiCl_4$, *i.e.*, by passing chlorine over the dioxide heated with carbon.

It gets easily hydrolysed yielding oxochloride.

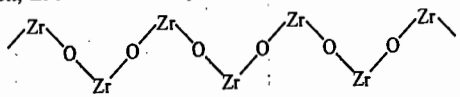
$$ZrCl_4 + H_2O \longrightarrow ZrOCl_2 + 2HCl$$

The oxochloride crystallises from the solution as the octahydrate, $ZrOCl_2.8H_2O$. $ZnCl_4$ resembles $TiCl_4$ in most of its properties.

$ZrBr_4$ and **ZrI_4** are also known. These are made by direct combination of the elements and are similar in properties to $ZrCl_4$. $ZrBr_4$ is yellow while ZrI_4 is red-brown in colour. ZrF_4 is also known as a white crystalline solid.

The trihalides **ZrX_3** are known but these are not stable. These are oxidised by water to +4 oxidation state.

Zr(IV) in Aqueous Solutions. The zirconyl ion, ZrO^{2+} exists in aqueous solutions alongwith the usual anions such as NO_3^-, SO_4^{2-}, etc. The compounds of ZrO^{2+} can be easily isolated from its aqueous solutions. $ZrO(NO_3)_2$ in solid state contains an oxygen-bridged chain, as shown.



Zriconyl nitrate solution is used for the removal of phosphate ions in qualitative analysis.

Complexes of Zirconium. Apart from the complex ions $[ZrX_6]^{2-}$ (X = halogen), some 7-coordinated complex ions of Zr are also known. Well known example is $[ZrF_7]^{3-}$.

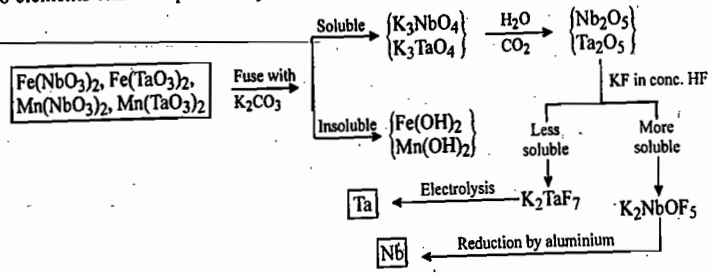
While Na_3ZrF_7 is pentagonal bipyramidal in structure, $(NH_4)_3ZrF_7$ has capped trigonal prismatic structure. In $Na_4[ZrF_8]$ and $[Cu(H_2O)_6][ZrF_8]$, the coordination number of Zr is 8. However, the structures of the two complexes are different. Thus, while the former complex has bi disphenoid structure, the latter has square antiprismatic structure.

NIOBIUM AND TANTALUM

Since niobium of Second transition series and tantalum of Third transition series occur together and have similar properties, it is convenient to discuss them together.

Occurrence. Both the elements are relatively rare and constitute nearly 3×10^{-5} percent of the earth's crust. Their important minerals are mixed niobate and tantalate of iron and manganese : $Fe(NbO_3)_2.Fe(TaO_3)_2$ and $Mn(NbO_3)_2.Mn(TaO_3)_2$. If the mineral contains more of niobium than of tantalum, it is called *columbite*. If it contains more of tantalum than of niobium, the mineral is called *tantalite*.

The two elements can be separated by the scheme shown below :



Properties and Uses. Both the metals are resistant to corrosion. Tantalum is more resistant than niobium. It is used, therefore, in chemical research as well as in construction of manufacturing plants. It is also used in making instruments. Niobium is used chiefly to prevent intergranular corrosion in special steels. Its carbide is used in making hard carbide tools.

They resist the attack by air, water, alkalies or hydrochloric acid. However, they dissolve in hot concentrated sulphuric acid as well as in aqua regia. They also dissolve in fused alkalies giving niobates and tantalates and evolving hydrogen. They also combine with non-metals, such as oxygen, nitrogen, halogens, etc., producing the oxides, nitrides and halides. The nitrides, NbN and TaN react with steam at high temperatures to yield the oxides, evolving ammonia.

The higher nitride, Ta_2N_5, is also formed but it is not stable.

The sulphides, NbS_2 and TaS_2 are also known. NbS_2 is formed by direct combination of the elements. TaS_2 is obtained by the reduction of Ta_2O_5 with CS_2 at high temperature.

COMPOUNDS OF NIOBIUM AND TANTALUM

Niobium and Tantalum, like vanadium, show oxidation states of +5, +4, +3 and +2 in their various compounds. The most stable oxidation state, however, is +5.

Compounds with +5 Oxidation State. 1. Oxides. Nb_2O_5 and Ta_2O_5 are prepared by the same methods as used in preparing V_2O_5. The hydrous pentoxides are also obtained as gelatinous precipitates on treating their pentahalides with water.

Both the compounds are inert and can be brought into solution only on treating them with hydrofluoric acid or by fusing them with sodium carbonate or sodium hydroxide.

$$Nb_2O_5 + 3Na_2CO_3 \longrightarrow 2Na_3NbO_4 + 3CO_2$$

Tantalum pentoxide reacts in the same manner but slowly.

Both the pentoxides are more stable than V_2O_5. Consequently, it is more difficult to reduce them to the lower oxides.

2. Halides. The pentafluorides are prepared by heating the metals, the pentoxides or pentachlorides in fluorine. They are white, volatile solids.

The other pentahalides are yellow to brown or purple-red solids. These are obtained by direct combination of the elements as well as by heating the pentoxides with carbon and the halogen concerned.

$$2Ta + 5I_2 \longrightarrow 2TaI_5$$

$$Nb_2O_5 + 5C + 5Cl_2 \longrightarrow 2NbCl_5 + 5CO$$

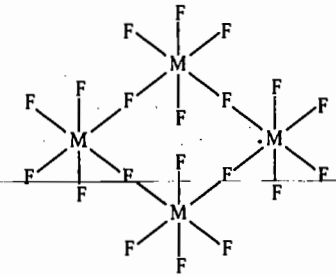
All the pentahalides can be sublimed in the atmosphere of the corresponding halogen without decomposition. In the vapour state, they are monomeric.

These halides are soluble in organic liquids including carbon tetrachloride and ether. These are readily hydrolysed by water to yield hydrous pentoxides and hydrohalic acids.

$$2TaCl_5 + 5H_2O \longrightarrow Ta_2O_5 + 10HCl$$

The chlorides act as Friedel-Craft catalysts.

Both NbF_5 and TaF_5 have cyclic tetrameric structures, as shown.



M = Nb or Ta

NbF_5 and TaF_5 react with $F^-(aq)$ to give $[MF_6]^-$ and $[MF_7]^{2-}$ (M is Nb or Ta). With very high concentration of F^- ions in aqueous solutions, TaF_5 forms $[TaF_8]^{3-}$ and NbF_5 forms $[NbOF_6]^{3-}$.

3. Oxohalides. The oxohalides of niobium are : $NbOCl_3$, $NbOBr_3$, $NbOI_3$ and NbO_2I. The oxohalides of tantalum are : $TaOCl_3$ and $TaOBr_3$. These are volatile solids though not so volatile as the corresponding pentahalides. The oxochlorides are white while the oxobromides are yellow.

The oxohalides can be prepared by the oxidation of the corresponding pentahalides. Thus,

$$2NbCl_5 + O_2 \longrightarrow 2NbOCl_3 + 2Cl_2$$

$$2TaCl_5 + O_2 \longrightarrow 2TaOCl_3 + 2Cl_2$$

The oxofluorides can also be prepared by heating the pentafluorides with silica. Thus,

$$2TaF_5 + SiO_2 \longrightarrow 2TaOF_3 + SiF_4$$

The oxohalides are monomeric in vapour state and get hydrolysed in water to give hydrous pentoxides.

Compounds of Lower Oxidation States. Niobium (IV) and Tantalum(IV) Oxides. NbO_2 is obtained by the reduction of Nb_2O_5 in a current of hydrogen at elevated temperature.

$$Nb_2O_5 + H_2 \longrightarrow 2NbO_2 + H_2O$$

TaO_2 is obtained by reduction of Ta_2O_5 by carbon at a high temperature:

$$Ta_2O_5 + C \longrightarrow 2TaO_2 + CO$$

These are dark-grey powders, insoluble in water and acids. They dissolve in hot aqueous alkalies.

The Lower Halides. The lower halides of Nb and Ta are prepared by reduction of the pentahalides on heating either with the metal itself or with aluminium. The oxidation state of the final product depends upon the intensity of the reduction process. The higher the temperature and larger the time of reduction, the lower is the oxidation state of the product obtained. Amongst the lower halides known are :

+4 *State* : NbF_4, $NbCl_4$, $NbBr_4$, NbI_4 ; $TaCl_4$, $TaBr_4$, TaI_4.

+3 *State* : NbF_3, $NbCl_{3.13}$, $NbBr_3$, NbI_3 ; $TaCl_{2.9-3.1}$, $TaBr_{2.9-3.1}$, TaI_3

+2 *State* : $NbF_{2.5}$, $NbCl_{2.67}$, $NbCl_{2.33}$, $NbBr_{2.67}$, $NaBr_2$, $NbI_{2.67}$; $NbCl_2$; $TaCl_{2.5}$, $TaBr_{2.5}$, $TaI_{2.33}$

It was previously thought that the lower halides of Nb and Ta are non-stoichiometric in nature. It has now been confirmed that most of them are **cluster compounds** whose structures are based on $[M_6X_{12}]^{2+}$ cluster units. The octahedral M_6 units are held together by multicentre M-M bonds over the six metal atoms and by halogen bridges along the twelve edges of the octahedron.

The tetrahalides are all dark solids and are diamagnetic. This is possible only if there is extensive M-M bonding in these compounds. They are also volatile above 300° C with the exception of NbF_4.

MOLYBDENUM

Molybdenum occurs mostly as *molybdenite*, MoS_2 and to a smaller extent as *molybdates* such as $PbMoO_4$ *(wulfenite)*. Molybdenite ore contains relatively small amount of MoS_2. The first step in the extraction, therefore, is to concentrate the ore by *froth floatation process*. The concentrate is then roasted in air so as to convert the sulphide into molybdenum trioxide, MoO_3.

$$2MoS_2 + 7O_2 \longrightarrow 2MoO_3 + 4SO_2$$

The crude oxide is dissolved in ammonia when ammonium molybdate is formed.

$$MoO_3 + 2NH_3 + H_2O \longrightarrow (NH_4)_2MoO_4$$

This compound is purified by repeated crystallisation and then heated strongly to get pure molybdenum trioxide.

$$(NH_4)_2MoO_4 \longrightarrow MoO_3 + 2NH_3 + H_2O$$

Molybdenum is recovered from the trioxide by reduction with hydrogen at 600° C.

$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$

Aluminothermic process is also used for this purpose.

$$MoO_3 + 2Al \longrightarrow Mo + Al_2O_3$$

The metal obtained by this method is 98—99 percent pure. Reduction of MoO_3 with calcium or zinc dust also yields the metal of about 99 per cent purity. Reduction with carbon, however, is to be avoided as in that case molybdenum carbide rather than molybdenum is obtained.

Properties. It is a silvery-white metal, fairly hard and melts at 2610° C.

It is not attacked by air at ordinary temperatures but when heated strongly (500–600° C) it gets slowly oxidised to the trioxide, MoO_3.

$$2Mo + 3O_2 \longrightarrow 2MoO_3$$

It is also attacked by the halogens giving the corresponding halides.

$$Mo + 3F_2 \longrightarrow MoF_6$$

$$2Mo + 5Cl_2 \longrightarrow Mo_2Cl_{10}$$

$$2Mo + 3Br_2 \longrightarrow 2MoBr_3$$

It does not react with sulphur and phosphorus.

It is only gradually attacked by acids. Hot and concentrated nitric acid oxidises the metal to the trioxide, MoO_3. However, it soon becomes passive.

It is not attacked by alkalies but dissolves in fusion mixture of KNO_3 and NaOH.

Uses. Molybdenum finds extensive applications in industry, the chief amongst which is in the manufacture of alloy steels. For this purpose, *ferromolybdenum* alloy which is industrially used for making molybdenum-steel, is prepared by heating molybdenite ore with iron pyrites, lime and coke in an electric furnace or by reducing a mixture of oxides of molybdenum and iron by the aluminothermic process. Steel containing 2 percent of molybdenum does not soften on heating and is, therefore, used for high-speed lathe tools. Steel containing molybdenum along with nickel (nickel-molybdenum steel) is used in making gun barrels. Steel containing molybdenum (2-3%) and chromium (about 60%) is acid-resistant. An alloy containing molybdenum (about 4%), nickel (about 79%) and iron (about 17%) has high magnetic permeability and is used in making magnetic cores. It is also used for the filament supports of electric lamps and as windings for resistance furnaces.

Molybdenum compounds are used as blue pigments for painting on porcelain as well as in silk and wool dyeing. Ammonium molybdate is used in the analysis of steel for the estimation of phosphorus.

COMPOUNDS OF MOLYBDENUM

Molybdenum mostly forms covalent compounds in which the metal is in oxidation states of +2, +3, +4, +5 and +6, the last being more important.

Compounds of Molybdenum(VI). Molybdenum trioxide, MoO_3. It is obtained by roasting molybdenite ore in air or boiling it with conc. nitric acid. It is an acidic oxide and dissolves in a strong alkali solution to give molybdate which contains MoO_4^{2-} ion. Lowering of *p*H of the molybdate solution yields a polymolybdate. The oxide MoO_3 sublimes easily. Moist MoO_3, on mild reduction, gives a blue coloured product. It is believed that on reduction, MoO_3 gets converted into Mo(IV) and Mo(V) oxides and hydroxides which are coloured compounds. MoO_3 is thermally and kinetically more stable than CrO_3. It may be pointed out here that whereas CrO_3 is a strong oxidising agent, MoO_3 has very mild oxidising character. This indicates higher stability of +6 oxidation state of Mo compared to Cr.

It dissolves in ammonia and when the solution in excess of ammonia is allowed to cool, crystals of **ammonium molybdate** separate out. Ammonium molybdate has *not* been assigned the simple formula $(NH_4)_2MoO_4$ but is represented as $(NH_4)_2Mo_7O_{24}.4H_2O$. *Ammonium molybdate is used as a laboratory reagent for the detection as well as elimination of phosphates. Its solution in dilute nitric acid containing* ammonium nitrate is the well known '*molybdate reagent*' which when added to a solution of a phosphate produces a yellow precipitate of ammonium phosphomolybdate, usually represented as $(NH_4)_3PO_4.12MoO_3$. The solution of ammonium molybdate in dilute acid deposits, if allowed to stand at a low temperature, yellow α-molybdic acid, $H_2MoO_4.H_2O$ which on heating to 70° C gives white β-molybdic acid, H_2MoO_4.

Molybdic acid in colloidal form, *i.e.*, **colloidal molybdic acid**, can be prepared by dialysing a solution of ammonium molybdate in hydrochloric acid.

The various molybdic acids as well as their salts give molybdic trioxide, MoO_3, on heating.

Polymolybdates. The salts of molybdic acid, *i.e.*, molybdates, give polymolybdates on acidification. The composition of the polymolybdate formed depends upon the *p*H of the solution, as shown below :

$$MoO_4^{2-} \xrightarrow{pH\ 6} [Mo_7O_{24}]^{6-} \xrightarrow{pH\ 2} [Mo_8O_{26}]^{4-} \xrightarrow{pH\ 1} MoO_3.2H_2O$$

The structure of these polymolybdates contains octahedral MoO_6 units which are joined together in a variety of ways, *i.e.*, by sharing corners and edges of MoO_6 octahedra. The type of linking of MoO_6 octahedra determines the type of the polymolybdate unit formed.

The polymolybdates obtained by the condensation of MoO_4^{2-} units alone are called **isopolymolybdates.** $[Mo_7O_{24}]^{6-}$ is an example.

Heteropolymolybdic Acids and Their salts. Heteropolymolybdates are formed when molybdate solutions containing other oxo anions, usually phosphate, silicate and arsenate, are allowed to crystallise together. The ratio of MoO_3 to PO_4^{3-} or SiO_4^{4-}, etc., condensed together is usualy 12 : 1 or 6 : 1. Other ratios are also known. The acidification of the solutions of heteropolymolybdates yields heteropolymolybdic acids. These are also called **condensed acids.** The examples are : $H_3PMo_{12}O_{40}$ (12-molybdophosphoric acid):$H_4SiMo_{12}O_{40}$ (12-molybdosilicic acid) and $H_3AsMo_{12}O_{40}$ (12-molybdoarsenic acid). Their salts are also known. Sodium and ammonium 12-molybdosphates ($Na_3PMo_{12}O_{40}$ and $[(NH_4)_3PMo_{12}O_{40}]$ are familiar examples. The acids and their salts are extensively hydrated. They have complicated structures.

The structure of heteropolymolybdates consists of tetrahedral PO_4^{3-}, SiO_4^{3-} or BO_4^{3-} ions surrounded by MoO_6 octahedral units. A well known example of heteropolymolybdate is the product obtained by mixing solutions of PO_4^{3-} and ammonium polymolybdate, *i.e.*, $(NH_4)_3[PO_4Mo_{12}O_{36}]$.

Mixed Oxides of Mo (VI). When MoO_3 is fused with the oxides of alkali and alkaline earth metals, mixed oxides are produced. The structures of these mixed oxides are quite complicated. Nevertheless, these contain MoO_6 octa-hedral units which are linked with each other through oxygens of these units.

Molybdenum hexafluoride, MoF_6. This is another important compound of Mo(VI). It is formed by direct combination of the elements. It forms colourless crystals melting at 17° C.

It reacts slowly with NaF to give a crystalline solid of composition $MoF_6.2NaF$.

It is more stable than CrF_6.

Other Halides and Oxohalides of Mo(VI). The dark coloured $MoCl_6$ and $MoBr_6$ are well known. These solids hydrolyse easily to produce molybdic acids. The oxohalides of M(VI) such as $MoOF_4$, $MoOCl_4$, MoO_2Cl_2, $MoOS_2$ are also known.

Compounds of Molybdenum(V). Molybdenum pentoxide, Mo_2O_5. It is obtained by heating molybdenum powder with molybdenum trioxide in nitrogen at 750° C.

$$Mo + 5MoO_3 \longrightarrow 3Mo_2O_5$$

It is a violet black powder and dissolves in acids on warming.

Molybdenum pentafluoride, MoF_5. It is prepared by the action of fluorine diluted with nitrogen on the metal at 400° C. It is also formed by the reduction of hexafluoride by the carbonyl of the metal.

$$5MoF_6 + Mo(CO)_6 \xrightarrow{25°\ C} 6MoF_5 + 6CO$$

It is a crystalline solid. It has a cyclic tetrameric structure in which four MoF_6 units are joined through Mo-F-Mo bridges to form a ring.

Molybdenum pentachloride, $MoCl_5$. It is prepared by heating the metal in chlorine. It is highly deliquescent and is hydrolysed in water to give the oxochloride $MoOCl_3$.

$$MoCl_5 + H_2O \longrightarrow MoOCl_3 + 2HCl$$

It is a dimer with the formula Mo_2Cl_{10} in the solid phase but is monomeric in solution phase, as for example , when it is dissolved in benzene. The compound Mo_2Cl_{10} does not contain any Mo-Mo bond.

The pentasulphide, Mo_2S_5, is also known as a black powder.

The compounds of pentavalent molybdenum produce deep red colouration with ammonium sulphocyanide due to the formation of $Mo(OH)_2(CNS)_3$.

Compounds of Molybdenum(IV). Molybdenum dioxide, MoO_2. It is obtained by heating the trioxide at 450° C in hydrogen.

$$2MoO_3 + 2H_2 \longrightarrow 2MoO_2 + 2H_2O$$

It is a violet powder. It is oxidised by nitric acid to the trioxide, MoO_3. MoO_2 is polymeric and contains Mo–Mo bonds in its structure.

Molybdenum tetrafluoride, MoF_4, is obtained by treating MoF_5 with molybdenum carbonyl at – 75° C when a compound of composition Mo_2F_9 is obtained which on heating to 150° C gives MoF_4. It is a nonvolatile solid.

Molybdenum tetrachloride, $MoCl_4$, is obtained by refluxing the solution of $MoCl_5$ in benzene, in a reducing atmosphere. It is also obtained on treating MoO_2 with carbon tetrachloride at 250° C.

$$MoO_2 + CCl_4 \longrightarrow MoCl_4 + CO_2$$

It is a dark red solid.

The sulphide of Mo(IV), *viz.*, molybdenum **disulphide, MoS_2,** is the naturally occurring *molybdenite* ore.

Compounds of Molybdenum(III). The existence of **molybdenum sesquioxide, Mo_2O_3,** has not been firmly established. However, the **trihydroxide, $Mo(OH)_3$,** appears as a black precipitate by adding alkali to a solution of molybdate reduced by zinc. It dissolves in acids forming salts. For example, with hydrochloric acid and sulphuric acid it gives chloride and sulphate of the formula $MoCl_3$ and $Mo_2(SO_4)_3$, respectively. **Molybdenum trifluoride, MoF_3,** is obtained by treating MoF_6 with Mo at about 400°C. It is a yellowish-brown non-volatile solid. **Molybdenum trichloride, $MoCl_3$,** can also be prepared by heating $MoCl_5$ in hydrogen at 250°C. It is a dark red solid, insoluble in cold water. It forms a stable complex ion $[MoCl_6]^{3-}$ when it reacts with Cl^-.

The **sulphide, Mo_2S_3,** is obtained as a precipitate on adding ammonium sulphide to a solution containing a salt of trivalent molybdenum.

Compounds of Molybdenum(II). The dichloride, $MoCl_2$, is obtained on heating the trichloride in an atmosphere of carbon dioxide.

$$2MoCl_3 \longrightarrow MoCl_2 + MoCl_4$$

The tetrachloride, being more volatile, distils off. It can also be prepared by passing chlorine over molybdenum heated at 120° C. It is an amorphous yellow solid, insoluble in water. The **dibromide** has the molecular formula, **Mo_6Br_{12}.** It is similar to chloride in most of its properties.

Mo_6Br_{12} is actually $[Mo_6Br_8]^{4+}.4Br^-$. The $[Mo_6Br_8]^{4+}$ unit consists of Mo_6 octahedral unit containing Mo-Mo bonds and Mo-Br-Mo bridges.

Blue Oxides. Blue oxides of molybdenum, known as *molydenum blues*, are prepared by the reduction of acidified solutions of molybdates by H_2S or SO_2. These contain oxides and hydroxides. Their compositions vary although the colour in each case remains blue. Thus, they have the compositions $MoO_{2.33}.H_2O$, $Mo_{2.5}(OH)_{2.5}$, $MoO_2(OH)$, etc.

Interstitial Compounds. Molybdenum combines with several non- metals including B, C, N and Si to form interstitial compounds. These are hard, refractory and chemically inert substances. These properties make them useful in the construction of kilns, jet engines, gas turbines and for the fabrication of cutting tools. The compositions of such compounds correspond to Mo_2C, MoN, MoC, Mo_2N, Mo_2B, MoB_2 and Mo_2B_5

Compounds containing Molybdenum in Unusual Oxidation States. The organometallic compound $(C_6H_6)_2Mo^+$ has Mo in +1 oxidation state whereas metal carbonyls $Mo(CO)_6$, $[Mo_2(CO)_{10}]^{2-}$ and $[M(CO)_5]^{2-}$contain the metal in zero, –1 and –2 oxidation states. This is in agreement with the general statement that pi-acceptor ligands stabilise lower oxidation states of the metal.

TECHNETIUM

Technetium-99 occurs in traces only, being a fission product of uranium. It has also been observed in the spectra of the sun and certain stars. Another isotope, technetium-97 was first made in 1937 by bombarding molybdenum with deuterons. Its half-life period is 90 days. Another isotope, technetium-95, with half-life period of 60 days is used as a tracer.

COMPOUNDS OF TECHNETIUM

Oxides. Three oxides of technetium having compositions TcO_2, TcO_3 and Tc_2O_7, in which the element is in +4, +6 and +7 states, respectively, are known. Amongst these, technetium dioxide, TcO_2 is the most stable. It sublimes at 1000° C. It is obtained by heating ammonium pertechnetate, NH_4TcO_4.

Technetium trioxide, TcO_3, is obtained by heating TcO_3Br. However, much is not known about this compound.

Technetium heptoxide, Tc_2O_7, is made by heating the metal or other oxides to 200° C in air. It is a pale-yellow hygroscopic solid. It melts at 300° C.

Pertechnic Acid and Pertechnetates. Pertechnic acid and pertechnetates are very well known. Pertechnic acid is made by dissolving Tc_2O_7 in water.

$$Tc_2O_7 + H_2O \longrightarrow 2HTcO_4$$

The solution , on evaporation, yields dark red crystals of the anhydrous acid. Thus, unlike $HMnO_4$, which is known only in solution, $HTcO_4$ is known in solid state as well.

Pertechnetates of alkali metals (*e.g.*,$KTcO_4$) are also known. These are obtained by dissolving Tc_2O_7 in alkalies. These are more stable than the permanganates and do not have oxidising properties. Pertechnetates react with potassium in ethanol to give $K_2[TcH_2]$.

Halides. The known halides of technetium are $TcCl_4$, $TcCl_6$ and TcF_6. The hexafluoride, TcF_6, has been studied in greater details. It exists as golden yellow crystals melting at 33° C It is obtained by heating the metal in fluorine.

The oxofluorides TcO_3F and TcO_3Cl are also known. The oxofluoride, $TcOF_3$, is obtained by the action of fluorine with TcO_2 at 150° C. It is a yellow solid having a low melting point.

Both TcS_2 and Tc_2S_7 are known.

RUTHENIUM

Ruthenium occurs in nature as an alloy of ruthenium, osmium and irridium. The metal is extracted by heating the alloy with a mixture of potassium hydroxide and potassium nitrate when ruthenium is converted into potassium ruthenate, K_2RuO_4. The mixture is then acidified and boiled to eliminate osmium as osmium tetroxide, OsO_4.

The solution is made alkaline and heated when ruthenium distils off as ruthenium tetroxide, RuO_4. This compound is finally reduced in a current of hydrogen to get ruthenium.

Properties. Ruthenium is a grey-white metal, fairly hard and very resistant to attack by acids or alkalies. It dissolves only when fused with alkaline oxidising mixture of KOH and KNO_3 (or $KClO_3$) yielding potassium ruthenate, K_2RuO_4.

It combines with oxygen at 500° C to form the oxide RuO_2. When heated it combines with sulphur to yield RuS_2, with fluorine to give RuF_3 and with chlorine to give $RuCl_3$.

It shows oxidation states of +2, +3, +4, +6 and +8. The first three states are more important.

Ruthenium is used as a hardening agent for platinum and for making hard inert alloys used in fountain-pen tips and gramophone needles.

COMPOUNDS OF RUTHENIUM

Ruthenium(II) compounds, $RuCl_2$ and RuO are known to exist. However, ruthenium(II) complexes, such as $[Ru(NH_3)_6]^{2+}$ and $[Ru(CN)_6]^{4-}$, are more stable than simple ruthenium(II) compounds.

Ruthenium shows special affinity towards pi acid ligands such as CO, PR_3, etc., with which it forms tetrahedral complexes. Another pi acid ligand, NO, forms a large number of mixed complexes with Ru(II). Examples are $[Ru(NO)Cl_5]^{2-}$ and $Ru[NO(CN)_5]^{2-}$. The Ru–NO linkage in the mixed nitroso complex is either straight or bent, *i.e.*, Ru–N= O or Ru—N⋝O

Ruthenium(III) complexes are also quite stable. Examples are $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5H_2O]^{3+}$.

Ruthenium shows special affinity towards pi acid ligands such as CO and even N_2. The affinity for N_2 is shown by the following reaction :

$$[Ru(NH_3)_5H_2O]^{3+} \xrightarrow{NaN_3} [Ru(NH_3)_5N_2]^{3+}$$

The N_2 complex further reacts as follows :

$$[Ru(NH_3)_5N_2]^{3+} + [Ru(NH_3)_5H_2O]^{3+} \longrightarrow [(H_3N)_5Ru\text{–}N_2\text{–}Ru(NH_3)_5]^{4+} + H_2O$$

RuO_2 is also known. It is a bluish black solid which contains ruthenium in +4 oxidation state.

RuO_4 containing Ru(VIII) is a yellow solid which dissolves in alkalies to give perruthenate and ruthenate, as shown below ;

$$4RuO_4 + 4OH^- \longrightarrow \underset{\text{Perruthenate containing Ru(VIII)}}{4RuO_4^-} + H_2O + O_2$$

$$4RuO_4 + 4OH^- \longrightarrow \underset{\text{Ruthenate containing Ru(VI)}}{4RuO_4^{2-}} + 2H_2O + O_2$$

Unusual Oxidation States of Ruthenium. Ruthenium exists in –2 oxidation state in $[Ru(CO)_4]^{2-}$ and in the zero oxidation state in $Ru(CO)_5$, $Ru_3(CO)_{12}$, etc. The π acid ligands are known to stabilise lower oxidation states as shown in the above examples.

RHODIUM

Rhodium occurs very rarely and constitutes only 10^{-7} per cent of the earth's crust. It occurs generally alloyed with platinum. In order to recover it, the alloy is fused with potassium hydrogen sulphate, $KHSO_4$, when rhodium dissolves to give $KRh(SO_4)_2$. It is extracted with hot water and then recrystallised. The compound when heated above 200° C in air, yields rhodium.

Properties. It is a silvery-white metal, soft and ductile. It is rather inert and dissolves only in hot concentrated sulphuric acid or in a mixture of hot concentrated hydrochloric acid and sodium chlorate. It is not attacked by chlorine or oxygen unless the temperature is raised to red heat.

On account of its inert nature, the metal is used for plating scientific instruments. Its alloy with platinum is used for making high-temperature scientific apparatuses including crucible, thermocouples.

The chief oxidation state of rhodium in most of its simple and complex compounds is +3. Rh_2O_3, $RhCl_3$, RhF_3 are examples of simple compounds while $K_2[RhCl_5]$ is an example of a complex salt of rhodium(III).

COMPOUNDS OF RHODIUM

The highest oxidation state of rhodium is +6 which the metal exhibits in RhF_6. This compound is unstable and highly reactive.

The compounds of Rh(V) are very rare and are unstable. RhF_5 is actually a cyclic tetramer in which four RhF_6 octahedra form a ring through Rh–F–Rh bonds. The structure of $(RhF_5)_4$ is similar to the tetrameric structure of NbF_5 and TaF_5 which has been discussed earlier.

The compound RhF_4 is unstable. Another compound of Rh(IV) is RhO_2 which is formed by the oxidation of an aqueous solution of Rh(III) compounds by a strong oxidising agent such as $NaBiO_3$ in the presence of an alkali.

The halocomplexes of Rh(IV) are slightly more stable than the simple Rh(IV) compounds. Thus, $K_2[RhCl_6]$ and $K_2[RhF_6]$ are slightly more stable than RhF_4 and RhO_2.

The +3 oxidation state of Rh is more stable than any other oxidation state of the metal. All the trihalides are known and are found to be quite stable. These halides, however, cannot be represented by simple structures. Their structures contain RhX_6 octahedra fused with one another through Rh–X–Rh bonds in such a manner that the aggregate structure is RhX_3. However, $RhCl_3.3H_2O$ is monomeric and has octahedral structure.

The complexes of Rh(III) are also very stable. Most of these are diamagnetic in character. The complex cation $[Rh(H_2O)_6]^{3+}$ is quite stable in aqueous solution whereas $[Co(H_2O)_6]^{3+}$ is oxidising. This indicates that Rh(III) salt solutions in water are more stable than Co(III) salt solutions. The anion $[RhCl_6]^{3-}$ is also quite stable.

Although pentahalide and heptahalide complex ions such as $[RhBr_5]^{2-}$ and $[RhBr_7]^{4-}$ are known, yet these are not very stable.

The basic acetate of rhodium has the formula $[Rh_3O(CH_3COO)_6(H_2O)_3]^+$ which is similar to the formula of basic acetate of chromium, *viz.*, $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$. The structure of basic acetate of rhodium is thus similar to the structure of basic acetate of chromium already shown in the last chapter.

A number of mixed metal hydrides of rhodium, whose stability is due to the presence of pi acid ligands, are also known. One such compound is $[Rh(R_3P)_2(H)Cl_2]^+$.

The +2 oxidation state of Rh is not very stable. However, the pi acceptor ligands stabilise this oxidation state. Rhodocene, $Rh^{II}(\eta^5\text{–}C_5H_5)_2$ is similar to ferrocene and cobaltocene in structure but it is much less stable.

The +1 oxidation state of Rh is quite common in complexes containing pi acid ligands such as PR_3 and CO.

Wilkinson's Catalyst. The complex $[RhCl(PPh_3)_3]$ is known as Wilkinson's catalyst. It has a square planar structure and is red-violet in colour. It is obtained by refluxing $RhCl_3.3H_2O$ with PPh_3. It is used as a catalyst in the **OXO process** in which CO and H_2 are added to the **end double bond** of alkenes forming aldehydes which on oxidation give carboxylic acids and on reduction give alcohols. Thus, the OXO process involving the use of Wilkinson's catalyst is of considerable industrial importance. Another trigonal bipyramidal compound trans$[Rh(CO)(H)(PPh_3)_3]$ is also employed as a catalyst in the process giving similar products.

The carbonyls $[Rh_6(CO)_{16}]$, $[Rh_4(CO)_{12}]$, etc., contain Rh in zero oxidation state whereas the complex anion $[Rh(CO)_4]^-$ contains Rh in –1 oxidation state.

PALLADIUM

Occurrence. Palladium occurs alloyed with other metals such as gold, copper, iron and nickel, in South Africa, Russia and Columbia. The chief source is Sudbury nickel ore which consists of platinum

as well as palladium in equal amounts mixed with sulphides of copper, nickel and iron. It is more abundant than any other of the platinum metals. It constitutes about 10^{-6} per cent of the earth's crust.

Extraction. The metal is extracted generally from the Sudbury nickel ore which is first concentrated and then digested with dilute aqua regia under pressure. The solution containing the chlorides of platinum and palladium is treated with ammonium chloride when a yellow precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is obtained. The precipitate is separated and ignited when spongy platinum is left behind. The solution now contains mostly palladium dichloride, $PdCl_2$. It is mixed with ammonia and concentrated by heating. On cooling, crystals of tetraammine palladium(II) chloride, $[Pd(NH_3)_4]Cl_2.H_2O$, separate out. These are redissolved in water and a small amount of hydrochloric acid is added to get a yellow precipitate of dichlorodiamminepalladium(II), $[PdCl_2(NH_3)_2]$. The precipitate is thoroughly washed and redissolved in ammonia to get once again the soluble tetraamminepalladium(II) chloride in the form of crystals. The cycle

$$[Pd(NH_3)_4]Cl_2 \underset{NH_3}{\overset{HCl}{\rightleftharpoons}} [PdCl_2(NH_3)_2]$$

is repeated about half a dozen times so as to get the palladium complex in as refined a state as possible. Ultimately, the tetrammine complex is heated strongly when it decomposes giving palladium in the form of a sponge or a fine powder. If the operations are carried out carefully, it is possible to get palladium of almost 99·5 per cent purity.

Alternatively, the metal may be extracted from its natural alloys with other metals of the family by taking advantage of the fact that this alone forms an insoluble cyanide. Thus, when the alloy is fused with potassium cyanide and the products extracted with water, $Pd(CN)_2$ separates out as a precipitate. On ignition, this decomposes to give the pure metal.

Properties. It is a silvery-white metal which is malleable and ductile. It melts at 1552° C.

It is not affected by air but when heated in air, a blue film of palladous oxide, PdO, is formed. It resists the attack of chlorine unless the temperature is raised to red heat. It combines directly with sulphur at high temperature forming the sulphide, PdS.

It dissolves in dilute nitric acid forming palladous nitrate, $Pd(NO_3)_2$ and in dilute sulphuric acid containing a small amount of nitric acid, to form palladous sulphate, $PdSO_4.2H_2O$

It dissolves in aqua regia to give H_2PdCl_6 which on evaporation and subsequent heating decomposes to give $PdCl_2$.

The most remarkable property of palladium is that it *absorbs hydrogen.* When heated to dull redness, it absorbs about 1000 times its own volume of hydrogen. If the temperature is raised further, the hydrogen is expelled. It is believed that in the absorption process, the hydrogen molecules break down into the hydrogen atoms which then fit into the palladium lattice.

Uses. Palladium is used in jewellery and in the formation of a white alloy with gold which serves as a substitute for platinum. This is because it is inert towards air and can take up polish easily. It is also used as a catalyst in several hydrogenation reactions. It appears that the catalytic performance in hydrogenation process is due to the dissociation of molecular hydrogen into atomic state. Since atomic hydrogen is far more reactive, the reaction is brought about very speedily and very efficiently.

COMPOUNDS OF PALLADIUM

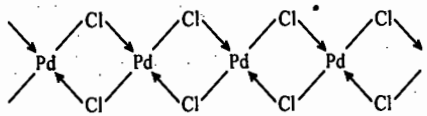
Palladium(0) Compounds. Palladium shows its zero oxidation state in its complexes formed by σ donor and pi acceptor ligands. One such complex is $[Pd(CO)(Ph_3)_3]$. Pure binary compounds of Pd(0), such as $Pd(CO)_4$, do not exist. The probable reason for this has been discussed in the Chapter on Pi-Acceptor Ligands.

Palladium(II) Compounds. Palladium forms a large number of compounds in which it has the oxidation state of +2. Some of the important compounds of Pd(II) are described below.

Palladous oxide, PdO. It is obtained by heating spongy palladium at 800°C in oxygen or by heating palladous nitrate, $Pd(NO_3)_2$. It is a black powder. It is insoluble in acids and even in aqua regia. It is a strong oxidising agent as on heating it decomposes into the metal and oxygen.

Palladous hydroxide, $Pd(OH)_2$. It is obtained as a precipitate on heating a solution of palladous nitrate. Unlike the oxide, it dissolves readily in acids. It starts decomposing when heated above 550° C.

Palladous chloride, $PdCl_2$. It is obtained by heating palladium in chlorine. It is a dark red solid which is highly soluble in water. The solution on evaporation yields crystals of $PdCl_2.2H_2O$. It is reduced by sulphur dioxide or carbon monoxide to palladium.



$PdCl_2$ exists as a chain polymer in the solid state, having the structure as shown.

Another form of $PdCl_2$ is a hexamer $(PdCl_2)_6$. It is not soluble in water. Its structure comprises of a complicated three-dimensional pattern of Pd and Cl atoms in which each Pd atom is surrounded by four Cl atoms in a square planar geometry. All the Cl atoms are bridging type. This form of $PdCl_2$ is known as β-$PdCl_2$.

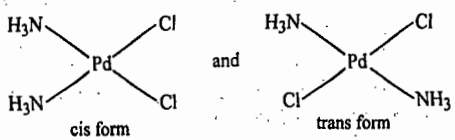
Palladous nitrate, $Pd(NO_3)_2$. It is obtained by dissolving palladium metal or palladous hydroxide in dilute nitric acid. The solution on evaporation yields brown deliquescent prism-like crystals.

Palladous sulphate, $PdSO_4.2H_2O$. This is obtained by dissolving palladium hydroxide in dilute sulphuric acid. It is a brown deliquescent solid.

Palladous cyanide, $Pd(CN)_2$. It is obtained as a precipitate on adding potassium cyanide to a solution of palladous chloride. The precipitate dissolves on adding excess of potasium cyanide to give the complex compound, $K_2[Pd(CN)_4].3H_2O$.

Complex Compounds of Palladium(II). A number of complex compounds of divalent palladium are known. Palladium ion, Pd^{2+}, in aqueous solution is hydrated and exists as the complex $[Pd(H_2O)_4]^{2+}$. It also forms a complex with ammonia $[Pd(NH_3)_4]^{2+}$. A solution of palladous chloride in hydrochloric acid contains the divalent complex anion, $[PdCl_4]^{2-}$. A solution of palladous chloride mixed with that of potassium chloride on evaporation yields crystals of potassium tetrachloropalladate(II), $K_2[PdCl_4]$.

Amongst the various ammine complexes, mention may be made of **tetramminepalladium(II) chloride,** $[Pd(NH_3)_4]Cl_2$, which is a pink solid and **dichlorodiamminepalladium(II),** $[Pd(NH_3)_2Cl_2]$, which is a yellow solid and exists in two forms : The cis form (commonly known as cis platin) is used in cancer therapy.



cis form trans form

Palladium(III) Compounds. Palladium(III) compounds are rather uncommon. Amongst the few compounds known, PdF_3 is important. This is obtained by heating the metal in a a current of fluorine at 500° C. The complex compounds, $Na_3[PdF_6]$ and $Na[PdF_4]$, though unstable, are known to exist.

Palladium(IV) Compounds. Very few compounds of Pd(IV) are known. PdO_2 is stable only in the hydrated form. Amongst the halogens, only fluorine forms the tetrahalide, PdF_4. The complexes of Pd(IV) are more stable than the Pd(IV) compounds. Well known complexes of Pd(IV) are $Na_2[PdX_6]$ and $Pd[X_4(NH_3)_2]$ (X = F, Cl, Br).

SILVER

Occurrence. It occurs native in a few places in Canada, United States of America and Mexico, mixed with varying amounts of copper and gold. Its most important ores are : *argentite* (*silver glance*), Ag_2S, *horn silver*, AgCl and *pyrargyrite* (*Ruby silver*), $Ag_2S.Sb_2S_3$

The ores are mixed with a large amount of rock, silica and clay. The silver content hardly exceeds 1 per cent.

Extraction. Silver is extracted from its ores generally by the **cyanide process.** In this process, the finely powdered ore is leached for several hours with a dilute (0·5%) solution of sodium cyanide, the mixture being all the time agitated by a current of air. Metallic silver, silver chloride and silver sulphide all pass into solution with the formation of the complex sodium dicyanoargenate(I), $Na[Ag(CN)_2]$. Sodium sulphide is at the same time largely oxidized to sodium sulphate by the air current.

The solution containing the silver complex is removed and treated with zinc dust when silver precipitates out.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

The precipitated silver is finally fused with borax or potassium nitrate to purify it.

It may also be purified by electrolytic process.

Physical Properties. Silver is a white lustrous metal, highly malleable and ductile. It is the best conductor of heat and electricity. It has a density of 10·5 g/c.c. and melts at 960·8° C. Molten silver can absorb oxygen which is given off on cooling causing violent spurting. The phenomenon is called *spitting of silver.*

Chemical Properties. Silver has a a poor chemical activity. Therefore, it is known as a *noble* metal. Following are its chief chemical properties.

1. Action of air. Silver is not attacked by air or moisture. But when exposed to air containing even traces of hydrogen sulphide, it turns black due to formation of a thin layer of silver sulphide on its surface.

2. Action of halogens. When heated strongly in a current of halogen gas or vapour, it forms the corresponding halide.

When an olefin is made to react with heated AgCl, it forms an **organometallic compound.**

$$AgCl + C_2H_4 \xrightarrow{\Delta} Ag(C_2H_4)Cl$$

3. Action of sulphur. Silver has great affinity for sulphur. When heated with sulphur powder, it forms silver sulphide.

4. Action of acids. The standard oxidation potantial for the reaction.

$$Ag\,(s) \longrightarrow Ag^+\,(aq) + e^-,$$

is –0·80 volt which is even lower than that of copper. Hence, it cannot displace hydrogen from dilute acids. Silver is, thus, not attacked by non-oxidising acids, *i.e.,* hydrochloric acid and dilute sulphuric acid. However, it reacts with nitric acid and concentrated sulphuric acid forming silver nitrate and silver sulphate, respectively.

$$3Ag + 4HNO_3\,(dil.) \longrightarrow 3AgNO_3 + 2H_2O + NO$$

$$Ag + 2HNO_3\ (conc.) \longrightarrow AgNO_3 + H_2O + NO_2$$

$$2Ag + 2H_2SO_4\,(conc.) \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$$

It is not attacked by aqua regia. Advantage is taken of this fact in separating it from gold (which is attacked by aqua regia.)

5. Action of alkali cyanides. Silver dissolves in sodium cyanide or potassium cyanide in the presence of air due to formation of the complex cyanide ion.

$$2Ag + H_2O + O_2 + 4CN^- \rightleftharpoons 2[Ag(CN)_2]^- + 2(OH^-)$$

Uses of Silver. 1. Silver is used in making coins, ornaments, silver ware, decoration pieces, etc. As silver itself is rather soft, for most purposes it is alloyed with copper. The silver alloy used for ornaments contains about 80 per cent silver and 20 per cent copper. 2. Silver compounds are used in plating articles made of baser metals.

Oxidation States. The normal oxidation state of silver is +1 in its compounds. A few compounds in which silver is in oxidation state of +2 have been reported but these are highly unstable. Silver is reduced readily in these compounds to +1 state. These compounds, therefore, act as strong oxidising agents. For example, an oxide, AgO, in which silver is in +2 oxidation state, is formed by passing ozone over silver. This decomposes readily to Ag_2O, giving out oxygen and thus acts as a strong oxidising agent,

$$2AgO \longrightarrow Ag_2O + O$$

Another compound of silver (II) is AgF_2. This is also unstable and is a powerful oxidising agent.

It is evident that the +2 state which is so important in the chemistry of copper is not stable at all in silver,

However, some complexes of silver in +2 oxidation state are more stable than its salts. Thus, the complexes, $[Ag(py)_4]^{2+}$, $[Ag(1,10\ phenanthrolin)_2]^{2+}$ are known to be reasonably stable and contain Ag^{2+} ion in a square planar environment.

The +3 oxidation state of Ag is still less common although $Na[AgF_4]$ has been prepared by heating a mixture of NaCl and AgCl in a current of fluorine.

Solubilities of Silver Halides. The solubility products of AgCl, AgBr and AgI at the room temperature are $2{\cdot}8 \times 10^{-10}$, $5{\cdot}0 \times 10^{-13}$ and $8{\cdot}5 \times 10^{-17}$, respectively. Thus, AgI is the least soluble silver halide.

The extremely low solubilities of AgCl, AgBr and AgI are surprising in view of the fact that salts of univalent cations with univalent anions are generally soluble. The abnormal insolubilities of silver halides other than silver fluoride are considered to be due to their *abnormally high lattice energies*. The reason for unusually high lattice energies lies in the strong van der Waals attraction between silver and halide ions in addition to the usual electrostatic attraction between the oppositely charged ions. Comparing AgCl with KCl, it is found that Ag^+ and K^+ ions are of about the same size, the ionic radii of Ag^+ and K^+ being 1·26 and 1·33 Å. However, Ag^+ ion has 46 electrons while K^+ ion has only 18 electrons. As a general rule, the larger the number of electrons in an ion, the stronger is its van der Waals attraction for neighbouring ions. Consequently, the lattice energy of AgCl should be much higher than that of KCl. This is found to be actually the case. The lattice energy of AgCl is 895·4 kJ mol^{-1} while that of KCl is 702·9 kJ mol^{-1}. Thus, more energy is needed to break the lattice of AgCl than that of KCl. Accordingly, silver chloride should be much less soluble than potassium chloride which is actually the case.

The lattice energies of AgBr and AgI are even higher because of greater number of electrons in their anions. Consequently, they are even less soluble than AgCl.

The lattice energy of AgF is the lowest because of the smallest number of electrons in its anion. This salt, therefore, is soluble in water.

Silver bromide is soluble in solutions containing high concentration of thiosulphate ion due to complex formation.

$$AgBr\ (s) + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$$

This reaction is made use of in fixing the image on the photographic plate since sodium thiosulphate dissolves away the whole of the unaffected silver bromide from the exposed film.

CADMIUM

Occurrence. Cadmium does not occur free in nature. Most of the zinc ores such as *calamine* or *zinc blende* contain 2–3% of cadmium. A mineral *greenockite* (CdS) is known but it is rare and not of commercial importance.

Extraction. During the distillation of cadmiferous zinc, the first product of distillation contains most of the cadmium, partly as oxide. From this crude sample, free cadmium is prepared by repeating the fractional distillation or by dissolving in dilute sulphuric acid and electrolysing the solution.

Properties. It is a soft, bluish white metal. It is malleable and ductile. Chemically it is similar to zinc though it is much less reactive. It burns in air to give brown fumes of the oxide. It burns in chlorine to form the chloride. Its reactions with acids are similar to those of zinc.

Cadmium differs from zinc in the fact that its sulphide can be precipitated in acid medium and that its oxide is not amphoteric.

Uses. Cadmium is used in the manufacture of a number of fusible alloys such as Wood's metal and Rose metal. Its amalgam is used in Weston standard cell. Cadmium rods are used as controlling rods in atomic reactors.

Aqueous Chemistry of Cd(II). The usual oxidation state of cadmium is +2. The Cd^{2+} ion is hydrated but to a smaller extent than Zn^{2+} ion. When hydrogen sulphide is passed through a solution containing Cd^{2+} ions, yellow precipitate of CdS results. Its solubility product is $1{\cdot}0 \times 10^{-28}$. It is used as a pigment under the name *cadmium yellow*.

Cadmium forms a number of complexes like $[Cd(NH_3)_4]^{2+}$, $[Cd(CN)_4]^{2-}$, $[CdI_4]^{2-}$, as already mentioned. A precipitate of cadmium hydroxide dissolves in ammonia due to formation of the complex $[Cd(NH_3)_4]^{2+}$.

The complex anion $[[CdCl_5]^{3-}$ has trigonal bipyramidal geometry. A number of octahedral complexes of Cd(II) are also known. Exmples are $[Cd(NH_3)_6]^{2+}$, $[Cd(en)_3]^{2+}$, etc.

Chemistry of Cd(I). The Cd–Cd bond is much weaker than Hg–Hg bond. That is why Hg_2^{2+} ion is quite stable whereas Cd_2^{2+} ion is very unstable. Cd_2^{2+} is formed only in the fused melts of the type $Cd\text{-}CdCl_2$.

Toxic Effects of Cadmium. Cadmium, if ingested, accumulates in kidneys. It causes malfunctioning of kindeys. It can also replace zinc in some useful enzymes of the body.

QUESTIONS

1. How does zirconium occur in nature? How is the metal extracted from its ores? Discuss its imporant properties and uses.
2. Discuss the occurence, preparation and properties of niobium and tantalum.
   Give a brief description of the compounds of niobium and tantalum in various oxidation states of the metals.
3. How is molybdenum extracted from its sulphide ore ? Discuss the important properties and uses of the metal.
4. Molybdenum forms compounds of all oxidation states varying from +2 to +6. Give a brief description of the compounds formed in different oxidation states of the metal.
5. How does rhodium occur in nature ? Describe its properties and uses.
6. How does palladium occur in nature ? How is the metal extracted from its ore ? Describe the important properties and uses of the metal. Name the important compounds of palladium.
7. Name the important ores of silver. How is the metal extracted from these ores. Discuss the important properties and uses of the metal.
8. Discuss the chemistry of Ag in +1 oxidation state. Why do the halides of silver differ so much in their solubilities. While KCl is highly soluble, AgCl is only sparingly soluble in water. Why is it so ?
9. How does cadmium occur in nature ? How is the metal extracted ? Discuss the important properties and uses of the metal.
10. Give the preparation, properties and uses of important compounds of cadmium.

24 THE ELEMENTS OF THE THIRD TRANSITION SERIES

The Third transition series consists of nine elements, excluding lanthanum which is discussed as a member of the lanthanide series because of its very close resemblance with the elements of this series. The nine members of the Third transition series are **hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold** and **mercury.** These elements are much more important than the elements of the Second transition series. The general characteristics of these elements have already been discussed in Chapter 21. Some of their physical constants are given in Table 1. The present chapter is aimed at describing the chemistry of the indivisual members of the series in some details.

HAFNIUM

Occurrence. It occurs in zirconium minerals, as already stated. In fact, it was first discovered in these minerals by X-ray methods. Most of the zirconium minerals contain this element, ordinarily, only upto 0·1 per cent but occasionally upto 7 per cent concentration as well.

Extraction. Separation of hafnium from zirconium, however, is very difficult on account of their very close resemblance. However, it is now possible to do so by ion-exchange chromatography or fractional solvent extraction.

The method based on **ion-exchange chromatography** has been discussed in details in the next chapter.

In another method of separation, advantage is taken of the fact that the halides of both the elements, *i.e.*, $HfCl_4$ and $ZrCl_4$, form stable complexes with phosphoryl chloride, $POCl_3$. The two complexes formed are $[(HfCl_4)_2(POCl_3)_2]$ and $[(ZrCl_4)_3(POCl_3)_2]$. These two differ in their boiling points by 5° C. This helps in separating the two complexes and subsequently the two elements from each other.

There is very close resemblance between hafnium and zirconium as also in their compounds.

TANTALUM

The chemistry of tantalum has already been discussed along with that of niobium in the last chapter.

TUNGSTEN

Occurrence. The minerals containing tungsten are :

(*i*) *Wolframite* which is a mixture of iron and manganese tungstates $[(Fe, Mn)WO_4]$.

(*ii*) *Scheelite* which consists of calcium tungstate, $CaWO_4$.

(*iii*) *Cuproscheelite,* which is copper tungstate, $CuWO_4$.

Extraction. The metal is generally extracted from the wolframite ore. The ore is concentrated by eletromagnetic process as it contains magnetic impurities. The concentrated ore is roasted with sodium carbonate in excess of air when sodium tungstate is produced while iron and manganese are converted to their respective oxides. The reactions are represented as below:

$$4FeWO_4 + 4Na_2CO_3 + O_2 \longrightarrow 2Fe_2O_3 + 4CO_2 + 4Na_2WO_4$$

$$2MnWO_4 + 2Na_2CO_3 + O_2 \longrightarrow 2MnO_2 + 2CO_2 + 2Na_2WO_4$$

The roasted mass is extracted with hot water to dissolve sodium tungstate. The insoluble ferric oxide and manganese dioxide are removed by filtration. The solution is treated with dilute acid when tungsten

TABLE 1

Important Physical Constants of Elements of the Third Transition Series

Elements and their atomic numbers	Outer electronic configuration	Atomic mass (a.m.u.)	Atomic volume (ml)	Density (g ml^{-1})	Melting point (°C)	Boiling point (°C)	Atomic radius (Å)	Stable oxidation	Ionic radius oxid. state	First ionization states (kJ mol^{-1})	Heat of fusion for stable (kJ mol^{-1})	Heat of vaporisation energy (kJ mol^{-1})
Hf (72)	$5d^2\ 6s^2$	178·49	13·60	13·1	2222	5400	1·58	+4	0·81	531.4	21·7	648·5
Ta (73)	$5d^3\ 6s^2$	180·95	10·90	16·6	2996	5425	1·46	+5	0·73	577.4	28·4	753·1
W (74)	$5d^5\ 6s^1$	183·85	9·53	19·3	3410	5930	1·39	+ 6	0·68	769·8	33·7	774·0
Re (75)	$5d^5\ 6s^2$	186·21	8·85	21·0	3180	5900	1·37	+2 to +7	—	761·5	33·0	636·0
Os (76)	$5d^6\ 6s^2$	190·21	8·43	22·6	2700	5500	1·26	+4, +6	0·67 (+4)	841·0	2628	690·0
Ir (77)	$5d^7\ 6s^2$	192·30	8·54	22·5	2454	5300	1·26	+3, +4	0·60 (+4)	887·1	27·6	648·5
Pt (78)	$5d^8\ 6s^2$	195·10	9·10	21·4	1769	4530	1·29	+2, +4	0·52 (+2)	866·1	21·7	564·8
Au (79)	$5d^{10}\ 6s^1$	196·97	10·20	19·3	1063	2970	1·44	+1, +3	1·37 (+1)	891·2	12·7	365·3
Hg (80)	$5d^{10}\ 6s^2$	200·59	14·81	13·6	−38·4	357	1·57	+2	1·10	1008.3	2·3	58·2

trioxide, WO_3, is thrown down as a precipitate. This is washed and dried and reduced to the metal by heating with carbon, zinc or aluminium.

$$WO_3 + 2Al \longrightarrow Al_2O_3 + W$$

Properties. It is hard and has a silvery-white lusture. It has a very high melting point which is close to 3410° C. It is higher than that of any other metal. Its specific gravity (19·3) is close to that of gold. Due to its high melting point, it cannot be easily cast into rods or wires. A special technique has been devised for this purpose. The powder is compressed into a rod and heated in an atmosphere of hydrogen while a strong electric current is also passed so as to raise it to about 3000° C. As a result of this, the powder gets converted into a compact mass which can then be rolled and hammered at 1500° C and drawn into wires.

Tungsten resists the action of air, oxygen or chlorine unless heated to bright redness.

It is not attacked by acids. However, it dissolves in fused alkalies or fused oxidising agents like potassium chlorate.

Uses. Tungsten wire, prepared as above, because of its extremely high melting point and low volatility is used largely in making filaments for electric lamps.

Another major use of tungsten is in making special steel consisting of 14–20% tungsten and 3–5% chromium. This steel, due to its extreme hardness even at high temperature, is used in making tools for high speed lathes. Tungsten also forms useful alloys with chromium and cobalt.

Sodium tungstate is used as a mordant in dyeing and for 'fire proofing' of certain varieties of fabrics.

COMPOUNDS OF TUNGSTEN

Tungsten, like chromium, shows oxidation states of 2, 3, 4, 5 and 6. The compounds in which tungsten is in +6 oxidation state are more important.

Oxides. Tungsten Trioxide, WO_3. This is the most important oxide of tungsten. It is obtained from *wolframite,* as has been described above. It is a yellow powder, insoluble in water and has amorphous nature. It dissolves in alkalies forming *tungstates.* When heated mildly in a current of hydrogen, it changes into **tungsten dioxide, WO_2** which is a brown powder. It is soluble in water. It has a complicated structure containing W–W bonds.

The oxide WO_3, when fused with alkali or alkaline earth oxides, gives **mixed oxides** whose structures and properties are very similar to those of the corresponding mixed oxides of Mo.

Tungstic Acid and Tungstates. The acid H_2WO_4 is obtained as a precipitate when a solution of any tungstate is treated with hydrochloric acid. If precipitation takes place from a cold solution, α-tungstic acid, $H_2WO_4.H_2O$, is produced but if the precipitation takes place from a hot solution, β-tungstic acid, H_2WO_4, is produced., The former variety is white in colour and is very slightly soluble in water while the latter variety is yellow in colour and is insoluble in water as well as in acids except hydrofluoric acid. When dissolved in hydrofluoric acid it changes into hydrofluorotungstic acid, $H_2WO_2F_4$.

When WO_3 dissolves in sodium hydroxide solution, sodium tungstate, Na_2WO_4, is formed. While CrO_4^{2-} is strongly oxidising, WO_4^{2-} is a very mild oxidising agent.

On lowering the *p*H of tungstate solution, **isopolytungstates** are formed. These compounds have complicated structures containing the WO_6 octahedral units joined in a variety of ways by sharing the corners or edges of the octahedral units.

When WO_4^{2-} co-condenses with PO_4^{3-}, SiO_4^{4-} and BO_4^{3-}, **heteropolytungstates** are formed. Their structures are similar to those of heteropolymolybdates. A well known example of a heteropolytungstic acid is phosphotungstic acid, $H_3PO_4.12WO_3$.

Halides. Tungsten also forms a number of **halides** which are covalent. The examples are : WF_6, WCl_6, WCl_5, WCl_4, Their structures and properties are similar to those of the corresponding halides of molybdenum.

Tungsten Bronzes. By reducing alkali metal tungstates (*e.g.*, Na_2WO_4 or K_2WO_4) with tungsten, *deeply coloured* substances are obtained. These substances, called **tungsten bronzes**, are unreactive towards common acids (except HF) and alkalies, but are good conductors of electicity. They have metallic lustre and have the general formula M_xWO_3 (where M = Li, Na or K). The value of $x < 1$. These are, evidently, non-stoichiometric substances in which M^+ ion is always present in interstitial sites created by three-dimensional network formed due to corner sharing of WO_6 octahedra.

Tungsten bronzes can also be prepared by (*i*) heating the alkali metal tungstates in a current of hydrogen. (*ii*) reducing the tungstates electolytically. (*iii*) reducing WO_3 with alkali metals in the vapour phase.

The colours of tungsten bronzes depend upon the amount of alkali or alkaline earth metal ions. These ions, depending upon their amount, produce varying extents of lattice defects and hence impart different colours to the tungsten bronzes. Thus, the colour of Na_xWO_3 varies from golden yellow ($x = 0·9$) to blue violet ($x = 0·3$). The electrons produced due to ionisation of alkali metal M to M^+ ions in these tungsten bronzes are completely delocalised over the whole of the lattice and are, therefore, free to move throughout the lattice. As a result, the tungsten bronzes become conducting. The tungusten bronzes with $x < 0·3$ are as good conductors as metals. The conductance of tungsten bronzes decreases with increase in temperature. The tungsten bronzes are largely used as metallic paints.

Tungsten Blues. Like molybdenum blues, tungsten also forms **tungsten blues** by similar methods. Like molybdenum blues, they have varied compositions as $WO_{2·67}(OH)_{0·33}$ and $WO_{2·7}(OH)_{0·1}$.

RHENIUM

Rhenium was discovered only in 1925. The reason is that for several years before 1925, the element was looked for in manganese ores. But this element actually occurs in molybdenum ores, particularly in the mineral *molybdenite.* At some places, this mineral contains upto 20 parts per million (ppm) of rhenium as the sulphide ReS_2 or the oxide ReO_2. Both the sulphide and oxide are readily reduced to yield the metal.

COMPOUNDS OF RHENIUM

Oxides. Amongst the oxides of rhenium are the dioxide, trioxide, pentoxide and heptoxide (*i.e.*, ReO_2, ReO_3, Re_2O_5 and Re_2O_7). The oxidation states of the metal in these compounds, evidently, are +4, +5, +6 and +7, respectively.

ReO_2 is obtained by heating Re_2O_7 with the metal at 600° C . At higher temperatures, this compound reverts back to Re_2O_7 and Re.

ReO_3 is made by heating Re_2O_7 with rhenium at 300° C. It exists in two forms : *red* and *purple.* When heated strongly, it disproportionates as

$$3ReO_3 \longrightarrow Re_2O_7 + ReO_2$$

Perrhenic Acid and Perrhenates. Perrhenic acid is obtained as colourless solution on dissolving Re_2O_7 in water.

$$Re_2O_7 + H_2O \longrightarrow 2HReO_4$$

The acid is also obtained by oxidising the metal on heating in nitric acid or by passing chlorine in a suspension of ReO_2

$$2ReO_2 + 3Cl_2 + 4H_2O \longrightarrow 2HReO_4 + 6HCl$$

It has not been possible to isolate anhydrous perrhenic acid. The solution when heated gives back Re_2O_7.

Perrhenic acid is a strong monobasic acid. It reacts with magnesium, iron and zinc, evolving hydrogen. It is not a strong oxidising agent. However, it can oxidise HBr to bromine and HI to iodine.

Alkali metal perrhenates (*e.g.*, $KReO_4$ and $NaReO_4$) are also known. These are colourless and stable compounds. Sodium perrhenate and ammonium perrhenate are very soluble in water. Potassium perrhenate,

however, is much less soluble. It appears as a precipitate when KCl and $HReO_4$ solutions are mixed.

$$KCl + HReO_4 \longrightarrow \underset{\text{ppt.}}{KReO_4} + HCl$$

Ammonium perrhenate when heated in nitrogen gives the nitride Re_3N and the metal.

Perrhenates are comparatively more stable and, therefore, are not used as oxidising agents. Perrhenates are reduced by K metal in C_2H_5OH to give the hydride complex anion $[ReH_9]^{2-}$.

Halides and Oxohalides. A number of halides of rhenium in which the element is in +3, +4, +5, +6 and +7 oxidation states, are known, A number of **oxohalides** are also known. These are given in Table 2.

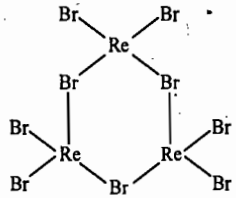
TABLE 2

Halides and Oxohalides of Rhenium

Oxidation state	Halides and Oxohalides
+3	$ReCl_3$, $ReBr_3$, ReI_3, $[Re_3Br_{10}]^-$, $[Re_3Br_{11}]^{2-}$
+4	ReF_4, $ReBr_4$, ReI_4, $[ReCl_6]^{2-}$, $[ReBr_6]^{2-}$
+5	ReF_5, $ReCl_5$, $ReBr_5$, $ReOF_3$
+6	ReF_6, $ReCl_6$, $ReOF_4$, $ReOCl_4$, $ReOBr_4$
+7	ReF_7, $ReOF_5$, ReO_2F_3

Preparation of some of the more important halides is given below :

$ReBr_3$ is obtained by direct combination of the elements at 300° C. It is a dark green solid. It has a trimeric structure as shown. The lines between the atoms in this structure do not show the exact bond order. $ReCl_3$ and ReI_3 have similar structure. $(ReBr_3)_3$ adds up KBr to give $K[Re_3Br_{10}]$, $K_2[Re_3Br_{11}]$ and $K_3[Re_3Br_{12}]$.



$ReCl_5$ is also made by heating the metal in chlorine. When heated in an inert atmosphere, it decomposes into **$ReCl_3$** which is a violet crystalline solid. It reacts with water to give perrhenic acid

$$3ReCl_5 + 8H_2O \longrightarrow HReO_4 + 2ReO_2\text{ (hydrated)} + 15HCl$$

$ReBr_4$ and **ReI_4** are obtained by reducing perrhenic acid with HBr and HI, respectively.

Unusual Oxidation States of Rhenium. Re has zero oxidation state in $[Re_2(CO)_{10}]$ and +1 oxidation state in $[ReCl(CO)_5]$. The +2 oxidation state is not very common. However, complexes such as $[ReCl_2(\text{pyridine})_2]$ are known to be fairly stable.

OSMIUM

Osmium occurs in nature as an alloy of osmium and iridium usually contaminated with ruthenium. In order to **recover osmium,** the alloy is fused with alkaline oxidising mixture of potassium hydroxide and potassium nitrate when ruthenium is converted into the soluble potassium ruthenate, K_2RuO_4, After dissolving and acidifying, the mixture is boiled when osmium distils over as osmium tetroxide, OsO_4. The latter is reduced to osmium on treatment with hydrogen or any other reducing agent.

The potential of the oxidation half reaction

$$Os(s) + 4H_2O \longrightarrow OsO_4 + 8H^+ + 8e^-$$

is −0·85 volt which means that the potential of the reverse reaction is +0·85 volt. This is an appreciable positive value. Hence, osmium tetroxide can be easily reduced in acidic medium.

Properties. It is a grey white, brittle and fairly hard metal. It is inert in the bulk state. It does not dissolve easily even in aqua regia. Although it is not attacked by air, it is attacked by pure oxygen even at 200° C forming volatile tetroxide, OsO_4.

Due to its hardness and inertness, its alloy with iridium is used in making tips of fountain pens.

It reacts with alkaline oxidising agents to give compounds like Na_2OsO_4 and K_2OsO_4. When heated it reacts with sulphur giving OsS_4, with fluorine giving OsF_6 and with chlorine giving $OsCl_4$.

It shows oxidation states of +2, +3, +4, +6 and +8 in its compounds. The important oxidation states are +4 and +6.

The +4 state is exhibited in the compounds, OsO_2 and $OsCl_4$. The +6 state is represented by the osmate ion, $[OsO_4]^{2-}$ in sodium or potassium osmate and also in OsF_6 which is obtained by heating osmium with flourine.

The +8 state is exhibited in the oxide OsO_4. This is the most important compound of osmium and is also known as **osmic acid.**

Osmium tetroxide, OsO_4. Osmium tetroxide is a solid melting at 40° C and boiling at 100° C. It is highly volatile and its vapours are corrosive to animal tissue and hence very dangerous, particularly for the eyes.

It is a strong oxidising agent and gets reduced easily even by dust or grease to OsO_2.

OsO_4 is used as a catalyst in organic chemistry., particularly for the addition of OH groups at carbon-carbon double bond on treatment with hydrogen peroxide. It is a good catalyst for several other reactions also but it gets poisoned easily and is, therefore, not very popular.

Osmium forms a number of complex compounds with ammonia and cyanide ions as the ligands.

Unusual Oxidation States. Like ruthenium, osmium also forms a number of complexes with p_i acid ligands such as CO in which osmium is present in −2 or zero oxidation state. Examples are $[Os(CO)_4]^{2-}$, $[Os(CO)_5]$, $[Os_3(CO)_{12}]$, etc.

IRIDIUM

Iridium occurs in nature as an alloy of osmium and ruthenium. In order to recover it from the alloy, osmium and ruthenium are first eliminated in the manner described under the respective metals. Iridium is recovered by appropriate treatment as the slightly soluble ammonium hexachloroiridiate, $(NH_4)_2[IrCl_6]$. This substance is decomposed on heating to get iridium.

Properties. It is a silvery-white metal which is brittle but fairly hard. It is used as an additive to platinum for hardening. It is extremely resistant to attack of acids. In bulk state it does not dissolve even in aqua regia. It dissolves in a mixture of concentrated hydrochloric acid and sodium chlorate in a sealed tube (*i.e.*, under pressure) at about 150° C.

It combines with chlorine at red heat to give the trichloride $IrCl_3$ and with fluorine at 600° C to give the hexafluoride, IrF_6.

It combines with oxygen when heated above 1000° C to give IrO_2.

COMPOUNDS OF IRIDIUM

The highest oxidation state of iriduim is +6. The compound IrF_6 is known but is quite unstable.

Iridium pentafluoride IrF_5 has a structure similar to that of RhF_5 and MoF_5 and is better represented as $(IrF_5)_4$. The oxidation state of Ir in IrF_5 is evidently +5.

The +4 oxidation state of Ir is quite stable. The tetrahalides of Ir are known. When Ir is heated in a current of oxygen, it gets converted to IrO_2

A number of complexes of Ir(IV) are also known. Some of these are $[IrCl_6]^{2-}$, $[IrCl_3(H_2O)_3]^+$, $[IrCl_4(H_2O)_2]$, $[IrCl_5(H_2O)]^-$ and $[Ir(C_2O_4)_3]^{2-}$. The last complex is optically active.

All the halides of Ir(III) are insoluble in water. These are all polymeric containing Ir-halogen-Ir bonds in their structure. The hydrated halides of Ir(III) are monomeric and soluble in water. When alkali is added to an aqueous solution of Ir^{3+}, hydrated Ir_2O_3 gets precipitated. Iridium basic acetate, $[Ir_3O(CH_3COO)_6(H_2O)_3]^+$ has structure similar to that of basic acetate of Rh and Cr which has been described earlier.

The +2 oxidation state of Ir is not very common although $IrCl_2$ (having a polymeric structure with Ir-Cl-Ir bridges) is known. Some phosphine complexes of this state are known.

Vsaka's compound, trans $[IrCl(CO)(PPh_3)_2]$, is yellow in colour and has the capability of coordinating aerial O_2. The yellow coloured Vsaka's compound turns orange when it takes up oxygen. When flushed with nitrogen, it releases oxygen and again turns yellow.

$[Ir(PF_3)_4]^-$ and $[Ir_4(CO)_{12}]$ contain Ir in −1 and zero oxidation state, respectively.

PLATINUM

Platinum is one of the most important and useful elements of the Third transition series.

Occurrence. It occurs only to the extent of 5×10^{-7} per cent in the earth's crust. But in view of its concentrated deposits, its extraction is relatively easier. It occurs mostly in the native state mixed with other metals of the platinum family (Pd and Rh) as well as with copper, iron and gold. Thus, the ore obtained from Urals (Russia) contains about 76% Pt, 11·7% Fe, 4·3% Ir, 4·1% Cu, 1·4% Pd, 0·5% Os, 0·3% Pb, mixed with sand. The platinum metal deposits also occur in California (U.S.A.), Brazil, Canada, Borneo and Australia.

Extraction. The heavier metallic particles are first separated from alluvial sand and gravel by washing. Gold, if present, is removed by the amalgamation process. The rest of the ore is digested with aqua regia which dissolves all the platinum metals forming chlorides, except osmium which is separated thereby. The solution containing chlorides of the metals of the platinum family (Pt, Pd and Rh) is evaporated to dryness and the residue heated to 175° C. Palladium and rhodium tetrachlorides are thus converted into the lower chlorides, $PdCl_2$ and $RhCl_2$, which are insoluble while platinum tetrachloride and iridium tetrachloride remain as such. On adding water, platinum tetrachloride together with iridium tetrachloride (which is present in small quantity only) passes into solution while the lower chlorides of palladium and rhodium remain as the residue.

The solution is acidified and ammonium chloride is added when the sparingly soluble salt, $(NH_4)_2PtCl_6$, gets precipitated.

$$PtCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2PtCl_6$$

The iridium tetrachloride remains in solution.

The precipitate of ammonium chloroplatinate is ignited when it decomposes to give spongy platinum.

$$(NH_4)_2PtCl_6 \longrightarrow 2NH_4Cl + 2Cl_2 + Pt$$

It is heated to redness and hammered to get the metal in the form of coherent sheets.

Properties. Platinum is a white metal with a silvery lustre, melting at a high temperature of 1769° C. It has a very high density of 21·4 g/c.c. It is malleable and ductile. It can be rolled into foils or drawn into very thin wires.

It has about the same coefficient of expansion as glass and, therefore, platinum wires and foils can be sealed into glass without cracking.

It is more reactive than osmium and iridium. It is, however, considerably more resistant to acids than palladium.

Pure platinum is not attacked even by hot and concentrated hydrochloric, nitric and sulphuric acids. If the metal is impure, it is slightly attacked by sulphuric acid. However, it is attacked by hot aqua regia forming chloroplatinic acid, $H_2[PtCl_6]$, commonly known as platinum chloride.

$$Pt + 2HCl + 4Cl \longrightarrow H_2[PtCl_6]$$

It also dissolves slowly in HCl particularly in the presence of air.

Platinum is commonly considered to be an inert element. This is, however, not quite correct. It is attacked by fused alkalies, nitrates and peroxides. Therefore, platinum crucibles should not be employed for heating such substances. It is also attacked by carbon disulphide vapours when a compound of composition $PtCS_2$ is formed.

It is also attacked by fluorine and chlorine at red heat. With fluorine it gives PtF_4 and with chlorine it gives $PtCl_2$.

It combines with oxygen at high temperature and pressure to give the oxide PtO.

Platinum, specially when it exists in finely divided state, absorbs an appreciable quantity of hydrogen and when in fused state, it absorbs oxygen. The volume of hydrogen absorbed may be as high as 900 times of its own volume at 80° C under a pressure of 1 atmosphere. Platinum is used, therefore, as a catalyst, like palladium, in a number of hydrogenation processes. The mechanism of absorption of hydrogen by platinum is the same as that by palladium.

Platinum forms alloys with a number of metals.

It exercises oxidation states of +2 and +4 in its compounds. A number of complexes containing platinum in both these states are also known. The +3, +5 and +6 oxidation states are also known. Examples are $PtCl_3$, PtF_5 and PtO_3. The +5 and +6 oxidation states, however, are rare.

The +4 oxidation state is more important, *e.g.*, PtF_4, PtO_2.

Platinum differs from the other elements of its family in forming alkyl derivatives by a Grignard reaction.

Uses. 1. Since platinum is not attacked by air, oxygen or water, it is used in jewellery and on account of its bright lustre, it is used for ornamental purposes. It is also used in dentistry.

2. As it is not attacked by strong acids even at high temperatures, it is used in chemical apparatus such as crucibles, dishes, etc. For the same reason, it is used as electrodes in various electrolytic processes.

3. Since it can be drawn into extremely thin wires and foils, it is used in making a number of instruments required for various scientific purposes.

4. It is used as an important catalyst in the form of *platinised asbestos*, which is prepared by soaking asbestos in a solution of platinic chloride containing a little of hydrochloric acid and ammonium chloride. Some important reactions catalysted by platinum include

(*i*) Combination of sulphur dioxide and oxygen to form sulphur trioxide in the contact process for the manufacture of sulphuric acid.

(*ii*) Oxidation of ammonia to nitric oxide in Ostwald's process for the manufacture of nitric acid.

(*iii*) Oxidation of methyl alcohol to formaldehyde.

COMPOUNDS OF PLATINUM

Some of the important compounds of platinum in various oxidation states are described below.

Compounds of Platinum(0). A well known compound in which Pt occurs in zero oxidation state is $Pt[(CO)_2(PPh_3)_2]$. Platinum, like palladium, does not form a pure binary metal carbonyl, $Pt(CO)_4$. The reason for this has been discussed in the chapter on Pi Acceptor Ligands.

Compounds of Platinum(I)

Platinum monochloride, PtCl. As already stated, platinum shows variable valency. Univalent platinum is represented by platinum monochloride, PtCl. It is obtained by heating platinum(II) chloride with platinum at 581–583° C.

$$PtCl_2 + Pt \longrightarrow 2PtCl$$

However, it is not known in pure state.

Compounds and Complexes of Platinum(II)

Platinum(II) chloride, $PtCl_2$. The typical bivalent platinum is represented by platinum(II) chloride. This is obtained by heating platinum(IV) chloride at 580° C.

$$PtCl_4 \longrightarrow PtCl_2 + Cl_2$$

It is a green grey powder insoluble in water. It dissolves in hydrochloric acid and metal chloride solutions forming complex ion $[PtCl_4]^{2-}$.

$$PtCl_2 + 2Cl^- \longrightarrow [PtCl_4]^{2-}$$

Thus, with hydrochloric acid and potassium chloride, the following complex compounds are formed.

$$PtCl_2 + 2HCl \longrightarrow H_2[PtCl_4]$$

$$PtCl_2 + 2KCl \longrightarrow K_2[PtCl_4]$$

Complex platinum(II) chlorides are also obtained by the reduction of complex platinum(IV) chlorides by sulphur dioxide, etc.

$$H_2[PtCl_6] + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl + H_2[PtCl_4]$$

Potassium tetrachloroplatinate(II) may also be obtained by warming a paste of potassium

hexachloroplatinate(IV) with cuprous chloride.

$$K_2[PtCl_6] + Cu_2Cl_2 \longrightarrow 2CuCl_2 + K_2[PtCl_4]$$

Most of the tetrachloroplatinate(II) complexes are soluble in water yielding red solutions.

The complex anion $[PtCl_4]^{2-}$ is diamagnetic. It has a square planar geometry.

Potassium tetracyanoplatinate(II), $K_2[Pt(CN)_4].3H_2O$. It is obtained by mixing a solution of potassium cyanide with platinum(II) chloride in proper proportions and evaporating to crystallisation.

$$PtCl_2 + 2KCN \longrightarrow Pt(CN)_2 + 2KCl$$

$$Pt(CN)_2 + 2KCN \longrightarrow K_2[Pt(CN)_4]$$

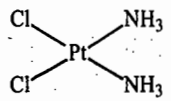
Potassium tetracyanoplatinate(II) is used in photography.

Barium tetracyanoplatinate(II), $Ba[Pt(CN)_4].H_2O$. It is a very important compound of bivalent platinum and is prepared by treating chloroplatinic acid with barium hydroxide solution and hydrocyanic acid and passing in sulphur dioxide till the solution becomes colourless.

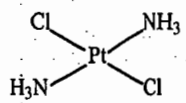
$$H_2[PtCl_6] + 5Ba(OH)_2 + 4HCN + SO_2 \longrightarrow Ba[Pt(CN)_4] + BaSO_4 + 3BaCl_2 + 8H_2O$$

The complex anion $[Pt(CN)_4]^{2-}$ is diamagnetic and, like $[PtCl_4]^{2-}$, it has a square planar geometry.

Diamminedichloroplatinum(II). This complex exists in two isomeric forms, *viz.*, *cis* diamminedichloroplatinum(II) and *trans* diamminedichloro-platinum(II), whose structures are given below.



cis



trans

The *cis* isomer, commonly known as ***cis* platin,** is used in the treatment of cancer.

Platinum(II) iodide, PtI_2. It is obtained as a black insoluble powder on heating platinum(II) chloride with potassium iodide solution.

$$PtCl_2 + 2KI \longrightarrow PtI_2 + 2KCl$$

Compounds and Complexes of Platinum(IV).

Platinum(IV) chloride, $PtCl_4$. This is one of the best known compounds of platinum. It is obtained by heating chloroplatinic acid in a current of chlorine at 370° C.

$$H_2[PtCl_6] \longrightarrow PtCl_4 + 2HCl$$

It is a reddish brown, crystalline solid, readily soluble in water, the solution having acidic reaction. The solution has been found to contain the complex compound $H_2[PtCl_4(OH)_2]$. On electrolysis, the platinum is discharged at the anode as a part of the anion $[PtCl_4(OH)_2]^{2-}$.

Chloroplatinic acid, $H_2[PtCl_6]$. It is the best known complex of platinum(IV). It is prepared by the action of aqua regia on platinum.

$$2HNO_3 + 8HCl + Pt \longrightarrow H_2[PtCl_6] + 4H_2O + 2NOCl$$

The solution is evaporated to drive off nitric acid before crystallising chloroplatinic acid.

Chloroplatinic acid is a reddish brown crystalline substance associated with 6 molecules of water of crystallisation, $H_2[PtCl_6].6H_2O$.

On heating in chlorine at 360–370° C, it decomposes into platinum (IV) chloride.

$$H_2[PtCl_6] \longrightarrow PtCl_4 + 2HCl$$

Chloroplatinic acid is a strong dibasic acid, ionising as

$$H_2[PtCl_6] \longrightarrow 2H^+ + [PtCl_6]^{2-}$$

It forms stable salts. The lithium and sodium salts ($Li_2PtCl_6.6H_2O$, $Na_2PtCl_6.6H_2O$) are soluble while the potassium and ammonium salts (K_2PtCl_6 and $(NH_4)_2PtCl_6$) form yellow precipitates. These salts decompose on heating leaving a residue of platinum.

$$K_2PtCl_6 \longrightarrow Pt + 2KCl + 2Cl_2$$

Some other well known complexes of Pt(IV) are $[Pt(NH_3)_6]^{4+}$, $[Pt(NH_3)_5Cl]^{3+}$, etc.

Organometallic Compounds of Platinum. These have been discussed in Chapter 33 on Organometallic Compounds.

GOLD

Occurrence. Gold occurs in native state either scattered in sand and gravel (*alluvial or placer gold*) or mixed intimately in quartz (*vein gold*). It also occurs, to a small extent, in combined state. The mineral *sylvanite* contains a telluride of silver and gold [(Au, Ag)Te_2].

Metallurgy. Different methods are adopted for the extraction of gold according to the nature of its source.

Extraction of Placer Gold. When gold is mixed with sand, silt or gravel, its separation is affected by taking advantage of its much higher specific gravity (19·3). The ore–sand mixture is thoroughly washed with a powerful current of water in long *sluices*. A sluice is an inclined channel with a number of small troughs provided with cleats, along the bottom. The heavier particles of gold settle down and collect in the troughs while the lighter particles of silt, sand and gravel are carried away by the current of water. This process is known as **placer mining.**

Sometimes it is necessary to throw a powerful stream of water on the deposits to wash away the gravel, etc. The process is then known as **hydraulic mining.**

Extraction of Vein Gold. It is popularly known as **vein mining** and is employed for the extraction of gold from hard auriferous quartz rocks. The rock is blasted at the quarry and the bigger lumps are broken to a smaller size by means of rock crushers. It is then carried to the factory and subjected to the following treatment for the extraction of gold from it.

1. Pulverization. The smaller pieces of auriferous quartz are finely pulverized by means of a battery stamp mill. Each of these mills consists of a mortar box enclosing a die and a moving stamp. The stamps weigh over a thousand pounds each and they fall about a hundred times per minute through a height of about 20 cm. The auriferous quartz pieces are fed from one side into the mill and pounded by the stamp. The pulverized matter is carried off by a current of water through a screen provided at the other end of the mill. The coarser particles, if any, are retained and pulverized again.

2. Amalgamation. The water slurry carrying the finer particles is next passed over amalgamated copper plates placed in a sloping position in front of each stamp mill. Free gold present in the slurry is retained by the mercury and the tailings drop into a dump. The gold amalgam is scraped from the copper plates after every 2 hours and collected into a pit below called the mercury well. The used-up copper plates are replaced by the new amalgamated plates. Nearly 75 to 80% of the total gold originally present in the quartz is thus recovered. The rest passes into the tailings.

3. Distillation. The gold amalgam so collected is squeezed between rubber blocks and then distilled in iron retorts. Mercury distils over (and is collected for further use) while gold is left in the retort. Gold particles recovered from the retort are fused with a flux like borax and made into a solid lump or bar on cooling.

4. Recovery of gold from the tailings. The tailings contain 20–25% of the gold originally present in the quartz rock. For its recovery, the tailings are again passed over amalgamated plates. This results in the recovery of 15–20% more gold, while about 10–12% of it escapes into the earthy slime or gangue.

5. *Treatment of gangue.* *The remaining 10–15% of gold is extracted from the gangue with the* help of the MacArthur–Forest cyanide process.

Extraction of Mineral Gold. The minerals in which gold is present in a combined state are first of all subjected to roasting in order to remove easily oxidizable impurities like sulphur, tellurium, arsenic,

antimony, etc. The roasted ore is then subjected to the MacArthur-Forest cyanide process or the Plattner's chlorine process, described below.

a. **MacArthur–Forest Cyanide Process.** This process is based on the fact that in the presence of atmospheric oxygen, gold dissolves in a solution of potassium cyanide with the formation of the cyanide complex :

$$4Au + 8KCN + 2H_2O + O_2\,(air) \longrightarrow 4K[Au(CN)_2] + 4KOH$$

The finely powdered roasted ore is filled in large vats made of cement or iron and consisting of false wooden bottoms with holes. A solution of potassium cyanide (0·5%) percolates all through for 12–24 hours.

From the complex cyanide solution, the metal gold is precipitated by zinc shavings.

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4 + 2Au$$

For this purpose, the solution is run through wooden troughs containing zinc shavings.

b. **Plattner's Chlorine Process.** The roasted ore is placed in vats with false bottoms, moistened and then saturated with a current of chlorine from underneath and left as such for a day. The gold chloride ($AuCl_3$) thus formed is leached with water. The solution is transferred to a separate tank where it is treated with ferrous sulphate to precipitate gold.

$$AuCl_3 + 3FeSO_4 \longrightarrow Au + FeCl_3 + Fe_2(SO_4)_3$$

Refining of Gold. Gold obtained by any of the above processes is impure and is generally contaminated with other metals like silver, copper, lead and some other baser metals. Lead and the other baser metals are removed by cupellation while silver and possibly a small amount of copper remains. The removal of silver and copper from gold is known as **parting** and can be achieved by the following methods.

1. Chlorine parting. The impure gold is melted in a fire-clay crucible and dry chlorine is bubbled through the melt by means of clay pipes. At first, fumes of baser metal chlorides are evolved, then silver is converted to silver chloride and the gold remains unaffected. Silver chloride forms a scum on the surface of the molten metal and can be easily skimmed off. The pure gold is tapped out of the crucible into small ingots.

2. Parting with sulphuric acid. It is based on the fact that while silver and copper dissolve in hot concentrated sulphuric acid, gold remains unaffected. It is found, however, that if the percentage of gold in the impure sample is more than 25%, the sample is not attacked by the acid. More silver is, therefore, added to the sample till an alloy containing about 25% of gold is obtained. This is treated with boiling concentrated sulphuric acid when silver and copper dissolve leaving gold behind.

$$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$$

In this process, since the gold content in the sample has to be reduced to 25% or one quarter before the acid treatment, it is sometimes called **quartation.** Formerly, nitric acid was used for the purpose but now it has been replaced by the cheaper sulphuric acid.

3. Electro-refining. Blocks of impure gold are made the anode in an electrolytic cell containing a solution of gold chloride ($AuCl_3$) in hydrochloric acid. Thin plates of pure gold constitute the cathodes. On electrolysis, pure gold is deposited on the cathode. Silver forms silver chloride which remains as a deposit near the anode. Gold thus obtained is 99·9% pure. For a higher purity, if desired, the metal is put to a second electrolytic refining.

Physical Properties. Gold is a yellow metal, highly malleable and ductile. It has a specific gravity of 19·3. It is soft and, therefore, for use in coinage and jewellery, it is necessary to alloy it with silver or copper. It is a very good conductor of heat and electricity.

Chemical Properties. Chemically, gold is rather inert. It has been valued for its *nobility,* that is, for its resistance to chemical attack of air, moisture, carbon dioxide, hydrogen sulphide and even most of the acids.

1. Action of acids. The oxidation potential of gold is extremely low being –1·50 volts. Hence it is not attacked by hydrofluoric acid, hydrochloric acid, sulphuric or nitric acid. It dissolves, however, in

aqua regia forming chloroauric acid, $HAuCl_4$.

$$3HNO_3 + 11HCl + 2Au \longrightarrow 2HAuCl_4 + 6H_2O + 3NOCl$$

2. Action of the halogens. Gold is attacked by the halogens forming the respective halides, AuX_3. When heated with iodine, gold forms aurous iodide, AuI (auric iodide is unstable).

3. Action of potassium cyanide solution. Gold dissolves in alkali cyanide solution in the presence of air or oxygen, forming complex cyanide ion, $[Au(CN)_2]^-$.

$$4Au + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Au(CN)_2] + 4KOH$$

Colloidal Gold. Colloidal solutions of gold can be prepared either by Bredig's method or by reducing gold chloride solution by a reducing agent such as formaldehyde, hydrazine hydrate, yellow phosphorus, carbon monoxide, etc. Sols of different colours, red, blue, purple or reddish purple, are obtained by different methods. The difference in colour is due to difference in the size of the colloidal particles obtained.

When gold is precipitated along with another colloid, a solid colloidal solution of purple tint, commonly known as **purple of Cassius,** is obtained. This is done by adding a mixture of stannous chloride and stannic chloride solutions to a solution of gold chloride. The resulting product probably consists of stannic hydroxide containing colloidal particles of gold.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 2Au + 3SnCl_4$$

$$SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl$$

Purple of Cassius is generally used for making ruby glass and high class pottery.

Uses of Gold. Gold is a precious and noble metal. Since it retains its bright surface untarnished, it is used for making ornaments, jewellery and frames of watches. Generally, small quantities of copper are added to make it harder. It is also used for making coins.

Gold is also used for plating the baser metals such as copper, silver, etc.

The purity or fineness of gold is generally expressed in *carats*, pure gold being known as 24 carats. Gold coin is 22 carats, *i.e.*, 22 parts gold and 2 parts impurity. Most of the ornaments and jewellery in India are made of 22 carat gold.

Compounds of Gold. Gold commonly exhibits oxidation states of +1 and +3. The +3 oxidation state is more stable. Gold(I) ion is unstable as it undergoes disproportionation in solution.

$$3Au^+ \rightleftharpoons Au^{3+} + 2Au$$

The equilibrium constant of the reaction, given by $K = [Au^{3+}]/[Au^+]^3 = 10^{10}$, shows that there can be only traces of gold (I) ion in aqueous solution.

Gold (I) is, however, stable in its insoluble or complex compounds.

The most important compound of gold, in which it exhibits a stable +3 oxidation state, is $AuCl_3$. In the solid state, it has a dimeric structure in which Cl atoms form the bridges. $AuCl_3$ when dissolved in organic solvents is called **liquid gold** which is used in paints.

The only known compound of gold in its +5 oxidation state is AuF_5. This is a dark red polymeric solid which is diamagnetic in character.

Gold in –1 Oxidation State. There is at least one case where it has been established that gold has an oxidation state of –1. When gold and cesium are fused together in equal proportions, the mass obtained does not behave as an alloy. Nor does it conduct electricity. It has been established that the mass is actually a salt with the composition Cs^+Au^-.

Complex Compounds of Gold. Gold, like copper and silver, forms complex compounds both in +1 and +3 oxidation states. Some of the important complex compounds are given below.

Potassium dicyanoaurate(I), $K[Au(CN)_2]$. It is obtained

1. By dissolving gold (I) oxide in excess of potassium cyanide solution.

$$Au_2O + 4KCN + H_2O \longrightarrow 2K[Au(CN)_2] + 2KOH$$

2. By treating gold with a dilute solution of KCN in the presence of atmospheric oxygen.

$$4Au + 8KCN + O_2 + 2H_2O \longrightarrow 4K[Au(CN)_2] + 2KOH$$

The $[Au(CN)_2]^-$ complex ion is linear in geometry.

Sodium dithiosulphatoaurate(I), $Na_3[Au(S_2O_3)_2]$. This is obtained by adding gold(III) chloride to *hypo* solution.

$$4Na_2S_2O_3 + AuCl_3 \longrightarrow Na_3[Au(S_2O_3)_2] + Na_2S_4O_6 + 3NaCl$$

Hypo is oxidized to sodium tetrathionate while trivalent gold is reduced to monovalent state.

Potassium tetracyanoaurate(III), $K[Au(CN)_4]$. It is obtained by treating a hot saturated solution of gold (III) chloride with potassium cyanide. The solution on crystallization yields crystals of potassium tetracyanoaurate(III).

$$AuCl_3 + 4KCN \longrightarrow K[Au(CN)_4] + 3KCl$$

Chloroauric acid, $H[AuCl_4]$. When gold is dissolved in aqua regia, a yellow solution of chloroauric acid is obtained. On crystallization, yellow crystals of chloroauric acid are formed. The sodium and potassium salts of this acid can be prepared by treating calculated amounts of alkali chlorides with gold trichloride.

$$AuCl_3 + KCl \longrightarrow K[AuCl_4]$$

Bromoauric acid, $H[AuBr_4]$. This is made by heating gold(III) bromide with hydrogen bromide. It is a red solid, soluble in water.

Fulminating Gold, AuN_2H_3. When concentrated ammonia is added to gold (III) hydroxide or oxide, a yellowish or greenish substance is formed which is named **fulminating gold**.

It is also obtained as a precipitate when gold(III) chloride solution is treated with ammonia.

Fulminating gold has a variable composition, the formula approximating to $HN{=}Au{-}NH_2$. It is a highly explosive substance. It explodes violently when heated or struck with a hammer.

MERCURY

Occurrence. Small quantities of mercury occur in free state, disseminated in rocks. Its ore, *cinnabar*, HgS, is found chiefly in Spain and Italy.

Extraction. Cinnabar (HgS) is crushed dry and screened into two grades. The large size pieces, richer in the ore, are sorted and subjected to a combined process of roasting and distillation.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

Various types of furnaces have been used for this purpose but the most important is the *Idrian furnace* (cf. Chapter 10).

Purification. Mercury obtained as above contains iron and zinc as the main impurities. Some dust particles and mercury oxide are also present in the form of a scum which, however, can be removed by squeezing mercury through chamois leather. It may be further purified by vacuum distillation.

Physical Properties. It is a silvery-white metal and liquid at ordinary temperature. It may be recalled that metal atoms in a transition metal are bonded together through both the covalent bonding and metallic bonding. The covalent bonding, which is much stronger than the metallic bonding, is mainly responsible for the hardness of the metal. It involves the overlapping of *d* orbitals of the metal atoms containing unpaired electrons. The weaker metallic bonding is due to attraction between metal cations and negatively charged free electrons surrounding these cations *(electron sea model)*. These free electrons come from the valence *s* subshells of the transition metal atoms. Therefore, the strength of the metallic bonding, which imparts electrical conductivity to the metal, depends upon the tendency of valence. electrons to get free from the atoms of the metal.

Since mercury atoms have no unpaired *d* electrons, there is no covalent bonding between them. Therefore, the attraction between mercury atoms is quite low. Consequently mercury is soft compared to other transition metals. Further, the ionisation energy required to remove the valence *s* electrons of mercury

is very high with the result that the metallic bonding between the mercury atoms is also weak compared to such bonding in other transition metals. This further reduces the attraction between mercury atoms so that, unlike other *d*-block elements, mercury is liquid at room temperature. It freezes at –38·4° C to a crystalline solid which is malleable and ductile. It boils at 357° C giving colourless vapour, the density of which shows its molecules to be monoatomic. The vapours in cold do not conduct electricity but when hot they conduct electricity giving out characteristic mercury spectrum, rich in ultra-violet rays. This is the principle of mercury vapour lamp. It forms amalgam with all metals except iron and platinum.

Chemical Properties. 1. Action of oxygen. Mercury is not attacked by oxygen or air at ordinary temperatures but when heated above 350° C, it slowly combines with oxygen forming mercuric oxide.

$$2Hg + O_2 \longrightarrow 2HgO$$

2. Action of halogens. Mercury combines readily with halogens forming halides, for example,

$$Hg + Cl_2 \longrightarrow HgCl_2$$

3. Action of acids. The oxidation potential of Hg is –0·85, *i.e.*, much less than that of hydrogen. Hence, it is not attacked by dilute hydrochloric acid and sulphuric acid in cold but hot concentrated sulphuric acid reacts with mercury to form mercury(I) sulphate and sulphur dioxide.

$$2Hg + 2H_2SO_4 \longrightarrow Hg_2SO_4 + 2H_2O + SO_2$$

With excess of acid, mercury(I) sulphate is further oxidised to mercury(II) sulphate.

$$Hg_2SO_4 + 2H_2SO_4 \longrightarrow 2HgSO_4 + SO_2 + 2H_2O$$

The reaction with nitric acid is not simple. The products obtained depend upon the temperature and concentration of the acid. Warm dilute nitric acid forms mercury(I) nitrate and nitric oxide.

$$6Hg + 8HNO_3 \longrightarrow 3Hg_2(NO_3)_2 + 4H_2O + 2NO$$

With concentrated nitric acid, mercury (II) nitrate is formed and nitrogen dioxide is evolved.

$$Hg + 4HNO_3 \longrightarrow Hg(NO_3)_2 + 2H_2O + 2NO_2$$

Uses. It is used for filling thermometers. manometers, vacuum pumps, diffusion pumps, etc . Mercury vapour lamps are used as a source of ultraviolet light. Mercury and its compounds are extensively used in medicine. Amalgams of various metals are used for producing hydrogen at controlled rate. It is used as an electrode in a number of electrolytic processes.

Oxidation States of Mercury. Mercury displays oxidation states of +1 and +2 in its compounds. In this respect it differs from zinc and cadmium which show +2 oxidation state only. Mercurous ion (*i.e.*, mercury in +1 state) is unique in the sense that it consists of two atoms linked by a covalent bond formed by 6*s* electrons of the two Hg^+ ions. Hg_2^{2+} ion is diamagnetic.

The Hg_2^{2+} ion in aqueous solution is stable towards disproportionation to Hg and Hg^{2+} ion, *i.e.*, the reaction

$$Hg_2^{2+}(aq) \rightleftharpoons Hg^{2+}(aq) + Hg$$

proceeds forward to a very small extent only. But, if we add to the above aqueous solution a reagent which *removes* Hg^{2+} in the form of a precipitate, the equilibrium shifts towards the right meaning thereby that more of Hg_2^{2+} disproportionates into Hg and Hg^{2+}, If the precipitating reagent for Hg^{2+} is present in excess, then almost the entire amount of Hg_2^{2+} disproportionates into Hg and the precipitate of the compound containing Hg^{2+}.

Thus, when hydrogen sulphide is passed through an aqueous solution of mercury(I) nitrate, the products are mercury(II) sulphide and free mercury.

$$Hg_2^{2+} + H_2S \longrightarrow HgS + Hg + 2H^+$$

Similarly, when sodium hydroxide is added to an aqueous solution of mercury(I) ions, mercury(II) oxide and mercury are obtained.

$$Hg_2^{2+} + 2OH^- \longrightarrow HgO + Hg + H_2O$$

Thus, it is not possible to prepare mercury(I) sulphide or mercury(I) oxide.

Mercury(I) salts are generally very little soluble in water.

When aqueous ammonia is added to mercury(I) chloride, the solid turns black due to the formation of finely divided mercury.

$$Hg_2Cl_2(s) + 2NH_3 \longrightarrow Hg(NH_2)Cl + Hg + NH_4^+ + Cl^-$$

The compound $Hg(NH_2)Cl$ is white but it is masked by the dark colour of mercury.

This serves as a test for distinguishing between $AgCl$ and Hg_2Cl_2. The former dissolves while the latter turns black on the addition of aqueous ammonia.

Complexes of Hg(II). Mercury in +2 oxidation state is found in soluble or insoluble salts and in complex ions. A solution of $HgCl_2$ (mercury (II) chloride) contains only a small concentration of Hg^{2+} or Cl^- ions in comparison to the concentration of undissociated $HgCl_2$ molecules. This is because $HgCl_2$ is a covalent compound. If excess of chloride ion is added to the solution of the salt, the complex $[HgCl_4]^{2-}$ is formed.

When dissolved in ammonia, complexes containing one, two, three and four ammonia molecules are known to be formed. With four molecules, the ammonia complex has the formula $[Hg(NH_3)_4]^{2+}$.

With cyanide ion, the complex, as expected, is $[Hg(CN)_4]^{2-}$

Both the complexes are stable, $[Hg(CN)_4]^{2-}$ is even more stable than $[Hg(NH_3)]^{2+}$.

Compounds containing Hg_3 and Hg_4 Units. The compounds such as $Hg_3(AlCl_4)_2$ and $Hg_4(AsF_6)_2$ are also known. Although Hg–Hg bond length in these compounds is comparable to the one in Hg_2^{2+} compounds, the exact mode of bonding in these compounds is not clear. An interesting non-stoichiometric compound approximating to the composition $[Hg_{2.85}(AsF_6)]_n$ is known to be a good conductor of electricity at room temperature and becomes superconductor at low temperatures.

Toxic Effects of Mercury. Mercury vapours are toxic and, if inhaled, can cause giddines, tremors, lung damage and brain damage. Mercury has sufficient vapour pressure even at room temperature to cause harm.

Inorganic mercury salts and organic mercury compounds are extremely poisonous. The Hg^{2+} ions, if accumalated in the body, cannot be removed easily. Aryl and alkyl mercury compounds are so poisonous that they can cause brain damage, deafness and even death.

Comparison of the Proprties of Elements of First Transition Series with those of the Elements of Second and Third Transition Series

For comparing the properties of the elements of the First transition series with those of the elements of Second and Third transition series, it is helpful to divide the elements of the three series into groups of three elements each. The first group (scandium group), thus, consists of the three elements, scandium, yttrium and lanthanum (excluding the radioactive actinium) belonging, respectively, to the first, second and Third transition series. The second group (titanium group) consists of titanium, zirconium and hafnium while the third group (vanadium group) comprises of vanadium, niobium and tantalum and so on. The last group (zinc group) consists of zinc, cadmium and mercury.

If we recall the properties of the elements of the three transition series, we observe that while the elements of Second and Third transition series have similar properties, the elements of the First transition series have considerably different properties from those of the elements of the Second and Third transition series. The main points of difference are discussed below.

1. Ionic Radius. The ionic radii of the elements of Second transition series are larger than those of their cogeners of the First transition series in each group. This is because of the increased number of electrons and higher principal quantum numbers in the elements of the Second transition series. On account of lanthanide contraction, there is very little difference in the ionic radii of the elements of the Second and Third transition series in a given group. For instance, the ionic radii of Ni^{2+}, Pd^{2+} and Pt^{2+} in a square planar ligand environment are 0·63 Å, 0·78 Å and 0·74 Å, respectively. Obviously, while the ionic radii of the elements of the Second and Third transition series in this group are practically the same, the ionic radius of their cogener of the First transition series is much shorter. The same conclusion is drawn

from the ionic radii of Co^{3+}, Rh^{3+} and Ir^{3+} in octahedral ligand environment which are 0·69 Å, 0·81 Å and 0·82 Å, respectively.

2. Coordination Number. While coordination numbers 7 and 8 are quite common for the first few members in each of the Second and Third transition series, these coordination numbers are quite rare for the elements of the First transition series.

3. Metal–Metal Bonding. The transition elements of the Second and Third transition series in a given group have greater tendency to form compounds containing M–M bonds than their cogener of the First transition series. Thus, in the vanadium group, while Nb and Ta form complexes of the type $[Nb_6Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{2+}$, vanadium does not. In the manganese group, while Tc and Re form complexes of the type $[TcCl_8]^{2-}$ and $[Re_2Cl_8]^{2-}$, Mn does not. Similarly, in the chromium group, while Mo and W form complexes of the type $[Mo_6X_8]^{4+}$ and $[W_6X_8]^{4+}$ (X=halogen), no such complex is known for Cr.

4. Oxidation States. The lower oxidation states, especially +2 and + 3, which so dominate the chemistry of the elements of the First transition series, are of relatively little importance for most of the elements of the Second and Third transition series. In the cobalt group, for instance, while Co^{2+} ion is a very stable species in aqueous medium, Rh^{2+} and Ir^{2+} ions are hardly known. While the complex $[Co(NH_3)_6]^{3+}$ for Co^{3+} ion is highly stable in aqueous medium, no such complex is known for Rh^{3+} and Ir^{3+} ions. In the manganese group, while Mn^{2+} ion is highly stable, Tc^{2+} and Re^{2+} ions are not so stable. The latter ions occur only in some metal clusters and complexes of pi acceptor ligands. In the chromium family, a large number of complexes of Cr^{3+} ion are known whereas Mo^{3+} and W^{3+} ions form relatively fewer complexes.

The higher oxidation state is generally more stable for the elements of the Second and Third transition series than for the elements of the First transition series. For example, RuO_4, WCl_6, PtF_6 are quite stable whereas FeO_4, $CrCl_6$, NiF_6 are not known. In the chromium group, $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ are highly stable and are not easily reduced whereas $[CrO_4]^{2-}$ is a very strong oxidising agent and is easily reduced. Similarly, in the manganese group, $[MnO_4]^-$ is a very strong oxidising agent whereas $[TcO_4]^-$ and $[ReO_4]^-$ are highly stable.

QUESTIONS

1. How does tungsten occur in nature? How is the metal extracted ? Describe the important properties and uses of the metal.
2. How does osmium occur in nature? How is the metal extracted ? Describe the important properties of the metal.
3. Describe the important compounds of osmium in various oxidation states of the metal.
4. Write what you know about iridium.
5. How does platinum occur in nature? How is it extracted from its ores? Discuss its important properties and uses.
6. Why is platinum called noble metal? How would you explain its noble character? How would you account for the oxidation states exhibited by platinum?
7. Describe the important compounds of platinum in various oxidation states of the metal.
8. Write a note on the complexes of platinum.
9. What are the important ores of gold? How is the metal extracted from its ores? Discuss its important uses. What is fulminating gold?
10. What are the important oxidation states of gold? Why does Au^+ exist only in traces in aqueous solutions?
11. How is gold extracted from its ores? Discuss the chemical reactions involved in the method employed.
12. How does mercury occur in nature? How is the metal extracted ? Describe its important properties and uses. Why is mercury liquid at ordinary temperature ? Why is it not possible to prepare mercury(I) sulphide or mercury(I) oxide ?
13. Discuss the main points of difference in the properties of the elements of the First transition series with those of the elements of the Second and Third transition series.

25 THE *f* BLOCK ELEMENTS. THE INNER TRANSITION ELEMENTS

The ***f* block elements** are those which have partly filled *f* subshells of the third to the outermost (antepenultimate), *i.e.*, (n–2)th energy shells in their elementary or ionic state. These elements are also called **inner transition elements** and are divided into two series, *viz.*,

(*i*) *The Lanthanide Series*

(*ii*) *The Actinide Series*

In lanthanides, it is the 4*f* subshell which is being successively filled while in actinides, it is the 5*f* subshell which is being successively filled.

THE LANTHANIDE SERIES

Lanthanum (Z = 57) and the next fourteen elements (Z = 58 – 71) which follow it are called **lanthanides** or **lanthanones**. *These fifteen elements closely resemble one another and form a distinct group with lanthanum as the prototype ;* hence the name *lanthanides* or *lanthanones*. The reason why they resemble lanthanum so closely lies in their electronic configurations. The configuration of lanthanum is $[Xe]5d^1 6s^2$. In the succeeding fourteen elements, 14 electrons are successively added to the empty 4*f* subshell of the lanthanum configuration. Thus, while in cerium, the element immediately following lanthanum, one 4*f* electron is added to the lanthanum configuration, in lutetium, the last element of the series, fourteen 4*f* electrons are added to the lanthanum configuration. Hence, the configurations of cerium and lutetium are $[Xe]4f^1 5d^1 6s^2$ and $[Xe]4f^{14} 5d^1 6s^2$, respectively. Since the number of electrons in the outermost, as well as the penultimate shell, remains the same, all the fifteen lanthanides resemble one another very closely. Strictly speaking, only 13 elements from Ce to Yb are *f* block elements because in lanthanum ($5d^1 6s^2$) the 4*f* subshell is completely empty, while in lutetium ($4f^{14} 5d^1 5s^2$), the 4*f* subshell is completely filled. However, all the elements from La to Lu have similar chemical and physical properites and hence are considered together. The reason for their similar properties is that the 4*f* electrons in which alone they differ are embedded in the interior while 5*d* and 6*s* electrons which are alike are exposed more to the surroundings. This aspect will be discussed a little later in this chapter.

Occurrence. The lanthanides were originally called rare earth elements. The word 'earth' was used because they occurred as oxides (which in early usage meant earth) and the word 'rare' was used because their occurrence was believed to be very scarce. Now many elements occur even more rarely than the lanthanides. Hence, although they are not abundant by any means, they are not considered to be rare in the sense in which this word was used before. Their substantial deposits occur in several countries, particularly in India, Scandinavia, U.S.A. and Russia. The most commonly occurring lanthanide is cerium which constitutes about 3×10^{-4} per cent of the earth's crust. *Monazite sand* is the most important mineral containing lanthanides. It is essentially a lanthanide orthophosphate. Some monazite deposits contain appreciable amounts of thorium also. In some cases the concentration of thorium may amount to as much as 30 per cent.

The abundance with which these elements occur in the earth's crust is shown in Table 1. The number of naturally occurring isotopes is also shown in the last column.

TABLE 1

Abundance of Lanthanides

Element	Symbol	Atomic number	Abundance (ppm of earth's crust)	Number of naturally occurring isotopes
Lanthanum	La	57	0·7	1
Cerium	Ce	58	66	4
Praseodymium	Pr	59	9·1	1
Neodymium	Nd	60	40	7
Promethium	Pm	61	—	0
Samarium	Sm	62	7·0	7
Europium	Eu	63	2·1	2
Gadolinium	Gd	64	6·1	7
Terbium	Tb	65	1·2	1
Dysprosium	Dy	66	4·5	7
Holmium	Ho	67	1·4	1
Erbium	Er	68	3·5	6
Thulium	Tm	69	0·5	1
Ytterbium	Yb	70	3·1	7
Lutetium	Lu	71	0·8	2

It is interesting to note that elements with even atomic numbers are relatively more abundant and aslo have a larger number of isotopes. The elements with odd atomic numbers are less abundant and do not have more than two isotopes. Promethium (Z = 61) does not occur in nature. It has been made artificiallly by radioactive disintegration.

Properties of Lanthanides

1. Electronic Configurations. Electronic configurations of lanthanides are given in Table 2. There is, however, some doubt regarding these configurations. This arises from the complexity of the electronic spectra of these elements. According to one view, the configurations are as given in column 3. According to another view, the configurations are as given in column 4. As can be seen, according to the latter view, the solitary 5*d* electron shifts into 4*f* subshell in all cases except in gadolinium (Z = 64) where such a shift destroys the symmetry of a half-filled *f* subshell and in lutetium (Z = 71) where the *f* subshell is already completely filled and cannot accommodate any additional electron. These days, the latter view is more accepted.

TABLE 2

Electronic Configurations and Oxidation States of Lanthanides

Element	Atomic Number	Electronic Configuration	Alternative Probable Configuration	Oxidation States
La	57	$[Xe]\ 5d^1\ 6s^2$		+3
Ce	58	$[Xe]\ 4f^1\ 5d^1\ 6s^2$	$[Xe]\ 4f^2\ 6s^2$	+3, +4
Pr	59	$[Xe]\ 4f^2\ 5d^1\ 6s^2$	$[Xe]\ 4f^3\ 6s^2$	+3, +4
Nd	60	$[He]\ 4f^3\ 5d^1\ 6s^2$	$[Xe]\ 4f^4\ 6s^2$	+2, +3, +4
Pm	61	$[Xe]\ 4f^4\ 5d^1\ 6s^2$	$[Xe]\ 4f^5\ 6s^2$	+3
Sm	62	$[Xe]\ 4f^5\ 5d^1\ 6s^2$	$[Xe]\ 4f^6\ 6s^2$	+2, +3
Eu	63	$[Xe]\ 4f^6\ 5d^1\ 6s^2$	$[Xe]\ 4f^7\ 6s^2$	+2, +3
Gd	64	$[Xe]\ 4f^7\ 5d^1\ 6s^2$	$[Xe]\ 4f^8\ 6s^2$	+3
Tb	65	$[Xe]\ 4f^8\ 5d^1\ 6s^2$	$[Xe]\ 4f^9\ 6s^2$	+3, +4
Dy	66	$[Xe]\ 4f^9\ 5d^1\ 6s^2$	$[Xe]\ 4f^{10}\ 6s^2$	+3, +4
Ho	67	$[Xe]\ 4f^{10}\ 5d^1\ 6s^2$	$[Xe]\ 4f^{11}\ 6s^2$	+3
Er	68	$[Xe]\ 4f^{11}\ 5d^1\ 6s^2$	$[Xe]\ 4f^{12}\ 6s^2$	+3
Tm	69	$[Xe]\ 4f^{12}\ 5d^1\ 6s^2$	$[Xe]\ 4f^{13}\ 6s^2$	+2, +3
Yb	70	$[Xe]\ 4f^{13}\ 5d^1\ 6s^2$	$[Xe]\ 4f^{14}\ 6s^2$	+2, +3
Lu	71	$[Xe]\ 4f^{14}\ 5d^1\ 6s^2$	$[Xe]\ 4f^{14}\ 5d^1\ 6s^2$	+3

All the lanthanides have been allotted one single position in the periodic table on account of the great similarity in their electronic configurations and chemical properties.

2. Oxidation States. The common oxidation state of all the lanthanides is +3. Lanthanum shows +3 oxidation state through the loss of both of the 6*s* electrons and also the solitary *d* electron. The configuration of La^{3+} ion, evidently, is that of xenon which is highly stable. It is very difficult, therefore, to remove another electron from this structure. Hence, a higher oxidation state for lanthanum is not possible ordinarily. In other words, it is not possible, ordinarily, to have La^{4+} ion. Similarly, gadolinium and lutetium also form only the tripositive M^{3+} ions. This is because the removal of three

electrons yields the stable [Xe]$4f^7$ configuration for Gd^{3+} ion in which the *f* subshell is exactly half-filled and the stable [Xe]$4f^{14}$ configuration for Lu^{3+} ion in which the *f* subshell is fully filled. In these cases, therefore, any oxidation state other than +3 would not occur. In other lanthanides, other oxidation states, +2 and +4 in particular, also occur. But these states are always less stable than the +3 state which is characteristic of this family. The outer electronic configurations of lanthanides in different oxidation states are given in Table 3. The configuration of neutral atoms are also included in the table for easy reference.

TABLE 3

Outer Electronic Configurations of Lanthanides in Different Oxidation States

Element	Oxidation States	Outer Electronic Configuraton of :			
		M	M^{2+}	M^{3+}	M^{4+}
La	+3	$5d^16s^2$	—	$5d^06s^0$	—
Ce	+3, +4	$4f^26s^2$	—	$4f^16s^0$	$4f^06s^0$
Pr	+3, +4	$4f^36s^2$	—	$4f^26s^0$	$4f^16s^0$
Nd	+2, +3, +4	$4f^46s^2$	$4f^46s^0$	$4f^36s^0$	$4f^26s^0$
Pm	+3	$4f^56s^2$	—	$4f^46s^0$	—
Sm	+2, +3	$4f^66s^2$	$4f^66s^0$	$4f^56s^0$	—
Eu	+2, +3	$4f^76s^2$	$4f^76s^0$	$4f^66s^0$	—
Gd	+3	$4f^75d^16s^2$	—	$4f^76s^0$	—
Tb	+3, +4	$4f^96s^2$	—	$4f^86s^0$	$4f^76s^0$
Dy	+3, +4	$4f^{10}6s^2$	—	$4f^96s^0$	$4f^86s^0$
Ho	+3	$4f^{11}6s^2$	—	$4f^{10}6s^0$	—
Er	+3	$4f^{12}6s^2$	—	$4f^{11}6s^0$	—
Tm	+2, +3	$4f^{13}6s^2$	$4f^{13}6s^0$	$4f^{12}6s^0$	—
Yb	+2, +3	$4f^{14}6s^2$	$4f^{14}6s^0$	$4f^{13}6s^0$	—
Lu	+3	$4f^{14}5d^16s^2$	—	$4f^{14}6s^0$	—

The +2 and +4 oxidation states are shown by those elements which by doing so attain the stable f^0, f^7 and f^{14} configurations. For example, cerium (Ce) and terbium (Tb) attain f^0 and f^7 configurations, respectively, when they go into +4 oxidation state, as shown below:

$$Ce^{4+} : [Xe]\ 4f^0 \ ; \ Tb^{4+} : [Xe]\ 4f^7$$

Similarly, europium and ytterbium acquire the f^7 and f^{14} configurations, respectively, when they change into +2 oxidation state, as shown below :

$$Eu^{2+} : [Xe]\ 4f^7 \ ; \ Yb^{2+} : [Xe]\ 4f^{14}$$

These facts explain why these elements excercise oxidation states other than +3 as well. This argument, however, does not hold good when we find that samarium and thulium also show oxidation state of +2, even though the M^{2+} ions have f^6 and f^{13} configurations, respectively:

$$Sm^{2+} : [Xe]\ 4f^6 \ ; \ Tm^{2+} : [Xe]\ 4f^{13}$$

It may be noted that M^+ ions of these metals would have acquired f^7 and f^{14} configurations and according to the general rule that exactly half-filled and completely filled shells are highly stable, the +1 oxidation state of these elements should have been more stable. But, samarium and thulium do not form M^+ ions at all.

Similarly, praseodymium (Pr) shows oxidation state of +4 giving M^{4+} ion with f^1 configuration but does not show oxidation state of +5 although M^{5+} ion would have attained f^0 (*i.e.*, empty *f* shell) configuration which would have been more stable. It is also seen that neodymium gives M^{4+} ion with f^2 configuration and not M^{6+} ion with f^0 configuration although the latter should have been more stable.

It is evident from the above discussion that although special stability associated with empty, half-filled ad completely filled *f* subshells (*i.e.*, f^0, f^7 and f^{14} structures) is an important factor, there are some other factors which are of equal or even greater importance in determining the stabilities of the oxidation states. These factors are based on highly complicated thermodynamic and kinetic considerations which are still not quite certain.

The M^{4+} ions in aqueous solution have a tendency to change readily into M^{3+} ions. The standard potential of the reduction half-cell reaction involving reduction of Ce^{4+}, for instance, is 1·61 volt.

$$Ce^{4+} + e^- \longrightarrow Ce^{3+} \qquad E^\circ = 1{\cdot}61 \text{ volt}$$

This indicates that Ce^{4+} ion is as strong an oxidising agent as MnO_4^- ion. Other +4 lanthanide ions like Pr^{4+} and Tb^{4+} are even more powerful oxidising agents.

3. Ionic Radii. Lanthanide Contraction. The radii of M^{3+} ions, which are the most stable, are given in Table 4.

TABLE 4

Ionic Radii of Lanthanides

Ion	Radius (Å)	Ion	Radius (Å)
La^{3+}	1·15	Tb^{3+}	1·00
Ce^{3+}	1·11	Dy^{3+}	0·99
Pr^{3+}	1·09	Ho^{3+}	0·97
Nd^{3+}	1·08	Er^{3+}	0·96
Pm^{3+}	1·06	Tm^{3+}	0·95
Sm^{3+}	1·04	Yb^{3+}	0·94
Eu^{3+}	—	Lu^{3+}	0·93
Gd^{3+}	1·02		

This table shows very clearly how ionic size decreases as we move along the lanthanide series from lanthanum to lutetium. It will be seen that on going from La^{3+} to Lu^{3+}, the ionic radius shrinks from 1·15 Å to 0·93 Å. *The steady decrease in ionic radius all along the series amounting in all to 0·22 Å, is called the* **lanthanide contraction.**

Consequences of Lanthanide Contraction. Lanthanide contraction, as will be seen shortly, is an important factor in allowing the *separation of lanthanides* from one another. Not only that ; the lanthanide contraction has a highly significant effect on the relative properties of the elements which precede and follow the lanthanides in the periodic table. The radius of La^{3+} ion, for example, is 0·21 Å larger than that of Y^{3+} ion which lies immediately above it in the periodic table (Table 5). On that basis, if the fourteen lanthanides had not occurred between Zr and Hf, the atomic radius of Hf^{4+} ion should have been greater than that of Zr^{4+} ion (which lies immediately above it) by about 0·2 Å. But the occurrence of lanthanide contraction of about the same order almost exactly cancels the expected increase. The result is that Hf^{4+} and Zr^{4+} ions have almost identical radii. Zirconium (Z = 40) and hafnium (Z = 72) have, therefore, almost identical chemical properties.

TABLE 5

Atomic (Covalent) Radii of Elements Preceding and Following the Lanthanides

21	22	23	24	25	26	27	28
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1·44	1·32	1·22	1·17	1·17	1·17	1·16	1·15
39	40	41	42	43	44	45	46
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
1·62	1·45	1·34	1·29	—	1·24	1·25	1·28
57 58 to 71	72	73	74	75	76	77	78
La	Hf	Ta	W	Re	Os	Ir	Pd
1·69	1·44	1·34	1·30	1·28	1·26	1·26	1·28

14 lanthanides

Similarly, as a result of lanthanide contraction, the atomic (covalent) radii of the elements which follow the lanthanides, *e.g.*, Hf, Ta, W, etc., are very similar to those of the elements of the previous row. This will be evident from Table 5.

It is seen that the normal increase in size from Sc → Y → La disappears after the lanthanides and the pairs of elements : Zr–Hf, Nb–Ta, Mo–W, etc., possess almost the same size. The properties of these pairs of elemens are also very similar.

It is thus *a direct consequence of lanthanide contraction that elements of the Second and Third transition series resemble each other much more closely than do the elements of the First and Second transition series.*

Cause of Lanthanide Contraction. The lanthanide contraction, although more pronounced, is similar to the contraction that was encountered in *d* block (transition) elements. The cause is also the same in both cases. As we move through the lanthanide series, 4*f* electrons are being added one at each step. The mutual shielding effect of *f* electrons is very litttle, being even smaller than that of *d* electrons. This is due to the shape of the *f* orbitals. The nuclear charge, however, increases by one at each step. Hence the inward pull experienced by the 4*f* electrons increases. This causes a reduction in the size of the entire $4f^n$ shell. The sum of the successive reductions gives the total lanthanide contraction.

It may be noted (Table 5) that the decrease in size, although continuous, is not regular. The decrease is much more in the case of the first 6 elements than in the case of subsequent elements. The properties of lanthanide compounds, accordingly, show some divergence from regularity.

4. Colour. Some of the trivalent ions of lanthanides are coloured in the solid state as well as in aqueous solution. These colours are shown in Table 6.

TABLE 6

Colour of Lanthanide Ions

Ion	Number of 4*f* electrons	Colour	Ion	Number of 4*f* electrons	Colour
La^{3+}	0	Colourless	Tb^{3+}	8	Pale pink
Ce^{3+}	1	Colourless	Dy^{3+}	9	Yellow
Pr^{3+}	2	Green	Ho^{3+}	10	Pale yellow
Nd^{3+}	3	Lilac	Er^{3+}	11	Pink
Pm^{3+}	4	Pink	Tm^{3+}	12	Pale green
Sm^{3+}	5	Yellow	Yb^{3+}	13	Colourless
Eu^{3+}	6	Pale pink	Lu^{3+}	14	Colourless
Gd^{3+}	7	Colourless			

The colour appears to depend upon the number of *f* electrons. The colour of ions containing *xf* electrons is about the same as those with (14–*x*) *f* electrons. This shows that the 4*f* orbitals are the main cause of colour. The absorption bands in the visible region of electronic spectra of rare earth ions in their compounds arise because of the absorption of light in the visible range resulting in the transition of the electrons of the ions from the lower energy *f* orbitals to the higher energy *f* orbitals. A rare earth ion thus appears to be of the colour which is complementary to the colour of the light absorbed. This type of *change* in the arrangement of *f* electrons due to absorption of light is called **f–f transition.**

A remarkable characteristic of the spectra of the tripositive lanthanide ions is the *sharpness of the individual bands*. Many of these bands are *linelike* and become even narrower as the temperature is lowered. This is, again, due to the fact that the electrons in the 4*f* orbitals are effectively shielded from the surroundings by the overlying electrons in the 5*s* and 5*p* orbitals of the rare earth ions and hence absorption bands arise merely from electronic transitions within the 4*f* level. Such transitions are more forbidden than the *d–d* transitions of the transition metal ions since 4*f* electrons of lanthanide ions are much less affected by the ligand electrons than the electrons in the *d* orbitals of transition metal ions in their complexes. Therefore, the selection rules are more strictly followed for transitions in the compounds of lanthanides than in the compounds of transition metals.

5. Magnetic Properties. The La^{3+}, Lu^{3+}, Ce^{4+} and Yb^{2+} ions which have $4f^0$ or $4f^{14}$ electronic configurations are *diamagnetic*. The rest of the trivalent lanthanide ions which contain unpaired electrons in the 4*f* orbitals are *paramagnetic*. The magnetic properties of the lanthanides are different from those of the transition elements. In general, the magnetic moments arise from two types of motion of electron. The spin motion of electron around its own axis produces magnetic moment called *spin magnetic moment* while the orbital motion of electron atound the nucleus produces magnetic moment called *orbital magnetic moment*. The observed magnetic properties of a substance are thus the result of both the spin magnetic moment and the orbital magnetic moment.

In the case of compounds of transition elements (*d* block elements), the *d* electrons of the metal ions interact strongly with the electrons of the ligands (atoms, ions or molecules) surrounding the metal ion. Due to the electric field of the ligands, the orbital motion of the electrons gets restricted and thereby the orbital magnetic moment of these electrons gets almost quenched. The magnetic moment of *d* block elements thus arises mainly from the contribution of spin motion of the electrons. The simple relationship based on the spin contribution of the electron, *viz.*,

$$\mu = \sqrt{n(n+2)}$$

where *n* is the number of unpaired electrons, roughly accounts for the magnetic properties of *d* block elements. However, *the above relationship is not valid in the case of f block elements*. In these elements, the 4*f* orbitals are well shielded from the surroundings by the overlying 5*s* and 5*p* subshells. As a result, the electric field of the ligands surrounding the ion does not restrict the orbital motion of the

electrons. Thus, orbital contribution, which was ignored in the case of *d* block elements, cannot be ignored in the case of *f* block elements. The magnetic moment in such cases is given by the relationship

$$\mu = g\sqrt{J(J+1)}$$

where J is the total angular momentum quantum number.

The few values of magnetic moment calculated by the above expression are seen to be in good agreement (with a few exceptions) with the experimental values (Table 7).

TABLE 7

Magnetic Moments (Theoretical and Experimental) of Tripositive Lanthanide Ions

Ion	Magnetic Moment		Ion	Magnetic Moment		Ion	Magnetic Moment	
	Experimental	Theoretical		Experimental	Theoretical		Experimental	Theoretical
La^{3+}	0	0	Sm^{3+}	1·4 – 1·7	0·84	Ho^{3+}	10·4 – 10·7	10·60
Ce^{3+}	2·3 – 2·5	2·54	Eu^{3+}	3·3 – 3·5	0	Er^{3+}	9·4 – 9·6	9·56
Pr^{3+}	3·4 – 3·6	3·58	Gd^{3+}	7·9 – 8·0	7·94	Tm^{3+}	7·1 – 7·5	7·56
Nd^{3+}	3·5 – 3·6	3·62	Tb^{3+}	9·5 – 9·8	9·72	Yb^{3+}	4·3 – 4·9	4·54
Pm^{3+}	—	2·68	Dy^{3+}	10·4 – 10·6	10·65	Lu^{3+}	0	0

The experimental magnetic moments of tripositive lanthanide ions are plotted in Fig. 1 against their respective atomic numbers. La^{3+} ion is diamagnetic ($\mu = 0$) because of its f^0 configuration. The value increases upto Nd^{3+} ion and then drops to 1·47 for Sm^{3+} ion. It starts rising again, becoming maximum for Dy^{3+} ion when it is about 11. It again starts dropping becoming zero for Lu^{3+} (f^{14} configuration) which is diamagnetic.

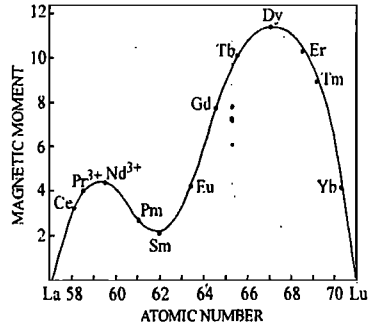


Fig. 1. Magnetic moments of tri-positive lanthanide ions.

6. Oxidation Potentials. The standard oxidation potentials of lanthanides for the half reaction

$$M(s) \longrightarrow M^{3+}(aq) + 3e^-$$

are given in Table 8.

TABLE 8

Standard Oxidation Potentials ($E°$)

[$M(s) \longrightarrow M^{3+}(aq) + 3e^-$]

Element	$E°$ (volts)	Element	$E°$ (volts)	Element	$E°$ (volts)	Element	$E°$ (volts)
La	2·52	Pm	2·42	Tb	2·39	Tm	2·27
Ce	2·48	Sm	2·41	Dy	2·35	Yb	2·28
Pr	2·47	Eu	2·41	Ho	2·32	Lu	2·25
Nd	2·44	Gd	2·40	Er	2·30		

The values are quite high and are in accord with their electropositive character. There is, however, a trend towards a *slight decrease in the oxidation potential (or electropositive character). This, evidently,* is consistent with the slight decrease in the ionic radius due to the lanthanide contraction.

7. Basic Character. All the lanthanides form trivalent ionic compounds. Their hydroxides, $M(OH)_3$, are ionic and basic in character. They are stronger bases than $Al(OH)_3$ but weaker than $Ca(OH)_2$. Since ionic size decreases from La^{3+} to Lu^{3+}, the basicity of hydroxides decreases in the same order. Thus, $La(OH)_3$ is the strongest and $Lu(OH)_3$ is the weakest base.

8. Solubility of Compounds. The nitrates, chlorides, sulphates, perchlorates and salts of oxoacids of the lanthanides are soluble while the oxalates, carbonates and fluorides are insoluble in water. This is just like the corresponding compounds of Group 2 elements. Lanthanide sulphates, however, unlike the sulphates of Group 2 elements, are soluble in water.

9. Double Salts. A number of double salts with the corresponding salts of Group 1 elements or of ammonia are known, *e.g.*, $Na_2SO_4.La_2(SO_4)_3.8H_2O$. *These double salts can be separated in the form of well-defined crystals from their aqueous solution. This helps in the separation of the lanthanides from* one another, as will be seen shortly.

Amongst the important double salts formed by lanthanides are :

(*i*) *Carbonates, e.g.,* $K_2CO_3.Ce_2(CO_3)_3.3H_2O$

(*ii*) *Nitrates, e.g.,* $3Mg(NO_3)_2.2R(NO_3)_3.24H_2O$

(*iii*) *Sulphates, e.g.,* $(NH_4)_2SO_4.R_2(SO_4)_3.8H_2O$, where R stands for a lanthanide element.

10. Chemical Reactivity. The lanthanides differ from one another only in the number of 4*f* electrons. Since these electrons are very effectively shielded from interaction with other elements by the overlying 5*s*, 5*p* and 6*s* electrons, *they show very little difference in their chemical reactivity.*

The lanthanides are highly reactive, silvery-white metals which tarnish readily on exposure to air. In finely divided state, they all burn in air giving the sesquioxide of the formula M_2O_3, except cerium which gives CeO_2. Ytterbium, however, resists the action of air even at 1000°C due to formation of a protective coating of its oxide.

The lanthanides combine with hydrogen. The reaction is exothermic. However, initial heating to 300°C is necessary to start the reaction. The heat of the reaction is sufficient to keep the reaction going thereafter. The resulting hydrides MH_2 and MH_3 are stable.

The lanthanides also react with other non-metals like halogens, sulphur, phosphorus, nitrogen, carbon and silicon forming corresponding compounds.

They decompose water evolving hydrogen slowly in cold but rapidly on heating.

They have strong electropositive character as indicated by their high oxidation potentials (Table 8).

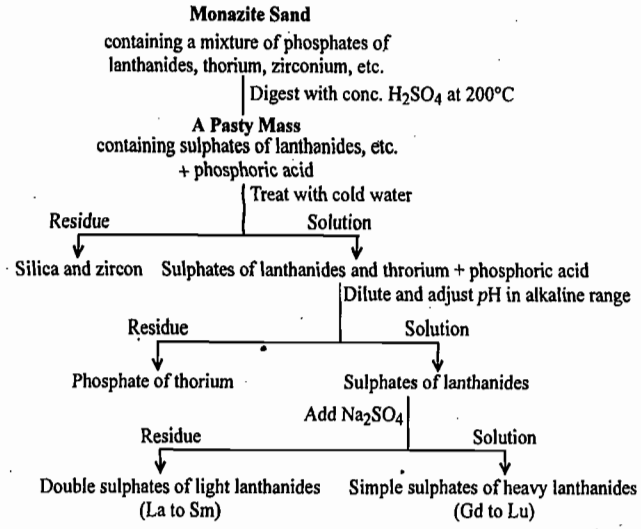
11. Complexes. Lanthanide ions, in spite of the high charge (+3), have low charge density because of their large size. They connot, therefore, cause much polarization and, consequently, they have only a weak tendency to form complexes. Their complexes with unidentate ligands are very few. However, complexes with a few chelating ligands such as β-diketones, oximes and ethylenediaminetertraacetic acid (EDTA) are fairly common. The lanthanides do not form complexes with π bonding ligands such as CO, NO, CNR, etc. The tendency to form complexes and their stability increases with increasing atomic number. Advantage is taken of this fact in their separation from one another.

Extraction of a Mixture of Lanthanides from Monazite Sand. Monazite sand is the best known mineral containing the lanthanide elements. It is essentially a mixture of phosphates, RPO_4 (where R stands for a lanthanide element) containing upto 12 per cent of thorium together with small amounts of zirconium, iron and titanium in the form of silicates. The mineral is digested with hot concentrated sulphuric acid at 200°C in the form of a paste when the phosphates change into the corresponding sulphates. The paste is separated by centrifugation and treated with cold water. The sulphates are more soluble in cold water than in hot water and, therefore, pass into solution. Silica (SiO_2), zircon ($ZrSiO_4$), etc., being insoluble, get eliminated. Thorium left in solution is removed as insoluble phosphate on diluting and adjusting the *p*H of the solution in the alkaline range.

The solutoin containing now only sulphates of the lanthanide elements is treated with sodium sulphate. This results in dividing the lanthanides into two groups. The light lanthanides (La to Sm) are thrown down as the double sulphates having variable composition while the heavier lanthanides (Gd to Lu) remain in solution (as simple sulphates). The precipitated double sulphates are treated with hot NaOH when they are converted into a mixture of oxides and hydroxides. The mixture is washed to remove sodium sulphate formed in the process and dried in air at 100°C. Cerium gets oxidised to cerium oxide,

CeO_2, during the drying process and, therefore, gets separated by itself. The method is summed up in the flow sheet.

The lanthanides are then separated from one another by various techniques as discussed below.



Separation of the Lanthanides

The properties of metal ions are determined by their size and charge. Since all the lanthanide ions are of about the same size and also carry the same charge, being typically trivalent, their properties are almost identical. The separation of lanthanides from one another, therefore, is as problematic as the separation of isotopes. Recently, methods based on *repeated fractional crystallisation, solvent extraction, fractional precipitation, ion exchange chromatography*. etc., which take advantage of slight differences of properties like solubility, complex ion formation and hydration, arising from very slight size differences of their trivalent ions, have been used. These methods are discussed below in brief.

1. Repeated Fractional Crystallisation. Formation of simple salts like nitrates, sulphates, bromates, oxalates as well as double salts like $2La(NO_3)_3.3Mg(NO_3)_2.24H_2O$, which form nice crystals, have been made use of in the separation of the lanthanide elements. Advantage is taken of slight differences in their solubilities in water.

2. Solvent Extraction. The partition coefficients of the salts of these metals between water and organic solvents are slightly different. To take an example, the partition coefficient of $Gd(NO_3)_3$ between water and normal butyl alcohol is 1·06 times greater than that of $La(NO_3)_3$. This means that $Gd(NO_3)_3$ can be separated from $La(NO_3)_3$ by continuous extraction with water from a solution of these salts in butyl alcohol.

3. Fractional Precipitation. If only a small amount of a precipitating agent is added to a mixture of lanthanide salts, the substance having the lowest solubility product will precipitate out first. Thus, if sodium hydroxide is added to a solution of lanthanide nitrates, $Lu(OH)_3$, which is the weakest base and has the lowest solubility product, is precipitated first while $La(OH)_3$, which has the highest solubility product, is precipitated last. A partial separation takes place in this manner. However, by redissolving the precipitate, the process can be repeated a number of times until complete separation is affected.

4. Change of Oxidation State. As already discussed, some of the lanthanides show +2 and +4 oxidation states in addition to the +3 oxidation state which is most characteristic of all the elements of the family. The properties of the M^{2+} and M^{4+} ions are different from those of the usual M^{3+} ions. To take an example, cerium can be separated from a mixture of trivalent ions of all other lanthanides by oxidising it to Ce^{4+} state by reacting it with alkaline $KMnO_4$. Now, Ce^{4+} ion has a greater charge than Ce^{3+} ion. Accordingly, it is smaller in size and, therefore, less basic and less soluble. It can be precipitated as $Ce(OH)_4$ by the addition of a small amount of an alkali leaving all the trivalent lanthanide ions in solution. It has been possible to have 99 percent pure cerium from a mixture containing only 40 per cent cerium by this method.

Europium can be separated from a mixture of trivalent lanthanide ions by reducing it first to the +2 oxidation state by means of zinc amalgam. Eu^{2+} ion can then be precipitated as $EuSO_4$ which is insoluble in water. The sulphates of all the trivalent lanthanides, on the other hand, are soluble in water.

5. Ion Exchange Chromatography. This is the most successful and the most rapid method for the separation of lanthanides. We shall first explain a few terms which are used frequently in the discussion of this technique. These terms are :

Cation exchange. Cation exchange is a chemical reaction in which free mobile cation of a solid (called ion exchanger) is exchanged for different ions of similar charge present in solution.

Cation exchanger. Cation exchanger is usually an insoluble solid, organic or inorganic, which contains cationic groups capable of undergoing exchage with other ions of similar charge present in solution. It has an open network structure. The open structure permits free entry and escape of the ions present in solution.

It has been well known that soils, clays and certain minerals such as zeolites, are able to exchage some of the cations they contain with other cations in solution. This property is also possessed by ***synthetic resins*** which are now widely used as ion exchangers. These are organic polymers with three-dimensional network to which ion exchange properties are imparted by attachment of ionic groups to the network. The cation exchange properties are imparted by the introduction of acid groups such as carboxylic (COOH), sulphonic (SO_3H) and phenolic (OH). In these resins, the hydrogen ions are mobile and exchangeable with other cations. The anions (*e.g.*, COO^-, SO_3^{2-} and O^{2-}) remain attached to the resin network. When such a resin is placed in a solution of a salt, some of the H^+ ions of the resin enter the solution and an equivalent quantity of the cations of salt get attached to the resin. The reaction with a trivalent lanthanide ion may be represented as

$$M^{3+} + 3H\text{-Resin} \rightleftharpoons M(\text{Resin})_3 + 3H^+$$

The reaction is reversible as represented above.

Cation exchange capacity. The capacity of an ion to undergo the exchange reaction depends upon the ***charge*** and the ***size*** of the hydrated ion in solution. Under similar conditions, the capacity increases with increase in the charge on the ion (*i.e.*, the valency of the ion) and decreases with increase in the size of the hydrated ion.

When hydrated ions of the same size are compared, it has been found that the ionic charge plays an important role in determinig their capacity to undergo the exchange reactions. According to this view, the capacity amongst cations decreases in the order :

$$Th^{4+} > Al^{3+} > Ca^{2+} > Na^+$$

For ions carrying the same charge, the size of the hydrated ions is more important. Thus, amongst the univalent cations, the capacity decreases in the order :

$$H^+ > Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+$$

Amongst the doubly charged cations, the capacity decreases in the order :

$$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+}$$

If the active ion in a resin is polyvalent and it is desired to exchange it by an ion of lower valency, the exchange is favoured invariably by using much higher concentration of the solution.

Efficiency of the resin. The ion exchange capacity of a resin determines the quality, *i.e.*, the efficiency of the resin for exchange process. This depends upon the total number of ion-active groups per unit mass of the material. The greater the number of the ion-active groups, the greater is the capacity of the resin for the exchange process. The efficiency of the resin also depends upon the degree of cross-linking ; the greater the cross-linking, the higher the efficiency of the resin.

The technique which is used for the separation of lanthanide ions with the help of cation exchangers is known as **cation exchange chromatography.** In this technique, the solution containing a mixture of lanthanide ions is passed through a column packed with particles of a suitable cation exchange resin. The cations in solution undergo exchange with the hydrogen or any other cation that may be present in the ion exchanger. The cation which has the maximum capacity to undergo the exchange process is held

near the top and the other cations are held further down the column in the order of their decreasing capacities to undergo the exchange reaction. Another solution containing a stronger exchanger such as H^+ ions, is then used as an ***eluent.*** The function of the eluent is to release the lanthanide ions held on the resin. Dilute hydrochloric acid is a good eluent in many cases. It is allowed to percolate slowly through the column. Hydrogen ions displace the other cations held on the resin.

$$M(\text{Resin})_3 + 3H^+ \longrightarrow 3H\text{-Resin} + M^{3+}$$

The eluate, *i.e.*, the liquid coming out from the bottom of the column, contains *first* the component (cation) which was *least firmly held* on the resin. It is followed by other components (cations) in the order of increasing strengths with which they are held by the resin. Thus, the eluate coming out *last* from the bottom of the column is that which was *most firmly held* by the resin.

In the case of lanthanides, the ionic radii of tripositive ions decrease with increasing atomic number (lanthanide contraction), *i.e.*, as we move from La to Lu. As the ionic size decreases, the degree of hydration increases and, therefore, the radii of *hydrated* lanthanide (III) ions *increase* with increasing atomic number. Consequently, the tenacity with which the cations are held by the anionic sites of the exchange resin decreases as we move from La to Lu. Hence, if the mixed tripositive lanthanides are held as a band at the top of cation exchange column and then eluted, say, with hydrochloric acid, the heavier members come out first and the lighter members come out last. Thus, out of a mixture of La^{3+}, Ho^{3+} and Lu^{3+} ions, for example, the Lu^{3+} ion emerges first and the La^{3+} ion comes out last from the bottom of the column. But, since in the lanthanides, the ionic sizes do not vary much, the separation by this technique is only partial.

In order to get a better separation, citrate solution is used (instead of HCl) as the eluent. In this case, complex anions are formed between the various lanthanide cations and the citrate ions. Generally, ammonium citrate buffer of *p*H 2·8 – 3·4 is used as the eluent. As the stability of such complexes increases with decreasing size of cations, it is evident that the stability of complex ions formed by the lanthanide (III) ions increases with increasing atomic number, *i.e.*, as we move from La^{3+} to Lu^{3+}. It may be noted that as soon as the citrate buffer is added, the lanthanide ions no longer remain hydrated and their radii decrease with increase in atomic number (lanthanide contraction). The greater stability of a complex enhances its preference for the aqueous phase. Hence, during elution with a citrate buffer solution, the Lu^{3+}-citrate complex ion having maximum stability and hence maximum preference for the aqueous mobile phase (eluent) comes out first while the La^{3+}-citrate complex having minimum stability and minimum preference for aqueous phase comes out last. A typical elution curve of lanthanide ions using buffered ammonium citrate solution as the eluent is shown in Fig. 2.

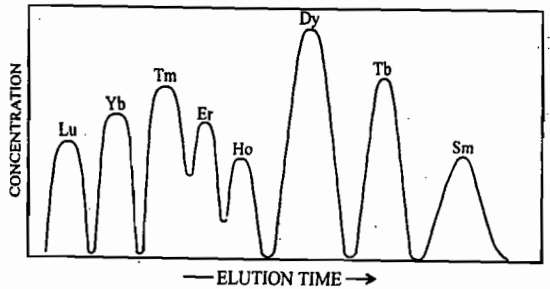


Fig.2. Separation of lanthanides by ion-exchange chromatography

6. By Complex Formation. Lanthanide oxalates are insoluble in water but they can be dissolved by complexing with ethylenediamineteraacetic acid (EDTA). These complexes differ in their stabilities towards acids. The least stable complex is destroyed first and changes to the oxalate while the most stable complex is destroyed last on the addition of an acid.

Production of Lanthanide Metals. The lanthanide metals can be produced by the following four methods :

1. Electrolysis of the fused chlorides. The method is similar to that used in the metallurgy of calcium.

2. Electrolysis of CeO_2 in fused CeF_2. This method is used in the production of cerium and is similar to the method employed in the metallurgy of aluminium.

3. **Reduction of anhydrous chlorides with sodium.** The reduction takes place at a high temperature above 1000°C. The method is used for the production of lighter lanthanides such as La, Ce and Ga.

4. **Reduction of anhydrous fluorides with magnesium.** The reduction in this case also takes place at temperature above 1000°C. The method is used in the production of heavier lanthanides because their fluorides are less volatile than the chlorides. The loss by evaporation is, therefore, small when fluorides are used instead of the chlorides.

Uses of Lanthanides. Lanthanides and their salts find important uses in industry and laboratory.

1. Steel mixed with La, Ce, Pr and Nd is used in the manufacture of flame throwing tanks.
2. Ce–Mg alloys are used for the manufacture of flash light powders.
3. Since cerium absorbs both heat and ultraviolet light, cerium glass is used in glare-reducing spectacles.
4. Oxides of cerium are used in gas mantles.
5. Cerium salts are used in qualitative analysis as well as for dyeing cotton. They are also used as catalysts.
6. Lanthanide salts have recently been used in lasers. Neodymium oxide dissolved in selenium oxochloride serves as a powerful liquid laser.

LANTHANUM

Lanthanum occurs alongwith cerium and neodymium, etc., as oxide in a Swedish mineral called *cerite*. It also occurs as $La_2(CO_3)_3.8H_2O$ in the mineral *lanthanite*. It is obtained in relatively pure state by reduction of its trichloride with calcium at 1000° C.

It is a silvery-white metal but gets tarnished on exposure to air. It is malleable and ductile and can be hammered into foils and drawn into wires. It burns easily to give the sesquioxide La_2O_3. It reacts with water, slowly in cold but rapidly on heating, liberating hydrogen in each case. This is due to its high oxidation potenitial (Table 8) and hence strong electropositive character.

Lanthanum reacts with hydrogen yielding the hydrides of composition LaH_2 and LaH_3. The reaction is exothermic but initial heating to 300–400° C is often required. The hydrides are highly stable even upto 900° C.

Lanthanum also reacts with several other non-metals including oxygen, halogens, sulphur, nitrogen, phosphorus, carbon, silicon, etc. When heated in oxygen, it burns energetically yielding the oxide La_2O_3. When heated in nitrogen or ammonia, it gives a black nitride, LaN, which is decomposed in water evolving ammonia. Thus, when heated in air, lanthanum gives a mixture of the oxide, La_2O_3 and the nitride, LaN.

Compounds of Lanthanum. Lanthanum exists in +3 oxidation state in most of its stable compounds. A few important compounds are considered below.

Lanthanum Oxide, La_2O_3. It is obtained as a snow-white powder by heating the carbonate or oxalate. When dropped in water, it changes into hydroxide evolving a large amount of heat. This behaviour is similar to that of lime.

It is sparingly soluble in water. It is basic in character and dissolves readily in dilute acids. It is used in the manufacture of the so-called 'Crookes' glass as it can absorb ultraviolet rays to some extent.

Lanthanum Halides, LaX_3. ***Lanthanum fluoride*** is obtained as a white gelatinous precipitate by adding hydrofluoric acid to a lanthanum salt solution. If the solution is allowed to stand for some time, the crystals of composition $LaF_3.3H_2O$ separate out. It is insoluble in dilute but soluble in concentrated mineral acids.

Lanthanum chloride is obtained as anhydrous $LaCl_3$ on heating a mixture of lanthanum oxide and carbon in a current of chlorine. It is a white deliquescent powder and is readily soluble in water. It crystallises out from aqueous solution as the heptahydrate, $LaCl_3.7H_2O$.

Lanthanum bromide and ***lanthanum iodide*** are also known and are prepared by similar methods.

Lanthanum Sulphate, $La_2(SO_4)_3$. It is prepared by reacting lanthanum oxide with dilute sulphuric acid. On adding a potassium salt to a solution of lanthanum sulphate, a double salt of composition, $La_2(SO_4)_3.3K_2SO_4.8H_2O$ separates out as white crystalline precipitate. Similar double sulphates with Na_2SO_4 and Li_2SO_4 can also be prepared. These are very sparingly soluble in water.

Anhydrous lanthanum sulphate is known as a white powder. It is hygroscopic, freely soluble in ice-cold water. On warming a concentrated solution, the sparingly soluble nonahydrate, $La_2(SO_4)_3.9H_2O$, separates out.

Lanthanum Nitrate, $La(NO_3)_3.6H_2O$. It is obtained by treating lanthanum oxide with dilute nitric acid. It separates out from water as the hexahydrate, $La(NO_3)_3.6H_2O$. It consists of large deliquescent prisms. The double salt, $La(NO_3)_3.2NH_4NO_3.4H_2O$, lanthanum ammonium nitrate, crystallises out from a concentrated solution of the two salts.

Lanthanum Carbonate, $La_2(CO_3)_3$. It occurs in nature as the mineral *lanthanite*, $La_2(CO_3)_3.8H_2O$. It is obtained as a white precipitate on adding ammonium carbonate to a solution of lanthanum nitrate. If excess of the reagent is added, the precipitate dissolves in it to some extent. When allowed to stand, crystals of lanthanum ammonium carbonate separate out.

THE ACTINIDE SERIES

Actinium ($Z = 89$) and the succeeding elements upto lawrencium ($Z = 103$), are called **actinides**. The outer electronic configuration of actinium is $5f^0 6d^1 7s^2$. In the succeeding fourteen elements, 14 electrons are successively added to the empty $5f$ subshell. Thus, just as in *lanthanides*, the antepenultimate $4f$ subshell is filled successively by the addition of one electron at a time, similarly, in *actinides*, the antepenultimate $5f$ subshell is filled successively by the addition of one electron at each step. Just as lanthanum is the prototype of the lanthanides, actinium is the prototype of the actinides. Lanthanides constitute the First Inner Transition Series while actinides constitute the Second Inner Transition Series. Since, in these elements, the number of electrons in the outermost as well as the penultimate shell remains the same, all the actinides resemble one another very closely.

Sources of Actinides. The chief source of thorium and uranium are the widely distributed thorium and uranium ores. Thorium is mostly obtained from monazite sands while uranium is mostly obtained from pitchblende and carnotite. Actinium and protactinium occur in all uranium ores as decay products of ^{235}U. None of the elements heavier than uranium occurs in nature.

TRANSURANIC ELEMENTS

During the last about 40 years, a number of elements beyond uranium, *i.e.*, beyond atomic number 92, have been prepared in the laboratory through nuclear reactions. These elements are known as **transuranic elements.** They are all *f* block elements.

Preparation of Transuranic Elements. It was found by Seaborg at the University of California that when ^{238}U is bombarded with neutrons of a certain critical velocity, one neutron is captured per atom of uranium giving rise to an element of a higher mass number.

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + \gamma \text{ rays}$$

This new isotope of uranium is much more radioactive than the natural uranium. It emits a beta particle and gives a new element of atomic number 93 which does not occur in nature. This element is named **neptunium.**

$$^{239}_{92}U \longrightarrow ^{239}_{93}\mathbf{Np} + ^{0}_{-1}e$$

Neptunium also is radioactive and emits a beta particle giving another new element of atomic number 94, known as **plutonium.**

$$^{239}_{93}Np \longrightarrow ^{239}_{94}\mathbf{Pu} + ^{0}_{-1}e$$

Actually three isotopes of plutonium with mass numbers 236, 238 and 239 are formed.

The next two elements, *viz.*, **americium** (At. No. 95) and **curium** (At. No. 96) were obtained by the bombardment of ^{238}U with alpha particles, as illustrated below.

$$^{238}_{92}U + ^{4}_{2}He \longrightarrow ^{241}_{94}Pu + ^{1}_{0}n$$

In fact, two isotopes of plutonium with mass numbers 241 and 239 are produced which undergo the following nuclear reactions :

$$^{241}_{94}Pu \longrightarrow ^{241}_{95}Am + ^{0}_{-1}e$$

$$^{239}_{94}Pu + ^{4}_{2}He \longrightarrow ^{242}_{96}Cm + ^{1}_{0}n$$

Californium (At. No. 98) was synthesised by the bombardment of curium with accelerated alpha particles. Two isotopes of the element are fomed.

$$^{242}_{96}Cm + ^{4}_{2}He \longrightarrow ^{246}_{98}Cf + \gamma \text{ rays}$$

$$^{242}_{96}Cm + ^{4}_{2}He \longrightarrow ^{244}_{98}Cf + 2^{1}_{0}n$$

Einsteinium (At. No. 99) was obtained by the bombardment of an isotope of californium (mass number 250) with neutrons. The californium isotope of mass number 253 obtained during the bombardment, yielded einsteinium as a result of β-ray emission, as illustrated below.

$$^{250}_{98}Cf + ^{1}_{0}n \longrightarrow ^{251}_{98}Cf + \gamma \text{ rays}$$

$$^{251}_{98}Cf + ^{1}_{0}n \longrightarrow ^{252}_{98}Cf + \gamma \text{ rays}$$

$$^{252}_{98}Cf + ^{1}_{0}n \longrightarrow ^{253}_{98}Cf + \gamma \text{ rays}$$

$$^{253}_{98}Cf \longrightarrow ^{253}_{99}Es + ^{0}_{-1}e$$

Fermium (At. No. 100) was obtained by the bombardment of einsteinium with neutrons when the isotope of einsteinium (mass number 254) formed during the process yielded fermium as a result of β-ray emission.

$$^{253}_{99}Es + ^{1}_{0}n \longrightarrow ^{254}_{99}Es + \gamma \text{ rays}$$

$$^{254}_{99}Es \longrightarrow ^{254}_{100}Fm + ^{0}_{-1}e$$

The next three elements, namely, **mendelevium** (At. No. 101), **nobelium** (At. No. 102) and **lawrencium** (At. No. 103) were also synthesised through nuclear reactions, as illustrated below :

$$^{253}_{99}Es + ^{4}_{2}He \longrightarrow ^{256}_{101}Md + ^{1}_{0}n$$

$$^{246}_{96}Cm + ^{12}_{6}C \longrightarrow ^{254}_{102}No + 4^{1}_{0}n$$

$$^{250}_{98}Cf + ^{11}_{5}B \longrightarrow ^{257}_{103}Lw + 4^{1}_{0}n$$

The transuranic elements obtained as above were separated from their respective target materials and the irradiated nuclear fuels by following certain specialised techniques such as ion exchange, solvent extraction, carrier precipitation, fluoride volatilization, etc. The discussion of these techniques is, however, beyond the scope of the book.

Electronic Configurations. There is some uncertainty with regard to outer electronic configurations of these elements. There is doubt whether thorium, protactinium and uranium contain any 5*f* electrons at all. It has been suggested that in these elemens the additional electrons enter the 6*d* subshell and not 5*f* subshell and that the entry into the 5*f* subshell begins only after uranium. According to this suggestion, the elements following uranium, in which the 5*f* subshell is definitely being filled, are called **urenides**. The uncertainty with respect to the entry of elctrons in 5*f* or 6*d* subshell is due to the fact that both these subshells are of almost equal energy. Not only this ; the nuclei of these elements are also unstable and

undergo radioactive decay. In some cases, the determinations have been extremely difficult on account of only miniute amounts of the elements that could be obtained for experimental purposes.

The probable electronic configurations of these elements, accepting the view that entry into 5*f* subshell begins with actinium, are given in Table 9. The general electronic configuration may be written as $[Rn]5f^{1-14}\,6d^{0-1}\,7s^2$. These configurations are even less certain than those given for the lanthanides in Table 2. The important oxidation states of the elements are also included in the table.

TABLE 9

Probable Electronic Configurations and Oxidation States of Actinides

Element	Symbol	Atomic number	Electronic configurations	Oxidation states*
Actinium	Ac	89	[Rn] $6d^1\,7s^1$	(+2), +3, (+4)
Thorium	Th	90	[Rn] $5f^1\,6d^1\,7s^2$	(+3), +4, (+5)
Protactinium	Pa	91	[Rn] $5f^2\,6d^1\,7s^2$	(+3), +4, +5, +6
Uranium	U	92	[Rn] $5f^3\,6d^1\,7s^2$	+3, +4, +5, +6
Neptunium	Np	93	[Rn] $5f^4\,6d^1\,7s^2$	+3, +4, +5, +6
Plutonium	Pu	94	[Rn] $5f^5\,6d^1\,7s^2$	+3, +4, +5, +6
Americium	Am	95	[Rn] $5f^7\,6d^0\,7s^2$	+3, (+4),
Curium	Cm	96	[Rn] $5f^7\,6d^1\,7s^2$	+3, (+4)
Berkeylium	Bk	97	[Rn] $5f^8\,6d^1\,7s^2$	+3, +4
Californium	Cf	98	[Rn] $5f^{10}\,6d^0\,7s^2$	+3
Einsteinium	Es	99	[Rn] $5f^{11}\,6d^0\,7s^2$	+3
Fermium	Fm	100	[Rn] $5f^{12}\,6d^0\,7s^2$	+3
Mendelevium	Md	101	[Rn] $5f^{13}\,6d^0\,7s^2$	+3
Nobelium	No	102	[Rn] $5f^{14}\,6d^0\,7s^2$	—
Lawrencium	Lr	103	[Rn] $5f^{14}\,6d^1\,7s^2$	—

* Less stable oxidation states are given in brackets.

Properties. All these elements are radioactive and are α-ray emitters. Thorium and uranium have sufficiently long half-life periods ($1{\cdot}39\times10^{10}$ years for ^{232}Th and $4{\cdot}50\times10^{9}$ years for ^{238}U) and this is the reason why they have been occurring in nature all the time. The half-life periods of the rest of the elements are shorter than the age of the earth (25×10^{9} years). Hence, the transuranic elements (*i.e*, urenides) do not occur in nature and have been prepared by artificial means using nuclear reactors. However, neptunium and plutonium have been isolated in traces from uranium minerals.

Some physical constants of the first seven members of the actinide series are given in Table 10.

TABLE 10

Some Physical Constants of Actinides

Element	Melting point (°C)	Boiling point (°C)	Heat of vaporisation (kJ mol^{-1})	Density at 25°C(g ml^{-1})
Actinium	1050	—	293	
Thorium	1750	3000-4200	544-740	11·72
Protactinium	1875	—	—	15·35
Uranium	1132	3818	—	19·04
Neptunium	640	—	—	20·45
Plutonium	639·5	3235	—	19·74
Americium	850–1200	2607	—	11·87

All the known actinides are silvery-white metals which are highly electropositive and reactive. They tarnish rapidly in air due to the formation of coating of oxides. Finely divided thorium burns spontaneously in air. The actinides react with most non-metals especially when heated.

They resist the attack of alkalies and are also less reactive towards acids. They form compounds which in aqueous solution give simple trivalent ions (hydrated) such as Ac^{3+}, U^{3+}, Np^{3+}, Pu^{3+}, Am^{3+}, etc. In this respect, the actinide elements resemble the lanthanide elements. The ions of actinide elements are paramagnetic like those of the lanthanides.

All the actinides, except thorium and americium, have high densities. They exhibit isomorphism.

Oxidation States. Actinides exhibit oxidation states of +2, +3, +4, +5 and +6. The +2 state is shown only by actinium and thorium in a few compounds, *e.g.*, $ThBr_2$, ThI_2, ThO and ThS. The +3 oxidation state is most common (as in lanthanides). This state is shown by all the actinide elements. The +3 oxidation state becomes more and more stable with increase in atomic number. The +4 oxidation state is shown by the first 8 elements (Ac to Cm) only. The +5 oxidation state is shown by five elements from Th to Pu whereas the +6 oxidation state is exhibited only by four elements (Pa to Pu).

The various oxidation states exhibited by the actinides are reproduced in Table 11.

TABLE 11

Oxidation States Exhibited by Actinides

Element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Er	Fm	Md
At. No.	89	90	91	92	93	94	95	96	97	98	99	100	101
Oxidation States	+2	+2											
	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4	+4					
		+5	+5	+5	+5	+5							
			+6	+6	+6	+6							

Ionic Radii of Actinide Elements. The ionic radii of the actinide elements decrease gradually as we move along the actinide series (Table 12). Thus, on going from Ac^{3+} to Cm^{3+} ion, the ionic radius decreases from 1·11 to 0·98Å. There is also a steady decrease in the radii of An^{4+} ions (An = actinide). This steady decrease in the ionic radii with increase in the positive charge of the nucleus is called **actinide contraction** and is analogous to lanthanide contraction. This contraction in ionic radii of An^{3+} and An^{4+} ions may be attributed to the addition of successive electrons to an inner *f* subshell (*i.e.*, 5*f*). Thus, at each step, the nuclear charge (*i.e.*, atomic number) increases which is not compensated due to poor shielding effect of the 5*f* electrons. Hence, as the atomic number increases, the inward pull experienced by the 5*f* electrons increases. Consequently, steady decrease in ionic radii occurs in actinide series.

TABLE 12

Ionic Radii of Actinides

Element	Atomic number	Ionic radius An^{3+} (Å)	Ionic radius An^{4+} (Å)
Ac	89	1·11	0·99
Th	90	1·08	0·96
Pa	91	1·05	0·93
U	92	1·03	0·92
Np	93	1·01	0·92
Pu	94	1·00	0·90
Am	95	0·99	0·89
Cm	96	0·98	0·88

Colours of Ions. Actinide ions are generally coloured. The appearance of colour depends upon the number of 5*f* electrons. The ions without 5*f* electrons (*i.e.*, fully filled 5*d* subshell and no 5*f* subshell) or seven 5*f* electrons (exactly half-filled *f* subshell) are colourless, as expected. The ions containing 2 to 6 electrons in the 5*f* subshell are coloured (Table 13). The colours arise out of electronic transitions between various energy states within the 5*f* subshell (***f–f* transitions**).

TABLE 13

Colours of Actinide Ions in Aqueous Solutions

Ion	Number of 5*f* electrons	Colour
Ac^{3+}	0	colourless
U^{3+}	3	red
Np^{3+}	4	blue
Pu^{3+}	5	violet
Am^{3+}	6	pink
Cm^{3+}	7	colourless
Th^{4+}	0	colourless
U^{4+}	2	green
Np^{4+}	3	yellowish-green
Pu^{4+}	4	yellowish-brown
Am^{4+}	5	pink
Cm^{4+}	6	pale yellow

Formation of Complexes. Actinides have greater tendency to form complexes in comparison to lanthanides. Most of the actinide halides form complex ions with alkali metal halides. Thorium tetrachloride, for instance, forms complexes such as $KThCl_5$ and K_2ThCl_6 with KCl. Thorium tetrachloride and tetrabromide also form complexes with pyridine. Of the chelates, those with EDTA and oxime are so well known.

Actinides can also form complexes with π bonding ligands such as alkyl phosphines, thioethers, etc.

Comparison with Lanthanides. Since in actinides also, the *f* subshell is being filled, hence these are also called *f* block elements, like the lanthanides. The two series of elements have a close relationship with each other. There are a number of *notable similarities* between them but there are also some *important differences*. The differences arise mainly because of lower binding energies of 5*f* electrons in actinides than those of 4*f* electrons in lanthanides. The 5*f* electrons also provide less effective shielding than the 4*f* electrons. They have much greater tendency to form complexes than the lanthanides.

The actinides, unlike lanthanides, show a variety of oxidation states, as shown in Table 11. Uranium, for example, shows oxidation states of +3, +4, +5 and +6 in many of its compounds. The U^{3+} ion in aqueous solution reduces water liberating hydrogen gas and gets itself oxidised to U^{4+} state. The latter is slowly oxidised by air to form UO_2^{2+} ion called the uranyl ion.

The dominant oxidation state in actinides, however, remains +3 as in lanthanides. The properties of actinides are very similar to those of lanthanides when both are in +3 state. However, for thorium and protactinium, the +3 oxidation state is unimportant. For these elements, +4 and +5 states, respectively, predominate. Thus, thorium resembles hafnium while protactinium resembles tantalum.

It may be noted that curium shows only +3 oxidiation state. This is due to stable configuration of the half-filled 5*f* subshell which is left after the removal of the two *s* and one *d* electron in the formation of cm^{3+} ion.

Most of the actinide ions, like the lanthanide ions, are coloured. Thus, U^{4+} is green, U^{3+} is red and UO_2^{2+} is yellow. Many of the actinide ions are paramagnetic.

Absorption spectra of actinides also consist of sharp lines like those of lanthanides. The reason is the same as given for the lanthanides.

THORIUM

Thorium was discovered in 1882 in a Norwegian mineral and was named after the Scandinavian god, Thorium. Its radioactive character was established by Madam Curie and Professor Schmidt in 1898.

Occurrence. Thorium constitutes nearly 0·0012 per cent of earth's crust and is about three times more abundant than uranium. The important minerals of thorium are : *thorianite* (thorium oxide), *thorite* (thorium silicate), *cheralite* (silicates and phosphates of Th, Ca and Ce) and *manazite* (phosphates of Ce, Y, La and Th).

Monazite sands constitute the most important source of thorium. These are found largely in Brazil, India, Sri Lanka, U.S.A, Canada and Australia. In India deposits of monazite are found on the sea coast of Kerala state.

Extraction of Thorium from Monazite. Indian monazite sand is of topmost grade in the world. Its chemical composition is as follows :

$$ThO_2 = 9{\cdot}4\%,\ CeO_2 = 28{\cdot}5\%,\ U_3O_8 = 0{\cdot}37\% \text{ and } P_2O_5 = 25{\cdot}9\%$$

Owing to the presence of rare earth impurities which in chemical properties resemble thorium, the extraction of thorium becomes quite difficult. The process of extraction involves the following steps.

1. Concentration and formation of thorium dioxide. The ore is freed from a major chunk of silicious impurities either by mechanical washing or by magnetic separation and is then treated with concentrated sulphuric acid in cast iron pans. The resultant pasty mass in added to cold water, stirred thoroughly and then allowed to stand. Impurities such as sillica and unattacked minerals settle down. The supernatant liquid which contains phosphates of thorium and rare earth elements, is syphoned off. The acid solution is partially neutralised by ammonia or alkali hydroxide or magnesia mixture when thorium, being more electropositive than the rare earths, gets precipitated as thorium phosphate alongwith comparatively smaller amounts of phosphates of rare earths. The precipitate is removed, dissolved in minimum quantity of acid and then neutralised as before to again precipitate the phosphate of thorium. The process is repeated several times and in this way the amount of phosphates of rare earths is reduced considerably.

The precipitate of thorium phosphate obtained as above is dissolved in nitric acid (about 6M) and treated with potassium iodate in the presence of hydrogen peroxide when thorium gets precipitated as thorium iodate. The rare earth phosphates remain in solution.

The precipitate of thorium iodate is dissolved in hydrochloric acid and reprecipitated as thorium oxalate to eliminate zirconium.

The thorium oxalate is then ignited to get thorium dioxide, ThO_2.

2. Preparation of thorium metal. The preparation of thorium from thorium dioxide is rather difficult because the metal is highly reactive in its molten state. The various methods employed for the recovery of the metal are briefly discussed below.

1. Thorium dioxide, obtained as above, is heated at 950°C with calcium in a steel bomb using calcium chloride as a flux.

$$ThO_2 + 2Ca \xrightarrow{950°C} 2CaO + Th$$

2. In another method, thorium dioxide is first converted into thorium chloride or thorium fluoride by heating with carbon is a current of chlorine or fluorine.

$$ThO_2 + 2C + 2Cl_2 \longrightarrow ThCl_4 + 2CO$$
$$ThO_2 + 2C + 2F_2 \longrightarrow ThF_4 + 2CO$$

The thorium chloride or fluoride is then reduced with electropositive metals such as Na, Ca and Mg.

$$ThCl_4 + 4Na \longrightarrow Th + 4NaCl$$
$$ThF_4 + 2Ca \longrightarrow Th + 2CaF_2$$

Zinc chloride is used as a flux during reduction with calcium.

3. Electrolytic method. In this method, metallic thorium is obtained by electrolysing a fused mixture of ThF_4–KCl–NaCl employing a lead cathode and a graphite anode. Electrolysis is carried out at a temperature of 800°C employing a current density of 70 amperes per kilogram of the electrolyte. Thorium is deposited as a powder on the cathode and is scraped off from time to time. The powder is washed with dilute nitric acid, dried and converted into ingots.

4. Pure thorium can also be obtained by heating the crude metal powder in iodine vapours to form volatile thorium iodide which is isolated and thermally decomposed on an incandescent filament at about 1100–1200°C to yield pure thorium.

$$\underset{\text{Crude}}{Th} + 2I_2 \longrightarrow ThI_4$$

$$ThI_4 \xrightarrow{1100-1200°C} \underset{\text{(Pure)}}{Th} + 2I_2$$

Properties. Thorium has a high melting point of 1750°C. It exists in amorphous as well as crystalline states. At very low temperatures it has super conductivity though at ordinary temperatures, the conductivity is very low.

Thorium undergoes transformation from a face centred cubic structure to a body centred cubic structure at about 1400°C. It forms many intermetallic compounds of the type $ThMn_2$, $ThMn_{1\cdot2}$, Th_7Co_3, Th_7Fe_3, ThNi, Th_2Cu, $ThCu_2$, etc.

When heated in air, it burns brilliantly with emission of sparks forming the dioxide.

$$Th + O_2 \longrightarrow ThO_2$$

The metal is fairly strongly electropositive in character. It resembles lanthanide metals in its chemical reactivity. Thus, when exposed to air, it gets tarnished. It is attacked by oxygen at 250°C, by nitrogen at 800°C and by water at its boiling point.

It combines with hydrogen vigorously when heated forming thorium hydride.

$$Th + 2H_2 \longrightarrow ThH_4$$

It is attacked only slowly by dilute hydrofluoric, nitric and sulphuric acids but not by dilute hydrochloric acid. It is, however, attacked slowly by concentrated hydrochloric acid. Hot and concentrated hydrochloric acid gives a black residue approximating to the composition $ThO_{1\cdot3}Cl_{0\cdot3}H_{1\cdot3}$. It is rendered passive when placed in strong nitric acid.

Thorium is radioactive and yields a series of disintegrtion products (Thorium series).

Uses. 1. The most important and strategic use of thorium is in the manufacture of fuel rods for atomic reactors.

2. Its oxide, ThO_2, finds wide application in the preparation of *incandescent gas mantles*. These mantles consist of a mixture of 99 per cent thorium oxide and 1 per cent cerium oxide. The small amount of cerium oxide is essential because otherwise thorium oxide itself gives only poor light.

3. Thorium salts find wide application as medicines in the treatment of cancer.

4. Thorium nitrate is used for the titration of flluorides using methyl red as the indicator.

COMPOUNDS OF THORIUM

Thorium commonly exhibits an oxidation state of +4 in its ionic and covalent compounds. An oxidation state of +2 is also exhibited in some of its compounds but this state is not so important chemically.

Oxides. Thorium forms only one stable oxide, *viz.*, the dioxide, ThO_2. Its high heat of formation (– 1226·5 kJ) speaks for its high stability.

It exists in amorphous as well a crystalline forms. The amorphous form is obtained by heating the metal in air or by igniting its nitrate. The crystalline form is obtained by heating the amorphous oxide with potassium orthophosphate. This may also be obtained by fusing thorium fluoride with sodium carbonate.

$$ThF_4 + 2Na_2CO_3 \longrightarrow ThO_2 + 2CO_2 + 4NaF$$

ThO_2 can also be obtained from monazite sand, as already discussed.

Thorium dioxide melts at 3000°C and boils at 4400°C. It is slightly soluble in water and dilute acids but readily soluble in hot concentrated sulphuric acid. It is highly refractory.

When heated strongly with boron and carbon, it forms the boride and the carbide, respectively.

Thoria (ThO_2) is used mainly in the preparation of gas mantles. It is also used as a refractory material as well as a catalyst in many organic reactions. It finds use in welding operations, in X-ray machines and also in medicines.

URANIUM

Uranium was discovered by Klaproth in 1789 in a specimen of pitchblende. Metallic uranium was prepared in 1840 by Peligot by the reduction of anhydrous uranium tetrachloride with potassium in a closed platinum crucible.

Occurrence. Uranium is widely distributed in a variety of rocks as well as in sea water. The latter contains about 2×10^{-6} g of uranium per litre. Important ores of uranium are *pitchblende* (or *uranite*) and *carnotite*. Other ores are : *fergusonite*, *samarskite*, *autosite* and *uronophane*.

Extraction of Uranium. The first step in the extraction of uranium is the isolation of pure uranium oxide from the ores.

1. Isolation of Uranium Oxide, U_3O_8, from Uranium Ores.

a. Uranium Oxide from Pitchblende. Uranium oxide from pitchblende ore is obtained by two processes.

First Process. The first process involves the following steps :

1. The ore is crushed to a fine powder and concentrated by gravity process.

2. The concentrated ore is roasted in a reverberatory furnace in the presence of excess air to remove sulphur, arsenic and other volatile impurities

3. The roasted ore which contains U_3O_8 is mixed with sodium carbonate and sodium nitrate and the whole mass is heated to fusion resulting in the formation of sodium uranate.

$$U_3O_8 + 3Na_2CO_3 + \underset{\text{(from } NaNO_3)}{\frac{1}{2}O_2} \longrightarrow 3Na_2UO_4 + 3CO_2$$

4. The fused mass is extracted with hot water and the solution is treated with an excess of ammonium carbonate when impurities such as aluminium, nickel, cobalt and manganese get precipitated as basic carbonates while uranium remains in solution as ammonium uranyl carbonate, $(NH_4)_4UO_2(CO_3)_3$.

5. The solution is neutralised with dilute sulphuric acid and evaporated to dryness when ammonium diuranate, $(NH_4)_2U_2O_7$, is obtained as a heavy yellow precipitate. On calcination, the diuranate yields uranium oxide, U_3O_8.

$$3(NH_4)_2U_2O_7 \longrightarrow 2U_3O_8 + 6NH_3 + 3H_2O + O_2$$

Alternatively, the roasted ore (after step 2) is heated with dilute sulphuric acid for about 16–24 hours in the presence of an oxidising agent, such as MnO_2. This oxidises the U_3O_8 present in the roasted ore to soluble uranyl sulphate, UO_2SO_4. When ammonium carbonate is added to the solution, ammonium uranyl carbonate, $(NH_4)_2UO_2(CO_3)_3$, is crystallised out which on ignition gives U_3O_8.

$$UO_2SO_4 + 3(NH_4)_2CO_3 \longrightarrow (NH_4)_4UO_2(CO_3)_3 + (NH_4)_2SO_4$$

$$3(NH_4)_4UO_2(CO_3)_3 \longrightarrow U_3O_8 + 9CO_2 + 12NH_3 + 6H_2O + O$$

Second Process. Klaproth's Process. In this process, the pitchblende ore is treated with nitric acid or aqua regia and the resulting solution is evaporated to dryness. The dry mass is then extracted with hydrochloric acid. The filtrate is then treated with nitric acid and neutralised with ammonium carbonate. On boiling this solution, uranium, zinc and cobalt get precipitated as oxides. The precipitate is again treated with hydrochloric acid when the oxides of zinc and cobalt get dissolved leaving behind the oxide of uranium which is insoluble in HCl.

b. Uranium Oxide from Carnotite Ore. Uranium oxide from the carnotite ore is obtained as follows.

The powdered mineral is fused with porassium bisulphate and the cold mass is extracted with water. The solution is subjected to crystallisation when crystals of double sulphates of vanadium and uranium are obtained. The crystals are treated first with zinc and sulphuric acid and then with ammonia and ammonium carbonate when all the vanadium present gets completely precipitated as carbonate which is removed by filtration. The filtrate containing ammonium diuranate is evaporated to dryness and then ignited to get the black oxide of uranium, U_3O_8.

2. Production of the Metal from the Oxide

From the black oxide of uranium, U_3O_8, the metal is obtained as follows.

1. The oxide is heated with charcoal or hydrogen when it is reduced to the uranium dioxide, UO_2. It cannot be reduced further to uranium on heating with hydrogen even at such a high temperature as 2500°C.

2. The dioxide is heated with chlorine when yellow crystalline uranyl chloride, UO_2Cl_2, is obtianed.

$$UO_2 + Cl_2 \longrightarrow \underset{\text{Uranyl chloride}}{UO_2Cl_2}$$

3. Uranyl chloride is heated with carbon while a stream of chlorine continues to pass. This results in the formation of uranium tetrachloride, UCl_4, which sublimes readily.

$$UO_2Cl_2 + Cl_2 \longrightarrow UCl_4 + O_2$$

4. Finally, the uranium tetrachloride is heated with sodium to get metallic uranium.

$$UCl_4 + 4Na \longrightarrow U + 4NaCl$$

Alternatively and more conveniently, uranium dioxide, UO_2, obtained as above is treated with hydrofluoric acid to get uranium tetrafluoride, UF_4, which is reduced by magnesium to get the metal.

$$UO_2 + 4HF \xrightarrow{\text{Heat}} UF_4 + 2H_2O$$

$$UF_4 + 2Mg \longrightarrow U + \underset{\text{Slag}}{2MgF_2}$$

Yet another method is to reduce the uranium dioxide, UO_2, by calcium hydride at 980°C or by aluminium (Goldschmidt process).

$$3UO_2 + 4Al \longrightarrow 3U + 2Al_2O_3$$

Physical properties. Uranium has a silvery-white lusture. It melts at 1132°C and is malleable and ductile. Its specific gravity is 19·05. It forms a wide range of intermetallic compounds such as U_6Mn, U_6Ni, USn_3, etc. It has several isotopes of which ^{235}U and ^{233}U are important for nuclear energy.

Chemical properties. Chemically, uranium is highly reactive. It easily gets tranished in moist air to form the oxide.

It burns in oxygen at 170°C with a brilliant flame forming U_3O_8.

It reacts with steam between 150–250°C to form a mixture of oxide and hydride.

$$7U + 6H_2O \longrightarrow 3UO_2 + 4UH_3$$

It dissolves readily in dilute hydrochloric acid. In nitric acid it dissolves at a moderate rate while in sulphuric acid and hydrofluoric acid, the rate of dissolution is very slow.

It does not react with alkalies.

It combines directly with halogens. It burns in fluorine forming green volatile tetrafluroide. It catches fire in chlorine at 180°C and in bromine at 240°C forming the corresponding halides. It reacts with iodine vapours at 260°C to form the tetraiodide, UI_4.

It reacts with hydrogen at 600°C under pressure to form the well defined hydride, UH_3.

Uses. 1. The most important use of uranium is in the production of nuclear energy by the process of nuclear fission.

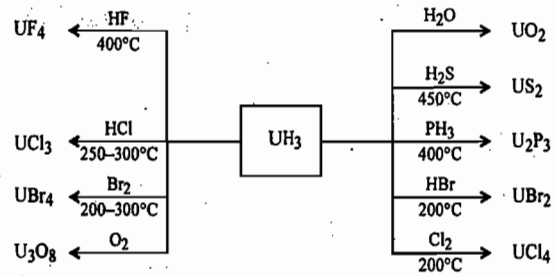
2. Uranium salts find use in textile industry, ceramic industry as well as in medicine.

COMPOUNDS OF URANIUM

Uranium forms a number of compounds in which the metal is in oxidation states of +2, +3, +4, +5 and +6. Compounds of tetravalent and hexavalent uranium are the most stable.

Some of the important compounds of uranium are described below.

Uranium Hydride, UH_3. The metal reacts with hydrogen at 500–600°C under 120 atm pressure to form uranium hydride which is a black powder. Like the metal it conducts electricity. Chemically it is very reactive and inflames in air. It is more suitable than the metal for the preparation of various other compounds of uranium, as shown :



Oxides. The well known oxides of uranium are UO_2, UO_3 and U_3O_8. The first is basic and forms uranous salts while UO_3 behaves as an acidic oxide.

The **dioxide, UO_2,** is obtained by the reduction of U_3O_8 with CO or by heating sodium-uranium hexachloride in a current of carbon dioxide and extracting the cooled product with water. It is black to reddish brown in colour, with a specific gravity varying from 6·94 to 10·82.

It forms uranous salts with acid radicals. It combines with chlorine at red heat forming uranyl chloride, UO_2Cl_2. It reduces silver nitrate to metallic silver.

$$4AgNO_3 + UO_2 \longrightarrow 2Ag_2O + U(NO_3)_4$$

$$U(NO_3)_4 + 2Ag_2O \longrightarrow UO_2(NO_3)_2 + 2Ag + 2AgNO_3$$

The **trioxide, UO_3**, is obtained :

1. By heating uranyl carbonate at 300°C

$$UO_2CO_3 \longrightarrow UO_3 + CO_2$$

2. By heating ammonium diuranate at 250°C for about 30 hours.

$$(NH_4)_2U_2O_7 \longrightarrow 2UO_3 + H_2O + 2NH_3$$

3. By heating uranyl nitrate at 250°C.

$$2UO_2(NO_3)_2 \longrightarrow 2UO_3 + 4NO_2 + O_2$$

UO_3 is an orange-yellow or brick-red powder, with a specific gravity of 1·29.

It is an amphoteric oxide dissolving in acids to form **uranyl salts** and in alkalies to form **uranates** and **diuranates**.

$$UO_3 + 2HCl \longrightarrow \underset{\text{Uranyl chloride}}{UO_2Cl_2} + H_2O$$

$$UO_3 + H_2SO_4 \longrightarrow \underset{\text{Uranyl sulphate}}{UO_2SO_4} + H_2O$$

$$UO_3 + 2NaOH \longrightarrow \underset{\text{Sodium uranate}}{Na_2UO_4} + H_2O$$

$$2UO_3 + 2NaOH \longrightarrow \underset{\text{Sodium diuranate}}{Na_2U_2O_7} + H_2O$$

The **oxide U_3O_8** is obtained from the trioxide by heating at 700°C.

$$3UO_3 \xrightarrow{700°C} U_3O_8 + 1/2\ O_2$$

All the oxides readily dissolve in nitric acid to give UO_2^{2+} salts. When heated with S_2Cl_2 at 450°C, all of them form UCl_4.

Uranates. Uranates are obtained by the fusion of uranium oxides with alkaline earth carbonates. These are orange or yellow in colour.

$$2UO_3 + Li_2CO_3 \longrightarrow Li_2U_2O_7 + CO_2$$

$$Li_2U_2O_7 + Li_2CO_3 \longrightarrow 2Li_2UO_4 + CO_2$$

$$Li_2UO_4 + Li_2CO_3 \longrightarrow Li_4UO_5 + CO_2$$

A very common uranate, ammonium diuranate, is obtained by the addition of aqueous ammonia to uranyl nitrate solution.

Uranium Halides. The halides of uranium are important for their role in the production of nuclear energy.

The well known **fluorides** are the trifluoride, the tetrafluoride and the hexafluoride

1. The trifluoride, UF_3, is obtained by the reduction of the tetrafluoride with aluminium.

$$3UF_4 + Al \xrightarrow{900°C} 3UF_3 + 2AlF_3$$

It is a non-volatile, green crystalline solid, insoluble in water as well as in dilute acids.

2. The tetrafluoride, UF_4, is obtained by heating UO_2 with HF at 400°C.

$$UO_2 + 4HF \xrightarrow{400°C} UF_4 + 2H_2O$$

It is a green, non-volatile, non-hygroscopic solid soluble in water.

3. The hexafluoride, UF_6, is the most important halide as it is used in the separation of ^{235}U from ^{238}U. It is obtained by the direct fluorination of uranium tetrafluoride.

$$UF_4 + F_2 \longrightarrow UF_6$$

It is a highly reactive fluorinating agent and reacts with most of the organic compounds yielding hydrogen fluoride, carbonised matter and either UO_2F_2 or UF_4. It is a colourless, volatile compound which forms uranyl fluoride (UO_2F_2) with water.

The other fluorides are U_2F_9 (black) and UF_5 (white blue).

Chlorides. The known chlorides are the trichloride, the tetrachloride and the hexachloride.

1. The trichloride, UCl_3, is obtained by heating the tetrachloride in dry hydrogen or nitrogen or ammonia.

It is a dark red, hygroscopic substance freely soluble in water.

2. The tetrachloride, UCl_4, is formed when uranium burns in chlorine. It is also prepared by passing dry chlorine through a mixture of U_3O_8 and carbon at red heat. It is the most stable of the chlorides. It is soluble in acetone and ethyl acetate but insoluble in benzene and chloroform.

3. The hexachloride, UCl_6, is a green, non-volatile solid and forms uranyl chloride with water. It is the most reactive of all the chlorides.

The only other chloride known is uranium pentachloride, UCl_5.

Bromides. The tribromide and the tetrabromide are the only known bromides.

The tribromide, UBr_3, is formed by distilling the tetrabromide in nitrogen. It forms dark brown, hygroscopic, needle-like crystals.

The tetrabromide, UBr_4, forms black or brown hygroscopic crystals which are hydrolysed by water.

Iodides. The only known iodide is UI_4 which is obtained when a mixture of iodine and uranium is heated in a sealed tube at 500°C. In moist air it is oxidised to oxoiodide, UO_2I_2.

Uranyl salts. These are the most important and stable salts of uranium in which uranium has a valency of six.

Uranyl nitrate, $UO_2(NO_3)_2.6H_2O$. It is the most common and stable compound of uranium. It is obtained by dissolving uranium trioxide in nitric acid. It forms yellow deliquescent crystals exhibiting green fluorescence. It is soluble in water and ether. It is the most important compound of uranium. It is used for the volumetric estimation of phosphates as it gives yellow precipitate of uranyl ammonium phosphate, $UO_2(NH_4)PO_4$ when mixed with a phosphate solution. The end point is detected by using potassium ferrocyanide as the external indicator. The colour changes to brown when uranyl nitrate is present even in slight excess.

Uranyl acetate, $UO_2(C_2H_3O_2)_2.2H_2O$. It is prepared by dissolving uranium trioxide in acetic acid. It is a yellow crystalline solid, soluble in water. It is used as a reagent for the estimation of phosphate in the same way as uranyl nitrate. It is also used for the detection of sodium which is precipitated as its double salt with zinc or magnesium having the formula $NaMg[UO_2(C_2H_3O_2)_3]_3.9H_2O$.

Uranyl sulphate. $UO_2SO_4.3H_2O$. It is obtained by the action of concentrated sulphuric acid on hydrated UO_3.

$$UO_3 + H_2SO_4 \longrightarrow UO_2SO_4 + H_2O$$

It is a yellow crystalline solid. It forms the hydrate $UO_2SO_4.3H_2O$.

PLUTONIUM

Plutonium, named after the planet Pluto, was discovered in 1940 at the University of California by Seaborg, MacMillan, Kennedy and Wahl. It is a man-made element of unique importance in chemical engineering and in the release of nuclear energy. Its numerous isotopes are all prepared synthetically. *Of these the fissionable isotope ^{239}Pu was discovered in 1941 by Kennedy and Seaborg.*

Occurrence. In nature it occurs in minute concentrations in uranium-bearing ores like *Canadian pitchblende* where it was first discovered in 1943. The isotope involved was ^{239}Pu. No other isotope has been detected to occur in nature. The other important ores of plutonium are *Colorado pitchblende, fergusonite* and *carnotite*.

Production of Plutonium. It is produced mainly from uranium in nuclear reactors. Natural uranium contains a large proportion of ^{238}U whereas ^{235}U is present only to the extent of 0·7%. The interaction of slow neutrons with ^{238}U present in natural uranium gives rise to plutonium as the end product in the following nuclear reactions :

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + \gamma \text{ rays}$$

$$^{239}_{92}U \longrightarrow ^{239}_{93}Np + \beta \text{ rays}$$

$$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + \beta \text{ rays}$$

Plutonium, being chemcally different from uranium, can be separated relatively easily. Plutonium undergoes nuclear fission in the same way as does ^{235}U thereby releasing a tremendous amount of energy. It is estimated that energy released by a gram of plutonium is equal to that released by about 30 tons of T.N.T. This forms the basis of the manufacture of **plutonium bomb**. The fission of plutonium can also be carried out in a controlled manner. The energy thus released is utilised for several peaceful purposes.

Properties. There are six allotropic forms of metallic plutonium below its melting point of 639°C. These are :

(*i*) α Pu (monoclinic), specific gravity 19·74.

(*ii*) β Pu (body centred monoclinic), specific gravity 17·65.

(*iii*) γ Pu (face centred orthorhombic), specific gravity 17·19.

(*iv*) δ Pu (face centred cubic), specific gravity 15·92.

(*v*) η Pu (face centred tetragonal), specific gravity 15·90.

(*vi*) ε Pu (body centred cubic), specific gravity 16·48.

It forms intermetallic compounds with Al, Be, Co, Fe, Mn, Ni and Ag. Examples are : $PuAl_2$, $PuAl_3$, $PuBe_3$, $PuCo_2$, $PuFe_2$, $PuMn_2$, $PuNi_2$, $PuNi_5$, Pu_2Ni_7, etc.

In aqueous solution it is similar to uranium and neptunium in having 4 oxidation states, *viz.*, +3, +4, +5, +6. The ions in aqueous solution possess characteristic colours ; Pu^{3+} is blue lavender, Pu^{4+} is yellowish brown, PuO_2^{2+} is pink-orange. No solution of pure PuO_2^{2+} has yet been prepared. The formation of complexes alters the colours of the ions and the aqueous ions formed are strongly paramagnetic.

Uses. 1. ^{239}Pu is mainly used for fuelling atomic reactors. The heat of radioactive decay is used for the generation of electricity.

2. It is used for the manufacture of plutonium bomb as also for the release of nuclear energy for peaceful purposes.

COMPOUNDS OF PLUTONIUM

Very few of the plutonium compounds are obtained from aqueous solutions. They are invariably the result of reactions in solid and gas phases.

Hydrides. These are prepared by the action of hydrogen on plutonium at 150 to 200°C. PuH_2 has the fluorite structure whereas PuH_3 has the hexagonal structure. They are of special importance because their thermal decomposition gives the metal in a finely divided state which, in turn, is a useful starting material for the preparation of many other compounds.

Oxides. PuO, Pu_2O_3, Pu_4O_7 and PuO_2 are the known oxides. Of these, PuO_2, plutonium dioxide, is the most stable and the most important. It was the first compound of the element to be isolated in the pure form. It is used as the starting material in the synthesis of other compounds of plutonium.

Halides. Excepting the tri-iodide, hexafluoride and oxofluoride, all other halides are prepared by halogenation of the dioxide or the oxalate of Pu^{3+} at a temperature of 700°C.

PuF_3 is obtained by the following reaction :

$$2PuO_2 + H_2 + 6HF \xrightarrow{500°C} 2PuF_3 + 4H_2O$$

PuF_4 is obtained by the addition of alkali fluoride to plutonium salts in +4 state. PuF_3 is obtained from PuF_4 by reaction with fluorine.

$$PuF_4 + F_2 \longrightarrow PuF_6$$

PuF_6 is quite unstable.

The tri-iodide, PuI_3, is obtained from the metal by reaction with hydriodic acid at 400°C. The tetrachloride and the tetrabromide have not been prepared in solid state.

All the trihalides are appreciably volatile at moderate temperatures. They are hygroscopic except for the trifluoride.

A few compounds of plutonium are prepared from the aqueous solutions by precipitation, evaporation or crystallisation procedures. Crystals of plutonium nitrate, $Pu(NO_3)_4 \cdot 5H_2O$, are obtained by slow evaporation in air of a concentrated solution of plutonium (V) nitrate in nitric acid. The chloride or sulphate is soluble in water.

A large number of chelate complexes of plutonium have also been prepared.

QUESTIONS

1. (*a*) What are *f* block elements ? Why are they so called ?
   (*b*) Discuss the electronic configurations and oxidation states of lanthanides.
2. (*a*) How do lanthanides occur in nautre ? Describe the procedures generally adopted for their separation.
   (*b*) Discuss the position of lanthanides in the periodic table.
   (*c*) Compare briefly the chemistry of elements of *d* block with those of *f* block.
3. (*a*) What are lanthanides ? Discuss their electronic structures and the similarity of their properties.
   (*b*) What is lanthanide contraction ? How would you account for it ? What are its important consequences ?
   (*c*) Why does lanthanum exhibit only +3 oxidation state whereas certain other elements of *f* block show +2 and +4 oxidation state also.
4. (*a*) Give the general electronic configuration of lanthanides. Explain
   (*i*) the filling of 4*f* subshell in th lanthanide series.
   (*ii*) the anomalous oxidation states of +2 and +4 shown by some elements in the series.
   (*b*) What are the problems in the separation of lanthanides from one another ? Discuss the ion exchange and solvent extraction methods for the separation of lanthanides.
5. (*a*) What are actinides ? Why are they so called ? Give their electronic configurations.
   (*b*) Write a brief note on the preparation of transuranic elements.
   (*c*) Actinides have greater tendency to form complexes than lanthanides. Explain.
6. (*a*) How does thorium occur in nature ? How is the metal extracted from monazite sand ?
   (*b*) How does thorium react with hydrogen and oxygen ?
   (*c*) List important uses of thorium.
7. (*a*) What are inner transition elements ? How are they classified further ?
   (*b*) Explain the following :
   (*i*) Filling of 4*f* sublevel is not regular in the lanthanide series.
   (*ii*) The +3 oxidation state is the characteristic oxidation state of lanthanides though their atoms contain only 2 ($6s^2$) outermost electrons.
8. (*a*) Why do the lanthanides form a closely knit group of similar chemical and physical properties ?
   (*b*) How is uranium extracted from its ores ?

9. (*a*) What are the important ores of uranium ? How is the metal extracted from pitchblende ?
   (*b*) Give important properites and uses of uranium ?
   (*c*) How is uranium trioxide prepared ? How does it react with acids and alkalies ?
   (*d*) How is U_3O_8 obtained from uranium trioxide ?
10. (*a*) In what ways are the observed oxidation states of lanthanides related to their electronic configurations ?
   (*b*) Compare and explain the relative tendencies of lanthanides and actinides to form complexes.
   (*c*) What is lanthanide contraction and what are its consequences ? Would you expect analogous actinide contraction ?
   (*d*) Discuss the use of uranium and plutonium as nuclear fuels.
11. (*a*) Discuss the chemistry of various steps involved in the extraction of thorium from monazite and of uranium from pitchblende.
   (*b*) Predict the number of unpaired electrons in the following ions : Ce^{4+}, Yb^{2+}, Eu^{2+}, Lu^{3+}
   (*c*) Write a brief note on the halides of uranium.
12. (*a*) Discuss the paramagnetic behaviour of *d* block and *f* block elements.
   (*b*) Account for the colour exhibited by the lanthanide compounds.
   (*c*) Describe briefly the various methods used for the separation of lanthanides. Which method, in your opinion, is preferable ?
13. Complete the following reactions :

   (*i*) $UO_3 + 2NaOH \longrightarrow$

   (*ii*) $UH_3 + Br_2 \xrightarrow{200\text{–}300°C}$

   (*iii*) $7U + 6H_2O \longrightarrow$

   (*iv*) $Th + 2C + 2Cl_2 \longrightarrow$

   (*v*) $ThCl_4 + Na \longrightarrow$

COORDINATION COMPOUNDS. PART I

WERNER'S THEORY, NOMENCLATURE, STEREOCHEMISTRY AND ISOMERISM

26

It is well known that when solutions containing two or more salts in stoichiometric (*i.e.*, simple molar) proportions are allowed to evaporate, crystals of new compounds separate out. These new compounds fall in two categories : (*i*) *Double Salts* and (*ii*) *Coordination Compounds.*

1. Double Salts. Double salts are *those compounds which exist only in crystal lattices but break down into their constituent compounds when dissolved in water or any other solvent.* Their physical and chemical properties remain essentially the same as those of the individual compounds. Some well known double salts are :

Mohr's salt	:	$FeSO_4.(NH_4)_2SO_4.6H_2O$
Potash alum	:	$Al_2(SO_4)_3.K_2SO_4.24H_2O$
Carnallite	:	$KCl.MgCl_2.6H_2O$

These compounds are stable in the solid state but when the lattice is disrupted on dissolution in water or any other solvent, they decompose into their individual components. Their solutions, therefore, have the same properties as a mixture of the individual components. For example, a solution of Mohr salt shows the same physical and chemical properties as a mixture of solutions of ferrous sulphate and ammonium sulphate.

2. Coordination Compounds. Coordination compounds are *those compounds which retain their identities even when dissolved in water or any other solvent and their properties are completely different from those of the constituents.* For example, when aqueous ammonia is added to green solution of nickel chloride, the colour changes to purple. The Ni^{2+} ions almost disappear from the solution. Ammonia enters into an intimate association with Ni^{2+} ion yielding a new ion of composition $[Ni(NH_3)_6]^{2+}$. Such an ion is called a **complex ion.** The solution, on evaporation, yields purple crystals of a compounds corresponding to the formula $[Ni(NH_3)_6]Cl_2$. Such a compound is called a **coordination** (or **complex**) **compound.** If the crystals are dissolved in water, there is no evidence for the existence of free Ni^{2+} ions or ammonia molecules. The properties of the complex compound are entirely different from those of free Ni^{2+} ions or ammonia. The compound ionises in solution as

$$[Ni(NH_3)_6]Cl_2 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 2Cl^-$$

and can be recovered as such on evaporating the solution.

The complex compounds formed by the association of one or more molecules of **ammonia** with metal cations are called **ammines.** These were amongst the earliest complex compounds discovered. A large number of complex compounds of different types are now known. For example, a precipitate of silver cyanide dissolves in a solution of potassium cyanide to give a soluble complex compound, $K[Ag(CN)_2]$.

$$AgCN + KCN \longrightarrow K[Ag(CN)_2]$$

This compound ionises in solution to give K^+ ion and the complex ion, $[Ag(CN)_2]^-$.

$$K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]^-$$

There is no evidence for free silver or cyanide ions as such in the solution. Some other common examples of coordination compounds are $[Co(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$, $[Pt(NH_3)_2Cl_4]$, etc.

A few more examples of coordination compounds which we come across in *qualitative analysis* may also be considered. A confirmatory test for the detection of copper (II) involves the formation of a deep blue colour on the addition of ammonia solution to a solution of copper (II) salt, say, $CuSO_4$. This is due to the formation of the complex ion, $[Cu(NH_3)_4]^{2+}$ which has intense blue colour.

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$

Copper ions in aqueous solution are actually extensively hydrated giving complex ions of composition $[Cu(H_2O)_4]^{2+}$. The addition of ammonia to such a solution, therefore, involves substitution of water molecules by ammonia molecules. It would be more correct to write the above chemical equation as

$$[Cu(H_2O)_4]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + 4H_2O$$

To take another example from qualitative analysis, consider the separation of silver chloride from the precipitate of AgCl, Hg_2Cl_2 and $PbCl_2$ formed in Group I of the scheme for the detection of basic radicals. We add aqueous ammonia solution to the precipitate when silver chloride dissolves due to the formation of the complex ion, $[Ag(NH_3)_2]^+$.

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$Ag^+ + 2NH_3 \rightleftharpoons \underset{\text{(Soluble)}}{[Ag(NH_3)_2]^+}$$

Mercurous chloride and lead chloride do not form complex ions and, therefore, they do not dissolve.

Sulphides of antimony, arsenic and tin are separated from the sulphides of the remaining elements of Group II of the scheme by adding a solution of yellow ammonium sulphide. The soluble complex ions formed in solution are $[SbS_4]^{3-}$, $[AsS_4]^{3-}$ and $[SnS_3]^{2-}$. The sulphides of other elements of this group do not form such complexes and, therefore, remain undissolved.

Definitions and Terminology

Coordination Complexes and Complex Ions. A **coordination complex** may be defined as *a compound that results from the combination of two or more stable chemical species and retains its identity in the solid as well as dissolved state.* A water-soluble coordination compound almost invariably contains a **complex ion.** Thus, $[Cu(NH_3)_4]SO_4$ contains the complex ion $[Cu(NH_3)_4]^{2+}$ while $K[Ag(CN)_2]$ contains the complex ion $[Ag(CN)_2]^-$, and so on. A **complex ion** may be defined as *an electrically charged ion which consists of a central metal atom or ion surrounded by a group of ions or neutral molecules.* For example, $[Ni(NH_3)_6]^{2+}$ is a complex ion in which the central nickel ion, Ni^{2+}, is surrounded by six ammonia molecules. Similarly, the complex ion $[PtCl_2(NH_3)_4]^{2+}$ consists of the central platinum ion, Pt^{4+}, surrounded by four ammonia molecules and two chloride ions. The complex ion may be positively charged as, for example, $[Co(NH_3)_6]^{3+}$ or negatively charged as, for example, $[Ag(CN)_2]^-$. Sometimes, the complex is a neutral species as well. The well known examples are $[CoCl_3(NH_3)_3]$ and $[PtCl_4(NH_3)_2]$ complexes.

Central Ion and Ligands. The *cation* to which one or more neutral molecules or ions are coordinated is called the **central ion** while the *molecules* or *ions* so attached are called **ligands.** Thus, in the complex ion, $[Ni(NH_3)_6]^{2+}$, the Ni^{2+} ion is the *central ion* and the molecules of ammonia are the *ligands.* Similarly, in the complex ion, $[Fe(CN)_6]^{3-}$, the Fe^{3+} ion is the *central ion* while the cyanide ions are the *ligands.*

The ligands are attached to the central metal ion through coordinate bonds. It is essential, therefore, that while the central ion should have vacant orbitals, the ligands should have lone pairs of electrons in their valence orbitals which can be donated to the central ion. The atom in the ligand which can donate the electron pair is called **donor atom** or **coordinating atom.** For example, in ammonia, nitrogen is the donor atom and in water, oxygen is the donor atom.

Coordination Number. As will be shown shortly, the ligands are attached to the central ion through coordinate bonds. The *total number of ligands attached to a central ion is called the* **coordination number** *of that ion.* For example, the coordination number of Ag^+ ion in $[Ag(CN)_2]^-$ is 2, the coordination number of Cu^{2+} ion in $[Cu(NH_3)_4]^{2+}$ is 4 whereas the coordination number of Co^{3+} ion in $[CoCl_3(NH_3)_3]$ is 6.

The most common coordination numbers exhibited by metal ions are 2, 4 and 6. However, in some cases coordination numbers 3, 5, 7, 8, 9 and 12 also occur.

Coordination Sphere. *The central ion together with molecules or ions coordinated to it constitute what is termed as* **coordination sphere.** It may be noted that in writing formulae of complex ions, the central ion along with its coordination sphere is written inside square brackets, [ ], as, for example, $[Ag(CN)_2]^-$.

Charge on a Complex Ion. *The charge carried by a complex ion is the algebraic sum of charges carried by the central ion and the ligands coordinated to it.* Thus, $[Cu(NH_3)_4]^{2+}$ carries a charge of +2 because Cu^{2+} ion carries a charge of +2 and ammonia molecule is neutral. Similarly, $[Fe(CN)_6]^{4-}$ carries a charge of −4 because Fe^{2+} ion has a charge of +2 and six CN^- ions carry together a charge of −6. The complex ion, $[CoCl(NH_3)_5]^{2+}$, carries a net charge of +2 because it is formed by the coordination of one Co^{3+} ion with five neutral molecules of ammonia and one Cl^- ion.

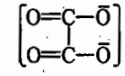
A coordination compound sometimes may not have any charge. For example, the complex $[CoCl_3(NH_3)_3]$ carries no charge because Co^{3+} ion carries a charge of +3, ammonia molecules are neutral and three Cl^- ions carry together a charge of −3.

Types of Ligands. A ligand contains one or more than one donor atoms for coordination with the central ion. Accordingly, various ligands may be classified as follows :

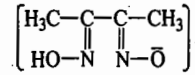
1. Unidentate or monodentate ligands. Ligands which donate only one pair of electrons and can thus coordinate to the central ion through only one atom, are known as **unidentate** or **monodentate ligands.** The common examples are

$$NH_3, H_2O, Cl^-, Br^-, CN^-, OH^-, NO_2^-, CO, \text{etc.}$$

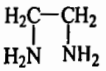
2. Bidentate ligands. Ligands which have two donor atoms and, therefore, have the tendency to attach to the central ion through two donor atoms are called **bidentate ligands.** The examples of bidentate ligands are :



Oxalate anion



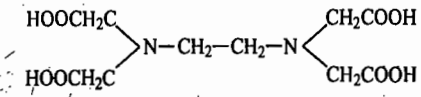
Dimethyl glyoximate anion



Ethylenediamine

3. Polydentate ligands. Ligands which coordinate with the central ion through more than two donor atoms present in the molecule are called **polydentate ligands.** These are called *tridentate* (three), *tetradentate* (four), *pentadentate* (five) and *hexadentate* (six) ligands depending upon the number of coordinating donor atoms present in their molecules.

Ethylene diamine tetraacetic acid (EDTA), for example, is an important *hexadentate* ligand. It binds through *two* nitrogen and *four* oxygen atoms of the four COOH groups to a central metal ion.



(see Table 1)

The various ligands which generally take part in the formation of complexes are shown in Table 1.

The structures of the ligands and their commonly used symbols are also given in this table.*

TABLE 1
Important Ligands Forming Complexes

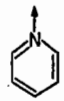
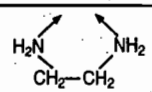
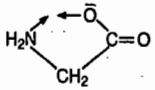
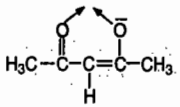
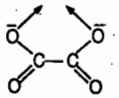
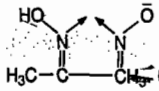
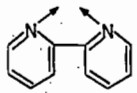
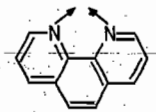
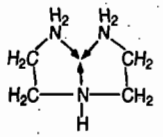
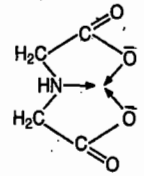
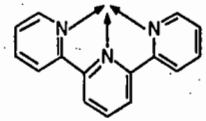
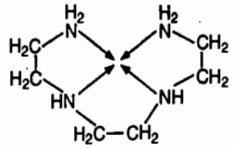
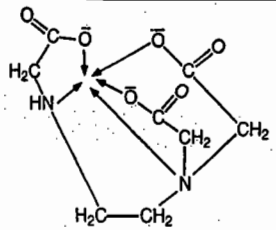
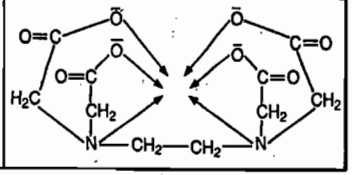
Type of Ligand	Name of Ligand	Symbol	Structure Showing only linkage sites (by ⟶) to metal ions
Unidentate	Water	aqua	
	Ammonia	ammine	
	Pyridine	py	
Bidentate	Ethylenediamine	en	
	Glycinate anion	gly	
	Acetylacetonate anion	acac	
	Oxalate anion	ox	
	Dimethylglyoximate anion	DMG	
	2, 2′ Dipyridyl	dipy	
	1, 10 Phenanthroline	phen	
Tridentate	Diethylene triamine	dien	

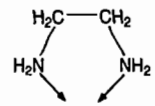
TABLE 1 (*Contd.*)

Type of Ligand	Name of Ligand	Symbol	Structure Showing linkage sites (by ⟶) to metal ions
Tridentate	Iminodiacetate anion	—	
	2, 2′, 2″ Terpyridine	tcry	
Tetradentate	Triethylene tetraamine	trien	
Pentadentate	Ethylenediamine triacetate anion	—	
Hexadentate	Ethylenediamine tetraacetate anion	EDTA	

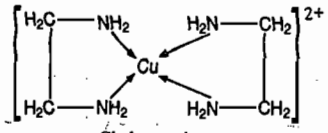
Note : The arrows in the above Table indicate the linkage sites only. These do not represent coordination bonds.

Chelating Ligands and Chelates. *When a bidenate or a polydentate ligand is attached through two or more donor atoms to the same central metal ion forming a* **ring structure,** the ligand is called **chelating ligand.** *The resulting complex is called a* **chelate.**

For example, when a bidentate ligand such as ethylenediamine coordinates through both the nitrogen atoms and results in the formation of a *ring structure,* it is called chelating ligand. The complex ion, $[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$ formed is thus a chelate cation, as illustrated below :

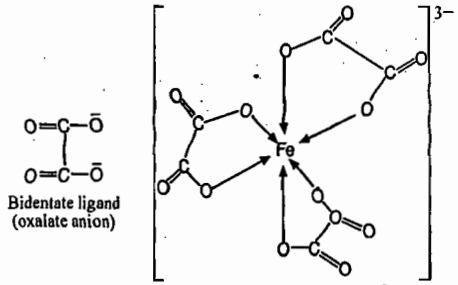


Bidentate ligand acting as chelating ligand.



Chelate cation

Similarly, oxalate anion acts as a chelating ligand in the formation of a chelate anion, $[Fe(C_2O_4)_3]^{3-}$, as shown below :



Chelate anion $[Fe(C_2O_4)_3]^{3-}$

Neutral chelates are also commonly known. Examples are $[Ni(DMG)_2]$ and $[Fe(acac)_3]$.

The chelating ligands form more stable complexes than the ordinary unidentate ligands.

The exact date of preparation of the first coordination compound is not exactly known. The discovery of hexaamminecobalt (III) chloride, $CoCl_3.6NH_3$, by Tassaert, in 1798, is generally regarded as the beginning of coordination chemistry. The formation of this orange coloured compound by Tassaert was quite intriguing in face of valency considerations. It was difficult for chemists to understand as to why two stable molecules such as $CoCl_3$ and NH_3 could combine to form another stable molecule. Later on, many such compounds were prepared and their properties studied.

Physical Methods Used in the Study of Complexes. Cryoscopic and electrical conductance measurements are used frequently in the study of complexes. By cryoscopic measurement (*i.e.,* by measuring depression in freezing point of aqueous solution of an ionic compound), it is possible to know the *number of particles, i.e., ionic species,* furnished by one molecule of the compound. NaCl, for example, gives nearly twice the depression in freezing point expected from unionised salt. This is because it dissociates to give Na^+ and Cl^- ions. Similarly, $BaCl_2$ and Na_2SO_4 give nearly three times while $AlCl_3$ and $LaCl_3$, if completely dissociated, give nearly four times the normal depression in freezing point.

Measurement of molar conductance, Λ_m, at large dilutions gives information with regard to the *number of electrical charges, i.e.,* the sum of the charges on positive and negative ions furnished by a molecule of the compound in aqueous solution. Thus, molar conductance of NaCl (2 charges : Na^+ and Cl^-) is 114 S m^2 mol^{-1} while that of $BaCl_2$ (4 charges : Ba^{2+} and $2Cl^-$) is 238 S m^2 mol^{-1} and that of $LaCl_3$ (6 charges : La^{3+} and $3Cl^-$) is 401 S m^2 mol^{-1}. We may take roughly 60 S m^2 mol^{-1} as the contribution of each charge towards molar conductance.

Knowing the number of particles from cryoscopic measurements and the number of charges furnished by a molecule of a complex compound from conductance measurements, it is possible to work out the structure of that complex compound. The conclusions arrived at in the case of different ammines of cobalt(III) are given in Table 2.

TABLE 2

Structures of Various Ammines of Co(III) determined by Cryoscopic and Conductance Measurements

Molecular formula of the complex compound	Number of particles (ionic or molecular) determined from cryoscopic measurements	Molar conductance Λ_m (S m^2 mol^{-1})	Number of electrical charges determined from Λ_m	Structure of the complex compound
1. $CoCl_3.6NH_3$	4	300	6	$[Co(NH_3)_6]^{3+}3Cl^-$
2. $CoCl_3.5NH_3$	3	262	4	$[CoCl(NH_3)_5]^{2+}2Cl^-$
3. $CoCl_3.4NH_3$	2	102	2	$[CoCl_2(NH_3)_4]^+Cl^-$

Similar observations and conclusions made in the case of ammines of platinum(IV) are given in Table 3.

TABLE 3

Structures of Various Ammines of Pt(IV) determined by Cryoscopic and Conductance Measurements

Molecular formula of the complex compound	Number of particles (ionic or molecular) determined from cryoscopic measurements	Molar conductance Λ_m (S m^2 mol^{-1})	Number of electrical charges determined from Λ_m	Structure of the complex compound
1. $PtCl_4.6NH_3$	5	524	8	$[Pt(NH_3)_6]^{4+}4Cl^-$
2. $PtCl_4.5NH_3$	4	404	6	$[PtCl(NH_3)_5]^{3+}3Cl^-$
3. $PtCl_4.4NH_3$	3	230	4	$[PtCl_2(NH_3)_4]^{2+}2Cl^-$
4. $PtCl_4.3NH_3$	2	97	2	$[PtCl_3(NH_3)_3]^+Cl^-$
5. $PtCl_4.2NH_3$	1	0	0	$[PtCl_4(NH_3)_2]$
6. $KPtCl_5.NH_3$	2	109	2	$K^+[PtCl_5(NH_3)]^-$
7. K_2PtCl_6	3	256	4	$K_2^+[PtCl_6]^{2-}$

The number of ions supplied by a complex compound can also be determined by **precipitation reactions**. For example, the number of chloride ions given by various ammines can be determined by the addition of silver nitrate. From the amount of silver chloride formed per mole of the complex compound, the number of chloride ions can be calculated. For example, when the coordination compound, $CoCl_3.6NH_3$ is treated with excess of silver nitrate, all the three chlorine atoms are precipitated as AgCl whereas when $CoCl_3.5NH_3$ is treated with excess of $AgNO_3$, only two chlorine atoms are precipitated. This means that in the first compound, all the three chlorine atoms behave as Cl^- ions whereas in the second case only two chlorine atoms behave as Cl^- ions. Similarly, the number of chloride ions which are precipitated in the case of $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ is found to be 1 and none, respectively. These observations support the structural formulae of these compounds as given in column 5 of Table 2.

The recent methods that are now employed for the study of complexes are based on spectroscopy, magnetic susceptibility, X-ray diffraction , etc.

WERNER'S COORDINATION THEORY

In 1823, Werner put forward his famous theory of coordination to explain the formation and structures of complex compounds. In recognition of his work in this field, he was awarded the Nobel Prize in chemistry. Werner is rightly called the father of coordination chemistry.

The **important postulates of Werner's coordination theory** are as follows :

1. In coordination compounds, the metal atoms exhibit two types of valency, *viz., the primary valency* and *the secondary valency.* The primary valency is ionizable and is non-directional whereas the secondary valency is non-ionizable and is directional. In modern terminology, the primary valency corresponds to *oxidation state* and the secondary valency corresponds to the *coordination number.*

2. Every metal atom has a fixed number of secondary valencies, *i.e.,* it has a fixed coordination number.

3. The metal atom tends to satisfy both its primary as well as secondary valencies. Primary valencies are satisfied by negative ions whereas secondary valencies are satisfied either by negative ions or by neutral molecules. In certain cases, a negative ion may satisfy both types of valencies.

4. The secondary valencies are always directed towards fixed positions in space and this leads to *definite geometry* of the coordination compound. For example, if a metal ion has six secondary valencies, these are arranged octahedrally around the central metal ion. If the metal ion has four secondary valencies, these are arranged in either tetrahedral or square planar arrangement around the central metal ion. The secondary valencies, thus, determine the **stereochemistry** of the complex. On the other hand, the primary valency is non-directional.

Let us try to explain the structures of various cobalt ammines on the basis of Werner's theory. In all these compounds, cobalt exhibits primary valency (oxidation state) of *three* and secondary valency (coordination number) of *six*. The secondary valencies are represented by thick lines and the primary

valencies by broken lines.

1. $CoCl_3.6NH_3$ Complex. In this compound, the coordination number of cobalt is 6 and all the 6 secondary valencies represented by solid lines are occupied by NH_3 molecules. The chloride ions are bonded to Co by three primary valencies. The primary valencies in this structure as well as in all subsequent structures are represented by dotted lines for convenience of understanding. These are non-directional in character. These chloride ions are instantaneously precipitated on the addition of silver nitrate. The total number of ions in this case is 4, three chloride ions and one complex ion, as indicated in column 4 of Table 2. The central ion and the neutral molecules or ions (ligands) satisfying secondary valencies are written in a square bracket while writing the formula of the complex compound. Thus, the complex may be formulated as $[Co(NH_3)_6]Cl_3$ and may be represented as shown in Fig. 1. The primary valencies, as already discussed, are ionizable and, therefore, all the chloride ions would get precipitated on the addition of silver nitrate.

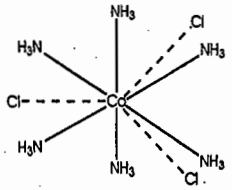


Fig. 1. Structure of $CoCl_3.6NH_3$ complex
Number of Cl^- ions precipitated = 3
Total number of ions = 4

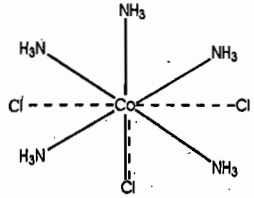


Fig. 2. Structure of $CoCl_3.5NH_3$ complex.
Number of Cl^- ions precipitated = 2.
Total number of ions = 3.

2. $CoCl_3.5NH_3$ Complex. In this compound, the coordination number of cobalt remains 6 but now five positions are occupied by NH_3 molecules and the sixth position by one of the chloride ions. This chloride ion exhibits a *dual behaviour* as it is held by a secondary as well as a primary valency. We have indicated here the secondary valency by full line and the primary valency by a broken line, as shown in Fig. 2. The full line in figures 1 to 4 signifies the direction of the metal–ligand bond whereas the broken line indicates an ionic bond which is non-directional.

This structure satisfies the 3 primary and 6 secondary valencies of cobalt. The addition of silver nitrate, however, will precipitate only two chloride ions which are linked by purely primary valencies. The total number of ions in this case is 3, two chloride ions and one complex ion, as indicated in Table 2.

Thus, the complex may be formulated by writing five ammonia molecules and one chloride ion inside the square brackets and two chloride ions outside the brackets, *i.e.*, as $[CoCl(NH_3)_5]Cl_2$.

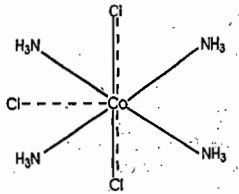


Fig. 3. Structure of $CoCl_3.4NH_3$ complex.
Number of Cl^- ions precipitated = 1
Total number of ions = 2

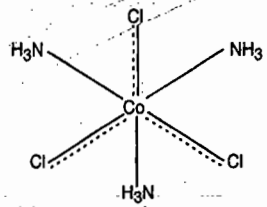


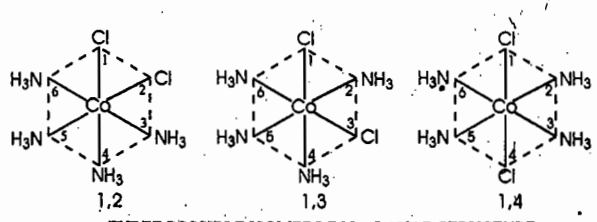
Fig. 4. Structure of $CoCl_3.3NH_3$ complex.
Number of Cl^- ions precipitated is nil.
It is a neutral molecule.

3. $CoCl_3.4NH_3$ Complex. In this compound, two chloride ions exhibit dual behaviour of satisfying both primary and secondary valencies. This is shown in Fig. 3. It will give precipitate with silver nitrate corresponding to only one Cl^- ion and the total number of ions in this case is 2, as indicated in Table 2. It may, therefore, be formulated as $[CoCl_2(NH_3)_4]Cl$.

4. $CoCl_3.3NH_3$ Complex. In this compound, three chloride ions satisfy primary as well as secondary valencies, as shown in Fig. 4. It is clear from the figure that no Cl^- ion will be precipitated on the addition of silver nitrate at room temperature. Therefore, the complex behaves as a neutral non-conducting molecule. It may be formulated as $[CoCl_3(NH_3)_3]$.

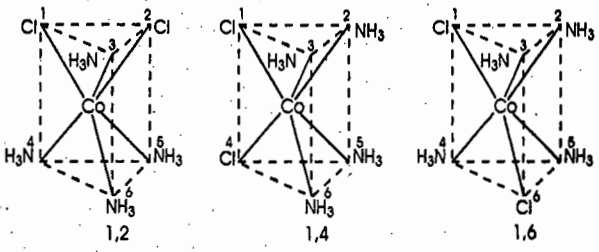
Werner also explained the structures of ammines of Pt^{4+}. In all these complexes, platinum exhibits a primary valency of *four* and secondary valency of *six*. The structures of these complexes are given in the last column of Table 3.

Werner's Theory and Isomerism. Werner examined complexes of a number of metals including cobalt, chromium, copper, silver, etc., in a similar way. He established the existence of definite coordination numbers of various cations. He then turned his attention towards the *geometrical arrangements* of the coordinated groups around the central cation and *explained successfully the cause of optical and geometrical isomerism of these compounds.* Some elementary discussion of this work is given below. It is to be noted that Werner did not have the advantage of sophisticated techniques based on X-ray diffraction and spectroscopy at that time. It required immense imaginative, hard and talented work by him and his team to arrive at correct conclusions.



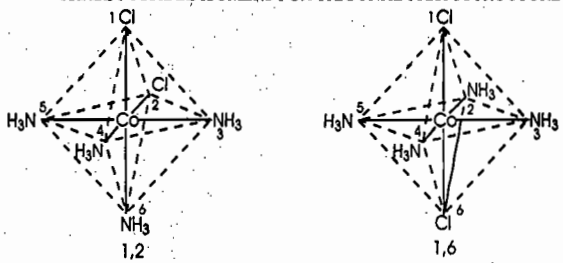
THREE POSSIBLE ISOMERS FOR PLANAR STRUCTURE

Consider the complex compound $[CoCl_2(NH_3)_4]Cl$. Werner argued that *theoretically three structures are possible* for this compound. These are *planar, trigonal prism* and *octahedral.* The number of possible isomers is 3 for planar, 3 for trigonal prism and 2 for octahedral structure, as shown in Fig. 5.



THREE POSSIBLE ISOMERS FOR TRIGONAL PRISM STRUCTURE

Since only *two isomers* of the compound could be isolated experimentally, the conclusion arrived at by Werner was that the geometrical arrangement of the coordinated groups around the central atom in this compound was *octahedral.* In the case of several other complexes in which the coordination number of the central atom was six, Werner was able to conclude that in all these cases the six-coordinated complexes have octahedral geometry.



TWO POSSIBLE ISOMERS FOR OCTAHEDRAL STRUCTURE

Fig. 5. Various possible isomers for planar, trigonal prism and octahedral structures of the complex ion $[CoCl_3(NH_3)_4]^+$.

He then studied the geometry of the complexes in which the coordination number of the central atom is 4. He argued that in such cases there are *two possible structures, viz., square planar* and *tetrahedral.*

Considering the complex compound of platinum, $[PtCl_2(NH_3)_2]$, in which the coordination number of the metal is 4, he found that it existed in two isomeric forms, *cis* and *trans*. This implies that all the four ligands lie in the same plane. The structure, therefore, should be square planar and the geometrical arrangement for *cis* and *trans* forms should be as represented in Fig. 6.

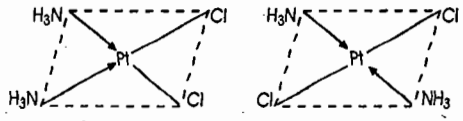


Fig. 6. Cis and trans forms of the complex $[Pt(NH_3)_2Cl_2]$.

Werner could actually isolate the two geometrical isomers. If the molecule had tetrahedral structure, only one geometrical isomer would have been possible.

However, certain complex compounds with four ligands around the central atom do have *tetrahedral structure.* In such cases only one geometrical isomer is possible. But, if this structure is *asymmetric* then it gives rise to *optical isomerism.* Accordingly, two optical isomers would be possible in a complex compound of the type MA_2B_2 as shown in Fig. 7.

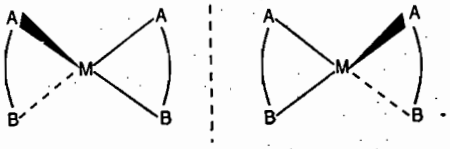


Fig. 7. Two optical isomers of the compound MA_2B_2.

Nomenclature of Coordination Compounds

The nomenclature of coordination compounds as recommended by the IUPAC (International Union of Pure and Applied Chemists), is given below.

Before discussing the nomenclature of coordination compounds let us explain how to write the formula of a complex compound. While writing the **formula of a coordination complex species**, the central atom is written first, anionic ligands are listed next which are followed by the neutral ligands. If there are more than one anionic ligands, they are listed in the alphabetical order according to the first symbols of their formulae (and not their names). An exactly similar procedure is followed if there are more than one neutral ligands. The polyatomic ligands are written in parentheses. Thus the complex, triamminebromochloroiodocobalt(III) is written as $[CoBrClI(NH_3)_3]$ according to the IUPAC nomenclature. and not as $[Co(NH_3)_3ClBrI]$.

The complicated organic ligands may be listed in the formula with their commonly accepted abbreviated names in parentheses. It should be remembered, however, that *their places in the formula are decided by the first symbols of their formulae* and not by the first letters of their common names. There should be no space between the cationic and anionic species while writing the formulae.

The complete formula of the coordination sphere is enclosed in a square bracket. The oxidation state of the metal in the coordination sphere may be written as a superscript in roman numeral if necessary.

The overall charge on the coordination species is written outside the square bracket as a superscript in which the number is written before the sign of the charge. Examples are : $[Fe(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$, etc.

The student should note that the procedure of writing the formula of a coordination complex species is different from the procedure of naming it. This would be clear from the ensuing discussion.

The following rules, as recommended by IUPAC, are applied for naming the coordination compounds.

1. Order of naming ions. In ionic coordination complexes, *the cation is named first and then the anion* (*cf.* compounds numbered 1–5, Table 4).

The non-ionic coordination complexes, *i.e.*, neutral complexes, however, are given a one-word name (*cf.* compounds numbered 6 and 7, Table 4).

2. Naming the coordination sphere. In naming the coordination sphere (whether it is constituted by cations, anions or neutral molecules), the ligands are named first and then the central metal ion.

3. Names of ligands. The names of negative ligands end in *o* and of positive ligands (which are rare) end in *ium*. The neutral ligands are named as such. This rule is illustrated in the brief list given below.

(*i*)	Negative Ligands	Names	Negative Ligands	Names	Negative Ligands	Names
	Cl^-	Chloro	F^-	Fluoro	Br^-	Bromo
	CN^-	Cyano	CH_3COO^-	Acetato	SO_4^{2-}	Sulphato or tetraoxosulphato
	COO^- | COO^-	Oxalato	CO_3^{2-}	Carbonato or trioxocarbonato	NO_2^-	Nitrito-N or dioxonitrato-N

(*i*)	Negative Ligands	Names	Negative Ligands	Names	Negative Ligands	Names
	ONO^-	Nitrito-O or dioxonitrato-O	NO_3^-	Nitrato or trioxonitrato	OH^-	Hydroxo
	NH_2^{2-}	Amido	NH^{2-}	Imido	SCN^-	Thiocyanato-S
	H^-	Hydrido	NCS^-	Thiocyanato-N	O_2^{2-}	Peroxo

(*ii*)	Positive Ligand	Name	Positive Ligand	Name	Positive Ligand	Name
	NO^+	Nitrosonium	NO_2^+	Nitronium	$NH_2NH_3^+$	Hydrazinium

(*iii*)	Neutral ligand	Name	Neutral Ligand	Name	Neutral Ligand	Name
	$H_2NCH_2CH_2NH_2$	Ethylenediamine	C_5H_5N	Pyridine	$(C_6H_5)_3P$	Triphenylphosphine

However, there are a few exceptions in naming neutral ligands. For example, H_2O, NH_3, NO and CO are named as below :

H_2O Aqua NO Nitrosyl NH_3 Ammine CO Carbonyl

4. Order of naming the ligands. According to the latest IUPAC convention, the ligands are named in the *alphabetical order* irrespective of their being neutral, negatively or positively charged. For example, to name the complex ion $[PtCl(NO_2)(NH_3)_4]^+$, the ligands are named in the order : ammine, chloro and nitrito-N.

Thus, the order of naming the ligands in coordination complexes is different from their listing in the formulae of coordination complexes.

5. Numerical prefixes to indicate the number of ligands. When more than one simple ligands (such as chloro, nitro, oxalato, etc.,) of a particular kind are present in the complex, the prefixes *di, tri, tetra, penta, hexa,* etc., are used to indicate their number. However, if the ligands have complex names such as ethylenediamine, triphenylphosphine, ethylenediaminetetra-acetato, etc., which themselves contain the affixes di, tri, etc., (or if writing di, tri, tetra, etc., before the names of ligands creates some ambiguity.), their numbers two, three, four, etc., are indicated by prefixes such as *bis, tris, tetrakis,* etc.

For example, to indicate two simple ligands such as chloro, bromo, ammine, etc., we use the prefix *di* but to indicate two complex ligands such as ethylenediamine, we use *bis*(ethylenediamine). It may be noted that the name of the complex ligand after the prefix bis, tris, tetrakis, etc., is given in parentheses. Similarly, two molecules of ethylamine coordinated to a metal will be named as *bis*(ethylamine) since writing them as diethylamine would create confusion because the latter may be taken to have an altogether different meaning. Likewise, $[Fe(NCCH_3)_6]Br_2$ should be named as *hexakis*(methylisocyanide)iron(II)bromide and not as hexa(methylisocyanide)iron(II)bromide.

6. Ending of names. When the complex is *anionic,* the name of the central metal atom ends in *ate.* For cationic and neutral complexes, the name of the metal is given without any characteristic ending. For example, the coordination compound $K[PtCl_5(NH_3)]$, which contains the anionic complex $[PtCl_5(NH_3)]^-$, is named as potassium amminepentachloroplatinate(IV). The coordination compound $Ca_2[Fe(CN)_6]$, which contains the anionic complex $[Fe(CN)_6]^{4-}$, is named as calcium hexacyanoferrate(II). The compound $[Fe(H_2O)_6]SO_4$, which contains the cationic complex $[Fe(H_2O)_6]^{2+}$, is named as hexaaqua iron(II) sulphate.

It may be noted that for anionic complexes, the Latin names of the metals are commonly used, as, for example, *cuperate* for Cu, *ferrate* for Fe, *argentate* for Ag, *stannate* for Sn, *aurate* for Au, etc.

7. Oxidation state of the central ion. The oxidation state of the central ion is designated by a Roman numeral (such as II, III, IV) in parentheses at the end of the name of the complex *without a space between the two.* To take a few examples,

$[PtCl(NO_2)(NH_3)_4]SO_4$ is named as tetramminechloronitrito-N platinum(IV) sulphate

$K_3[Al(C_2O_4)_3]$ is named as potassium trioxalatoaluminate(III)

$Na[Au(CN)_2]$ is named as sodium dicyanoaurate(I)

$K_4[Ni(CN)_4]$ is named as potassium tetracyanonickelate(II)

It may be noted that for zero oxidation state, the letter 0 is written in parentheses and for a negative oxidation state, the minus sign is used before the Roman numeral. Thus,

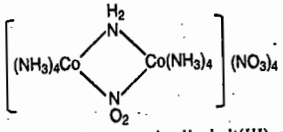
$[Fe(CO)_5]$ is named as penta carbonyl iron (0)

$Na[Co(CO)_4]$ is named as sodium tetracarbonylcobaltate(–I)

Alternately, the *charge on the whole coordination entity* is written in the Arabic numbers followed by the sign of the charge in paratheses. Thus, $[PtCl(NO_2)(NH_3)_4]SO_4$ may also be named as tetramminechloronitrito-N platinum(+2)sulphate and $Na[Au(CN)_2]$ may also be named as sodium dicyanoaurate (–1). This type of nomenclature has a special advantage where the oxidation state of the central atom is not unambiguously known.

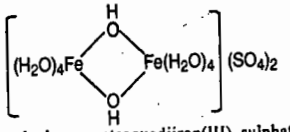
8. Bridging groups. For ligands which act as bridges between two metal atoms, the Greek letter μ is written before their names. The prefix μ is repeated before the name of each kind of bridging ligand. This may be illustrated by the following examples :

(*i*)



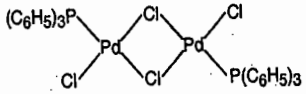
μ–amido–μ–nitrito–N tamminedicobalt(III) nitrate.
or μ–amido–μ (dioxonitrao–N) octaamminedicobalt(III) nitrate
or μ–amido–μ (nitrito–N) octoamminedicobalt(+3) nitrate.

(*ii*)



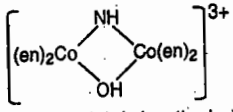
di–μ–hydroxo–octaaquadiiron(III) sulphate.
or di–μ–hydroxo–octaaquadiiron(+3) sulphate.

(*iii*)



di–μ–chloro–dichlorobis(triphenylphosphine)dipalladium(II)

(*iv*)



μ–hydroxo–μ–imido–tetrakis(ethylenediamine) dicobalt (+3) ion.

9. Points of attachment. If a ligand can coordinate through one or the other atom, then the point of attachment of the ligand is indicated by putting the symbol of the atom through which coordination occurs after the name of the ligand. For example, nitro group can coordinate either through N (written as NO_2^-) or through O (written as ONO^-). In such cases, different names are used for alternative modes of attachment, as, for example,

NO_2^- (through N) is called nitrito-N (previously called nitro)

ONO^- (through O) is called nitrito-O (previously called nitrito)

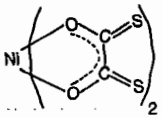
Similarly, thiocyanate ion can coordinate through S (written as SCN^-) or through N (written as NCS^-). For these, different names are used as shown below :

SCN^- : thiocyanato-S NCS^- : thiocyanato-N

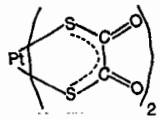
Accordingly, the names of some complexes containing these ligands are as follows :

$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrito-Ncobalt(III)
$[Co(NH_3)_5(ONO)]SO_4$	Pentaamminenitrito-Ocobalt(III) sulphate
$(NH_4)_2[Pt(SCN)_6]$	Ammonium hexathiocyanato-Splatinate(IV)
$(NH_4)_3[Cr(NCS)_6]$	Ammonium hexathiocyanato-Nchromate(III)

In the case of multidenate ligands in which only some of the atoms (not all) coordinate with the central atom, the complex formed is named in such a manner that the coordinating atoms are easily identified. The examples are :

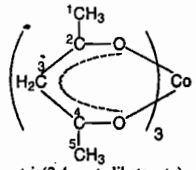


bis(dithiooxalato–O–O') nickel(II)



bis(dithiooxalato–S–S') platinum(II)

Sometimes it becomes necessary to identify the positions of coordinating atoms by numbering the atoms of the chelating ligands. Thus, $(acac)_3Co$ (where acac is acetylacetonate anion) can be named as tris(2,4 pentadiketonato) cobalt(III)



tris(2,4 pentadiketonato) cobalt(III)

Recently IUPAC has suggested the use of kappa (κ) convention to distinguish the actual coordinating atom/atoms in the ligands. Thus, $[Co(ONO)(NH_3)_5]^{2+}$ will be named as pentaamminenitrito-κ-O-cobalt(III) ion and $[Co(NCS)NH_3)_5]^{2+}$ will be named as pentaamminethiocyanato-κ-N-cobalt(III) ion.

Both the conventions discussed above to distinguish the coordinating atom/ atoms in bidentate or multidenate ligands, are, however, valid according to IUPAC.

10. Naming of geometrical isomers. Geometrical isomers are generally named by the use of terms **cis** to designate *adjacent positions* and **trans** to designate *opposite positions* of the ligands. For square planar complexes (*cf.* Fig. 8) for instance, the 1, 4 and 2, 3 positions are *cis* while 1, 3 and 2, 4 positions are *trans* with respect to each other. The student is quite familiar with this practice being followed in a variety of geometrical isomers encountered in organic chemistry.

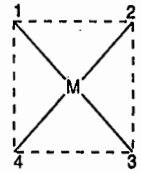


Fig. 8. *cis* and *trans* positions in a square planar complex.

11. Naming of optical isomers. Dextro and laevo rotatory optically active compounds are designated by (+) and (–) or by *d* and *l*, respectively. For example, dextrorotatory $K_3[Ir(C_2O_4)_3]$ is named as potassium(+)trioxalatoiridate(III) or potassium (*d*-) trioxalatoiridate(III). This is a familiar practice followed for differentiating between optical isomers amongst organic compounds.

12. Abbreviations for complicated molecules. For complicated molecules, abbreviations are generally used. Thus, for ethylendiamine, the abbreviation *en* is used ; for pyridine, *py* is used while for acetylacetanato *acac* is used. Thus, $[CoCl_2(NH_2CH_2CH_2NH_2)_2]_2SO_4$, is written as $[CoCl_2(en)_2]_2SO_4$.

Nomenclature of Polynuclear Complexes. The bridging ligands in polynuclear complexes are named first and the metal–metal bonds, if present, are given in paratheses after the names of polynuclear complexes. For example, the complex, $[CoCu_2Sn(CH_3)(\mu\text{-}C_2H_3O_2)_2(C_5H_5)]$ is named as di (μ-acetato) (cyclopentadienyl)(methyl)cobaltdicoppertin. Since all the ligands are organic compounds and since naming them without parentheses would have led to confusion, we have put each ligand in a parentheses.

Similarly, the complex $[Re_2Br_8]^{2-}$ or $[(ReBr_4)_2]^{2-}$ or $[Br_4ReReBr_4]^{2-}$ is named as bis(tetrabromorhenate) (Re–Re)(–2) or octabromodirhenate (Re–Re)(–2) and the complex $[Mn_2(CO)_{10}]$ or $[Mn(CO)_5]_2$ is named as bis (pentacarbonylmanganese) (Mn–Mn) or decacarbonyldimanganese (Mn–Mn).

The complex compound $[(NH_3)_4(H_2O)Cr\text{–}NH_2\text{–}Cr(NH_3)_4(H_2O)]Br_5$ is named as μ-amido-octaamminediaquadichromium(III)bromide.

The M–M bonds are indicated by italicized atomic symbols separated by a longer dash and are enclosed in parentheses placed after the names of central atoms but before the parentheses containing the ionic charge.

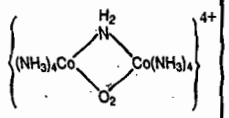
In order to illustrate further the use of the above nomenclature, the formulae and names of some typical coordination compounds are given in Table 4.

TABLE 4

Nomenclature of Some Typical Coordination compounds

Formula	Name
1. $[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
2. $[Co(CO_3)(NH_3)_4]Cl$	Tetraamminecarbonatocobalt(III) chloride
3. $K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
4. $[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
5. $Na_3[Co(NO_2)_6]$	Sodium hexanitrito-Ncobaltate(III)
6. $[PtCl_4(NH_3)_2]$	Diamminetetrachloroplatnium(IV)
7. $[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrito-Ncobalt(III)

Continued

8.	$[CoCl(ONO)(en)_2]^+$	Chlorobis(ethylenediammine)nitrito-Ocobalt(III)ion
9.	$[Ag(CN)_2]^-$	Dicyanoargentate(I)anion
10.	$[CoCl_2(en)_2]SO_4$	Dichlorobis(ethylenediamine)cobalt(III) sulphate
11.		μ-amido-μ-superoxo-octamminedicobalt(III) ion
*12.	$Na_2[CrOF_4]$	Sodium tetrafluoroxochromate(IV)
13.	$[Cu(NH_3)_4]SO_4$	Tetraamminecopper(II)sulphate
14.	$[Cr(H_2O)_6]Cl_3$	Hexaaquachromium(III) chloride
15.	$Na_2[SiF_6]$	Sodium hexafluorosilicate(IV)
16.	$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
17.	$[Pt(NH_3)_4][PtCl_4]$	Tetraammineplatinum(II)tetrachloroplatinate(II)
18.	$K_4[Mo(CN)_8]$	Potassium octacyanomolybdate(IV)
19.	$[PtCl_2(NH_3)_4][PtCl_4]$.	Tetraamminedichloroplatinum(IV)tetrachloroplatinate(II)
20.	$K_3[Fe(CN)_5NO]$	Potassium pentacyanonitrosylferrate(II) or potassium pentacyanonitrosylferrate (–3) (second name is better, why ?)
21.	$[PdI_2(NOO)_2(H_2O)_2]$	Diaquadiododinitrito-Npalladium(IV)
22.	$[Co(en)_3]_2(SO_4)_3$	Tris(ethylenediamine)*cobalt*(III) sulphate
23.	$[(NH_3)_5Co\text{-}NH_2\text{-}Co(NH_3)_4(H_2O)]Cl_5$	μ-amido-nonaammineaquadicobalt(III) chloride
24.	$Na_2[Ni(EDTA)]$	Sodium ethylenediaminetetraacetatonickelate(II)
25.	$K[BF_4]$	Potassium tetrafluoroborate(III)
26.	$[Cr(PPh_3)(CO)_5]$	Pentacarbonyltriphenylphosphinechromium(0)

*CrO^{2+}, CrO_2^{2+}, NbO^{3+}, TiO^{2+}, UO_2^{2+}, etc., exist as distinct cationic groups in many compounds. Therefore, O is always written alongwith the metal in the formulae of their coordination compounds.

Effective Atomic Number (EAN)**

In the formation of a complex, each ligand is considered to be donating one electron pair to the central metal ion. *The total number of electrons which the central metal ion appears to possess in the complex including those gained by it in bonding, is called the* **effective atomic number** *of the central metal ion.*

It was found that in many cases ligands are added until the central metal ion gets the same number of electrons as are present in the next noble gas. Accordingly, the effective atomic number in a complex should be equal to 36 (electrons in krypton), 54 (electrons in xenon) or 86 (electrons in radon).

To illustrate this, consider the complex ion, $[Co(NH_3)_6]^{3+}$. The atomic number of cobalt is 27. The number of electrons in Co^{3+} ion is 24. Each of the six ammonia molecules donates a pair of electrons so that EAN becomes $24 + 2 \times 6 = 36$. This is the same as the atomic number of krypton. Some other examples of complexes obeying the above rule are listed in Table 5.

TABLE 5

Complexes Obeying Effective Atomic Number Rule

Complex	Central metal ion	Atomic number of central metal	Number of electrons in metal ion	Electrons gained from ligands	EAN
$[Pt(NH_3)_6]^{4+}$	Pt^{4+}	78	74	12	86
$[Pt(NH_3)_5Cl]^{3+}$	Pt^{4+}	78	74	12	86
$[Pt(NH_3)_3Cl_3]^+$	Pt^{4+}	78	74	12	86
$[PtCl_6]^{2-}$	Pt^{4+}	78	74	12	86
$[Fe(CN)_6]^{4-}$	Fe^{2+}	26	24	12	36
$[Co(NH_3)_6]^{3+}$	Co^{3+}	27	24	12	36
$[Ni(CO)_4]$	Ni	28	28	8	36
$[Cu(CN)_4]^{3-}$	Cu^+	29	28	8	36

** The students are advised to refer to 18-electron rule also which is given in Chapter 34 on Organometallic Compounds.

However, many stable complexes are known in which the EAN is a few units above or below the number of electrons in the next noble gas. This is shown in Table 6.

TABLE 6

Complexes Not Obeying Effective Atomic Number Rule

Complex	Central metal ion	Atomic number of central metal	Number of electrons in metal ion	Electrons gained from ligands	EAN
$Pt(NH_3)_4]^{2+}$	Pt^{2+}	78	76	8	84
$[Ni(NH_3)_6]^{2+}$	Ni^{2+}	28	26	12	38
$[Fe(CN)_6]^{3-}$	Fe^{3+}	26	23	12	35
$[Cr(NH_3)_6]^{3+}$	Cr^{3+}	24	21	12	33

Stability of Complex Ions

Most of the complex ions are quite stable. However, they do dissociate, in aqueous solutions, to a slight extent, to establish an equilibrium with the central metal ion and the ligands from which they are derived. Thus, for example, in aqueous solution containing silver-ammonia complex ion, $[Ag(NH_3)_2]^+$, the following equilibrium exists :

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

The equilibrium constant, K, designated K_{dis} and given by the following expression,

$$K_{dis} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+}$$

is 6×10^{-8}. The shows that the degree of dissociation of the complex ion is extremely small. In other words, the complex ion is highly stable.

The above equilibrium constant is called the *dissociation constant* of the complex ion. Evidently, the smaller the value of the dissociation constant, the greater will be the stability of the complex. The *reciprocal of dissociation constant* is, therefore, called **stability constant** of the complex ion. The greater the value of the stability constant, the greater will be the stability of the complex ion, evidently.

The stability constant of the complex ion $[Ag(NH_3)_2]^+$ is the equilibrium constant of the reverse reaction, $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$. Accordingly,

$$K_{st} \text{ or } K = \frac{1}{K_{dis}} = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$$

The stability constant K of the complex ion $[Ag(NH_3)_2]^+$ is, thus, $1/(6\times10^{-8})=1{\cdot}67\times10^7$.

The dissociation constants and stability constants of some common complex ions are given in Table 7.

TABLE 7

Dissociation Constants and Stability Constants of Some Common Complex Ions

Complex ion equilibrium	Dissociation constant	Stability constant
$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$	$1{\cdot}0 \times 10^{-12}$	$1{\cdot}0 \times 10^{12}$
$[Co(NH_3)_6]^{3+} \rightleftharpoons Co^{3+} + 6NH_3$	$6{\cdot}2 \times 10^{-36}$	$1{\cdot}6 \times 10^{35}$
$[Ag(S_2O_3)_2]^{3-} \rightleftharpoons Ag^+ + 2S_2O_3^{2-}$	$6{\cdot}1 \times 10^{-14}$	$1{\cdot}6 \times 10^{13}$
$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$	$1{\cdot}8 \times 10^{-19}$	$5{\cdot}4 \times 10^{18}$
$[Hg(CN)_4]^{2-} \rightleftharpoons Hg^{2+} + 4CN^-$	$4{\cdot}0 \times 10^{-42}$	$2{\cdot}5 \times 10^{41}$
$[Fe(SCN)]^{2+} \rightleftharpoons Fe^{3+} + SCN^-$	$1{\cdot}0 \times 10^{-3}$	$1{\cdot}0 \times 10^3$

It follows from the values given in Table 7 that while $[Hg(CN)_4]^{2-}$ ion is the most stable, $[Fe(SCN)]^{2+}$ ion is the least stable of the various complex ions listed in Table 7.

Factors affecting the Stability of a Complex Ion. The stability of a complex ion depends to a large extent on : 1. *The nature of the central ion* 2. *The nature of the ligand* and 3. *The chelate effect.*

1. The nature of the central ion. In general, the greater the positive charge density, *i.e.*, charge/size ratio, also called ionic potential, on the central ion, the greater is the stability of its complexes. In other words, the greater the charge and the smaller the size of an ion, *i.e.*, the larger the charge/radius ratio of an ion), the greater is the stability of its complexes. For instance, Fe^{3+} ion carries a higher charge and has a smaller size than Fe^{2+} ion. Hence, positive charge density is higher on Fe^{3+} than on Fe^{2+} ion. The complexes of Fe^{3+} ion are, therefore, more stable. This is illustrated by the fact that while stability constant of $[Fe(CN)_6]^{3-}$ is about 10^{31}, that of $[Fe(CN)_6]^{4-}$ is only about 10^6.

Similarly, the stability constant of $[Co(CN)_6]^{3-}$ in aqueous medium, *viz.*, about 10^{64}, is much higher than the stability constant of $[Co(CN)_6]^{4-}$, *viz.*, about 10^{20}, as the former complex ion contains Co^{3+} and the latter contains Co^{2+}.

The order of stability of complexes of some of the ions carrying the same charge but differing in ionic radii also support the above view, in general :

Order of stability	Cu^{2+} >	Ni^{2+} >	Co^{2+} >	Fe^{2+} >	Mn^{2+}
Ionic radius (Å)	0·69	0·78	0·82	0·83	0·91

All these ions carry the same charge but the size increases as one moves from Cu^{2+} to Mn^{2+}. Hence, complexes of Cu^{2+} are most stable while those of Mn^{2+} are least stable.

Similar trends are observed for the stability constants of trivalent lanthanide complex ions in aqueous medium.

Electronegativity of the central ion also influences the stability of its complexes. The greater the electronegativity of the central ion, the greater is the stability of its complexes. This is because the bonding between a central ion and a ligand is due to the donation of electron pairs by the ligands. Hence, a strongly electron-attracting central ion will give stable complexes.

To sum up : The greater the positive charge density (*i.e.*, charge/size ratio) and the greater the electronegativity of the central ion, the greater is the stability of the complex formed by it.

Metal ions that are *hard acids* form more stable complexes with ligands containing coordinating N, O, F, etc., atoms and form comparatively less stable complexes with ligands containing coordinating P, S, Cl, etc., atoms. The metal ions that are *soft acids* form more stable complexes with ligands containing coordinating P, S, Cl, etc. atoms and comparatively less stable complexes with ligands containing coordinating N, O, F, etc., atoms.

Metal ions having large negative electrode potentials ($E^{\circ}_{M^{n+},M}$), such as Li^+, Ba^{2+}, Mg^{2+}, Al^{3+}, etc., have a lesser tendency to attract electrons and hence have more tendency to form complexes with ligands having highly electronegative atoms such as N, O, F, etc., so that the negative charge of the ligands remains mostly centred on the ligands. On the other hand, metal ions having large positive electrode potentials ($E^{\circ}_{M^{n+},M}$) such as Pd^{2+}, Pt^{2+}, etc., have greater tendency to accept electrons and thus form more stable complexes with ligands containing highly polarizable coordinating atoms such as P, S, Cl, etc. In such complexes, the electron charge of the ligand is easily polarised towards the complexed metal ion having positive electrode potential.

2. The nature of the ligand. In general, the more basic a ligand, the greater is the ease with which it can donate its lone pairs of electrons and, therefore, the greater is the stability of the complexes formed by it. Thus, CN^- and F^- ions and NH_3 molecules, which are strong bases, are good ligands to form stable complexes. For anionic ligands, the higher the charge and the smaller the size, the more stable is the complex formed. Thus, F^- ion gives more stable complexes than does Cl^- ion.

The nucleophilicity (*i.e.*, sigma electron pair donating capability), the pi accepting capacity, the dipole moment and the polarisability of negatively charged or neutral ligands are some other factors which determine the stabilities of complexes.

3. The chelate effect. The complexes containing chelate rings are known to be *more stable* than those containing similar but unidentate ligands. This effect is known as **chelate effect.**

The following stability constant data on the complexes of bivalent metal ions of the metals of the First transition series establish better stability of complexes containing chelating agent compared to the stability of their complexes with unidentate ligands.

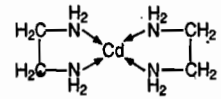
M stands for :	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
log *K* of $[M(NH_3)_4(H_2O)_2]^{2+}$	–	3·7	5·3	7·8	12·6
log *K* of $[M(en)_2(H_2O)_2]^{2+}$	4·9	7·7	10·9	14·5	20·2
log *K* of $[M(trien)(H_2O)_2]^{2+}$	5·8	8·8	12·8	14·7	20·6

Let us consider the formation of complexes from the hydrated cadmium ion $[Cd(H_2O)_4]^{2+}$ with methylamine and ethylenediamine (en) as the ligands, in aqueous medium :

(*i*) $[Cd(H_2O)_4]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+} + 4H_2O$

(*ii*) $[Cd(H_2O)_4]^{2+} + 2(en) \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O$

The complex formed by ethylenediamine is a chelate, as shown :



The stability constants of the complexes with CH_3NH_2 and ethylene diamine are known to be $3{\cdot}10\times10^6$ and $3{\cdot}2\times10^{10}$, respectively. It is clear that the chelate is 10,000 times more stable than the other complex. Let us see why it is so.

The value of ΔH° for both the above reactions (*i*) and (*ii*) is known to be practically the same, *viz.*, about –57 kJ. Thermodynamically, the stability of a species depends upon the value of ΔG° which should be large and negative. ΔG°, in turn, is equal to $\Delta H^{\circ} - T\Delta S^{\circ}$. The greater stability of $[Cd(en)_2]^{2+}$ complex than that of $[Cd(CH_3NH_2)_4]^{2+}$ complex should be due to its greater positive value of ΔS° since ΔH° is the same for both the reactions (*i*) and (*ii*).

In reaction (*i*), 4 molecules of CH_3NH_2 displace 4 molecules of H_2O coordinated to Cd^{2+} ion to form the complex ion $[Cd(CH_3NH_2)_4]^{2+}$ so that the number of molecules on the products side is the *same* as the number of molecules on the reactants side. As a consequence, there is very little change in the extent of randomness in going from reactants to products ; that is, ΔS° for the reaction is nearly zero. Therefore, for this reaction, the contribution of ΔS° to ΔG° is nearly zero so that $\Delta G^{\circ} \simeq \Delta H^{\circ} \simeq -57$ kJ. The driving force for reaction (*i*) thus comes mainly from the decrease in the enthalpy of the reaction.

In reaction (*ii*), two molecules of ethylenediamine displace four molecules of H_2O. There is thus release of two extra molecules resulting in an increase in the number of molecules on the products side and hence an increase in the disorder or entropy of the system. ΔS° is thus positive for this reaction. Consequently, ΔG° is equal to -57 kJ $- T\Delta S^{\circ}$. Evidently, ΔG° has a larger negative value. This accounts for the greater stability of the $[Cd(en)_2]^{2+}$ complex.

If, instead of the bidentate ethylenediamine ligand, we use the tetradentate triethylenetetramine (trien) ligand for the formation of the chelate, then one molecule of the ligand would displace 4 molecules of H_2O :

(*iii*) $[Cd(H_2O)_4]^{2+} + \text{trien} \rightleftharpoons [Cd(\text{trien})]^{2+} + 4H_2O$

Accordingly, there would be a release of *3 extra molecules* and hence a corresponding increase in the randomness or entropy of the system, *i.e.*, ΔS° would have a larger positive value. As a result, ΔG° would have a larger negative value. The complex formed would, therefore, be more stable than even the complex formed with ethylenediamine as the ligand. It follows from the above discussion that the larger the number of coordination centres on a ligand, the greater would be the stability of the chelate formed.

There are several cases where ΔH° for the formation of a chelate is positive but still the chelate is stable. It is so because ΔS° for the formation of such a chelate is so large and positive that $T\Delta S^{\circ}$ more than compensates the effect of positive ΔH° so that ΔG° ($= \Delta H^{\circ} - T\Delta S^{\circ}$) still remains negative. For instance, the value of ΔH° for the reaction

$$Ni[(en_2(H_2O)_2]^{2+} + \underset{\text{Tetradentate ligand}}{N(CH_2CH_2NH_2)_3} \rightleftharpoons \underset{\text{Chelate}}{Ni[N(CH_2CH_2NH_2)_3(H_2O)_2]} + 2en$$

is +13 kJ but $T\Delta S^{\circ}$ for the reaction is 23·7 kJ so that $\Delta G^{\circ} = -10{\cdot}7$ kJ. The complex, therefore, is stable.

An **alternative explanation** for the chelate effect is that after one end of the chelating agent attaches with the metal ion, the other end is very close and is in a better position to attack the metal ion than a free unidentate ligand moving in the solution at random. This renders the formation of the chelate much easier compared to the formation of the complex with the unidentate ligand, other conditions remaining the same.

It may be mentioned that steric factors and the size of the chelate ring are also important in determining the stability of a chelate complex. Thus, chelate complexes involving five-membered rings are highly stable whereas those involving six-membered rings are found to become stable when extended pi bonding electron delocalisation occurs. Complexes involving seven and eight-membered rings are quite unstable.

Determination of Stability of Complexes from Thermodynamic Data. Stabilities of complexes can be determined by evaluating their stability constants from thermodynamic data, as illustrated below.

Consider the formation of a complex (ML_n) *aq*, in aqueous medium, according to the reaction

$$[M(H_2O)_n]\,(aq) + n\,L\,(aq) \overset{K}{\rightleftharpoons} ML_n\,(aq) + nH_2O$$

and let ΔH be the enthalpy of this reaction (the charges on the species are not shown.)

The ligands are attached with the central metal ion, step by step, as shown below :

$$[M(H_2O)_n]\,(aq) + L\,(aq) \overset{K_1}{\rightleftharpoons} [M(H_2O)_{n-1}L]\,(aq) + H_2O\,; \quad \text{Enthalpy of reaction} = \Delta H_1$$

$$[M(H_2O)_{n-1}]\,(aq) + L\,(aq) \overset{K_2}{\rightleftharpoons} [M(H_2O)_{n-2}L_2]\,(aq) + H_2O\,; \quad \text{Enthalpy of reaction} = \Delta H_2$$

.....

.....

$$[M(H_2O)L_{n-1}]\,(aq) + L\,(aq) \overset{K_n}{\rightleftharpoons} [ML_n]\,(aq) + H_2O\,; \quad \text{Enthalpy of reaction} = \Delta H_n$$

Evidently, the enthalpy of the overall reaction, *viz.*, ΔH, would be the sum of the enthalpies ΔH_1, ΔH_2, etc., of the stepwise reactions and K would be equal to $K_1 K_2 K_3 \cdots\cdots K_n$, *i.e.*, the product of all the stepwise stability constants. The enthalpies of various reactions correspond to differences in bond energies of $M \leftarrow OH_2$ and $M \leftarrow L$ bonds. They also include differences in enthalpies of solvation of the complex species formed and the ligands.

We know from thermodynamics that

$$\Delta G^\circ = -RT \ln K \qquad \text{(van't Hoff reaction isotherm)} \qquad ...(1)$$

$$= -RT \ln K_1 K_2 \cdots\cdots K_n$$

where ΔG°, the standard free energy change of the reaction, measures the ease of the formation of the complex $[ML_n]$ (*aq*).

Further,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad ...(2)$$

where ΔS° is the standard entropy change of the reaction. From Eqs. 1 and 2,

$$\Delta H^\circ - T\Delta S^\circ = \Delta G^\circ = -RT \ln K = -2{\cdot}303\,RT \log K \qquad ...(3)$$

Thus, knowing the standard entropies and the standard enthalpies of the various species involved, log K and hence K can be evaluated. Thus, from the appropriate data, the values of K_1, K_2, K_3, etc., can be determined.

Consider, for instance, the log K values obtained as above, for the set of the following four reactions, taking place in aqueous medium :

$$[Cu(H_2O)_6]^{2+}\,(aq) + NH_3\,(aq) \overset{K_1}{\rightleftharpoons} [Cu(H_2O)_5NH_3]^{2+}\,(aq) + H_2O\,; \quad \log K_1 = 4{\cdot}3$$

$$[Cu(H_2O)_5NH_3]^{2+}\,(aq) + NH_3\,(aq) \overset{K_2}{\rightleftharpoons} [Cu(H_2O)_4(NH_3)_2]^{2+}\,(aq) + H_2O\,; \quad \log K_2 = 3{\cdot}6$$

$$[Cu(H_2O)_4(NH_3)_2]^{2+}\,(aq) + NH_3\,(aq) \overset{K_3}{\rightleftharpoons} [Cu(H_2O)_3(NH_3)_3]^{2+}\,(aq) + H_2O\,; \quad \log K_3 = 3{\cdot}0$$

$$[Cu(H_2O)_3(NH_3)_3]^{2+}\,(aq) + NH_3\,(aq) \overset{K_4}{\rightleftharpoons} [Cu(H_2O)_2(NH_3)_4]^{2+}\,(aq) + H_2O\,; \quad \log K_4 = 2{\cdot}3$$

The replacement of four molecules of water takes place in the normal way. The replacement of the fifth H_2O molecule is quite difficult and that of the sixth H_2O molecule cannot take place to any significant extent in aqueous medium. In fact, the complex $[Cu(NH_3)_6]^{2+}$ is formed only in non-aqueous liquid ammonia.

It readily follows from the log K values given above that $K_1 > K_2 > K_3 > K_4$ which means that the stability goes on decreasing from $[Cu(H_2O)_5NH_3]^{2+}$ to $[Cu(H_2O)_2(NH_3)_4]^{2+}$. This observation can be explained

as follows : In the complex $[Cu(H_2O)_6]^{2+}$, the ligand NH_3 can replace any of the *six* water molecules coordinated to Cu^{2+} ion whereas in $[Cu(H_2O)_5NH_3]^{2+}$, only *five* such replaceable sites are available which can be attacked by another NH_3 molecule to give $[Cu(H_2O)_4(NH_3)_2]^{2+}$. In the subsequent two complexes, there is further decrease in the number of attackable sites for NH_3 molecules. Thus, the ease of formation of $[Cu(H_2O)_5NH_3]^{2+}$, $[Cu(H_2O)_4(NH_3)_2]^{2+}$, $[Cu(H_2O)_3(NH_3)_3]^{2+}$ and $[Cu(H_2O)_2(NH_3)_4]^{2+}$ decreases in the order of their mention and so does their stability.

It has been established experimentally that the formation of certain complex species predominates within a given ligand concentration range. However, such ligand concentration ranges overlap with one another. It is only in very low and very high concentration ranges that a single complex species can be formed. Fig. 9 depicts qualitatively the plots of fractions of complexes of Cu^{2+} *vs* log[NH_3] for the first four steps involving replacement of H_2O molecules by NH_3 molecules, mentioned above. As can be seen, the plots overlap with one another.

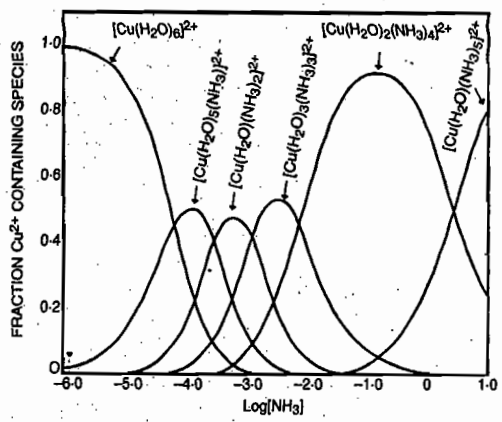


Fig. 9. The complex ions present in aqueous solutions containing Cu^{2+} and NH_3.

Apart from the statistical factor discussed as above, some other factors such as the change in the hybridisation of the orbitals of the metal ion, change in the state of spin of the metal ion, change in the geometry and the coordination number, etc., are also known to influence the stability of complexes. Sometimes, these factors even overweigh the statistical factor. Consider, for instance, the following set of reactions in aqueous medium:

$$[Fe(H_2O)_6]^{2+} + \text{bipyridyl} \overset{K_1}{\rightleftharpoons} [Fe(\text{bipyridyl})(H_2O)_4]^{2+} + 2H_2O$$

$$[Fe(\text{bipyridyl})(H_2O)_4]^{2+} + \text{bipyridyl} \overset{K_2}{\rightleftharpoons} [Fe(\text{bipyridyl})_2(H_2O)_2]^{2+} + 2H_2O$$

$$[Fe(\text{bipyridyl})_2(H_2O)_2]^{2+} + \text{bipyridyl} \overset{K_3}{\rightleftharpoons} [Fe(\text{bipyridyl})_3]^{2+} + 2H_2O$$

It has been experimentally observed that the order of stability constants is $K_1 > K_2 < K_3$ which is contrary to the order $K_1 > K_2 > K_3$ expected from statistical considerations alone. The reason is that while $[Fe(\text{bipyridyl})(H_2O)_4]^{2+}$ and $[Fe(\text{bipyridyl})_2(H_2O)_2]^{2+}$ are high spin complex ions having the $t_{2g}^4 e_g^2$ configuration with CFSE of 4 Dq, the complex ion $[Fe(\text{bipyridyl})_3]^{2+}$ is low spin having t_{2g}^6 configuration with CFSE of 24 Dq. This CFSE factor, which makes the complex ion $[Fe(\text{pyridyl})_3]^{2+}$ more stable than the other two products in the above set of reactions, overweighs the statistical factor.

Let us now consider the replacement of H_2O by Cl^- in the complex $[Hg(H_2O)_6]^{2+}$ in aqueous medium. This replacement reaction involves the following steps :

(*i*) $[Hg(H_2O)_6]^{2+}\,(aq) + Cl^- \overset{K_1}{\rightleftharpoons} [HgCl(H_2O)_5]^+\,(aq)$
Octahedral → Octahedral

(*ii*) $[HgCl(H_2O)_5]^+\,(aq) + Cl^- \overset{K_2}{\rightleftharpoons} [HgCl_2(H_2O)_4]\,(aq)$
Octahedral → Trans octahedral

(*iii*) $[HgCl_2(H_2O)_4]\,(aq) + Cl^- \overset{K_3}{\rightleftharpoons} [HgCl_3(H_2O)]^-\,(aq)$
Trans octahedral → Tetrahedral

(*iv*) $[Hg(Cl_3(H_2O)]^-\,(aq) + Cl^- \overset{K_4}{\rightleftharpoons} [HgCl_4]^{2-}\,(aq)$
Tetrahedral → Tetrahedral

As can be seen, in reactions (*iii*) and (*iv*), the coordination number of Hg reduces from 6 to 4. This may be explained as follows :

The covalent radius of oxygen atom is much smaller than the ionic radius of chloride ion. Therefore, there is room for the coordination of 6 molecules of H_2O through the smaller-sized oxygen atoms. There is room to accommodate one or two Cl^- ions also in place of H_2O molecules so that the coordination number of Hg in reactions (*i*) and (*ii*) is 6. However, with more than two bigger-sized Cl^- ions as ligands the coordination number of Hg reduces to 4 due to steric effects as also due to electrostatic repulsive interactions amongst the negatively charged Cl^- ions. The chloro complexes of many other bivalent transition metal ions show similar behaviour.

The experimentally observed order of stability constants in the above reactions is $K_1 > K_2 >>> K_3 > K_4$. The much higher stability of $[HgCl_2(H_2O)_4]$ compared to that of $[HgCl_3(H_2O)]^-$ cannot be explained on the basis of statistical factor alone. Nevertheless, we can clearly observe that the coordination number of Hg^{2+} ion, the hybridisation of Hg orbitals and the geometry of the two complex ions are different. It follows, therefore, that probably all the above mentioned factors alongwith the statistical factor are responsible for relatively much higher stability of $[HgCl_2(H_2O)_4]$ compared to that of $[HgCl_3(H_2O)]^-$.

Irving William Series

A plot of log K for octahedral high spin complexes of some bivalent metal ions of the First transition series formed with oxalate anion ligand is shown in Fig. 10. Similar plots are obtained for ligands other than oxalate anion as well.

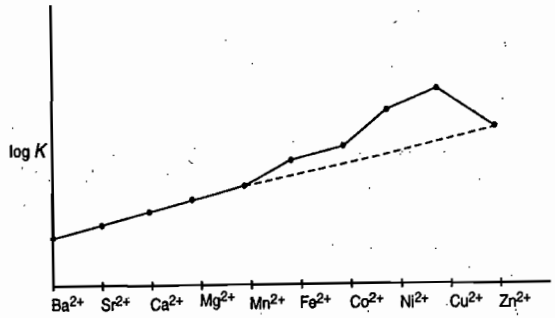


Fig. 10. Plot of log K for bivalent metal ions of Irving William Series

The metal ions Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} have also been included in the series because of their relevance in the present discussion. As can be seen from Fig. 10, the values of log K for complexes of the bivalent ions increase in the order :

$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The above series is known as **Irving William Series.**

The log K values, which reflect the stability of metal–ligand bonds, inceases regularly from Ba^{2+} to Mg^{2+} because the polarising power (*i.e.*, charge/size ratio) for these cations also increases in the order $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$. There is a sharp increase in log K values *beyond* Mn^{2+} for Fe^{2+} (d^6), Co^{2+} (d^7), Ni^{2+} (d^8) and Cu^{2+} (d^9) ions. This is due to the fact that the octahedral complexes of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} are additionally stabilised by CFSEs.

The stability of octahedral complexes of Zn^{2+}, where CFSE is zero, is obviously less than that of octahedral complex of Cu^{2+} and falls on the line representing the stabilities of the octahedral complexes of Ba^{2+}, Ca^{2+}, Mg^{2+} and Mn^{2+} where also CFSEs are zero (Fig. 10).

As can be seen from the plot, the log K of Cu^{2+} complex is higher than that of Ni^{2+} complex although CFSE of Cu^{2+} (d^9) is less than that of Ni^{2+} (d^8). The extra stability of the Cu^{2+} complex is provided by Jahn-Tellar effect. (cf. Chapter 29).

Experimental Determination of Stability Constants. The stability constants of complexes can be determined by conventional methods as also by modern techniques.

In cases where the rate of reaction is slow, as, for example, in the reaction

$$[Co(NH_3)_5Cl]^{2+} + H_2O \underset{}{\overset{K}{\rightleftharpoons}} [Co(NH_3)_5(H_2O)]^{3+} + Cl^-; \qquad (K \approx 10^{-5} \text{ at } 25°C)$$

the concentration of Cl^- can be determined by titration against $AgNO_3$ solution. Knowing the initial concentration of $[Co(NH_3)_5Cl]^{2+}$, the equilibrium constant K can be easily determined.

Conventional instrumental methods involving *p*H-metery, conductometery and polarography can also be employed, wherever permissible, for determining the stability constants of complexes.

The spectroscopic techniques can be employed to determine the concentrations of the reactants and the products if they absorb in different ranges of electromagnetic radiations. For example, in the above reaction showing the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$, the reactant $[Co(NH_3)_5Cl]^{2+}$ and the product, $[Co(NH_3)_5H_2O]^{3+}$, have different colours, *i.e.*, they absorb in different ranges. Hence, their concentrations can be conveniently measured with the help of spectroscopic techniques. IR, NMR and ESR techniques are also employed for determining the concentrations of reactants and products for evaluating the stability constants of complexes in some specific cases.

In some cases, distribution methods based on the difference in distribution coefficients of species in water and some suitable immiscible solvent, are also employed.

Stabilisation of Unstable Oxidation State. There are a number of cases where unstable ions get stabilised on the formation of complexes. A few examples are given below.

1. Complexes of copper(I) ion. It is well known that copper(I) ion, Cu^+, is unstable in aqueous solution as it readily undergoes disproportionation into copper(II) ion.

$$2Cu^+(aq) \longrightarrow Cu + Cu^{2+}(aq)$$

However, the complexes of Cu^+ ion such as $[Cu(CN)_4]^{3-}$ and $[Cu(NH_3]_4]^+$ are quite stable in aqueous solutions.

2. Complexes of cobalt(III) ion. Cobalt(III) ion, Co^{3+}, is unstable in aqueous solution. However, its complex ions $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$ are highly stable. Thus, although salts like $CoCl_3$ are difficult to prepare and when prepared are unstable, the complex compounds such as $[Co(NH_3)_6]Cl_3$ are prepared easily and are highly stable.

3. Complexes of iron (II). Iron (II) ion, Fe^{2+}, is not stable in air. Iron (II) compounds are fairly readily oxidised to iron(III) compounds sometimes on mere exposure to air. The complexes formed by Fe^{2+} ion, however, are highly stable. Thus, although iron (II) cyanide, $Fe(CN)_2$, is unstable, potassium ferrocyanide, $K_4[Fe(CN)_6]$, is highly stable. Iron (II) ion, can, thus, be stabilised by the formation of the complex ion, $[Fe(CN)_6]^{4-}$.

STEREOCHEMISTRY OF COORDINATION COMPOUNDS WITH DIFFERENT COORDINATION NUMBERS

The ligands adopt a definite geometry around the central metal ion depending upon the coordination number of the ion. The arrangement of the coordinated ligands is such that the electrostatic repulsion between them is minimum. We shall consider the stereochemistry of complexes with coordination numbers varying from 2 to 9. It is pertinent to mention here that the lines between metal and ligands in the figures do not show the exact bond order or the type of linkage. These lines merely indicate a chemical association between the metal and the ligands.

Coordination Number 2. There are only *two* possible arrangements for compounds with coordination number 2 : (*i*) *Linear* (*ii*) *Bent.*

When the central ion utilises the *two hybrid orbitals* for bonding with the ligands and does not contain any lone pair of electrons, it forms *linear complexes.* But, when the central ion utilises, apart from the two hybrid orbitals, one or more additional hybrid orbitals for accommodating *lone pairs of electrons*, it forms *bent complexes.*

The linear arrangement is adopted by complexes of Cu(I), Au(I) and Ag(I). Examples are : $[CuCl_2]^-$, $[Au(CN)_2]^-$, $[Ag(NH_3)_2]^+$, etc.

Examples of complexes having non-linear arrangements are rare.

Coordination Number 3. This coordination number is uncommon, rather rare. Several compounds which from their stoichiometry appear to be 3-coordinate, are found upon examination to have higher coordination numbers. The complex compound $K[Cu(CN)_2]$ is an example of true 3-coordination. Some other complex compounds which on X-ray examination have been found to be 3-coordinate are : tris(trimethylphosphinesulphide)copper(I)perchlorate, $[Cu(SP(CH_3)_3)_3]^+[ClO_4]$, tris(triphenylphosphine)platinum(0), $[(C_6H_5)_3P)_3Pt]$ and triiodomercurate (II) anion, $[HgI_3]^-$. In all these complexes, the geomettry is *trigonal planar*, as shown in Fig. 11 for $[HgI_3]^-$. The iodide ions are arranged at the three corners of an approximate equilateral triangle while Hg atom lies at the centre.

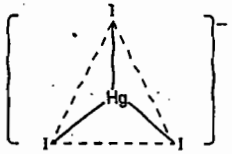


Fig. 11 Trigonal planar arrangement in $[HgI_3]^-$ complex ion.

Coordination Number 4. In this case, the two principal geometries encountered are : (*1*) *Tetrahedral* (*2*) *Square Planar*

1. Tetrahedral geometry. This geometry is common amongst complexes of transition as well as non-transition elements. Some of the common examples are : $[BeF_4]^{2-}$, $[BF_4]^-$, $[ZnCl_4]^{2-}$, $[Cd(CN)_4]^{2-}$, $[MnCl_4]^{2-}$, etc. The geometry of $[BeF_4]^{2-}$ is shown in Fig. 12.

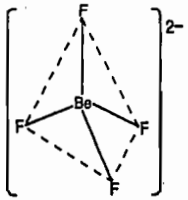


Fig. 12. Tetrahedral geometry of $[BeF_4]^{2-}$.

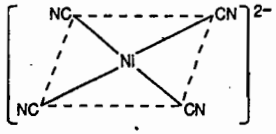


Fig. 13. Square planar geometry of $[Ni(CN)_4]^{2-}$.

2. Square planar geometry. This geometry is common amongst complexes of transition elements only. The common examples are $[PtCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[PdCl_4]^{2-}$, etc. The geometry of $[Ni(CN)_4]^{2-}$ is shown in Fig. 13.

Coordination Number 5. Complexes with coordination number 5 like those with coordination number 3, are rather rare. Several complexes in which the metal ion was considered to be having coordination member 5 were later on shown to have the metal ion with different coordination number. For example, X-ray studies have shown that the compound $(NH_4)_3[ZnCl_5]$, in which the complex ion $[ZnCl_5]^{3-}$ was considered to involve coordination number 5, actually consists of tetrahedral $[ZnCl_4]^{2-}$ ions and separate Cl^- ions in its lattice.

Similarly, the crystalline compound, $Cs_3[CoCl_5]$, in which the complex ion $[CoCl_5]^{3-}$ was considered to involve coordination number 5, has been found to contain $[CoCl_4]^{2-}$ ions and separate Cl^- ions in its lattice.

Two principal geometries in the case of compounds in which this coordination number has been established are :

(*1*) *Trigonal Bipyramidal* (*2*) *Square Pyramidal*

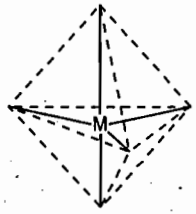


Fig. 14. Trigonal bipyramidal structure of complexes such as $Fe(CO)_5$, $[MoCl_5]^-$, $[CuCl_5]^{3-}$, $[SnCl_5]^-$, etc.

1. Trigonal bipyramidal geometry. In this case the ligands lie at the vertices of trigonal bipyramid, as shown in Fig. 14. This geometry is shown by complexes such as $[Fe(CO)_5]$, $[MoCl_5]^-$, $[CuCl_5]^{3-}$ and $[SnCl_5]^-$.

2. Square pyramidal geometry. In this case, the ligands lie at the vertices of a square pyramid, as shown in Fig. 15. An example is furnished by the complex $[SbF_5]^{2-}$. Other examples are $[VO(acac)_2]$ and $[Ni\{(C_6H_5)_3P\}_2Br_3]^-$.

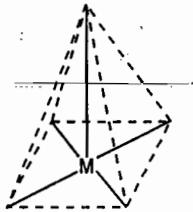


Fig. 15. Square pyramidal structure exhibited by $[SbF_5]^{2-}$ complex.

Coordination Number 6. Coordination number 6 is most common and has been extensively studied. The regular geometric arrangement is **octahedral** although due to distortions the geometry changes to

tetragonal. Octahedral geometry is shown by a large number of complexes such as $[Cu(NH_3)_6]^{2+}$, $[FeF_6]^{3-}$, $[TiF_6]^{2-}$, $[PtF_6]^{4-}$ and $[SbF_6]^-$. The octahedral geometry of $[FeF_6]^{3-}$ is shown in Fig. 16. An example of tetragonally distorted octahedron is furnished by $[CoCl_2(NH_3)_4]^+$ ion.

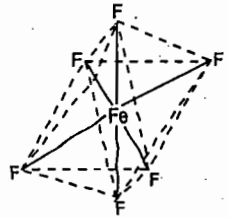


Fig. 16. Octahedral geometry of $[FeF_6]^{3-}$ ion.

Coordination Number 7. There are only a few compounds in which coordination number is 7. *Three geometrical forms known in this case are as follows :*

1. One of these which is most regular is ***pentagonal bipyramidal.*** This geometry is found in $[UO_2F_5]^{3-}$, $[UF_7]^{3-}$ and $[ZrF_7]^{3-}$. The pentagonal bipyramidal geometry of $[UO_2F_5]^{3-}$ is shown in Fig. 17.

2. The second arrangement is supposed to result from the addition of a seventh atom at the centre of one face of a ***distorted octahedron***. An example is furnished by $[NbOF_6]^{3-}$, as shown in Fig. 18.

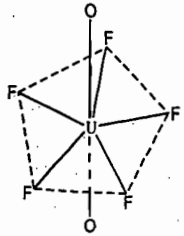


Fig. 17. Pentagonal bipyramidal geometry of $[UO_2F_5]^{3-}$complex.

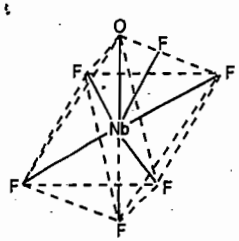


Fig. 18. Structure of $[NbOF_6]^{3-}$ complex.

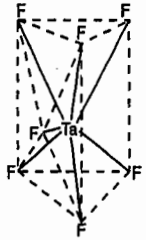


Fig. 19. Structure of $[TaF_7]^{2-}$ complex.

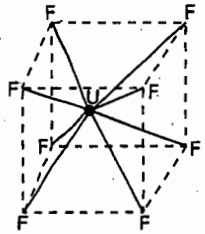


Fig. 20. The cubic structure of $[UF_8]^{3-}$complex.

3. The third arrangement is derived by putting a seventh atom above the centre of one of the rectangular faces of a ***trigonal prism.*** This arrangement occurs in $[NbF_7]^{2-}$ and $[TaF_7]^{2-}$ ions. The structure of $[TaF_7]^{2-}$ is shown in Fig. 19.

Coordination Number 8. This coordination number is most common after coordination numbers 6 and 4. Three types of geometries in the case of such compounds are known. These are :

1. Cubic 2. Square Antiprism and *3. Dodecahedral*

1. Cubic geometry. The most symmetrical arrangement is simple cubic. This occurs, however, only in the case of a few compounds, as, for example, in $[UF_8]^{3-}$, as illustrated in Fig. 20.

2. Square antiprism geometry. This depicts a distortion in the cubic geometry which is adopted to minimise the repulsion between the anions. The common examples are $[TaF_8]^{-3}$, $[ReF_8]^{2-}$and $[Zr(acac)_4]$.

The square antiprism structure of $[TaF_8]^{3-}$ is shown in Fig. 21.

3. Dodecahedral geometry. This type of geometry is exhibited by complexes such as $[Mo(CN)_8]^{4-}$ and $[Zr(ox)_4]^{4-}$. The geometry of $[Mo(CN)_8]^{4-}$ is shown in Fig. 22.

Coordination Number 9. There is only one symmetrical arrangement known for this coordination number. This is derived from a *trigonal prism* by placing the three additional atoms outside the centres of the three vertical faces.

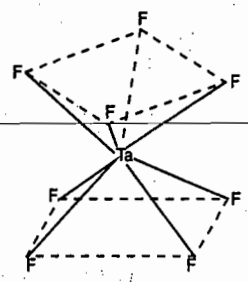


Fig. 21. Square antiprism structure of $[TaF_8]^{3-}$complex.

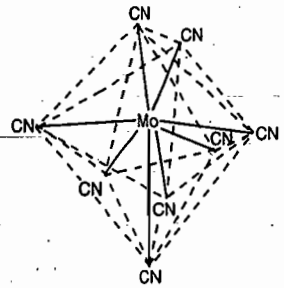


Fig. 22. Dodecahedral structure of $[Mo(CN)_8]^{4-}$.

As an example, we may consider the compound $[Nd(BrO_3)_3].9H_2O$ which contains $[Nd(H_2O)_9]^{3+}$ as the complex ion in which the central ion Nd^{3+} has coordination number 9 (Fig. 23).

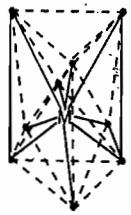


Fig. 23. Structure of $[Nd(H_2O)_9]^{3+}$.

ISOMERISM IN COORDINATION COMPOUNDS

It may be recalled that *the compounds having the same molecular formula but different structures and hence different physical and chemical properties are called* **isomers.** The phenomenon of the existence of such compounds is known as **isomerism.** Coordination compounds give rise to a wide variety of isomers due to different types of linkages and different structural arrangements of the constituent atoms.

Isomerism in coordination compounds may be divided into two main types :

(*A*) *Structural Isomerism* (*B*) *Stereo Isomerism*

These two types are further subdivided as shown below :

Isomerism in Coordination Compounds

Structural Isomerism	**Stereo Isomerism**
1. Ionisation isomerism	1. Geometrical isomerism
2. Hydrate isomerism	2. Optical isomerism
3. Coordination isomerism	
4. Linkage isomerism	
5. Coordination position isomerism	

A. STRUCTURAL ISOMERISM

The different types of structural isomerism are discussed below.

1. Ionisation Isomerism. In this type of isomerism, the difference arises from the positions of groups within or outside the coordination sphere. Therefore, these isomers give different ions in solution, hence the name ionisation isomerism. For example, there are two distinct compounds of the formula $Co(NH_3)_5BrSO_4$. One of them is *red-violet* and gives a precipitate with $BaCl_2$ indicating that sulphate ion is outside the coordination sphere. The second one is *red* and does not give precipitate with $BaCl_2$ but gives a precipitate of AgBr with silver nitrate indicating that now bromide ion is outside the coordination sphere. The structures of the two compounds and their modes of ionisation, therefore, should be as follows :

Colour of the Compound	*Structure and Mode of Ionisation*
Red-violet	$[CoBr(NH_3)_5]SO_4 \longrightarrow [CoBr(NH_3)_5]^{2+} + SO_4^{2-}$ Pentaamminebromo cobalt(III) sulphate
Red	$[CoSO_4(NH_3)_5]Br \longrightarrow [CoSO_4(NH_3)_5]^{+} + Br^{-}$ Pentaamminesulphato cobalt(III) bromide

Other compounds showing this type of isomerism are :

(*i*) $[CoCl_2(NH_3)_4]NO_2$ and $[Co(Cl)(NO_2)(NH_3)_4]Cl$

(*ii*) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

2. Hydrate Isomerism. This type of isomerism, which is similar to ionisation isomerism discussed above, arises from replacement of a coordinated group by water of hydration. As an example, we may consider the following three isomers having the molecular formula $CrCl_3.6H_2O$:

$$[Cr(H_2O)_6]Cl_3,\ [CrCl(H_2O)_5]Cl_2.H_2O \text{ and } [CrCl_2(H_2O)_4]Cl.2H_2O$$

They differ largely from one another in their physical and chemical properties, as illustrated below

$[Cr(H_2O)_6]Cl_3$ violet	It does not lose water when treated with conc. H_2SO_4 and three chloride ions are precipitated with $AgNO_3$
$[CrCl(H_2O)_5]Cl_2.H_2O$ green	It loses one water molecule when treated with conc. H_2SO_4 and two Cl^- ions are precipitated with $AgNO_3$
$[CrCl_2(H_2O)_4]Cl.2H_2O$ green	It loses two water molecules on treatment with conc. H_2SO_4 and one Cl^- ion is precipitated with $AgNO_3$

Another example is furnished by the following two isomers :

$$[CoCl(en)_2(H_2O)]Cl_2 \text{ and } [CoCl_2(en)_2]Cl.H_2O$$

3. Coordination Isomerism. This type of isomerism is observed in the case of compounds comprising of both cationic and anionic complexes. The examples are :

(*i*) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(*ii*) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

This type of isomerism is also shown by compounds in which the metal ion is the same in both cationic and anionic complexes. For example,

$[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(CN)_2(NH_3)_4][Cr(CN)_4(NH_3)_2]$

$[Pt(NH_3)_4][PtCl_4]$ and $PtCl(NH_3)_3][PtCl_3(NH_3)]$

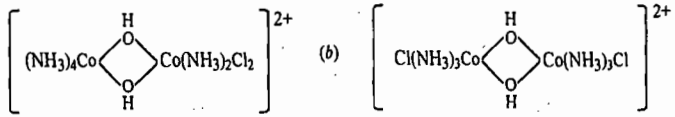
4. Linkage Isomerism. In some ligands, there are two atoms which can donate their lone pairs. For example, in NO_2^- ion, the nitrogen atom as well as the oxygen atom can donate their lone pairs. This gives rise to isomerism. If nitrogen donates its lone pair, one particular compound will be formed. If oxygen does so, a different compound (although having the same molecular formula) is obtained. For example, two different pentaamminecobalt(III)chlorides, each containing the NO_2 group in the complex ion, have been prepared. These are :

$[Co(NO_2)(NH_3)_5]Cl_2$ Pentaamminenitrito-Ncobalt(III)chloride

$[Co(ONO)(NH_3)_5]Cl_2$ Pentaamminenitrito-Ocobalt(III)chloride

Other ligands which give rise to linkage isomerism are CN (cyano) and NC (isocyano) and SCN (thiocyanato) and NCS (isothiocyanato).

5. Coordination Position Isomerism. This type of isomerism is exhibited by bridged complexes and results from different placement of ligands, as shown below :



It will be seen that in (*a*) and (*b*), ammonia and chloro ligands are differently placed relative to the two cobalt atoms.

B. STEREOISOMERISM

As already mentioned, stereoisomerism involves two types of isomerism, *viz.,geometrical isomerism* and *optical isomerism.* These are discussed below.

1. Geometrical Isomerism. Geometrical isomerism is due to ligands occupying different positions around the central ion. The ligands occupy positions either *adjacent to one another or opposite to one another.* These are referred to as *cis* form and *trans* form, respectively. This type of isomerism is, therefore, also referred to as *cis-trans* **isomerism.**

A much larger variety of geometrical isomerism is available in coordination compounds than even in organic compounds. *This is due to different coordination numbers,* varying from 2 to 9, commonly encountered in these compounds. Geometrical isomerism is not possible for complexes having coordination numbers 2 and 3 because in these arrangements all the positions are adjacent to one another. Geometrical isomerism of compounds with coordination numbers 4 and 6 is most important and is discussed below.

Geometrical isomerism in complexes of coordination number 4. *As discussed earlier, complexes* having coordination number 4 adopt either tetrahedral or square planar geometry. Cis-trans isomerism is not possible in tetrahedral complexes because all the four lignads are adjacent to one another. However, cis-trans isomerism is very common amongst square planar complexes of the following types :

a. Complexes of the *type* Ma_2b_2 can exist in *cis* and *trans* forms, as represented in Fig. 24.

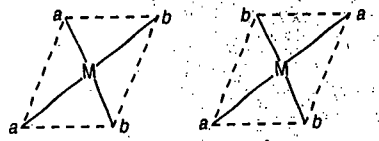


Fig. 24. The *cis* and *trans* forms of the complex Ma_2b_2.

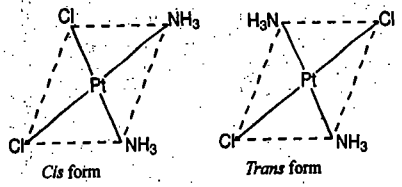


Fig. 25. The *cis* and *trans* forms of the complex $[PtCl_2(NH_3)_2]$.

Amongst the best known examples are the complexes of platinum(II) and palladium(II), such as $[PtCl_2(NH_3)_2]$, $[Pd(NO_2)_2(NH_3)_2]$ and $[PtCl_2(py)_2]$.

The *cis* and *trans* isomers of the complex $[PtCl_2(NH_3)_2]$ are represented in Fig. 25.

Cis-trans isomers can be readily distinguished from one another by X-ray diffraction technique.

b. In a complex of the type Ma_2bc also, there are *cis* and *trans* isomers depending upon whether the two '*a*' groups are adjacent or opposite to each other (Fig. 26.).

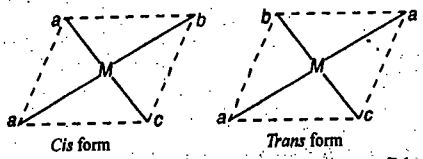


Fig. 26. The cis and trans forms of complex of the type $[Ma_2bc]$.

A common example of this type of complex is $[Pt(py)_2NH_3Cl]$.

c. Square planar complexes of the *type Mabcd* produce three isomers. The structures of these isomers can be written by fixing the position of one ligand (say, *a*) and placing the other ligands *b, c* and *d* trans to it (Fig. 27).

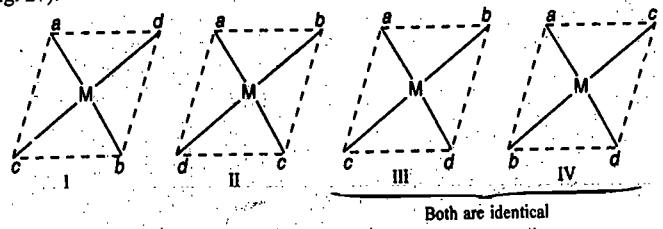


Fig. 27. The three isomeric structures of the complex *Mabcd*.

The fourth structure in which *a* is trans to *d* is identical to the third. The example is furnished by the cation $[Pt(NO_2)(C_5H_5N)(NH_3)(NH_2OH)]^+$. The three structures of the complex are represented in Fig. 28.

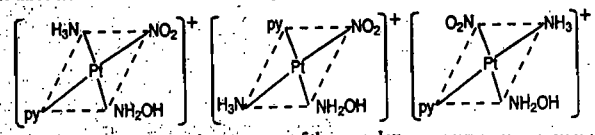


Fig. 28. The three isomeric structures of the complex $[Pt(NO_2)(C_5H_5N)(NH_3)(NH_2OH)]^+$ written by fixing the position of NH_2OH.

d. Geometrical isomerism cannot occur in complexes of the type Ma_4, Ma_3b or Mab_3 because all possible spatial arrangements for any of these complexes will be exactly equivalent.

e. The square planar complexes containing unsymmetrical bidentate ligands such as $[M(ab)_2]$ also show geometrical isomerism. For example, the complex $[Pt(gly)_2]$ where gly stands for $NH_2CH_2COO^-$ exists in *cis* and *trans* forms, as shown in Fig. 29.

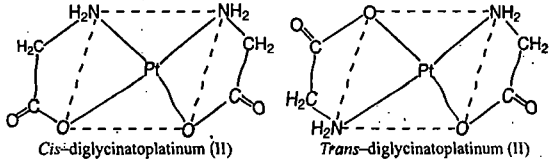


Fig. 29. *Cis* and *trans* forms of the complex $[Pt(gly)_2]$.

Geometrical isomerism in complexes of coordination number 6. The complexes having coordination number 6 adopt *octahedral* geometry. The octahedral complexes also exhibit geometrical isomerism.The complexes of the type Ma_6 and Ma_5b would not show geometrical isomerism. The different types of octahedral complexes exhibiting geometrical isomerism are discussed below.

a. Complexes of the type Ma_4b_2 or Ma_2b_4 or Ma_4bc show geometrical isomerism. For example, the structures of cis (violet) and trans (green) forms of tetraamminedichlorochromium(III) ion are shown in Fig. 30.

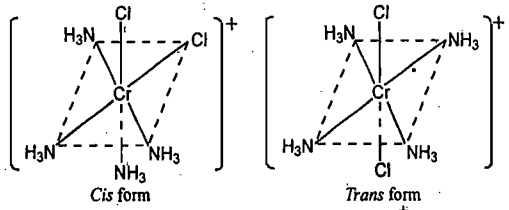


Fig. 30. The *cis* and *trans* forms of $[CrCl_2(NH_3)_4]^+$ complex.

A large number of other octahedral complexes of these types, where *M* is Co(III), Cr(III), Rh(III), Pt(IV), have been prepared.

b. Complexes of the type Ma_3b_3 exist in only two isomeric forms. The two isomers of the compound $[RhCl_3(py)_3]$ are shown in Fig. 31.

It is seen that in the cis form, like groups occupy the corners of one of the triangular faces of the octahedron while in the trans form, they do not.

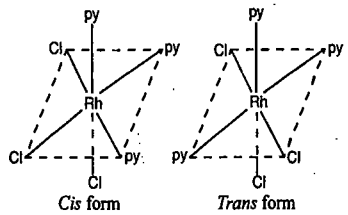


Fig. 31. The *cis* and *trans* forms of the complex $[RhCl_3(py)_3]$.

c. In the case of complexes of the type $[Mabcdef]$, in which all the ligands are different, there is a possibility for the existence of 15 different geometrical forms. However, the only compound of this type that has been prepared so far is

$$[PtBrClI(NO_2)(C_5H_5N)(NH_3)]$$

It has been possible to isolate only *three* different forms of this compound.

d. The complexes of the type $[M(aa)_2b_2]$ or $[M(aa)_2bc]$ containing bidentate ligands (*aa*) show geometrical isomerism. The other two ligands may be the same (b_2) or different (*bc*). The common examples are $[M(en)_2bc]$ where *M* is Co (III), Cr(III), Ir(III), Rh(III), Pt(IV) and *b* and *c* are ligands such as NO_2^-, I^-, Br^-, Cl^-, NH_3, py, etc. For example, the complex $[Co(en)_2Cl_2]^+$, where en is $H_2NCH_2CH_2NH_2$, exists in *cis* and *trans* forms, as shown in Fig. 32.

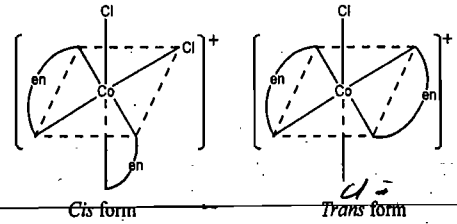


Fig. 32. *Cis* and *trans* forms of complex $[Co(en)_2Cl_2]^+$ ion.

2. Optical Isomerism. There are certain substances which can rotate the plane of polarised light. These are called **optically active** substances. *The optically active isomers of a compound which rotate the plane of polarised light equally but in opposite directions are called* **enantiomers.** The isomer which rotates the plane of polarised light to the right is called **dextro rotatory** designated as *d* and the one which rotates the plane of polarised light to the left is called **laevo rotatory** designated as *l*. The *d* and *l* isomers are mirror images of each other just as left hand is mirror image of the right hand. *The essential*

requirement for a substance to show optical activity is that the substance should not have a plane of symmetry in its structure. The optical isomers have identical physical and chemical properties. They differ only in the direction in which they rotate the plane of polarised light.

We would discuss here optical isomerism in complexes of coordination numbers 4 and 6 only.

Optical isomerism in complexes with coordination number 4. Tetrahedral complexes with coordination number 4 should exhibit optical isomerism because there is no plane of symmetry in their molecules. However, this has *not* been found to be the case. The first tetrahedral metal complex in which the central ion was surrounded by four *different* ligands was prepared in 1963 but it has not been possible to resolve it into *d* and *l* forms. However, tetrahedral complexes of Be(II), B(III) and Zn(II), containing two symmetrical bidentate ligands, can be resolved into optically active forms. For example, the complex bis(benzoylacetonato)beryllium(II) has been shown to exist in two optical forms, as shown in Fig. 33.

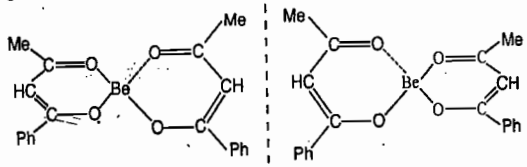
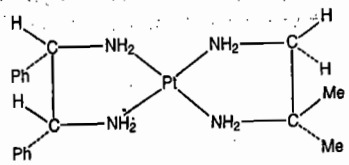


Fig. 33. The two optical isomers of tetrahedral bis (benzoylacetonato) beryllium (II) complex.

It may be noted that 4 different groups around the central atom are not essentially required for optical activity. All that is required is that the molecule should be *asymmetric* so that it can exist in two forms which are mirror images of each other, as shown above. Evidently, the two structures do not superimpose on each other.

Square planar complexes are seldom optically active. This is because all the ligands and the metal atom lie in the same plane. The molecule has a plane of symmetry (the plane of the molecule is the plane of symmetry) and this cannot exhibit optical isomerism. One such compound which has, however, been resolved into two forms is as shown.



As can be seen, it has no plane of symmetry that is why it is optically active.

Optical isomerism in complexes with coordination number 6. The most well known cases of optical isomerism occur among octahedral complexes. The common examples are complexes which contain bidentate ligands. These complexes fall under the following categories :

a. Complexes of the Type $[M(aa)_3]$ where *aa* = bidentate ligand. The complexes such as $[Co(en)_3]Cl_3$, $[Cr(ox)_3]^{3-}$, etc., exist as optical isomers because they form non-superimposable mirro images, as illustrated in Figs. 34 and 35.

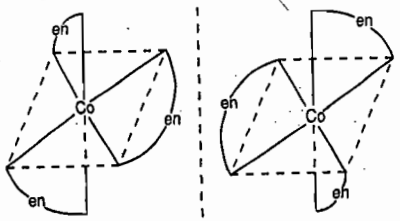


Fig. 34. The two optical isomeric forms of the complex $[Co(en)_3]^{3+}$

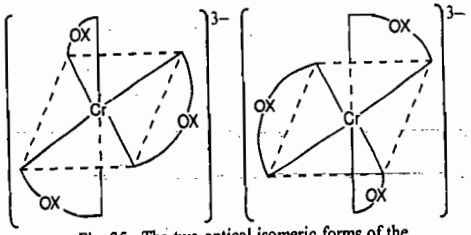


Fig. 35. The two optical isomeric forms of the complex $[Cr(ox)_3]^{3-}$

b. Complexes of the Type $[M(aa)_2b_2]$ **or** $[M(aa)_2bc]$. It has already been shown (Fig. 30) that these complexes form geometrical isomers (cis and *trans* forms). It is interesting to note that the *trans form does now show optical isomerism, i.e.,* it cannot be resolved into optical isomers. The reason is that the molecule in this case is symmetric. On the other hand, *the cis isomer is asymmetric* and can be resolved into *d* and *l* isomers. For example, the complex ion dichlorobis(ethylenediamine)rhodium(III) $[RhCl_2(en)_2]^+$

exists in the form of three isomers (*trans* optically inactive ; *cis* (*d*) and *cis* (*l*). The resolution of the *cis* isomer of the complex into *d* and *l* forms is shown in Fig. 36.

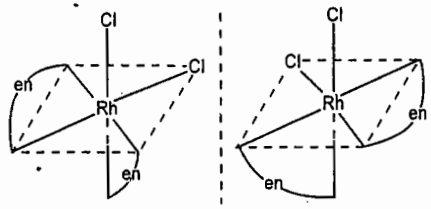


Fig. 36. Optically active isomers of *cis* $[RhCl_2(en)_2]^+$.

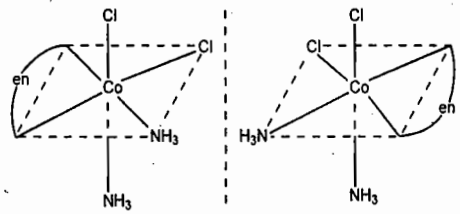


Fig. 37. Optical isomers of $[CoCl_2(en)(NH_3)_2]^+$.

c. Complexes of the type $[M(aa)_2c_2]$. The complexes containing only one symmetric bidentate ligand also show optical isomerism. For example, the complex ion $[CoCl_2(en)(NH_3)_2]^+$ exists in *d* and *l* forms, as shown in Fig. 37).

d. Complexes containing hexadentate ligands. The complexes containing hexadentate ligands such as ethylenediaminetetraacetato (EDTA) also show optical activity. For example, the complex $[Co(EDTA)]^-$ exists in two forms, *d* and *l*, as shown in Fig. 38.

e. Complexes containing unidentate ligands. The complexes of the type [*Mabcdef*] are also expected to show optical isomerism. A complex of this type can theoretically have 15 geometrical forms, each of which should be optically active.

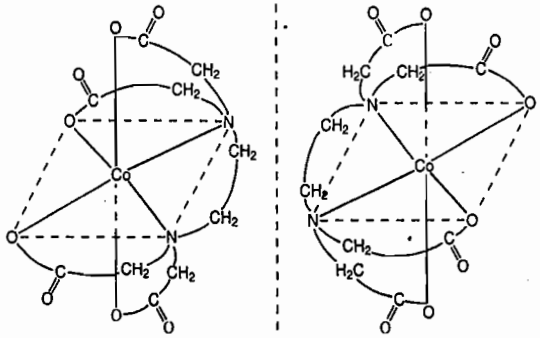


Fig. 38. Optical isomers of $[Co(EDTA)]^-$.

QUESTIONS

1. What are coordination compounds ? How do they differ from double salts ?
2. Define the following terms giving suitable examples :
   (*a*) Complex compound (*b*) Ligand (*c*) Coordination number (*d*) Coordination sphere.
3. How are ligands classified as unidentate, bidentate and polydenate ligands ? Explain with examples.
4. (*a*) Define chelating ligands and chelates. Give examples.
   (*b*) Give one example of hexadentate ligand.
   (*c*) Give one example of a bridging ligand and a bridged complex.
5. (*a*) What are the important postulates of Werner's theory of coordination compounds?
   (*b*) The two complexes $PtCl_4.2NH_3$ and $PtCl_4.2KCl$ do not give precipitates of AgCl when treated with $AgNO_3$. The conductance studies indicate zero and three moles of ions per mole of the complex respectively in their solutions. Write the structures of these compounds.
   (*c*) How does Werner's coordination theory account for nonionic nature of the complex $CoCl_3.3NH_3$?
6. How was Werner able to show that the only geometry possible for a complex with coordination number 6 is octahedral ?
7. *Briefly discuss the IUPAC system of nomenclature for coordination compounds with reference to*
   (*a*) *names of ligands* (*b*) *order of naming ligands*
   (*c*) prefixes to give the number of ligands and (*d*) oxidation state of the central metal atom.
8. Write the names of the following complexes according to IUPAC system
   (*a*) $K_3[Al(C_2O_4)_3]$ (*b*) $K_4[Ni(CN)_4]$ (*c*) $[PtCl(NO_2)(NH_3)_4]SO_4$ (*d*) $[Co(en)_3]Cl_3$
   (*e*) $NH_4[Cr(NCS)_4(NH_3)_2]$ (*f*) $K[AgF_4]$ (*g*) $[PtCl_2(NH_3)_4][PtCl_4]$ (*h*) $Na[Au(CN)_2]$

9. Write the formulae of the following complexes
   (*a*) Diamminechloro(ethylenediamine)nitrito-Nplatinum(IV) chloride (*b*) Calcium hexacyanoferrate(II)
   (*c*) Chlorobis(ethylenediamine)nitrito-Ocobalt(III) chloride (*d*) Tetracarbonylnickel(0)
   (*e*) Iron hexacyanoferrate(II) (*f*) Hexaaquanickel(II)perchlorate
   (*g*) Tetraamminechloronitrito-Nplatinum(IV)sulphate (*h*) μ-amido-μ-nitrito-Noctaamminedicobalt(III)nitrate
   (*i*) Dichlorobis(ethylenediamine)cobalt(III)sulphate
10. Write the formula of the complex ion tetraamminechloronitrito-Ncobalt(III). Identify the ligand, coordination number and coordination sphere in this complex. How many ions per mole would be given by this complex in aqueous solution ?
11. (*a*) Combination of Pt(IV), NH_3, Cl^- and K^+ results in the formation of seven complexes and one such complex is $[Pt(NH_3)_6]Cl_4$.
   (*i*) Write the formulae of the other six members of the series.
   (*ii*) Name these complexes according to IUPAC system of nomenclature.
   (*iii*) Which of these will have highest molar conductivity ?
   (*iv*) Which of these is non-ionic ? Explain the structure of this complex on the basis of Werner's theory of coordination compounds.
   (*b*) Formulate the following complexes of cobalt :
   (*i*) Triamminetrichlorocobalt(III) (*ii*) Dichlorobis(ethylenediamine)cobalt(III)sulphate
   (*iii*) Tris(ethylenediamine)cobalt(III)chloride (*iv*) Sodium tetracarbonylcobaltate(–I)
   (*v*) Tetraamineaquabromocobalt(III)nitrate
12. Name the different kinds of isomerism possible in coordination complexes. Give one example of each kind.
13. (*a*) What do you understand by optical isomers ? Why do square planar complexes not exhibit optical isomerism ?
   (*b*) Discuss the optical isomerism exhibited by complexes of coordination numbers 4 and 6.
   (*c*) Name the type of isomerism exhibited by the following isomers :
   (*i*) $[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(CN)_2(NH_3)_4][Cr(CN)_4(NH_3)_2]$
   (*ii*) $[CoCl_2(py)_2(H_2O)_2]Cl$ and $[CoCl_3(py)_2(H_2O)].H_2O$
   (*iii*) $[PtBr_2(NH_3)_4]Cl_2$ and $[PtCl_2(NH_3)_4]Br_2$ (*iv*) $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(ONO)(NH_3)_5]Cl_2$
14. (*a*) How many isomers are possible for each of the following complexes :
   (*i*) $[CoCl_3(NH_3)_3]$ (*ii*) $[CoCl_2(NH_3)_4]^+$ (*iii*) [Co(EDTA)]
   (*b*) Give one example of coordination isomerism.
15. (*a*) What is meant by coordination number ? Discuss the geometries adopted by complexes with coordination numbers varying from 2 to 9.
16. (*a*) The complex $CoCl_3.2(en)$ contains only one chloride ion which can be precipitated as AgCl on the addition of $AgNO_3$.
   (*i*) Draw structures of all the possible geometrical and optical isomers.
   (*ii*) Name the geometrical isomers according to IUPAC system.
   (*b*) Why do square planar complexes not show optical isomerism ?
   (*c*) Why do tetrahedral complexes not show geometrical isomerism ?
   (*d*) Discuss with examples the stereochemistry of complexes having coordination number 8.
17. What is meant by stability of a complex ion ? On what factors does the stability of a complex ion depend ? Explain giving suitable examples.
18. The complexes congtaining chelate rings are more stable than those containing similar but unidentate ligands. Why is it so ?
19. Explain, giving suitable examples, how stability of complexes is determined from thermodynamic data.
20. Unstable ions get stabilised on the formation of complexes. Illustrate giving suitable examples.
21. (*a*) What do you understand by stereoisomerism. Discuss the stereoisomerism of complexes of the type $[M(aa)_3]$ and $[M(aa)_2b_2]$ where aa=bidentate ligand and *b*=unidentate ligand.
   (*b*) Discuss the following with at least one example in each case :
   (*i*) Ionisation isomerism (*ii*) Coordination position isomerism
   (*iii*) Coordination isomerism (*iv*) Linkage isomerism
22. (*a*) Name the following complexes :
   (*i*) $K_2[OsCl_5NH_3]$ (*ii*) $K_3[Fe(CN)_5CO]$ (*iii*) $NH_4[Cr(NCS)_4(NH_3)_2$ (*iv*) $K_2[Ni(CN)_4]$
   (*b*) What are the coordination numbers of different metal ions in the above complexes ?
23. (*a*) Discuss the stereochemistry of complexes exhibiting coordination numbers 5 and 7.
   (*b*) Write a short note on optical isomerism.

COORDINATION COMPOUNDS. PART II

27

MODERN THEORIES OF METAL – LIGAND BOND

Three modern theories have been developed to explain the bonding involved in and the properties of coordination complexes. These are

1. *The Valence Bond Theory*
2. *The Crystal Field Theory*
3. *The Molecular Orbital Theory.*

All the above theories have been discussed below in appropriate details.

THE VALENCE BOND THEORY

The valence bond theory has been developed mostly by Pauling. Although the other two theories are now more useful in understanding the bonding in coordination complexes yet it is desirable to be familiar with the valence bond treatment also. This is because considerable amount of research in coordination chemistry has been inspired by this theory.

The **main points of the valence bond theory** may be summed up as follows :

1. The *central metal ion* in the complex makes available an adequate number of empty orbitals for the formation of coordinate bonds with suitable ligands. The number of empty orbitals made available for the purpose is equal to the coordination number of the central ion.

2. The appropriate atomic orbitals (*s*, *p* and *d*) of the metal hybridise to give an equal number of new orbitals of equivalent energy, called *hybrid orbitals.* The hybrid orbitals are directed towards the ligand positions according to the geometry of the complex, as given in Table 1.

3. The *d* orbitals involved in hybridisation may be inner, *viz.*, (n–1)*d* orbitals or the *outer*, *viz.*, n*d* orbitals. For example, octahedral hybridisation may be either $(n-1)d^2sp^3$ or nsp^3d^2 (Table 1). The complexes thus formed are referred to as **low spin** and **high spin** complexes, respectively. The reason for this nomenclature would be discussed shortly.

4. Each ligand has at least one orbital containing a lone pair of electrons.

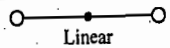
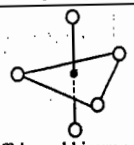
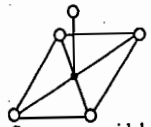
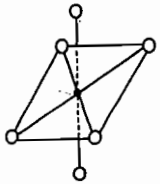
5. The empty hybrid orbitals of metal ion overlap with the fully filled orbitals of the ligand, forming the ligand–metal coordinate bond. The number of such bonds varies with the number of empty orbitals made available by the central ion.

The valence bond theory has been able to account for many stereochemical and magnetic properties of coordination compounds. We know that a substance which does not contain any unpaired electron is *repelled by magnetic field.* It is said to be *diamagnetic.* On the other hand, a substance which contains one or more unpaired electrons is *attracted by a magnetic field.* It is said to be *paramagnetic.** Knowing the magnetic behaviour, it is possible to predict the number of unpaired electrons, the type of hybridisation involved in the formation of a given complex and hence its geometry as well. Alternatively, if the geometry of the complex is known, it is possible to predict the magnetic properties (*viz.*, diamagnetic or paramagnetic character) of the complex and the number of unpaired electrons present in the metal ion of the complex.

* Magnetic properties of metal complexes have been discussed in greater details in a later part of this chapter.

TABLE 1

Coordination Numbers, Hybridised Orbitals and Molecular Geometry of Various Coordination Complexes

C.N.	Hybridised Orbitals	Molecular Geometry	Examples
2	sp	 Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[Zn(NH_3)_4]^{2+}$
4	dsp^2 The d orbital involved is $d_{x^2-y^2}$ of the inner, *i.e.*, $(n-1)$th shell.	Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
5	dsp^3 The d orbital involved is d_{z^2} of the inner, *i.e.*, $(n-1)$th shell.	 Trigonal bipyramidal	$[Fe(CO)_5]$
5	sp^3d The d orbital inolved is $d_{x^2-y^2}$ of the outer, *i.e.*, the nth shell.	 Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3 or sp^3d^2 The d orbitals involved are d_{z^2} and $d_{x^2-y^2}$ of the inner, *i.e.*, $(n-1)$th shell in the first case and of the outer, *i.e.*, nth shell in the second case.	 Octahedral	$[Co(NH_3)_6]^{2+}$ Co utilises $(n-1)d$ orbitals; $[CoF_6]^{3-}$ Co utilises nd orbitals

We may now take a few examples to illustrate the valence bond theory. In this treatment, the orbitals are designated by circles. The electrons in each orbital are indicated by half arrows. The orbitals which are involved in hybridisation are enclosed within rectangular boxes.

Examples of Square Planar and Tetrahedral Complexes. In this category we shall consider complexes of nickel in which the coordination number of the metal ion is 4. The typical examples are offered by $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$.

1. Tetracyanonickelate(II) ion, $[Ni(CN)_4]^{2-}$. The nickel (II) ion has $3d^8$ as its outer electronic configuration and according to Hund's rule, it will have two unpaired electrons, as shown in Fig. 1(*a*). Depending upon the type of hybridisation, there are two possible ways in which the complexes of nickel with coordination number 4 may be formed. If the complex involves $4sp^3$ hybridisation, it would have

tetrahedral structure. If, on the other hand, the complex involves $3d4sp^2$ hybridisation, it would have *square planar structure.*

For the formation of tetrahedral structure, the $3d$ orbitals would remain unaffected and, therefore, the two unpaired d electrons would remain as such. Consequently, the complex would be paramagnetic like the Ni^{2+} ion itself.

On the other hand, for the formation of square planar structure through dsp^2 hybridisation, one of the $3d$ orbitals should be empty and available for hybridisation. This is possible if, due to the energy made available by the approach of ligands, the two unpaired d electrons are paired up thereby making one of the $3d$ orbitals empty. There would thus be no unpaired electron and the complex would be diamagnetic.

We know from experiment that the complex ion $[Ni(CN)_4]^{2-}$ is diamagnetic indicating that the hybridisation involved in this case is $3d4sp^2$, as represented in Fig. 1 (*b*). Consequently, the structure of the complex would be *square planar.* The empty hybrid orbitals of the metal overlap with the fully filled orbitals of cyanide ions to form metal–ligand coordinate bonds, as shown in the figure. The dotted arrows represent electron pairs donated by CN^- ions.

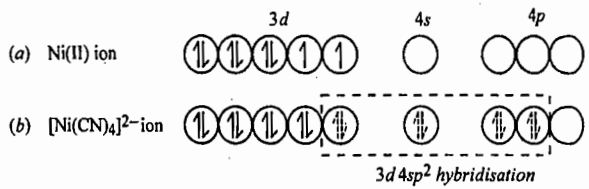


Fig. 1. Formation of square planar $[Ni(CN)_4]^{2-}$ complex, involving $3d\,4sp^2$ hybridisation of Ni^{2+} ion orbitals.

2. Tetrachloronickelate(II) ion, $[NiCl_4]^{2-}$. The nickel(II) ion has two unpaired electrons, as shown in Fig. 2(*a*). As discussed above, if the complex of nickel with coordination number 4 is paramagnetic, it would involve $4sp^3$ hybridisation and its structure would be *tetrahedral.* If the complex is diamagnetic, it would involve $3d4sp^2$ hybridisation and it would have *square planar structure.*

The magnetic measurements of the complex $[NiCl_4]^{2-}$ show that it is paramagnetic and has two unpaired electrons.* Evidently, in this case the $3d$ orbitals remain undisturbed and $4sp^3$ hybridisation occurs resulting in *tetrahedral structure* of the complex. As is evident from Fig. 2(*b*), there are two unpaired electrons in the complex.

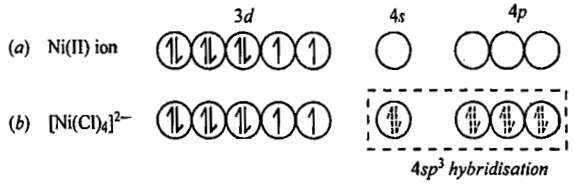


Fig. 2. Formation of tetrahedral $[NiCl_4]^{2-}$ complex involving sp^3 hybridisation of Ni^{2+} orbitals. Dotted arrows represent electron pairs donated by Cl^- ions.

The valence bond treatment for some other complexes with square planar and tetrahedral configurations is given in Table 2.

Examples of Octahedral Complexes. Octahedral complexes are the most common and have been studied most extensively. We may consider, as an illustration, the formation of complexes of cobalt(III) on the basis of valence bond theory.

1. Complexes of Cobalt(III). Hexaamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$. The outer electronic configuration of cobalt(III) ion is $3d^6$. Four of the $3d$ orbitals are singly filled and one $3d$ orbital has a pair of electrons. This is shown in Fig. 3(*a*). Octahedral complexes are formed through $3d^24sp^3$ hybridisation for which the

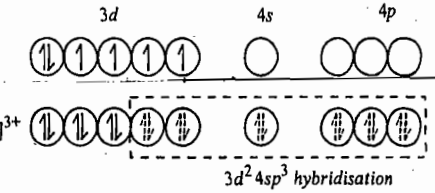


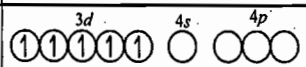
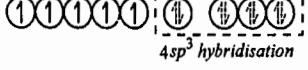
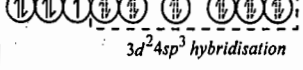
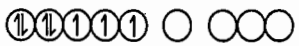
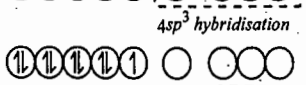
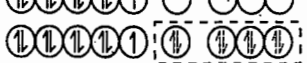
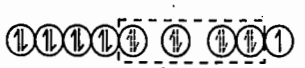
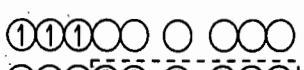
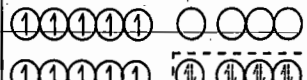
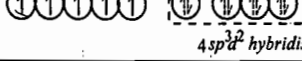
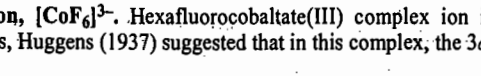
Fig. 3. Formation of octahedral complex, $[Co(NH_3)_6]^{3+}$, involving $3d^2\,4sp^3$ hybridisation of Co^{3+} ion orbitals.

*Magnetic measurements help to calculate the magnetic moment from which the number of unpaired electrons can be calculated. The details are given in a subsequent section in this chapter.

metal atom must have two of its $3d$ orbitals empty. This is achieved by the pairing of the two $3d$ electrons as a result of the energy released due to the approach of the ligands. This is shown in Fig. 3(*b*). This results in the formation of an octahedral complex. As is evident from the figure, the complex does not contain any unpaired electron and is, therefore, diamagnetic. Since the central atom utilises the inner (n–1)d orbitals for forming d^2sp^3 hybrid orbitals, such a complex is called *inner orbital complex*. In the formation of an inner orbital complex, the electrons of the metal atom are forced to pair up and hence the complex would either be diamagnetic or would have lesser number of unpaired electrons compared to their number in the free metal ion. Such a complex is called ***low spin complex.***

TABLE 2

Application of Valence Bond Theory to Some Complexes

Ion/Complex	No. of unpaired electrons as obtained from magnetic studies	Electronic Configuration and Hybridisation	Structure of Complex
Mn^{2+}			
$[MnCl_4]^{2-}$	5	 $4sp^3$ *hybridisation*	Tetrahedral
$[Mn(CN)_6]^{4-}$	1	 $3d^24sp^3$ *hybridisation*	Octahedral
Co^{2+}			
$[CoCl_4]^{2-}$	3	 $4sp^3$ *hybridisation*	Tetrahedral
Cu^{2+}			
$[CuCl_4]^{2-}$	1	 $4sp^3$ *hybridisation*	Tetrahedral
$[Cu(NH_3)_4]^{2+}$	1	 $3d4sp^2$ *hybridisation*	Square planar
Cr^{3+}			
$[Cr(NH_3)_6]^{3+}$	3	 $3d^24sp^3$ *hybridisation*	Octahedral
Fe^{3+}			
$[FeF_6]^{3-}$	5	 $4sp^3d^2$ *hybridisation*	Octahedral

Hexafluorocobaltate(III) ion, $[CoF_6]^{3-}$. Hexafluorocobaltate(III) complex ion is known to be paramagnetic. To account for this, Huggens (1937) suggested that in this complex, the $3d$ orbitals remain

undisturbed while the *outer* $4d$ orbitals are involved in hybridisation, as shown in Fig. 4 (*b*).

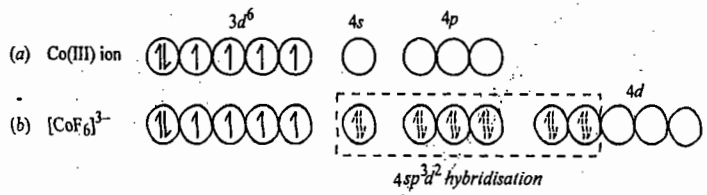


Fig. 4. Formation of octahedral $[CoF_6]^{3-}$ complex involving $4sp^3d^2$ hybridisation of Co^{3+} ion orbitals.

It is clear from the figure that there are four unpaired electrons in this complex and hence it is paramagnetic. Such a complex in which the metal ion utilises outer nd orbitals is called *outer orbital complex.*

The outer orbital complex has a larger number of unpaired electrons than their number in inner orbital complex of the same metal ion since the configuration of the metal ion remains undisturbed on complexation. Such a complex is also called ***high spin complex.***

The valence bond treatment for some other octahedral complexes is presented in Table 2.

Shortcomings of Valence Bond Theory. The valence bond theory successfully establishes a correlation between metal to ligand bonding geometry of coordination compounds. However, like any other theory, it is also not free from flaws. It has several shortcomings some of which are discussed below.

1. Although the theory gives a pictorial representation of bonding in coordination compounds, it does not have a sound theoretical basis and is essentially qualitative in nature. It does not say anything about the electronic excited states and energies associated with them. As a result, the theory fails to predict the number, positions and the intensities of the bands observed in electronic spectra of coordination compounds.

2. According to valence bond theory, the magnetic moment of a complex originates from the magnetic field generated by the spin of electrons in the metal ion. The theory gives no credence to the magnetic field generated by the orbital motion of electrons. This is a big flaw because magnetic field is generated not only by the spin motion but also by the orbital motion of electrons. The correct magnetic moment would thus be given by the combination of μ_{spin} and $\mu_{orbital}$. This is the reason why the experimental μ value generally differs from the calculated μ_{spin} value.

3. According to valence bond theory, the complex ion $[Cu(NH_3)_4]^{2+}$ and similar other square planar complexes of Cu(II), utilise $4dsp^2$ hybridised orbitals for bonding with the ligands. The valence bond theory suggests that the transfer of an unpaired $3d$ electron of Cu(II) to the higher energy $4p_z$ orbital is essential to bring about $4dsp^2$ hybridisation. However, the ESR spectra reveal that the unpaired electron in such complexes is not permanently located in the $4p_z$ orbital of Cu(II). The valence bond theory also suggests that it would be easier to oxidise Cu(II) to Cu(III) in its square planar complexes since the removal of electron from the higher energy $4p_z$ orbital would be quite easy. But, it is contrary to facts. For instance, the oxidation of $[Cu(NH_3)_4]^{2+}$ to $[Cu(NH_3)_4]^{3+}$ does not occur at all.

4. The valence bond theory does not explain satisfactorily why some complexes of a metal ion in a particular oxidation state are *low spin* (inner orbital) while some other complexes of the same metal ion in the same oxidation state are *high spin* (outer orbital) complexes. For instance, while $[Co(NH_3)_6]^{3+}$ is diamagnetic, $[CoF_6]^{3-}$ is paramagnetic. According to valence bond theory, Co^{3+} in the former complex utilises the inner (n–1)d orbitals for d^2sp^3 hybridisation whereas Co^{3+} in the latter complex utilises the outer nd orbitals for sp^3d^2 hybridisation. What factors compel Co^{3+} to utilise d orbitals of different principal shells in $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ is not explained by the valence bond theory.

5. The correlation worked out by valence bond theory between the geometry of a complex and its magnetic behaviour is sometimes quite misleading. For example, according to valence bond theory, the

square planar complexes of Ni(II) should be *diamagnetic*. This is because Ni(II) can easily make an inner $(n-1)dnsp^2$ hybridisation by rearranging the eight electrons in the four remaining $(n-1)d$ orbitals thereby giving rise to a square planar geometry with no unpaired electron, as shown in Fig. 5.

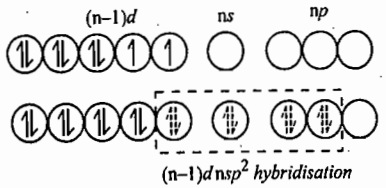


Fig. 5. The diamagnetic square planar complex of Ni(II). The complex has no unpaired electron.

This may lead to the conclusion that *all square planar complexes of* Ni(II) *should be diamagnetic.* But actually it is not so. We come across quite a few square planar complexes of Ni(II) which are *paramagnetic.* Valence bond theory does make an attempt to explain this observation by postulating that in such complexes one of the unpaired $(n-1)d$ electrons of Ni^{2+} gets transferred to the vacant $4p_z$ orbital to vacate the $(n-1)d$ orbital which is required for $(n-1)d\,nsp^2$ hybridisation to form a *square planar complex.* Such a complex would contain two unpaired electrons as shown in Fig. 6 and would thus be *paramagnetic.* But it is difficult to explain why such excitation of electron occurs in one square planar complex but not in the other.

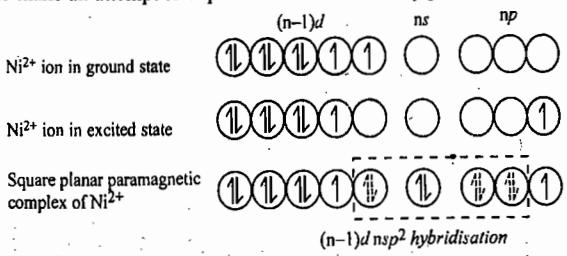


Fig. 6. The paramagnetic square planar complex of Ni(II). The complex has two unpaired electrons.

CRYSTAL FIELD (C.F.) THEORY

The crystal field theory developed by H. Bethe and V. Bleck (1935) proved to be far more successful in explaining the bonding in and the properties of coordination complexes than the valence bond theory. According to the **crystal field theory,** *bonding between a central metal ion and its ligand arises from purely electrostatic interactions.* If the ligand is an anion, the attraction towards the cation is as that between any oppositely charged particles. If the ligand is a neutral molecule such as NH_3 or H_2O, the negative end of the dipole is attracted towards the central positive ion.

Knowing the arrangement of ligands around the central metal ion, assuming the bonds between metal ion and the ligands to be purely electrostatic and considering the metal ion and the ligands as *point charges* q_1 and q_2, separated by a distance r, the metal–ligand bond energies for various complexes can be calculated using the Coulomb's law, *viz.*, $B.E. = -q_1q_2/r$. The values obtained were found to be in close agreement with those obtained experimentally in the case of non-transition metal complexes. The values were, however, too low compared to the experimentally observed values, in the case of transition metal complexes. The cause of discrepancy, according to the crystal field theory, *lies in the manner of the orientation of the d orbitals in space,* as explained below.

Orientation of *d* Orbitals and Crystal Field Splitting of Energy Levels

As shown in Chapter 1, the *d* orbitals can be divided into two groups depending upon the nature of their orientation in space. One of the groups consists of three orbitals which are oriented in the regions in between the coordinate axes while the other group comprises of two orbitals which are oriented along the axes. In the case of a free metal ion, all the five *d* orbitals have the same energy, *i.e.,* they are **degenerate,** meaning energetically alike. Consider a hypothetical case in which the set of five *d* orbitals of the metal ion is spherically surrounded by a uniformly spread negative charge such as the one created by the presence of negative lignads around the central metal ion. The electrostatic repulsion between *d* electrons and the said charge would result in *uniform increase* in the energies of *d* orbitals. In other words, although the orbitals acquire higher energy, they would still remain *degenerate.* Now consider that the negative charge surrounding *d* orbitals of the metal ion gets concentrated in a number of point charges such as the negative ligands in certain specific positions. The energy of the orbitals *lying in the directions of the point charges would be raised to a larger extent than that of the orbitals lying in between the point charges* because the electrons in the former type of *d* orbitals would experience greater repulsion from point charges than the electrons in the latter type of *d* orbitals. This means that some of the *d* orbitals would get associated with a higher energy than the other *d* orbitals. *The splitting of five degenerate d orbitals of the metal ion into sets of orbitals having different energies is called* **crystal field splitting.** The concept forms the *basis of crystal field theory.* In the crystal field theory we consider ligands as point charges.

The number of ligands and their arrangement around the central metal ion will naturally affect the relative energies of the five *d* orbitals. In other words, *the magnitude and the type of the crystal field splitting will be different in complexes of different geometries in which metal ions have different coordination numbers.* We would illustrate this concept by considering complexes with coordination numbers 6 and 4 which are the most common. The discussion would be restricted to the most common structures which are *octahedral, square planar* and *tetrahedral.*

Crystal Field Splitting in Octahedral Complexes. In an octahedral complex, the co-ordination number is 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron, as shown in Fig. 7.

The three axes *X, Y* and *Z* pointing along the corners of the octahedron are also shown. Let us suppose that the metal ion M^{n+} has a single *d* electron (d^1 configuration). In the free ion, when there are no ligands, the electron can occupy any one of the five *d* orbitals because all are of the same energy. Such orbitals having the same energy are called degenerate orbitals, as already mentioned.

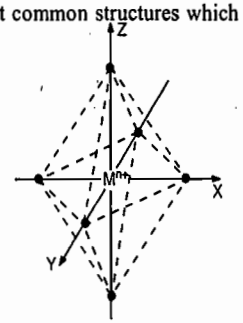


Fig. 7. Six ligands at the corners of an octahedron surrounding the metal ion, M^{n+}.

However, in the octahedral complex MX_6, all the five *d* orbitals will not remain of equal energy. This can be easily understood from the following discussion.

As already explained, the two orbitals, $d_{x^2-y^2}$ and d_{z^2} are oriented *along the axes* while the remaining three orbitals, *viz.*, d_{xy}, d_{yz} and d_{zx} are oriented *in between the axes.*

In the case of **octahedral complexes,** the former two orbitals are designated as e_g orbitals while the latter three orbitals are designated as t_{2g} orbitals. As the six ligands approach the central ion *along the axes,* the electron, if present in the e_g *orbitals, is repelled more by the ligand electrons than if it is present in the* t_{2g} *orbitals.* In other words, *the energy of the* d_{z^2} and $d_{x^2-y^2}$ *orbitals increases much more than the energy of the* d_{xy}, d_{yz} *and* d_{zx} *orbitals.* (It should be remembered that when a charge is repelled by a similar charge, its potential energy increases. The greater the repulsion, the greater is the increase of potential energy). Thus, in octahedral complexes, the five *d* orbitals split up into two sets : one set consisting of two orbitals of higher energy (e_g orbitals) and the other set consisting of three orbitals of lower energy (t_{2g} orbitals). The crystal field splitting in an **octahedral complex** is illustrated in Fig. 8.

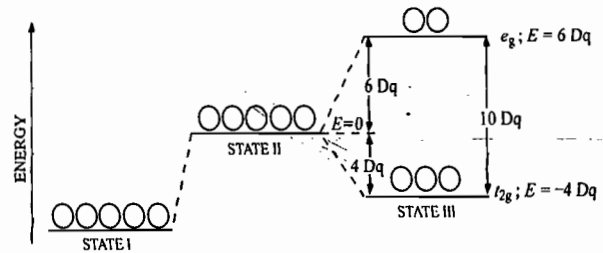


Fig. 8. Crystal field splitting in an octahedral complex.

The state I represents degeneracy of all the five *d* orbitals in the isolated central ion. The state II represents *hypothetical* degeneracy of all the orbitals at a higher energy level since the negative charge of all the ligands is *assumed* to be uniformly affecting the electrons in the *d* orbitals of the metal ion. The state III represents *crystal field splitting,* discussed above.

The crystal field splitting is measured in terms of the energy difference between t_{2g} and e_g orbitals Δ_o (the subscript o indicating octahedral complex). The crystal field splitting is generally measured in terms of a parameter, Dq. (The value of Dq varies from ligand to ligand as shown in the next chapter). By convention, Δ_o is taken to be equal to 10 Dq.

It can be shown that for an octahedral system, the energy of the t_{2g} orbitals is 4 Dq or 0·4 Δ_o *less* than the energy of the hypothetical degenerate *d* orbitals which would result if crystal field splitting is ignored (Fig. 8, state II). It follows, therefore, that the energy of the e_g orbitals is 6 Dq or 0·6 Δ_o *above* that of the hypothetical degenerate *d* orbitals. (The total energy of the unsplit *d* orbitals must be equal to the energy of the split *d* orbitals).

Crystal Field Stabilization Energy (CFSE). We know that an electron always prefers to occupy an orbital of a lower energy. It is evident that if an octahedral complex contains one *d* electron, that electron will reside in one of the t_{2g} orbitals. This orbital has an energy – 4 Dq or – 0·4 Δ_o compared to the energy (taken as zero) of the hypothetical degenerate orbitals of state II (Fig. 8). Thus, the complex will be 4 Dq or 0·4 Δ_o *more stable* than predicted by the pure electrostatic theory. Evidently, the energy of the complex would now be less. The decrease in energy = 0 – (– 4 Dq) = 4 Dq is called the crystal field stabilisation energy (CFSE) of the complex under consideration. The **crystal field stabilisation energy (CFSE)** may thus be defined as *the lowering in the energy of a transition metal ion in a given ligand environment due to crystal field effects.* [The splitting of *d* orbitals (or of energy terms which arise due to electrostatic repulsions amongst *d* electrons)* of a metal ion due to electrostatic crystal field potential of ligands and the consequences thereof are known as **crystal field effects**].

The qualitative procedure commonly adopted for calculating CFSEs of the complexed metal ions containing more than one *d* electrons is to assume that the interelectronic repulsions amongst *d* electrons do not affect the CFSEs much. Therefore, CFSEs are calculated by this qualitative procedure by considering the splitting of *d* orbitals alone. For each electron entering into a t_{2g} orbital, the crystal field stabilisation energy is 4 Dq. Hence, for each electron entering into an e_g orbital, the destabilisation energy would be 6 Dq. Working on this basis, it is possible to calculate crystal field stabilisation energies for various metal ions in octahedral complexes.

For example, for a d^2 system, the two electrons will occupy t_{2g} orbitals. The crystal field stabilisation energy, CFSE = 0 – 2(– 4 Dq) = 8 Dq, provided it is assumed that the changes in the interelectronic repulsions amongst the *d* electrons due to crystal field effects do not appreciably alter the stabilisation energy of the complex. Similarly, for a d^3 system, CFSE = 0 – 3(– 4 Dq) = 12 Dq.

However, for a d^4 system, there are two possibilities :

1. All the four electrons may occupy t_{2g} orbitals. One electron obviously gets paired. The electronic configuration may be written as $(t_{2g})^4$.

2. Three electrons occupy t_{2g} orbitals and one electron goes to one of the higher e_g orbitals. The configuration may then be written as $(t_{2g})^3(e_g)^1$.

The actual configuration may be decided on the basis of Δ_o and the **pairing energy** (*P*), *i.e., the energy required to pair the electrons with one another.* The pairing energy is evidently related to the energy of electrostatic repulsion amongst the *d* electrons. The configuration (1) is possible if $\Delta_o > P$, *i.e.*, Δ_o is greater than the energy of electrostatic repulsions amongst *d* electrons. In this case, the complex has less number of unpaired electrons and is called *low spin complex or strong field complex.* On the other hand, configuration (2) is possible if $\Delta_o < P$, *i.e.*, Δ_o is less than the energy of electrostatic repulsions amongst *d* electrons. In that case, the maximum number of electrons remain unpaired and the complex is called *high spin complex or weak field complex.*

A more exact procedure for calculating CFSEs of high spin complexes is to include in calculations the effects of interelectronic repulsions amongst the *d* electrons alongwith the effects of splitting of *d* orbitals due to crystal field effects. The results obtained with or without including the effect of interelectronic

*A detailed discussion of energy terms is given in Chapter 29.

repulsions, however, are identical except for d^2, d^7 (high spin) metal ions in weak field octahedral ligand environments and for d^3, d^8 metal ions in tetrahedral ligand environments. In these particular cases, the more exact procedure gives CFSEs of 6 Dq instead of 8 Dq.

In low spin complexes, the effects of interelectronic repulsions amongst the *d* electrons are *quite small* compared to the effects of splitting of *d* orbitals. *The CFSEs of low spin complexes are, therefore, estimated by neglecting the interelectronic repulsion factor.*

The crystal field stabilisation energies for metal ions having different numbers of *d* electrons in octahedral complexes are given in Table 3.

TABLE 3
Crystal Field Stabilisation Energies for Metal Ions having Different Number of *d* Electrons in Octahedral Complexes.

No. of *d* electrons in metal ions	Distribution of Electrons (High Spin) t_{2g} e_g	CFSE*	Distribution of Electrons (Low Spin) t_{2g} e_g	CFSE
1	↑ ○ ○ ○ ○	4 Dq		
2	↑ ↑ ○ ○ ○	6 Dq**		
3	↑ ↑ ↑ ○ ○	12 Dq		
4	↑ ↑ ↑ ↑ ○	6 Dq	↑↓ ↑ ↑ ○ ○	16 Dq
5	↑ ↑ ↑ ↑ ↑	0	↑↓ ↑↓ ↑ ○ ○	20 Dq
6	↑↓ ↑ ↑ ↑ ↑	4 Dq	↑↓ ↑↓ ↑↓ ○ ○	24 Dq
7	↑↓ ↑↓ ↑ ↑ ↑	6 Dq**	↑↓ ↑↓ ↑↓ ↑ ○	18 Dq
8	↑↓ ↑↓ ↑↓ ↑ ↑	12 Dq		
9	↑↓ ↑↓ ↑↓ ↑↓ ↑	6 Dq		
10	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0		

* Calculated by including the effects of interelectronic repulsions amongst the *d* electrons and the effects of *d* orbital splitting.

** CFSEs of these configurations are 8 Dq if we consider the effects of *d* orbital splitting alone and neglect the effects of interelectronic repulsions amongst the *d* electrons.

Crystal Field Splitting in Tetrahedral Complexes. The coordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate corners of a cube, as shown in Fig. 9.

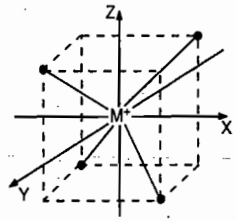


Fig. 9. Tetrahedral arrangement of four ligands around the metal ion.

It can be shown that in a tetrahedral structure, none of the *d* orbitals points exactly towards the ligands.

The three *d* orbitals d_{xy}, d_{yz} and d_{xz} are pointing close to the direction in which ligands are approaching while the two orbitals $d_{x^2-y^2}$ and d_{z^2} are lying in between the ligands. As a result of this, the energy of the former three orbitals increases compared to the energy of the latter two orbitals because the electrons in the former orbitals would be repelled by ligand electrons more strongly than electrons in the latter orbitals. Thus, the *d* orbitals are again split into two groups *but in a reverse order*.. The three orbitals, d_{xy}, d_{yz} and d_{xz}, designated as t_2 orbitals, now have higher energy than the two orbitals $d_{x^2-y^2}$ and d_{z^2}, designated

as e orbitals. This is diagrammatically shown in Fig. 10.

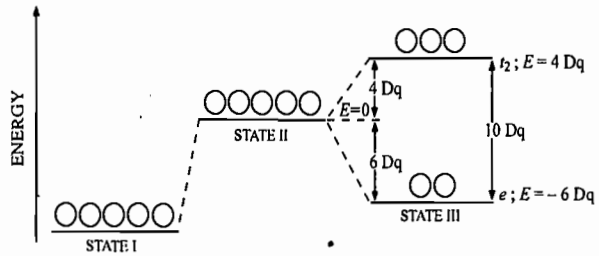


Fig. 10. Crystal field splitting in tetrahedral complexes. State II represents a hypothical state since it is assumed that negative charge of ligands uniformly affects the charge of d electrons.

The crystal field splitting (*i.e.*, the energy difference between the two sets of orbitals), in this case, is denoted by Δ_t, the subscript t indicating tetrahedral complexes. It is less than Δ_o observed in the case of octahedral complexes, discussed earlier. It has been estimated that $\Delta_t \approx -4/9\Delta_o$; the minus sign denotes that the order of splitting in tetrahedral complexes is the reverse of that in octahedral complexes. The smaller value of Δ_t as compared to Δ_o is partly due to lesser number of ligands in the tetrahedral field.

Since an electron prefers to move into a region of lower energy for reasons of stability, it follows that if a tetrahedral complex contains a d electron, that electron will reside in one of the $d_{x^2-y^2}$ and d_{z^2} orbitals.

An electron going into either of the $d_{x^2-y^2}$ and d_{z^2} orbitals is *stabilised* by 6 Dq (or $0{\cdot}6\Delta_t$) while that going into any of the other three orbitals is *destabilised* by 4 Dq (or $0{\cdot}4\,\Delta_t$).

The CFSEs for tetrahedral complexes having different electronic configurations can also be calculated by following the same procedure as for octahedral complexes. For a d^1 system, for example, CFSE = 0 –(–6 Dq) = 6 Dq and for a d^2 system, CFSE = 0–(–12 Dq) = 12 Dq. For a d^3 system, both low spin and high spin states are possible. However, no tetrahedral complex with low spin configuration has been formed. This is due to the fact that crystal field splitting energy in tetrahedral field is comparatively small and it is always less than the pairing energy. Therefore, pairing does not occur and the complexes are high spin complexes. The CFSE for a d^3 system, taking into consideration the d orbital splitting as well as repulsions amongst d electrons, is 6 Dq.

The CFSEs for complexes with metal ions having different configurations of d orbitals in tetrahedral field are given in Table 4.

TABLE 4
Crystal Field Stabilisation Energies for Tetrahedral Complexes with Metal Ions having different Electronic Configurations

Electronic configuration	Distribution of Electrons e	t_2	CFSE
d^1	↑	○○○	6 Dq
d^2	↑↑	○○○	12 Dq
d^3	↑↑	↑○○	6 Dq*
d^4	↑↑	↑↑○	4 Dq
d^5	↑↑	↑↑↑	0
d^6	↑↓↑	↑↑↑	6 Dq
d^7	↑↓↑↓	↑↑↑	12 Dq
d^8	↑↓↑↓	↑↓↑↑	6 Dq*
d^9	↑↓↑↓	↑↓↑↓↑	4 Dq
d^{10}	↑↓↑↓	↑↓↑↓↑↓	0

*CFSEs of these configurations are 8 Dq if we consider the effect of d orbital splitting alone and neglect the effects of interelectronic repulsions amongst the d electrons.

Crystal Field Splitting in Tetragonal and Square planar Complexes. The splitting of d orbitals in tetragonal and square planar complexes can be understood by gradually *withdrawing two ligands lying along the Z axis from an octahedral complex.*

As the ligands lying on the Z axis are moved away, the ligands in the XY plane tend to approach the central ion more closely. As a result of this, the electrons in d orbitals in the XY plane experience greater repulsion from the electrons of ligands in a tetragonal complex than in an octahedral complex. This causes an increase in the energy of d orbitals in XY plane, *i.e.*, an increase in the energy of $d_{x^2-y^2}$ and d_{xy} orbitals in tetragonal complexes compared to their energies in octahedral complexes, as illustrated in Fig. 11.

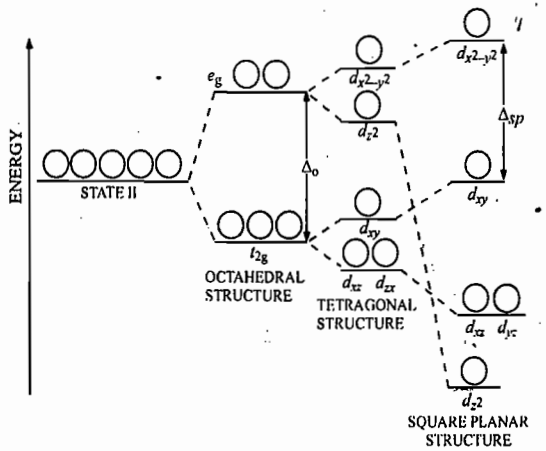


Fig. 11. Crystal field splitting in octahedral, tetragonal and square planar complexes.

Further, since the ligands lying on the Z axis have been moved away, the electrons in the d orbitals along the Z axis as well as in the XZ and YZ planes *experience relatively smaller repulsions* from the electrons of the ligands. This results in appreciable fall in the energy of d_{z^2} orbital as well as d_{xz} and d_{yz} orbitals. These changes are shown in Fig. 11. The structure in which the two trans ligands are at a different distance as compared to the other four ligands in XY plane is called **tetragonal structure.**

As the trans ligands lying along the Z axis *drop out completely,* a **square planar complex** ML_4 is formed. This is accompanied by a *further rise* in the energies of $d_{x^2-y^2}$ and d_{xy} orbitals and a *further fall* in the energies of d_{z^2}, d_{xz} and d_{yz} orbitals, as illustrated in Fig. 11. The crystal field splitting in the case of the square planar complex is indicated by Δ_{sp}.

Magnetic Properties of Metal Complexes and Crystal Field Theory. An important application of crystal field theory has been in understanding magnetic properties of transition metal complexes. As already discussed in Chapter 21, an electron, because of its orbital and spin motions, produces magnetic field whose strength is measured in units of Bohr magneton (B.M.) which is given by

$$\text{B.M.} = eh/4\pi mc$$

where h is Planck's constant, c is the velocity of light, e is the charge on the electron and m is its mass.

If an orbital contains *paired electrons,* the magnetic moment of one electron is cancelled by the equal and opposite magnetic moment of the other. Such substances get repelled by an applied magnetic field and are called ***diamagnetic.***

A substance having orbitals with one or more *unpaired* electrons, however, has a definite magnetic moment and it is attracted by a magnetic field. Such substances are said to be ***paramagnetic.***

The greater the number of unpaired electrons in a substance, the greater is the magnetic moment of the substance. It has been shown that magnetic moment of a substance containing n unpaired electrons is approximately equal to $\sqrt{n(n+2)}$ Bohr magnetons. This relationship has been employed for calculating the number of unpaired electrons in a substance. The values of n calculated by this expression for different magnetic moments are given in Table 5.

TABLE 5
Number of Unpaired Electrons Calculated From Magnetic Moments

Magnetic Moment ** (Bohr magneton)	Number of Unpaired Electrons
0	0
1·73	1
2·83	2
3·87	3
4·90	4
5·92	5

** The observed magnetic moments are slightly different from these values since the magnetic moments generated due to orbital motion of unpaired electrons have not been included in the formula, $\mu = \sqrt{n(n+2)}$.

A simple device, known as **Guoy's balance***, is generally used for measuring paramagnetism. The method, in brief, consists in placing a sample under examination in a magnetic field and measuring its weight. If the substance is paramagnetic, it will weigh more in the presence of a magnetic field than in its absence. The increase in weight is a measure of paramagnetism of the substance. The larger the number of unpaired electrons in a substance, the greater is the increase in its weight in a magnetic field.

Consider now the complexes of cobalt(III). From experiment we learn that its complex $[Co(NH_3)_6]^{3+}$ is *diamagnetic* while its complex $[CoF_6]^{3-}$ is *paramagnetic*. The cobalt(III) ion has six *d* electrons. This shows that while in the complex $[Co(NH_3)_6]^{3+}$, there is no unpaired electron, in the complex $[CoF_6]^{3-}$, there must be some unpaired electrons. Magnetic measurements indicate that the latter complex contains four unpaired electrons.

This observation can be explained in the light of the crystal field theory. In the octahedral complexes of Co(III), the *d* orbitals split up into two sets of orbitals, t_{2g} and e_g. The first three electrons of the central atom would singly occupy the low energy t_{2g} orbitals as per Hund's rule. The fourth and the fifth electron may either pair up with the electrons in t_{2g} orbitals or may occupy the higher energy e_g orbitals, depending upon the magnitude of Δ_o and *P*.

If Δ_o is small, the energy required to pair up the fourth and the fifth electron with the electrons in the lower *d* orbitals would be higher than that required to place the electrons in the higher *d* orbital. As a result, a lower energy high spin complex would be more stable. In a high spin complex, the sixth electron is paired up with the electron in the lower *d* orbital out of compulsion. In $[CoF_6]^{3-}$ complex, Δ_o is small so that a high spin complex with four unpaired electrons is formed (Fig. 12*a*). On the other hand, if Δ_o is large, the energy required to pair up the fourth, fifth and sixth electron with the electrons in the lower *d* orbitals would be less than that required to place the electron in higher *d* orbitals. Therefore, a low spin complex of lower energy would be more stable. In $[Co(NH_3)_6]^{3+}$ complex, Δ_o is large and hence a low spin complex with no unpaired electron results (Fig. 12*b*). Similarly, the magnetic behaviour of other octahedral complexes having central atom with seven or eight *d* electrons can be explained with the help of crystal field theory.

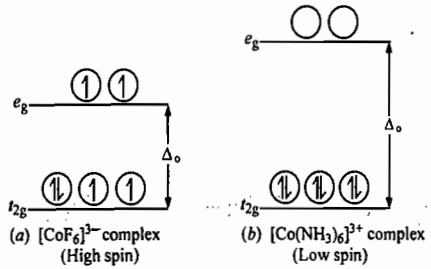


Fig. 12. Magnitude of crystal field splitting energy in low spin and high spin complexes of cobalt(III).

The number of unpaired electrons in octahedral and tetrahedral complexes having different configurations are given in Table 6.

While the pairing energy *P* depends upon the principal energy level *n* of the *d* electrons involved, crystal field splitting energy Δ depends upon a number of factors. These factors are discussed below.

Factors influencing the magnitude of Crystal Field Splitting. The following factors influence the magnitude of crystal field splitting.

1. Nature of the ligands. The crystal field splitting depends on the nature of the ligands. The greater the ease with which the ligands can approach the central ion, the greater is the crystal field splitting caused by it. Therefore, the ligands with large negative charge, small size and having good sigma donor and pi acceptor powers will give large crystal field splitting as they can approach the central ion closely.

In the following series, known as **spectrochemical series***, the ligands are arranged in the order in which they produce increasing values of Δ (or 10 Dq) with a particular metal ion :

$$I^- < Br^- < Cl^- < F^- < ox^{2-} \approx H_2O < py \approx NH_3 < en < NO_2^- < CN^- < CO$$

The ligands which produce small Δ (or 10 Dq) like I^-, Br^-, etc., are known as *weak field ligands* and those which produce large Δ (or 10 Dq) like CO, CN^-, etc., are called *strong field ligands*.

* Guoy's balance and spectrochemical series have been discussed in details in Chapter 30.

TABLE 6

Number of Unpaired Electrons in Octahedral and Tetrahedral Complexes.
[(*a*) is the configuration for high spin and (*b*) is the configuration for low spin complexes]

Electronic Configuration		Octahedral Complex (t_{2g} set)	Octahedral Complex (e_g set)	Number of unpaired electrons	Tetrahedral Complex (*e* set)	Tetrahedral Complex (t_2 set)	Number of unpaired electrons
d^1		↑ ○ ○	○ ○	1	↑ ○	○ ○ ○	1
d^2		↑ ↑ ○	○ ○	2	↑ ↑	○ ○ ○	2
d^3		↑ ↑ ↑	○ ○	3	↑ ↑	↑ ○ ○	3
d^4	(*a*)	↑ ↑ ↑	↑ ○	4	↑ ↑	↑ ↑ ○	4
	(*b*)	↑↓ ↑ ↑	○ ○	2			
d^5	(*a*)	↑ ↑ ↑	↑ ↑	5	↑ ↑	↑ ↑ ↑	5
	(*b*)	↑↓ ↑↓ ↑	○ ○	1			
d^6	(*a*)	↑↓ ↑ ↑	↑ ↑	4	↑↓ ↑	↑ ↑ ↑	4
	(*b*)	↑↓ ↑↓ ↑↓	○ ○	0			
d^7	(*a*)	↑↓ ↑↓ ↑	↑ ↑	3	↑↓ ↑↓	↑ ↑ ↑	3
	(*b*)	↑↓ ↑↓ ↑↓	↑ ○	1			
d^8		↑↓ ↑↓ ↑↓	↑ ↑	2	↑↓ ↑↓	↑↓ ↑ ↑	2
d^9		↑↓ ↑↓ ↑↓	↑↓ ↑	1	↑↓ ↑↓	↑↓ ↑↓ ↑	1
d^{10}		↑↓ ↑↓ ↑↓	↑↓ ↑↓	0	↑↓ ↑↓	↑↓ ↑↓ ↑↓	0

2. Oxidation state of the metal ion. The oxidation state of the metal ion also influences the magnitude of crystal field splitting. The metal ion with higher oxidation state causes larger crystal field splitting than is done by the ion with lower oxidation state. For example, the crystal field splitting energy Δ_o for $[Co(H_2O)_6]^{3+}$ complex in which the oxidation state of cobalt is +3, is 18,600 cm^{-1} whereas for the complex $[Co(H_2O)_6]^{2+}$ in which the oxidation state of Co is +2, Δ_o is 9,300 cm^{-1}. Similarly, for the complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$ in which iron has oxidation state +3 and +2, respectively, Δ_o is 13,700 cm^{-1} and 10,400 cm^{-1}, respectively.

3. Size of *d* orbitals (Transition series). The extent of crystal field splitting for similar complexes of a metal in the same oxidation state increases by about 30 to 50% on going from 3*d* series (First transition series) to 4*d* series (Second transition series). The increase is almost of the same magnitude (30 – 50%) on going from 4*d* series (Second transition series) to 5*d* series (Third transition series).

This may be explained on the basis that 4*d* orbitals in comparison to 3*d* orbitals are bigger in size and extend farther into space. As a result, the electrons in 4*d* orbitals can interact more strongly with the electrons in the ligand orbitals and, therefore, the crystal field splitting is more. Similarly, 5*d* orbitals are bigger than 4*d* orbitals and hence Δ_o for complexes of the elements of the Third transition series is more than that for Second transition series. This is evident from the following data :

$[Co(NH_3)_6]^{3+}$ Configuration $3d^6$ Δ_o = 23,000 cm^{-1}
$[Rh(NH_3)_6]^{3+}$ Configuration $4d^6$ Δ_o = 34,000 cm^{-1}
$[Ir(NH_3)_6]^{3+}$ Configuration $5d^6$ Δ_o = 41,000 cm^{-1}

This is the reason why almost all the octahedral complexes of metals of Second and Third transition series are low spin or strong field complexes.

4. Geometry of the complex. As mentioned earlier, the crystal field splitting energy of tetrahedral complexes (Δ_t) is nearly half the value for octahedral complexes ($\Delta_t \approx -4/9\,\Delta_o$). As a result, the splitting energy for tetrahedral complexes, in general, is small as compared to the pairing energy P. The tetrahedral complexes are, therefore, mostly *high spin complexes.*

Colour of Transition Metal Complexes

A substance exhibits colour because it has the property to absorb certain radiations from the visible region of spectrum. If, for example, the radiations corresponding to red light are absorbed, the reflected light will consist of radiations corresponding to wave lengths of complementary colours, of blue colour in particular. The substance, therefore, will appear to have blue colour. Hydrated copper(II) ions, for example, absorb red light and thus appear blue.

In the case of the transition metal complexes, the energy difference between the two sets of d orbitals (Δ) is usually small. The excitation of an electron from lower energy d orbitals to higher energy d orbitals (*e.g.*, from t_{2g} to e_g orbitals in octahedral complexes and from e to t_2 orbitals in tetrahedral complexes) is, therefore, very easy and can be achieved even by the absorption of low energy radiations of the visible region. As a result of the absorption of some selected wave lengths of visible light, the complexes appear coloured.

If λ is the wave length of radiations absorbed, the energy associated with it is given by $E = hc/\lambda$ where c is the velocity of light and h is the Planck's constant. Consider, for example, the octahedral complex $[Ti(H_2O)_6]^{3+}$. In this complex, the metal ion has d^1 configuration. In ground state this electron occupies one of the t_{2g} orbitals. It absorbs radiations in the green and yellow regions around 5000 Å wave length. The energy corresponding to this wave length, as calculated by the above expression, is about 240 kJ per mole. This energy is, therefore, equal to Δ_o which is required to excite the solitary electron to one of the e_g orbitals. Since, radiations from green and yellow regions are absorbed by the complex, the solution of the complex $[Ti(H_2O)_6]^{3+}$ looks purple which is the complementary colour of the absorbed radiations.

Since the differences in energy levels of t_{2g} and e_g orbitals (Δ_o values) vary with the nature of the ions, the nature of the ligands and the geometries of complexes formed, they absorb radiations from different regions of the visible light. Thus, the octahedral hydrated cobalt(II) complex $[Co(H_2O)_6]^{2+}$ absorbs in the blue region of the visible light. Its aqueous solution, therefore, appears pink (red). The tetrahedral cobalt(II) complexes of the type $[CoX_4]^{2-}$ need smaller energy for the excitation of their d electrons since $\Delta_t < \Delta_o$ and, therefore, they absorb in red region of the visible spectrum. These complexes, therefore, appear blue.

Similarly, it may be mentioned that since $[Co(NH_3)_6]^{3+}$ needs larger energy for excitation of its t_{2g} electrons, it absorbs in blue region. Hence it appears orange in solution. Another complex ion of cobalt(III), namely, $[Co(CN)_6]^{3-}$, requires still higher energy for excitation of its t_{2g} electrons. It absorbs in violet region and, therefore, its solution appears yellow.

It may be noted that only those transition metal complexes are coloured which have incomplete d subshells and in which the excitation of electrons from a lower energy set of d orbitals to a higher energy set is possible. The transition metal ions having completely filled or completely empty d subshells are colourless. Thus, complexes of $Cu^+(d^{10})$, $Zn^{2+}(d^{10})$, $Ag^+(d^{10})$, Sc^{3+} (d^0), $Ti^{4+}(d^0)$, etc., are colourless.

MODIFIED CRYSTAL FIELD THEORY. THE LIGAND FIELD THEORY

As discussed above, the crystal field theory assumes that the source of metal–ligand bond is the pure electrostatic interaction between the metal ion and the ligand. The theory predicts the splitting of d orbitals as being due to the electrostatic potential of the ligands to which the d electrons of the metal ions get exposed. The crystal field theory can explain the spectra of metal ions and of complexes on the assumption that these arise from the transition of electrons from lower energy d orbitals to higher energy d orbitals. However, the positions and intensities of spectral bands calculated on the basis of crystal field theory do not always coincide with those determined experimentally. There are frequent deviations.

Apart from this, a pure electrostatic interaction between the metal ion and the ligands fails to explain the relative positions of ligands in the spectrochemical series.

According to **ligand field theory**, the metal-ligand bonding is not exclusively due to electrostatic interaction between the metal ion and the ligand as postulated in the crystal field theory. On the other hand, there is concrete evidence to show that covalent bonding between the metal ion and the ligand also makes significant contribution towards the metal–ligand bonding in coordination complexes. This evidence is provided by the following facts :

Evidence of Covalent Bonding

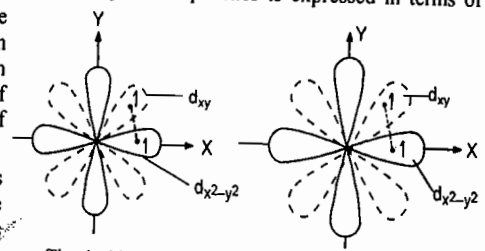
1. Lande's splitting factor, g.** The Lande's splitting factor g which is employed to predict the magnetic behaviour of transition metal complexes can also determine the extent of delocalisation (or penetration) of d electrons of the metal ion into the orbitals of the ligand. The value of g determined experimentally shows that the d electrons of the metal ion are almost always delocalised to some extent into the ligand orbitals. This can happen only due to the overlapping of the d orbitals of the metal ion with the ligand orbitals through covalent bonding. It has been deduced from the value of g that even in the bonds of F^- ions with metal ions in fluoro compounds, which are conventionally taken as ionic, there is around 5% covalent character.

2. Electron spin resonance (ESR) spectra. The ESR spectral studies conducted on the complexes of paramagnetic metal ions reveal the presence of unpaired electrons in the molecular orbitals formed due to the overlapping of orbitals of the ligand and the metal ion.

3. Nuclear magnetic resonance (NMR) spectra. The NMR spectral studies clearly indicate that the spin of an unpaired electron of a metal ion interacts with the nuclear spin of ^{19}F in the fluoro complex of a paramagnetic metal ion. This electron spin–nuclear spin interaction is possible only if the unpaired electron spends more than negligible time on the ^{19}F-nucleus. This is possible through the overlapping of orbitals of the ligand and the metal ion, *i.e.*, through covalent bonding.

4. Interelectronic repulsion the nephelauxetic effect. Electrons in the partly filled d orbitals of a metal ion repel one another and give rise to a number of energy levels depending upon the arrangement of these electrons in the d orbitals. The energy of each of these levels can be expressed in terms of some interelectronic repulsion parameters called *Racah repulsion parameters B* and *C*. The energy gap between two such energy levels which have the same spin multiplicity can be expressed in terms of Dq and B and the energy gap between two energy levels having different spin multiplicities is expressed in terms of Dq, B and C. It is observed experimentally that the magnitude of these interelectronic reulsion parameters always decreases on the complexation of the metal ion. This is possible only if interelectronic repulsion between the d electrons of the metal ion decreases on complexation.

The magnitude of interelectronic repulsion is inversely proportional to the distance r between the regions of maximum charge density of the d orbitals which are occupied by the electrons. This repulsion would decrease only if the distance r increases or if the lobes of d orbitals (containing the electrons) extend in space, as illustrated in Fig. 13.



The d orbitals of free metal ion. The extended d orbitals of complexed metal ion.

Fig. 13. The extension of the d orbitals in space in complexed metal ion.

** The magnetic moment μ of a transition metal ion is given by $\mu = g\sqrt{J(J+1)}$ where g is known as Lande's splitting factor. The value of g is given by the expression

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

where S is a quantum number which describes the total spin angular momenta of all the electrons, L is a quantum number which describes total orbital angular momentum and J is a quantum number which describes total angular momentum resulting from the coupling of spin and orbital angular momenta of electrons in a metal ion.

The extension of the lobes of the *d* orbitals which means the expansion of the *d* electron charge cloud, is known as **nephelauxetic effect** (from Greek, meaning 'cloud expanding').

The extension of *d* orbitals of the complexed metal ion in space occurs obviously to maximise the overlap of these orbitals with the orbitals of the ligand. This is an essential condition for covalent bonding. In other words, *it is the covalent bonding in metal–ligand bond which decreases the interelectronic repulsion parameters when a free metal ion gets complexed.* The larger the decrease in the interelectronic repulsion parameters, the greater is the extent of covalent bonding in metal–ligand bond of the complex. The capability of *d* orbitals of different metal ions to extend themselves in space forms the basis of the nephelauxetic series. Since the interelectronic repulsion parameters almost always decrease on complexation of a metal ion, the metal–ligand bonds in all the complexes must contain some contribution from covalent bonding.

5. Nuclear quadrupole resonance (NQR) studies. The NQR data on the complexes containing halide ions as the ligands clearly show that the metal–halogen bond is partly ionic and partly covalent in character.

The ligand field theory assumes, however, that the extent of covalent character in metal–ligand bond is generally low as compared to the extent of the ionic character of the bond with the result that the conclusions arrived at by the crystal field theory are still valid to a large extent.

MOLECULAR ORBITAL THEORY

The molecular orbital theory, although more complicated than the valence bond and crystal field theories, explains more satisfactorily the nature of bonding involved in coordination complexes.

For proper understanding of the molecular orbital theory of metal-ligand bond, we are to refresh our knowledge of the group theory and the terminology used therein which have been discussed in Chapter 3. Thus, we are to recall that the symbols *a*, *e* and *t* stand, respectively, for non-degenerate, doubly degenerate and triply degenerate* orbitals. The symmetry symbol for a particular orbital of the metal may be different in different environments. Thus, a set of *p* orbitals of a metal has t_{1u} symmetry in octahedral environment whereas it has t_2 symmetry in tetrahedral environment.

We are also to recall that for an effective combination of atomic orbitals to form molecular orbitals, the following requirements are needed to be met with :

1. The symmetry of the combining atomic orbitals must be the same so that the additive combination of atomic orbitals permits the maximum overlap of orbitals.

2. The difference in the energies of the combining orbitals is not large.

3. If the two atomic orbitals are of unequal energies, then the bonding molecular orbital would have more characteristics of the lower energy atomic orbital and the antibonding molecular orbital would have more characteristics of the higher energy atomic orbital. The greater the difference in the energies of the combining atomic orbitals, the greater would be the incorporation of the character of the lower energy atomic orbital in the bonding molecular orbital and the greater would be the incorporation of the character of the higher energy atomic orbital in the antibonding molecular orbital.

We shall now discuss the molecular orbital theory to explain the nature of bonding in coordination complexes.

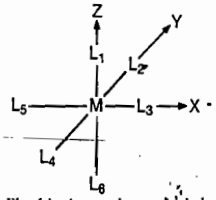


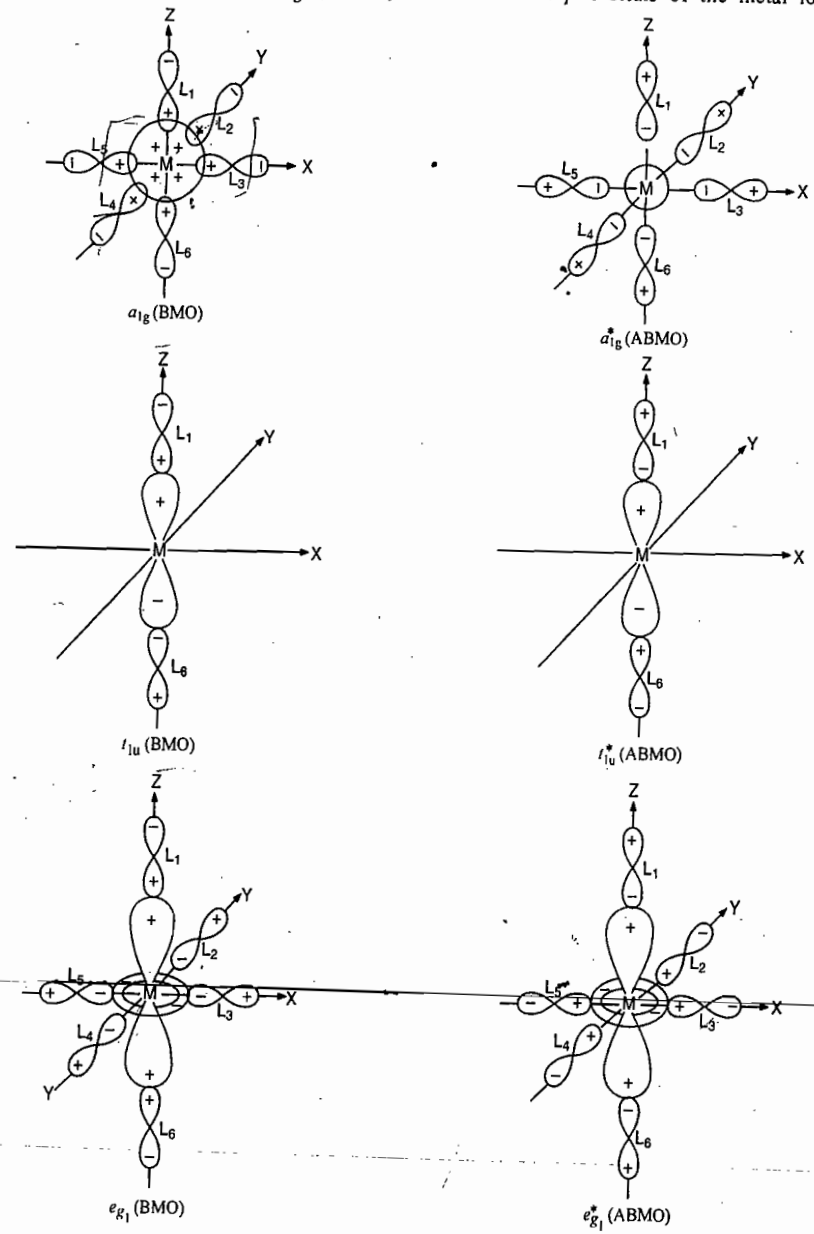
Fig. 14. A metal surrounded octahedrally by six ligands.

Sigma Bonding in Octahedral Complexes

Consider a metal ion surrounded octahedrally by six ligands and suppose that each ligand has a filled p_σ orbital on it which is capable of forming σ bond with the metal ion represented as M without charge for the sake of convenience (Fig. 14).

*Degenerate orbitals are orbitals of the same energy. Doubly and triply degenerate orbitals imply two orbitals of the same energy and three orbitals of the same energy, respectively.

The first step is to identify the metal orbitals and the combinations of p_σ orbitals of the ligand which are best suited to permit σ overlaps in the ± X, ± Y and ± Z directions. It can be easily shown with the help of the group theory that the combinations of p_σ orbitals of the ligand and the orbitals of the metal ion which combine with such combinations of p_σ orbitals of the ligand to form molecular orbitals, must have the a_{1g}, e_g and t_{1u} symmetries. In octahedral environment, the *s* orbital of the metal has a_{1g} symmetry, the two d_{z^2} and $d_{x^2-y^2}$ orbitals have e_g symmetry while the three *p* orbitals of the metal ion have



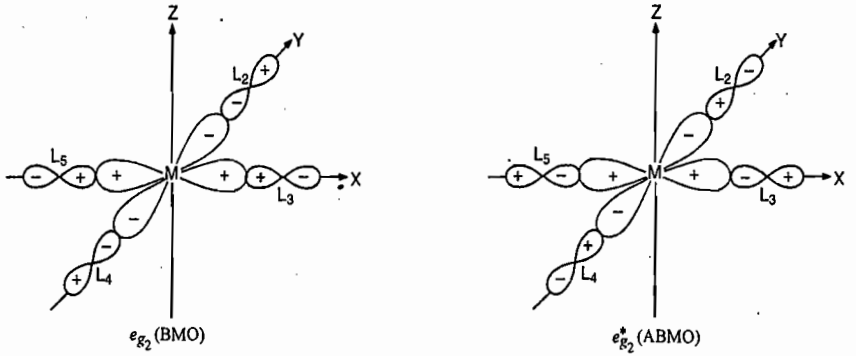


Fig. 15. The formation of a_{1g}, a^*_{1g}, t_{1u}, t^*_{1u}, e_g, e^*_g molecular orbitals.

t_{1u} symmetry. Hence the s orbital of the metal with a_{1g} symmetry would combine with p_σ ligand orbital combinations of a_{1g} symmetry to form a_{1g} bonding molecular orbitals (BMOs) and a^*_{1g} antibonding molecular orbitals (ABMOs), as shown in Fig. 15.

From the figure it is clear that the ligand orbitals have such orientations in bonding molecular orbitals that they give maximum positive overlap with the metal ion orbitals.

Similarly, the three p orbitals of the metal ion with t_{1u} symmetry combine with p_σ ligand–orbital combinations of t_{1u} symmetry to form t_{1u} bonding molecular orbitals and t^*_{1u} antibonding molecular orbitals. One such bonding t_{1u} and one such antibonding t^*_{1u} molecular orbital, obtained by combing p_z metal orbital with ligand orbital combinations of appropriate symmetries, are shown in Fig. 15. (Other t_{1u} and t^*_{1u} molecular orbitals can be easily drawn in a similar manner). Likewise, d_{z^2} and $d_{x^2-y^2}$ orbitals of the metal ion with e_g symmetry combine with p_σ ligand–orbital combinations of e_g symmetry to form e_g bonding molecular orbital and e^*_g antibonding molecular orbitals. A qualitative diagram representing relative energies of these molecular orbitals in the case of an octahedral complex is shown in Fig. 16.

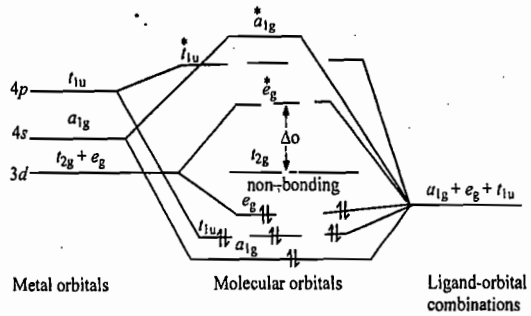


Fig. 16. Relative energies of sigma molecular orbitals in octahedral complexes.

The six filled p_σ orbitals of the ligands contribute 6×2 = 12 electrons to the molecular orbitals. These may be considered to be filling the bonding molecular orbitals, a_{1g}, t_{1u} and e_g. The electrons previously present in the d orbitals of the free metal ion may thus be considered to be distributed between t_{2g} non-bonding and e_g anti-bonding molecular orbitals of the complex. The energy gap between t_{2g} and e^*_g is, thus, equivalent to the crystal field splitting parameter Δ_o of the crystal field theory. However, in the crystal field theory, both the t_{2g} and e_g sets of orbitals are composed of pure d orbitals of the metal ion whereas according to molecular orbital theory, e_g molecular orbitals of the octahedral complex containing only sigma bonds between the metal ion and the ligand, have some ligand orbital character also. Out of the two sets of orbitals, t_{2g} non-bonding orbitals are pure metal d orbitals (*i.e.*, d_{xy}, d_{yz} and d_{zx} orbitals) whereas e^*_g antibonding molecular orbitals have a major contribution from e_g orbitals of the metal ion (*i.e.*, d_{z^2} and $d_{x^2-y^2}$ orbitals) and only minor contribution from the ligand orbitals. Therefore, it can be said that the electrons previously belonging to the free metal ion are accommodated in those molecular orbitals of the octahedral complex which are the pure d orbitals or which have a major contribution from d orbitals of the metal ion.

Pi Bonding in Octahedral Complexes

Consider each ligand of the octahedral complex having two mutually perpendicular p orbitals which are together perpendicular to the p_σ orbital and are capable of forming pi bonds. For example, each halide ion in an octhedral halide complex has two p orbitals of this type which are mutually perpendicular to each other and also perpendicular to p_σ orbital. Similarly, each cyanide ion in an octahedral cyanide complex has two mutually perpendicular π^* orbitals of this type. There will be in all 12 such orbitals on the six ligands. It can be shown with the application of the group theory that $t_{1g} + t_{2g} + t_{1u} + t_{2u}$ combinations of these twelve orbitals of the ligands are most suited for giving maximum pi overlap when combined with the orbitals of the metal ion of the same symmetry. There are no metal ion orbitals with t_{2u} and t_{1g} symmetry and the metal ion orbitals with t_{1u} symmetry are better suited for σ overlap. Hence only the t_{2g} orbitals of the metal ion overlap with t_{2g} combinations of the orbitals of the ligands to form t_{2g} bonding and t^*_{2g} antibonding pi molecular orbitals. Pictorial representation of the bonding and the antibonding molecular orbitals resulting from the overlap of one of the metal ion t_{2g} orbitals (*viz.*, d_{xy} orbital) and one of the t_{2g} combinations of the pi bonding ligand orbitals, is shown in Fig. 17.

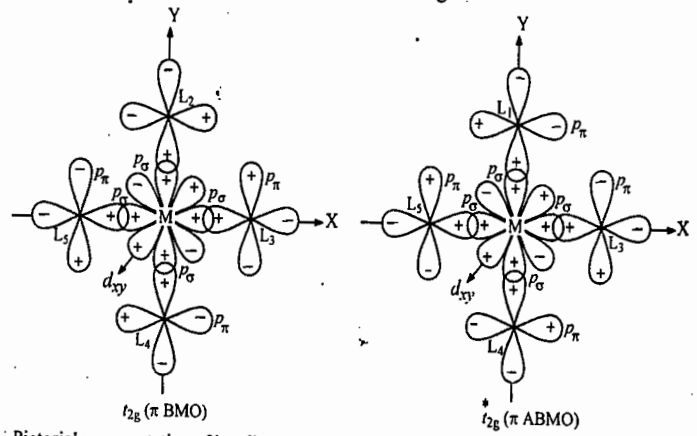


Fig. 17. Pictorial representation of bonding and antibonding molecular orbitals resulting from the overlap of one of the metal t_{2g} orbitals and the combination of π bonding ligand orbitals of the same symmetry.

It may be noted from the figure depicting bonding molecular orbitals that the orientation of the ligand p_π orbitals is such that they give maximum positive overlap with the metal ion orbitals.

The molecular orbital energy level diagram depicting both sigma and pi molecular orbitals in octahedral complexes is shown in Fig. 18.

If the ligands have filled p_π orbitals perpendicular to their p_σ orbitals (as in halide ions), then there are 12×2 + 6×2 = 36 electrons contributed by the ligands to the molecular orbitals of the complex. These electrons may be considered to be filling the bonding molecular

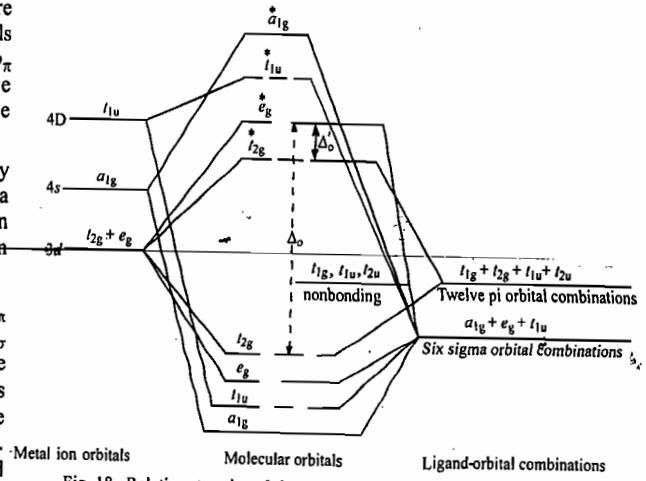


Fig. 18. Relative energies of sigma and pi bonding molecular orbitals in octahedral complexes.

orbitals upto the $t_{1g} + t_{1u} + t_{2u}$ level. The electrons previously present in the d orbitals of the free metal ion may be considered to be distributed between t_{2g}^* and e_g^* orbitals. Both the sets of these antibonding molecular orbitals have major contribution from the metal ion d orbitals. The energy separation between t_{2g}^* and e_g^* (Δ'_o) is equivalent to crystal field splitting parameter of the crystal field theory. But, if the ligands have empty π orbitals (*e.g.*, π^* in CN^- ion), then the ligands contribute $12\times0 + 6\times2 = 12$ electrons to the molecular orbitals of the complex. *These electrons may be considered to be filling the bonding molecular orbitals upto the e_g level. The n electrons previously present in the d orbitals of the* metal ion may be considered to be distributed between the t_{2g} and e_g^* molecular orbitals. The t_{2g} orbitals have mixed contribution from ligand orbitals and metal ion d orbitals. In this case, the energy separation between t_{2g} and e_g^* (Δ_o) is equivalent to crystal field splitting parameter of the crystal field theory which is obviously greater than Δ'_o. This is the reason why ligands such as CN^-, CO, etc., containing empty p_π orbitals, generally form low spin complexes ($\because \Delta_o > P$) whereas the ligands such as F^-, Cl^-, etc., containing filled pi orbitals (*i.e.*, orbitals containing filled p orbitals perpendicular to p_σ orbitals) generally form high spin complexes ($\because \Delta'_o < P$).

Sigma Bonding in Tetrahedral Complexes

The molecular orbital treatment of tetrahedral complexes is similar to the molecular orbital treatment of octahedral complexes. A tetrahedral complex may be thought to be derived from a cube with p_σ orbitals of the ligand directed towards the metal ion, as shown in Fig. 19. It can be shown by group theory that both the metal ion orbitals and the combinations of p_σ orbitals of the ligands which are most suited to form sigma bonds in the M – L directions have a_1 and t_2 symmetries. The orbital of the metal ion with a_1 symmetry in tetrahedral environment is the s orbital. But there are two sets of orbitals of the metal ion with t_2 symmetry in this environment. These are: the set of three p orbitals and the set of three d orbitals, *i.e.*, d_{xy}, d_{xz} and d_{yz} orbitals. The d_{z^2} and $d_{x^2-y^2}$ orbitals of the metal have e symmetry in tetrahedral environment and do not take part in sigma bonding as there are no combinations of p_σ orbitals of the ligands of e symmetry. A simple sigma molecular orbital energy level diagram of a tetrahedral complex is shown in Fig. 20.

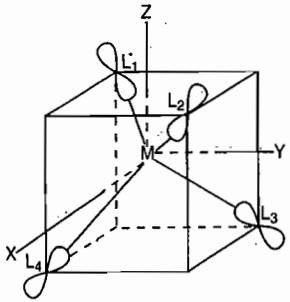


Fig. 19. A metal ion surrounded tetrahedrally by four ligands.

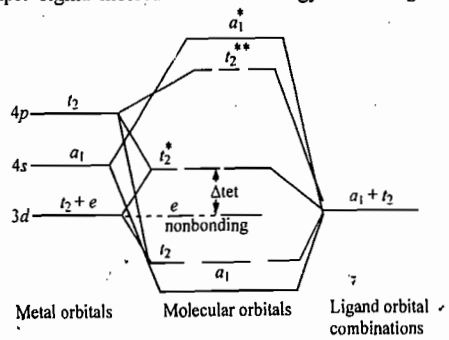


Fig. 20. Relative energies of sigma molcular orbitals in tetrahedral complexes.

The molecular orbitals t_2, t_2^* and t_2^{**} will have contribution from all the t_2 orbitals of the metal ion (*i.e.*, the set of p orbitals and d_{xy}, d_{yz}, d_{zx} orbitals) and the t_2 orbitals of the ligand. That is, these molecular orbitals will have a mixed contribution from the p and d orbitals of the metal ion. The four ligands contribute $4\times2 = 8$ electrons towards bonding which may be considered to be occupying the a_1 and t_2 bonding molecular orbitals. The electrons previously present in the d orbitals of the free metal ion may, therefore, be considered to be distributed in the $e - t_2^*$ set. The e orbitals are the non-bonding metal ion d_{z^2} and $d_{x^2-y^2}$ orbitals whereas t_2^* orbitals have a major contribution from the metal ion d (and p) orbitals. The energy difference between e and t_2^* orbitals is equivalent to the crystal field splitting parameter Δ_t of the crystal field theory. However, according to the crystal field theory, both e and t_2 orbitals are pure d orbitals whereas according to the molecular orbital theory, e orbitals are pure metal d orbitals and t_2^* orbitals have a mixed d, p orbitals character.

Pi Bonding in Tetrahedral Complexes

Suppose each ligand contains two p orbitals, apart from p_σ orbital which are capable of forming pi bond. These orbitals on each ligand are perpendicular to each other and to the p_σ orbital. There would, obviously, be eight such orbitals on the four ligands of the complex which can be shown by group theory to give combinations of ($t_1 + t_2 + e$) symmetry. These are best suited for pi bonding with the metal ion *orbitals of the same symmetry. But there are no metal ion orbitals with t_1 symmetry and the metal ion* orbitals with t_2 symmetry are better suited for sigma overlap. Hence, the metal ion orbitals with e symmetry preferentially combine with the combinations of ligand orbitals of the same symmetry to give e bonding and e^* antibonding molecular orbitals. The energy separation $e - t_2^*$ or $e^* - t_2^*$ in the event of pi bonding is generally less than the pairing energy (P). Therefore, tetrahedral complexes are almost always high spin complexes.

Sigma and Pi Bonding in Square Planar Complexes

Consider a square planar complex anion $[PtCl_4]^{2-}$ which belongs to D_{4h} symmetry point group. It can be shown by the application of group theory that the metal orbitals capable of forming sigma bonds with the ligands are $d_{x^2-y^2}$ (b_{1g}), s(a_{1g}), d_{z^2} (a_{1g}) and p_x, p_y(e_u). The symbols in parentheses give the symmetries of the respective metal ion orbitals in D_{4h} environment, the four p_σ ligand orbitals (one on each Cl^-) can be linearly combined to give four ligand–sigma orbital combinations which have the symmetries a_{1g}, b_{1g} and e_u. These ligand–sigma orbital combinations and metal ion orbitals of the same symmetry give molecular orbitals, as shown in Fig. 21.

Since the ligand orbitals are of considerably lower energy than the orbitals of the metal ion, all bonding molecular orbitals are closer in energy to the ligand orbital combinations and have major contribution from ligand orbitals. The bonding molecular orbitals, therefore, can be considered as essentially ligand orbitals. Similarly, all antibonding molecular orbitals, which are closer in energy to the metal ion orbitals, have major contribution from metal ion orbitals and can be considered as essentially metal ion orbitals.

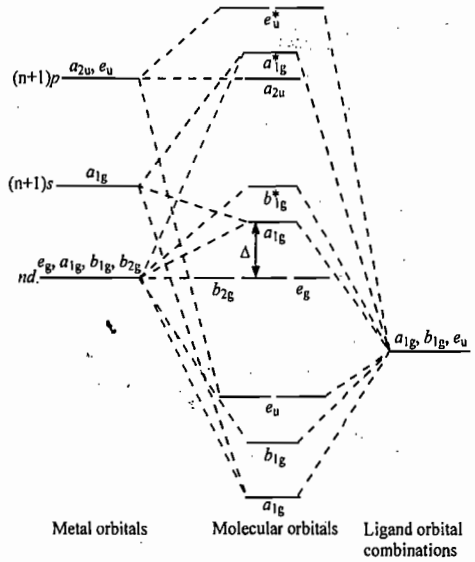


Fig. 21. Sigma molecular orbital diagram for square planar complex having D_{4h} symmetry

As is evident from Fig. 21, eight electrons from p_σ orbitals of four Cl^- ions and eight electrons from d orbitals of the metal ion belonging to the complex anion under discussion, get accommodated in eight molecular orbitals upto a_{1g}.

The sigma molecular orbital diagram given in Fig. 21 is an oversimplification of the actual bonding in the squar planar $[PtCl_4]^{2-}$ complex because each Cl^- also has two filled p_π orbitals, perpendicular to p_σ orbital. The eight linear combinations of these eight p_π ligand orbitals which are capable of forming pi bonds with the orbitals of central metal ion are of the symmetries a_{2g}, b_{2u}, e_u, a_{2u}, e_g and b_{2g}. The metal ion orbitals capable of forming pi bonds in square planar complexes of the type $[PtCl_4]^{2-}$ are d_{xy}(b_{2g}); d_{xz} and d_{yz}(e_g); p_z(a_{2u}) and p_x and p_y (e_u). These metal ion orbitals and ligand pi orbital combinations of the same symmetries give pi bonding and antibonding molecular orbitals. Therefore, a complete MO treatment of bonding in square planar $[PtCl_4]^{2-}$ complex should include both sigma and pi bonding effects.

A composite molecular orbital energy level diagram showing both σ and π molecular orbitals in $[PtCl_4]^{2-}$ complex is given in Fig. 22.

It is clear from Fig. 22 that ligand pi orbital combinations a_{2g} and b_{2u} remain non-bonding and are localised on the ligands because there are no orbitals of these symmetries available with the metal ion. The e_u metal orbitals are both sigma and pi bonding. Since there is one set of sigma as well as one set of pi ligand orbital combinations of e_u symmetry, there are three sets of molecular orbitals formed because of the combinations of one set of metal ion orbitals of e_u symmetry and two sets of ligand orbital combinations of this symmetry. The lowest energy e_u set of molecular orbitals is mainly σ bonding, the higher energy e_u set of molecular orbitals is mainly π bonding and the highest energy e_u set of molecular orbitals is both π antibonding (π*) and σ antibonding (σ*). Each set of e_u orbitals contains two orbitals of equal energy.

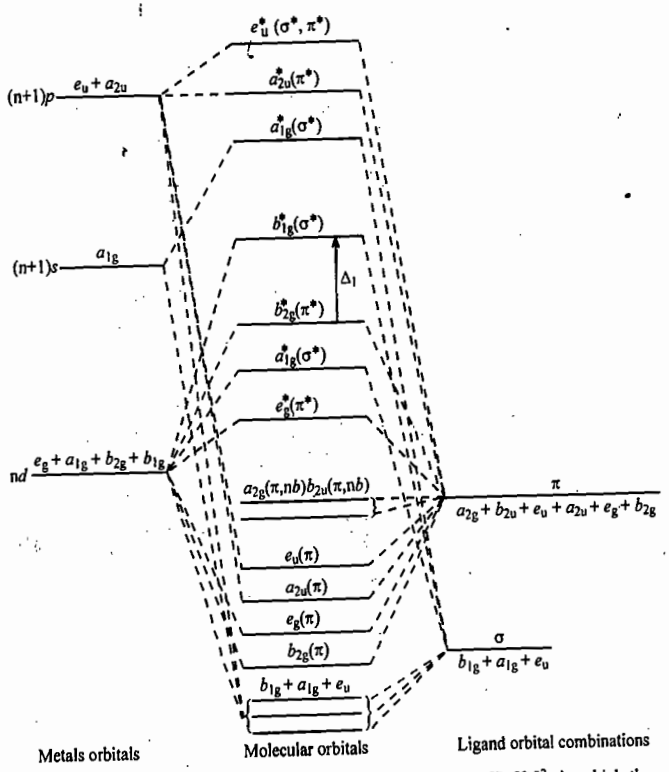


Fig. 22. Molecular orbitals of a square planar (D_{4h}) complex, $[PtCl_4]^{2-}$ in which the ligands are acting as both σ and pi donors.

The p_σ and p_π orbitals of four Cl^- ligands contribute 24 electrons which fill the twelve bonding and nonbonding molecular orbitals which are essentially ligand orbitals. The eight metal ion electrons may be considered to be occupying e_g^*, a_{1g}^* and b_{2g}^* orbitals which are essentially metal ion orbitals.

The part of Fig. 22 which accommodates metal ion *d* electrons is shown below :

$b^*_{1g}(\sigma^*)$	$d_{x^2-y^2}$
$b^*_{2g}(\pi^*)$	d_{xy}
$a^*_{1g}(\sigma^*)$	d_{z^2}
$e^*_g(\pi^*)$,	d_{xz}, d_{yz}

The above diagram is similar to the diagram showing splitting of *d* orbitals of a metal ion in a square planar complex due to crystal field effects. Thus, both crystal field theory and molecular orbital theory predict similar type of *d* orbital splitting in a square planar complex. But the molecular orbital theory has an edge over crystal field theory in the sense that the former not only explains the *d–d* transitions but also the L→M charge transfer transitions occurring in the complex. For instance, the excitation of electron from a filled nonbonding or bonding orbital (essentially ligand orbital) by electromagnetic radiation to b^*_{1g} (essentially a metal ion orbital) leads to transfer of electronic charge from ligands to metal ion within the complex. Such electronic excitations give rise to highly intense charge transfer bands in the electronic spectra of square planar complexes.

QUESTIONS

1. (*a*) What are the basic postulates of valence bond theory ?
   (*b*) What is the difference between an inner orbital complex and an outer orbital complex ? Discuss with one example each.
   (*c*) What is the number of unpaired electrons in tetrahedral $[Ni(CO)_4]$ complex ?
2. (*a*) Discuss in detail the valence bond theory to explain metal–ligand bonding in coordination compounds.
   (*b*) What are the important limitations of valence bond theory ?
3. (*a*) How does valence bond theory explain the shapes and magnetic properties of four-coordinated complexes of Ni^{2+} ? Illustrate your answer by giving suitabl examples.
   (*b*) The complex ion $[Co(NH_3)_6]^{3+}$ is octahedral and diamagnetic, the complex ion $[CoF_6]^{3-}$ is also octahedral but paramagnetic. How does valence bond theory account for this observation ?
4. (*a*) How does the valence bond theory account for the following facts :
   (*i*) $[Ni(CN)_4]^{2-}$ is diamagnetic and square planar.
   (*ii*) $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral
   (*iii*) $[Ni(CO)_4]$ is diamagnetic and tetrahedral ?
5. (*a*) How do the *d* orbitals split when a transition metal ion is placed in octahedral crystal field of ligands ?
   (*b*) Give the number of unpaired electrons in a strong and weak octahedral field for (*i*) Cr^{2+} (*ii*) Co^{2+} (*iii*) Fe^{3+}.
   (*c*) Explain the effect of the nature of ligands on the magnitude of Δ.
6. (*a*) Describe the bonding in $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ in terms of valence bond theory and crystal field theory.
   (*b*) How will you account for the non-existence of tetrahedral complexes with low spin configurations ?
7. (*a*) Discuss carefully and concisely the splitting of *d* orbitals in the case of
   (*i*) Octahedral complexes (*ii*) Tetrahedral complexes (*iii*) Square planar complexes
8. (*a*) Bring out clearly how the crystal field theory explains satisfactorily the magnetic properties of complexes of transition metals.
   (*b*) Discuss the structures of the following complexes on the basis of the crystal field theory :
   $[Co(NH_3)_6]^{3+}$ $[CoF_6]^{3-}$ $[Fe(H_2O)_6]^{2+}$ $[Fe(CN)_6]^{4-}$
9. What is crystal field theory ? How does it differ from the valence bond theory ? How does this theory account for the fact that $[CoF_6]^{3-}$ is paramagnetic but $[Co(NH_3]_6]^{3+}$ is diamagnetic, though both are octahedral ?
10. (*a*) Giving a neat diagram to explain how the *d* orbital energy levels split when transition metal ion is placed in the centre of a tetrahedral field.
    (*b*) Which complex has larger crystal field splitting :
    (*i*) $[Co(CN)_6]^{3-}$ or $[Co(NH_3)_6]^{3+}$ (*ii*) $[Co(H_2O)_6]^{2+}$ or $[Co(H_2O)_6]^{3+}$
    (*iii*) $[Co(NH_3)_6]^{3+}$ or $Rh(NH_3)_6]^{3+}$
    Give reasons for your answer.
    (*c*) What relationship exists between Δ (the crystal field splitting) and the pairing energy (*P*) in determining whether a given complex will be high spin or low spin ?
11. (*a*) Give the sequence of energy levels of *d* orbitals in square planar crystal field.
    (*b*) How does crystal field theory explain the colour of coordination complexes ?
12. (*a*) Define crystal field stabilization energy. Calculate its value for the following systems :
    (*i*) d^5 low spin octahedral (*ii*) d^5 high spin octahedral
    (*iii*) d^4 tetrahedral (*iv*) d^6 tetrahedral
13. Give evidence to establish that metal–ligand bonding in coordination complexes is not purely electrostatic in nature as is assumed in crystal field theory. In what respects does the ligand field theory differ from the crystal field theory ?
14. (*a*) Explain what is meant by nephelauxetic effect. How does this effect explain the contribution of covalent bonding in metal–ligand bonds ?
    (*b*) What conclusions can be drawn from the observed value of *g* (Lande's splitting factor) about the nature of metal–ligand bonding in coordination complexes ?
15. (*a*) Discuss the sigma and pi metal–ligand bonding in transition metal complexes with reference to tetrahedral transition metal complexes.
16. (*a*) Explain with the help of the molecular orbital theory why Cl^- acts as a weak ligand whereas CN^- acts as a strong ligand in octahedral transition metal complexes.
    (*b*) Why is molecular orbital theory preferred over crystal field theory in explaining metal–ligand bonding in transition metal complexes ?
17. Discuss sigma and pi bonding in square planar complexes by constructing a composite molecular orbital diagram for $[PtCl_4]^{2-}$

28 COORDINATION COMPOUNDS. PART III

QUANTITATIVE TREATMENT OF CRYSTAL FIELD THEORY

Crystal field theory explaining adequately the splitting of *d* orbitals into two sets of orbitals having different energies under the influence of electrostatic ligand field potential in octahedral and tetrahedral complexes has been discussed *qualitatively* in Chapter 27. The present chapter describes the *quantitative treatment* of the crystal field theory for explaining the splitting of *d* orbitals in metal ions subjected to octahedral crystal field potential, tetragonal crystal field potential and tetrahedral crystal field potential.

A. Metal Ions Subjected to Octahedral Crystal Field Potential. Derivation of Expression for determining V_{oct}

Consider a single electron in the degenerate set of *d* orbitals of a metal ion M^{n+} placed at the origin of the Cartesian coordinate system. Let this metal ion be surrounded octahedrally by six ligands placed at the points *i* (*i* = 1, 2, 3, ... 6) along the X, Y and Z directions. Assume that each of these ligands is represented by a point charge. Suppose that the *d* electron, at any particular instant, is present at the point *j* (*x*, *y*, *z*). The electrostatic potential $V_{oct}(x, y, z)$ experienced by the *d* electron at *j* from the octahedron of point charges of ligands is given by

$$V_{oct}(x, y, z) = \sum_{i=1}^{i=6} e^2 z_i / r_{ij} \qquad ...(1)$$

where r_{ij} is the distance between the ligand point charge $-z_i e$ and the point *j*. The effect of the electrostatic potential V_{oct} on the single *d* electron system is evaluated by applying **zeroth order perturbation method** (*i.e.*, the perturbation method for the degenerate systems) on the system as follows :

Suppose H_0 is the Hamiltonian, E_0 is the energy and ψ_1, ψ_2, ψ_3, etc., are the eigen wave functions of the degenerate set of *d* orbitals of the free metal ion M^{n+} containing a single *d* electron. As a result of the surrounding of the metal ion by the six ligand charges octahedrally, the Hamiltonian changes from H_0 to say, $H_0 + H'$ where H' is $V_{oct}(x, y, z)$ which is much smaller than H_0. Under such a situation $\psi_1, \psi_2, \psi_3 ... \psi_n$, etc., will no longer be the eigen wave functions of the changed system nor will the energy of the changed system be E_0. Let $E_0 + E'$ be the energy of the changed system. According to zeroth order perturbation, the wave functions of the perturbed system may still be represented as a linear combination of degenerate wave functions of the *d* orbitals of the free metal ion. Thus, the wave function ψ' for the changed system can be written as

$$\psi' = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + C_4\psi_4 + C_5\psi_5 \qquad ...(2)$$

where $\psi_1, \psi_2, \psi_3, \psi_4, \psi_5$ are real wave functions of degenerate *d* orbitals.

The wave equation for the perturbed system can, therefore, be written as

$$(H_0 + H')\psi' = (E_0 + E')\psi'$$

Applying the LCAO method, the following secular equations are obtained :

$$C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) + C_3(H_{13} - ES_{13}) + C_4(H_{14} - ES_{14}) + C_5(H_{15} - ES_{15}) = 0$$
$$C_1(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) + C_3(H_{23} - ES_{23}) + C_4(H_{24} - ES_{24}) + C_5(H_{25} - ES_{25}) = 0$$
$$C_1(H_{31} - ES_{31}) + C_2(H_{32} - ES_{32}) + C_3(H_{33} - ES_{33}) + C_4(H_{34} - ES_{34}) + C_5(H_{35} - ES_{35}) = 0$$
$$C_1(H_{41} - ES_{41}) + C_2(H_{42} - ES_{42}) + C_3(H_{43} - ES_{43}) + C_4(H_{44} - ES_{44}) + C_5(H_{45} - ES_{45}) = 0$$
$$C_1(H_{51} - ES_{51}) + C_2(H_{52} - ES_{52}) + C_3(H_{53} - ES_{53}) + C_4(H_{54} - ES_{54}) + C_5(H_{55} - ES_{55}) = 0$$

The secular determinant obtained from the above set of equations is :

$$\begin{array}{c|ccccc|} & \psi_1 & \psi_2 & \psi_3 & \psi_4 & \psi_5 \\ \hline \psi_1 & H_{11}-E & H_{12} & H_{13} & H_{14} & H_{15} \\ \psi_2 & H_{21} & H_{22}-E & H_{23} & H_{24} & H_{25} \\ \psi_3 & H_{31} & H_{32} & H_{33}-E & H_{34} & H_{35} \\ \psi_4 & H_{41} & H_{42} & H_{43} & H_{44}-E & H_{45} \\ \psi_5 & H_{51} & H_{52} & H_{53} & H_{54} & H_{55}-E \end{array} = 0$$

In the above determinant,

$$E = E_0 + E'$$

$$H_{11} = \int_{-\infty}^{+\infty} \psi_1^* (H_0 + H') \psi_1 \, d\tau_1 \text{ and so on}$$

$$H_{12} = \int_{-\infty}^{+\infty} \psi_1^* (H_0 + H') \psi_2 \, d\tau_2 \text{ and so on}$$

The following values of S_{ij} have already been inserted in the above determinant.

$$S_{11} = \int_{-\infty}^{+\infty} \psi_1^* \psi_1 \, d\tau = 1 \text{ and so on}$$

$$S_{12} = \int_{-\infty}^{+\infty} \psi_1^* \psi_2 \, d\tau_1 \, d\tau_2 = 0 \text{ and so on.}$$

Before we begin solving the above secular determinant, we should remember that we are interested in finding out only the changes that occur in the energy of *d* orbitals of the metal ion when it is subjected to octahedral crystal field potential of the ligands. We may, therefore, arbitrarily take the energy of the free metal ion, E_0, as zero.

The single-electron wave functions are conventionally written as (*n*, *l*, *m*). If these wave functions belong to the same set of wave functions (having same *n* and same *l*), they are written simply as (*m*). Thus, the wave functions $\psi_1, \psi_2, \psi_3, \psi_4$ and ψ_5 belonging to the set of *d* orbitals of the *d* metal ion are written as (+2), (+1), (0), (–1) and (–2), respectively.

Taking the energy of the free metal ion to be zero, H_{aa} reduces into H'_{aa} which is equal to $\int_{-\infty}^{+\infty} \psi_A^* | H' | \psi_A d\tau_A$, *i.e.*, $\int_{-\infty}^{+\infty} \psi_A^* | V_{oct} | \psi_A d\tau_A$ and H_{ab} reduces into H'_{ab} which is equal to $\int_{-\infty}^{+\infty} \psi_A^* | H' | \psi_B d\tau_A d\tau_B$ *i.e.*, $\int_{-\infty}^{+\infty} \psi_A^* | V_{oct} | \psi_B d\tau_A d\tau_B$.

Hence, the above secular determinant can be written in the following manner taking (+2), (+1), (0), (–1) and (–2) instead of $\psi_1, \psi_2, \psi_3, \psi_4$ and ψ_5, respectively and taking the energy of the free metal ion E_0 to be equal to zero.

$$\begin{array}{c|ccccc|} & (+2) & (+1) & (0) & (-1) & (-2) \\ \hline (+2) & H'_{+2,+2}-E' & H'_{+2,+1} & H'_{+2,0} & H'_{+2,-1} & H'_{+2,-2} \\ (+1) & H'_{+1,+2} & H'_{+1,+1}-E' & H'_{+1,0} & H'_{+1,-1} & H_{+1,-2} \\ (0) & H'_{0,+2} & H'_{0,+1} & H'_{0,0}-E' & H'_{-1,-1} & H_{0,-2} \\ (-1) & H'_{-1,+2} & H'_{-1,+1} & H_{-1,0} & H'_{-1,-1} & H_{-1,-2} \\ (-2) & H'_{-2,+2} & H'_{-2,+2} & H_{-2,0} & H'_{-2,-1} & H'_{-2,-2}-E' \end{array} = 0$$

where $H'_{m,m'} = \int_{-\infty}^{+\infty} (m)^* \,|\, H \,|\, (m')\, d\tau = \int_{-\infty}^{+\infty} (m)^* \,|\, V_{oct} \,|\, (m')\, d\tau$

(m may or may not be equal to m')

Remembering that $H' = V_{oct}(x, y, z)$, *i.e.* $= \sum_{i=1}^{i=6} ze^2/r_{ij}$, we can evaluate the elements of the integral provided r_{ij} is known. The quantity r_{ij} is determined with the help of the expression :

$$\frac{1}{r_{ij}} = \sum_{n=0}^{n=\infty} \sum_{m=-m}^{m=+m} \frac{4\pi}{2n+1} \frac{r_<^n}{r_>^{n+1}} Y_{nj}^m \, Y_{ni}^{m*} \qquad ...(4)$$

where Y_{ni}^{m*} and Y_{nj}^m are spherical harmonics of points i_{1-6} and j for particular values of n and m, $r_<$ means that r is lesser of the distances of the points i and j from the origin and $r_>$ implies greater of the distances of the points i and j from the origin. Since the point j, at which the electron is present at any instant, is located within the octahedron of ligand charges, $r_<$ can be written simply as r. Likewise, $r_>$, which is the metal-to-ligand distance, can be written simply as a. Accordingly, the above expression can be written as :

$$\frac{1}{r_{ij}} = \sum_{n=0}^{n=\infty} \sum_{m=-n}^{m=+n} \frac{4\pi}{2n+1} \frac{r^n}{a^{n+1}} Y_{n_j}^m \, Y_{n_i}^{m*} \qquad ...(5)$$

The various parameters involved are shown in Fig. 1.

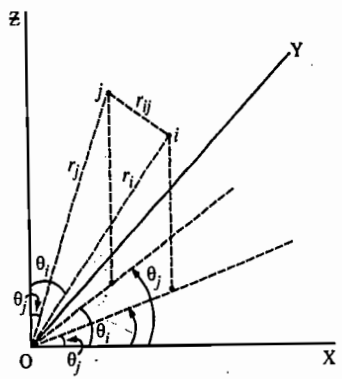


Fig. 1. Depiction of various parameters involved in the determination of octahedral crystal field potential at a particular point.

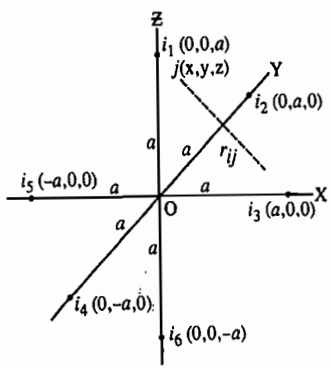


Fig. 2. Coordinates of points at which various ligands are placed in an octahedral complex.

In the present case, all the ligand charges are placed at the points i which are located on the ±X, ±Y and ±Z axes as shown in Fig. 2.

All the metal–ligand distances are a. The coordinates of the points i are $(0, 0, \pm a)$ along ±Z axis, $(0, \pm a, 0)$ along ±Y axis and $(\pm a, 0, 0)$ along ±X axis. All the angles θ_i and ϕ_i are thus known for the points i_{1-6}. One of the r_{ij} distance is shown in Fig. 2. The location of the remaining five r_{ij}s can be visualised. n and m are integers. For any n, the values of m range from $-n$ to $+n$ (including zero).

As already mentioned,

$$V_{oct}(x, y, z) = \sum_{i=1}^{i=6} \frac{ze^2}{r_{ij}} = Ze^2 \left[\frac{1}{r_{i_1 j}} + \frac{1}{r_{i_2 j}} + \frac{1}{r_{i_3 j}} + \frac{1}{r_{i_4 j}} + \frac{1}{r_{i_5 j}} + \frac{1}{r_{i_6 j}} \right] \qquad ...(6)$$

Let us find out all the $\frac{1}{r_{ij}}$ s with the help of expression (5) for different values of n and m.

Taking $n = 0$, the only value possible for m is zero. Hence,

$$\frac{1}{r_{i_1 j}} = \frac{4\pi}{1} \frac{r^0}{a^{0+1}} Y_{0j}^0 \, Y_{0i}^{0*} \qquad ...(7)$$

The spherical harmonic Y_0^0 is independent of θ and φ and has the same value for all is and the point j. The value of Y_0^0 is thus $\frac{1}{2\pi}$. Accordingly,

$$\frac{1}{r_{i_1 j}} = \frac{1}{r_{i_2 j}} = \frac{1}{r_{i_3 j}} = \frac{1}{r_{i_4 j}} = \frac{1}{r_{i_5 j}} = \frac{1}{r_{i_6 j}} \qquad ...(8)$$

$$= \frac{4\pi}{a} \times \frac{1}{2\sqrt{\pi}} \times \frac{1}{2\sqrt{\pi}} = \frac{1}{a} \qquad ...(9)$$

$$\therefore \quad V_{oct} = Ze^2 \left[\frac{1}{a} + \frac{1}{a} + \frac{1}{a} + \frac{1}{a} + \frac{1}{a} + \frac{1}{a} \right] \qquad ...(10)$$

$$= 6Ze^2/a \text{ when } n = 0 \text{ and } m = 0 \qquad ...(11)$$

The evaluation of $\frac{1}{r_{ij}}$ for odd values of n is not necessary since it can be shown that $\int (m)^* \,|\, V_{oct}, n = \text{odd} \,|\, (m')\, d\tau$ or $\int (m)^* \,|\, \frac{Ze^2}{r_{ij}} \; (n = \text{odd}) \,|\, (m')\, d\tau$ parts of the elements of the determinant vanish if (m) and (m') are the d orbital wave functions having $l = 2$. Hence, we shall consider only even values of n for calculating the rest of the fragments of $\frac{1}{r_{ij}}$ and hence of V_{oct}. Table 1 gives the values of θ_i and ϕ_i for the points i_1 to i_6.

TABLE 1

θ_i and ϕ_i Values for the Points i_1 to i_6 located on Different Axes

Position of the Ligand	θ_i	ϕ_i
i_1 on +Z axis $(0, 0, a)$	0	–
i_6 on –Z axis $(0, 0, -a)$	π	–
i_2 on +Y axis $(0, a, 0)$	π/2	π/2
i_4 on –Y axis $(0, -a, 0)$	π/2	–π/2
i_3 on +X axis $(a, 0, 0)$	π/2	0
i_5 on –X axis $(-a, 0, 0)$	π/2	π

Taking $n = 2$ and $m = 0$, we have

$$\frac{1}{r_{ij}} = \frac{4\pi}{5} \times \frac{r^2}{a^3} Y_{2j}^0 \, Y_{2i}^{0*} \quad ...(12)$$

$$= \frac{4\pi}{5} \times \frac{r^2}{a^3} Y_{2j}^0 \left(\frac{5}{8}\right)^{1/2} (2\pi)^{-1/2} (3\cos^2\theta_i - 1) \quad ...(13)$$

$$[\because Y_{2i}^{0*} = Y_{2i}^0 = \left(\frac{5}{8}\right)^{1/2} (3\cos^2\theta_i - 1)(2\pi)^{-1/2} e^{i0\phi}]$$

(The values of spherical harmonics Y of any point are given in Chapter 1)

$$\therefore \quad V_{\substack{oct \\ n=2, m=0}} = Ze^2 \sum_{i=1}^{i=6} \frac{1}{r_{ij}} = Ze^2 \left[\frac{1}{r_{i_1j}} + \frac{1}{r_{i_2j}} + \frac{1}{r_{i_3j}} + \frac{1}{r_{i_4j}} + \frac{1}{r_{i_5j}} + \frac{1}{r_{i_6j}}\right] \quad ...(14)$$

$$= [2 - 1 - 1 - 1 - 1 + 2] \, Ze^2 \frac{4\pi}{5} \frac{r^2}{a^3} \left(\frac{5}{8}\right)^{1/2} (2\pi)^{-1/2} Y_{2j}^0 = 0 \quad ...(15)$$

[The above values are obtained by substituting the values of θ_i and ϕ_i for all the six points in expression (5) for $\frac{1}{r_{ij}}$]

Taking $n = 2$ and $m = -1$, we have

$$\frac{1}{r_{ij}} = \frac{4\pi}{5} \frac{r^2}{a^3} Y_{2j}^{-1} \, Y_{2i}^{-1*} = \frac{4\pi}{5} \frac{r^2}{a^3} Y_{2j}^{-1} \left(\frac{15}{4}\right)^{1/2} \cos\theta_i \sin\theta_i (2\pi)^{-1/2} e^{+i\phi} \quad ...(16)$$

$$[\because Y_{2i}^{-1*} = Y_{2i}^{+1} = \left(\frac{15}{4}\right)^{1/2} \cos\theta_i \sin\theta_i \, (2\pi)^{-1/2} e^{+i\phi}]$$

$$\therefore \quad V_{\substack{oct \\ (n=2, m=-1)}} = Ze^2 \sum_{i=1}^{i=6} \frac{1}{r_{ij}} = Ze^2 \left[\frac{1}{r_{i_1j}} + \frac{1}{r_{i_2j}} + \frac{1}{r_{i_3j}} + \frac{1}{r_{i_4j}} + \frac{1}{r_{i_5j}} + \frac{1}{r_{i_6j}}\right] \quad ...(17)$$

Substituting the values of θ_i and ϕ_i for all the six points in expression (5) for $\frac{1}{r_{ij}}$, we get

$$V_{\substack{oct \\ (n=2, m=-1)}} = Ze^2 [0 + 0 + 0 + 0 + 0 + 0] \left(\frac{15}{4}\right)^{1/2} (2\pi)^{-1/2} Y_{2j}^{-1} = 0 \quad ...(18)$$

Similarly, it can be shown that

$$V_{\substack{oct \\ n=2, m=+1}} = 0 \quad (\because \textcircled{H}_{l,+m} = \textcircled{H}_{l,-m}; \ \textcircled{H} \text{ designates Hamiltonian}) \quad ...(19)$$

Taking $n = 2$ and $m = -2$, we have

$$\frac{1}{r_{ij}} = \frac{4\pi}{5} \frac{r^2}{a^3} Y_{2j}^{-2} \, Y_{2i}^{-2*} \quad ...(20)$$

$$= \frac{4\pi}{5} \frac{r^2}{a^3} Y_{2j}^{-2} \left(\frac{15}{16}\right)^{1/2} \sin^2\theta_i \, (2\pi)^{-1/2} e^{+i2\phi} \quad ...(21)$$

$$[\because Y_{2i}^{-2*} = Y_{2i}^{+2} = \left(\frac{15}{16}\right)^{1/2} \sin^2\theta_i \, (2\pi)^{-1/2} e^{+i2\phi}]$$

$$\therefore \quad V_{\substack{oct \\ (n=2, m=-2)}} = Ze^2 \sum_{i=1}^{i=6} \frac{1}{r_{ij}} = Ze^2 \left[\frac{1}{r_{i_1j}} + \frac{1}{r_{i_2j}} + \frac{1}{r_{i_3j}} + \frac{1}{r_{i_4j}} + \frac{1}{r_{i_5j}} + \frac{1}{r_{i_6j}}\right] \quad ...(22)$$

Substituting the values of θ_i and ϕ_i for all the six points in expression (5) for $\frac{1}{r_{ij}}$, we have

$$V_{\substack{oct \\ (n=2, m=-2)}} = Ze^2 [0 + 1 \times e^{+i\pi} + 1 \times e^0 + 1 \times e^{-i\pi} + 1 \times e^{i2\pi} + 0] \frac{4\pi}{5} \frac{r^2}{a^3} \left(\frac{15}{16}\right)^{1/2} (2\pi)^{-1/2} Y_{2j}^{-2} \quad ...(23)$$

$$= Ze^2 [0 + \cos\pi + i\sin\pi + 1 + \cos\pi - i\sin\pi + \cos 2\pi + i\sin 2\pi + 0] \frac{4\pi}{5} \frac{r^2}{a^3} \left(\frac{15}{16}\right)^{1/2} (2\pi)^{-1/2} Y_{2j}^{-2} \quad ...(24)$$

(applying $e^{\pm im\phi} = \cos m\phi + i \sin m\phi$)

$$= Ze^2 [0 - 1 + 1 - 1 + 1 + 0] \frac{4\pi}{5} \frac{r^2}{a^3} \left(\frac{15}{16}\right)^{1/2} (2\pi)^{-1/2} Y_{2j}^{-1} = 0 \quad ...(25)$$

Similarly, it can be shown that

$$V_{\substack{oct \\ n=2, m=2}} \text{ is also equal to zero.} \quad ...(26)$$

Taking $n = 4$ and $m = 0$, we have

$$\frac{1}{r_{ij}} = \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^0 \, Y_{4i}^{0*} \quad ...(27)$$

$$= \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^0 \left(\frac{9}{128}\right)^{1/2} (35\cos^4\theta_i - 30\cos^2\theta_i + 3) \sqrt{\frac{1}{2\pi}} \quad ...(28)$$

$$\therefore \quad V_{\substack{oct \\ (n=4, m=0)}} = Ze^2 \sum_{i=1}^{i=6} \frac{1}{r_{ij}} = Ze^2 \left[\frac{1}{r_{i_1j}} + \frac{1}{r_{i_2j}} + \frac{1}{r_{i_3j}} + \frac{1}{r_{i_4j}} + \frac{1}{r_{i_5j}} + \frac{1}{r_{i_6j}}\right] \quad ...(29)$$

$$= Ze^2 \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^0 \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} [8 + 3 + 3 + 3 + 3 + 8] \quad ...(30)$$

$$= Ze^2 \frac{4\pi}{9} \frac{r^4}{a^5} \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} 28 \, Y_{4j}^0 \quad ...(31)$$

It can be shown that V_{oct} ($n = 4$, $m = \pm 1$), V_{oct} ($n = 4$, $m = \pm 2$) and V_{oct} ($n = 4$ and $m = \pm 3$) are all equal to zero. The reader may verify it by taking spherical harmonics of $Y_{4i}^{\pm 1}$, $Y_{4i}^{\pm 2}$ and $Y_{4i}^{\pm 3}$ which are given in Chapter 1.

Taking $n = 4$ and $m = -4$, we have

$$\frac{1}{r_{ij}} = \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^{-4} \, Y_{4i}^{-4*} \quad ...(32)$$

$$= \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^{-4} \left(\frac{315}{256}\right)^{1/2} \sin^4\theta_i \, (2\pi)^{-1/2} e^{+i4\phi} \quad ...(33)$$

$$\therefore \quad V_{\underset{(n=4,\, m=-4)}{\text{oct}}} = Ze^2 \sum_{i=1}^{i=6} \frac{1}{r_{ij}} \qquad ...(34)$$

$$= Ze^2 \left[\frac{1}{r_{i_1 j}} + \frac{1}{r_{i_2 j}} + \frac{1}{r_{i_3 j}} + \frac{1}{r_{i_4 j}} + \frac{1}{r_{i_5 j}} + \frac{1}{r_{i_6 j}} \right] \qquad ...(35)$$

Substituting the values of θ_i and ϕ_i for all the six points in expression (5) for $\frac{1}{r_{ij}}$, we get

$$V_{\underset{(n=4,\, m=-4)}{\text{oct}}} = Ze^2 \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^{-4} \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} [0+1+1+1+1+0] \qquad ...(36)$$

$$= Ze^2 \frac{4\pi}{9} \frac{r^4}{a^5} \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} \times 4 Y_{4j}^{-4} \qquad ...(37)$$

In a similar manner, V_{oct} $(n = 4, m = +4)$ can be evaluated.

It can be shown easily that V_{oct} $(n = 4, m = +4)$ is equal to $Ze^2 \frac{4\pi}{9} \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} 4 Y_{4j}^{+4}$.

The expansion of $\frac{1}{r_{ij}}$ for $n > 4$ is not required because we are dealing with single d electron wave functions in which case the expansions with $n > 2l$ become redundant.

Based on the above discussion, we may express the value of V_{oct} as follows :

$$V_{\text{oct}} = \frac{6Ze^2}{a} + Ze^2 \frac{4\pi}{9} \frac{r^4}{a^5} \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} \times 28 Y_4^0 + Ze^2 \frac{4\pi}{9} \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} \times 4 (Y_{4j}^{-4} + Y_{4j}^{+4}) \qquad ...(38)$$

$$= \frac{6Ze^2}{a} + Ze^2 (2\pi)^{1/2} \left(\frac{49}{18}\right)^{1/2} Y_4^0 \frac{r^4}{a^5} + Ze^2 \left(\frac{35}{36}\right)^{1/2} (2\pi)^{1/2} \left(Y_4^{-4} + Y_4^{+4}\right) \frac{r^4}{a^5} \qquad ...(39)$$

$$= \frac{6Ze^2}{a} + \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2 r^4}{a^5} \left[Y_4^0 + \left(\frac{5}{14}\right)^{1/2} \left(Y_4^4 + Y_4^{-4}\right) \right] \qquad ...(40)$$

Having determined V_{oct}, let us proceed to evaluate the elements of the 5 × 5 determinant which are of the form :

$$\text{Ⓗ}_{m,\, m'} = \int (m)^* \, | V_{\text{oct}} | \, (m') \, d\tau \qquad ...(41)$$

$$= \int (m)^* \left| \frac{6Ze^2}{a} + \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2 r^4}{a^5} \left[Y_4^0 + \left(\frac{5}{14}\right)^{1/2} \left(Y_4^4 + Y_4^{-4}\right) \right] \right| (m') \, d\tau \qquad ...(42)$$

$$= \int (m)^* \left| \frac{6Ze^2}{a} \right| (m') \, d\tau + \int (m)^* \left| \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2 r^4}{a^5} \left[Y_4^0 + \left(\frac{5}{14}\right)^{1/2} \left(Y_4^4 + Y_4^{-4}\right) \right] \right| (m') \, d\tau \qquad ...(43)$$

The first integral which is $\int (m)^* \left| \frac{6Ze^2}{a} \right| (m') \, d\tau$ becomes zero in all the off diagonal elements where

$m \neq m'$ since in such cases, the integral becomes $\frac{6Ze^2}{a} \int (m)(m') \, d\tau$ which is obviously zero. This integral becomes $\frac{6Ze^2}{a}$ if $m = m'$ $\left(\text{since } \frac{6Ze^2}{a} \int (m)^* (m) \, d\tau = \frac{6Ze^2}{a} \right)$ whatever be the wave function (m) taken. In other words, the first integral $\int (m)^* \left| \frac{6Ze^2}{a} \right| (m') \, d\tau$ is uniformly equal to $\frac{6Ze^2}{a}$ for all the diagonal elements (where $m = m'$) independent of the wave function of the integral. The integral $\int (m)^* \left| \frac{6Ze^2}{a} \right| (m) \, d\tau$ of the diagonal elements corresponds to a uniform change in the energy of the five d orbitals. As stated above, we are interested only in knowing the changes that take place in the relative energies of d orbitals due to crystal field effect. Therefore, the first integral $\int (m)^* \left| \frac{6Ze^2}{a} \right| (m') \, d\tau$ is not considered further. Only the integral $\int (m)^* \left| \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2 r^4}{a^5} \left[Y_4^0 + \left(\frac{5}{14}\right)^{1/2} \left(Y_4^4 + Y_4^{-4}\right) \right] \right| (m') \, d\tau$ needs to be evaluated for all the elements of the determinant in order to evaluate changes that occur in the energies of d orbitals due to crystal field effect. The effective V_{oct} causing changes in the relative energies of d orbitals is, therefore, given by

$$V_{\text{oct}} = \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2 r^4}{a^5} \left[Y_4^0 + \left(\frac{5}{14}\right)^{1/2} \left(Y_4^4 + Y_4^{-4}\right) \right] \qquad ...(44)$$

Let us evaluate the second integral, *viz.*,

$$\int (m)^* \left| \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2 r^4}{a^5} \left[Y_4^0 + \left(\frac{5}{14}\right)^{-1/2} (Y_4^4 + Y_4^{-4}) \right] \right| (m') \, d\tau$$

to find out all $\text{Ⓗ}_{m,\, m'}$ (m may or may not be the same as m') of the determinant.

We can rewrite this integral as

$$\text{Ⓗ}_{m,\, m'} = \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2}{a^5} \int R_{n,2}^* \, r^4 . R_{n,2} \, r^2 dr \int_0^{\pi} \int_0^{2\pi} Y_2^{m^*} \left| Y_4^0 \right| + \left(\frac{5}{14}\right)^{1/2} \left(Y_4^4 + Y_4^{-4}\right) Y_2^{m'} \sin\theta \, d\theta \, d\phi \qquad ...(45)$$

where $R_{n,2}$ is the radial part of d orbital wave functions and $Y_2^{m^*}$ and $Y_2^{m'}$ are the spherical harmonics part of the d orbital wave functions (m^*) and (m'), respectively. $R_{n,2}$ is the same for all d orbital wave functions having the same n.

The radial part of the integral $\int R_{n,2}^* \, r^4 R_{n,2} \, r^2 dr$ is $\overline{r_2^4}$ which is the average of the fourth power of the radius of d electron.

The above expression can be rewritten as

$$\text{Ⓗ}_{m,\, m'} = \left(\frac{49}{18}\right)^{1/2} (2\pi)^{1/2} \frac{Ze^2 \overline{r_2^4}}{a^5} \left[\int_0^{\pi} \int_0^{2\pi} Y_2^{m^*} \left| Y_4^0 \right| Y_2^{m'} \sin\theta \, d\theta \, d\phi + \right.$$

$$\left. \left(\frac{5}{14}\right)^{1/2} \int_0^{\pi} \int_0^{2\pi} Y_2^{m^*} \left| Y_4^4 \right| Y_2^{m'} \sin\theta \, d\theta \, d\phi + \left(\frac{5}{14}\right)^{1/2} \int_0^{\pi} \int_0^{2\pi} Y_2^{m^*} \left| Y_4^{-4} \right| Y_2^{m'} \sin\theta \, d\theta \, d\phi \right] \qquad ...(45a)$$

The above expression contains three integrals. The integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{*}\,|\,Y_4^0\,|\,Y_2^{m'}\sin\theta\, d\theta\, d\phi$ can be rewritten as $\int_0^{\pi} \textcircled{H}_2^{m}\,|\,\textcircled{H}_4^0\,|\,\textcircled{H}_2^{m'}\sin\theta\, d\theta \left(\frac{1}{2\pi}\right)^{3/2}\int_0^{2\pi} e^{im^*\phi}\times e^{i0\phi}\times e^{im'\phi}d\phi$. The ϕ part of this integral, *viz.*, $\int_0^{2\pi} e^{i(m^*+0+m')d\phi}$ will always be zero unless (m^*+0+m') is equal to zero. If $(m^*+0+m')=0$, the ϕ part of the integral becomes $\int_0^{2\pi} d\phi$ *which is* equal to $[\,\phi\,]_0^{2\pi}$ or 2π. Thus, (m^*+0+m') must be zero and hence $-m+0+m'$ should be equal to zero in order that ϕ part has non zero value which means that $m=m'$. Thus, the ϕ part as well as the whole of the integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{m^*}\,|\,Y_4^0\,|\,Y_2^{m'}\sin\theta\, d\theta\, d\phi$ will be zero unless $m=m'$, or this integral will be non zero for the diagonal elements only (where $m=m'$) and will be non zero for all the off diagonal elements (where $m\neq m'$).

The integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{m^*}\,|\,Y_4^4\,|\,Y_2^{m'}\sin\theta\, d\theta\, d\phi$ can be similarly written as

$$\int_0^{\pi} \textcircled{H}_2^{m^*}\,\textcircled{H}_4^4\,\textcircled{H}_2^{m'}\sin\theta\, d\theta\left(\frac{1}{2\pi}\right)^{3/2}\int_0^{2\pi} e^{im^*\phi}\times e^{i4\phi}\times e^{im'\phi}\, d\phi$$

The ϕ part of the integral $\int_0^{2\pi} e^{i(m^*+4+m')\phi}d\phi$ will always be zero unless (m^*+4+m') is zero. If $(m^*+4+m')=0$, the integral becomes $\int_0^{2\pi} e^{i0\phi}d\phi$ or $\int_0^{2\pi} d\phi$ which gives a non zero value equal to 2π under the given limits. In other words, the integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{m^*}\,|\,Y_4^4\,|\,Y_2^{m'}\sin\theta\, d\theta\, d\phi$ will be non zero only if $(m^*+4+m')=0$ or $-m+m'=-4$ or when $m=2$ and $m'=2$. This means that only the integral $\int_0^{\pi}\int_0^{2\pi} Y_4^4\, Y_2^{-2}\sin\theta\, d\theta\, d\phi$, which occurs only in $\textcircled{H}_{2,-2}$ element of the determinant, will be non zero. The integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{m^*}\,|\,Y_4^4\,|\,Y_2^{m'}\sin\theta\, d\theta\, d\phi$ for all other values of m and m' will be zero and hence, all other elements, except $\textcircled{H}_{2,-2}$ of the determinant, will be zero.

Similarly, the third integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{m^*}\,|\,Y_4^{-4}\,|\,Y_2^{m'}\sin\theta\, d\theta\, d\phi$ which can be rewritten as $\int_0^{\pi} \textcircled{H}_2^{m^*}\,\textcircled{H}_4^{-4}\,\textcircled{H}_2^{m}\sin\theta\, d\phi\int_0^{2\pi} e^{i(m^*-4+m')\phi}d\phi$ will be non zero only if $m^*-4+m'=0$ or $(-m)-4+m'=0$ or $m=-2$ and $m'=2$. This means that only the integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{-2*}\, Y^{-4}\, Y_2^{2}\sin\theta\, d\theta\, d\phi$, which occurs only in the element $\textcircled{H}_{-2,\,2}$ of the determinant will be non zero. Accordingly, the integral $\int_0^{\pi}\int_0^{2\pi} Y_2^{m^*}\, Y_4^{-4}\, Y_2^{m}\sin\theta\, d\theta\, d\phi$ for all other values of m and m' will be zero, ~~that is, this integral will be~~ zero for all other elements except $\textcircled{H}_{-2,2}$.

It is now simple to reduce the 5×5 determinant to the following form :

$$\begin{vmatrix}
K(2\pi)^{-1/2}\int_0^{\pi}\textcircled{H}_2^{2*}\,\textcircled{H}_4^0\,\textcircled{H}_2^{2}\sin\theta\, d\theta - E & 0 & 0 & 0 & K(2\pi)^{-1/2}\left(\frac{5}{14}\right)^{1/2}\int_0^{\pi}\textcircled{H}_2^{2*}\,\textcircled{H}_4^4\,\textcircled{H}_2^{-2}\sin\theta\, d\theta \\
0 & K(2\pi)^{-1/2}\int_0^{\pi}\textcircled{H}_2^{1*}\,\textcircled{H}_4^0\,\textcircled{H}_2^{1}\sin\theta\, d\theta - E & 0 & 0 & 0 \\
0 & 0 & K(2\pi)^{-1/2}\int_0^{\pi}\textcircled{H}_2^{0*}\,\textcircled{H}_4^0\,\textcircled{H}_2^{0}\sin\theta\, d\theta - E & 0 & 0 \\
0 & 0 & 0 & K(2\pi)^{-1/2}\int_0^{\pi}\textcircled{H}_2^{-1*}\,\textcircled{H}_4^0\,\textcircled{H}_2^{-1}\sin\theta\, d\theta - E & 0 \\
K(2\pi)^{-1/2}\left(\frac{5}{14}\right)^{1/2}\int_0^{\pi}\textcircled{H}_2^{-2*}\,\textcircled{H}_4^{-4}\,\textcircled{H}_2^{+2}\sin\theta\, d\theta & 0 & 0 & 0 & K(2\pi)^{-1/2}\int_0^{\pi}\textcircled{H}_2^{-2*}\,\textcircled{H}_4^0\,\textcircled{H}_2^{-2}\sin\theta\, d\theta - E
\end{vmatrix} = 0$$

where K is $\left(\frac{49}{18}\right)^{1/2}(2\pi)^{1/2}(2\pi)^{-1/2}Ze^2r_2^4/a^5$

The calculated values of the integrals involved in the above determinant are as follows :

$$\int_0^\pi \Theta_2^{|2|}\,\Theta_4^0\,\Theta_2^{|2|}\sin\theta\,d\theta = \frac{\sqrt{2}}{14} \qquad \int_0^\pi \Theta_2^0\,\Theta_4^0\,\Theta_2^0\sin\theta\,d\theta = \frac{\sqrt{18}}{7}$$

$$\int_0^\pi \Theta_2^{|1|}\,\Theta_4^0\,\Theta_2^{|1|}\sin\theta\,d\theta = -\frac{\sqrt{8}}{7} \qquad \int_0^\pi \Theta_2^{|2|}\,\Theta_4^{|4|}\,\Theta_2^{|2|}\sin\theta\,d\theta = \frac{\sqrt{35}}{7}$$

$$\therefore\ K(2\pi)^{-1/2}\int_0^\pi \Theta_2^{2*}\Theta_4^0\Theta_2^2\sin\theta\,d\theta = \left(\frac{49}{18}\right)^{1/2}(2\pi)^{1/2}\frac{Zer_2^{\overline{4}}}{a^5}(2\pi)^{-1/2}\frac{\sqrt{2}}{14}$$

$$= \frac{1}{6}\frac{Ze^2r_2^{\overline{4}}}{a^5} \qquad ...(46)$$

Similarly, $$K(2\pi)^{-1/2}\int_0^\pi \Theta_2^{-2}\Theta_4^0\Theta_2^{-1}\sin\theta\,d\theta = \left(\frac{49}{18}\right)^{1/2}(2\pi)^{1/2}\frac{Zer_2^{\overline{4}}}{a^5}(2\pi)^{-1/2}\frac{\sqrt{2}}{14}$$

$$= \frac{1}{6}\frac{Ze^2r_2^{\overline{4}}}{a^5} \qquad ...(47)$$

$$K(2\pi)^{-1/2}\int_0^\pi \Theta_2^{1*}\Theta_4^0\Theta_2^1\sin\theta\,d\theta = \left(\frac{49}{18}\right)^{1/2}(2\pi)^{1/2}\frac{Zer_2^{\overline{4}}}{a^5}(2\pi)^{-1/2}\left(-\frac{\sqrt{8}}{7}\right)$$

$$= -\frac{4}{6}\frac{Ze^2r_2^{\overline{4}}}{a^5} \qquad ...(48)$$

Similarly, $$K(2\pi)^{-1/2}\int_0^\pi \Theta_2^{-1*}\Theta_4^0\Theta_2^{-1}\sin\theta\,d\theta = -\frac{4}{6}\frac{Ze^2r_2^{\overline{4}}}{a^5} \qquad ...(49)$$

Also $$K(2\pi)^{-1/2}\int_0^\pi \Theta_2^{0*}\Theta_4^0\Theta_2^0\sin\theta\,d\theta = \left(\frac{49}{18}\right)^{1/2}(2\pi)^{1/2}\frac{Ze^2r_2^{\overline{4}}}{a^5}(2\pi)^{-1/2}\frac{\sqrt{18}}{7} = \frac{Ze^2r_2^{\overline{4}}}{a^5} \qquad ...(50)$$

and $$K(2\pi)^{-1/2}\int_0^\pi \Theta_2^{2*}\Theta_4^4\Theta_2^{-2}\sin\theta\,d\theta = K(2\pi)^{-1/2}\int_0^\pi \Theta_2^{-2*}\Theta_4^{-4}\Theta_2^{+2}\sin\theta\,d\theta$$

$$= \left(\frac{49}{18}\right)^{1/2}(2\pi)^{-1/2}(2\pi)^{-1/2}\frac{\sqrt{35}}{8}\frac{Ze^2r_2^{\overline{4}}}{a^5}\left(\frac{5}{14}\right)^{1/2} = \frac{5Ze^2r_2^{\overline{4}}}{6a^5} \qquad ...(51)$$

Therefore, the 5 × 5 determinant becomes :

$$\begin{vmatrix} \frac{Ze^2r_2^{\overline{4}}}{6a^5}-E' & 0 & 0 & 0 & \frac{5Ze^2r_2^{\overline{4}}}{6a^5} \\ 0 & \frac{-4Ze^2r_2^{\overline{4}}}{6a^5}-E' & 0 & 0 & 0 \\ 0 & 0 & \frac{Ze^2r_2^{\overline{4}}}{6a^5}-E' & 0 & 0 \\ 0 & 0 & 0 & \frac{-4Ze^2r_2^{\overline{4}}}{6a^5}-E' & 0 \\ \frac{5Ze^2r_2^{\overline{4}}}{6a^5} & 0 & 0 & 0 & \frac{Ze^2r_2^{\overline{4}}}{6a^5}-E' \end{vmatrix} = 0$$

The quantity $\frac{35Ze}{4a^5}$ is termed as D and the quantity $\frac{2er_2^{\overline{4}}}{105}$ is called q so that

$$Dq = \frac{35Ze}{4a^5}\times\frac{2er_2^{\overline{4}}}{105} = \frac{Ze^2r_2^{\overline{4}}}{6a^5}.$$

As is clear from the parameters involved in the expression for Dq, the quantity Dq varies from ligand to ligand and from metal ion to metal ion. Dq is thus not a constant quantity, it varies from one complex to another.

Putting $\frac{Ze^2r_2^{\overline{4}}}{6a^5}$ as Dq, the above determinant is written as

$$\begin{array}{c|ccccc|} & (+2) & (+1) & (0) & (-1) & (-2) \\ \hline (+2) & Dq-E' & 0 & 0 & 0 & 5Dq \\ (+1) & 0 & -4Dq-E' & 0 & 0 & 0 \\ (0) & 0 & 0 & 6Dq-E' & 0 & 0 \\ (-1) & 0 & 0 & 0 & -4Dq-E' & 0 \\ (-2) & 5Dq & 0 & 0 & 0 & Dq-E' \end{array} = 0$$

The above determinant can be reduced to the following sub determinants :

1. First Sub Determinant. The first of such sub determinants is

$$\begin{array}{c|cc|} & (+2) & (-2) \\ \hline (+2) & Dq-E' & 5Dq \\ (-2) & 5Dq & Dq-E' \end{array} = 0$$

for which the following secular equations can be written :

$$C_{+2}(Dq-E') + C_{-2}(5Dq) = 0$$
$$C_{+2}(5Dq) + C_{-2}(Dq-E') = 0$$

The above secular equations obviously correspond to the linear combination $C_{+2}(+2) + C_{-2}(-2)$.

The solution of this sub determinant gives the quadratic equation

$$(Dq-E')^2 - 25(Dq)^2 = 0$$

or $$(Dq-E'+5Dq)(Dq-E'-5Dq) = 0$$

This equation gives two values of E', *viz.*, $E' = 6Dq$ and $E' = -4Dq$. Putting $E' = 6dq$ in one of the secular equations of this determinant, we get

$$C_{+2}(Dq-6Dq) + C_{-2}(5Dq) = 0$$

which gives $$C_{-2} - C_{+2} = 0$$

or $$C_{+2} = C_{-2} \qquad ...(52)$$

Since the corresponding wave function $C_{+2}(+2) + C_{-2}(-2)$ has to be a normalised wave function, hence

$$(C_{+2})^2 + (C_{-2})^2 = 1 \qquad ...(53)$$

From Eqs. 52 and 53, we get $C_{+2} = \frac{1}{\sqrt{2}}$ and $C_{-2} = -\frac{1}{\sqrt{2}}$ so that the wave function $\frac{1}{\sqrt{2}}[(+2)+(-2)]$ is associated with $E' = 6Dq$.

Again, putting $E' = -4Dq$ in the same secular equation, we get

$$C_{+2}(Dq + 4Dq) + C_{-2}(5Dq) = 0$$

or

$$C_{+2} + C_{-2} = 0 \qquad ...(54)$$

Since the wave function has to be normalised, hence,

$$(C_{+2})^2 + (C_{-2})^2 = 1 \qquad ...(55)$$

From Eqs. 54 and 55, we get $C_{+2} = \frac{1}{\sqrt{2}}$ and $C_{-2} = -\frac{1}{\sqrt{2}}$ so that the wave function $\frac{1}{\sqrt{2}}[(+2)-(-2)]$ is associated with $E' = -4Dq$.

2. Second Sub Determinant. The second sub determinant of 5 × 5 determinant is

$$\begin{array}{c|cc|c} & (+2) & (-1) & \\ \hline (+1) & -4Dq - E' & 0 & \\ & & & =0 \\ (-1) & 0 & -4Dq - E' & \end{array}$$

for which the following secular equations can be written :

$$C_{+1}(-4Dq - E') + C_{-1}(0) = 0 \qquad ...(56)$$

$$C_{+1}(0) + C_{-1}(-4Dq - E') = 0 \qquad ...(57)$$

Secular equation (56) gives $E' = -4Dq$ which is entirely due to the contribution of (+1). The contribution of wave function (–1) is 0 becomes $C_1^2 = 0$. Thus, the wave function (+1) has the energy $E' = -4Dq$. Similarly, from Eq. 57, we obtain that wave function (–1) has the energy $E' = -4Dq$. Thus, both (+1) and (–1) remain degenerate even in the presence of V_{oct} and both have energy $E' = -4Dq$. Therefore, the acceptable linear combinations of the two (+1) and (–1) degenerate wave functions will also be associated with the same energy $E' = -4Dq$. Thus,

$$\frac{1}{\sqrt{2}}[(+1)+(-1)] \text{ has energy } E' = -4Dq$$

and $$\frac{1}{\sqrt{2}}[(+1)+(-1)] \text{ also has energy } E' = -4Dq$$

The procedure of obtaining acceptable normalised linear combinations of degenerate wave functions has already been discussed in Chapter 1.

3. The third sub determinant of the 5 × 5 determinant is as shown which obviously shows that the wave function (0) has energy $E' = 6Dq$.

$$\begin{array}{c|c|} & (0) \\ \hline (0) & 6Dq - E' \end{array} = 0$$

To **sum up**, the **changes in the energies of *d* orbitals** of the *d* metal ion surrounded octahedrally by the six ligands are :

$$\left.\begin{array}{ll} \frac{1}{\sqrt{2}}[(+2)+(-2)], \textit{ i.e., } d_{x^2-y^2} \text{ orbital} \\ 0, \qquad \textit{i.e., } d_{z^2} \text{ orbital} \end{array}\right] \quad E' = 6Dq$$

$$\left.\begin{array}{l} \frac{1}{\sqrt{2}}[(+1)+(-1)], \textit{ i.e., } d_{xz} \text{ orbital} \\ \frac{1}{\sqrt{2}}[(+1)-(-1)], \textit{ i.e., } d_{yz} \text{ orbital} \\ \frac{1}{\sqrt{2}}[(+2)-(-2)], \textit{ i.e., } d_{xy} \text{ orbital} \end{array}\right] \quad E' = -4Dq$$

The above results are depicted in Fig. 3.

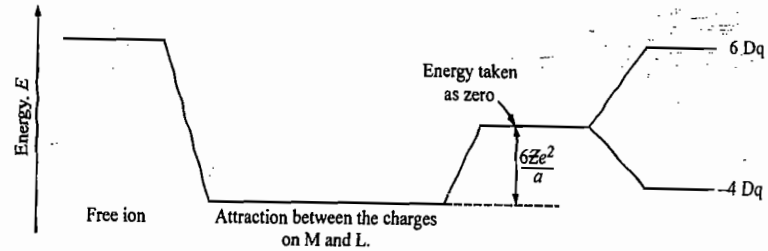


Fig.3. Diagram showing the changes in the energies of the *d* orbitals of the metal ion surrounded octahedrally by six ligand charges.

B. Metal Ion Subjected to Tetragonal Crystal Field Potential. Derivation of Expression for determining $V_{tetragonal}$

Let us consider the d' metal ion tetragonally surrounded by six ligands taken as point charges. As shown in Fig. 4, the M–L distances along the Z direction are different from the M–L distances along the X direction or Y direction. The expansion of $\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}}$ for n=0 and m = 0 is given by

$$\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}} = \frac{4\pi}{1}\frac{r^0}{a}\sum_{i=2}^{i=5} Y_{0i}^0 Y_{0i}^{0*} + \frac{4\pi}{1}\frac{r^0}{b}\sum_{i=1,6} Y_{0j}^0 Y_{0i}^{0*} \qquad ...(58)$$

$$= \left[4\pi\frac{1}{a}\frac{1}{2\sqrt{\pi}}\frac{1}{2\sqrt{\pi}}4 + 4\pi\frac{1}{b}\frac{1}{2\sqrt{\pi}}\frac{1}{2\sqrt{\pi}}2\right]Ze^2 \qquad ...(59)$$

$$= \frac{4Ze^2}{a} + \frac{2Ze^2}{b} \qquad ...(60)$$

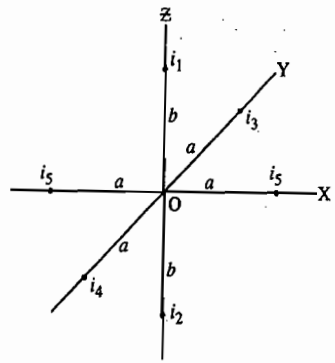


Fig. 4. Depiction of M–L distances along various axes in the case of a tetragonal complex.

The expansion of $\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}}$ when $n = 2$ and $m = 0$, is given by

$$\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}} = Ze^2\left[\frac{4\pi r^2}{a^3}\sum_{i=2}^{i=6} Y_{2j}^0 Y_{2i}^{0*} + \frac{4\pi r^2}{b^3}\sum_{i=1,6} Y_{2j}^0 Y_{2i}^{0*}\right] \qquad ...(61)$$

$$= \left(\frac{5}{8}\right)^{1/2}(2\pi)^{-1/2}\frac{Ze^2r^2}{a^3}4\pi Y_{2j}^0(-4) + \frac{4\pi r^2}{b^3}Y_{2j}^0\left(\frac{5}{8}\right)^{1/2}(2\pi)^{-1/2}(4)Y_{2j}^0 \qquad ...(62)$$

$$= 4\pi r^2 Ze^2\left(\frac{5}{8}\right)^{1/2}(2\pi)^{-1/2} \times 4\left[\frac{1}{b^3} - \frac{1}{a^3}\right]Y_{2j}^0 \qquad ...(63)$$

The expansions of $\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}}$ when n=2, m=±1 and n=2, m=±2, can be shown to be zero.

The expansion of $\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}}$, when $n = 4$ and $m = 0$, is given by

$$\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}} = Ze^2\left[\frac{4\pi}{9}\frac{r^4}{a^5}\sum_{i=2}^{i=5} Y_{4j}^0 Y_{4i}^{0*} + \frac{4\pi}{9}\frac{r^4}{b^5}\sum_{i=1,6} Y_{4j}^0 Y_{4i}^{0*}\right] \quad ...(64)$$

$$= \frac{4\pi}{9} Ze^2 r^4 \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} \times 4\left[\frac{3}{a^5}+\frac{4}{b^5}\right] Y_{4j}^0 \quad ...(65)$$

Expansions of $\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}}$ when $n = 4$ and $m = \pm 1, \pm 2$ and ± 3, can be shown to be zero.

Let us now write down the expression for the expansion of $\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}}$ when $n = 4$ and $m = -4$.

$$\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}} = \frac{Ze^2 4\pi r^4}{9a^5}\sum_{i=1}^{i=5} Y_{4j}^{-4} Y_{4i}^{-4*} + \frac{Ze^2 4\pi r^2}{9b^5}\sum_{i=1,6} Y_{4j}^{-4} Y_{4i}^{-4*} \quad ...(66)$$

$$= \frac{Ze^2 4\pi r^4}{9a^5}(2\pi)^{-1/2}\left(\frac{315}{256}\right)^{1/2} Y_{4j}^{-4} \times 4 \quad ...(67)$$

Similarly, the expansion of $\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}}$ when $n = 4$ and $m = 4$, is given by

$$\sum_{i=1}^{i=6} \frac{Ze^2}{r_{ij}} = \frac{Ze^2 4\pi r^4}{9a^5}\left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} Y_{4j}^{+4} \times 4 \quad ...(68)$$

Thus, the overall $V_{\text{tetragonal}}$ is given by

$$V_{\text{tetragonal}} = \frac{4Ze^2}{a} + \frac{2Ze^2}{b} + 2(2\pi)^{1/2} Ze^2\left[\left(\frac{5}{2}\right)^{1/2} 2r^2\left(\frac{1}{b^3}-\frac{1}{a^3}\right) Y_2^0\right]$$
$$+ r^4\left[(72)^{-1/2}\left(\frac{3}{a^5}+\frac{4}{b^5}\right) Y_4^0 + \left(\frac{35}{144}\right)^{1/2}\frac{1}{a^5}(Y_4^{+4}+Y_4^{-4})\right] \quad ...(69)$$

In the above expression, the subscript j is not written for the sake of convenience since all Ys in this expression are Ys.

Since the quantity $\frac{4Ze^2}{a}+\frac{2Ze^2}{b}$ is independent of the coordinates of j and it uniformly lifts the energies of all the five d orbitals, the $V_{\text{tetragonal}}$, which is actually responsible for causing a split in the d orbitals of the d' metal ion, is given by

$$V_{\text{tetragonal}} = 2(2\pi)^{1/2} Ze^2\left(\frac{5}{2}\right)^{1/2} 2r^2\left(\frac{1}{b^3}-\frac{1}{a^3}\right) Y_2^0$$
$$+ r^4\left[(72)^{-1/2}\left(\frac{3}{a^5}+\frac{4}{b^5}\right) Y_4^0 + \left(\frac{35}{144}\right)^{1/2}\frac{1}{a^5}(Y_4^{+4}+Y_4^{-4})\right] \quad ...(70)$$

A square planar crystal field is produced by $V_{\text{tetragonal}}$ if the ligands along the Z axis are taken away upto infinity. That is, $\frac{1}{b} = 0$. Accordingly, $V_{\text{sq planar}}$ is given by

$$V_{\text{sq planar}} = 2(2\pi)^{1/2} Ze^2\left(\frac{5}{2}\right)^{1/2}\frac{2r^2}{-a^3} Y_2^0 + \frac{r^4}{a^5}\left[(72)^{-1/2} 3Y_4^0 + \left(\frac{35}{144}\right)^{1/2}(Y_4^4+Y_4^{-4})\right] \quad ...(71)$$

$$= 2(2\pi)^{1/2} Ze^2\left[\left(\frac{5}{2}\right)^{1/2} 2\left(\frac{-r^2}{a^3}\right) Y_2^0\right] + \frac{r^4}{a^5}(8)^{-1/2}\left[Y_4^0 + \left(\frac{35}{18}\right)^{1/2}(Y_4^{+4}+Y_4^{-4})\right] \quad ...(72)$$

C. Metal Ion in a Tetrahedral Crystal Field Potential. Derivation of Expression for determining V_{tet}

Let us consider a tetrahedron inside a cube of length $2l$. Let the metal ion be placed at the centre of the cube which is also the origin (O) of the Cartesian coordinate system, as shown in Fig. 5. Let the ligands be at the positions 1, 2, 3, 4 forming a tetrahedron and let the M–L distance be a. From the point A, lying at the centre of the upper face of the cube and on the Z axis, draw a perpendicular on one of the sides, as shown.

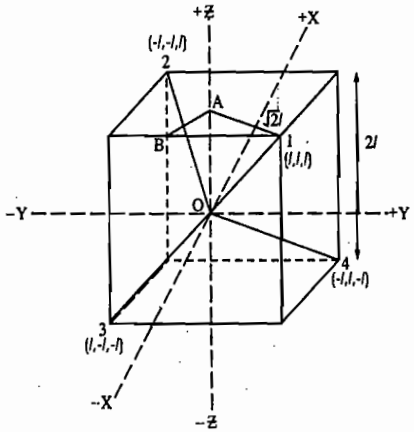


Fig.5. Depiction of the coordinates of points at which various ligands are placed in a tetrahedral complex.

In the right angled triangle AB1,

$$AB^2 + B1^2 = A1^2 \text{ or } l^2 + l^2 = A1^2 \text{ or } A1 = \sqrt{2l}$$

In the right angled triangle AO1,

$$AO^2 + A1^2 = O1^2 \text{ or } l^2 + 2l^2 = a^2 \text{ or } 3l^2 = a^2 \text{ or } l = \frac{a}{\sqrt{3}}$$

Therefore, the coordinates of the points 1 and 2 are $\left(\frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}\right)$ and $\left(-\frac{a}{\sqrt{3}}, -\frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}\right)$, respectively.

For point 1, $\cos\theta_1 = \frac{l}{a} = \frac{a}{\sqrt{3}} \times \frac{1}{a} = \frac{1}{\sqrt{3}}$ and $\phi_1 = 45°$ or $\frac{\pi}{4}$

For point 2, $\cos\theta_2 = \frac{l}{a} = \frac{a}{\sqrt{3}} \times \frac{1}{a} = \frac{1}{\sqrt{3}}$ and $\phi_2 = 180 + 45$ or $\frac{5\pi}{4}$

For point 3, $\cos\theta_3 = -\frac{l}{a} = -\frac{a}{\sqrt{3}} \times \frac{1}{a} = -\frac{1}{\sqrt{3}}$ and $\phi_3 = \frac{7\pi}{4}$

For point 4, $\cos\theta_4 = -\frac{l}{a} = -\frac{a}{\sqrt{3}} \times \frac{1}{a} = -\frac{1}{\sqrt{3}}$ and $\phi_4 = \frac{3\pi}{4}$

$\sin\theta_1$, $\sin\theta_2$, $\sin\theta_3$ and $\sin\theta_4$ for the four points is the same, *viz.*, $+\sqrt{\frac{2}{3}}$ (θ_1, θ_2, θ_3 and θ_4 lie between 0 and π).

Thus, each of $\sin\theta_1$, $\sin\theta_2$, $\sin\theta_3$ and $\sin\theta_4$ must have a positive value.

Let us now evaluate $Y_{0i}^{0}, Y_{2i}^{0}, Y_{2i}^{\pm1}, Y_{2i}^{\pm2}, Y_{4i}^{0}, Y_{4i}^{\pm1}, Y_{4i}^{\pm2}, Y_{4i}^{\pm3}$ and $Y_{4i}^{\pm4}$ for all the four points i (*i.e.*, 1, 2, 3 and 4) of the tetrahedron :

(*i*)
$$\sum_{i=1}^{i=4} Y_{0i}^{0^*} = \sum_{i=1}^{i=4} Y_{0i}^{0} = \frac{1}{2\sqrt{\pi}} \times 4 \qquad ...(73)$$

(*ii*)
$$\sum_{i=1}^{i=4} Y_{2i}^{0^*} = \sum_{i=1}^{i=4} Y_{2i}^{0} = \sum_{i=1}^{i=4} \left(\frac{5}{8}\right)^{1/2} (2\pi)^{-1/2} (3\cos^2\theta_i - 1)$$

$$= \left(\frac{5}{8}\right)^{1/2} (2\pi)^{-1/2} \sum_{i=1}^{i=4} (3\cos^2\theta - 1) = 0 \qquad ...(74)$$

(*iii*)
$$\sum_{i=1}^{i=4} Y_{2i}^{-1^*} = \sum_{i=1}^{i=4} Y_{2i}^{+1} = \sum_{i=1}^{i=4} \left(\frac{15}{4}\right)^{1/2} (2\pi)^{-1/2} \cos\theta_i \sin\theta_i \, e^{i\phi}$$

$$= \left(\frac{15}{4}\right)^{1/2} (2\pi)^{-1/2} \left[e^{i\pi/4} + e^{i5\pi/4} - e^{i7\pi/4} - e^{i3\pi/4}\right] \frac{\sqrt{2}}{3}$$

$$= \left(\frac{15}{4}\right)^{1/2} (2\pi)^{-1/2} \frac{\sqrt{2}}{3} \left[\cos\frac{\pi}{4} + i\sin\frac{\pi}{4} + \cos\frac{5\pi}{4} + i\sin\frac{5\pi}{4} - \cos\frac{7\pi}{4} - i\sin\frac{7\pi}{4} - \cos\frac{3\pi}{4} - i\sin\frac{3\pi}{4}\right] \frac{\sqrt{2}}{3}$$

$$= \left(\frac{15}{4}\right)^{1/2} (2\pi)^{-1/2} \frac{\sqrt{2}}{3} \left[\frac{1}{\sqrt{2}} + i\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} - i\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} + i\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}} - i\frac{1}{\sqrt{2}}\right] = 0 \qquad ...(75)$$

(*iv*) Similarly,
$$\sum_{i=1}^{i=4} Y_{2i}^{+1^*} = 0 \qquad ...(76)$$

(*v*)
$$\sum_{i=1}^{i=4} Y_{2i}^{-2^*} = \sum_{i=1}^{i=4} Y_{2i}^{+2}$$

$$= \left(\frac{5}{16}\right)^{1/2} (2\pi)^{-1/2} \sum_{i=1}^{i=4} \sin^2\theta e^{i2\phi}$$

$$= \left(\frac{5}{16}\right)^{1/2} (2\pi)^{-1/2} \frac{\sqrt{2}}{3} \left[e^{i\pi/2} + e^{i5\pi/2} + e^{i7\pi/2} + e^{i3\pi/2}\right]$$

$$\left[\cos\frac{\pi}{2} + i\sin\frac{\pi}{2} + \cos\frac{5\pi}{2} + i\sin\frac{5\pi}{2} + \cos\frac{7\pi}{2} i\sin\frac{7\pi}{2} + \cos\frac{3\pi}{2} + i\sin\frac{3\pi}{2}\right]$$

$$= \left(\frac{5}{16}\right)^{1/2} (2\pi)^{-1/2} \left(\frac{2}{3}\right) [0 + i + 0 + i + 0 - i + 0 - i] = 0 \qquad ...(77)$$

(*vi*) Similarly,
$$\sum_{i=1}^{i=4} Y_{2i}^{+2^*} = \sum_{i=1}^{i=4} Y_{2i}^{-2} = 0 \qquad ...(78)$$

(*vii*)
$$\sum_{i=1}^{i=4} Y_4^{0^*} = \sum_{i=1}^{i=4} Y_4^{0}$$

$$= \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} \sum_{i=1}^{i=4} (35\cos^4\theta_i - 30\cos^2\theta_i + 3)$$

$$= \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} \left(\frac{35}{9} - \frac{30}{3} + 3\right) \times 4$$

$$= \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} \times 28 \times \left(\frac{-4}{9}\right) \qquad ...(79)$$

(*viii*) Similarly, it can be shown that

$$\sum_{i=1}^{i=4} Y_4^{\pm^*} = 0; \sum_{i=1}^{i=4} Y_4^{\pm2^*} = 0 \text{ and } \sum_{i=1}^{i=4} Y_4^{\pm3^*} = 0 \qquad ...(80)$$

(*ix*)
$$\sum_{i=1}^{i=4} Y_4^{-4^*} = \sum_{i=1}^{i=4} Y_{4i}^{+4} = \sum_{i=1}^{i=4} \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} \sin 4\theta_i \, e^{+i4\phi}$$

$$= \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} \frac{4}{9} (e^{i\pi} + e^{i5\pi} + e^{i7\pi} + e^{i3\pi})$$

$$= \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} \frac{4}{9} (-1 - 1 - 1 - 1)$$

$$= \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} \times 4 \times \left(\frac{-4}{9}\right) \qquad ...(81)$$

(*x*) Similarly,

$$\sum_{i=1}^{i=4} Y_4^{+4} = \sum_{i=1}^{i=4} Y_4^{-4} = \left(\frac{315}{256}\right)^{1/2} (2\pi)^{-1/2} \times 4 \times \left(\frac{-4}{9}\right)$$

Let us now calculate V_{tet} experienced by the d' metal ion. Remembering that $Y_{0j}^{0} = Y_{0i}^{0}$,

$$V_{tet} = Ze^2 \left[\sum_{i=1}^{i=4} \frac{4\pi}{a} Y_{0j}^{0} Y_{0i}^{0} + \sum_{i=1}^{i=4} \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^{0} Y_{4i}^{0^*} + \sum_{i=1}^{i=4} \frac{4\pi}{a} \frac{r^4}{a^5} Y_{4j}^{+4} Y_{4i}^{+4^*} + \sum_{i=1}^{i=4} \frac{4\pi}{9} \frac{r^4}{a^5} Y_{4j}^{-4} Y_{4i}^{-4^*}\right]$$

$$= Ze^2 \frac{4\pi}{a} \frac{1}{2\sqrt{\pi}} \frac{1}{2\sqrt{\pi}} \times 4Ze^2 \frac{r^4}{a^5} \frac{4\pi}{9} Y_{4j}^{0} \left(\frac{9}{128}\right)^{1/2} (2\pi)^{-1/2} 28 \times \left(\frac{-4}{9}\right)$$

$$+ \frac{Ze^2 r^4}{a^5} \times \frac{4\pi}{9} (2\pi)^{-1/2} \left(\frac{315}{256}\right)^{1/2} \times 4 \times \left(\frac{-4}{9}\right) \left(Y_{4j}^{+4} + Y_{4j}^{-4}\right)$$

$$= \frac{4Ze^2}{a} + (2\pi)^{1/2}\left(\frac{49}{18}\right)^{1/2}\frac{Ze^2r^4}{a^5}Y_{4j}^0\left(\frac{-4}{9}\right) + (2\pi)^{1/2}\left(\frac{35}{36}\right)^{1/2}\left(Y_{4j}^4 + Y_{4j}^{-4}\right)\frac{Ze^2r^4}{a^5}\left(\frac{-4}{9}\right)$$

$$= \frac{4Ze^2}{a} + \left(\frac{49}{18}\right)^{1/2}(2\pi)^{1/2}\frac{Zer^4}{a^5}\left[Y_{4j}^0 + \left(\frac{5}{14}\right)^{1/2}\left(Y_{4j}^{+4} + Y_{4j}^{-4}\right)\right] \times \left(\frac{-4}{9}\right) \quad ...(82)$$

Since there is only one type of Y in the above expression, *viz.*, Y_j, we can drop the subscript j for the sake of convenience. Also, the component $\frac{4Ze^2}{a}$ of V_{tet} does not cause a split in the energy of d orbitals since it is independent of the position of d electron location. Therefore, V_{tet} which causes split in the d orbitals is obtained by omitting $\frac{4Ze^2}{a}$ from the expression. Thus,

$$V_{tet} = \left(\frac{49}{18}\right)^{1/2}(2\pi)^{1/2}\frac{Zer^4}{a^5}\left[Y_4^0 + \left(\frac{5}{14}\right)^{1/2}\left(Y_4^{+4} + Y_4^{-4}\right)\right] \times \left(\frac{-4}{9}\right) = -\frac{4}{9}V_{oct} \quad ...(83)$$

As can be seen from Fig. 6, eight corners of a cube constitute two concentric tetrahedra. Hence,

$$V_{cube} = 2\,V_{tet} = 2\left(\frac{-4}{9}V_{oct}\right) = -\frac{8}{9}V_{oct} \quad ...(84)$$

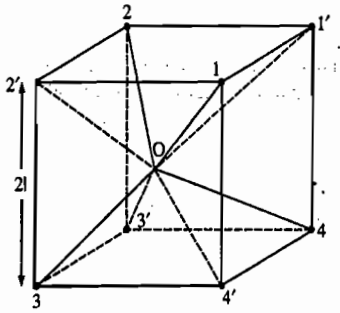


Fig. 6. The concentric tetrahedra constituted by 8 corners of a cube.

The fact that $V_{tet} = -\frac{4}{9}V_{oct}$, is very significant. This shows that if the metal ion containing a single d electron is subjected to both octahedral crystal field potential and tetrahedral crystal field potential due to the same set of ligands taken as point charges, the splitting of d orbitals of the metal ion caused by V_{tet} will only be $-\frac{4}{9}$th of the splitting caused by V_{oct} provided the M–L distances in both the octahedral and the tetrahedral environments of the metal ion are identical. The – sign signifies that the order of the splitting of d orbitals of the metal ion in tetrahedral ligand environment will be **opposite** to the splitting of d orbitals in octahedral ligand environment.

Comparison of Theoretical Value of Dq with Experimentally Observed Dq

It is difficult to evaluate Dq from the expression $Dq = Ze^2\overline{r_2^4}/6a^5$, since the exact magnitude of $\overline{r_2^4}$ is generally not known. The rough calculations yield Dq = ~100 cm^{-1} whereas the experimentally observed value of Dq is nearly 10 time the roughly calculated value of *Dq*.

Even if we represent the ligands as electrical dipoles instead of considering them as point charges (as has been done in the above treatment), the roughly calculated value of Dq again comes out to be = ~100 cm^{-1}. It appears, therefore, that apart from the electrostatic interactions between the ligands and the metal ion, there must be considerable overlap between the metal ion orbitals and the ligand orbitals. However, the Dq value is calculated by considering only the electrostatic interactions, completely ignoring the effect of the overlap between the metal ion orbitals and the ligand orbitals. Nevertheless, the electrostatic crystal field model is still useful in giving the effect of ligand environment on relative energies of d orbitals of the metal ion as well as in predicting fairly accurately the trends in a number of thermodynamic and spectroscopic properties of complexed metal ions. It is useful to remember that the stability of the M–L bond due to crystal field effects is only about $\frac{1}{10}$th of the overall stability of the M–L bond.

An Alternative Expression for V_{oct} in Terms of Cartesian Coordinates

Consider Fig. 7(*a*) in which the metal ion is placed at the origin O of the Cartesian coordinates and L_1, L_2, ..., L_6 are the positions of the six ligands arranged octahedrally around the metal ion. Let P be the position of the single d electron with charge e at a distance r from the origin (*i.e.* OP = r) at any instant and let a be the distance between the metal ion and the ligand. The electrostatic potential at P (x, y, z) due to ligand L_1 is given by

$$V_1 = \frac{Ze^2}{d_1} \quad ...(85)$$

where d_1 is the distance between the point P and the position of the ligand L_1 (Fig. 7*a*).

Applying the cosine law, the distance d_1 in ΔL_1PO is given by

$$d_1 = (a^2 + r^2 - 2ar\cos\theta_1) \quad ...(86)$$

where θ_1 is the angle between r and a taken along the axis containing L, as shown in Fig.7. In general, the distance d_i between the ligand L_i located on any of the three axes and the point P(x, y, z) is given by

$$d_i = \sqrt{a^2 + r^2 - 2ar\cos\theta_i} \quad ...(87)$$

where θ_i is the angle between the line OP and the axis on which the ligand L_i is located. Thus,

$$d_i = a \times \sqrt{1 + \left(\frac{r}{a}\right)^2 - \frac{2r}{a}\cos\theta_i}$$

or

$$\frac{1}{d_i} = \frac{1}{a \times \sqrt{1 + \left(\frac{r}{a}\right)^2 - \frac{2r}{a}\cos\theta_i}} \quad ...(88)$$

$$= \frac{1}{a \times \sqrt{1 - 2qt + q^2}} \quad ...(89)$$

where $t = \cos\theta_i$ and $q = \frac{r}{a}$.

The expansion of the expression $\frac{1}{\sqrt{1 - 2qt + q^2}}$ is carried out in terms of Legendre polynomial assuming that r is less

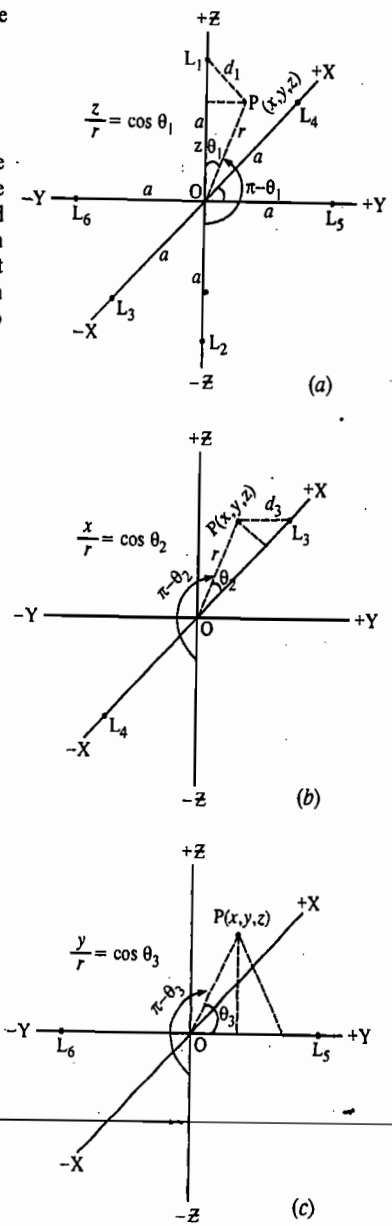


Fig.7. Depiction of various parameters in terms of Cartesian coordinates for the determination of octahedral crystal field potential at a particular point.

than a meaning thereby that the small probability of d electron being outside the sphere of radius a is negligible and is thus ignored. Accordingly,

$$\frac{1}{\sqrt{1-2qt+q^2}} = \sum_{l=0}^{l=\infty} P_r(t)\, q^l \quad \text{where } l \text{ is any number.}$$

or
$$P_l(t)\, q^l = \frac{1}{2^l \lfloor l} \frac{d^l}{(dt)^l}(t^2-1)^l \qquad ...(90)$$

Thus,

$$\frac{1}{d_i} = \frac{1}{a}\sum_{l=0}^{l=\infty} P_l(\cos\theta_i)\left(\frac{r}{a}\right)^l \qquad ...(91)$$

$$P_0(\cos\theta_i) = \frac{1}{2^0 \lfloor 0} \frac{d^0}{dt^0}(t^2-1)^0 = 1 \qquad ...(92)$$

$$P_1(\cos\theta_i) = \frac{1}{2^1 \lfloor 1} \frac{d}{dt}(t^2-1)^1 = t = \cos\theta_i \qquad ...(93)$$

$$P_2(\cos\theta_i) = \frac{1}{2^2 \lfloor 2} \frac{d^2}{dt^2}(t^2-1)^2 = \frac{1}{8}\frac{d^2}{dt^2}(t^4-2t^2+1)$$

$$= \frac{1}{8}(4\times 3t^2 - 2\times 2\times 1) = \frac{1}{2}(3\cos^2\theta_i - 1) \qquad ...(94)$$

$$P_3(\cos\theta_i) = \frac{1}{2^3 \lfloor 3} \frac{d^3}{dt^3}(t^6-3t^4+3t^2-1)$$

$$= \frac{1}{8\times 3\times 2}(6\times 5\times 4t^3 - 3\times 4\times 3\times 2t) = \frac{1}{48}(120t^3 - 72t)$$

$$= \frac{1}{48}\times 24(5t^3-3t) = \frac{1}{2}(5\cos^3\theta_i - 3\cos\theta_i) \qquad ...(95)$$

$$P_4(\cos\theta_i) = \frac{1}{2^4 \lfloor 4} \frac{d^4}{dt^4}(t^2-1)^4 = \frac{1}{16}\times\frac{1}{4\times 3\times 2\times 1}\frac{d^4}{dt^4}(t^2-1)^4$$

$$= \frac{1}{16\times 24}\frac{d^4}{dt^4}(t^8-4t^6+6t^4-4t^2+1)$$

$$= \frac{1}{16\times 24}(8\times 7\times 6\times 5t^4 - 4\times 6\times 5\times 4\times 3t^2 + 6\times 5\times 4\times 3\times 2\times 1)$$

$$= \frac{1\times 48}{16\times 24}[35\cos^4\theta_i - 30\cos^2\theta_i + 3]$$

$$= \frac{1}{8}(35\cos^4\theta_i - 30\cos^2\theta_i + 3) \qquad ...(96)$$

Evaluation of $(P_l \cos\theta_i)$ terms with $l > 4$ is not needed since their contribution for d electrons with $l = 2$, will be zero.

Let us now calculate the electrostatic potential experienced by the d electrons of the metal ion due to the presence of various ligands with the help of the data given above.

The electrostatic potential V_1 experienced by the d electron of the metal ion present at the point P from ligand L_1 is given by

$$V_1 = \frac{Ze^2}{d_1} = \frac{Ze^2}{a}\sum_{l=1}^{l=\infty}\left(\frac{r}{a}\right)^l P_l\cos\theta_1$$

$$= \frac{Ze^2}{a}\left(\frac{r}{a}\right)^0\times 1 + \frac{Ze^2}{a}\left(\frac{r}{a}\right)^1\cos\theta_1 + \frac{Ze^2}{a}\left(\frac{r}{a}\right)^2\times\frac{1}{2}(3\cos^2\theta_1 - 1)$$

$$+ Ze^2\left(\frac{r}{a}\right)^3\times\frac{1}{2}5(\cos^3\theta_1 - 3\cos\theta_1) + \frac{Ze^2}{a}\left(\frac{r}{a}\right)^4\frac{1}{8}(35\cos^4\theta_1 - 30\cos^2\theta_1 + 3) \qquad ...(97)$$

Similarly, the electrostatic potential V_2 at point P due to ligand L_2 is given by

$$V_2 = \frac{Ze^2}{a} + \frac{Ze^2}{a}\left(\frac{r}{a}\right)^1\cos(\pi-\theta_1) + \frac{Ze^2}{a}\times\frac{1}{2}(3\cos^2(\pi-\theta) - 1) + \frac{Ze^2}{a}\left(\frac{r}{a}\right)^3\frac{1}{2}(5\cos^3(\pi-\theta_1) - 3\cos(\pi-\theta_1)$$

$$+ \frac{Ze^2}{a}\left(\frac{r}{a}\right)^4\times\frac{1}{8}(35\cos^4(\pi-\theta_1) - 30\cos^2(\pi-\theta_1) + 3 \qquad ...(98)$$

or
$$V_2 = \frac{Ze^2}{a} - \frac{Ze^2}{a}\left(\frac{r}{a}\right)\cos\theta_1 + \frac{Ze^2}{a}\left(\frac{r}{a}\right)^2\times\frac{1}{2}(3\cos^2\theta_1 - 1)$$

$$- \frac{Ze^2}{a}\left(\frac{r}{a}\right)^3\times\frac{1}{2}(5\cos^3\theta_1 - 3\cos\theta_1) + \frac{Ze^2}{a}\left(\frac{r}{a}\right)^4\times\frac{1}{8}(35\cos^4\theta - 30\cos^2\theta) + 3 \qquad ...(99)$$

Thus,

$$V_1 + V_2 = \frac{2Ze^2}{a}\left[1 + \left(\frac{r}{a}\right)^2\times\frac{1}{2}(3\cos^2\theta_1 - 1) + \left(\frac{r}{a}\right)^4\times\frac{1}{8}(35\cos^4\theta_1 - 30\cos^2\theta_1 + 3\right] \qquad ...(100)$$

$$= \frac{2Ze^2}{a}\left[1 + \left(\frac{r}{a}\right)^2\times\frac{1}{2}\left(\frac{3z^2}{r^2} - 1\right) + \left(\frac{r}{a}\right)^4\times\frac{1}{8}\left(35\frac{z^4}{r^4} - \frac{30z^2}{r^2} + 3\right)\right] \qquad ...(101)$$

Now consider Fig. 7(*b*) in which the ligands L_3 and L_4 are located on the X-axis at a distance a from the origin O and P, as usual, is the point at which the d electron is positioned at any instant. The angles θ_2 and $\pi - \theta_2$ are as shown. It can be easily shown that in this case, $V_3 + V_4$ is given by

$$V_3 + V_4 = \frac{2Ze^2}{a}\left[1 + \left(\frac{r}{a}\right)^2\times\frac{1}{2}(3\cos^2\theta_2 - 1) + \left(\frac{r}{a}\right)^4\times\frac{1}{8}(35\cos^4\theta_2 - 30\cos^2\theta_2 + 3)\right]$$

$$= \frac{2ze^2}{a}\left[1 + \left(\frac{r}{a}\right)^2\frac{1}{2}\left(\frac{3x^2}{r^2} - 1\right) + \left(\frac{r}{a}\right)^4\frac{1}{8}\left(35\frac{x^4}{r^4} - 30\frac{x^2}{r^2} + 3\right)\right] \qquad ...(102)$$

Finally, consider Fig. 7(*c*) in which the ligands L_5 and L_6 are located on the Y-axis at distance *a* from the origin. Ths angles θ_3 and $(\pi - \theta_3)$ are as shown in the figure. It can be readily shown that $V_5 + V_6$ is now given by

$$V_5 + V_6 = \frac{2Ze^2}{a}\left[1+\left(\frac{r}{a}\right)^2\frac{1}{2}(3\cos^2\theta_3 - 1)+\left(\frac{r}{a}\right)^4\frac{1}{8}(35\cos^4\theta_3 - 30\cos^2\theta_3 + 3)\right]$$

$$= \frac{2Ze^2}{a}\left[1+\left(\frac{r}{a}\right)^2\frac{1}{2}\left(\frac{3y^2}{r^2}-1\right)+\left(\frac{r}{a}\right)^4\frac{1}{8}\left(35\frac{y^4}{r^4}-30\frac{y^2}{r^2}+3\right)\right] \quad ...(103)$$

The overall octahedral electrostatic potential, V_{oct}, is given by

$$\text{Overall } V_{oct} = \frac{6Ze^2}{a}+\frac{1}{2}\left(\frac{3(x^2+y^2+z^2)}{r^2}-3\right)\left(\frac{r}{a}\right)^2\frac{2Ze^2}{a}$$

$$+\frac{1}{8}\left(\frac{r}{a}\right)^4\frac{2Ze^2}{a}\left[\frac{35(x^4+y^4+z^4)}{r^4}-\frac{30(x^2+y^2+z^2)}{r^2}+9\right]$$

$$= \frac{6Ze^2}{a}+0+\frac{1}{8}\left(\frac{r}{a}\right)^4\frac{2Ze^2}{a}\left[\frac{35(x^4+y^4+z^4)}{r^4}-30+9\right]$$

$$= \frac{6Ze^2}{a}+\frac{1}{8}\left(\frac{r}{a}\right)^4\frac{2Ze^2}{a}\frac{1}{r^4}[35(x^4+y^4+z^4)-21r^4]$$

$$= \frac{6Ze^2}{a}+\frac{1}{8}\frac{r^4}{a^4}\frac{2Ze^2}{a}\frac{1}{r^4}35\left[x^4+y^4+z^4-\frac{3r^4}{5}\right]$$

$$= \frac{6Ze^2}{a}\times\frac{35Ze}{4a^5}\times e\left[x^4+y^4+z^4-\frac{3r^4}{5}\right]$$

$$= \frac{6Ze^2}{a}\times De\left[x^4+y^4+z^4-\frac{3r^4}{5}\right] \quad ...(104)$$

where $D = \frac{35Ze}{4a^5}$, as already described.

The quantity $\frac{6Ze^2}{a}$ is independent of the position of *d* electron of the metal ion. This term, therefore, does not cause a split of *d* orbitals. It uniformly lifts the energy of all the five *d* orbitals upto the same extent. Thus, the V_{oct} which actually changes the relative energies of *d* orbitals is written by omitting $\frac{6Ze^2}{a}$ as stated previously as well. Thus, V_{oct} in terms of Cartesian coordinates is written as

$$V_{oct} = De\left[x^4+y^4+z^4-\frac{3}{5}r^4\right] \quad ...(105)$$

where D is $\frac{35ze}{4a^5}$.

QUESTIONS

1. Derive an expression for calculating the electrostatic crystal field potential which is responsible for splitting the *d* orbitals in the case of :
   (*a*) an octahedral complex.
   (*b*) a tetrahedral complex.
   (*c*) a tetragonal complex.
2. Establish mathematically that in an octahedral complex, because of crystal field potential, the energy of e_g orbitals gets raised by 6 Dq and that of t_{2g} orbitals gets lowered by 4 Dq.
3. Establish mathematically that in a tetrahedral complex, because of crystal field potential, the energy of d_{xy}, d_{yz}, d_{zx} orbitals gets raised by 4 Dq and the energy of $d_{x^2-y^2}$ and d_{z^2} orbitals gets lowered by 6 Dq.
4. Establish mathematically that $\Delta_t = -\frac{4}{9}\Delta_o$ where Δ_t is crystal field splitting in a tetrahedral complex and Δ_o is crystal field splitting in an octahedral complex.
5. Derive an expression for calculating V_{oct} in terms of Cartesian coordinates.

29 COORDINATION COMPOUNDS. PART IV

SOME THERMODYNAMIC ASPECTS OF CRYSTAL FIELD EFFECTS AND JAHN–TELLER EFFECT

• CRYSTAL FIELD EFFECTS

The splitting of *d* or *f* orbitals of a complexed metal ion due to electrostatic crystal field potential of ligands experienced by *d* or *f* electrons (or of energy terms which arise due to electrostatic repulsion amongst *d* electrons)* and the effects of such splittings on any property of the complexed metal ion are known as **crystal field effects.**

Crystal Field Effects on Ionic Radii. Let us consider crystalline compounds of metal ions carrying the same charge and belonging to the same transition series which are surrounded by the same set of anions in the same geometric environment. The ionic radii of such metal ions are expected to *decrease smoothly* with increase in the effective nuclear charge Z_{eff} provided the electron charge distribution in each metal ion remains the same in all directions, *i.e.,* it remains spherically symmetrical. In order to explain this, let us consider **the variation in the ionic radii of lanthanide ions** carrying the same charge, in crystalline compounds of these ions formed with the same anion, say, X^-. All the electrons in the fully occupied 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, 4*s*, 4*p*, 5*s* and 5*p* orbitals of lanthanide ions have spherical distribution of their charge around the nucleus. Had the 4*f* orbitals of lanthanide ions in their compounds with X^- anions *remained degenerate,* the electrons present in these orbitals would not have had any specific preference for any particular *f* orbital and hence the charge distribution of 4*f* electrons would have also been spherical. In such a case, their ionic radii would have decreased regularly from $4f^0$ to $4f^{14}$ configurations owing to a regular increase in Z_{eff} in going from $4f^0$ to $4f^{14}$ ions. However, the 4*f* orbitals of lanthanide ions *do split* due to the crystal field effects as do the *d* orbitals of transition metal ions. Therefore, the electrons do have preference for the lower lying 4*f* orbitals of the lanthanide ions in their compounds and the electronic charge does get concentrated more in certain directions depending upon the shapes of the 4*f* orbitals which these electrons occupy. But the factor causing the splitting of the 4*f* orbitals, *i.e.,* the repulsion between the 4*f* electrons and the negative charge of surrounding anions X^-, *is of a small magnitude* because the 4*f* electrons are well shielded from the influence of the anionic charge by the intervening electrons of the lanthanide ions. As a result, the distribution of charge of 4*f* electrons still remains practically spherically symmetrical. Therefore, the lanthanide ions do show a smooth decrease in their ionic radii with gradual increase in the number of 4*f* electrons (and hence a gradual increase in Z_{eff}) from $4f^0$ to $4f^{14}$ configurations. The smooth variation of ionic radii of trivalent lanthanide ions in similar crystal environment with increase in the number of 4*f* electrons is shown in Fig. 1.

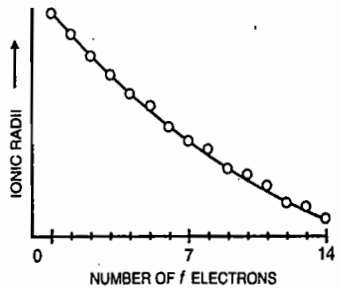


Fig. 1. Variation of ionic radii of lanthanide ions with increase in the number of 4*f* electrons.

Let us now consider the **variation in the ionic radii of divalent cations of the metals of the First transition series** in their crystalline compounds MX_2 (*e.g.,* metal halides) in which each metal ion is octahedrally surrounded by six anions X^-. The ionic radii of these cations are plotted in Fig. 2. The

* A detailed dissussion on energy terms is given in the next chapter.

ionic radius of Ca^{2+} ion, that is, the cation of the Main Group element immediately preceding the elements of the First transition series, is also included in the plot because of its specific relevance to the present discussion. Since there are no *d* electrons in Ca^{2+} ion, there will be no crystal field effects and hence no splitting of *d* orbitals by X^-.

As can be seen from Fig. 2, a smooth curve shown by dotted line can be drawn through the three points which indicate the radii of Ca^{2+}, Mn^{2+} and Zn^{2+} ions. The distribution of electron charge around the nucleus of Ca^{2+} ion (configuration $1s^2, 2s^2p^6, 3s^2p^6$) is *spherical* because of the fully filled *s* and *p* orbitals. The electronic configurations of Mn^{2+} ion (high spin) and Zn^{2+} ion, *viz.,* $t_{2g}^3 e_g^2$ and $t_{2g}^6 e_g^4$, are such that there is no splitting of *d* orbitals in these ions by the negative charge of the ligand X^-, *i.e.,* $\Delta_0 = 0$. Therefore, the 3*d* electrons of these metal ions generate a uniform electron charge round their nuclei. In other words, the electron charge distribution around the nuclei of Ca^{2+}, Mn^{2+} (high spin) and Zn^{2+} ions *remains spherically symmetrical.* Therefore, their ionic radii, which are determined from the extent of the approach of the X^- anions towards the positively charged metal ions, vary smoothly with increase in Z_{eff} or with increase in the number of 3*d* electrons. The number of *d* electrons increases from 0 in Ca^{2+} to 5 in Mn^{2+} to 10 in Zn^{2+}. The ionic radii of all other bivalent metal ions do not exhibit a smooth variation. These radii decrease *irregularly,* as shown by the solid line in Fig. 2. Their values invariably remain below their expected values, considering the effect of Z_{eff} alone. This is due to non-uniform or non-spherical distribution of charge of 3*d* electrons around their nuclei because of the splitting of the *d* orbitals under the influence of octahedral electrostatic potential of the surrounding X^- ligands as a result of which the electrons have preference for certain lower energy *d* orbitals compared to the higher energy *d* orbitals. Since the octahedral ionic radius of Sc^{2+} ion has not been determined with certainty as the +2 oxidation state of Sc is not stable, hence the solid line does not show the point corresponding to the octahedral ionic radius of Sc^{2+} ion.

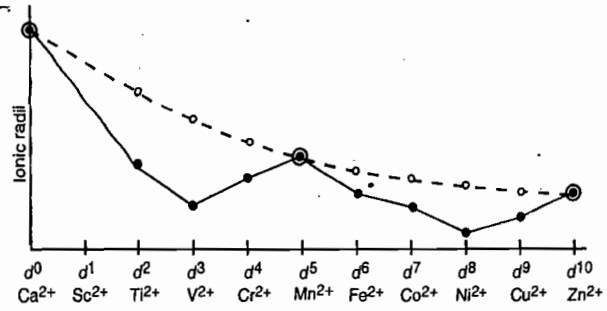


Fig. 2. Variation of ionic radii of divalent ions of the metals of the First transition series in octahedral environment of halide ions in their crystalline compounds MX_2. Hollow circles indicate hypothetical ionic radii expected in the absence of crystal field effects

The electronic configuration of Ti^{2+} ion in octahedral environment of X^- ligands is t_{2g}^2 so that the charge of the two *d* electrons is concentrated in those regions of space which lie in between the *X*, *Y* and *Z* axes along which the six X^- anions are placed. There is no concentration of charge due to these two electrons along the Ti^{2+}– X^- directions. This is because the regions of maximum electron charge density of t_{2g} orbitals, *viz.,* d_{xy}, d_{xz} and d_{yz} orbitals, lie in between the axes. Thus, due to abnormally low repulsion between the negative charge of *d* electrons and the negative charge of the anions X^- in the Ti^{2+}– X^- directions, the ligands X^- are drawn closer to Ti^{2+} ion as a result of greater electrostatic attraction between them as compared to such electrostatic attraction that would have existed if the *d* orbitals had remained degenerate resulting in a spherical distribution of charge of the electrons around the nucleus of Ti^{2+} ion. The spherical distribution of charge would have resulted from an equal probability of the two electrons to occupy any of the five *d* orbitals. Such a hypothetical spherical distribution of charge around the Ti^{2+} nucleus would have resulted in greater concentration of *d* electronic charge in the Ti^{2+}– X^- direction. This would have reduced the extent of approach of X^- towards Ti^{2+} due to greater repulsion between the *d* electronic charge and the negative charge of the ligand X^- in the direction of the bond compared to the extent of approach of X^- towards Ti^{2+} in the actual situation in which the electronic charge of the two electrons in t_{2g} orbitals is only concentrated *in between* Ti^{2+}– X^- directions and *not* in the Ti^{2+}–X^- directions. Thus, due to the crystal field splitting of the *d* orbitals of Ti^{2+} ion, the octahedral ionic radius of Ti^{2+} ion is rendered smaller than the value expected if there was no crystal field effect, that is, the value expected from the consideration of Z_{eff} alone.

In V^{2+} ion in octahedral environment of X^-, the effect of crystal field splitting is still more prominent because there are now three t_{2g} electrons whose charges are again concentrated *in between* the V^{2+}–X^- directions and not *in* the V^{2+}–X^- directions. The three *d* electrons, therefore, provide still less hindrance to attraction between the V^{2+} and X^- ions compared to the effect if the charge due to these three electrons had been spherically distributed around the V^{2+} nucleus in the event of non-splitting of *d* orbitals. Thus, a greater attraction between V^{2+} ion and surrounding X^- ions compared to such attraction between Ti^{2+} and X^- ions, results in a shorter V^{2+}–X^- distance. Consequently, the octahedral ionic radius of V^{2+} ion is smaller than that of Ti^{2+} ion. It is also smaller than its value if there was no crystal field effect, that is, its value expected from the consideration of Z_{eff} alone.

In the case of high spin Cr^{2+} ion with configuration $t_{2g}^3 e_g^1$, three electrons occupy the t_{2g} orbitals as in V^{2+} ion and the fourth electron occupies an e_g (*i.e.*, d_{z^2} or $d_{x^2-y^2}$) orbital whose regions of maximum electron density lie straight in the directions of Cr^{2+}–X^- bonds. Hence, compared to the approach of X^- towards V^{2+}, the approach of X^- towards Cr^{2+} becomes more difficult. This happens because of considerable repulsion between the charge of e_g electron and the negative charge of X^- in the direction of Cr^{2+}–X^- bond. As a result, the octahedral ionic radius of Cr^{2+} ion is larger than that of V^{2+}. But, it is still smaller than the value expected if there was no crystal field effect, that is, the value expected from the consideration of Z_{eff} alone. This is because the *d* electron charge is still more concentrated in between the directions of Cr^{2+}–X^- bonds (*i.e.*, in between the axes) than straight in the direction of Cr^{2+}–X^- bonds as a result of which the approach of X^- towards Cr^{2+} is still easier compared to the ease if the charge of the four *d* electrons had been uniformly distributed around the nucleus.

For high spin Mn^{2+} ion ($t_{2g}^3 e_g^2$), Δ_o is zero. Each *d* orbital of high spin Mn^{2+} ion, therefore, contains one electron resulting in a spherical distribution of charge around the nucleus. Hence the octahedral radius of high spin Mn^{2+} ion has the value as expected from the consideration of Z_{eff} alone.

The same sequence of events as described above in the case of Ca^{2+}, Ti^{2+}, V^{2+}, Cr^{2+} ions and Mn^{2+}, is repeated in the second half of the transition series, *i.e.*, in the case of high spin Fe^{2+}, Co^{2+} and Ni^{2+} ions with configurations $t_{2g}^4 e_g^2$, $t_{2g}^5 e_g^2$ and $t_{2g}^6 e_g^2$, respectively. With increase in the number of t_{2g} electrons, as we move from Mn^{2+} towards Ni^{2+} through Fe^{2+} and Co^{2+}, the *d* electron charge gets more and more concentrated in between the directions of M^{2+}–X^- bonds (M = Fe, Co or Ni) with the result that the approach of X^- towards M^{2+} becomes increasingly easier as we move from Mn^{2+} to Fe^{2+} to Co^{2+} to Ni^{2+}. Hence not only the radii of Fe^{2+}, Co^{2+} and Ni^{2+} ions decrease as we move from Fe^{2+} to Ni^{2+} through Co^{2+}, their values are even lesser than the values expected from consideration of Z_{eff} alone, *i.e.*, the values which could be obtained if there had been a uniform distribution of electronic charge around their nuclei in the absence of any crystal field effect.

In going from Ni^{2+} ($t_{2g}^6 e_g^2$) to Cu^{2+} ion ($t_{2g}^6 e_g^3$) in octahedral environment of X^- anion, the ninth *d* electron gets added to an e_g orbital whose regions of maximum electron charge density are straight in the directions of Cu^{2+}–X^- bonds. Therefore, the repulsion between *d* electron charge and negative charge on X^- increases in these directions making the approach of X^- towards Cu^{2+} more difficult than a similar approach of X^- towards Ni^{2+}. Therefore, the octahedral ionic radius of Cu^{2+} ion is larger than that of Ni^{2+} ion.

Because of the splitting of *d* orbitals, the *d* electron charge around the nucleus of Cu^{2+} is not spherical and is still less concentrated in the directions of Cu^{2+}–X^- bonds. Due to this, the approach of X^- towards Cu^{2+} becomes easier compared to the ease if there were a spherical or uniform distribution of *d* electron charge. Hence its ionic radius is smaller than the value expected from the consideration of Z_{eff} alone, *that is, the value expected if there had been no crystal field effect.*

Zn^{2+} ion with $t_{2g}^6 e_g^4$ configuration in octahedral environment of X^- does not show any splitting of its *d* orbitals since $\Delta_o = 0$. The *d* electron charge is, therefore, uniformly distributed in all directions. As a result, the octahedral ionic radius of Zn^{2+} ion has the value expected from the consideration of Z_{eff} alone.

Crystal Field Effects on Lattice Energies. As mentioned above, the *d* orbitals of transition metal ions split into t_{2g} and e_g sets of orbitals when these are surrounded octahedrally by six ligands. This results in preferential filling of lower energy t_{2g} orbitals compared to the filling of higher energy e_g orbitals of transition metal ions in their octahedral compounds. Had there been no splitting of *d* orbitals, their degeneracy would not have been lifted and their energy would have been higher than the energy of the t_{2g} orbitals. Thus, splitting of *d* orbitals of the metal ions imparts extra stability equal to crystal field stabilisation energy (CFSE) to the octahedral transition metal compounds. Therefore, *the observed lattice energies of such octahedral compounds are higher than the energies calculated if there had been no crystal field effects.*

Let us consider fluorides of transition metals of the First transition series. In crystalline state, each transition metal ion is surrounded octahedrally by six F^- ions. In CaF_2 (d^0 case), there is no crystal field effect and the distribution of electron charge around the Ca^{2+} nucleus is spherical because of the presence of fully filled *s* and *p* orbitals. In MnF_2 (d^5 case) and ZnF_2 (d^{10} case) also the distribution of electron charge around the nuclei is spherical because there is no splitting of *d* orbitals since $\Delta_o = 0$. The ionic radii of Ca^{2+}, Mn^{2+} and Zn^{2+} ions, therefore, are influenced solely by Z_{eff}. Since Z_{eff} increases smoothly from Ca^{2+} to Mn^{2+} to Zn^{2+} ion, the ionic radii of these three ions should decrease smoothly in the same order. Therefore, the lattice energies of CaF_2, MnF_2 and ZnF_2 should increase smoothly in the order of their mention. The lattice energy is inversely proportional to the interionic distance. Since the radius of the anion is the same in all these compounds, the lattice energy should be inversely proportional to the ionic radius of the metal ion. This is actually found to be the case as is evident from the plot of lattice energy *vs* the number of *d* electrons (Fig. 3) in which an almost straight line can be drawn through three points *P*, *K*, *L* which show the lattice energies of CaF_2, MnF_2 and ZnF_2.

However, the points showing the observed lattice energies of all other bivalent metal fluorides of the series depict irregular variation (Fig. 3). Also, the points showing the observed lattice energies of these fluorides lie above the points which show their hypothetical energies in the absence of any crystal field effects (Fig. 3).

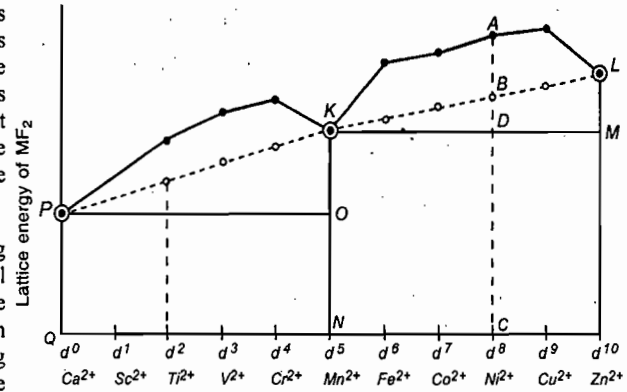


Fig. 3. Plot of lattice energy *vs.* number of *d* electrons of bivalent metal fluorides of the First transition series. Hollow circles (o) indicate hypothetical lattice energies expected in the absence of any crystal field effects and solid dots (•) indicate the observed lattice energies.

Remembering that all halide ions are weak field ligands, the extra stability due to crystal field splitting in the crysalline fluorides ScF_2, TiF_2, VF_2, CrF_2, FeF_2, CoF_2, NiF_2 and CuF_2 is 4 Dq, 6 Dq, 12 Dq, 6 Dq, 4 Dq, 6 Dq, 12 Dq and 6 Dq, respectively. (In the complexes of weak field ligands, the magnitude of splitting in *d* orbitals is less than electron repulsion effects amongst *d* electrons of metal ion. The real CFSEs for **weak field** complexes are, therefore, calculated by considering both inter electron repulsion as well as *d* orbital splitting effects). The difference between the observed lattice energy and the hypothetical lattice energy in the absence of crystal field effects gives the crystal field stabilisation energy (CFSE), *i.e.*, the extra stabilization of the crystal lattice due to crystal field effects.

Let us determine the CFSE of NiF_2. The observed lattice energy of NiF_2 is 3063·5 kJ mol^{-1}, as represented by *AC* in Fig. 3. This is equal to the hypothetical lattice energy *BC* in the absence of any

crystal field effects plus the extra stabilisation energy *AB*, that is, the CFSE. The hypothetical lattice energy *BC* can be easily obtained from the right angled triangle *KLM*. It is a simple problem of geometry to show that $BD = (3/5)LM$ and *LM* is the difference between the observed lattice energies of MnF_2 and ZnF_2 for which there are no crystal field effects and for which CFSE is 0. The observed lattice energies of ZnF_2 and MnF_2 are 2986·1 and 2782·4 kJ mol^{-1}, repectively. Hence,

$$\therefore\ BD = 3/5\,(2986{\cdot}1 - 2782{\cdot}4) = 122{\cdot}2 \text{ kJ mol}^{-1}$$

Hypothetical lattice energy in the absence of crystal field effects,

$$BC = BD + DC = 122{\cdot}2 + 2782{\cdot}4 = 2904{\cdot}6 \text{ kJ mol}^{-1}.$$

$$\text{CFSE for } NiF_2 = \text{Observed lattice energy} - \text{hypothetical lattice energy}$$
$$= 3063{\cdot}5 - 2904{\cdot}6 = 158{\cdot}9 \text{ kJ mol}^{-1}$$

From CFSE, the crystal field splitting, *i.e.*, the energy difference between t_{2g} and e_g orbitals can be easily calculated. In the case of NiF_2, for instance, the CFSE in octahedral ligand environment is 12 Dq. Thus,

$$12 \text{ Dq} = 158{\cdot}9 \text{ kJ mol}^{-1}$$
$$\therefore\ \Delta_o = 10 \text{ Dq} = (158{\cdot}9 \text{ kJ mol}^{-1} \times 10\text{Dq}/12\text{Dq}) = 132{\cdot}4 \text{ kJ mol}^{-1}$$

The same procedure can be followed for determining CFSEs of other metal fluorides from their lattice energy data. (It may be recalled that the crystal field splitting in octahedral environment is denoted by Δ_o which, by convention, is taken to be equal to 10 Dq.)

It may be worth mentioning that the hypothetical lattice energies in the absence of any crystal field effects for FeF_2, CoF_2 and CuF_2 are $KN + (1/5)LM$, $KN + (2/5)LM$ and $KN + (4/5)\,LM$, respectively. Similarly, for TiF_2, VF_2 and CrF_2 these lattice energies are $PQ + (2/5)KO$, $PQ + (3/5)KO$ and $PQ + (4/5)KO$, respectively.

Curves almost similar to the one presented in Fig. 3 for bivalent metal fluorides are obtained for the lattice energies of bivalent metal chlorides, bromides and iodides with the only difference that the bend at MnX_2 in the line obtained by joining points showing lattice energies of CaX_2, MnX_2 and ZnX_2 becomes more prominent which is probably due to greater polarizability of the comparatively bigger halide ions. As a result of polarisation of electron charge cloud of bigger halide ion by the metal ion, some covalent character also gets incorporated into the M^{2+}–X^- bond. Since the polarising powers of Ca^{2+}, Mn^{2+} and Zn^{2+} ions are different, the extent of covalent character introduced in the M^{2+}–X^- bonds of their halides is also different. Therefore, the lattice energies of CaX_2, MnX_2 and ZnX_2 (X^- is a bigger halide ion) have varying contributions from covalent character of M^{2+}–X^- bonding, apart from the usual contributions from electrostatic interactions between cations and anions. This varying covalent contribution leads to bending of the line obtained by joining points showing lattice energies of CaX_2, MnX_2 and ZnX_2. Such a bending is minimum for flourides of these metal ions because F^- ion is least polarisable and, therefore, the extent of covalent character in M^{2+}–F^- bond is minimum. There is a similar varying covalent character in M^{2+}–X^- bonds of other metal halides of the series which is difficult to determine experimentally and which causes error in the determination of CFSEs of these halides from the lattice energy data. The prominence of the bend at MX_2 increases with increase in the size of the ligand X^-, as expected.

Lattice energies (experimental values) of the halides of the bivalent metals of the First transition series are given in Table 1.

TABLE 1

Lattice Energies in kJ mol^{-1} of Halides of Ca and Bivalent Metals of the First Transition Series

Anion	Ca^{2+}	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
F^-	2607	—	2757	2770	2887	2782	2929	2979	3063	3067	2987
Cl^-	2234	—	2477	2548	2569	2502	2611	2690	2753	2786	2711
Br^-	2133	—	2393	2489	2506	2435	2540	2619	2699	2740	2644
I^-	2054	—	2309	2397	2397	2360	2477	2531	2619	2669	2581

The student is advised to calculate the CFSEs as well as Δ_o values for the various halides following the procedure described above.

It may be mentioned again that abnormal increase in the observed lattice energies of the bivalent metal halides compared to the values expected in the absence of crystal field effects is linked with the abnormal decrease in the ionic radii of these metal ions due to crystal field effects compared to the expected values of their ionic radii in the absence of crystal field effects. *The decrease in ionic radius results in a decrease in the interionic distance between the metal ion and the halide ion which, in turn, results in an increase in* the lattice energy since the lattice energy is inversely proportional to the interionic distance. Thus, the lattice energies of metal halides are higher in the presence of crystal field effects than in their absence.

As discussed earlier in Chapter 6 on the Structure of Solids, the lattice energy per mole of a crystal with oppositely charged ions at the equilibrium distance r_0 is given by

$$U_0 = -\frac{N_A A z^2 e^2}{r_0}\left(1 - \frac{1}{n}\right) \qquad ...(1)$$

Had there been no crystal field effects, the interionic distances should have been higher than r_0, say, *r*, as explained above. The lattice energy per mole, *U*, in the absence of crystal field effects would, therefore, be given by

$$U = -\frac{N_A A z^2 e^2}{r} + \frac{N_A B}{r^n} \qquad ...(2)$$

where *B* is the Born repulsion term which is equal to $Az^2e^2r_0^{n-1}/n$*. Substituting the value of *B* in the above equation, we get

$$U = -\frac{N_A A z^2 e^2}{r} + \frac{N_A}{r^n} \times \frac{A z^2 e^2 r_0^{n-1}}{n} \qquad ...(3)$$

$$= -\frac{N_A A z^2 e^2}{r}\left[1 - \frac{1}{n}\left(\frac{r_0}{r}\right)^{n-1}\right] \qquad ...(4)$$

Dividing Eq. 3 by Eq. 1, we get,

$$\frac{U}{U_0} = \frac{r_0}{r(n-1)}\left[n - \left(\frac{r_0}{r}\right)^{n-1}\right] \qquad ...(5)$$

or

$$1 - \frac{U}{U_0} = 1 - \frac{r_0}{r(n-1)}\left[n - \left(\frac{r_0}{r}\right)^{n-1}\right] \qquad ...(6)$$

or

$$\frac{U_0 - U}{U_0} = 1 - \frac{r_0}{r(n-1)}\left[n - \left(\frac{r_0}{r}\right)^{n-1}\right] \qquad ...(7)$$

$U_0 - U$ is, evidently, the extra stabilization of the crystal lattice due to crystal field effects, *i.e.*, $U_0 - U$ gives the crystal field stabilization energy (CFSE). Thus,

$$\frac{\text{CFSE}}{U_0} = 1 - \frac{r_0}{r(n-1)}\left[n - \left(\frac{r_0}{r}\right)^{n-1}\right] \qquad ...(8)$$

In Eq. 8, U_0 is the lattice energy of the metal halide determined experimentally. The equilibrium interionic distance r_0 is known from X-ray data. The interionic distance *r* can be known from the plot of ionic radii as a function of the number of *d* electrons, as shown in Fig. 2 for the metal halides. This plot permits easy evaluation of the ionic radius of a particular ion in the absence of crystal field effects (this parameter is given by a point on the dotted curve which is directly above the point indicating the actual ionic radius of the metal). Knowing the ionic radius of the metal ion as also of the halide ion, the interionic distance *r* can be determined. The value of the Born exponent *n* for the bivalent metal fluorides

* In order that *u* is minimum, $\frac{du}{dr}$ must be zero. Therefore, $\frac{du}{dr} = 0 = \frac{+N_A A Z^2 e^2}{r_0^2} - \frac{nN_A B}{r_0^{n+1}}$ $\therefore\ B = AZ^2e^2 r_0^{n-1}/n$

is 7. Knowing U_0, r, r_0 and n, CFSE can be readily determined. Eq. 8, thus, provides an alternative procedure for determining CFSEs for the metal halides.

A similar trend in the lattice energies is shown by trivalent metal halides of the First transition series. The only difference is that the bend at $M(d^5)X_3$ in the curve joining $M(d^0)X_3$, $M(d^5)X_3$ and $M(d^{10})X_3$ is more prominent. This is due to the greater polarizing power of $M^{3+}(d^n)$ ion compared to $M^{2+}(d^n)$ ion which introduces greater covalent character in $M(d^n)X_3$ compared to $M(d^n)X_2$.

Crystal Field Effects on Heats of Ligation. The heat of ligation for a metal ion is defined as the heat evolved when one mole of the metal ions in gaseous state react with the required number of ligands to produce one mole of the complex species in the gaseous state. Thus,

$$M^{n+}(g) + mL^{l-}(g) \xrightarrow{L^{n+}} [ML_m]^{(+n-ln)}(g)$$

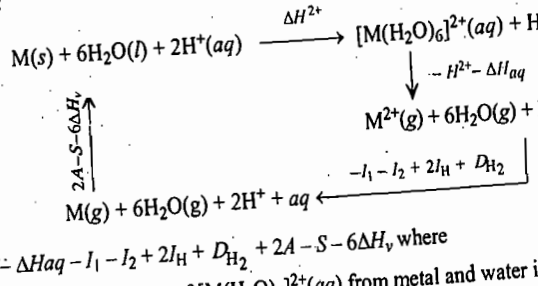
In the above equation, L^{n+} stands for the heat of ligation of $(n-1)$-valent metal ion and is assigned a negative sign as per the convention.

Heats of Ligation with Water as the Ligand. Heats of Hydration. We shall first consider heats of ligation which can also be called the **heats of hydration** of bivalent metal ions of the First transition series when the ligand is H_2O. The heat of ligation in this case would be the heat evolved when one mole of $[M(H_2O)_6]^{2+}$ (*gaseous*) is formed from one mole of M^{2+} ions (*gaseous*) and 6 moles of H_2O molecules (*gaseous*). The heat of ligation in this case is symbolised as H^{2+} and is negative as per the convention. Thus,

$$M^{2+}(g) + 6H_2O(g) \xrightarrow{H^{2+}} [M(H_2O)_6]^{2+}(g)$$

It is to be noted that heat of hydration is different from the heat of aquation which is the heat evolved when one mole of $[M(H_2O)_6]^{2+}(g)$ is aquated.

The heats of hydration of metal ions are determined indirectly with the help of the Born-Haber cycle, as illustrated below :



Thus, $H^{2+} = \Delta H^{2+} - \Delta Haq - I_1 - I_2 + 2I_H + D_{H_2} + 2A - S - 6\Delta H_v$ where

ΔH^{2+} is the enthalpy of formation of $[M(H_2O)_6]^{2+}(aq)$ from metal and water in their standard states

I_1 and I_2 are the first and second ionisation energies of the metal

I_H is the ionization energy of H

D_{H_2} is the bond dissociation energy of H_2

S is the sublimation energy of the metal

ΔH_v is the heat of vaporization of water

A is the heat of aquation of proton

ΔHaq is the heat of aquation of $[M(H_2O)_6]^{2+}$

The heats of hydration of the bivalent metal ions of the First transition series are given in Table 2.

Since H_2O is a weak field ligand, all $[M(H_2O)_6]^{2+}$ complex ions formed would be of high spin.

TABLE 2

Heats of Hydration of Bivalent Metal Ions of First Transition Series

Ion	$-H^{2+}$ (kJ mol^{-1})	Ion	$-H^{2+}$ (kJ mol^{-1})
Ca^{2+}	2469		
Sc^{2+}	—	Fe^{2+}	2845
Ti^{2+}	2732	Co^{2+}	2916
V^{2+}	2778	Ni^{2+}	2996
Cr^{2+}	2795	Cu^{2+}	3000
Mn^{2+}	2736	Zn^{2+}	2933

In the absence of any crystal field effects, the extent of electrostatic attraction between M^{2+} and the negative end of H_2O dipole should have increased smoothly from Ca^{2+} to Zn^{2+} due to an expected regular decrease in their ionic radii as explained earlier. In that event the hydration energies would have increased smoothly from Ca^{2+} to Zn^{2+}. Since in the case of Ca^{2+}, Mn^{2+} and Zn^{2+}, there are no crystal field effects, as already explained, the hydration energy curve obtained by joining the points showing H^{2+} for Ca^{2+}, Mn^{2+} and Zn^{2+} gives almost a straight line (Fig. 4) as expected.

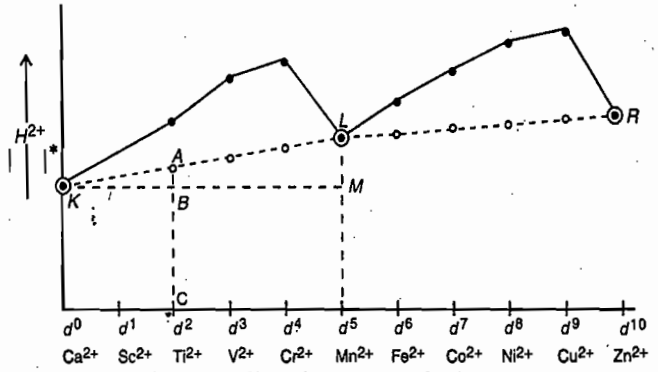


Fig. 4. Heat of hydration *vs* number of *d* electrons.

In the case of other bivalent ions, however, there is splitting of *d* orbitals by the H_2O molecules as a result of which the radii of these ions become smaller compared to their radii expected in the absence of crystal field effects. Consequently, the hydration energies of these ions obtained experimentally are higher than the hypothetical hydration energies expected in the absence of crystal field effects (Fig. 4). The difference between the experimental hydration energy and the hypothetical hydration energy obviously gives CFSE.

In the absence of any crystal field effects, all the points showing hydration energies of M^{2+} ions should have fallen on the dotted curve *KLR* obtained by joining the points for Ca^{2+}, Mn^{2+} and Zn^{2+}. This places at our disposal a convenient procedure for determining the CFSEs from the observed heats of hydration of the ions given in Table 2.

For instance, let us determine the heat of hydration of Ti^{2+} ion. The experimental value of H^{2+} for Ti^{2+} is 2732 kJ mol^{-1} and the values for Ca^{2+} and Mn^{2+} ions are 2469 and 2736 kJ mol^{-1}, respectively.

In the right angled triangle *KLM*,

$$AB = (2/5)\,LM = 2/5\,(2736 - 2469) = 107 \text{ kJ mol}^{-1}$$

$$\left.\begin{array}{l}\text{The hypothetical } H^{2+} \text{ for } Ti^{2+} \text{ ion}\\ \text{in the absence of cystal field effects}\end{array}\right\} = AC = BC + AB = 2469 + 107 = 2576 \text{ kJ mol}^{-1}$$

$$\therefore \quad \text{CFSE of } [Ti(H_2O)_6]^{2+} = 2732 - 2576 = 156 \text{ kJ mol}^{-1}$$

The student is advised to determine CFSEs in other cases with the help of the data given in Table 2.

The plots of heats of hydration of trivalent ions are similar to those of the bivalent ions except for the fact that the bend at $Fe^{3+}(d^5)$ is slightly more prominent than the corresponding bend at $Mn^{2+}(d^5)$. This is due to greater polarizing power of M^{3+} ion which increases the extent of covalent character in M^{3+}–OH_2 bond. Because of the more prominent bend, the CFSEs of trivalent metal complexes calculated from H^{3+} data are less reliable than those calculated for the bivalent metal complexes from H^{2+} data.

Heats of Ligation involving Ligands other than Water. As mentioned earlier, the heat of ligation of a metal ion is defined as the heat released when one mole of the metal ions in gaseous state react with the

* The magnitude of any quanity without considering positive or negative sign is written as |quantity|.

required number of ligands to produce one mole of the complex species in gaseous state. Heat of ligation is a negative quantity. Thus, we may write

$$M^{n+}(g) + mL^{l-}(g) \xrightarrow{L^{n+}} [ML_m]^{(+n-lm)}(g)$$

However, the thermodynamic data for this reaction is not easily available. In order to study the above reaction, therefore, we make use of the easily available stability constant data for the reaction

$$[M(H_2O)_6]^{n+}(aq) + 6L \underset{}{\overset{\Delta H}{\rightleftharpoons}} [ML_6]^{n+}(aq) + 6H_2O(l) \qquad ...(i)$$

This reaction actually represents the replacement of coordinated water by another ligand L in aqueous medium. The equilibrium constant of this reaction is obviously related with the stability of the complex $[ML_6]^{n+}(aq)$ and is thus known as the stability constant of $[ML_6]^{n+}(aq)$.

Consider the following set of reactions :

$$6H_2O(l) \xrightarrow{6\Delta H_v} 6H_2O(g)$$

$$M^{n+}(g) + 6H_2O(g) \xrightarrow{H^{n+}} [M(H_2O)_6]^{n+}(g)$$

$$[M(H_2O)_6]^{n+}(g) + aq \xrightarrow{\Delta H_1(aq)} [M(H_2O)_6]^{n+}(aq)$$

$$[M(H_2O)_6]^{n+}(aq) + 6L \overset{\Delta H}{\rightleftharpoons} [ML_6]^{n+}(aq) + 6H_2O(l)$$

$$[ML_6]^{n+}(aq) \xrightarrow{-\Delta H_2(aq)} [ML_6]^{n}(g) + aq$$

Adding, we get $\quad M^{n+}(g) + 6L \xrightarrow{L^{n+}} [ML_6]^{n+}(g) \qquad ...(ii)$

where $L^{n+} = 6\Delta H_v + H^{n+} + \Delta H_{1(aq)} - \Delta H_{2(aq)} + \Delta H$.

The magnitude of $6\Delta H_v + \Delta H_1(aq) - \Delta H_2(aq)$ is small compared to that of $H^{n+} + \Delta H$. Therefore,

$$L^{n+} \simeq H^{n+} + \Delta H \qquad ...(iii)$$

The equilibrium constant K for reaction (i) in aqueous medium is given by the expression

$$K = \frac{[ML_6]^{n+}(aq)}{[M(H_2O)_6]^{n+}(aq)[L]^6} \qquad ...(iv)$$

The equilibrium constant K is clearly the stability constant of the complex ion. The greater the stability of the complex $[ML_6]^{n+}(aq)$, the greater is the value of K.

We know from thermodynamics that

$$\Delta G = -RT \ln K$$

where $\quad \Delta G = \Delta H - T\Delta S$

$$\therefore \quad \Delta H = -RT \ln K + T\Delta S \qquad ...(v)$$

Thus, knowing the stability constant K, we can evaluate ΔH, Further, knowing ΔH and H^{n+}, we can evaluate L^{n+}, the heat of ligation of the ion.

As mentioned above, $L^{n+} \simeq H^{2+} + \Delta H$. Therefore, L^{n+}, being dependent on H^{n+}, would also vary with increase in the number of d electrons as does H^{n+}. Accordingly, $|L^{n+}|$ of metal ions with the same charge having configurations d^0, d^5 and d^{10} (where there is no splitting of d orbitals) should increase smoothly as does their $|H^{n+}|$. This is actually found to be so. A plot of $|L^{2+}|$ *vs* number of d electrons present in Ca^{2+}, Mn^{2+} and Zn^{2+} ions of the First transition series is found to be an almost

straight line ascending from $Ca^{2+}(d^0)$ to $Mn^{2+}(d^5)$ and from $Mn^{2+}(d^5)$ to $Zn^{2+}(d^{10})$. But all other points representing heats of ligation $|L^{2+}|$ of other bivalent ions of the series lie above this line because the ligated metal ions, $[ML_6]^{2+}$ are further stabilised due to CFSE which becomes available to them because of splitting of d orbitals in these cases.

In nut-shell, the curves obtained by plotting $|L^{2+}|$ *vs* number of d electrons present in the bivalent metal ions of the First transition series are similar in character to those obtained by plotting $|H^{2+}|$ or lattice energy *vs* the number of d electrons in these ions. The plots for $|L^{n+}|$ are, therefore, not given.

It may be mentioned that the replacement of H_2O by any other unidentate ligand L, as represented in Eq. (i), does not take place in one step. For instance, the replacement of H_2O by NH_3 takes place through a number of successive equilibrium reactions, as shown below :

$$[M(H_2O)_6]^{n+} + NH_3 \overset{K_1}{\rightleftharpoons} [M(NH_3)(H_2O)_5]^{n+} + H_2O$$

$$[M(NH_3)(H_2O)_5]^{n+} + NH_3 \overset{K_2}{\rightleftharpoons} [M(NH_3)_2(H_2O)_4]^{n+} + H_2O$$

.....

.....

$$[M(NH_3)_5H_2O]^{n+} + NH_3 \overset{K_6}{\rightleftharpoons} [M(NH_3)_6]^{n+} + H_2O$$

The ΔH accompanying the replacement of one H_2O molecule is determined from K_1, of two H_2O molecules from K_1K_2, of three H_2O molecules from $K_1K_2K_3$ and so on.

A plot of $|\Delta H|$ *vs* the number of moles of N-containing unidenate ligand (say, pyridine) attached to one mole of metal ions in the product is a linear graph whose slope depends upon the nature of the particular metal ion and the ligand. The plots obtained in the case of Fe^{2+} and Ni^{2+} ions with pyridine and NH_3 as coordinated water replacing ligands are shown in Fig. 5*a* and 5*b*. It can be seen from the plots that for a particular ligand the slope of the line for Fe^{2+} is less than the slope of the line for Ni^{2+}. This relative order of slopes for the two metal ions remains always unaltered whatever be the ligand employed to replace water coordinated to Fe^{2+} and Ni^{2+}.

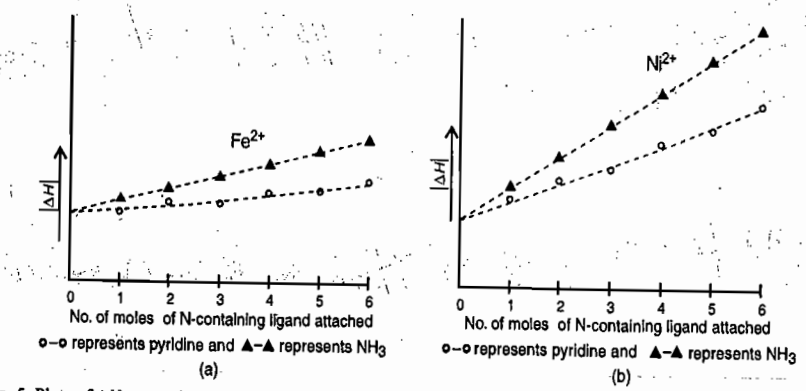


Fig. 5. Plots of ΔH *vs* number of moles of N-containing ligands attached to one mole of the metal ions in the product.

The general replacement reaction may be written as

$$[M(H_2O)_6]^{2+} + (1 \text{ to } 6) \text{ N-containing unidentate ligands}$$
$$\rightleftharpoons [M(H_2O)_{5 \text{ to } 0}(\text{N-containing unidentate ligands})_{1 \text{ to } 6}]^{2+}$$

A unidentate ligand which is stronger than water will form products $[M(H_2O)_5L]^{2+}$, $[M(H_2O)_4L_2]^{2+}$ .....$[M(H_2O)L_5]^{2+}$, $[ML_6]^{2+}$, in which the average electrostatic crystal field potential generated by H_2O and the ligand around M^{2+} will go on increasing with increase in the number of ligands in the product.

This would obviously go on increasing the energy gap between t_{2g} and e_g set of orbitals of metal ion and hence the magnitude of | Dq |, as we move from $[M(H_2O)_6]^{2+}$, $[M(H_2O)_5L]^{2+}$, etc., to $[ML_6]^{2+}$. This means that the magnitude of CFSE, which obviously depends on the magnitude of Dq, goes on increasing with increase in the number of ligands L attached with the metal ion in the product. Therefore, the enthalpy of the replacement reaction also goes on increasing with increase in the number of ligands L which replace the water molecules. Consider, for illustration, the stepwise replacement of coordinated H_2O molecules of $[Ti(H_2O)_6]^{2+}$ with the ligand NH_3. We assume that the geometry of the product obtained at each step is approximately octahedral. The CFSE for Ti^{2+} in octahedral environment is known to be 8 Dq. However, Dq is not a constant unit since its magnitude increases with increase in the electrostatic crystal field potential generated by the mixed set of H_2O and NH_3 ligands around Ti^{2+} ion. This is because the electrostatic crystal field potential generated by NH_3 ligand is higher than the one generated by H_2O ligand. The electrostatic crystal field potential around Ti^{2+} thus goes on increasing as we move from $[Ti(H_2O)_6]^{2+}$, $[Ti(H_2O)_5(NH_3)]^{2+}$, etc., to $[Ti(NH_3)_6]^{2+}$. As a result, the magnitude of | Dq | (and hence of | 8 Dq |) goes on increasing in the same order.

Each type of water-replacing ligand, reacting with a particular metal ion, generates a different slope of the line obtained by plotting ΔH *vs* the number of moles of the ligand attached per mole of the metal ion. But the relative order of the slopes thus obtained by employing any particular ligand with different metal ions of the series remains unaltered whether that ligand is unidentate like NH_3, pyridine, an alkylamine, etc., or it is bidentate like ethylene diamine, dipyridyl, etc. Thus the relative order of slopes, whatever be the water-replacing ligand, is found to vary in the order : $Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+}$.

We have already mentioned in the text that Dq is not a constant quantity and its magnitude varies directly with the strength of the crystal field generated by the ligand around the metal ion. Since ΔH of water replacement reactions also depends upon the difference between the stability of $[M(H_2O)_6]^{2+}$ and $[M(H_2O)_{5\ to\ 0}(L)_{1\ to\ 6}]^{2+}$ due to crystal field effects, an increase in ΔH also indicates an increase in the magnitude of CFSE or in the magnitude of Dq. Therefore, the slope of the line obtained by plotting ΔH *vs* the number of ligands attached in the product is directly linked with the magnitude of Dq of the product. Since the magnitude of Dq of the product depends upon the crystal field strength of the ligand attached with the product, the slope of the above mentioned line also depends upon the crystal field strength of the ligand. The following observations can be made from the plots of | ΔH | *vs* the number of ligands attached in the water replacement reactions :

1. For a particular metal ion, the magnitude of the slope depends upon the crystal field strength of the ligand which replaces coordinated water to form the product.

2. The magnitude of | Dq | goes on increasing, for a particular metal ion, with increase in the number of water molecules replaced in forming the product. This amounts to saying that the energy gap between the two sets of *d* orbitals, (*viz.*, t_{2g} and e_g), which is dependent on the magnitude of | Dq |, goes on increasing (or the strength of electrostatic potential generated by the mixed ligands attached to the metal ion goes on increasing) with increase in the number of ligands attached to the metal ion in the product.

3. The slope of the line obtained for the replacement of coordinated H_2O molecules by a bidentate N-containing ligand (like en) is higher than that by a similar monodentate ligand (like NH_3), as shown in Figs. 6*a* and *b*.

Thus, a bidentate ligand generates a stronger electrostatic field than a similar monodentate ligand.

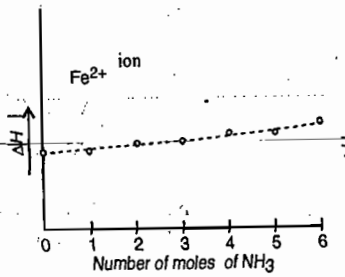


Fig. 6(a). Number of moles of NH_3 attached with one mole of Fe^{2+}.

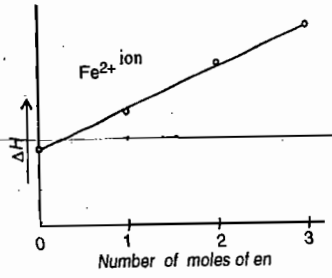


Fig. 6(b). Number of moles of (en) attached with one mole of Fe^{2+}

4. The slopes of the lines using the same coordinated water-replacing ligand depend upon the nature of the metal ions. In the water replacement reaction involving ammonia, the variation of the slope is in the order : $Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+}$. This order remains unaltered if we use any other ligand, instead of NH_3, for replacing coordinated water from the same series of metal ions.

It follows from the above discussion that ligands can be placed in a series in such a way that those which generate the least magnitude of Dq and hence the least separation of the two sets of *d* orbitals of any metal ion are placed at one end while those which generate the greatest magnitude of Dq and hence the highest separation of the two sets of *d* orbitals are placed at the other end of the series. Such a series is similar to spectrochemical series which is also based on the order of increase in the magnitude of Dq. However, Dq in spectrochemical series is obtained from spectroscopic data.

A similar series can be constructed for the metal ions belonging to the same transition series, by arranging the magnitudes of the slopes of lines obtained by plotting | ΔH | against the number of moles of the ligands attached with each metal ion in the increasing order. For obtaining such lines, the ligand attached with each metal ion is kept the same. A part of such a series comprises of $Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+}$, as already mentioned above.

TABLE 3

Crystal Field Stabilisation Energies of Metal Ions in Octahedral and Tetrahedral Ligand Environments

Configuration of Metal Ion	CFSE for Octahedral Geometry	CFSE for Tetrahedral Geometry
d^0, d^5	0	0
d^1, d^6	4 Dq_{oct}	6 Dq_{tet}
d^2, d^7	6 Dq_{oct}*	12 Dq_{tet}
d^3, d^8	12 Dq_{oct}	6 Dq_{tet}*
d^4, d^9	6 Dq_{oct}	4 Dq_{tet}
d^5, d^{10}	0	0 Dq_{tet}

* Calculated by taking into consideration the effects of *d* orbital splitting as well as the interelectronic repulsions amongst the *d* electrons. CFSEs of these configurations would be 8 Dq if we consider effects of *d* orbital splitting alone and neglect interelectronic repulsions amongst the *d* electrons.

Crystal Field Effects on the Geometry of Coordination Complexes. In order to study the crystal field effects on the geometry of coordination complexes, let us consider the crystal field stabilisation energies (CFSEs) of metal ions in their weak octahedral and tetrahedral ligand environments. In such cases, the electrostatic crystal fields generated by ligands (which cause splitting of *d* orbitals) are smaller in magnitude than the electron repulsion effects amongst *d* electrons. The CFSEs given in Table 3 have been calculated by taking into consideration both the effects.

Recalling that for a particular metal ion and a particular ligand, Dq_{tet} is 4/9th of Dq_{oct}, we can make some predictions about the type of geometry which a particular ion would prefer for its coordination complex. For instance, the metal ions with d^3 and d^8 configurations are much more stabilised in octahedral environment of ligands (CFSE = 12 Dq_{oct}) than in tetrahedral environment of ligands (CFSE = (6 Dq_{oct} × 4/9 = 2·7 Dq_{oct}). If we try to change the octahedral ligand environments of such metal ions to tetrahedral ligand environments, there will be a considerable loss of stability (equal to 9·3 Dq_{oct}) accompanying such a change. Therefore, the crystal field theory predicts preference for an octahedral geometry over a tetrahedral geometry for the coordination complexes of such metal ions.

For complexes of metal ions with d^0, d^5 (high spin) and d^{10} configurations, there is no stabilisation (due to crystal field effects) of either an octahedral or a tetrahedral geometry of the coordination complexes of such metal ions. Therefore, crystal field theory predicts equal probability for the occurrence of both the geometries of such complexes provided no other factors influencing the geometries are taken into account.

In the case of complexes of metal ions with d^1 and d^6 (high spin) configuration, the loss in stability due to crystal field effects in going from octahedral to tetrahedral geometry is 4 Dq_{oct} – (6 Dq_{oct} × 4/9) = 1·33 Dq_{oct}. However, the magnitude of this loss is quite small so that if, any factor other than crystal field effects, favours tetrahedral geometry by a stabilisation factor of magnitude greater than 1·33 Dq_{oct}, the complexes formed would be tetrahedral.

For complexes of metal ions with configurations d^2 and d^7 (high spin), the loss in stability in going from octahedral to tetrahedral geometry is 0·67 Dq_{oct}. The crystal field theory thus predicts that tetrahedral

complexes of such ions should be formed easily provided any other factor stabilises the tetrahedral geometry by any amount more than 0·67 Dq_{oct}.

The actual observations are in conformity with the predictions made by the crystal field theory. It is observed that while the complexes of metal ions with d^3 and d^8 configurations are predominantly octahedral, the tetrahedral complexes of metal ions with d^0, d^5 (high spin), d^6 (high spin), d^7 (high spin) and d^{10} configurations are also quite common. For instance, while V^{2+} and Ni^{2+} ions predominantly form octahedral complexes, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Zn^{2+} ions form a number of tetrahedral complexes as well.

One must remember while arguing the probability of existence of a particular geometry that the stability imparted to a metal–ligand bond because of CFSE is only about 1/10th of the normal stability of the metal–ligand bond. The overall stability of the bond depends upon several factors besides CFSE. Some of these factors are attraction between metal ions and the ligands, repulsion between like charges on the ligands, steric interactions between the ligands, the extent of covalent character in the metal–ligand bond, etc. Any of these factors may overweigh CFSE factor and may stabilise one geometry over the other specially when the difference between the CFSEs of octahedral and tetrahedral geometries is small.

Crystal Field Effects and Spinel Structures of Some Oxides. A number of oxides with the general formula $M^{2+}M'^{3+}_2O_4$ (M′ may be the same as M) adopt spinel structure. In the spinel structure, the anion lattice is composed of cubic closely packed O^{2-} anions. This type of packing of O^{2-} anions generates both tetrahedral and octahedral holes in the lattice. The bivalent and trivalent metal cations occupy these octahedral and tetrahedral holes of the spinel lattice. The manner in which the cations are distributed amongst the tetrahedral and octahedral holes gives rise to two different classes of spinel structures called *normal* and *inverted spinels*.

Normal spinels have all the bivalent cations in tetrahedral holes and trivalent cations in octahedral holes of the spinel lattice.

Inverted spinels have all the bivalent cations and half the trivalent cations in octahedral holes. The remaining trivalent cations are in tetrahedral holes.

Tetrahedral holes in spinel lattice are commonly referred to as *A* sites and the cations occupying such holes are written as A^{n+}. Similarly, octahedral holes in spinel lattice are commonly referred to as *B* sites and the cations occupying such holes are written as B^{n+}. Thus, in this nomenclature, the formula of normal spinel is $A^{2+}B^{3+}_2O_4$ and of the inverted spinel is $A^{3+}B^{2+}B^{3+}O_4$.

The O^{2-} anions are weak field ligands. Therefore, the metal ions surrounded by these anions (octahedrally or tetrahedrally) experience weak crystal field potential due to these anions and, therefore, have high spin configurations.

It is experimentally known that whereas Mn_3O_4 has a normal spinel structure, Fe_3O_4 has inverted spinel structure. But, Co_3O_4 again has normal spinel structure. This change of spinel structure in going from Mn_3O_4 to Fe_3O_4 to Co_3O_4 cannot be explained on the basis of variation in the ionic radii, the number of *d* electrons in the metal ions or any other factor except for the crystal field effects.

We can explain the spinel structures of Mn_3O_4, Fe_3O_4 and Co_3O_4 if we assume that

1. The distribution of bi and trivalent ions amongst *A* and *B* sites does not appreciably affect the lattice energy. But it does affect the crystal field stabilisation energy.
2. Other things being equal, the value of 10 Dq for a trivalent ion is 1·5 times that of a bivalent ion of the same element.
3. The value of 10 Dq is reduced by a factor of 4/9 on going from a *B* (*i.e.*, octahedral) site to an *A* (*i.e.*, tetrahedral) site for a given metal ion.

Taking Dq for B^{2+} as the standard unit of measurement and remembering that O^{2-} anions create weak field environments around metal ions and, therefore, generate high spin configurations of these ions, let us calculate crystal field stabilisation energies for bivalent and trivalent metal ions in octahedral (*i.e.*, *B*) and in tetrahedral (*i.e.*, *A*) holes on the basis of the above assumptions.

B^{2+} ions having d^4, d^5, d^6, d^7 high spin configurations have crystal field stabilisation energies of 6 Dq, 0, 4 Dq and 6 Dq, respectively, whereas B^{3+} ions having the same high spin configurations have crystal field stabilisation energies of 1·5 × 6 Dq, 0, 1·5 × 4 Dq and 1·5 × 6 Dq, respectively. Similarly, A^{2+} ions having d^4, d^5, d^6, d^7 configurations have crystal field stabilisation energies of 4/9 × 4 Dq, 0, 4/9 × 6 Dq, 4/9 × 12 Dq, respectively whereas A^{3+} ions having the same configurations have 3/2 × 4/9 × 4 Dq, 0, 3/2 × 4/9 × 6 Dq and 3/2 × 4/9 × 12 Dq, respectively.

The normal spinel structure for Mn_3O_4 is $A^{2+}(d^5)B^{3+}_2(d^4)O_4$. Therefore, crystal field stabilisation energy for this structure is 0 + 2 × 9Dq = 18Dq.

The inverted spinel structure for Mn_3O_4 is $A^{3+}(d^4)B^{3+}(d^4)B^{2+}(d^5)O_4$. Therefore, crystal field stabilisation energy for this structure is 8/3 Dq + 9 Dq + 0 = 11·67 Dq. Hence, Mn_3O_4 should have a more stable normal spinel structure, as it actually has.

The normal spinel structure for Fe_3O_4 is $A^{2+}(d^6)B^{3+}_2(d^5)O_4$. Therefore, crystal field stabilisation energy for this structure is (8/3 Dq + 0 + 0 = 2·67 Dq. The inverted spinel structure for Fe_3O_4 is $A^{3+}(d^5)B^{3+}(d^5)B^{2+}(d^6)O_4$. Therefore, crystal field stabilisation energy for this structure is 0 + 0 + 4 Dq = 4 Dq. Hence, Fe_3O_4 should have a more stable inverted spinel structure, as it actually has.

The normal spinel structure for Co_3O_4 is $A^{2+}(d^7)B^{3+}_2(d^6)O_4$. Therefore, crystal field stabilisation energy for this structure is 16/3 Dq + 2 × 6 Dq = 17·3 Dq. The inverted spinel structure for Co_3O_4 is $A^{3+}(d^6)B^{3+}(d^6)B^{2+}(d^7)O_4$. Therefore crystal field stabilisation energy for this structure is 4 Dq + 6 Dq + 6 Dq = 16 Dq. Hence, Co_3O_4 should have a more stable normal spinel structure, as it actually has.

Thus, crystal field effects successfully explain the type of spinel structure which Mn_3O_4, Fe_3O_4 and Co_3O_4 adopt.

JAHN–TELLER EFFECT

It was stated by Jahn and Teller that *any non-linear molecular system in orbitally degenerate electronic state* (*i.e.*, a state which represents more than one electronic arrangements of the same energy) *would be unstable and that it would get stabilised by undergoing distortion in its geometry and thus by causing a split in its orbitally degenerate electronic state.* The above statement is known as **Jahn–Teller effect.** The distortion in the geometry of the non-linear molecular system thus produced is known as **Jahn—Teller distortion.** The lowering of symmetry of the non-linear system due to Jahn-Teller effect always occurs in a manner which results in decrease in the energy of the system. *Jahn-Teller distortion is, therefore, automatic for the non-linear molecular systems of the above mentioned type.*

Let us consider an octahedral complex of Cu^{2+} ion with unidentate ligands L^-. The Cu^{2+} ion in a *perfect* octahedral ligand environment has the ground state electronic configuration $t^6_{2g}\,e^3_g$ which represents two electronic arrangements $t^6_{2g}\,d^2_{z^2}\,d^1_{x^2-y^2}$ and $t^6_{2g}\,d^1_{z^2}\,d^2_{x^2-y^2}$ of equal energy. Because of the Jahn-Teller effect the octahedral symmetry of the complex will be automatically lowered to tetragonal symmetry to stabilise the complex. This is explained as follows :

The t_{2g} orbitals of Cu^{2+} ion in octahedral ligand environment are completely occupied in the ground state. Therefore, the electron charge density due to the six t_{2g} electrons will be uniformly distributed in all directions. The same is the case with the charge density of electrons in the inner shells which are completely filled.

The three electrons in e_g orbitals of an octahedral Cu^{2+} complex can be placed in two equivalent ways as follows :

1. Two electrons in d_{z^2} orbital and one electron in $d_{x^2-y^2}$ orbital of Cu^{2+} ion.
2. Two electrons in $d_{x^2-y^2}$ orbital and one electron in d_{z^2} orbital of Cu^{2+} ion.

In possibility (1), the d electron charge density will obviously become higher in Z direction than in X or Y direction. The screening of the positive charge on Cu^{2+} nucleus by d electrons will, therefore, be more in Z direction than in X or Y direction. The negative charge on the ligand L^- along the Z direction will thus be less attracted by the nuclear charge on Cu^{2+} ion than the negative charge on the ligand along X and Y directions. Consequently, the Cu^{2+}–ligand attraction along Z direction will be less than the Cu^{2+}–ligand attraction along X and Y directions. As a result, the ligands along Z direction will move away from the metal ion whereas the ligands along X and Y directions will draw nearer to the metal ion. In other words, *the octahedral geometry of the complex will get distorted to tetragonal geometry* which is elongated along Z direction and compressed along X and Y directions, as shown in Fig. 7.

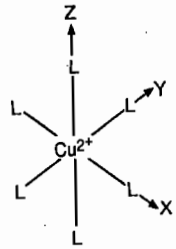
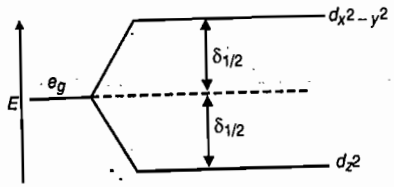


Fig. 7. Distortion of octahedral geometry of $[CuL_6]^{2+}$ tetragonal geometry due to Jahn–Tellar effect, if there are more electrons in d_{z^2} orbital than in $d_{x^2-y^2}$ orbital.

Because of the elongation of metal–ligand bonds along the Z direction, the electrostatic repulsion experienced by d electrons of the metal ion from the negative charge on the ligands along the Z direction becomes less than the similar repulsion experienced by electrons along the X and Y directions. Due to this, the d_{z^2} orbital will be of lower energy and $d_{x^2-y^2}$ orbital will be of higher energy. In this way, the degeneracy of the two orbitals gets lifted. This is illustrated in Fig. 8.

Since the distortion of octahedral geometry to tetragonal geometry is automatic, that is, without the supply of any energy from outside, the overall energy of the split orbitals remains equal to the overall energy of the unsplit orbitals. Thus, if we tentatively assume the overall energy of the unsplit d_{z^2} and $d_{x^2-y^2}$ orbitals to be zero, the energy of the lower energy d_{z^2} orbital plus the energy of the higher energy $d_{x^2-y^2}$ orbital after their split due to the lowering of symmetry should be equal to zero. This conclusion is expressed by the statement *that the 'centre of gravity of the split orbitals is maintained'*. This is known as **'centre of gravity rule'** for the energies of the split orbitals relative to the energies of the unsplit orbitals.



8. Lifting of the degeneracy of e_g orbitals of $[CuL_6]^{2+}$ due to Jahn—Tellar effect when there are more electrons in d_{z^2} orbital than in $d_{x^2-y^2}$ orbital.

It can be safely concluded that, in general, whenever there are more electrons in d_{z^2} orbital than in $d_{x^2-y^2}$ orbital of an octahedral complex of any metal ion, the distortion of octahedral geometry to tetragonal geometry would occur by elongation of its metal–ligand bond along the Z direction and that the energy of the d_{z^2} orbital becomes lower than the energy of the $d_{x^2-y^2}$ orbital (Fig. 8.)

In possibility (2), in which the $d_{x^2-y^2}$ orbital has two electrons and the d_{z^2} orbital one electron, these are the negative charges on the ligands along X and Y directions which are less attracted by the nuclear charge on Cu^{2+} ion because of more effective screening of the latter by d electrons in X and Y directions. This results in elongation of metal–ligand bonds along X and Y directions and a contraction of metal–ligand bonds along Z direction. This implies that the octahedral geometry of Cu^{2+} ion complex gets distorted to tetragonal geometry which gets elongated along X and Y directions and compressed along Z direction, as shown in Fig. 9.

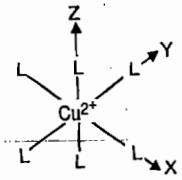


Fig. 9. Distortion of octahedral geometry of $[CuL_6]^{2+}$ to tetragonal geometry due to Jahn–Tellar effect if there are more electrons in $d_{x^2-y^2}$ orbital than in d_{z^2} orbital.

Further, in possibility (2), the electrostatic replusion experienced by d electrons of Cu^{2+} from the negative charge on the ligands along X and Y directions will be less than the similar repulsion experienced by d electrons from the negative charge on the ligands along Z direction. As a result, the $d_{x^2-y^2}$ orbital becomes of lower energy and d_{z^2} orbital becomes of higher energy.

In this way, the degeneracy of the two orbitals gets lifted. This is shown in Fig. 10.

It can be easily shown that, in general, whenever there are more electrons in $d_{x^2-y^2}$ orbital than in d_{z^2} orbital of an octahedral complex of any metal ion, the octahedral geometry would get distorted to tetragonal geometry by elongation of its metal–ligand bonds along X and Y directions as a result of which the energy of $d_{x^2-y^2}$ orbital becomes lower than the energy of d_{z^2} orbital (Fig. 10)

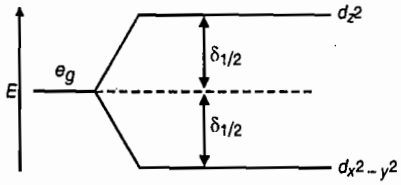


Fig. 10. Lifting of the degeneracy of e_g orbitals in $[CuL_6]^{2+}$ complex due to Jahn–Tellar effect when there are more electrons in $d_{x^2-y^2}$ orbital than in d_{z^2} orbital.

Apart from octahedral complexes of Cu^{2+} ion having $t_{2g}^6 e_g^3$ ground state configuration, the other octahedral complexes which show Jahn-Teller effect due to unequal number of electrons in e_g orbitals (*i.e.*, d_{z^2} and $d_{x^2-y^2}$ orbitals) comprise of metal ions with the ground state configurations, $t_{2g}^6 e_g^1$ and $t_{2g}^3 e_g^1$. In both these configurations, the electronic charge due to t_{2g} electrons is uniformly distributed and, therefore, the type of distortion in geometry depends upon the e_g orbital (d_{z^2} or $d_{x^2-y^2}$)which the electron occupies.

Let us now consider an octahedral complex of a metal ion with t_{2g}^1 configuration in ground state. The solitary electron can be present in any of the three t_{2g} orbitals. If the electron is present in d_{xy} orbital of the t_{2g} set, it would screen the nucleus of the metal ion more effectively in XY plane than in XZ or YZ plane.This wouldreduce the attraction between the nuclear charge on the metal ion and the negative charge on the ligands in XY plane. As a result, the octahedral geometry of the complex would get distorted by elongation of the metal–ligand bonds in XY plane. In such a situation, the repulsion between d electrons of the metal ion and the negative charge on the ligands would become less in the XY plane compared to such a repulsion in the XZ or YZ plane, resulting in a decrease in the energy of the d_{xy} orbital and an increase in the energies of d_{xz} and d_{yz} orbitals, as illustrated in Fig. 11. The changes in the energies of the orbitals would obviously be governed by the centre of gravity rule.

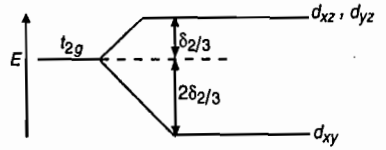


Fig. 11. Lifting of degeneracy of t_{2g} orbitals in an octahedral complex of a metal ion with t_{2g}^1 configuration when the solitary electron is present in d_{xy} orbital.

If, on the other hand, the electron is present in either of the d_{xz} and d_{yz} orbitals, it will screen the nucleus of the metal ion more effectively in the XZ or the YZ plane compared to the XY plane. This would result in a decrease of attraction between the positive nuclear charge on the metal ion and the negative charge on the ligands along the Z direction and an increase in such attraction along the X and Y directions. As a result, the metal–ligand bonds get elongated along the Z direction whereby the octahedral geometry gets distorted to tetragonal geometry.

Since the ligands along Z axis move away from the metal ion while those along X and Y axes come nearer, the d electron would be repelled less by the negative charge on the ligands along Z direction whereas it will be repelled more by the negative charge on the ligands along X and Y directions. This increases the energy of d_{xy} orbital and decreases the energies of d_{xz} and d_{yz} orbitals, as illustrated in Fig. 12.

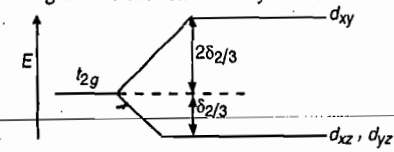


Fig. 12 Lifting of the degeneracy of t_{2g} orbitals in an octahedral complex of a metal ion with t_{2g}^1 configuration when the solitary electron is present in d_{xz} or d_{yz} orbital.

The changes in energies of these orbitals will again obey the centre of gravity rule.

It is pertinent to add here that the energies of both d_{xy} and $d_{x^2-y^2}$ orbitals (being functions of the same variables x and y) alter in a similar manner due to distortion of octahedral geometry by Jahn–Teller effect. The relative energies of all the five d orbitals in the two possible tetragonal distortions are given

below in Figs. 13 and 14.

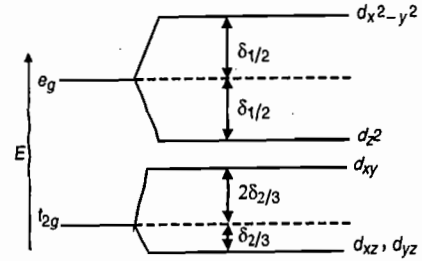


Fig 13. Tetragonal distortion caused by elongation of M–L bonds along Z direction

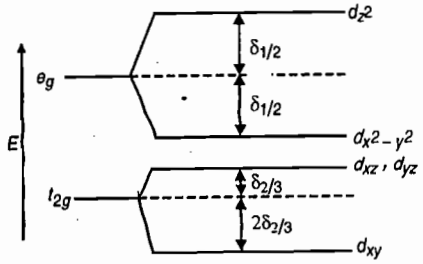


Fig. 14. Tetragonal distortion caused by compression of M–L bonds along Z direction.

It may be noted that Jahn–Teller effect is operative not only in the case of complexes formed with negatively charged ligands but also in the case of complexes formed by neutral ligands such as NH_3, H_2O, CO, NO, etc., which are dipolar in character. The only difference in the two types of complexes is that while in the former category of complexes, the *d* electrons of the metal ion are repelled by the negative charges on the ligands, in the latter category, the *d* electrons are repelled by the negatively charged poles of dipolar neutral ligands.

It is pertinent to point out that the Jahn–Teller effect shown by t_{2g} orbitals (designated as δ_2) is much weaker than that shown by e_g orbitals (designated as δ_1), *i.e.*, $\delta_2 << \delta_1$. The reason for this is that in t_{2g} orbitals the regions of maximum charge density lie *in between* the *X*, *Y* and *Z* directions and not directly *in* the *X*, *Y* and *Z* directions along which the ligands are placed whereas in e_g orbitals, the regions of maximum charge density lie directly *in the directions* along which the ligands are placed. As a result, an electron placed in any of the t_{2g} orbitals would shield the positive charge on the nucleus of the metal ion much less effectively in the *X*, *Y* and *Z* directions, *i.e.*, along the directions of the ligands than what an electron placed in any of the e_g orbitals would do along these directions. Therefore, the magnitude of Jahn—Teller effect, which is related to the extent of screening of the nuclear charge of the metal ion by the *d* electrons in the directions of the ligands, is smaller in octahedral complexes of metal ions with ground state configurations t_{2g}^1, t_{2g}^2, t_{2g}^4 and t_{2g}^5 than in complexes of metal ions with ground state configurations $t_{2g}^6 e_g^1$, $t_{2g}^6 e_g^3$, $t_{2g}^3 e_g^1$, etc. In fact, it has not been possible to detect Jahn-Teller distortion in octahedral complexes of metal ions with ground state configurations t_{2g}^1, t_{2g}^2, t_{2g}^4 and t_{2g}^5 (except from indirect spectroscopic evidence) because the magnitude of the effect is comparatively very small. Nevertheless, these complexes do get somewhat more stabilised due to Jahn–Teller effect. We can, in fact, theoretically predict the type of Jahn–Teller distortion which these complexes would undergo depending upon the electronic configuration of the metal ion. This is illustrated in Table 4.

TABLE 4

Prediction of the Type of Distortion to be produced in Octahedral Complexes due to Jahn-Teller Effect

Configuration of metal ion	Stabilisation obtained by distortion of octahedral geometry caused due to :		Prediction of Distortion *E* : Elongation along Z-axis *C* : Compression along Z-axis
	Elongation of M–L bonds along Z-axis	Compression of M–L bonds along Z-axis	
t_{2g}^1	$\delta_2/3$	$2\delta_2/3$	*C*
t_{2g}^2	$2\delta_2/3$	$\delta_2/3$	*E*
t_{2g}^4 **	$\delta_2/3$	$2\delta_2/3$	*C*
t_{2g}^5 **	$2\delta_2/3$	$\delta_2/3$	*E*

** δ_2 <<< pairing energy

As already stated, the predictions made in Table 4 cannot be verified experimentally as the magnitude of the splitting of t_{2g} orbitals is very very small.

Let us now see if we can predict the type of distortion that can be produced due to Jahn-Teller effect in octahedral complexes of metal ions with ground state configurations $t_{2g}^6 e_g^1$ and $t_{2g}^6 e_g^3$. We shall take into consideration the case of octahedral complex of Cu^{2+} ion ($t_{2g}^6 e_g^3$). (The low spin complex of Co^{2+} ion ($t_{2g}^6 e_g^1$) would exhibit similar behaviour).

The distribution of electrons in t_{2g} and e_g orbitals of an octahedral complex of Cu^{2+} and the two possible distortions produced due to Jahn–Teller effect are shown in Figs. 15 and 16.

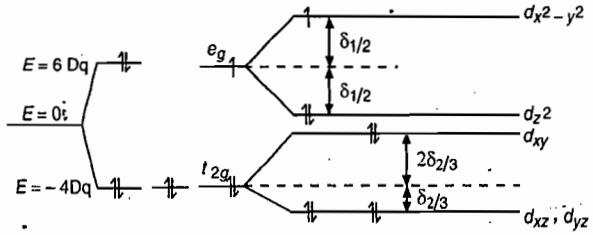


Fig. 15. Elongation of octahedral complex along Z axis.

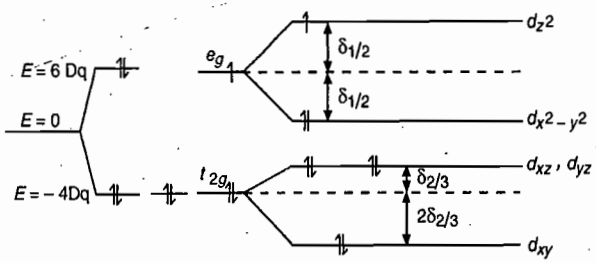


Fig. 16. Compression of octahedral complex along Z axis.

The decrease in energy accompanying the two possible distortions that occur due to Jahn-Teller effect may be calculated as follows :

Possibility 1. Elongation along Z axis :

Energy of the complex corresponding to Possibility (1) is given by

$$E_1 = 4 \times (-4\,Dq - \delta_2/3) + 2 \times (-4\,Dq + 2\,\delta_2/3) + 2 \times (6\,Dq - \delta_1/2) + 1 \times (6Dq + \delta_1/2)$$
$$= -6\,Dq - \delta_1/2$$

Energy of the complex without distortion is given by

$$E_2 = 6 \times (-4\,Dq) + 3 \times 6\,Dq = -6\,Dq$$

Decrease in energy due to Jahn-Teller distortion is given by

$$E_2 - E_1 = -6\,Dq - (-6\,Dq - \delta_1/2) = \delta_1/2$$

Thus, increase in stability due to Jahn-Teller distortion = $\delta_1/2$

Possibility 2. Compression along Z axis :

Energy of the complex corresponding to Possibility (2) is given by

$$E_3 = 2 \times (-4\,Dq - 2\,\delta_2/3) + 4\,(-4\,Dq + \delta_2/3) + 2 \times (6\,Dq - \delta_1/2) + 1 \times)6\,Dq + \delta_1/2)$$
$$= -6\,Dq - \delta_1/2$$

Energy of the complex without distortion is given, as above, by $E_2 = -6\,Dq$

Decrease in energy due to Jahn-Teller distortion is given by

$$E_2 - E_3 = -6\,Dq - (-6\,Dq - \delta_1/2) = \delta_1/2$$

Thus, increase in stability due to Jahn-Teller distortion = $\delta_1/2$

It is evident from the above calculations that both the distortions stabilise the octahedral complex to the same extent. It is, therefore, difficult to predict as to which of the two possible distortions would occur in the octahedral complex due to Jahn-Teller effect. Of course, as revealed by experimental observations, the common distortion involves *elongation* of the Cu–ligand bonds along one axis (say, Z-axis). For instance, in the CuF_2 crystal lattice in which each Cu^{2+} ion is surrounded by six F^- ions, two of the six F^- ions immediately surrounding the Cu^{2+} ion are at a distance of 2·27 Å and the remaining four F^- ions are at a distance of 1·93 Å. The distortion thus leads to tetragonal geometry. In some cases, the Jahn-Teller effect is so strong that Cu^{2+}–ligand bonds get elongated so much along the Z-axis that the resulting distorted octahedral complex acquires a square planar geometry instead of a tetragonal geometry.

Some copper(II) octahedral complexes, however, are known to exist in the other tetragonal geometry in which the Cu–ligand bonds are shorter along one direction (say, Z direction). A well known example is $K_2[CuF_4]$ in whose crystal each Cu^{2+} ion has six F^- ions as immediate neighbours, as shown in Fig. 17.

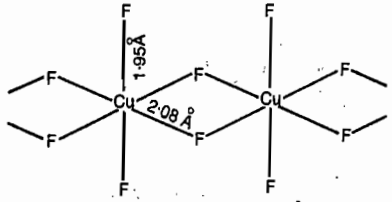


Fig. 17. The structure of $[CuF_4]^{2-}$ ion in solid state. (Charges on Cu and F not shown)

As shown above, some of the F^- ions form a common neighbourhood to two Cu^{2+} ions so that the overall formula of the complex ion is $[CuF_4]^{2-}$. The lines between Cu^{2+} and F^- ions simply indicate the association between the two and not the exact bond order.

To sum up :

1. Jahn–Teller distortions occur in octahedral complexes in which the metal ions have the ground state configurations, $t_{2g}^3e_g^1$, $t_{2g}^4e_g^1$, $t_{2g}^4e_g^2$, $t_{2g}^5e_g^2$, $t_{2g}^6e_g^1$ and $t_{2g}^6e_g^3$, t_{2g}^1, t_{2g}^2, t_{2g}^4 and t_{2g}^5.

2. Jahn–Teller distortions are automatic and are not imposed on the system.

3. Jahn-Teller effect is operative not only in complexes with anionic ligands but also in complexes with neutral dipolar ligands.

4. Jahn–Teller effect shown by t_{2g} orbitals (δ_2) is much weaker than that shown by e_g orbitals (δ_1), *i.e.*, $\delta_2 << \delta_1$.

Jahn–Teller Effect and Electronic Spectra of Complexes. Electronic absorption bands in the spectra of coordination complexes are associated with *d–d* transitions which arise due to the excitation of electrons of the metal ions from lower energy *d* orbitals to higher energy *d* orbitals. Obviously, only that frequency (ν) of electromagnetic radiation would be absorbed which matches with frequency ν of the energy gap ΔE (Fig. 18) between the energies of the two *d* orbitals involved in the electronic transition.

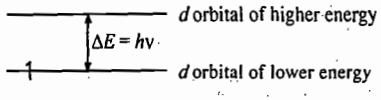


Fig. 18 Energy gap between the energies of the two *d* orbitals involved in the electronic transition.

It is evident that the absorption band would appear at frequency ν.

Let us consider, for example, the octahedral complex of Ti^{3+} ion, *viz.*, $[Ti(H_2O)_6]^{3+}$. In this complex the metal ion has d^1 configuration. In ground state, this electron occupies one of the t_{2g} orbitals, the e_g orbitals remaining vacant. This complex absorbs radiations in the visible region around 5000 Å wave length. The energy absorbed excites the solitary electron to one of the e_g orbitals. The $t_{2g}^1 \rightarrow e_g^1$ electron transition should give rise to a single symmetrical absorption band in the spectrum of $[Ti(H_2O)_6]^{3+}$. But actually it is not so. The observed absorption bond is unsymmetrical, as shown in Fig 19, which appears to be the result of overlapping of more than one absorption bands. This can be accounted for on the basis

of Jahn–Teller effect, as follows :

Table 4 predicts that the ground state electronic arrangement in which the solitary electron is present in d_{xy} orbital of the complexed metal ion is slightly more stable. As explained earlier, because of the presence of this electron in d_{xy} orbital, the octahedral geometry of the complex would get distorted to tetragonal geometry in which the Ti – OH_2 bonds along *Z* axis are shorter than those along *X* and *Y* axes (Jahn-Teller effect) and the energy of d_{xy} orbital becomes less than the energies of d_{zx} and d_{yz} orbitals. However, since the energy gap δ_2 between d_{xy} and (d_{xz}, d_{yz}) is much smaller than the average width of an electronic absorption band, the gap δ_2 can neither account for absorption of electromagnetic radiation in the visible region nor can it account for the asymmetry in the electronic absorption band of $[Ti(H_2O)_6]^{3+}$.

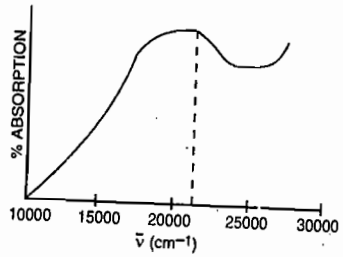


Fig. 19. Unsymmetrical absorption band observed in the spectrum of $[Ti(H_2O)_6]^{3+}$.

The electron present in d_{xy} orbital on excitation may occupy either (*i*) $d_{x^2-y^2}$ orbital leaving d_{z^2} orbital vacant or (*ii*) d_{z^2} orbital leaving $d_{x^2-y^2}$ orbital vacant. If the electron occupies $d_{x^2-y^2}$ orbital in the exited state it will have its charge polarised more in the *XY* plane in that state and if it occupies d_{z^2} orbital it will have its charge polarised more along the *Z* direction. This gives rise to two electronic arrangements in the excited state which will be of different energy.

Thus, lowering of the symmetry of $[Ti(H_2O)_6]^{3+}$ from octahedral to tetragonal due to Jahn–Teller effect splits the excited state and makes possible two electronic transitions or electronic jumps, *viz.*, $d_{xy}^1 \rightarrow d_{x^2-y^2}^1$ and $d_{xy}^1 \rightarrow d_{z^2}^1$, as shown in Fig. 20 which should give rise to two absorption bands.

Since the energy difference δ_2 between d_{xy} and (d_{xz}, d_{yz}) is very small, the population difference between d_{xy} and (d_{xy}, d_{yz}) levels is also very small. Therefore, the ground state of $[Ti(H_2O)_6]^{3+}$ is often written as t_{2g}^1 instead of d_{xy}^1 so that the two transitions are more commonly called $t_{2g}^1 \rightarrow d_{x^2-y^2}^1$ and $t_{2g}^1 \rightarrow d_{z^2}^1$ instead of $d_{xy}^1 \rightarrow d_{x^2-y^2}^1$ and $d_{xy}^1 \rightarrow d_{z^2}^1$ transitions, respectively.

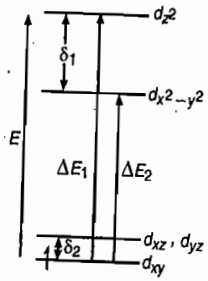


Fig. 20. Splitting of the excited state energy levels due to Jahn-Tellar effect in $[Ti(H_2O)_6]^{3+}$ in the distorted geometry making possible two electronic transitions.

The energy gap ΔE_1 ($E_{d_{z^2}} - E_{d_{xy}}$) is not very different from the energy gap ΔE_2 ($E_{d_{x^2-y^2}} - E_{d_{xy}}$). Therefore, the two transitions are of close energy giving rise to two bands at close frequencies which overlap to give a composite absorption band as shown in Fig. 19.

Although so far we have considered a slightly more stable tetragonal distortion for $[Ti(H_2O)_6]^{3+}$ ions in which Ti–OH_2 bonds along the *Z* direction are shorter than the rest of such bonds, there is also present, a considerable fraction of the complex ions, at any moment, containing the other possible tetragonally distorted geometry in which Ti–OH_2 bonds along the Z direction are elongated compared to other such bonds due to the following reason :

As is obvious from Table 4, the distorted geometry (*C*) of $[Ti(H_2O)_6]^{3+}$ obtained by compression of Ti^{3+}–OH_2 bonds along Z axis is *stabler* by $\delta_2/3$ over its distorted geometry (*E*) obtained by elongation of Ti–OH_2 bonds along *Z* axis. But the difference $\delta_2/3$ in the energies of the two distorted geometries *C* and *E* of the complex ion $[Ti(H_2O)_6]^{3+}$ is very small and the thermal energy available at room temperature to these complex ions in the distorted geometry *C* is sufficiently enough to allow these ions to change their geometry to *E*. Thus, there are two factors which determine the geometry of the complex ions :

1. Jahn–Teller effect which tends to favour the disorted geometry *C* for $[Ti(H_2O)_6]^{3+}$ in which d_{xy} is the lowest energy orbital.

2. The thermal energy available to the complex ions which tends to equalise the population of the complex ions in the two distorted geometries *C* and *E*. Due to this, an equilibrium condition between the populations of the complex ions in the two distorted geometries exists. This is known as **dynamic Jahn-Teller effect**. One of the requirements for the occurrence of dynamic Jahn–Teller effect is that the energy gap between the split up t_{2g} and/or e_g orbitals should be small.

If in an octahedral complex, the energy gap between the split up t_{2g} and/or e_g orbitals is quite high, the thermal energy available at room temperature will no longer be sufficient to influence the population of the complex molecules in any of the distorted geometries. Hence Jahn-Teller effect will solely determine the stabler distorted geometry which the complex molecules will acquire. In other words, in such a case, all the complex molecules will exist in only one stable distorted geometry. This is known as **static Jahn–Teller effect.**

The complex ion $[Ti(H_2O)_6]^{3+}$ exhibits, in all probability, dynamic Jahn–Teller effect so that at room temperature the complex ions having both the types of distorted geometries exist in equilibrium. The electron absorption spectra of $[Ti(H_2O)_6]^{3+}$ will, therefore, be an average of the electron absorption spectra of the two distorted geometries. We have already discussed the electron absorption spectra of $[Ti(H_2O)_6]^{3+}$ in the distorted geometry *C*. Let us now see what type of electron absorption spectra will be observed for the complex ions having the other distorted geometry *E* in which Ti^{3+}–OH_2 bonds along *Z* axis are longer than such bonds along *X* and *Y* directions.

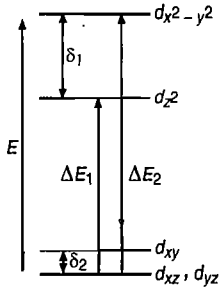


Fig. 21 Splitting of the excited state energy levels due to Jahn-Tellar effect in $[Ti(H_2)_6]^{3+}$ in the distorted geometry *E* making possible two electronic transitions.

The ground state for such a geometry will obviously be $(d_{xz}, d_{yz})^1$. The excited state $d^1_{z^2}$ will be of lower energy than the excited state $d^1_{x^2-y^2}$. We shall again observe two transitions, $(d_{xz}, d_{yz})^1$ or $t^1_{2g} \rightarrow d^1_{z^2}$ and $(d_{xz}, d_{yz})^1$ or $t^1_{2g} \rightarrow d^1_{x^2-y^2}$, as shown in Fig. 21.

Since ΔE_1 $(E_{d_{z^2}} - E_{d_{xz},d_{yz}})$ is not much different from ΔE_2 $(E_{d_{x^2-y^2}} - E_{d_{xz},d_{yz}})$, the two transitions will again give rise to two overlapping bands or an average unsymmetric band. Thus, an unsymmetric absorption band will be observed whether the complex ion $[Ti(H_2O)_6]^{3+}$ has the distorted geometry *C* or *E* or whether an equilibrium exists between *C* and *E* due to dynamic Jahn-Teller effect.

Let us now consider the octahedral complx of Cu^{2+}, *viz.*, $[Cu(H_2O)_6]^{2+}$. Most of the octahedral complexes of Cu^{2+} exhibit tetragonal distortion because of Jahn–Teller effect in which Cu–ligand bonds along *Z* axis are elongated compared to the bonds in the *XY* plane. We shall, therefore, discuss the electronic absorption spectrum of this geometry only.

The order of the energies of *d* orbitals in tetragonal geometry of the complex are as shown in Fig. 22.

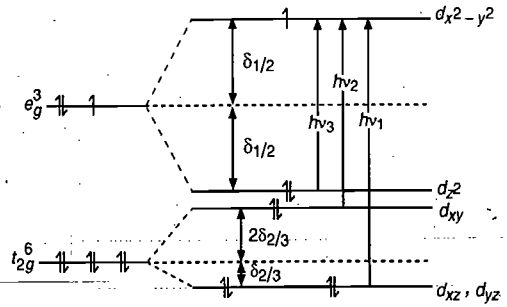


Fig. 22 Possible electronic transitions in tetragonal $[Cu(H_2O)_6]^{2+}$.

Unlike in octahedral Ti^{3+} complexes, there is considerable splitting of e_g orbitals in octahedral Cu^{2+} complexes due to Jahn–Teller effect as a result of which the energy of the d_{z^2} orbital is decreased to such an extent that it comes close to the energies of d_{xy} and (d_{xz}, d_{yz}) orbitals, as shown in the figure. Therefore, the energy required to excite an electron from any one of these orbitals to the partially vacant $d_{x^2-y^2}$ orbital is nearly of the same magnitude. Thus, the following three electronic transitions are

possible in electronic spectra of $[Cu(H_2O)_6]^{2+}$:

(*i*) Transition of an electron from d_{z^2} to partially vacant $d_{x^2-y^2}$ orbital by absorbing energy $h\nu_1$.

(*ii*) Transition of an electron from d_{xy} to partially filled $d_{x^2-y^2}$ orbital by absorbing energy $h\nu_2$.

(*iii*) Transition of an electron from d_{xz} to partially filled $d_{x^2-y^2}$ orbital by absorbing energy $h\nu_3$.

The three transitions of close energy would give rise to three absorption bands at close frequencies ν_1, ν_2 and ν_3 which overlap to give a composite, unsymmetric absorption band, as shown in Fig. 23.

If there had been no Jahn–Teller distortion, the spectrum would have consisted of a single symmetric band corresponding to the transition $t^6_{2g}e^3_g \rightarrow t^5_{2g}e^4_g$. The observed spectrum of the complex can thus be explained only on the basis of the Jahn–Teller effect.

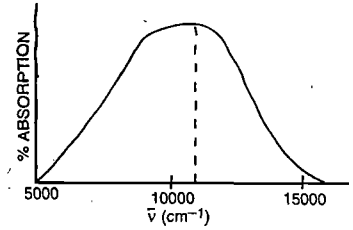


Fig. 23. Electronic spectrum of $[Cu(H_2O)_6]^{2+}$.

QUESTIONS

1. What are crystal field effects ? Discuss the crystal field effects on (*i*) ionic radii (*ii*) lattice energy (*iii*) heats of ligation (*iv*) geometry of coordination complexes.
2. Why do the ionic radii of Ca^{2+}, Mn^{2+} and Zn^{2+} show a smooth decrease whereas the ionic radii of the other bivalent metal ions of the First transition series show an irregular pattern ?
3. (*a*) Define crystal field stabilisation energy.

   (*b*) Why is lattice energy of an octahedral complex of a transition metal ion more than expected ? How can you calculate crystal field stabilisation energy from lattice energy ?
4. (*a*) Calculate crystal field stabilisation energy and 10 Dq of $FeBr_2$ if U_{MnBr_2} is 2435 kJ mole ; U_{FeBr_2} is 2540 kJ mole and U_{ZnBr_2} is 662 kJ mole.

   (*b*) How is it that the graph of ionic radii vs number of *d* electrons of Ca^{2+}, Mn^{2+} and Zn^{2+} in CaF_2, MnF_2 and ZnF_2 is almost a straight line whereas a similar graph of their ionic radii in $CaBr_2$, $MnBr_2$ and $ZnBr_2$ shows a bend at $MnBr_2$ in the line ?
5. (*a*) How can one calculate crystal field stabilisation energy from heats of hydration data of bivalent metal ions of the First transition series ?

   (*b*) The heats of hydration of Ca^{2+}, Cr^{2+} and Mn^{2+} are 2468 kJ mole, 2795 kJ mole and 2736 kJ mole respectively. Calculate the crystal field stabilisation energy of $[Cr(H_2O)]^{2+}_6$
6. How is heat of ligation related with the heat of hydration and the enthalpy of the reaction,

$$[M(H_2O)_6]^{n+}(aq) + 6L \overset{\Delta H}{\rightleftharpoons} [ML_6]^{n+}(aq) + 6H_2O$$

7. Discuss the stepwise replacement of water by another ligand L in $[Fe(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$. Based upon the above discussion, determine the relative positions of the metal ions in the spectrochemical series.
8. Explain why some metal ions have tendency to form mainly octahedral complexes whereas some others form both tetrahedral and octahedral complexes.
9. (*a*) State and explain Jahn–Teller effect.

   (*b*) Why are Jahn–Teller distortions automatic for the octahedral geometry of some metal ions?
10. Discuss the consequences of Jahn–Teller effect on the electronic spectra of octahedral complexes.
11. Explain the crystal structures of the following spinels : Co_3O_4, Mn_3O_4, Fe_3O_4.

30

COORDINATION COMPOUNDS. PART V

ELECTRON ABSORPTION SPECTROSCOPY AND MAGNETOCHEMISTRY OF TRANSITION METAL COMPLEXES

ELECTRON ABSORPTION SPECTRA OF TRANSITION METAL COMPLEXES

Electron absorption spectroscopy is the study of excitation of a chemical species from its ground state electronic energy level to an excited state electronic energy level by the absorption of electromagnetic radiation.

The study of electron absorption spectra, specially crystal field spectra of coordination complexes, gives important information about the colours of complexes, the magnitudes of energy gaps between ground electronic energy state and the excited electronic energy states of the metal ions in their complexes; the extent of covalent character in metal–ligand bonds, the geometry of complexes, the positions of metal ions and the ligands in the spectrochemical and nephelauxetic series, etc.

The crystal field spectra of coordination complexes arise due to excitation of a complexed transition metal ion from its ground *d* electronic energy level (*i.e.*, lowest energy arrangement of electron in *d* orbitals) to one of its excited *d* electronic energy levels (*i.e.*, one of the higher energy arrangements of electrons in *d* orbitals) because of the absorption of electromagnetic radiation by the complexed metal ion. The electromagnetic radiation absorbed by the complexed metal ion is utilised in promoting electrons from lower energy *d* orbitals to the higher energy *d* orbitals thereby causing changes in the overall arrangements of electrons in the *d* orbitals. For a proper understanding of electron absorption spectra of coordination complexes, a working knowledge of the following topics is necessary :

1. Atomic spectroscopy which deals with the consequences of interelectronic repulsions and magnetic interactions amongst electrons in the electronic configuration of an atom or an ion. Such interactions cause couplings of spin and angular momenta of electrons within a given electronic configuration which give rise to several degenerate and non-degenerate energy levels, known as the energy terms and the spectroscopic states. The transitions in these electronic energy levels of an atom or an ion due to absorption of electromagnetic radiation give rise to its electron absorption spectrum.
2. The effect of electrostatic crystal field generated by ligands on the energy terms of a given electronic configuration of metal ion in its complex which quite often splits the degenerate energy terms.
3. Basic concepts of electron absorption spectroscopy such as the selection rules and their relaxation.

We shall briefly discuss all these topics one by one before attempting to interpret the electron absorption spectra of coordination complexes.

ATOMIC SPECTROSCOPY

Orbital Angular Momentum and Spin Angular Momentum of an Electron

According to the prewave mechanical concepts, an electron moving in an orbit generates orbital angular momentum (*l*) which is a vector quantity and is perpendicular to the plane of the orbit containing the electron (Fig.1). This vector can be resolved along the three mutually perpendicular axes so that $(l) = \sqrt{(l_x)^2 + (l_y)^2 + (l_z)^2}$ where (l_x), (l_y) and (l_z) are components of (*l*) along X, Y and Z axes (Fig. 2).

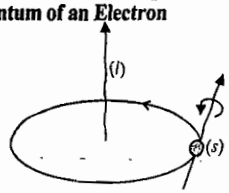


Fig. 1. Representation of spin and orbital angular momentum vectors associated with an electron.

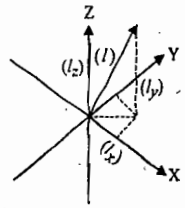


Fig. 2. Components of (*l*) along X, Y and Z axis.

The magnitude of vector (*l*) is equal to $\sqrt{l(l+1)}\ h/2\pi$ where *l* is the angular momentum quantum number. *Note that (l) and l represent different quantities.* The vector (*l*) is allowed (2*l* + 1) orientations or positions in space about any given direction (generally the Z direction) in such a manner that its component along this direction, *i.e.*, m_l, can have values ranging from $+lh/2\pi$ to $-lh/2\pi$ depending upon the orientation of the vector (*l*), as shown in Fig. 3 for (*l*) = (2).

If we apply an external magnetic field along the same direction (*i.e.*, the Z direction), it is the component of (*l*) along this direction, *viz.*, m_l, which interacts with the external magnetic field. If there are (2*l*+1) values of m_l, then, obviously, there would be (2*l*+1) interactions of m_l with the external magnetic field and each interaction of this type would be of different energy. In the absence of external magnetic field, however, all the orientations would be of equal energy and (*l*) may have any of the (2*l*+1) orientations in space.

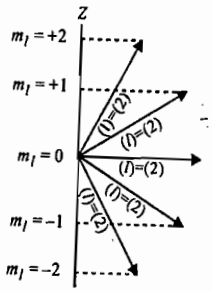


Fig. 3. Orientations of (*l*) = (2) along Z axis.

In order to explain finer points of atomic spectra it was suggested by G. Uhlenbeck and S. Gouldsmit that the electron, apart from moving in an orbit, is also spinning around its own axis. The spinning motion generates spin angular momentum (*s*) which is again a vector quantity and is directed along the spinning axis of the electron, as shown in Fig. 1. The magnitude of vector (*s*) is equal to $\sqrt{s(s+1)}\ h/2\pi$ where *s* is the spin quantum number. The position of vector (*s*) in space is also quantized in the sense that it is allowed a fixed number of orientations (*viz.*, two orientations) in space about any direction (taken as Z direction). Each orientation of vector (*s*) in space has component s_z or m_s along the Z direction. The two m_s values for the two orientations of (*s*) are $+\frac{1}{2}h/2\pi$ and $-\frac{1}{2}h/2\pi$, as shown in Fig. 4.

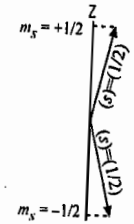


Fig. 4. Allowed orientations of (*s*) = (1/2)

In the absence of an external magnetic field, the two orientations will be of equal energy so that the electron may have its (*s*) vector in either of these orientations. But, in the presence of the external magnetic field along the Z direction, the interactions of m_s of each orientation with external magnetic field would be of different energy.

While referring to angular momentum, in general, the factor $h/2\pi$ is sometimes omitted for brevity although the presence of this factor should always be kept in mind while discussing angular momentum. Thus, the magnitude of orbital angular momentum (2) is written as $\sqrt{2(2+1)}$ instead of $\sqrt{2(2+1)}\ h/2\pi$. Similarly, the magnitude of spin angular momentum ($\frac{1}{2}$) is written as $\sqrt{1/2(1/2+1)}$ instead of $\sqrt{1/2(1/2+1)}\ h/2\pi$. The magnitude of $m_l = +1$ is written as +1 instead of $+1h/2\pi$. Similarly, the magnitudes of $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ are written as $+\frac{1}{2}$ and $-\frac{1}{2}$ instead of $+\frac{1}{2}h/2\pi$ and $-\frac{1}{2}h/2\pi$. Henceforth, we shall omit the factor $h/2\pi$ of the angular momentum from our discussion. We shall use small letters *l* and *s* in parentheses, *i.e.*, (*l*) and (*s*), for representing uncoupled angular momentum vectors of a single electron in a system and capital letters *L* and *S* in parentheses, *i.e.*, (*L*) and (*S*), for representing the resultant angular momentum vectors of a multielectron system. Small letters *l* and *s*, without parentheses, represent angular momentum quantam numbers of individual uncoupled electrons whereas capital letters *L* and *S* without parentheses represent angular momentum quantum numbers of coupled electrons in a multielectron system.

Coupling of Single Electron Angular Momenta

Since (*l*) and (*s*) of each electron in a given electronic configuration are vector quantities, hence, like all other vector quantities, these can be combined to give a resultant vector. The vectors (*l*) and (*s*) can combine together in a number of ways depending upon the type of interaction causing the combination. These interactions are : electrostatic repulsion interactions between electrons and magnetic interactions between magnetic fields generated by the orbital and spin motions of electrons. Each type of combination of single electron angular momenta, *i.e.*, (*l*)–(*l*), (*s*)–(*s*) or (*l*)–(*s*) has only a fixed number of discrete arrangements of the combining angular momenta and in each of these arrangements, the individual, single

electron angular momentum vectors are inclined to each other at some definite angles so that each arrangement has a definite resultant angular momentum depending upon the angle between the combining angular momenta. The two combining vectors precess about the direction of their resultant. Such vectors are said to have **coupled.**

The following types of coupling of single electron angular momentum vectors (l) and (s) are generally encountered in free atoms or ions of elements.

1. (s) – (s) or Spin – Spin Coupling. The spin angular momentum vectors (s_1) and (s_2) of two electrons in a fixed orientation can get coupled to give a resultant spin angular momentum vector (s). The single electron vectors (s_1) and (s_2) can couple only in certain fixed inclinations of (s_1) with (s_2) due to restrictions placed on coupling by quantum mechanics. Each fixed inclination of (s_1) with (s_2) will give its own resultant (S). Each fixed inclination of (s_1) with (s_2) will also have a different energy due to different electron spin exchange interactions.

The magnitude of resultant spin angular momentum (S) is equal to $\sqrt{S(S+1)}$ where S is the resultant spin quantum number. S can have values s_1+s_2 and s_1-s_2. This implies that the resultant spin angular momentum vector will also have two values. The vector (S) can have ($2S+1$) orientations about a particular direction (generally Z direction) due to quantum mechanical restrictions placed on the spin–spin coupling. Each orientation of vector (S) will have its own component along the Z direction known as S_z or M_S. There will, therefore, be ($2S+1$) values of M_s ranging from $+S$ to $-S$ for each (S).

We shall illustrate spin–spin coupling by considering a two-electron atom or ion in free state. The resultant spin quantum number S will have two values, *viz.*, $\frac{1}{2}+\frac{1}{2}$, *i.e.*, 1 and $\frac{1}{2}-\frac{1}{2}$, *i.e.*, 0. Therefore, the magnitude of vector (S) will also have two values, *viz.*, $\sqrt{1(1+1)}$ and $\sqrt{0(0+1)}$, commonly written as (1) and (0). The spin angular momentum vector (1) will have 2×1+1=3 orientations about the Z direction whose Z-components along this axis, *i.e.*, M_S values, will be –1, 0, +1, as shown in Fig. 5.

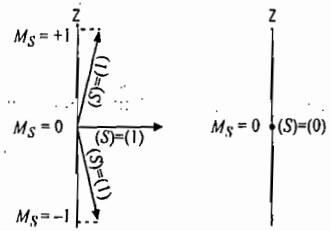


Fig. 5. Allowed orientations of (S) = (1) and (S) = (0).

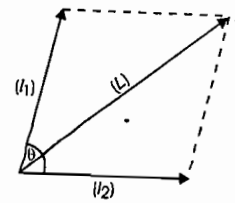
The spin angular momentum vector (0) has only one value of M_S, *viz.*, zero (Fig. 5).

If there are three electrons in an atom or an ion, the (s)–(s) coupling of any two electrons is considered first. The (s) vector of the third electron then couples with each of the (s) vectors separately by following the same rules as applicable to (s)–(s) coupling. Many-electron systems are also treated in a similar manner.

In an atom or an ion having orbitals of the same or similar energies, the electrons avoid being paired in a single orbital due to interelectronic repulsion. That is why the most stable arrangement is the one which has the maximum possible number of unpaired electrons. The electron spin exchange interactions in such an arrangement will be maximum if all the unpaired electrons have parallel spins. We have already discussed in Chapter 1 that the most stable electronic arrangement is the one which has maximum number of electronic spin exchange interactions. Thus, it is clear from the above discussion that the electronic arrangement with the highest value of (S) will be the most stable out of all the arrangments that are possible for a given configuration.

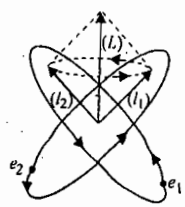
2. (l) – (l) Coupling or Orbital Coupling. This is the coupling of the orbital angular momentum vector (l_1) of one electron (e_1) with the orbital angular momentum vector (l_2) of the other electron (e_2). The coupling vectors (l_1) and (l_2) precess about a common axis while maintaining their mutual inclination and give rise to a resultant vector (L) along the common axis around which (l_1) and (l_2) precess. Because the angular momentum vector of an electron is perpendicular to the plane of rotation of electron, *i.e.*, to the orbit of electron, the planes of the orbits are, themselves, similarly inclined to each other as the coupling vectors (l_1) *and* (l_2). That is, for a particular combination of (l_1) and (l_2), the angle between the coupling vectors is the same as the angle between the two planes of the orbits in which (e_1) and (e_2) move.

The angle between the coupling vectors (l_1) and (l_2) is quantised so that only some fixed combinations of (l_1) with (l_2) are allowed. Each allowed combination of (l_1) with (l_2) will give a different resultant (L) depending upon the quantum mechanically allowed angle θ between (l_1) and (l_2). One such combination is shown in Fig. 6*a*.



(*a*)

Fig. 6*a*. Combination of (l_1) with (l_2). $\angle\theta$ is quantum mechanically allowed angle.



(*b*)

Fig. 6*b*. Electrostatic repulsion causing coupling of (l_1) and (l_2) in an allowed combination.

Each allowed combination of (l_1) and (l_2) which originates from similarly inclined planes of the orbits of the two electrons is associated with a definite energy which is determined by the extent of electrostatic repulsion between the two electrons which, in turn, depends upon the angle between the planes of the orbits of the two electrons and hence the angle between the combining (l_1) and (l_2). In other words, the energy associated with the resultant (L) of an allowed combination of (l_1) with (l_2) depends upon the angle between these two combining vectors.

For a particular combination of (l_1) with (l_2) to be stable, the electrostatic repulsion between e_1 and e_2 in their respective orbits should be minimum. For this, the two electrons should be on the opposite sides of the nucleus in which position they will be at maximum possible distance from each other. In order to maintain this distance, the electrons must move in the same direction and with the same velocity. Due to this, their (l_1) and (l_2) will also precess with the same velocity around a common axis which is also the direction of their resultant (L) (Fig. 6*b*). The strongest coupling between (l_1) and (l_2) (*i.e.*, the coupling associated with minimum energy) will occur when the orbital planes are parallel so that the directions of (l_1) and (l_2) are identical. In such a combination, therefore, the magnitude of (L) is the same as the sum of the magnitudes of (l_1) and (l_2).

The magnitude of resulting (L) is given by $\sqrt{L(L+1)}$ where L is resultant orbital angular momentum quantum number. It can have values ranging from l_1+l_2, l_1+l_2-1.....to l_1-l_2 or l_2-l_1 whichever is positive. The resultant (L) will vary with the quantum number L. Also since each resultant (L) is given by a definite inclination of (l_1) with (l_2), the number of values of (L) obtained is equal to the number of inclinations of (l_1) with (l_2) which are quantum mechanically allowed for coupling.

Each resultant orbital angular momentum vector (L) can have $2L+1$ orientations in space around any particular direction (often taken as Z direction) and each of $2L+1$ orientations has a component of (L) in the Z direction which is called (L_z) or M_L. Each allowed orientation of (L) makes a fixed solid angle with Z direction. (The situation is similar to the allowed orientations of (l) of single electron described in Chapter 1 (Fig. 18)). Thus, there are ($2L+1$) values of M_L for each (L). Fig. 7 shows orientations of (L) with L=3 and the corresponding L_z or M_L values. The quantum number M_L can be shown to be the combination of the single-electron m_l values of the two electrons. Let us consider that in the above example. The quantum number L=3 comes from an allowed combination l_1+l_2 of the two electrons one of which has l_1=1 and the other has l_2=2, *i.e.*, a p^1d^1 configuration. The possible m_l values of the first uncoupled electron are +1, 0, –1 and of the second uncoupled electron are +2, +1, 0, –1, –2. The value of M_L=3 of L=3 is the summation of m_{l_1} =+1 and m_{l_2} =+2. Similarly, M_L=+2 of L=3 is the summation of m_{l_1} =0 and m_{l_2} =+2 and so on.

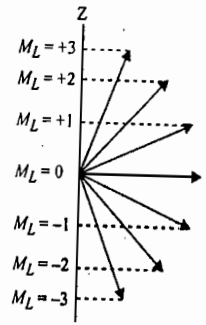


Fig. 7. Orientations of (L) with L=3 around Z direction.

For three-electron systems, we combine or couple each resultant orbital angular momentum vector (L) [obtained by the coupling of (l_1) and (l_2)] with (l_3) (the orbital angular momentum vector of third electron) exactly by the procedure described for the coupling of (l_1) with (l_2).

Just as the numerical values of l are given by symbols s, p, d, f, etc., similar but capital symbols are used for the numerical values of L. Thus,

for l =	0	1	2	3	4	5
the symbols are :	s	p	d	f	g	h
Similarly, for L =	0	1	2	3	4	5
the symbols are :	S	P	D	F	G	H

3. $(l)-(s)$ Coupling or Spin–Orbital Coupling of the Same Electron. The spin angular mometum vector (s_1) and orbital angular momentum vector (l_1) of the same electron may combine or couple to produce a resultant angular momentum vector (j) of that single electron. The angle between (l) and (s) is quantised. In other words, the vectors to be coupled are allowed certain specific inclinations or angles between them due to quantum mechanical restrictions placed on their coupling. In an allowed combination, the two vectors (l) and (s) belonging to the same electron precess about the direction of their resultant (j) (Fig. 8). More than one such inclinations or angles between (l_1) and (s_1) may be quantum mechanically allowed for coupling resulting in more than one resultant (j) value.

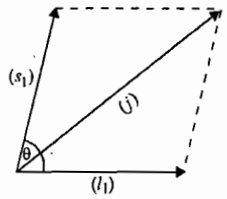


Fig. 8. Coupling of (l_1) and (s_1) of the same electron for an allowed inclination θ to give resultant (j)

The (l)–(s) coupling is magnetic in origin and can be best visualised if we hypothetically station curselves on the electron. The electron to us will then appear positioned at one place while the nucleus will appear to be moving around the electron. This motion of the nucleus around the electron will produce a magnetic field at the electron whose magnitude will depend upon the effective charge on the nucleus. The magnetic moment, μ_l generated in this way will interact with the magnetic moment μ_s generated due to the spinning of electron. The extent of this type of (l)–(s) coupling will tend to increase with the strength of magnetic field generated by the nucleus which will obviously increase with increase in effective charge on the nucleus. That is why the extent of $(l)-(s)$ coupling is greater for heavier atoms since their nuclei have greater effective charges than those of lighter atoms. The (l)–(s) coupling is not very significant for lighter elements.

The Energy Terms. Having discussed various types of angular momentum interactions, we shall describe the Russel–Saunders or $(L)-(S)$ coupling scheme and the $(j)-(j)$ coupling scheme for finding out **'energy terms'** of a given electronic configuration. But before we do that we shall illustrate the difference between an electronic configuration and an energy term. An electronic configuration is the assignment of a given number of electrons to a certain set of orbitals without caring about the electrostatic and other interactions between the electrons. For example, d^2 configuration tells us that there are two electrons in a set of five degenerate d orbitals. It does not tell us as to which d orbital is occupied and which is not.

It is important to note that for the same configuration, the placement of electrons even in degenerate orbitals may lead to electronic arrangements which may be of different energies. Consider the example of a metal ion with d^2 configuration. Let us say that we have a situation (a) in which the metal ion has one electron in $d_{x^2-y^2}$ orbital and one electron in d_{xy} orbital. Let us have another situation (b) in which the metal ion has one electron in $d_{x^2-y^2}$ orbital and one electron in d_{z^2} orbital. Now an electron in $d_{x^2-y^2}$ orbital has its regions of maximum electron charge density along the X and Y directions whereas an electron in d_{xy} orbital has the regions of maximum electron charge density in between the X and Y directions and an electron in d_{z^2} orbital has regions of maximum electron charge density mainly in the Z direction. Therefore, the two electrons in $d_{x^2-y^2}$ and d_{xy} orbitals, both of which have their electronic charge spread in the XY plane (situation a) will replel each other to a greater extent compared to the extent with which they will repel each other when present in $d_{x^2-y^2}$ and d_{z^2} orbitals (situation b). Both the situations (a) and (b) correspond to the same configuration but are associated with different energies. We can write many more arrangements for the d^2 configuration some of which will have different energies (non-degenerate arrangements due to different electrostatic repulsions between electrons) and some others will have the same energy (degenerate arrangements due to the same electrostatic repulsion between the electrons).

An **energy term** (or simply a **'term'**) is an energy level or a set of degenerate energy levels resulting from the electron–electron repulsions in an electronic arrangement or in a set of degenerate electronic arrangements of a configuration of a free atom or ion. It may again be emphasized that all the energy levels of an energy term are degenerate. Since electron–electron repulsions for all the electronic arrangements of a configuration may not be the same, there can be several energy terms in a configuration. The number of energy levels in a term is known as its degeneracy. The sum of degeneracies of all the terms of a configuration is obviously equal to the number of energy levels arising out of the configuration. Each energy level results from electron–electron repulsion in a distinct electronic arrangement of the configuration. In other words, the total number of energy levels arising out of a configuration is equal to the total number of electronic arrangements possible for that configuration.

Since it is very cumbersome to calculate the exact electron–electron repulsion in a many-electron system, a more convenient way to calculate the energy levels through $(l)-(l)$ and $(s)-(s)$ coupling effects (which are a direct consequence of electron–electron repulsions in a configuration) is adopted.

Just as each single electron wave function, which is used to calculate the energy of the single electron, is specified by the single electron quantum numbers l, m_l and m_s, each wave function of a many-electron system, which is used to calculate the energy of an electronic arrangement, is specified by the quantum numbers L, M_L and M_S.

Each energy level pertaining to an electronic configuration of a term in a many-electron system is associated with a distinct total wave function $\psi_{L,M_L} \cdot \psi_{M_S}$ which, when operated upon by the energy operator of the system, determines the energy of that level. ψ_{L,M_L} is known as the orbital part of the wave function whereas ψ_{M_S} is known as the spin part of the wave function.

An energy term is written as $^{(2S+1)}L$. The quantity $(2S+1)$ is known as spin multiplicity and gives the number of orientations of (S) in space {*i.e.*, the number of M_S values of (S)}. This means that there will be $2S+1$ spin wave fucntions, ψ_{M_S} and hence $(2S+1)$ spin energy levels for each orbital energy level corresponding to a particular orbital electronic arrangement of the term. Each orbital electronic arrangement has a distinct set of L, M_L values and each spin electronic arrangement has a distinct set of S, M_S values.

The resultant orbital angular momentum quantum number L in a term indicates the number of degenerate orbital energy levels contained in it. Since orbital angular momentum (L) corresponding to a term can have $2L+1$ orientations in space with respect to Z direction leading to an equal number of M_L values, there will be $2L+1$ orbital energy levels having $2L+1$ (L, M_L) sets in a term. In other words, the orbital degeneracy of a term is $2L+1$. As discussed above, each orbital energy level of a term is assigned a wave function ψ_{L,M_L} so that there are $2L+1$ wave functions corresponding to $2L+1$ orbital energy levels arising out of as many orbital arrangements of electrons in a term.

Since for each orbital energy level, there are $2S+1$ spin energy levels, the total number of energy levels or electronic arrangements (taking into consideration all possible electron spin interactions) in a term is given by the product of orbital degeneracy (*i.e.*, the number of orbital energy levels) and spin multiplicity (*i.e.*, the number of spin energy levels). That is, the total number of energy levels in a term designated as $^{(2S+1)}L$ is equal to $(2S+1)(2L+1)$. All the energy levels in a term are degenerate provided the energy of electronic arrangement of the term is solely determined from electrostatic interactions.

A ^3F term will have $3(2\times3+1) = 21$ energy levels of equal energy contained in it. (Here $2S+1 = 3$)

A ^3P term will have $3(2\times1+1) = 9$ energy levels of equal energy in it.

Let us, for the sake of practice, write down all the energy levels in a ^3P term (S=1, L=1) arising from p^2 configuration :

$M_L = -1$	$M_S = +1$	$M_L = 0$	$M_S = +1$	$M_L = +1$	$M_S = +1$
$M_L = -1$	$M_S = 0$	$M_L = 0$	$M_S = 0$	$M_L = +1$	$M_S = 0$
$M_L = -1$	$M_S = -1$	$M_L = 0$	$M_S = -1$	$M_L = +1$	$M_S = -1$

It can be seen that in a ^3P term of p^2 configuration, each orbital energy level ($L = 1$, $M_L = +1$; $L = 1$, $M_L = 0$; $L = 1$, $M_L = -1$) is repeated thrice so that the total energy levels of the term are **nine** as

expected. The other terms arising out of p^2 configuration are ^1D ($L = 2, S = 0$) and ^1S ($L = 0, S = 0$). The five energy levels contained in ^1D term are : $M_L = 2, M_S = 0$; $M_L = +1, M_S = 0$; $M_L = 0, M_S = 0$; $M_L = -1, M_S = 0$ and $M_L = -2, M_S = 0$. The only energy level contained in S term is $M_L = 0, M_S = 0$.

All the fifteen energy levels of the terms of p^2 configuration can be correlated with fifteen electronic arrangements of the configuration, as shown in Fig. 9. The m_l values +1, 0, −1 of p orbital ($l = 1$) are written above the boxes representing p orbitals. An upward arrow indicates an electron with $m_s = +1/2$ and a downward arrow with $m_s = -1/2$

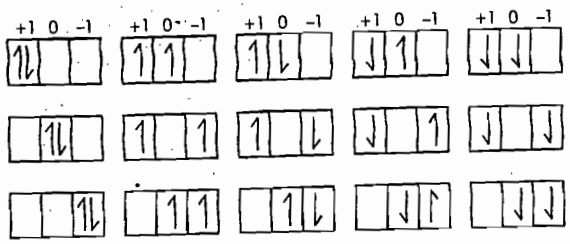


Fig. 9. Fifteen electronic arrangements of p^2 configuration.

As mentioned earlier, an energy term arises due to electrostatic interactions between the electrons of a configuration. The same electrostatic interactions cause $(l)-(l)$ and $(s)-(s)$ coupling also. There is another interaction acting on the electrons of a configuration. It is the magnetic interaction which causes coupling of spin angular momentum with orbital angular momentum. This interaction further splits the degenerate energy levels of a term to give rise to a number of **energy states** (or **spectroscopic states**). Thus, an energy term may be split into many energy states due to spin–orbit coupling. An energy state is written as $^{2S+1}L_J$ where J is the resultant angular momentum quantum number arising due to spin–orbit coupling. It may be mentioned that both energy terms (or terms) and energy states (or spectroscopic states) are in fact energy levels of the system. The energy levels or the set of energy levels resulting only from electron–electron repulsions in a configuration are called energy terms (or simply as terms) while those resulting from both electron–electron repulsions and magnetic interactions are called energy states or spectroscopic states.

There are two ways in which the energy states of a configuration may be derived :

1. We can write down all electronic arrangements of a configuration and calculate their energies due to actual interelectronic repulsion and magnetic interactions. It is, however, a very tedius method and is seldom used.

2. The second way is to apply orbital coupling, spin–spin coupling and spin–orbit coupling effects which are consequences of interelectronic repulsions and magnetic interactions, on the electrons of a configuration and find out the energy states.

Since the spin–spin coupling and orbital coupling effects arise due to interelectronic repulsion interaction and spin–orbit coupling effect arises due to magnetic interaction on electrons of a configuration, both the ways (1) and (2) lead to the same result. The way (2) is much easier to carry out than way (1) and shall be discussed in detail. That is, we shall derive energy states by considering spin–spin, orbital and spin–orbit coupling effects on electrons of a configuration.

Coupling Schemes. There are two ways in which the spin–spin, orbital and spin–orbit coupling effects can be applied on the electrons of a configuration. These are : **1. Russel-Saunders coupling scheme** which is applied to configurations of atoms or ions where interelectronic repulsions are much stronger than magnetic effects and **2. *(j) – (j)* coupling scheme** which is applied where magnetic effects acting on electrons of a configuration are stronger than interelectronic repulsion effect.

It is known that no atom or ion of interest conforms to conditions imposed by $(j) - (j)$ coupling. Therefore, Russel-Saunders coupling scheme is of greater importance to us and shall be discussed in greater details.

1. Russel-Saunders Coupling Scheme or $(L)-(S)$ Coupling Scheme

This scheme is applicable for most of the metal ions which are of interest in inorganic chemistry. It rightly assumes that for configurations of atoms or ions of lighter elements, the interelectronic repulsions

are far more important than spin–orbit coupling effects. Therefore, the effects with larger magnitude, *i.e.*, interelectronic repulsion effects (causing spin–spin and orbital coupling) are considered first on electronic configurations of free atoms or ions. These effects lead to energy terms of the configuration as already discussed. Each energy term of the configuration is then subjected to the effect of lesser magnitude, *i.e.*, magnetic effect or spin–orbit coupling effect leading to energy states or spectroscopic states. This scheme, therefore, involves the following steps :

1. The first step in this scheme is to find out the resultant orbital angular momenta (L) and resultant spin angular momenta (S) of all the electrons present in the configuration.

2. The second step is to write down all the possible terms in the configuration with the help of L and S. Some of these terms may really exist for a configuration and some may not.

3. The third step is to determine the terms which really exist out of all the possible terms of a configuration.

4. The fourth step is to couple the resultant spin angular mometum (S) with resultant orbital angular momentum (L) to arrive at different values of resultant angular momentum (J).

Let us find out the energy terms and energy states of a **free carbon atom** in its ground state.

The carbon atom has the ground state configuration $1s^2 2s^2 p^2$. A filled shell or filled set of orbitals will not contribute anything towards resultant spin angular momentum and resultant orbital angular momentum of electrons in a configuration. The electronic charge distribution of the paired up electrons in such cases is uniform in all the directions. Because of this, the paired up electrons in $1s$ and $2s$ orbitals of carbon atom will not contribute anything towards (L) and (S) of the configuration. Therefore, (L) and (S) of the configuration will entirely result from electrons in p orbitals.

We first couple spin angular momenta (1/2) and (1/2) of the two electrons to get two values of the resultant spin angular momentum (1) and (0) with the resultant spin quantum numbers having the values of 1 and 0, respectively. The spin multiplicity corresponding to (1) is $2 \times 1 + 1 = 3$ and corresponding to (0) is $2 \times 0 + 1 = 1$.

We now couple orbital angular momenta (l_1) and (l_2) of the two electrons. Since $l_1 = l_2 = 1$ for p electrons, the resultant (L) has values (1+1), (1+1−1) and (1+1−2) (*i.e.*, varying from (l_1+l_2) to (l_1-l_2) or (l_2-l_1) whichever is positive. That is, L has the values 2, 1 and 0.

Having found out all the possible values of L and S, we write down all the possible $^{(2S+1)}L$ terms for p^2 configuration. These terms are :

$$\underset{(L=2)}{^3D} \quad \underset{(L=1)}{^3P} \quad \underset{(L=0)}{^3S} \quad \text{and} \quad \underset{(L=2)}{^1D} \quad \underset{(L=1)}{^1P} \quad \underset{(L=0)}{^1S}$$

All these terms do not actually exist for p^2 configuration because the sum of energy levels contained in the terms of a configuration must be equal to the total number of electronic arrangements possible in it. Since for a p^2 configuration, there are only fifteen ways of arranging the two electrons in three p orbitals, the sum of energy levels of all the terms of the configuration must also be fifteen.

These fifteen electronic arrangements have already been shown in Fig. 9. Each arrangement has a distinct set of (M_L, M_S) values and a definite energy corresponding to this set. In these arrangements, M_L ($=\Sigma m_l$) equal to +2 occurs once (first arrangement in first row), M_L equal to +1 occurs four times (second to fifth arrangements in second row) and M_L equal to zero occurs five times (first to fifth arrangements in second row). Similarly, M_L equal to −1 occurs four times and M_L equal to −2 occurs only once.

It can also be seen that M_S ($= \Sigma m_s$) equal to +1, 0 and −1 occurs three, nine and three times, respectively, in these arrangements. It is evident from the above description that the number of M_L as also of M_S values is always equal to the number of electronic arrangements and hence is equal to the number of energy levels of a configuration.

The quantum number L relating to that (L) which includes the highest M_L of the arrangements (which is +2 in the present case) is obviously 2. Therefore, the set of fifteen energy levels pertaining to

fifteen arrangements of a p^2 or s^2p^2 configuration should contain a D term. It can be shown that the number of times any particular M_L appears in a term is equal to the spin multiplicity of that term. Since M_L equal to + 2 occurs only once in the arrangements, the spin multiplicity of the D term is 1. Spin multiplicity of a term is given by $2S + 1$. It is also equal to the number of M_S values that (S) can have. Since $2S + 1 = 1$ for the D term, $S = 0$ and M_S is also equal to zero.

The ^1D term ($L = 2$) includes the following five energy levels :

$$M_L = \pm 2,\quad M_S = 0;\qquad M_L = \pm 1,\quad M_S = 0;\qquad M_L = 0,\quad M_S = 0$$

If we substract the M_L and M_s values contained in ^1D term from the total (M_L, M_S) values of fifteen energy levels, we are left with $M_L = \pm 1$ occurring three times each, $M_L = 0$ occurring four times, $M_S = \pm 1$ occurring three times each and $M_S = 0$ occurring four times in the remaining ten energy levels.

Again, the quantum number L relating to that (L) which includes + 1 as the highest M_L is 1. Therefore, the next term of the configuration is a P term. Since $M_L = \pm 1$ occurs three times each in the term, its spin multiplicity is 3. In other words, each orbital energy level of the term with a particular M_L is associated with $M_S = +1, 0$ and -1. Since spin multiplicity given by $2S + 1$ is 3, hence $S = 1$. The ^3P term contains nine energy levels with the following sets of (M_L, M_S) values :

$$M_L = \pm 1,\quad M_S = +1;\qquad M_L = \pm 1,\quad M_S = 0;\qquad M_L = \pm 1,\quad M_S = -1;$$
$$M_L = 0,\quad M_S = +1;\qquad M_L = 0,\quad M_S = 0;\qquad M_L = 0,\quad M_S = -1;$$

After subtracting (M_L, M_S) values of these nine energy levels contained in the ^3P term, the only electronic energy level that remains has $M_L = 0$, $M_S = 0$, which constitutes nothing but a ^1S term. Thus, only ^3P, ^1D and ^1S terms exist for a p^2 configuration of a free atom or ion.

The total number of energy levels in these terms are $3(2\times 1 + 1) + 1(2 \times 2 + 1) + 1(1 \times 0 + 1) = 15$ [Total number of energy levels in all the terms of a configuration $= \Sigma(2S + 1)(2L + 1)$].

Let us now work out the energy terms that arise out of $1s^2\,2s^2\,3s^2p^6d^1$ configuration of a free Sc^{2+} ion. As already stated, a filled set of orbitals does not contribute towards (L) and (S). Since there is only one electron in the set of d orbitals of Sc^{2+} ion, M_L ($= \Sigma m_l$) is the same as m_l and M_S ($= \Sigma m_s$) is the same as m_s. There are ten ways of putting a single electron in the five degenerate orbitals, as illustrated below :

$M_L = +2$	$M_S = +1/2$	$M_L = +2$	$M_S = -1/2$
$M_L = +1$	$M_S = +1/2$	$M_L = +1$	$M_S = -1/2$
$M_L = 0$	$M_S = +1/2$	$M_L = 0$	$M_S = -1/2$
$M_L = -1$	$M_S = +1/2$	$M_L = -1$	$M_S = -1/2$
$M_L = -2$	$M_S = +1/2$	$M_L = -2$	$M_S = -1/2$

There is no other d electron to cause (l) – (l), (l) – (s) or (L) – (S) coupling. Therefore, all the ten electronic arrangements are of equal energy. Since the highest M_L is + 2 and each M_L occurs twice, the term which includes all the above mentioned energy levels is ^2D.

Following the procedure as illustrated above it can be seen that for a d^2 configuration of a free metal ion, the terms ^3S, ^3P, ^3D, ^3F, ^3G and ^1S, ^1P, ^1D, ^1F, ^1G are possible out of which only ^3F, ^3P, ^1G, ^1D, ^1S actually exist.

There are 45 ways of arranging two electrons in five d orbitals. Some of these arrangements are shown in Fig. 10. Each box represents a d orbital. The m_l values of the d orbitals are written over the boxes. An upward arrow, as mentioned earlier, indicates an electron with $m_s = +1/2$ and a downward arrow with $m_s = -1/2$. The student is advised to write similar arrangements for $M_L = -4, -3, -2$ and -1.

A perusal of all the electronic arrangements reveals that $M_L = \pm 4$ occurs one time each, $M_L = \pm 3$ occurs 4 times each, $M_L = \pm 2$ occurs 5 times each, $M_L = \pm 1$ occurs 8 times each and $M_L = 0$ occurs 9 times, making a total of 45. One can easily calculate from these arrangements that $M_S = \pm 1$ occurs 10 times each and $M_S = 0$ occurs 25 times.

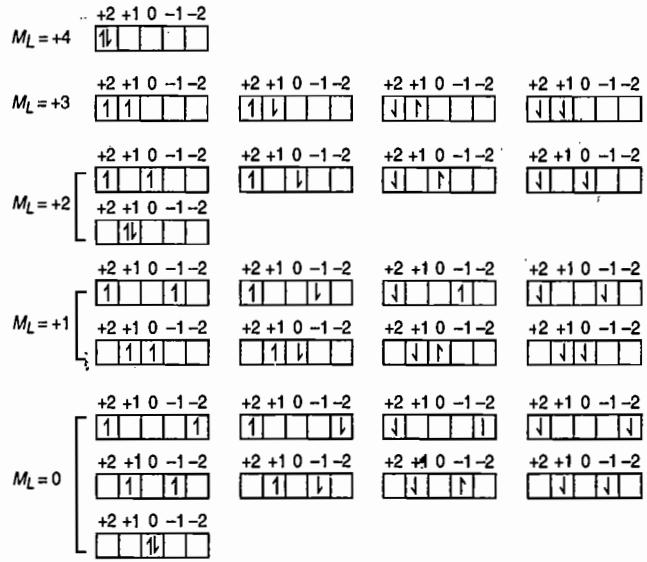


Fig. 10. Some of the forty five electronic arrangements of a d^2 configuration.

Proceeding in a similar manner as in the above example of a free carbon atom in its ground state, we find that the quantum number L relating to that (L) which includes + 4 as the highest M_L of the arrangements is obviously 4. Hence the term is G. Since there is only one $M_L = +4$ in the arrangements, the spin multiplicity is 1. The term is, therefore, ^1G. Since multiplicity is given by $2S + 1$, it is evident that $S = 0$ and M_S is also zero.

The nine (M_L, M_S) energy levels of the ^1G term are :

$M_L = +4$	$M_S = 0$	$M_L = +3$	$M_S = 0$	$M_L = +2$	$M_S = 0$
$M_L = +1$	$M_S = 0$	$M_L = 0$	$M_S = 0$	$M_L = -4$	$M_S = 0$
$M_L = -3$	$M_S = 0$	$M_L = -2$	$M_S = 0$	$M_L = -1$	$M_S = 0$

Subtracting (M_L, M_S) values of nine energy levels contained in the ^1G term from (M_L, M_S) values of forty five energy levels of this term, we are left with $M_L = \pm 3$ occurring 3 times each, $M_L = \pm 2$ occurring 4 times each, $M_L = \pm 1$ occurring 7 times each, $M_L = 0$ occurring 8 times ; $M_S = \pm 1$ occurring 10 times each and $M_S = 0$ occurring 16 times.

The next term should be the one in which $M_L = +3$ occurs thrice as the highest M_L. Following the procedure as mentioned above, it can be shown that this is a ^3F term with spin multiplicity equal to 3. Since spin multiplicity is given by $2S + 1$, hence $S = 1$ and $M_S = +1, 0$ and -1. The twenty one (M_L, M_S) energy levels of ^3F term may be written as follows :

$M_L = +3$	$M_S = +1, 0, -1$	$M_L = +2$	$M_S = +1, 0, -1$
$M_L = +1$	$M_S = +1, 0, -1$	$M_L = 0$	$M_S = +1, 0, -1$
$M_L = -3$	$M_S = +1, 0, -1$	$M_L = -2$	$M_S = +1, 0, -1$
$M_L = -1$	$M_S = +1, 0, -1$		

After subtracting (M_L, M_S) values of the ^3F term from the (M_L, M_S) values of twenty one energy levels of this term, we are left with $M_L = \pm 2$ occurring one time each, $M_L = \pm 1$ occurring 4 times each, $M_L = 0$ occurring 5 times ; $M_S = \pm 1$ occurring 3 times each and $M_S = 0$ occurring 9 times.

The next term of the configuration is D ($L=2$) which includes $+2$ as the highest M_L. Since $M_L=+2$ in the remaining energy levels occurs only once, the spin multiplicity is 1 and the term is, therefore, ^1D. Since $2S+1$ is 1, hence S is zero and M_S is also equal to zero. Since in this term, $M_L=\pm 2, \pm 1, 0$ occur only one time each and since $M_S=0$ occurs 5 times, the remaining (M_L, M_S) values of the energy levels are :

$M_L=\pm 1$ occurring 3 times each, $M_L=0$ occurring 4 times,

$M_S=\pm 1$ occurring 3 times each and $M_S=0$ occurring 4 times.

The quantum number L relating to that (L) which includes +1 as the highest M_L is 1. Hence the next term is P. Since $M_L=+1$ occurs thrice, the spin multiplicity is 3. The term is thus ^3P. The (M_L, M_S) values of energy levels contained in the ^3P term are :

$$M_L=+1,\ M_S=+1, 0, -1;\quad M_L=0,\ M_S=+1, 0, -1;\quad M_L=-1,\ M_S=+1, 0, -1$$

After subtracting the above (M_L, M_S) values from the remaining M_L, M_S values we are left with the energy level having both $M_L=0$ and $M_S=0$ occurring only once each. This energy level is evidently a ^1S term.

It follows from the above discussion that a free metal ion with d^2 configuration gives rise to ^3F, ^3P, ^1G, ^1D and ^1S terms. The total number of energy levels contained in these terms and given by $\Sigma(2S+1)(2L+1)$ are :

$$3(2\times 3+1)+3(2\times 1+1)+1(2\times 4+1)+1(2\times 2+1)+1(2\times 0+1)=45$$

This is exactly equal to the number of electronic arrangements of the configuration.

The energy terms of free metal atoms or ions with d^3, d^4 and d^5 configurations can be worked out in a similar manner. The energy terms of a d^3 configuration of a free atom or ion are ^4F, ^4P, ^2H, ^2G, ^2F, $2\times{}^2D$ and ^2P; the energy terms for a d^4 configuration are ^5D, ^3H, ^3G, $2\times{}^3F$, ^3D, $2\times{}^3P$, ^1I, $2\times{}^1G$, ^1F, $2\times{}^1D$ and $2\times{}^1S$ and the energy terms for a d^5 configuration of a free metal atom or ion are ^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, $2\times{}^2G$, ^2X, ^2F, $3\times{}^2D$, ^2P and ^2S.

We now come to the last step in the scheme, *i.e.*, to apply the effects of spin–orbit coupling to each term of a configuration. We shall discuss it in a little greater detail.

The mechanism of (L)–(S) coupling in a many-electron system is the same as that of (l) – (s) coupling for a single electron. The interactions causing (L) – (S) coupling are magnetic in nature and are much weaker than electrostatic interactions causing (l)–(l) and (s) – (s) coupling in the free atoms or ions in majority of the elements. That is why (L)–(S) coupling effect is considered as a perturbation to the main electrostatic repulsion effect in Russel-Saunders coupling scheme. (L)–(S) coupling in a many-electron system occurs to give the resultant angular momentum (J). The resultant vector (J) depends upon the angle of inclination θ between (L) and (S) which is quantised (Fig. 11). This means that only some definite number of combinations of (L) with (S) are allowed. Each such allowed combination will give its own resultant (J) depending upon θ between (L) and (S).

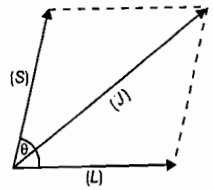


Fig. 11. Coupling of (L) with (S) for an allowed inclination θ between the two vectors.

The resultant angular momentum vector (J) has the magnitude $=\sqrt{J(J+1)}$ (in units of $h/2\pi$) where J is the angular momentum quantum number which can have values ranging from $L+S$ to $L-S$ or $S-L$ (whichever is positive). Each value of (J) is allowed $(2J+1)$ orientations in space about any particular direction (taken as Z direction) and each of these orientations has a component along Z direction called J_Z or M_J. Thus, M_J has values ranging from $-J$ to $+J$. The J states arising out of a term are written as $^{2S+1}L_J$. The energy states with the same J but different J_Z have same energies in the absence of any external magnetic field but have different energies in the presence of external magnetic field. For a metal ion with less than half-filled configurations, the J state of a term which is having lowest value of J forms the ground state of the term whereas it is the reverse for J states of a term with more than half-filled configurations. This can be explained by 'positive hole' or 'positive electron' formalism as will be discussed shortly.

The J energy states or Russel-Saunders states are of immense utility in explaining the spectra of atoms and ions of elements. That is why these are also known as spectroscopic states.

Coming back to the energy terms of s^2p^2 ground state configuration of carbon atom, *viz.*, ^3P, ^1P, ^1D, ^1S. The ^3P term has $L=1$, $S=1$. Therefore, quantum number J has the values $1+1$, $1+1-1$, $1+1-2$, *i.e.*, 2, 1, 0. Thus, the J energy states of the ^3P term are $^3P_0$, $^3P_1$ and $^3P_2$ out of which $^3P_0$ will form the ground state (since p orbitals are less than half full). A ^1D term has $L=2$ but has $S=0$. Therefore, there is no question of (L)–(S) coupling. Alternatively, we may say that J in this case is the same as L. Therefore, the energy state is $^1D_2$.

Similarly, we can find out the J energy states of a ^3F and a ^3P term arising out of d^2 configuration. The ^3F term of free metal ion with d^2 configuration forms the ground term. It has $L=3$, $S=1$ and hence the J states arising out of this ion are $^3F_2$, $^3F_3$, $^3F_4$ out of which $^3F_2$ will be of lowest energy and will form the ground state. Similarly, a ^3P term of d^2 configuration will split up into $^3P_0$, $^3P_1$, $^3P_2$ out of which $^3P_0$ will be of lowest energy. The terms of a d^8 configuration are split up in the same manner but the order of energies of the J states are reversed. Thus, out of the J states arising out of ^3F term, $^3F_4$ will be lowest in energy and will form the ground state while $^3P_2$ will be of lowest energy out of the states arising out of ^3P term of d^8 configuration. Although all the orientations of a particular (J) around Z direction are of equal energy in the absence of any external magnetic field, their interactions with an external magnetic field applied along Z direction will be different, *i.e.*, although the M_J levels of a particular J state are of equal energy in the absence of magnetic field, these split up in the presence of external magnetic field.

This happens because each M_J of a particular (J) will generate magnetic field of different magnitude around Z direction. Therefore, the interaction of external magnetic field and the magnetic field generated due to M_J in the Z direction will vary with the value of M_J. This is the origin of first order Zeeman effect. Fig. 12 gives the splittings of free ion terms of a d^2 and a d^8 configuration due to (L) – (S) or spin–orbit coupling.

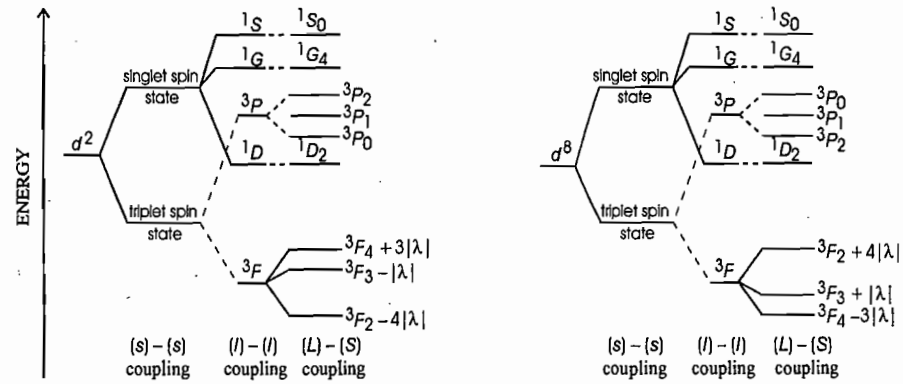


Fig. 12. Splitting of free ion terms of d^2 and d^8 configurations due to (L) – (S) coupling (Refer to the next section for the significance of λ term.

Relative Energies of Terms : Ground Terms. The calculation of energies of the terms of a configuration involves a complicated procedure the discussion of which is beyond the scope of this book. But we can find out the ground term of any configuration of free metal ions by applying Hund's rule. Take, for instance, d^1 to d^{10} configurations one by one. Draw five boxes for the five d orbitals ($l=2$ for d orbitals) with their (m_l) values in decreasing order written above the boxes. Go on filling the electrons in the boxes taking care that the electrons fill the d orbitals in such a way that these have maximum parallel spins and maximum M_L (*i.e.*, maximum Σm_l). Find out the total M_L and total M_S (*i.e.*, maximum Σm_s). Now take L such that M_L obtained from the arrangement forms the highest value for (L). (This way, L will have the same value as of M_L obtained from the arrangement). Take S such that M_S obtained from this arrangement forms

the highest value for (S). (This way, S will have the same value as M_S obtained from the arrangement). Calculate the spin multiplicity from the formula $2S+1$ and write down the ground term from L and $2S+1$. The ground terms which can be derived for d^1 to d^{10} configurations of free metal ions by this method are given in Table 1

TABLE 1

Derivation of Ground Terms for d^1 to d^{10} Configurations of Free Metal Ions

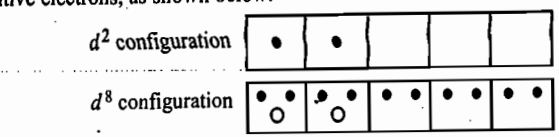
Configuration	Electronic Arrangement					M_L (Σm_l)	M_S (Σm_s)	L	S	Ground term	Ground state
	(+2)	(+1)	(0)	(−1)	(−2)						
d^1	↑					+2	+1/2	2	1/2	^2D	$^2D_{3/2}$
d^2	↑	↑				+3	+1	3	1	^3F	$^3F_2$
d^3	↑	↑	↑			+3	+3/2	3	3/2	^4F	$^4F_{3/2}$
d^4	↑	↑	↑	↑		+2	+2	2	2	^5D	$^5D_0$
d^5	↑	↑	↑	↑	↑	0	+5/2	0	5/2	^6S	$^6S_{5/2}$
d^6	↑↓	↑	↑	↑	↑	+2	+2	2	2	^5D	$^5D_4$
d^7	↑↓	↑↓	↑	↑	↑	+3	+3/2	3	3/2	^4F	$^4F_{9/2}$
d^8	↑↓	↑↓	↑↓	↑	↑	+3	+1	3	1	^3F	$^3F_4$
d^9	↑↓	↑↓	↑↓	↑↓	↑	+2	+1/2	2	1/2	^2D	$^2D_{5/2}$
d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	0	^1S	$^1S_0$

It can be seen from the above table that d^n has the same ground term as d^{10-n} ($n < 5$). In fact, not only the ground terms but all other terms of d^n and d^{10-n} configurations of free metal ions are the same. This is because of 'positive hole' or 'positive electron' formalism discussed below.

As already explained, the terms of a configuration arise because of electrostatic repulsions between the negatively charged electrons of a configuration. Now, imagine another configuration with the same number of hypothetical 'positively charged electrons' instead of negatively charged electrons. The magnitude of electrostatic repulsions between the hypothetical positively charged electrons of this configuration will be the same as the magnitude of electrostatic repulsions between the same number of negatively charged electrons of the previous configuration (The hypothetical positively charged electron is identical to negatively charged electron except for the positive charge on it). This will give rise to the same energy terms in both the configurations.

Let us take a configuration with two negatively charged electrons in d orbitals. The energy terms which arise out of this configuration due to interelectronic repulsion between the two electrons are ^3F, ^3P, ^1G, ^1D and ^1S. Now take a d^{10-2}, *i.e.*, d^8 configuration containing eight negatively charged electrons in its d orbitals. We can assume that this configuration is equivalent to the configuration in which d orbitals, besides being completely full of electrons, also contain two positively charged electrons, that is, we hypothetically add to d^8 configuration two negatively charged electrons so that the d orbitals are completely occupied and then add two positively charged electrons to compensate for the previously added two negatively charged electrons. The two positively charged electrons will experience similar electrostatic interactions as the two negatively charged electrons do. They will also obey Pauli's exclusion principle and Hund's rule.

In nutshell, the d^8 configuration can be hypothetically assumed to be a d^{10} configuration containing two positive electrons, as shown below.



(Solid dots show negatively charged and hollow dots show positively charged electrons)

The d^{10} configuration with completely full orbitals will not contribute anything to (L) and (S) but the two positively charged electrons will repel each other exactly in the same manner as the negatively charged electrons do in a d^2 configuration giving rise to the same energy terms for both d^2 and d^8 configurations.

We can similarly argue for the other pairs of d^n and d^{10-n} configurations to arrive at the same result. Thus, d^1, d^9; d^3, d^7 and d^4, d^6 configurations of free atoms or ions give rise to the same terms.

The resultant magnetic field due to coupling of the spin and orbital motions of a positively charged electron and a negatively charged electron which are moving in the same direction in the orbit and are spinning along the same axis in the same direction, will be in the opposite directions. That is why in one case (*i.e.*, in d^n configuration, n being <5), the J state with least spin orbit coupling quantum number J will be of lowest energy whereas in the other case (d^{10-n} configuration), it is the J state with the highest value of J which will be of lowest energy.

Two paramenters are in use to describe the strength of coupling between spin angular momentum and orbital angular momentum. The single electron spin–orbit coupling parameter ξ (zeta) measures the strength of coupling between spin and orbital angular momenta of a single electron of the configuration. It is a property of the configuration. The second parameter, which is the property of the term itself, is the spin–orbit coupling parameter λ. It is a measure of the strength of interaction between (L) and (S) of a term.

The two parameters are related to each other. The energies of the J states of the term are generally calculated in terms of λ. The parameter λ for a configuration, which consists of less than half full subshell, is a positive quantity and is written as $+|\lambda|$. It is a negative quantity and is written as $-|\lambda|$ for a configuration which consists of more than half full subshell. $|\lambda|$ is the absolute magnitude of the parameter without considering its positive or negative nature.

The energy separation between two adjacent J states of a term, arising out of a configuration having less than half-full d subshell, is given by

$$E_{J+1} - E_J = +|\lambda|(J+1) \quad ...(1)$$

Since the right hand side of this equation is positive, $E_{J+1} > E_J$. Therefore, in such a case, the state with lowest value of J will be of lowest energy out of all the states of the term. This type of splitting of a term into J states is known as **'normal multiplet.'**

But the energy separation between two adjacent J states of a term, which arise from a configuration consisting of more than half-full d subshell, is given by

$$E_{J+1} - E_J = -|\lambda|(J+1) \quad ...(2)$$

Since the right hand side of the above equation is a negative quantity, $E_{J+1} < E_J$. Thus, in such a case the state with the lowest energy will be the one having highest J and the state with the highest energy will be the one having lowest J. This type of splitting of the term into J states is known as **'inverted multiplet.'**

According to the centre of gravity rule, the centre of gravity of states of a term remains the same as that of the unsplit term. That is, if the energy of an unsplit term is taken as zero, then the sum of the energies of all the J states of the term is zero, that is,

$$\sum_{J=L-S}^{J=L+S} (2J+1)E_J = 0 \quad ...(3)$$

where E_J is the energy of the Jth state.

Let us consider the splitting of a ^3F term of a d^2 configuration. It splits up into $^3F_2$, $^3F_3$ and $^3F_4$ states, as shown earlier in Fig. 12. From Eq. 3, we have

$$(2\times2+1)E_2 + (2\times3+1)E_3 + (2\times4+1)E_4 = 0 \quad ...(4)$$

where E_2, E_3 and E_4 are the energies of $^3F_2$, $^3F_3$ and $^3F_4$ terms, respectively. From Eq. 2,

$$E_3 - E_2 = +3|\lambda| \text{ so that } E_3 = E_2 + 3|\lambda|$$

Similarly,

$$E_4 - E_3 = +4|\lambda| \text{ so that } E_4 = E_3 + 4|\lambda| = E_2 + 7|\lambda|$$

Substituting the values of E_3 and E_4 in Eq. 4, we have

$$5E_2 + 7(E_2 + 3\lambda) + 9(E_2 + 7\lambda) = 0 \quad ...(5)$$

or $$21E_2 = -84|\lambda| \text{ so that } E_2 = -4|\lambda|$$

Accordingly, $$E_3 = -|\lambda| \text{ and } E_4 = +3|\lambda|$$

It is evident from the above data that $^3F_2$ has the lowest energy $= -4|\lambda|$, as shown above in Fig. 12.

Let us now consider ^3F term of a d^8 configuration which consists of more than half full d subshell. This term also splits into F_2, F_3 and F_4 states, as shown in Fig.12. From Eq. 2,

$$E_4 - E_3 = -4|\lambda| \text{ so that } E_3 = E_4 + 4|\lambda|$$

Also $$E_3 - E_2 = -3|\lambda| \text{ so that } E_2 = E_3 + 3|\lambda| = E_4 + 7|\lambda|$$

From Eq. 3,

$$(2\times2+1)E_2 + (2\times3+1)E_3 + (2\times4+1)E_4 = 0 \quad ...(6)$$

Substituting the values of E_2 and E_3 in Eq. 6, we get

$$5(E_4 + 7|\lambda|) + 7(E_4 + 4|\lambda|) + 9E_4 = 0$$

or $$21E_4 = -63|\lambda| \text{ so that } E_4 = -3|\lambda|$$

Accordingly, $$E_3 = +|\lambda| \text{ and } E_2 = +4|\lambda|.$$

It is evident from the above data that the state $^3F_4$ lies lowest in energy $= -3|\lambda|$, as shown in Fig. 12.

The student is advised to work out the energies of the J states of ^3P terms of d^2 and d^8 configurations in a similar manner.

2. (j) – (j) Coupling Scheme

If, in a many-electron system, spin–orbit coupling effect is stronger than interelectronic repulsion effect, then, instead of the configuration being split up into terms due to $(s)-(s)$ or $(l)-(l)$ coupling, the coupling of the spin and orbital angular momentum of every individual electron occurs first to give the resultant angular momentum (j_i) which has a magnitude of $\sqrt{j_i(j_i+1)}\, h/2\pi$ where j_i is the resultant single electron angular momentum quantum number for the ith electron which can have values ranging from l_i+s_i, l_i+s_i-1..... to l_i-s_i or s_i-l_i (whichever is positive). The vector (j_i) can have $2j_i+1$ orientations in space about a particular direction (say, Z direction). Each of these orientations gives its own component along the Z direction which is called $j_i(z)$ or m_{j_i} whose value ranges from $-j_i$ to $+j_i$. These single electron resultant angular momentum vectors of different electrons then couple to give resultant angular momentum (J) which has a magnitude of $\sqrt{J(J+1)}\, h/2\pi$ where J is the resultant angular momentum quantum number and has values (for a two-electron system) ranging from j_1+j_2 to j_1-j_2 or j_2-j_1 (whichever is positive). Each value of resultant vector (J) has $(2J+1)$ orientations in space along Z direction and each orientation will have its own component along this direction called J_z or M_J which has values ranging from $-J$ to $+J$.

Russel–Saunders or $(L)-(S)$ coupling scheme is of greater utility compared to $(j)-(j)$ coupling scheme because no ion of interest to inorganic chemists has magnitude of spin–orbit coupling higher than interelectronic repulsions.

The heavy metal ions have both the interactions (*i.e.*, spin–orbit coupling and electrostatic interactions) of comparable magnitude. Therefore, these do not conform to either scheme and may require something in between.

EFFECT OF WEAK OCTAHEDRAL CRYSTAL FIELD POTENTIAL, V_{oct} AND TETRAHEDRAL CRYSTAL FIELD POTENTIAL, V_{tet} ON THE TERMS

We have stated above that all the energy levels in a term arising out of a d^n configuration of a free metal ion are degenerate. But it is not so when the metal ion is surrounded octahedrally by six ligands or tetrahedrally by four ligands. The negative charges on the anionic ligands or the electric dipoles of *neutral but polar ligands will generate an electrostatic crystal field potential which will act on the d* electrons of the metal ion causing a split in the terms. If the electrostatic interaction between d electrons of the metal ion and octahedral crystal field potential (V_{oct}) or tetrahedral crystal field potential (V_{tet}) generated by negative charges of the anionic ligands or electric dipoles of the neutral polar ligands is weaker than the electrostatic repulsive interactions amongst the d electrons themselves, then that octahedral or tetrahedral potential is known as **weak** V_{oct} or V_{tet}. The tetrahedral potential (V_{tet}) is always weak whatever be the nature of ligands surrounding the metal ion. This is so because V_{tet} is only 4/9th of V_{oct} in magnitude for the same metal ion and for the same set of ligands.

Thus, the order of various types of interactions acting on the d electrons of a metal ion configuration when it is octahedrally surrounded by six ligands (*assuming V_{oct} to be weak*) or when it is tetrahedrally surrounded by four ligands is : electrostatic repulsive interactions amongst d electrons of the metal ion causing $(l)-(l)$ and $(s)-(s)$ coupling and giving rise to terms $> V_{oct}$ or $V_{tet} >$ spin–orbit coupling interactions.

The spin–orbit coupling interactions which are very weak compared to repulsive interactions amongst d electrons as also the interactions between d electrons and weak V_{oct} have not been considered in the present discussion.

For studying the other two types of interactions, *viz.*, repulsive interactions amongst d electrons and interactions between d electrons and weak V_{oct} or V_{tet}, we shall first of all consider the stronger electrostatic repulsions amongst d electrons to obtain energy terms for a d^n configuration of a free transition metal ion and then consider the interactions between d electrons and weak V_{oct} or weak V_{tet} as a small perturbation on the energies of the levels contained in the term.

However, before we discuss the effect of weak V_{oct} or V_{tet} on S, P, D and F terms, it is worthwhile to define orbital degeneracy and spin multiplicity once again.

If we ignore the spin of electrons, the number of degenerate orbital energy levels or the number of degenerate arrangements of electrons in orbitals is known as **orbital degeneracy**. A P term contains three degenerate orbital arrangements and an F term contains seven such arrangements. Therefore, the orbital degeneracy of a P term is three and of an F term is seven. Orbital degeneracy of a term is equal to the number of M_L values of (L) of the term (that is, equal to $2L+1$).

The number of spin energy levels for each orbital energy level or the number of electron spin arrangements allowed for each orbital arrangement of a term is known as the **spin multiplicity** of the term. The spin multiplicity is given by the number of M_S values of (S) in a term.

The total number of degenerate energy levels or number of electronic arrangements in a term, taking care of electron spins also, is given by $(2S+1)(2L+1)$ and is known as the **total degeneracy** of a term.

Effect of Weak V_{oct} or V_{tet} on S term. An S term is orbitally non-degenerate. Therefore, it cannot be split by V_{oct} or V_{tet} whatever is the strength of electrostatic interaction between d electrons and the electrostatic crystal field potential V_{oct} or V_{tet}.

Effect of Weak V_{oct} or V_{tet} on P term. The three degenerate orbital energy levels contained in a P term of the configuration of a metal ion are not split when the metal ion is subjected to weak V_{oct} or V_{tet}. This is so because the three degenerate orbital arrangements of electrons of the P term still remain equally probable and, therefore, the d electron charge distribution in these arrangements remains uniform in all the directions. The symmetry of P term, unsplit by V_{oct} or V_{tet}, can be shown to be T_{1g} and T_1, respectively.

Effect of Weak V_{oct} and V_{tet} on D term. A D term is orbitally five-fold degenerate. For the D term of d^1 or d^6 configuration, the five energy levels corresponding to the five orbital arrangements of

electrons contained in a D term get split up into two groups when the metal ion with either of the above configurations is subjected to V_{oct}. The d electrons in the two of the five orbital arrangements will experience higher repulsion from octahedral crystal field potential compared to the repulsion experienced by d electrons in the other three arrangements. Thus, a D term derived from a d^1 or d^6 configuration of a metal ion splits up into T_{2g} and E_g energy levels when the metal ion is subjected to weak octahedral potential (Fig. 13). It can be shown quantitatively that the energies of T_{2g} and E_g levels are -4 Dq and $+6$ Dq, respectively, with respect to the energy of unsplit D term taken as zero.

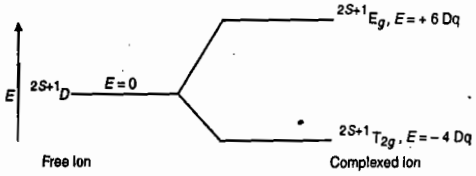


Fig. 13. Splitting of D term of d^1 or d^6 configuration when the metal ion is subjected to a weak V_{oct}.

The symbols A, B, E, T are symmetry symbols of orbital energy levels or arrangements. Non-degenerate orbital energy levels are given the symbols A and B, doubly degenerate E and triply degenerate energy levels T. The choice between A and B in the case of non-degenerate energy levels or arrangements and between 1 and 2 depends on some symmetry properties of orbital arrangements under a given geometric environment.

The splitting pattern is reversed when the metal ion is subjected to a tetrahedral crystal field potential because $V_{tet} = -4/9\, V_{oct}$. The sign of V_{tet} is opposite to that of V_{oct}. This means that the interaction between d electrons and the electrostatic crystal field potential will now cause a reversal of the splitting pattern (Fig. 14). It can be shown quantitatively that the energies of E and T_2 levels are -6 Dq and $+4$ Dq, respectively, with respect to the energy of unsplit D term taken as zero.

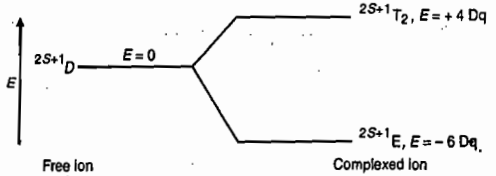


Fig. 14. Splitting of a D term of d^1 or d^6 configuration when the metal ion is subjected to V_{tet}.

One should also remember that, in general, the splitting of a term of d^n configuration ($n < 5$) is similar to the splitting of a term of d^{n+5} configuration of metal ions when both the metal ions are subjected to a similar weak crystal field potential. That is why the splittings of D term of d^1 and d^6 configurations of a metal ion under similar crystal field potential are also similar.

Another thing to note here is that the spin multiplicity of the parent term and of its splittings remain the same when the metal ion is subjected to weak V_{oct} or V_{tet}. This is because the crystal field potential is not of sufficient strength to overcome interelectronic repulsion caused by putting two electrons in the same orbital and hence to cause spin pairing.

The splitting of D term of a d^9 configuration of a metal ion subjected to weak V_{oct} or V_{tet} is the reverse of the splitting of D term of a d^1 configuration of a metal ion under similar environments. This is because of the positive hole or positive electron formalism as illustrated below :

A d^9 configuration is equivalent to a d^{10} configuration containing one hypothetical positive electron which behaves identically to an electron except for the positive charge. The electrostatic interaction experienced by this positive electron with crystal field potential will be of opposite sign to that experienced by an electron. This will cause the reversal of splitting pattern of D term in d^1 and d^9 configurations since d^9 is equivalent to d^{10+1e^+}. Since the electrons in d^{10} configuration will be uniformly repelled by V_{oct} or V_{tet} and will not cause any splitting, the splitting of D term of a d^9 configuration will be caused only due to the interaction of the positive electron and V_{oct} or V_{tet}. That is, the splitting pattern of D term of a d^9 configuration will be the reverse of the splitting of this term of a d^1 configuration under the influence of similar crystal field potential.

It is a general phenomenon that the splitting of a term in d^n configuration of a metal ion in a particular ligand environment is the reverse of the splitting of the same term in d^{10-n} configuration of the metal ion under similar environment ($n < 5$).

The splitting of D term of d^9 or d^4 configuration of a metal ion under weak V_{oct} is, therefore, as shown in Fig. 15. The energies of E_g and T_{2g} levels are -6 Dq and $+4$ Dq, respectively, with respect to the energy of unsplit D term taken as zero.

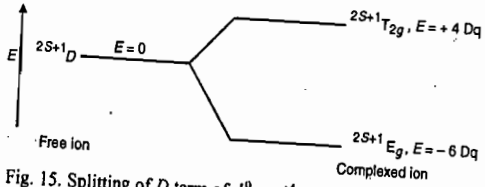


Fig. 15. Splitting of D term of d^9 or d^4 configuration of a metal ion under the influence of weak V_{oct}.

Similarly, the splitting of D term of d^9 or d^4 configuration of a metal ion under V_{tet} is the reverse of the splitting of D term of d^1 or d^6 configuration of the metal ion under similar ligand environment (Fig. 16). The energies of T_2 and E levels are -4 Dq and $+6$ Dq, respectively, with respect to the energy of unsplit D term taken as zero.

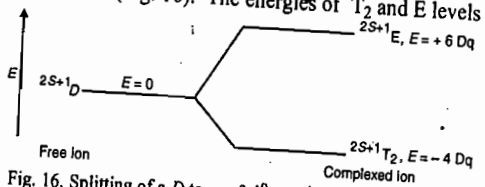


Fig. 16. Splitting of a D term of d^9 or d^4 configuration of a metal ion under V_{tet}.

One should not confuse between S, P, D, etc., terms and s, p, d, etc., orbitals. Small alphabets are used for orbitals and capital letters are used for the terms.

One should keep in mind that there is similarity between the splitting of a term and splitting of an orbital when the metal ion is placed in similar ligand environment. Thus, neither the terms S and P nor the orbitals s and p are split up when the d electrons of a metal ion are subjected to V_{tet} or V_{oct}. The D term is split into T_{2g} and E_g orbital energy levels while the d orbitals of the metal ion are split up into t_{2g} and e_g set when the metal ion is subjected to weak V_{oct}. We shall see that a similar situation occurs for F term and a set of f orbitals.

Splitting of F term under the influence of weak V_{oct} and V_{tet}. Just as the seven f orbitals of a metal ion split up into three sub-groups of 3, 3 and 1 orbitals when the metal ion is subjected to V_{oct} or V_{tet}, similarly an F term gets split up into three sub-groups of energy levels containing 3, 3 and 1 orbital energy levels in the group. Splitting of an F term arising out of d^2 or d^7 (*i.e.*, d^{2+5}) configuration of metal ions under the influence of weak V_{oct} is shown in Fig. 17. It can be shown quantitatively that the energies of T_{1g}, T_{2g} and A_{2g} energy levels are -6 Dq, $+2$ Dq, and $+12$ Dq, respectively, with respect to the energy of unsplit F term taken as zero.

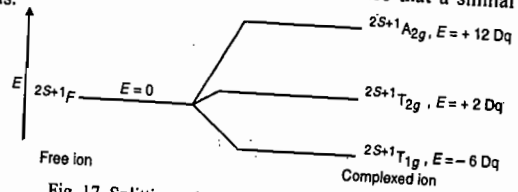


Fig. 17. Splitting of F term of a metal ion with d^2 or d^7 configuration under the influence of weak V_{oct}.

The splitting of the F term of d^2 or d^7 configuration of a metal ion under the influence of V_{tet} will, therefore, be reversed, as shown in Fig. 18. The energies of A_2, T and T_1 energy levels are -12 Dq, -2 Dq and $+6$ Dq, respectively, with respect to the energy of unsplit F term taken as zero.

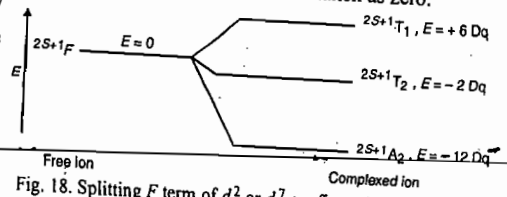


Fig. 18. Splitting F term of d^2 or d^7 configuration of a metal ion under the influence of V_{tet}.

Similarly, the splitting of F term of d^8 or d^3 configuration of a metal ion under weak V_{oct} will be the reverse of the splitting of F term for d^2 or d^7 (*i.e.*, d^{2+5}) configuration of the metal ion under similar ligand environment (Fig. 19). The energies of A_{2g}, T_{2g} and T_{1g} energy levels are -12 Dq, $+2$ Dq and $+6$ Dq, respectively, with respect to the energy of the unsplit F term taken as zero.

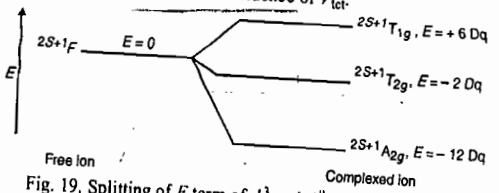


Fig. 19. Splitting of F term of d^3 and d^8 configuration of a metal ion under the influence of weak V_{oct}.

The splitting of the F term of d^3 or d^8 (*i.e.*, d^{3+5}) configuration of a metal ion under the influence of V_{tet} will be the reverse of the splitting shown above (see Fig. 20). The energies of T_1, T_2 and E_2 energy levels are -6 Dq, $+2$ Dq and $+12$ Dq, respectively, with respect to the energy of the unsplit F term taken as zero.

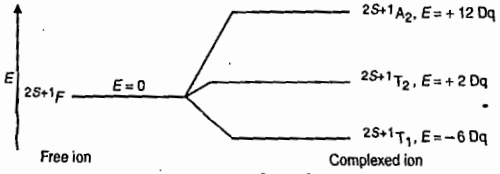


Fig. 20. Splitting of F term of d^3 or d^8 configuration of a metal ion under the influence of the V_{tet}.

As already stated, weak V_{oct} is not sufficiently strong to cause pairing of electron spins and will lead to only *high spin* configurations. Likewise, V_{tet}, also being less than half in magnitude of V_{oct}, is not sufficiently strong to cause pairing of electron spins and, therefore, gives rise to only high spin configurations. We should, therefore, calculate the spin multiplicities keeping the above mentioned facts in view.

From the above discussion on the splitting of terms under the influence of weak V_{oct} and V_{tet}, it is clear that

(*i*) The splitting of a term arising out of d^n or d^{n+5} ($n < 5$) configuration of a metal ion with similar ligand environment is of the same order and pattern.

(*ii*) The splitting of a term arising out of d^n configuration is the reverse of the splitting of the same term of d^{10-n} configuration of metal ion provided the two metal ions have similar ligand environment.

(*iii*) The splitting of a term arising out of d^n configuration under weak V_{oct} is the reverse of the splitting of the term of same configuration under V_{tet} and vice-versa.

(*iv*) The splitting of a term arising out of d^n configuration of a metal ion under the influence of weak V_{oct} is the same as its splitting arising out of d^{10-n} configuration under the influence of V_{tet} and vice-versa.*

It is to be noted that Dq is not a constant quantity. Its value not only varies with the nature of the metal ion and the ligand but it also depends upon the geometry of the complex.

BASIC CONCEPTS OF ELECTRON ABSORPTION SPECTROSCOPY

The transition metal compounds appear coloured because they absorb light of a particular wave length (or frequency) in the visible region. The colour shown by a compound is complementary to the colour of the light radiation absorbed. Table 2 shows the colour regions in which absorption of light radiation occurs alongwith the complementary colours observed for the transition metal compounds.

TABLE 2

Absorption of Electromegnetic Radiations by Transition Metal Compounds

Visible region in which absorption occurs	Frequency range of the visible region of absorption (cm^{-1})	Wave length range of the visible region of absorption (nm)	Complementary colour observed
Violet	26,300 – 23,800	380 – 420	Yellow/Green
Indigo	23,800 – 22,700	420 – 440	Yellow
Blue	22,700 – 20,800	440 – 480	Orange
Blue/Green	20,800 – 20,000	480 – 500	Red
Green	20,000 – 18,200	500 – 550	Purple
Yellow/Green	18,200 – 17,300	550 – 580	Violet
Yellow	17,300 – 16,400	580 – 610	Indigo
Orange	16,400 – 15,400	610 – 650	Blue
Red	15,400 – 12,800	650 – 780	Blue/Green

* Before applying the above rules, we should remember that a tetrahedron has no centre of symmetry. Therefore, none of the splittings of a term under the influence of V_{tet} is written with the symbol 'g'.

The extent or intensity of absorption of light of a particular wave length (frequency) by a species in solution phase is expressed in terms of molar extinction coefficient (or molar absorption coefficient), ε, given by

$$\varepsilon = \frac{1}{cl} \log \frac{I_0}{I}$$

in which c is the molar concentration of the solution, I_0 is the intensity of incident radiation and I is the intensity of light transmitted after passing through a column of length l of the solution of the species. The molar extinction coefficient ε is constant for a particular species and a particular wave length.

More accurately, the extent or intensity of absorption is measured in terms of oscillator strength, f, determined from the area under the absorption band in accordance with the equation,

$$\text{Oscillator strength,} \quad f = 4{\cdot}32 \times 10^{-9} \int_{\nu_1}^{\nu_2} \varepsilon d\nu$$

where ν, as usual, stands for frequency of absorption. The absorption band is obtained by plotting ε against ν (or $\bar{\nu}$) of the light radiation incident on the species (Fig. 21).

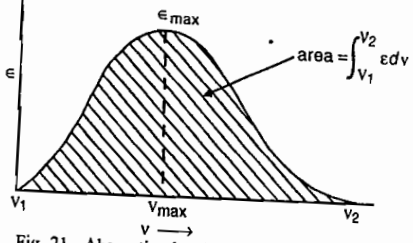


Fig. 21. Absorption band obtained by plotting ε against ν.

The radiant energy $h\nu$ absorbed by a molecule of the species promotes electrons from an orbital of lower energy to an orbital of higher energy of the molecule. This causes a change in the electron population and hence in the arrangement of electrons in the orbitals of the molecule. This means that the electronic arrangement in the orbitals of the molecule before the absorption of light energy is different from the electronic arrangement in its orbitals after the absorption of light. The electronic arrangements before and after the absorption of light are associated with different energies. The energy of an electronic arrangement is called energy level. We may thus say that the molecule occupies a different electronic energy level after absorption of light from the energy level it occupied before absorption. (Fig. 22).

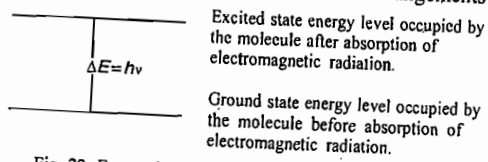


Fig. 22. Energy levels involved in electronic transition.

The promotion of electrons from an orbital of lower energy to an orbital of higher energy due to absorption of electromagnetic radiation which results in a change in the arrangement of electrons in the orbitals of the molecule is termed **electronic transition.** Each electronic transition causes an absorption band in the electronic spectrum of the molecular species. The number of absorption bands observed in the electronic spectrum of the species would, thus, correspond to the number of electronic transitions which occur due to absorption of radiation.

Experimentally, an absorption band is obtained as follows : The monochromatic light of a particular frequency is made to pass through the solution of the sample and the intensity of the light radiation before and after passing through the sample (*i.e.*, I_0 and I) are measured with the help of a spectrophotometer. We then go on varying the frequency of the incident light and measuring both I_0 and I. Measurements are spread over a range of frequencies. Only that frequency which exactly matches the frequency of the energy gap ΔE (= $h\nu$) between the two energy levels of the molecules of the sample would be absorbed and would appear with diminished intensity after passing through the solution of the sample. The frequencies both higher and lower than the frequency of the energy gap ΔE (= $h\nu$) will not be absorbed and would appear with the same intensity after passing through the solution. A graph is then plotted between ε and ν the frequency of light radiation incident upon the sample. This gives the absorption band (Fig. 21).

Selection Rules. It is not necessary that the light radiation of frequency ν, corresponding to the frequency ν of the energy gap ΔE (= $h\nu$) between the ground state electronic energy level and the excited

state electronic energy level will always be absorbed by the sample. The absorption of light radiation by a sample follows certain set rules known as **selection rules**. These are :

1. Spin Selection Rule. According to this rule, the electronic transitions from a lower to a higher electronic energy level of a molecule of the sample will take place *provided the two energy levels involved in the transition are of the same spin multiplicity*. For example, a $^3T_{1g} \rightarrow {}^3T_{2g}$ transition between the electronic energy levels of crystal field origin is allowed by the spin selection rule whereas $^3T_{1g} \rightarrow {}^1T_{2g}$ transition is not allowed (T stands for orbitally triply degenerate energy level). The electronic energy levels of crystal field origin are the energy levels derived from the electronic arrangements in *d* orbitals of transition metal ions in their coordination compounds. In $^3T_{1g} \rightarrow {}^3T_{2g}$ transition, the two energy levels involved have the same spin multiplicity, *viz.*, 3, whereas in $^3T_{1g} \rightarrow {}^1T_{2g}$ transition, the spin multiplicities of the two energy levels are 3 and 1. The above example has been illustrated further in Fig. 23.

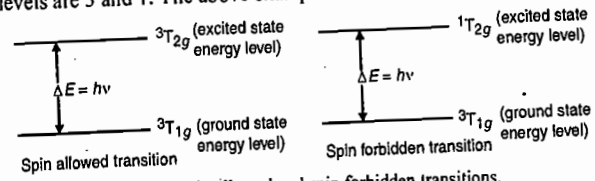


Fig. 23. Spin allowed and spin forbidden transitions.

The spin-orbit coupling [(*s*)−(*l*) coupling] may render spin forbidden transitions 'slightly allowed' but the intensities of absorption of the resulting bands are much lower than those of the spin allowed transitions.

2. Orbital Selection Rule or Leporte Selection Rule. According to the electric dipole mechanism, the electronic transition between two electronic energy levels represented by $\psi_{1\,elec}$ and $\psi_{2\,elec}$ will occur only *if there is change in the dipole moment during the transition*. Mathematically, the transition moment integral *Q*, given by Eq. 8, must be non-zero for the electronic transition to occur between the electronic energy levels $\psi_{1\,elec}$ and $\psi_{2\,elec}$.

$$Q = \int_{-\infty}^{+\infty} \psi_{1\,elec} |\vec{M}| \psi_{2\,elec}\, d\tau = \int_{-\infty}^{+\infty} \psi_{1\,elec} |\Sigma e\vec{r}| \psi_{2\,elec}\, d\tau \qquad ...(7)$$

The electric dipole moment operator $\vec{M}$ used in the above equation is defined as the distance between the centres of gravity of the positive and negative charges in a molecule times the magnitudes of the charges. The centre of gravity of positive charge in a molecule is fixed by the nuclei but the centre of gravity of negative charge is an average of the probability function of the moving electrons. The vector for the average distance from the nuclei in the molecule to a particular electron is represented by $\vec{r}$. The electric dipole vector $\vec{M}$ is then given by $\Sigma e\vec{r}$ with the summation carried over all the electrons in the molecule.

The transition dipole moment integral *Q* roughly represents the displacement of electronic charge in going from the ground electronic state ψ_{1elec} to the excited electronic state $\psi_{2\,elec}$ of the molecule. This means that *Q roughly represents the change in dipole moment during the transition.*

The transition dipole moment integral can be non-zero only if its integrand $\psi_{1\,elec} | \Sigma e\vec{r} | \psi_{2\,elec}$ is *totally symmetric*. This means that the integrand should have the same sign in $-\infty$ to 0 region and 0 to $+\infty$ region. If the signs of the integrand in the two regions are opposite (*i.e.*, if the integrand is unsymmetric), its summation (or integration) from $-\infty$ to 0 and from 0 to $+\infty$ would be zero. We can easily find out from the group theory without actual mathematical calculations whether the integrand would be symmetric or not or whether *Q* would be non-zero or zero. The group theory has been discussed in details in Chapter 3.

For a molecule having a centre of symmetry and containing the metal ion at this centre, as, for example, a complex with an octahedral, square planar or tetragonal symmetry in which the dipole moment operator $\Sigma e\vec{r}$ is *u* (or unsymmetric), one of the conditions for the integrand $\psi_{1\,elec} | \Sigma e\vec{r} | \psi_{2\,elec}$ to be totally symmetric or *g* and hence for *Q* to be non-zero is that one of ψ_{1elec} and ψ_{2elec} should be *g* (or symmetric) and the other *u* (or unsymmetric). The integrand would be unsymmetric (or *u*) and hence *Q*

would be zero if both $\psi_{1\,elec}$ and $\psi_{2\,elec}$ are *g* or both are *u***. Thus, in a molecule with a centre of symmetry, the electronic transitions $\psi_{1\,elec}(g) \longrightarrow \psi_{2\,elec}(g)$ and $\psi_{1\,elec}(u) \longrightarrow \psi_{2\,elec}(u)$ are not allowed. On the other hand, the transitions $\psi_{1\,elec}(g) \longrightarrow \psi_{2\,elec}(u)$ and $\psi_{1\,elec}(u) \longrightarrow \psi_{2\,elec}(g)$ may be allowed. The above statement constitutes the Leporte selection rule.

Molecules with a centre of symmetry are so chosen in the present discussion that the metal ion in each case always occupies the centre of symmetry. In such molecules, all the wave functions associated with the metal ion orbitals or with the electronic arrangements in the metal ion orbitals are either *g* or *u*. Thus, the wave functions for *d* and *s* orbitals are *g* whereas those for *p* orbitals are *u* in such molecules. Hence, all $d \rightarrow d$ transitions which are in fact $g \rightarrow g$ transitions, are not allowed whereas $d \rightarrow p$ $(g \rightarrow u)$, $s \rightarrow p$ $(g \rightarrow u)$, $p \rightarrow d$ $(u \rightarrow g)$ or $p \rightarrow s$ $(u \rightarrow g)$ transitions may be allowed in complexes having a centre of symmetry (*i.e.*, octahedral, tetragonal and square planar complexes). All crystal field electronic energy levels in complexes with a centre of symmetry are derived from the electronic arrangements in the *d* orbitals of *g* character. Therefore, the electronic transitions between two such crystal field electronic energy levels of such molecules are $g \rightarrow g$ transitions and are thus Leporte forbidden. For example, the three transitions between the crystal field electronic energy levels of $[Ni(H_2O)_6]^{2+}$ are $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and all of them are Leporte forbidden (A stands for orbitally non-degenerate energy level whereas $T_{1g}(F)$ and $T_{1g}(P)$, respectively, stand for orbitally triply degenerate energy levels arising out of *F* and *P* terms of the free metal ion when it is surrounded by six H_2O ligands).

It may be pointed out that apart from the $g \rightarrow u$ or $u \rightarrow g$ condition, there is another important condition of symmetry to be observed by the integrand $\psi_{1\,elec} | \Sigma e\vec{r} | \psi_{2\,elec}$ in order that *Q* is non-zero. Its discussion is based on the group theory and is given here only as a foot note* for the interested readers.

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* The following theoretical procedure is adopted to see whether the integrand $\psi_{1\,elec} | \Sigma e\vec{r} | \psi_{2\,elec}$ is totally symmetric or not, *i.e.*, whether *Q* is zero or non-zero :

Let the electronic energy levels $\psi_{1\,elec}$, $\psi_{2\,elec}$ and $\Sigma e\vec{r}$ transform as Γ_1, Γ_2 and Γ_r irreducible representations of the symmetry group to which the molecule belongs. The integrand will be totally symmetric and hence *Q* will be non-zero if the direct product $\Gamma_1 \times \Gamma_r \times \Gamma_2$ contains totally symmetric representation A_{1g} *if the molecule has a centre of symmetry* as in octahedral and tetragonal complexes or contains the representation A_1 *if the molecule has no centre of symmetry* as in tetrahedral complexes.

Suppose we wish to find out whether the electronic transition between crystal field energy levels $^3T_{1g} \rightarrow {}^3T_{2g}$ in $[V(H_2O)_6]^{3+}$, an octahedral complex ion, is allowed or not. In an octahedral symmetry group, the vector $\Sigma e\vec{r}$ transforms as T_{1u} of the group. The functions $\psi_{1\,elec}$ and $\psi_{2\,elec}$ obviously transform as T_{1g} and T_{2g} representations of the octahedral symmetry group. The direct product $\Gamma_1 \times \Gamma_r \times \Gamma_2$ then becomes $T_{1g} \times T_{1u} \times T_{2g}$ which when reduced, contains only *u* irreducible representations of the octahedral group character table. Since the direct product contains none of the *g* irreducible representations, the integrand is unsymmetrical and hence *Q* here is zero. The transition $T_{1g} \rightarrow T_{2g}$ of the octahedral complex is, therefore, not allowed. Following a similar procedure, we can see that none of the electronic transitions between the crystal field electronic energy levels of an octahedral complex are allowed if the selection rule is strictly applicable.

The *g* and *u* characters of irreducible representations can also be known from the products of gs and us of the components of the direct product. It is to be noted that $g \times g = g$; $g \times u = u$; $u \times g = u$, and $u \times u = g$. Therefore, all the representations contained in the direct product $T_{1g} \times T_{1u} \times T_{2g}$ will be *u* type since $g \times u \times g = u$.

Similarly, if in an octahedral complex, $\psi_{1\,elec}$ and $\psi_{2\,elec}$ are both *u* type, the direct product $\Gamma_{1u} \times \Gamma_{1u} \times \Gamma_{2u}$ will contain all representations of *u* type since $u \times u \times u = u$. Such a direct product cannot contain the term A_{1g} with the result that a $u \rightarrow u$ transition in the octahedral complexes is also forbidden. However, if one of $\psi_{1\,elec}$ and $\psi_{2\,elec}$ is *g* and the other is *u*, then the direct product $\Gamma_{1g} \times \Gamma_{1u} \times \Gamma_{2u}$ or $\Gamma_{1u} \times \Gamma_{1u} \times \Gamma_{2g}$ will, on reduction, contain all irreducible representations of *g* character since $u \times u = g$ so that $g \times u \times u$ or $u \times u \times g = g \times g = g$. If one of these irreducible representations is A_{1g}, the electronic transition $g \rightarrow u$ or $u \rightarrow g$ will be allowed.

It is to be noted that if all the irreducible representations contained in the direct product, $\Gamma_{1u} \times \Gamma_{1u} \times \Gamma_{2g}$ of the octahedral complex are of *g* type but none of these is A_{1g}, the electronic transition will not be allowed even through it may be of $g \rightarrow u$ or $u \rightarrow g$ type since *the integrand will be totally symmetric in such cases only if the direct product* contains the irreducible representation, A_{1g}.

** The symmetry of the integrand is given by the direct product of the symmetries of the terms in it. Also, $g \times u = u \times g = u$; $g \times g = g$; $u \times u = g$. The symmetry of the integrand, where ψ_1 is *g* and ψ_2 is *u*, is $g \times u \times u = g$. The symmetry of the integrand where ψ_1 and ψ_2 are both *g*, is $g \times u \times g = u$.

In the case of molecules with no centre of symmetry, as, for example, a tetrahedral complex, the crystal field energy levels of the metal ions do not have u or g character. However, the d orbitals from which the energy levels are derived do have a g character. Therefore, the electronic transitions between any two crystal field energy levels of a tetrahedral complex may be roughly considered as $g \rightarrow g$ which, of course, will not be as much allowed as the $g \rightarrow u$ or $u \rightarrow g$ transition.

A better procedure to know whether in a tetrahedral complex with no centre of symmetry, a particular crystal field transition is allowed or not, is based on the group theory. According to this procedure if the direct product $\Gamma_1 \times \Gamma_r \times \Gamma_2$ contains A_1 irreducible representation of the symmetry group to which the molecule belongs, Q will be non-zero and the electronic transition between the energy levels $\psi_{1\,elec}$ (transforming as Γ_1 representation of the symmetry group) and $\psi_{2\,elec}$ (transforming as Γ_2 representation of the symmetry group) will be allowed. Γ_r is the representation of the symmetry group to which $\Sigma e\vec{r}$ belongs. If the direct product $\Gamma_1 \times \Gamma_r \times \Gamma_2$ does not contain A_1, Q will be zero and the electronic transition will be forbidden.

Relaxation of Selection Rules

1. Relaxation of Spin Selection Rule. Even though an electronic transition may be spin forbidden, yet it is sometimes observed as a weak absorption band, *i.e.*, a band of very low intensity. This means that such a transition in some way becomes partly allowed. One of the reasons for spin forbidden transition becoming partly allowed is *spin–orbit coupling*.

Suppose a metal ion in a particular ligand environment has a ground state energy level ^{2A+1}X and an excited state energy level ^{2B+1}Y. Let the resultant spin quantum numbers A and B of the two energy levels be different. As a result, the electronic transition between the two energy levels would be spin forbidden. If the orbital angular momentum of the metal ion is not completely quenched, the resultant orbital angular momentum quantum numbers X and Y of the two states would be non-zero. In such a case, the spin–orbit coupling will occur leading to the splitting of the ground as well as excited state energy levels into a number of J states. The J states of the ground state energy levels are spread from X – A to X + A and those of the excited state energy levels are spread from Y – B to Y + B. This means that a spread of energy of ground and excited state energy levels due to their splitting into a number of J states will occur. This will bring some of the J states of ground state energy level nearer to some of the J states of the excited state energy level. Under such a circumstance, a J state of ground state energy level which is near a J state of excited state energy level 'mix' together to give an equal number of new energy levels provided the resultant angular momentum quantum number J of the mixing J states is the same. The new energy levels obtained due to this type of mixing may have the spin character of the original ground state as well as of the original excited state energy levels. In other words, some spin character of ground state energy level will also appear in the new excited state energy level obtained by the mixing of the ground and excited state energy levels as a result of the spin–orbit coupling. Under these circumstances, the electronic transition between the two energy levels becomes partly spin allowed. To illustrate the above discussion, suppose that for a metal ion, the ground state is $^1S_0$ and the excited state is ^3P so that the electronic transition $^1S \rightarrow {}^3P$ is spin forbidden. But the spin-orbit coupling will split the excited ^3P state into $^3P_0$, $^3P_1$ and $^3P_2$ states. Since the resultant angular momentum J of $^3P_0$ and the ground state $^1S_0$ is the same, these two states will combine or 'mix' to produce two new states one of which will be a little above $^3P_0$ and the other a little below $^1S_0$. The lower new state will obviously derive a little triplet character from $^3P_0$ and the higher new state will derive a little singlet character from $^1S_0$. Due to this mixed singlet triplet character of the new states, the forbidden $^1S \rightarrow {}^3P$ transition becomes partly allowed, as shown in Fig. 24.

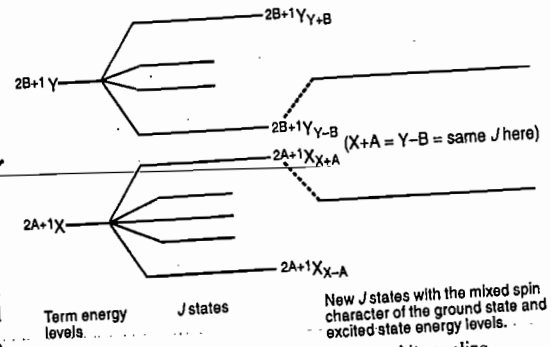


Fig. 24. 'Mixing' of states due to spin-orbit coupling.

2. Relaxation of Leporte Selection Rule. The Leporte selection rule gets relaxed due to several reasons two important of which are described below.

a. Lowering of molecular symmetry. Lowering of molecular symmetry sometimes makes an orbitally forbidden or Leporte forbidden transition fully allowed. We have discussed earlier that all electronic transitions of d–d origin in a metal ion surrounded by an octahedron of ligands involve only g type of energy levels and are, therefore, forbidden.

Now consider a metal ion surrounded by a tetrahedron of ligands instead of an octahedron of ligands. A regular tetrahedron has no centre of symmetry and hence the use of symbols g and u for the energy levels derived from d orbitals in a tetrahedral case is meaningless. Secondly, the set of p orbitals and d_{xy}, d_{xz}, d_{yz} orbitals of the metal ion in tetrahedral surroundings have the same symmetry t_2. Because of this, mixing of d and p orbitals of the metal ion, both of the same symmetry t_2, will occur in tetrahedral ligand environment. Therefore, all the above mentioned energy levels involved in crystal field electronic transitions of a tetrahedral complex are not purely derived from d orbitals and will also have varying amounts of p character incorporated in them. But, the p orbitals are assymmetric or of u type (why ?) whereas the d orbitals are of g type. It means that the crystal field energy levels of tetrahedral complexes apart from having g character derived from d orbitals will also have varying amounts of u character derived from p orbitals. Therefore, electronic transitions between any two of such energy levels will become partly allowed because both the ground and excited states will have different extent of g as well as u character. This is the reason why the intensity of absorption bands of electronic transitions of 'd–d' type are 200–1200 times weaker in octahedral complexes of the type $[ML_6]^{4-}$ than the intensity of absorption of similar transitions in tetrahedral complexes of the type $[ML_4]^{2-}$ where M is Ni, Co, Cu, etc., and L is any uninegative unidentate ligand capable of forming octahedral as well as tetrahedral complexes.

The complex ion $[Co(en)_2Cl_2]^+$ has two isomers, *viz.*, the lower symmetry cis isomer, cis $[Co(en_2)Cl_2]^+$ and the higher symmetry trans isomer, trans $[Co(en)_2Cl_2]^+$. While cis isomer has no centre of symmetry, the trans isomer has a centre of symmetry. Therefore, Leporte selection rule is better applicable to the trans isomer (why ?). As a result, the crystal field electronic transitions of d–d origin (*i.e.*, g–g type) are more Leporte forbidden in trans isomer than similar transitions in the cis isomer. (Due to lack of centre of symmetry in the cis isomer, the energy levels cannot be termed g or u if we apply symmetry rules strictly.) In other words, the intensity of absorption bands is lower in trans isomer than the intensity of bands in the cis isomer. Thus, the lowering of molecular symmetry relaxes Leporte selection rule and increases the intensity of absorption of crystal field transitions.

b. Dynamic distortion of symmetry. Vibronic coupling. While deriving the Leporte selection rule, the vibrational state of the molecule is ignored. In fact, the vibrations of atoms in a molecule can 'couple' with its electronic states and can render a forbidden electronic transition partly allowed. This phenomenon of coupling of vibrational state with the electronic state of a molecule is known as **vibronic coupling.**

We shall try to explain qualitatively the allowance of a Leporte forbidden transition due to vibronic coupling in an octahedral complex. Certain vibrational modes such as T_{1u} and T_{2u} (Fig. 25) of octahedral complex destroy its centre of symmetry so that the metal ion no longer lies at the centre of the regular octahedron. The electronic transitions between crystal field energy levels of octahedral molecules during such vibrational modes will no longer be g–g type and hence for molecules having a centre of symmetry and undergoing such vibrations, the Leporte selection rule no longer applies.

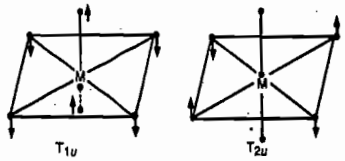


Fig. 25. T_{1u} and T_{2u} vibrations destroying center of symmetry in octahedral complex.

Normally, almost all the molecules of a species are present in the lowest vibrational state which is totally symmetric or has g character (say, $\psi_{1\,vib(g)}$. Suppose the electronic excited state couples with vibrational

state $\psi_{2\,vib}$. Then the transition moment integral Q would be given by

$$Q = \int \psi_{1elec}\, \psi_{1vib(g)} \,|\Sigma e\vec{r}|\, \psi_{2elec}\, \psi_{2vib}\, d\tau \qquad ...(8)$$

Suppose we are interested in finding out the allowance of an electronic transition between two crystal field energy levels $\psi_{1\,elec}$ and $\psi_{2\,elec}$ of an octahedral complex (having a centre of symmetry) in the event of vibronic coupling. In such a case, $\psi_{1\,elec}$, $\psi_{2\,elec}$ and $\psi_{1\,vib}$ are of g character. Therefore, the integrand of Q would be symmetric only if $\psi_{2\,vib}$ is of u character. The symmetry of dipole moment operator in this geometry is T_{1u}. The symmetry of the integrand of Q is then $g \times g\,|\times u\,|\times g \times u = g$. In other words, the excited electronic state should couple with a vibrational state of u type in order that the integrand may be symmetric and non-zero. Further, $\psi_{2vib(u)}$ coupling with the excited electronic state $\psi_{2\,elec}$ should be such that the direct product $\Gamma_{1\,elec} \times \Gamma_{1\,vib\,(g)} \times T_{1u} \times \Gamma_{2\,elec} \times \Gamma_{2\,vib(u)}$ contains the term A_{1g} of the octahedral group. Here Γs are the irreducible representations of the octahedral group to which ψ_{elec} and ψ_{vib} of the ground and excited states belong. We thus observe that a $g-g$ electronic transition which appears forbidden due to nonconsideration of molecular vibrations may become allowed because of vibronic coupling.

Widths of Absorption Bands

The absorption bands observed in electronic spectra are not sharp. These are generally broad, spreading over a range of frequencies. The broadening of the absorption bands is due to the following reasons.

1. Vibrational Bands. Each electronic energy level is associated with a number of vibrational levels. Therefore, a number of closely spaced bands corresponding to the vibrational level transitions are formed alongwith the absorption bands corresponding to the electronic transitions (Fig. 26). Since the closely spaced vibrational bands cannot be properly resolved, we generally obtain an average broad band enveloping all the closely spaced bands.

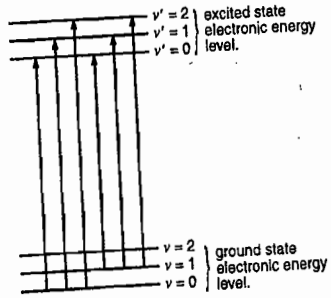


Fig. 26. Transitions involving vibrational levels of ground and excited electronic states.

2. Spin – Orbital Coupling. We have already seen that the ground state energy level as well as the excited state energy level further split up due to spin–orbital coupling giving rise to a number of closely spaced J states in each electronic energy level. As a result, a number of transitions of close energies are possible from the J states of the ground state energy level to the J states of the excited state energy level instead of a single electronic transition between the unsplit ground and excited state energy levels in the absence of spin–orbital coupling. Since these closely spaced transitions are not resolvable, we get an average broad band in the electronic spectrum.

3. Jahn–Teller Distortion. Jahn–Teller distortion may also lift the degeneracy of E and T levels, *i.e.*, orbitally doubly degenerate and triply degenerate energy levels. This would result in more than one closely spaced bands which may appear as an average broad band.

Relative Variation of Energy Levels under the Influence of Crystal Field Potential

The extent of absorption band broadening depends upon the slopes of the lines of the excited state energy level and the ground state energy level of the metal ion in its complex which are obtained when the energies of the levels are plotted as a function of the strength of the crystal field generated by a set of ligands which is measured in terms of Δ or 10 Dq (Fig. 27). In this figure, g.s. is the ground state energy level and e_1, e_2 are the excited state energy levels of the metal ion.

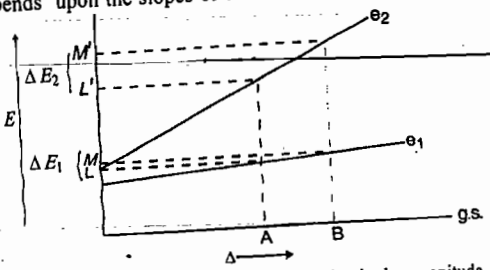


Fig. 27. Broadening caused due to variation in the magnitude of Δ or 10 Dq.

First of all we consider the electronic transitions between g.s. and e_1 the plots of which are almost parallel to each other (or have similar slopes). The quantity Δ or 10 Dq in an octahedral

or a tetrahedral complex of the metal ion is given by the equation,

$$10\,Dq = 10Ze^2\bar{r}^4/(6a^5)$$

where Ze is the charge on the ligand, $\bar{r}^4$ is the average of the fourth power of the radius of d orbitals of the metal ion and a is metal–ligand distance in the complex. It is clear from the above equation that Δ or 10 Dq is proportional to $1/a^5$. Now, in a molecular vibrational mode, metal–ligand bond distances (*i.e.*, a) contract and expand periodically thereby increasing and decreasing Δ or 10 Dq. Therefore, Δ or 10 Dq does not have an absolutely fixed value but has a range for any set of ligands around the metal ion. Let A and B represent the lower and upper limit of the range in Δ caused by a molecular vibrational mode of a complex having a particular set of ligands attached to the metal ion. The energy limits corresponding to A and B are L and M. Thus, LM (or ΔE_1) will be the range in the energy of electronic transition g.s. → e_1. Since the g.s. and e_1 energy levels are almost parallel (*i.e.*, their slopes are very similar), the energy range LM (or ΔE_1) will be very narrow. Since $\Delta E = h\Delta\nu$ where $\Delta\nu$ is the range or spread of frequencies of the absorption band corresponding to the transition g.s. → e_1, this band will be a narrow band.

Let us now consider the electronic transition g.s. → e_2 and apply the above procedure to find out the range $L'M'$ or ΔE_2 in the energy of this transition. Since the slopes of g.s. and e_2 energy levels differ considerably for the same lower and upper limits A and B of the range in Δ, the range ΔE_2 (or $L'M'$) in the energy of the transition g.s. → e_2 will be considerably spread. In other words, the absorption band corresponding to g.s. → e_2 will be quite broad as it will be spread over a wide range of frequencies. Absorption band will be narrow if the ground state and the excited state energy levels have similar slopes and will be broad if they have dissimilar slopes.

INTERPRETATION OF ELECTRON ABSORPTION SPECTRA OF COORDINATION COMPOUNDS

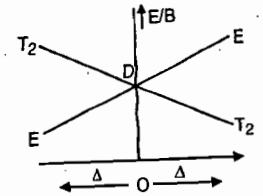
Orgel Diagrams. Orgel diagrams are used for the interpretation of the spin allowed absorption bands of spectra of crystal field or d–d origin in electronic spectra of tetrahedral and octahedral transition metal complexes. The spin allowed electronic transitions occur between the two energy levels which have the same spin multiplicity. Since the energy difference ΔE between electronic energy levels is generally greater than kT (k is Boltzmann constant and T is room temperature), almost all the molecules of the complex occupy the ground state energy level. The electronic transitions, therefore, occur from the ground state energy level. It means that any excited state energy level involved in the transition should also have the same multiplicity as the ground state energy level. Sometimes the spin forbidden transitions, *i.e.*, electronic transitions between energy levels of different spin multiplicity can also appear as absorption bands in the electronic spectra of certain complexes but the intensity of such bands is much lower than the intensity of spin allowed transitions. (The spin forbidden transitions are not discussed here). Following is the list of ground state energy terms (underlined) and excited state energy terms of the same multiplicity for various configurations of free metal ions.

Configurations	*Energy terms*
d^1, d^9	$\underline{^2D}$
d^2, d^8	$\underline{^3F}, {}^3P$
d^3, d^7	$\underline{^4F}, {}^4P$
d^4, d^6	$\underline{^5D}$

The energy levels obtained by the splitting of these energy terms when the metal ion is subjected to weak V_{oct} or V_{tet} will also have the same multiplicity as the unsplit terms because the electrostatic crystal field potential is not of sufficient strength to cause electron spin pairing. The other excited state terms which have different multiplicities than those of the ground state terms are omitted from the list because such excited states will not participate in spin allowed transitions.

Since only the terms listed above for each configuration will, normally, be involved in spin allowed electronic transitions, an energy level diagram showing the splitting of only these terms as a function of the strength of weak V_{oct} and V_{tet} will suffice for a simple interpretation of crystal field spectra which

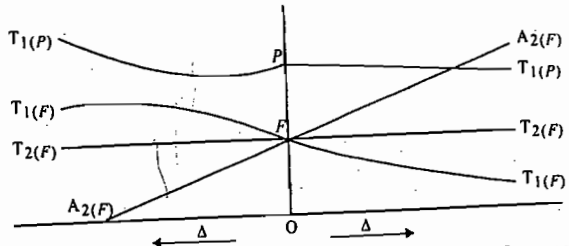
originate from d–d transitions of transition metal complexes. Such a diagram is known as **Orgel diagram** (Figs. 28*a* and *b*).



Orgel diagram for d^1, d^6 metal ion in tetrahedral ligand environment and d^9, d^4 metal ion in octahedral ligand environment

Orgel diagram for d^1, d^6 metal ion in octahedral ligand environment and for d^9, d^4 metal ion in tetrahedral ligand environment

Fig. 28 (*a*) Orgel diagram



Orgel diagram for d^2, d^7 metal ion in tetrahedral ligand environment and d^8, d^3 metal ion in octahedral ligand environment

Orgel diagram for d^2, d^7 metal ion in octahedral ligand environment and d^8, d^3 metal ion in tetrahedral ligand environment

Fig. 28(*b*) Orgel diagram

All the rules (*i*) to (*iv*) (described earlier under the heading Effect of Weak V_{oct} and V_{tet} on the Terms) for the splitting of terms are observed while drawing these diagrams. The abscissa in the diagrams shows the change in the strength of V_{oct} or V_{tet} and ordinate shows the corresponding change in the energies of the splittings of the parent terms. Only two diagrams suffice for the interpretation of spin allowed crystal field transitions of the metal ions with d^1, d^2, d^3, d^4, d^6, d^7, d^8 and d^9 configurations under the influence of weak V_{oct} or V_{tet}. The metal ion with d^5 configuration under the influence of weak V_{oct} or V_{tet} is a special case since no excited term of such a metal ion has the same multiplicity as the ground state term ^6S under these conditions. That is why all electronic transitions of crystal field origin (*i.e.*, of d–d origin) in the electronic spectra of Mn^{2+} are spin forbidden and show absorption bands of very low intensity. This is also the reason why many Mn^{2+} salts and complexes where each Mn^{2+} ion is octahedrally surrounded by a set of ligands, are lightly coloured.

It may be emphasised again that while drawing these diagrams, we have applied weak field conditions. That is, we have assumed the influence of d–d interelectronic repulsions to be stronger than the electrostatic interaction between V_{oct} or V_{tet} and d electrons on the energies of the metal ion in its complex. Therefore, while drawing these diagrams, we have first considered the generation of the energy terms of the free metal ion (*i.e.* P, F, etc.) due to d–d interelectronic repulsions and have *then* considered the influence of V_{oct} or V_{tet} on these terms.

Since weak field and strong field configurations for d^1, d^2, d^3, d^8, d^9 metal ions in octahedral ligand environment give rise to identical energy terms, Orgel diagrams can be used for interpreting electronic spectra of octahedral complexes of the above mentioned metal ions irrespective of the strength of crystal fields generated by the ligands around these metal ions.

How to Use Orgel Diagrams. We can use orgel diagrams for assigning electronic transitions of crystal field origin in weak field or high spin transition metal octahedral complexes and all tetrahedral complexes. The diagrams cannot be used for low spin or strong field complexes where V_{oct} is stronger than d–d interelectronic repulsions.

Although the diagrams are qualitatively drawn, these are easy to remember and use. In order to use Orgel diagram for any particular configuration of a metal ion under the influence of weak V_{oct} or V_{tet}, carry out the following operations :

1. Write down the spin multiplicity of ground and excited free ion terms in the diagram which you want to use.
2. Write down the same multiplicity for the term energy level obtained from splitting of terms under the influence of the given crystal field potential.
3. Write down the subscript g to all term energy levels if the metal ion is subjected to weak V_{oct}. Do not write down the subscript g if the metal ion is subjected to V_{tet}.
4. Show all possible transitions from ground state to various excited states.

Applications of Orgel Diagrams to Electronic Spectra of Transition Metal Complexes. We shall discuss the electronic transitions of crystal field or d–d-origin only with the help of Orgel diagrams. We shall consider one example for each type of metal ion configuration in a complex of the metal ion in weak field octahedral environment.

d^1 Metal ion in Octahedral Environment The electronic absorption spectrum of $[Ti(H_2O)_6]^{3+}$ consists of one absorption band of crystal field or d–d origin which appears around 20,400 cm^{-1}. The aqueous solution of the complex ion is purple in colour.

We take the right half of the Orgel diagram (Fig. 28*a*) which is meant for octahedral complexes of metal ions with d^1 configuration. On applying operations 1 to 4 listed above to the Orgel diagram, it transforms into Fig. 29*a*.

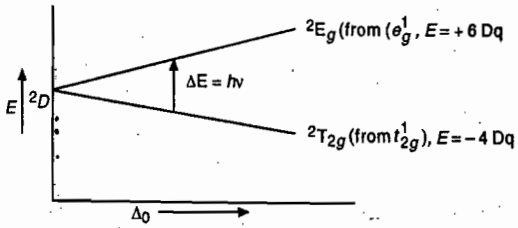


Fig. 29 *a*. Orgel diagram for d^1 configuration of metal ion in its octahedral complex.

There is only one electron in d orbitals of a free Ti^{3+} ion. Therefore, it has only one energy term, *i.e.*, ^2D. When Ti^{3+} ion is surrounded octahedrally by six water molecules, this electron enters t_{2g} set of orbitals. The ground state configuration of $[Ti(H_2O)_6]^{3+}$ has three degenerate energy levels corresponding to the three equivalent orbital electronic arrangements d_{xy}^1, d_{xz}^1 and d_{yz}^1 (called T_{2g} energy levels in (Fig. 29*a*). On absorption of radiation of frequency ν (matching ν of ΔE), the electron gets excited to one of the e_g orbitals. The energy gap ΔE depends on the strength of octahedral electrostatic crystal field potential generated by the ligands, *i.e.*, the water molecules surrounding the metal ion. The electron in the e_g orbitals has two degenerate orbital arrangements $d_{z^2}^1$ and $d_{x^2-y^2}^1$ of equal energy (called E_g levels). The absorption band at 20,400 cm^{-1} of crystal field origin can, therefore, be assigned to $^2T_{2g} \rightarrow {}^2E_g$ transition.

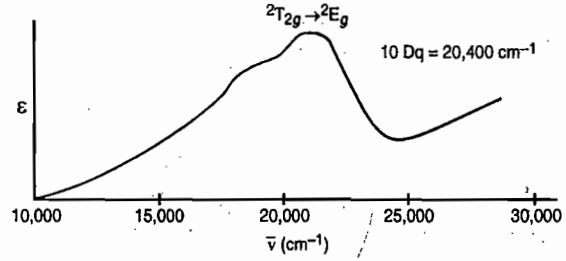


Fig. 29 *b*. Crystal field absorption band of $[Ti(H_2O)_6]^{3+}$ in aqueous solution.

The absorption band (Fig. 29 *b*) in the spectra of $[Ti(H_2O)_6]^{3+}$ appears to be composite because of the splitting of the excited state ^2E_g due to Jahn–Tellar effect.

d^6 Metal ion in Octahedral Environment. The aqueous solution of $[Fe(H_2O)_6]^{2+}$ is pale green in colour and its electronic spectrum shows an absorption band around 10,000 cm^{-1}. We can once again make use of the right half of the orgel diagram (Fig. 28*a*) for assigning this absorption band. The spin multiplicity of the free ion ground term and of the energy levels T_{2g} and E_g obtained from the splitting of the term is 5. The ground state energy level $^5T_{2g}$ originates from the configuration $t_{2g}^4\, e_g^2$ which has three degenerate energy levels corresponding to three orbital arrangements of equal energy, *viz.*, $d^1_{xz}\, d^1_{yz}\, d^2_{xy}\, d^1_{x2-y2}\, d^1_{z2}$; $d^2_{xz}\, d^1_{yz}\, d^1_{xy}\, d^1_{x2-y2}\, d^1_{z2}$; and $d^1_{xz}\, d^2_{yz}\, d^1_{xy}\, d^1_{x2-y2}\, d^1_{z2}$. The excited state energy level ^5E_g originates from $t_{2g}^3\, e_g^3$ configuration containing two degenerate energy levels corresponding to the arrangements $d^1_{xy}\, d^1_{xz}\, d^1_{yz}\, d^2_{z2}\, d^1_{x2-y2}$ and $d^1_{xy}\, d^1_{yz}\, d^2_{z2}\, d^2_{x2-y2}$. The absorption band observed is, therefore, assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition. The band appears to be a composite one due to the splitting of the excited state energy level ^5E_g into two non-degenerate energy levels due to Jahn–Tellar distortion. (Figs. 30 *a*, *b*, and *c*).

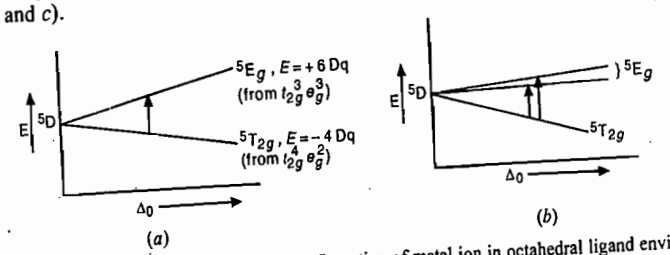
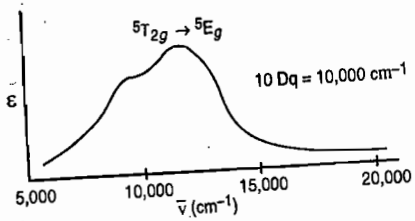


Fig. 30. (*a*) Orgel diagram for d^6 (high spin) configuration of metal ion in octahedral ligand environment. (*b*) Splitting due to Jahn-Tellar distortion of the excited state ^5E_g.



Figs. 30. (*c*) Electronic absorption band of crystal field origin for $[Fe(H_2O)_6]^{2+}$ complex ion in aqueous solution.

d^9 Metal ion in Octahedral Environment. The complex ion $[Cu(H_2O)_6]^{2+}$ in aqueous solution absorbs in the visible region around 12,000 cm^{-1} and gives blue coloured solutions.

We employ the left half of the Orgel diagram (Fig. 28*a*) for interpreting the electronic spectra of octahedral $[Cu(H_2O)_6]^{2+}$ complex of the metal ion having d^9 configuration. A spin multiplicity of 2 is written above the free ion energy term and the energy levels of the diagram since there is only one unpaired electron in the metal ion (Fig. 31). The ground state energy level ^2E_g of the complex originates from the configuration $t_{2g}^6\, e_g^3$ and contains two degenerate energy levels corresponding to the orbital arrangements $t_{2g}^6\, d^2_{z2}\, d^1_{x2-y2}$ and $t_{2g}^6\, d^1_{z2}\, d^2_{x2-y2}$. The excited state energy level originates from the configuration $t_{2g}^5 e_g^4$ and contains three degenerate energy levels from three degenerate orbital arrangements $d^2_{xz}\, d^2_{yz}\, d^1_{xy}\, e_g^4$, $d^1_{xz}\, d^2_{yz}\, d^2_{xy}\, e_g^4$ and $d^2_{xz}\, d^1_{yz}\, d^2_{xy}\, e_g^4$. The absorption band is, therefore, assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition. The composite nature of the band is due to Jahn–Tellar distortion. The absorption

band for $[Cu(H_2O)_6]^{2+}$ is also shown in Fig. 31 *b*.

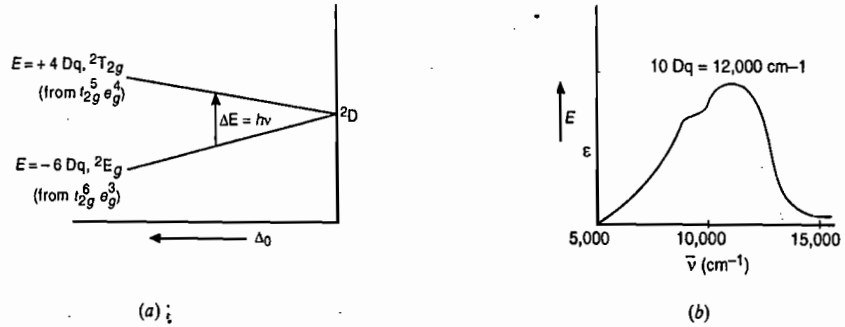
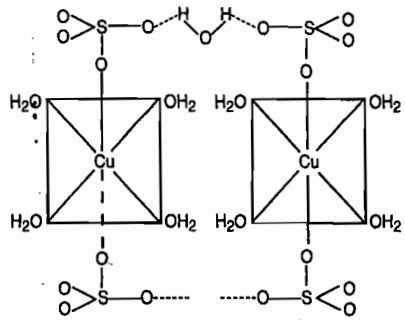


Fig. 31 (*a*). Orgel diagram for d^9 configuration of metal ion in octahedral ligand environment. (*b*). Electronic absorption band of crystal field origin of $[Cu(H_2O)_6]^{2+}$ complex ion in aqueous solutions.

The absorption spectrum of solid $CuSO_4.5H_2O$ can also be interpreted in a similar manner. The Cu^{2+} ion in the salt has octahedral enviroment of O atoms, as shown below :



The blue colour of the salt is due to its absorption around 12,000 cm^{-1} and the absorption band is assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition. As in the case of $[Cu(H_2O)_6]^{2+}$ complex ion, the band is asymmetric due to Jahn–Tellar distortion.

When we heat $CuSO_4.5H_2O$, the four planar coordinated water molecules escape resulting in the formation of $CuSO_4.H_2O$. The monohydrate is no more octahedrally surrounded by the coordinating O atoms of water molecule. Therefore, the splitting of *d* orbitals into t_{2g} and e_g occurring in the case of $CuSO_4.5H_2O$ will no longer occur in the case of $CuSO_4.H_2O$. The energy levels due to the splitting of *d* orbitals will also vanish and hence there is no question of the occurrence of crystal field electronic transition in the visible region in the case of $CuSO_4.H_2O$. In other words, we may say that since the electrons are now present in five degenerate *d* orbitals, there is no question of *excitation* of electrons from one *d* orbital to the other *d* orbital by absorption of energy. Hence, $CuSO_4.H_2O$ will be colourless. It may be worthwhile to mention that there is another sulphate of copper, namely Cu_2SO_4, which is also colourless. This should obviously be so because Cu^+ ion has a d^{10} configuration and hence there is no question of a transition of *d–d* origin occurring in its electronic spectra.

d^4 Metal ion in Octahedral Environment. The complex ion $[Cr(H_2O)_6]^{2+}$ shows an absorption band around 14,000 cm^{-1} and its aqueous solution is pale blue in colour (Fig. 32 *a*).

We shall use the left half of Orgel diagram (Fig. 28*a*) after writing down a spin multiplicity of 5 over each term and each energy level (see Fig. 32 *b*).

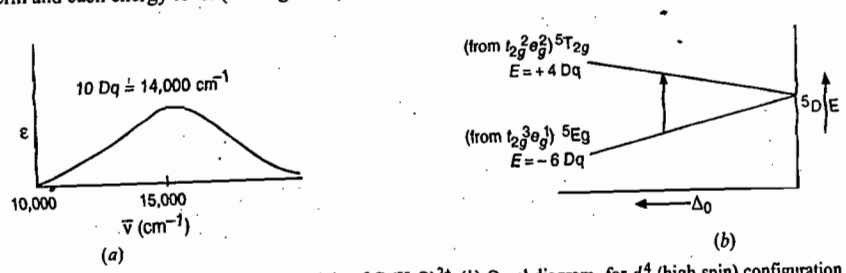


Fig. 32. (*a*) Electronic spectra of crystal field origin of $Cr(H_2O)_6^{2+}$ (*b*) Orgel diagram for d^4 (high spin) configuration of metal ion in octahedral ligand environment.

The ground state energy level ^5E_g originates from the doubly degenerate orbital arrangements $d^1_{xz}d^1_{yz}d^1_{xy}d^1_{z2}$ and $d^1_{xz}d^1_{yz}d^1_{xy}d^1_{x2-y2}$ of $t^3_{2g}e^1_g$ configuration. The excited state energy level $^5T_{2g}$ originates from triply degenerate orbital arrangements $d^1_{xz}d^1_{yz}d^1_{z2}d^1_{x2-y2}$, $d^1_{xy}d^1_{yz}d^1_{z2}d^1_{x2-y2}$ and $d^1_{xz}d^1_{xy}d^1_{z2}d^1_{x2-y2}$ of $t^2_{2g}e^2_g$ configuration. The absorption band at 14,000 cm^{-1}, therefore, appears due to $^5E_g \rightarrow {}^5T_{2g}$ transition.

By now it should be clear that each orbital energy level originates from a specific orbital arrangement of electrons in a configuration. Henceforth, we shall show, on the energy level diagram, the electronic configuration from which the energy levels are derived and shall leave it to the reader to verify the orbital degeneracy of the energy levels.

d^2 Metal Ions in Octahedral Environment. The complex ion $[V(H_2O)_6]^{3+}$ absorbs at 17,200 cm^{-1} and 25,600 cm^{-1} (Fig. 33*a*) and its aqueous solution is green in colour. We shall use the right half of the Orgel diagram (Fig. 28*b*) for assigning these absorption bands.

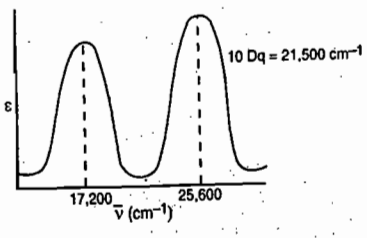


Fig. 33 (*a*). Electronic spectra of crystal field origin of $[V(H_2O)_6]^{3+}$ complex ion in aqueous medium.

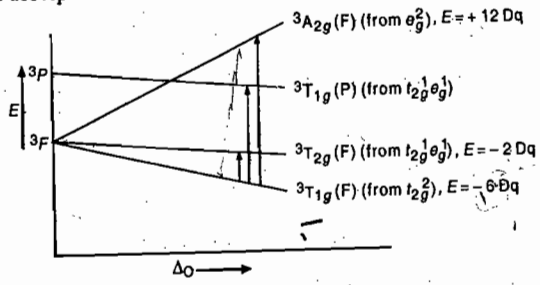


Fig. 33 (*b*). Orgel diagram for d^2 metal ion in octahedral ligand environment.

The energy terms arising out of d^2 configuration of free V^{3+} ion because of interelectronic repulsions between *d* electrons are ^3F, ^1G, ^1D, ^1S and ^3P out of which ^3F forms the ground state. The other term with the same multiplicity is ^3P. The ^3F term splits up into $^3T_{1g}(F)$, $^3T_{2g}$ and $^3A_{2g}$ whereas the ^3P term, which transforms as $^3T_{1g}(P)$ in octahedral symmetry, is not split and remains orbitally triply degenerate under the influence of weak V_{oct} generated by six water molecules acting as ligands. Thus we actually expect three absorption bands due to $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$; $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3T_{1g}(F) \rightarrow {}^3A_{2g}$ electronic transitions (Fig. 33*b*). But actually only two absorption bands at 17,200 cm^{-1} and 25,600 cm^{-1} are observed due to $^3T_{1g}(F) \rightarrow {}^3T_{2g}$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ electronic transitions. The third electronic transition

$^3T_{1g}(F) \rightarrow {}^3A_{2g}$ refers to the simultaneous excitation of both the electrons from t_{2g} to e_g orbitals and is forbidden.

Since $E_{^3T_{2g}} - E_{^3T_{1g}} = 17{,}200$ cm^{-1}, hence, 2 Dq − (−6 Dq) = 8 Dq = 17,200 cm^{-1}. Therefore, 10 Dq = 17,200 × 10/8 = 21,500 cm^{-1}

(More refined calculations yield 18,600 cm^{-1} as the value of 10 Dq. Such refined calculations are, however, beyond the scope of the book)

The electronic spectrum of $[V(ox)_3]^{3+}$ complex ion (ox^{2-} is oxalate anion) is similar to that of $[V(H_2O)_6]^{3+}$ except for minor differences in the positions and intensities of the two absorption bands observed.

d^7 Metal ion in Weak Octahedral Environment. The complex ion $[Co(H_2O)_6]^{2+}$ is pinkish violet in an aqueous solution and shows three absorption bands at 8000 cm^{-1}, 19,600 cm^{-1} and 21,600 cm^{-1} (Fig. 34*a*).

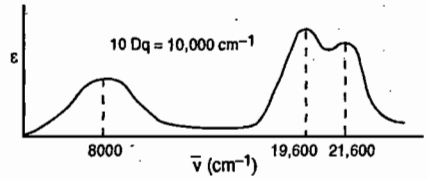


Fig. 34(*a*). Absorption bands of crystal field origin in the electronic spectrum of $[Co(H_2O)_6]^{2+}$ in aqueous medium.

We again use the right half of Orgel diagram (Fig. 28*b*) for assigning these bands. The ground state term of free Co^{2+} is ^4F and its only other term with the same multiplicity is ^4P. The ^4F term splits into $^4T_{1g}(F)$, $^4T_{2g}$ and $^4A_{2g}$ whereas the ^4P, *i.e.*, $^4T_{1g}(P)$, term remains unsplit under the influence of weak octahedral potential generated by six water molecules acting as ligands around the metal ion.

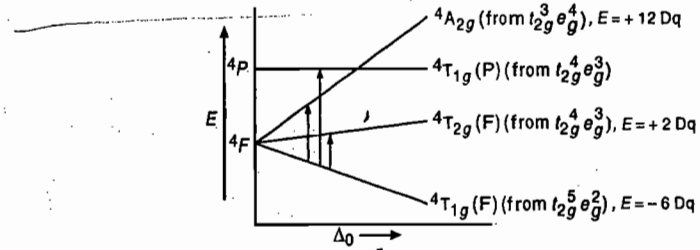


Fig. 34(*b*). Orgel diagram for d^7 metal ion in weak octahedral ligand environment.

The diagram shows three electronic transitions *viz.*, $^4T_{1g}(F) \rightarrow {}^4T_{2g}$; $^4T_{1g}(F) \rightarrow {}^4A_{2g}$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, corresponding to three absorption bands at 8,000, 19,600 and 21,600 cm^{-1}, respectively (Fig. 34*b*).

Since $E_{^4T_{2g}} - E_{^4T_{1g}} = 8000$ cm^{-1}, hence, 2 Dq − (−6 Dq) = 8 Dq = 8000 cm^{-1}. Therefore, 10 Dq = 8000 × 10/8 = 10,000 cm^{-1}

d^8 Metal ion in Octahedral Environment. The complex ion $[Ni(H_2O)_6]^{2+}$ shows greenish blue colour in aqueous medium and absorbs at 8,700, 14,500 and 25,300 cm^{-1} (Fig. 35*a*).

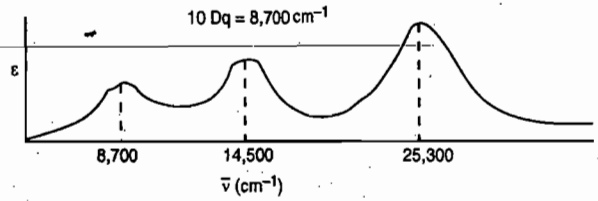


Fig. 35 (*a*). Absorption bands of crystal field origin in the electronic spectrum of $[Ni(H_2O)_6]^{2+}$.

We consider the left half of Orgel diagram (Fig. 28*b*) for assigning these bands. The free Ni^{2+} ion has the same energy terms as a free metal ion with d^2 configuration has. The ground term is ^3F and the other term of the same multiplicity as the ground term is ^3P. The energy term ^3F splits into $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}$ in that order whereas ^3P [*i.e.*, $^3T_{1g}(P)$] term remains unsplit under the influence of V_{oct}. The terms $^3T_{1g}(F)$ and $^3T_{1g}(P)$ do not cross because they are of the same symmetry (Fig. 35*b*).

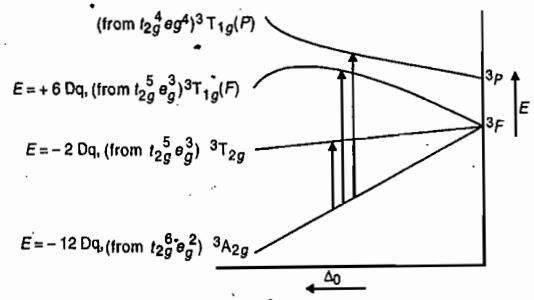


Fig. 35 (*b*). Orgel diagram for d^8 metal ion under octahedral ligand environment

Thus, the electronic transition $^3A_{2g} \rightarrow {}^3T_{2g}$ gives rise to 8,700 cm^{-1} absorption band ; the electronic transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ gives rise to 14,500 cm^{-1} absorption band and the electronic transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ gives rise to 25,300 cm^{-1} absorption band in the electronic spectrum of $[Ni(H_2O)_6]^{2+}$.

Since energy of $^3T_{2g} - {}^3A_{2g} = -2\ Dq - (-12\ Dq) = 8{,}700\ cm^{-1}$, hence 10 Dq = 8,700 cm^{-1}.

d^3 Metal ion in Octahedral Environment. The complex ion $[Cr(H_2O)_6]^{3+}$ gives light green solution in aquous medium and shows absorption bands at 17,000 cm^{-1} and 24,000 cm^{-1}. There is a weak absorption band at 37,000 cm^{-1} also (Fig. 36*a*).

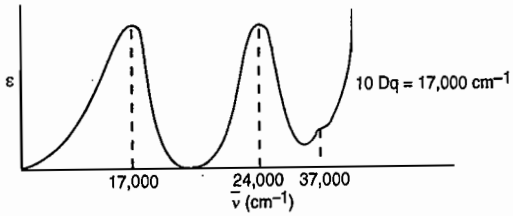
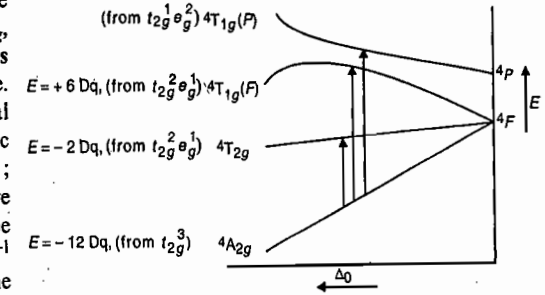


Fig. 36(*a*). Electronic spectrum of crystal field origin of $[Cr(H_2O)_6]^{3+}$ in aqueous medium.

We consider the left half of the Orgel diagram (Fig. 28 *b*) for assigning these absorption bands. The free d^3 ion has ^4F as the ground term. The other term of the same multiplicity is ^4P. While ^4F is split into $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}(F)$ in that order, the ^4P term is unsplit and remains orbitally triply generate. (It becomes $^4T_{1g}(P)$ term in octahedral symmetry). In this case three electronic transitions, *viz*, $^4A_{2g} \rightarrow {}^4T_{2g}$; $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ are possible which are responsible for three absorption bands at 17,000 cm^{-1}, 24,000 cm^{-1} and 37000 cm^{-1}, respectively, in the spectrum (Figs. 36 *a* and *b*).



Fig, 36(*b*). Orgel diagram for d^3 ion in octahedral ligand environment.

Since energy of $^4T_{2g} - {}^4A_{2g} = -2\ Dq - (-12\ Dq) = 17{,}000\ cm^{-1}$, hence, 10 Dq = 17,000 cm^{-1}.

The electronic spectrum of $[Cr(ox)_3]^{3-}$ in aqueous medium is similar to that of $[Cr(H_2O)_6]^{3+}$ and the absorption bands in the former can be assigned on similar lines.

We have taken the aquated species of metal ions for our studies because water is a *weak ligand* and generates *weak* V_{oct}, in general. The Orgel diagrams and the assignments made with their help are equally valid for other weak field complexes of the metal ions.

It is clear from the above discussion that, as stated earlier, the splitting of a term of d^n metal ion is the reverse of the splitting of the same term of d^{10-n} metal ion in the same ligand environment.

Metal Ions in Tetrahedral Environments. The metal ions under tetrahedral ligand environments also experience a weak field. Therefore, Orgel diagrams can be used to interpret their spectra also. While using the diagrams for tetrahedral complexes, it should be kept in mind that the symbol '*g*' is not to be used in the energy levels because a tetrahedron has no centre of symmetry.

The tetrahedral complexes are known for only a few of the metal ions of the First transition series. The following features generally complicate the assignment of bands in electronic spectra of tetrahedral complexes.

(*i*) The intensities of the absorption bands of crystal field origin in tetrahedral complexes are higher than in octahedral complexes due to '*d–p*' mixing. Due to this, it is not always easy to differentiate between the crystal field transitions and the 'allowed' charge transfer transitions in the electronic spectra of tetrahedral complexes.

(*ii*) The structural features observed in the absorption bands of crystal field origin due to vibronic coupling, spin–orbit coupling and due to low symmetry ligand field components are more pronounced in the electronic spectra of tetrahedral than in the electronic spectra of octahedral complexes. The structural features in an absorption band are sometimes so pronounced that they themselves may be mistaken for separate crystal field absorption bands of close energies.

We shall now discuss the elecronic spectra (only crystal field bands) of some metal ions in their tetrahedral complexes by using Orgel diagrams.

d^6 Metal ion in Tetrahedral Environment. The electronic spectrum of $[FeCl_4]^{2-}$ shows a crystal field broad absorption band around 4000 cm^{-1} (in the near IR region). We employ the left half of Orgel diagram (Fig. 28 *a*), after writing the appropriate multiplicities over the terms and the splittings, to interpret the absorption band observed. The absorption band is obviously due to the transition $^5E \rightarrow {}^5T_2$ (Fig. 37) and 10 Dq is 4,000 cm^{-1}.

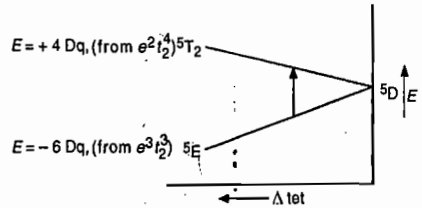


Fig. 37. Orgel diagram for d^6 configuration of metal ion in tetrahedral ligand environment.

d^7 Metal ion in Tetrahedral Environment. The electronic spectrum of the complex ion $[CoCl_4]^{2-}$ shows two absorption bands at 5,800 cm^{-1} (in the near IR region) and 15,000 cm^{-1} (in the visible region), as shown in Fig. 38(*a*). We employ the left half of Orgel diagram (Fig. 28*b*), after writing appropriate spin multiplicities, to interpret the crystal field spectra of the complex ion (Fig. 38*b*)

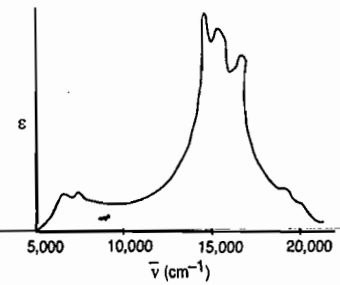


Fig. 38(*a*). Absorption bands of crystal field origin of aqueous solution of $[CoCl_4]^{2-}$

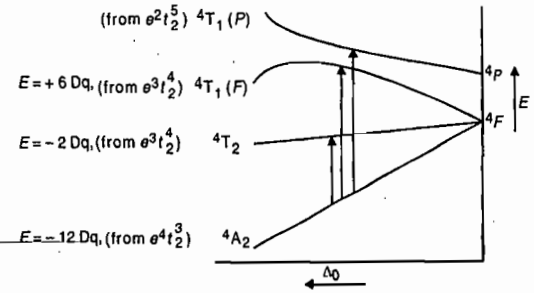


Fig. 38(*b*). Orgel diagram for d^7 configuration of metal ion in tetrahedral ligand environment.

The bands at 5,800 and 15,000 cm^{-1} are due to transitions $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$, respectively.

The absorption band of lowest energy, that is, due to the transition $^4A_2 \rightarrow {}^4T_2$, is expected at 3,500 cm^{-1}, in the near IR region and is, therefore, out of the range of common ultraviolet and visible range spectrophotometers.

We can calculate 10 Dq from 5,800 cm^{-1} absorption band. Thus, 6 Dq – (– 12 Dq) = 18 Dq = 5,800 cm^{-1}. Hence, 10 Dq = 5,800×10/18 = 3,220 cm^{-1}

The energy gap between $^4T_2$ and $^4A_2$ is also 10 Dq. Therefore, first transition should also appear at about 3,200 cm^{-1}.

***d^8* Metal ion in Tetrahedral Environment.** The solution of $[\{(C_6H_5)_3AsO\}_2NiCl_2]$ in benzene shows two absorption bands at 7,800 cm^{-1} and 14000–16,000 cm^{-1} (Fig. 39*a*). The complex has a distorted tetrahedral structure. The right half of the Orgel diagram (Fig. 28*b*), after writing appropriate multiplicities on the terms and the splittings, can be employed to interpret the electronic spectra of tetrahedral complex (Fig. 39*b*). The two absorbption bands have been assigned to the following transitions:

$^3T_1(F) \rightarrow {}^3A_2$ 7,800 cm^{-1}

$^3T_1(F) \rightarrow {}^3T_1(P)$ 16,000 cm^{-1}

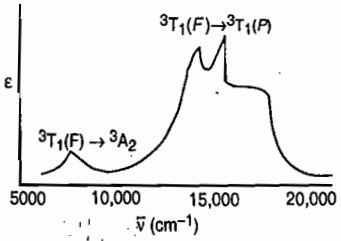


Fig. 39(*a*). Absorption bands of crystal field origin of $(C_6H_5)_3AsO)_2NiCl_2$ in aqueous medium.

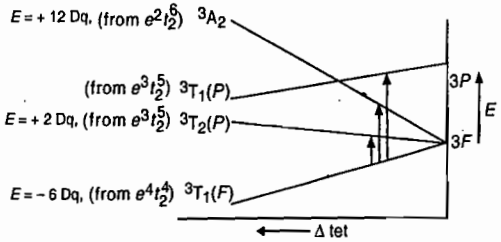


Fig. 39(*b*). Orgel diagram for d^8 configuration of metal ion in tetrahedral environment.

From Fig. 39(*b*), it is clear that the energy gap corresponding to the transition $^3T_1(F) \rightarrow {}^3A_2$ is 18 Dq.

Hence, 18 Dq = 7,800 cm^{-1} and, therefore, 10 Dq = 7,800×10/18 = 4,300 cm^{-1}

The transition of lowest energy, *i.e.*, $^3T_1(F) \rightarrow {}^3T_2(F)$ should show an absorption band at 3,500 cm^{-1} but is not observed since the frequency of absorption of this band falls in the IR region.

Charge Transfer Spectra (CT Spectra)

Charge transfer spectra originate from a redistribution of electron charge density within the molecule. Therefore, these spectra are also referred to as redox spectra. The appearance of charge transfer bands is connected with electron-donating and electron-accepting properties of ligands and the metal ions. The charge transfer within a complex can occur from the metal ion to the ligand as also from the ligand to the metal ion. The spectra corresponding to both of these charge transfers have been discussed in this section. The greater the oxidising power of the metal ion and the reducing power of the ligand, the lower is the energy and hence the frequency at which the charge transfer bands appear.

L → M Charge Transfer Spectra. In this type, we shall discuss the charge transfer spectra of hexahalo complex anions which contain ligands with fully filled π orbitals. These complex anions can be divided into two categories. In the first category are the halo complex anions of metal ions with d^4 and d^5 configurations. Well known examples are $[RuCl_6]^{2-}$ and $[IrBr_6]^{2-}$ anions. These complexes produce two charge transfer bands, one of lower intensity appearing at lower frequencies falling around 20,000 cm^{-1} and the other of higher intensity appearing at much higher frequencies falling between 40,000 and 80,000 cm^{-1}. The second category includes complexes of metal ions with d^6 configuration as, for example, $[IrBr_6]^{3-}$. In these complexes, the lower frequency bands are absent and only higher frequency bands are

formed. The charge transfer spectra of both of these categories of complexes are shown in Fig. 40.

In order to account for the above spectra, it has been suggested that the lower intensity lower frequency bands produced by the first category of complexes be assigned to the charge transfer transition $t_{1u}^n, t_{2u}^n \rightarrow t_{2g}^*$ and the higher intensity higher frequency charge transfer bands which are produced by both the categories of complexes be assigned to the charge transfer transitions $t_{1u}^n, t_{2u}^n \rightarrow e_g^*$.

Since in $[IrBr_6]^{3-}$, the t_{2g}^* orbitals are filled (as Ir^{3+} has d^6 configuration), the charge transfer transitions $t_{1u}^n, t_{2u}^n \rightarrow t_{2g}^*$ are not possible. Hence the lower intensity lower frequency charge transfer transitions are not possible in this case. Only the higher intensity higher frequency transitions $t_{1u}^n, t_{2u}^n \rightarrow e_g^*$ are possible.

In the case of halo complex anions of the first category in which the metal ions have d^4, d^5 configurations, there are vacancies in t_{2g}^* molecular orbitals and hence lower intensity lower frequency charge transfer transitions $t_{1u}^n, t_{2u}^n \rightarrow e_{2g}^*$ occur along with the other charge transfer transitions $t_{1u}, t_{2u} \rightarrow e_g^*$.

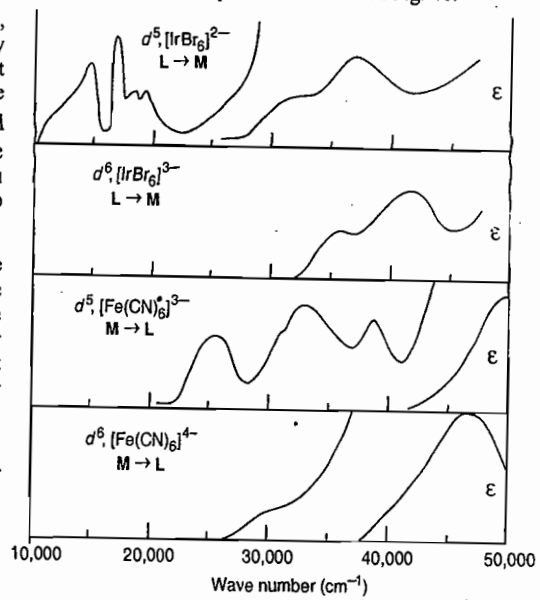


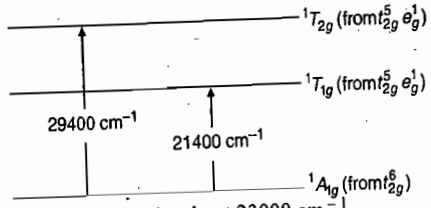
Fig. 40. L→M and M→L charge transfer bands in the spectra of some complex anions

M → L Charge Transfer Spectra. The charge transfer spectra of this type can be observed only when there are vacant orbitals localised on the ligands which are higher in energy than the filled molecular orbitals of the metal ions. Examples are furnished by the complexes $Cr(CO)_6$, $Mo(CO)_6$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, etc. These complexes show intense absorption bands in the region 35000 – 45000 cm^{-1} which have been assigned to charge transfer transitions from filled (mainly metal t_{2g} molecular orbitals) to vacant π* ligand orbital combinations t_{1u}^n, t_{2u}^n. The charge transfer transitions of this type in electronic spectra of complex anions $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are also shown in Fig. 40.

Electronic Absorption Spectra of Spin-paired (or Low Spin or Strong Field) Complexes. We have already discussed the electronic spectra of spin-free (high spin or weak field) octahedral complexes by taking into consideration the spectra of hexaaqua metal ions, $[M(H_2O)_6]^{n+}$ (water is a weak field ligand). However, our discussion on electronic spectra would be incomplete if we do not say a few words about the electronic spectra of spin-paired (low spin) octahedral complexes.

In spin-paired octahedral complexes, the spin multiplicity of the ground energy level of a complexed metal ion is less than that of the free metal ion. Such complexes comprise of strong field ligands which generate high magnitude of 10 Dq. The electronic absorption spectra of such complexes generally contain lower energy charge transfer bands which often extend into the visible region and thus tend to mask the absorption bands of crystal field origin which also appear in this region. However, these bands are associated with much lower energy than the charge transfer bands as a result of which the colours of spin-paired complexes are generally due to charge transfer absorptions rather than absorptions of crystal field origin. Therefore, the information obtained from spectra of spin-paired complexes is a good deal less than the information supplied by the spectra of spin-free complexes.

There is no distinction between the spin-free or spin-paired complexes of metal ions with d^1, d^2 and d^3 configurations. The assignment of crystal field bands in the spectra of spin-paired complexes of metal ions with d^4, d^5 and d^7 configurations are quite ambiguous because of simultaneous appearance of charge transfer bands as well as crystal field bands in the visible region.



The charge transfer spectrum which has been interpretted with a good deal of certainty is the one given by the spin-paired complex ion $[Co(en)_3]^{3+}$. The assignments for this spectrum are as shown.

The charge transfer bands appear at comparatively higher frequencies so that the crystal field bands are not masked by the charge transfer bands and are thus clearly observed. The 10 Dq in this complex has been calculated to be about 23000 cm^{-1}.

Rule of Average Environment. This rule, which is empirical in nature, states that 10 Dq of a complex $[MA_nB_{N-n}]$ containing ligands A and B, is a weighted average of 10 Dqs of the complexes $[MA_N]$ and $[MB_N]$ of the same geometry (N is the coordination number of the metal ion). According to the above rule, the 10 Dq for an octaheral complex of the form $[MA_nB_{6-n}]$ would be given by

$$10\ Dq = [n \times 10\ Dq \text{ of } MA_6 + (6-n) \times 10\ Dq \text{ of } MB_6]/6$$

Accordingly, for the complex ion $[Co(en)_2F_2]^+$, in which the two en ligands occupy four of the six available coordination sites and are thus equivalent to four unidentate ligands, would be given by

$$10\ Dq = \{4 \times 10\ Dq \text{ of } [Co(en)_3]^{3+} + 2 \times 10\ Dq \text{ of } [CoF_6]^{3-}\}/6$$
$$= (4 \times 23000 + 2 \times 13000)/6 = 20{,}000\ cm^{-1}$$

The experimental 10 Dq for the complex is known to be 21000 cm^{-1}.

The rule of average environment is specially useful when we wish to know the 10 Dq for an unstable or hypothetical complex $[MA_n B_{N-n}]$ whose electronic spectrum cannot be recorded. If the electronic spectra of MA_N and MB_N are available, we can easily calculate 10 Dq for the complex $[MA_nB_{N-n}]$ from this rule.

Spectrochemical Series

It is possible to arrange the metal ions in the following order of increasing 10 Dq when these metal ions are complexed with a particular ligand :

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Ir^{3+} < V^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{4+} < Re^{4+} < Pt^{4+}$$

($^1A_{1g}$ (from t_{2g}^6))

Similarly, various ligands when attached to a particular metal ion can also be arranged in the following order of increasing 10 Dq :

$$I^- < Br^- < NCS^- < F^- < urea < OH^- < CH_3COO^- < Ox^{2-} < H_2O < SCN^- < glycine < pyridine \sim NH_3 < en < SO_3^{2-} < dipyridyl < O^- phenanthrolene < NO_2^- < CN^- < CO$$

Such series of metal ions and ligands are known as **spectrochemical series.**

A plausible explanation for the above series of ligands can be offered on the basis of electronegativities, polarisabilities, polarising powers, permanent dipole moments and π bonding properties of these ligands.

Arguments on similar lines can be advanced for the above series of metal ions. These, however, are not entirely convincing.

There are many metal ions whose complexes with a particular ligand are not known. It is, therefore, not possible to determine 10 Dq for such complexes experimentally. An empirical solution to this problem has been suggested. Two parameters f and g have been assigned empirical values for various metal ions and ligands ; the products $f \times g \times 10^3$ cm^{-1} give the approximate 10 Dqs for the complexes involved. The empirical values for f and g for various combinations of ligands and metal ions are given in Table 3.

TABLE 3

Empirical Values of Parameters f and g for Various Combinations of Ligands and Metal Ions for Estimating 10 Dqs for Unknown Complexes

Metal Ion	Empirical value of g	Ligand	Empirical value of f
Co^{2+}	9·3	3 acac	1·21
Co^{3+}	19·0	6 H_2O	1·00
Cr^{3+}	17·0	6CH_3COO^-	0·96
Cu^{2+}	12·0	3en	1·28
Fe^{3+}	10·0	6OH –	1·70
Ni^{2+}	8·9	6 F –	0·90

According to the above data, the value of 10 Dq for $[Ni(H_2O)_6]^{2+}$ would be given by

$$10\ Dq = f \times g \times 10^3\ cm^{-1} = 8{\cdot}9 \times 1{\cdot}00 \times 10^3\ cm^{-1} = 8900\ cm^{-1}$$

The experimentally determined value of 10 Dq for this complex = 8700 cm^{-1}.

Similarly, 10 Dq for $[Co(en)_3]^{3+} = 9{\cdot}3 \times 1{\cdot}28 \times 10^3\ cm^{-1} = 23{,}000\ cm^{-1}$

Experimentally determined 10 Dq = 23,000 cm^{-1}

Nephelauxetic Series

It is possible to place various metal ions and ligands in a series based on the order in which another factor, *viz.*, ($B_{\text{free metal ion}} - B_{\text{complexed metal ion}}$), goes on increasing. In this factor, B stands for Racah interelectronic repulsion parameter which measures interelectronic repulsion amongst d electrons of the metal ion. Due to an increase in the size of the d orbitals which invariably occurs when the metal ion gets complexed, a decrease in the interelectronic repulsion amongst d electron of the metal ion always occurs. Therefore, B of the complexed metal ion is always less than B of free-metalion. The approximate value of B is calculated with the help of an empirical relation, $B = B_0(1 - hk) \times 10^3$ cm^{-1}, in which B_0 is Racah replusion parameter for free metal ion whose value for a given metal ion is very well known and h and k are arbitrary parameters which are assigned empirical values for various metal ions and ligands. These empirical values are given in Table 4.

TABLE 4

Empirical Values of Parameters h and k assigned to Various Metal Ions and Ligands

Metal Ion	Empirical value of h	Ligand	Empirical value of k
CO^{2+}	0·23	6 CN^-	
Co^{3+}	0·35	6 Br^-	2·3
Cr^{3+}	0·21	6 Cl^-	2·0
Fe^{3+}	0·24	6 OH^-	2·0
Mo^{3+}	0·07	3 en	1·5
Ni^{2+}	0·12	6 H_2O	1·4

According to the above data, the approximate value of B for $[Ni(H_2O)_6]^{2+}$ comes out to be $1080(1 - 0{\cdot}12 \times 1{\cdot}4) \times 10^3 = 898{\cdot}6$ cm^{-1}. The experimentally determined value is 905 cm^{-1}. (B_0 for Ni^{2+} ion = 1080cm^{-1}).

Based on the values of the factor ($B_{\text{free metal ion}} - B_{\text{complexed metal ion}}$), the metal ions and ligands are arranged in the following series, called the **nephelauxetic series** :

Metal Ions $Mn^{2+} \sim V^{2+} > Ni^{2+} \sim Co^{2+} > Mo^{3+} > Re^{4+} > Cr^{3+} > Re^{3+} > Ir^{3+} \sim Rh^{3+} > Co^{3+}$

Ligands $F^- > H_2O > urea > NH_3 > en \sim Ox^{2-} > SCN^- > Cl^- \sim CN^- > Br^- > I^-$

As can be seen, the above series some what resemble the spectrochemical series.

MAGNETOCHEMISTRY OF TRANSITION METAL COMPLEXES

The study of magnetic properties of coordination compounds has contributed a lot to our understanding of the chemistry of transition metal complexes, the stereochemistry of the central metal ion and the nature of the metal–ligand bonding. It is of interest, therefore, to describe the origin of the type of the magnetic behaviour exhibited by transition metal complexes.

As is well known, any moving charged particle produces a magnetic field. Accordingly, planetary electrons as well as nuclei of atoms are capable of producing magnetic fields although the magnetic field generated by a nucleus is about 10^4 times weaker than the magnetic field generated by a moving electron. Therefore, the magnetic phenomenon associated with electron motion remained of greater interest to chemists till the discovery of the phenomenon of nuclear magnetic resonance. The nuclear magnetic resonance has now become an extremely useful technique for studying the nature of inorganic as well as organic compounds. We shall, however, limit our discussion to the magnetic phenomenon associated with the motion of electron only. For nuclear magnetic resonance, the student is advised to refer to any good book on spectroscopy.

Before we discuss the magnetic behaviour of coordination compounds, it would be worthwhile to familiarise the student with a few terms which would be used frequently in this discussion. These terms are *magnetic induction, permeability, intensity of magnetisation* and *magnetic susceptibility.*

Magnetic induction. When a specimen of a magnetic material is placed in a magnetising field, magnetism is induced in the specimen. This phenomenon is called **magnetic induction**. The end of the specimen through which the magnetic lines of force enter becomes the south pole and the end from which these lines leave the specimen becomes the north pole. Magnetic induction is also defined as the total number of magnetic lines of force crossing a unit area (which is perpendicular to the direction of the magnetising lines of induction) around a point located within the specimen placed in the magnetising field. It is also termed as **magnetic flux density**. The magnetic lines of induction at any point within the specimen may be both more or less than the magnetic lines of induction at the same point if it is in air or vacuum.

Permeability. Permeability is defined as the ratio of the magnetic flux density at any point in the specimen to the strength of the magnetic field applied. If B is the magnetic flux density and H is the strength of the magnetic field applied, then permeability = B/H.

Intensity of magnetisation (I). It represents the extent to which a specimen gets magnetised when kept in a magnetising field. Quantitatively it is defined as the magnetic moment per unit volume, *i.e.*, $I = M/V$ where M, the magnetic moment, is given by the product of the pole strength and the distance between the magnetic poles of the specimen.

Magnetic susceptibility (K). It is the ratio of the intensity of magnetisation of the specimen of the material and the strength of the magnetic field applied, *i.e.*, $K = I/H$. It measures how easily the specimen can be magnetised. Since I is magnetic moment per unit volume, K ($=I/H$) would be expressed as per unit volume. That is why K is also known as **volume magnetic susceptibility**. Likewise, *gram magnetic susceptibility*, χ_g, is magnetic susceptibility per gram of the material. Thus, $\chi_g = K/d$ where d is the density of the material.

Molar magnetic susceptibility, χ, is magnetic susceptibility per mole of the substance. Evidently, $\chi = \chi_g \times M = KM/d$. It can be easily shown that $B = H + 4\pi I$ so that $B/H = 1 + 4\pi I/H = 1 + 4\pi K$. It is to be kept in mind that the symbols χ_A, χ_B and χ used in subsequent discussion stand, respectively, for magnetic susceptibility of atoms, bonds and molecules per mole, *i.e.*, per Avogadro's number of atoms, bonds and molecules, as the case may be.

ORIGIN OF MAGNETISM

The origin of magnetism in an atom lies in the motion of its negatively charged electrons. The overall magnetic moment of an atom is the resultant of the magnetic moment generated by the orbital motion of electrons, called *orbital magnetic moment* (μ_l) and the magnetic moment generated by the spin motion of electrons, called *spin magnetic moment* (μ_s). The generation of orbital magnetic moment and spin magnetic moment is shown pictorially in Fig. 41.

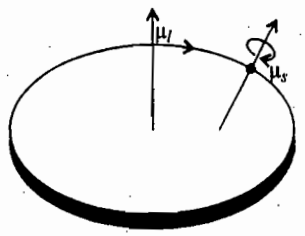


Fig. 41. Generation of orbital magnetic moment and spin magnetic moment.

Orbital Magnetic Moment (μ_l). A negatively charged electron moving in a circular orbit is similar to the flow of electric current in a circular wire. The electron motion, therefore, generates a magnetic field in a direction perpendicular to the plane of the orbit containing the electron. The moment of the magnetic field so generated is given by the product of the electric current and the surface area of the orbit. Thus,

$$\text{Orbital magnetic moment, } \mu_l = iA = (e\omega/2\pi c)\pi r^2 \qquad \ldots(9)$$

where r is the radius of the orbit, ω is the angular velocity of electron, c is the velocity of light and e is the electronic charge.

As discussed earlier *, an electron moving in an orbit generates orbital angular momentum (l) which is

* In prewave mechanical concepts, we picture the electron as a hard negatively charged sphere moving around the nucleus in a closed circular path called orbit. The terms orbital angular momentum and spin angular momentum were introduced as concepts to explain some spectral and magnetic properties of atoms and molecules.

perpendicular to the plane of the orbit and is given by

$$(l) = \sqrt{l(l+1)}\, h/2\pi$$

where l is the orbital angular momentum quantum number. It is to be noted that (l), the orbital angular momentum and l, the orbital angular momentum quantum number are distinctly different quantities.

Since the orbital angular momentum of a particle of mass m moving in a circle of radius r is given by $m\omega r^2$, hence

$$(l) = m\omega r^2 = \sqrt{l(l+1)}\, h/2\pi \qquad \ldots(10)$$

or

$$\omega r^2 = \sqrt{l(l+1)}\, h/2\pi m \qquad \ldots(11)$$

Substituting the above value of ωr^2 in Eq. 9, we have

$$\text{Orbital magnetic moment, } \mu_l = (e/2c)\sqrt{l(l+1)}\, h/2\pi m = \sqrt{l(l+1)}\left(\frac{eh}{4\pi mc}\right) = \sqrt{l(l+1)}\ \text{B.M.} \qquad \ldots(12)$$

Also

$$\frac{\mu_l}{(l)} = \frac{\mu_l}{\sqrt{l(l+1)}\, h/2\pi} = \frac{\sqrt{l(l+1)}\ \text{B.M.}}{\sqrt{l(l+1)}\, h/2\pi} = \frac{\sqrt{l(l+1)}}{\sqrt{l(l+1)}} = 1 \qquad \ldots(13)$$

The magnetic moment μ_l is measured in units of Bohr magneton (B.M.) which, as is evident from Eq. 13, is equal to $eh/4\pi mc$. Thus, for an electron moving in an orbit around the nucleus, μ_l in units of B.M. and (l) in units of $h/2\pi$ have the same magnitude, *viz.*, $\sqrt{l(l+1)}$ (cf. Eqs. 10 and 13). Both μ_l and (l) are vector quantities. These are collinear but *in opposite directions* and are perpendicular to the plane of the orbit.

Spin Magnetic Moment (μ_s). In order to explain certain spectral phenomena, Uhlenback and Goudsmit observed in 1926 that a moving electron possesses angular momentum in excess of orbital angular momentum. They ascribed the excess angular momentum to the spinning of the electron around its own axis. The negatively charged electron in its spin motion will also produce magnetic field whose moment is directed along the spin axis. They also postulated that the ratio of spin magnetic moment μ_s to the spin angular momentum (s) is twice the ratio of μ_l to (l) in their respective units of B.M. and $h/2\pi$. Since the ratio of μ_l to (l) in their respective units is 1, the ratio of μ_s to (s) should be 2. The ratio of spin magnetic moment to spin angular momentum is called **Lande splitting factor, g**. Thus,

$$\frac{\mu_s}{(s)} = \frac{\mu_s}{\sqrt{s(s+1)}} = g \qquad \ldots(14)$$

or

$$\mu_s = g\sqrt{s(s+1)} = 2\sqrt{s(s+1)}\ \text{B.M.} \qquad \ldots(15)$$

The spin angular momentum of the electron is equal to $\sqrt{s(s+1)}\, h/2\pi$ where s is the spin angular momentum quantum number. It is to be noted again that s and (s) represent different quantities. While (s) represents spin angular momentum, s represents spin angular momentum quantum number.

When we apply an external magnetic field, both μ_l and μ_s will interact with the applied magnetic field. Like small bar magnets, they will tend to align themselves (or their resultant will tend to align itself) with the applied magnetic field thereby reinforcing the applied magnetic field.

In a multielectron atom, which is of greater interest to us, the spin magnetic moments of individual electrons will interact with one another to give a resultant or an overall spin magnetic moment. In such a case we shall have to use the resultant spin angular momentum quantum number S for calculating the resultant spin magnetic moment, μ_S. Similarly, we shall have to use resultant orbital angular momentum quantum number L for calculating resultant orbital magnetic moment, μ_L.

The **overall magnetic moment** μ for a multielectron system will be a resultant of μ_S and μ_L provided (L) and (S) vectors do not couple or mix with each other. If (L) and (S) couple, then μ of the system will be calculated from the *resultant angular momentum quantum number J*.

Let us now explain the various types of magnetic phenomena encountered in magnetic studies of substances. These are : *1. Diamagnetism 2. Paramagnetism 3. Ferromagnetism* and *Antiferromagnetism*.

1. Diamagnetism

Diamagnetism arises from the motion of electrons, treated as charged particles, in an applied magnetic field. In a crude manner, it may be pictured as arising from the circulation of electric current in circular wires. The interaction between the electric current and the applied magnetic field causes the electronic orbits to precess (the Larmor precession) around the direction of the applied magnetic field. This Larmor precession of electronic orbits also produces a magnetic field whose direction is opposite to the direction of applied magnetic field. When a diamagnetic substance is placed in a magnetic field, the magnetic lines of force are deflected away from the substance. Diamagnetism is a very small effect but, since all materials contain electrons, it is invariably present in all substances. Importance of diamagnetism lies in the fact that the presence of a large number of diamagnetic atoms contributes appreciably towards the magnetic susceptibility of a substance. The atomic diamagnetic susceptibility per Avogadro's number of atoms of a material is mathematically given by the expression

$$\chi_A = -\frac{N_A e^2}{6mc^2}\sum_{i=1}^{i=n} \overline{r_i^2} = -2{\cdot}83\times10^{10}\sum_{i=1}^{i=n}\overline{r_i^2} \qquad ...(16)$$

where n is the number of electrons present in the atom, $\overline{r_i^2}$ is the mean square radius of the ith electron and N_A is Avogadro's number. Larger atoms with a larger number of electrons have greater diamagnetic susceptibility than smaller atoms with fewer electrons. The **molar diamagnetic susceptibility** of a compound, χ_{dia}, can be obtained to a good approximation by the summation of contributions from all the atoms and from all the bonds present in its molecule. The contributions from atoms are designated as χ_A and those from bonds are designated as χ_B. The values for χ_A and χ_B are referred to as **Pascal's constants** for the atoms and the bonds concerned.

The Pascal's constants for some common atoms and bonds are given in Table 5.

TABLE 5

Pascal's Constants for Atoms and Bonds

χ_A Values				χ_B Values	
Atom	χ_A ($\times10^{-6}$) (cm^3 mol^{-1})	Atom	χ_A ($\times10^{-6}$) (cm^3 mol^{-1})	Bond	χ_B ($\times10^{-6}$) (cm^3 mol^{-1})
H	−2·9	Br	−30·6	C=C	+5·5
C	−6·0	I	−44·6	C≡C	+0·8
C (aromatic)	−6·2	Mg^{2+}	−5·0	C=N	+8·2
N	−5·6	Zn^{2+}	−15·0	C≡N	+0·8
N (aromatic)	−4·6	Pb^{2+}	−32·0	N=N	+1·8
O	−4·6	Ca^{2+}	−10·4	N=O	+1·7
O_2 (carboxylate)	−7·9	Fe^{2+}	−12·8	C=O	+6·3
S	−15·0	Cu^{2+}	−12·8		
P	−26·3	Co^{2+}	−12·8		
F	−6·3	Ni^{2+}	−12·8		
Cl	−20·1				

Calculation of χ_{dia} with the help of Pascal's constants is illustrated below.

Calculation of χ_{dia} for pyridine,

Contributions of :

5 C atoms of aromatic ring	$= -31{\cdot}0\times10^{-6}$ cm^3 mol^{-1}
5 H atoms	$= -14{\cdot}5\times10^{-6}$ cm^3 mol^{-1}
1 N atom of aromatic ring	$= -4{\cdot}6\times10^{-6}$ cm^3 mol^{-1}
Total	$= -50{\cdot}1\times10^{-6}$ cm^3 mol^{-1}

Contributions of bonds is accounted for by using the ring values for carbon and nitrogen atoms.

Thus, χ_{dia} for pyridine $= \mathbf{-50{\cdot}1\times10^{-6}\ cm^3\ mol^{-1}}$

Calculation of χ_{dia} for acetone, $(CH_3)_2CO$:

Contributions of Atoms :

3 C atoms	$= -18{\cdot}0\times10^{-6}$ cm^3 mol^{-1}
6 H atoms	$= -17{\cdot}4\times10^{-6}$ cm^3 mol^{-1}
1 O atom	$= -4{\cdot}6\times10^{-6}$ cm^3 mol^{-1}

Contributions of Bonds :

1 C=O bond	$= +6{\cdot}3\times10^{-6}$ cm^3 mol^{-1}

Contributions of C–C and C–H bonds are known to be zero.

$$\therefore\ \chi_{dia} = \Sigma\chi_{Atom} + \Sigma\chi_{Bond} = -40{\cdot}0\times10^{-6}\ \text{cm}^3\ \text{mol}^{-1} + 6{\cdot}3\times10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$$

$$= \mathbf{-33{\cdot}7\times10^{-6}\ cm^3\ mol^{-1}}$$

It is to be noted that *diamagnetism is independent* of *temperature.*

Since in diamagnetic substances, the magnetic field induced is in the direction which is opposite to the direction of the magnetic field applied, χ_{dia} is always negative.

2. Paramagnetism

Substances which are freely magnetised in the direction of the magnetising field in which they are placed, are called **paramagnetic substances.** When a paramagnetic substance is placed in a magnetising field, the magnetic lines of force prefer to pass through the specimen rather than through air. That is, for such substances $B > H$ or $B/H > 1$ so that K is always positive.

Systems containing one or more unpaired electrons have a permanent magnetic moment, *i.e.,* the individual atoms or molecules of such substances behave as permanent magnets. This is because all the magnetic moments of electrons in these atoms or molecules do not cancel one another. Such atoms or molecules of paramagnetic substances which individually behave as permanent magnets are randomly oriented in the absence of an external magnetic field so that the net magnetic moment in these substances is zero.

When a paramagnetic substance is placed in an external magnetic field, the individual atoms or molecules behaving as permanent magnets align themselves in the same direction as that of the external field and are thus attracted towards the field. As a result, the paramagnetic substances allow a larger number of magnetic lines of induction to pass through them than through air. Magnetic susceptibility for such substances would be positive, as already mentioned. Since the number of atoms or molecules behaving as permanent magnets present in a unit volume of a substance is fixed, the magnetic susceptibility shown by the substance would be independent of the strength of the external field applied. However, the magnetic susceptibility of the substance would depend upon the temperature since the thermal agitation would tend to randomise the 'atomic' or 'molecular' magnetic dipoles which get aligned in the direction of the magnetic field applied. The magnetic susceptibility of a paramagnetic substance, χ_{para}, would, therefore, decrease with increase in temperature. The variation of χ_{para} with temperature is expressed as

$$\chi_{para} = C/T \qquad ...(17)$$

where C is a constant known as the Curie constant. The relation expressed by Eq. 17 is known as the **Curie law.**

It is observed, however, that for most of the substances, a plot of χ_{para} vs $1/T$ does not pass through the origin, *i.e.,* the Curie law is not obeyed. Curie and Weiss suggested the following correlation to account for the variation of χ_{para} with temperature.

$$\chi_{para} = C/(T-\theta) \qquad ...(18)$$

where θ is known as the Weiss constant. The above correlation, which is known as the **Curie-Weiss law,** is found to be more appropriate than the Curie law.

It is to be noted that magnetic susceptibility for paramagnetic substances measured experimentally is, in fact, the *net* magnetic susceptibility which is the sum of paramagnet (χ_{para}) and diamagnetic (χ_{dia}) contributions. Thus, to obtain the paramagnetic susceptibility, the diamagnetic susceptibility has to be subtracted from the net susceptibility. The diamagnetic susceptibility is obtained with the help of the Pascal's constants given in Table 5, as illustrated above. For precise work, the paramagnetic susceptibility, χ_{para}, is further corrected for temperature-independent paramagnetism which arises out of the mixing of the ground and excited states of the atoms or molecules under the influence of the applied magnetic field. Due to this mixing, there is a small contribution towards χ_{para} even in the absence of unpaired electrons in the substance. A detailed discussion of temperature-independent paramagnetism is beyond the scope of the book. Magnetic susceptibility corrected for diamagnetism and temperature-independent paramagnetism is designated as χ_{para}^{corr}. It can be shown from quantum mechanical calculations that

$$\chi_{para}^{corr} = N_A \mu_{eff}^2 / 3kT \qquad \text{... (19)}$$

where μ_{eff} is magnetic moment (in B.M.) per mole of the substance, N_A is Avogadro's number, k is Boltzmann constant and T is the absolute temperature. Substituting the values of various constants in Eq. 19, we get

$$\mu_{eff} = 2{\cdot}84\sqrt{\chi_{para}^{corr} T} \text{ B.M.} \qquad \text{... (20)}$$

Measurement of Magnetic Susceptibility

The most common technique employed for measuring magnetic susceptibility is the Guoy's method. However, some other methods such as Evan's NMR method, Faraday's method, Quinke's method are also used for measuring magnetic susceptibility. All these methods are described below.

1. Guoy's Method. The Guoy's method, in brief, consists in placing the sample under examination in a magnetic field and measuring its **weight** (mass × gravity). The apparatus is shown in Fig. 42.

The pole pieces of the magnet are usually cylindrical so that the magnetic field is symmetrical about the axis of the magnet. The magnetic field is strongest at the centre where the bottom of the sample column is placed. The magnetic field falls off rapidly in radial directions so that it is very small at the top of the sample column. The sample is taken either as a uniformly packed solid or as solution in a glass tube suspended from the balance. Under these conditions, there is an apparent change in the weight of the sample when the magnetic field is turned on. The change in weight of the sample is related to the magnetic susceptibility of the magnetic substance as follows :

$$\chi_1 = \frac{k_2 v + \left(\frac{2l}{H^2}\right) W}{W}$$

The derivation of this relation is given below.

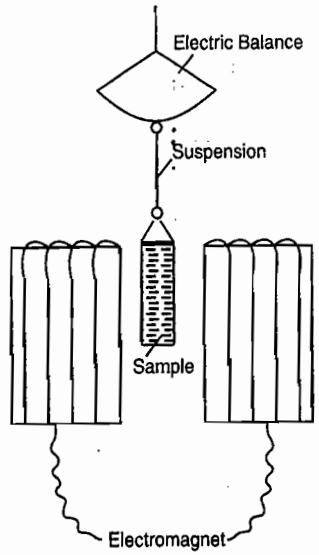


Fig. 42. Guoy's balance for measurement of magnetic susceptibility.

If the field gradient over the volume element dv of the sample is dH/dl, the force exerted by the magnetic field on the volume element dv is given by

$$dF = (k_1 - k_2)\, dv\, H\, (dH/dl) \qquad \text{...(21)}$$

$$= (k_1 - k_2)\, dl\, H\, (dH/dl) \qquad \text{...(22)}$$

$$= (k_1 - k_2)\, AH\Delta H$$

where k_1, k_2 are the volume susceptibilities of the sample and of the displaced medium (usually air), respectively, A is the area of cross-section of the tube of length l in which the sample is packed, dl is the length element corresponding to the volume element dv ; H is the strength of the magnetic field which is maximum at the bottom of the tube and approaches zero at the top of the sample.

Integrating both sides, we get

$$F = (k_1 - k_2) A \left[\frac{H^2}{2}\right]_0^H = (k_1 - k_2)\, AH^2/2 \qquad \text{...(23)}$$

The force F exerted by the magnetic field on the entire sample is equal to the *difference in the weights* of the sample when the field is switched off and switched on. Let us say it is w (= mg). The above equation, thus, becomes

$$w = (k_1 - k_2) AH^2/2 \qquad \text{...(24)}$$

or

$$\frac{2w}{AH^2} + k_2 = k_1 = \chi_1 \rho_1 = \chi_1 \frac{W}{v} \qquad \text{...(25)}$$

where χ_1 is the gram magnetic susceptibility of the sample, W is the actual weight of the sample, ρ_1 is the density of the sample and v is the volume of the sample.

$$\therefore \quad \chi_1 = \frac{v}{W}\left(\frac{2w}{AH^2} + k_2\right) = \frac{\frac{2wAl}{AH^2} + k_2 v}{W}$$

$$= \frac{k_2 v + \left(\frac{2l}{H^2}\right) w}{W} \qquad \text{...(26)}$$

k_2 for air is $+ 0{\cdot}029 \times 10^{-6}$. The volume v is determined by filling the tube with water upto that mark to which the sample was packed earlier. The temperature at which the experiment was carried out is recorded. Knowing the weight of water and its temperature, the volume of the tube upto which the sample was packed can be worked out.

The quantity $2l/H^2$ is dertermined by filling the powdered compound of known χ upto the same mark and recording the difference in the weights of the sample in the presence of the magnetic field and in its absence. Due correction is applied for the diamagnetism of the glass tube in which the sample is packed.

Suppose the weight of the glass tube without switching on the magnetic field is T and with switching on the magnetic field is $T + w_t$. Since glass is diamagnetic, w_t is a negative quantity so that the weight of the glass tube on switching on the magnetic field would decrease. Let us suppose that the weight of the glass tube filled with the sample without switching on the magnetic field is $T + W$ and on switching on the magnetic field, it is $T + w_t + W'$. Then the weight of the sample without switching on the magnetic field is $T + W - T = W$ and the weight of the sample on switching on the magnetic field is $T + w_t + W' - (T + w_t) = W'$. Hence, the change in the weight of the sample on switching on the magnetic field is $W' - W = w$.

The standard calibrant used for the measurement of magnetic susceptibility of solids is generally $Hg[Co(NCS)_4]$ which has χ equal to $+ 16{\cdot}44 \times 10^{-6}$ at 20°C, *decreasing* by $0{\cdot}05 \times 10^{-6}$ per degree rise in temperature. For measurement of magnetic susceptibility of solutions, a liquid calibrant is preferred. Water can be used as a calibrant. The χ of deoxygenated pure water is $- 0{\cdot}720 \times 10^{-6}$ at 20°C, *increasing* by $0{\cdot}0009 \times 10^{-6}$ per degree rise in temperature. A solution of Cs_2CoCl_4 (made directly from known amounts of CsCl and $CoCl_2.4H_2O$) can also be used as standard calibrant. The χ of this solution is given by

$$\chi = \left[\frac{6867f}{T+18} - 0{\cdot}72(1-f)\right] \times 10^{-6} \qquad \text{...(27)}$$

where f is the fraction by weight of Cs_2CoCl_4 and T is the temperature measured in K. A special apparatus is devised for measuring χ of samples at variable temperatures.

Sources of Error. 1. Loose packing of the sample leads to error in the volume of the sample.

2. There can be balance error in noting the change of weight of the sample, especially in the case of samples with low χ where change in weight is very small.

3. Lateral oscillations of the sample may cause error in weighing. Therefore, the apparatus must be kept in oscillation-free environments.

2. Evan's NMR Method. An NMR method has been devised by Evan for measuring magnetic susceptibility of paramagnetic substances in solution. In this method, a solution of the paramagnetic complex containing an internal standard (tetramethyl silance, abbreviated as TMS for non-aqueous solutions and tertiary butyl alcohol for aqueous solutions) is added to an inner tube whose length is far greater than its diameter. A solution of the same internal standard in the same solvent, the solution having the same concentration, is placed in the outer NMR tube. The inner tube is placed at the centre of the outer tube and is made coaxial with it, as shown in Fig. 43. When the tubes are spun and nmr recorded, two separate nmr lines, one corresponding to the internal standard in the pure solvent and the other corresponding to the internal standard present in the paramagnetic solution, would be observed because of different magnetic environments of the protons of the internal standard in the solution. The nmr signal of protons of the internal standard in the paramagnetic solution of the inner tube lies at a higher frequency. The contribution of magnetic susceptibility of the paramagnetic sample towards the absolute chemical shift of the nucleus, *viz.*, $\Delta\nu/\nu_0$, is given by

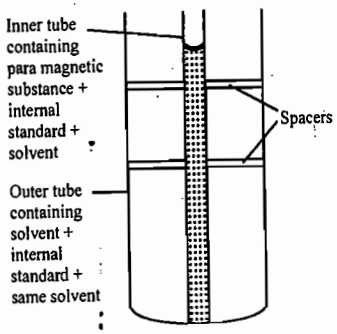


Fig. 43. Paramagnetic substance placed in a narrow tube enclosed in the NMR tube.

$$\frac{\Delta\nu}{\nu_0} = m\left(\frac{1}{3} - \alpha\right)\left[\chi - \chi_0\left(1 + \frac{\rho_0 - \rho_s}{m}\right)\right] \quad ...(28)$$

where $\Delta\nu$ is the difference in the nmr frequencies of the internal standard in the paramagnetic solution and in the solvent, ν_0 is the frequency of the NMR spectrometer, m is the mass of the paramagnetic solute in gram per cc, ρ_0 and ρ_s are the densities of the pure solvent and the solution and χ and χ_0 are gram magnetic susceptibilties per cc of the solution of the paramagnetic solute and of the pure solvent. The susceptibility χ_0 of the solvent is negative since the solvent is diamagnetic. For dilute solutions, ρ_0 is almost the same as ρ_s, that is, $\rho_0 - \rho_s \approx 0$ and, therefore, $(\rho_0 - \rho_s)/m \approx 0$. α is demagnetisation factor depending upon the direction of the magnetic field and the direction of the axis of the cylindrical sample tube.

The χ observed is related to χ_{para} and χ_{dia} by the expression

$$\chi_{observed} = \chi_{para} + \chi_{dia} \quad ...(29)$$

where χ_{dia} is diamagnetic susceptibility of the paramagnetic solution and is a negative quantity.

The measurement of χ_{dia} is, however, eliminated, as follows:

Another experiment is carried out in which the inner capillary tube is now filled with a solution of an analogous diamagnetic complex (*e.g.*, a complex of Zn^{2+}) having the same concentration in the same solvent and with the same internal standard. The outer tube contains the pure solvent with the same internal standard dissolved in it as in the main experiment. The frequencies of nmr signals of protons of internal standard obtained

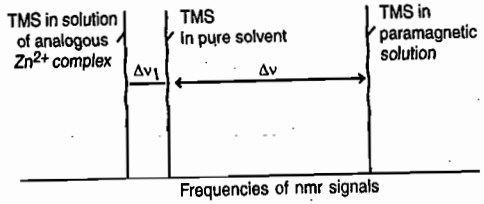


Fig. 44. Frequencies of nmr signals of protons of internal standard obtained under different conditions.

The chemical shift is now given by the equation

$$\frac{\Delta\nu_1}{\nu_0} = m\left(\frac{1}{3} - \alpha\right)\left[\chi_{dia} - \chi_0\left(1 + \frac{\rho_0 - \rho_s}{m}\right)\right] \quad ...(30)$$

since the contribution towards chemical shift is now predominantly from the diamagnetic ligands of the complex. Obviously, $\Delta\nu_1$ is now the difference in the frequencies of the nmr signals of the internal standard in the solution of the Zn^{2+} complex and in the solvent. It is a negative quantity. Also, for dilute solution $\rho_0 \approx \rho_s$ and, therefore, $\rho_0 - \rho_s/m \approx 0$.

Substracting Eq. 30 from Eq. 28, we get

$$\frac{\Delta\nu - \nu_1}{\nu_0} = m\left(\frac{1}{3} - \alpha\right)[\chi - \chi_{dia}] \quad ...(31)$$

$$= m\left(\frac{1}{3} - \alpha\right)\chi_{para} \quad \text{(vide Eq. 29)} \quad ...(32)$$

Thus, χ_{dia} gets eliminated.

Knowing χ_{para}, *viz.*, gram paramagnetic susceptibility per cc, from Eq. 32, the molar magnetic susceptibility, *i.e.*, susceptibility for 1 mole of the paramagnetic complex dissolved in 1000 cc of the solution can be easily calculated. Evidently, molar magnetic susceptibility will be equal to $1000 \times \chi_{para} \times M$ where M is the molar mass of the complex.

The Evan's method is particularly useful for working with *dilute* paramagnetic solutions. The Guoy's method in such cases is not suitable because the change in weight which is required to be measured in Guoy's method is insignificant in dilute solutions.

3. Faraday's Method. Eq. 21, appearing d in the derivation of the equation used in Guoy's method, can be written as

$$\partial F = (k_1 - k_2)\, dv\, H\frac{dH}{dl} \quad ...(33)$$

If the overall volume v of the sample is very small, then l of $A \times l$ (*i.e.*, v) is also very small (A is the area of cross section of the sample holder and l is the length upto which the sample is packed). In that case, $H\left(\frac{dH}{dl}\right)$ is practically constant over the *entire* sample. Let it be written as K. Hence, the above equation, on integration, gives

$$F = (k_1 - k_2)\, vHK \quad ...(34)$$

The force F is measured in terms of increase in the weight w (= mg) of the paramagnetic substance on the application of the magnetic field so that

$$F = w = (k_1 - k_2)\, vK \quad ...(35)$$

But,

$$k_1 = \chi_1\rho_1 = \chi_1 W/v \quad ...(36)$$

where χ_1, ρ_1 and W are the magnetic susceptibility, the density and the weight (without applying magnetic field) of the sample, respectively.

$$\therefore \quad w = (\chi_1(W/v) - k_2)\, vK = (\chi_1 W - k_2 v)\, K \quad ...(37)$$

or

$$\frac{w}{K} = \chi_1 W - k_2 v \quad ...(38)$$

where $K = H\dfrac{dH}{dl}$

or
$$\chi_1 = \left[w\left(\frac{1}{K}\right) + k_2 v \right] / W \qquad ...(39)$$

Since in Faraday's method, the volume of the sample has to be very small, the change in weight on applying external magnetic field is also very small. Hence, highly sensitive weighing techniques such as quartz fibre torsion balance and Sucksmith ring balance are used in noting the changes in weights of the samples in Faraday's method. These balances have accuracies greater than 10^{-7} g.

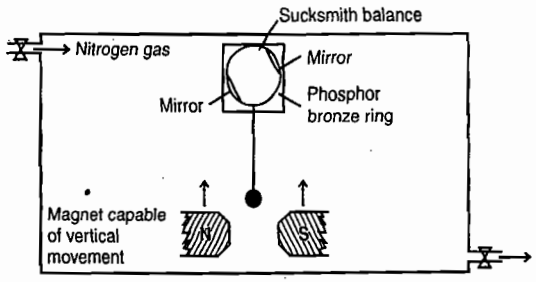


Fig. 45. Measurement of magnetic susceptibility by Faraday's method (using Sucksmith ring balance).

A **Sucksmith ring balance** used in Faraday's method consists of a phosphor bronze ring fixed at the top with specimen suspension attached to the bottom. The force exerted on the specimen by the magnetic field deforms the ring. This deformation is magnified about 200 times optically and recorded with a fair degree of accuracy.

For measurement at room temperature, only a small electromagnet is sufficient. The sample is place in a fused quartz bucket of small length and of about 1 mm diameter. The magnet is moved vertically from below the sample to a position above it. The balance readings are taken as the magnet is moved stepwise and the *difference* between the maximum weight and minimum weight recorded is taken as the change in weight of the sample resulting from the application of the magnetic field. The entire balance, the suspension and the sample system must have vibration-free environment. The evaluation of $k_2 v$ of Eq. 39 is eliminated by flushing the enclosed aparatus thoroughly with nitrogen gas which has $k \approx 0$. The appartus can be calibrated by working with a sample of known χ so that every quantity in Eq. 39, except $1K$, is known. This allows evaluation of $1/K$. Knowing w and W, the magnetic susceptibility χ_1 of the substance under investingation can be calculated.

Some of the **advantages** of Faraday's method are :

1. The apparatus is very compact.
2. Only a small amount of the sample is required for magnetic measurements.
3. The apparatus, with slight modification, can be used for measuring χ at different temeperatures.
4. The accuracy of the method is better than that of the Guoy's method.
5. The magnetic anisotropy of a single crystal of the sample can be studied by mounting the crystal along different axes.

However, the Faraday's method has some **disadvantages** also. These are :

1. Since the amount of the simple taken in this method is very small, even minute amounts of impurities can lead to big errors.
2. The sample has to be in a very *fine state of division*.
3. The equipment used is very delicate and needs to be handled with utmost care.
4. The equipment is unsuitable for measuring χ of solutions since even small amount of evaporation of the solvent can cause considerable error.

4. Quinke's Method. This method can be used for making magnetic measurements on solutions as well as on gases. In this method, a column of liquid is subjected to a magnetic field H which is maximum at the level of the meniscus but falls to zero at the bottom of the column, as shown in Fig. 46.

As discussed in Guoy's method, the force F exerted by an external magnetic field H on a paramagnetic sample is given by

$$F = \tfrac{1}{2}(k_1 - k_2)AH^2 \quad \text{(Eq. 23)} \qquad ...(40)$$

where k_1 is the volume magnetic susceptibility of the liquid, k_2 is the volume magnetic susceptibility of the gas above the liquid column and A is the area of cross section of the capillary tube containing the liquid. The pressure P of the liquid column is thus given by

$$P = F/A = 1/2(k_1 - k_2)H^2 \qquad ...(41)$$

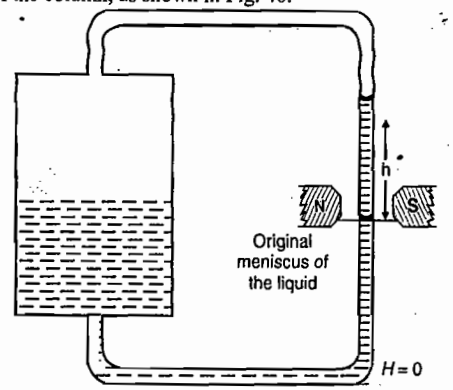


Fig. 46. Quinke's apparatus for measuring magnetic susceptibility.

When the magnetic field is switched on, the level of the liquid column rises if the liquid is paramagnetic and it falls if the liquid is diamagnetic with respect to the gas above the liquid. If the surface area of the reservoir containing the liquid is very large, the level of the liquid in the reservoir will remain unaffected by any change in the height of the liquid column in the capillary tube. Let h be the change in the height of the liquid column in the capillary tube containing the paramagnetic liquid when the magnetic field is switched on. Then,

$$P = h\rho_1 g = \tfrac{1}{2}(k_1 - k_2)H^2$$

or
$$\frac{2h\rho_1 g}{H^2} + k_2 = k_1 = \chi_1 \rho_1 \qquad ...(42)$$

where χ_1 and ρ_1 are gram magnetic susceptibility and density, respectively, of the liquid. The change in the height of the liquid (h) is measured with the help of a travelling microscope. The whole apparatus is kept in an enclosure whose temperature is kept constant by circulating water into it from a thermostat.

The apparatus is calibrated by using a liquid of known density (ρ) and magnetic susceptibility (χ) and by keeping the same gas above the liquid. If the volume magnetic susceptibility of the gas above the liquid (k_2) is known, the factor ($2g/H^2$) can be calculated from Eq. 42. Thus, knowing ($2g/H^2$), h, ρ_1 and k_2, the magnetic susceptibility of (χ_1) of the liquid under investigation can be calculated. Alternatively, if the magnetic susceptibility of the liquid (χ_1) is known, k_2 and hence χ_2 of the gas above the liquid can be determined.

We can also employ the 'null method' for determining magnetic susceptiblity of a liquid : After a change in the height of the liquid column (h) has occurred due to switching on the magnetic field, the pressure of the gas above the liquid is changed to bring back the liquid column to its original position in the capillary tube. Let P be the **change** in pressure. Eq. 42 can thus be rearranged as

$$2P/H^2 + k_2 = \chi_1 \rho_1 \qquad ...(43)$$

The apparatus is calibrated by using a liquid of known ρ and χ. Thus, knowing k_2, the volume magnetic susceptiblity of the gas used, $1/H^2$ of Eq. 43 is evaluated. Further, knowing the change in pressure (P), density of the liquid (ρ_1) and k_2 of the gas, the magnetic susceptibility of the liquid under investigation can be calculated with the help of Eq. 43.

Magnetic Titrations

If the addition of a reagent to a particular compound causes a change in the number of unpaired electrons in the compound, then the course of the reaction can be followed by conducting magnetic measurements after each addition of a fixed volume of the solution of the reagent. The apparatus, as shown in Fig. 47, is attached to a Guoy balance and the change in weight w (*i.e.*, the difference in weight with and without the application of the magnetic field) is noted after each addition of a fixed volume of the reagent solution. Apart from changing the weight of the solution during titration, the effect of adding the reagent solution to the sample under investigation is also to dilute the reactants and thereby to alter the field gradient acting over the reactants. In order to apply correction for this effect and to estimate the correct change in weight, a fresh lot of the same volume of the same solution of the compound is taken and diluted each time with the same volume of the *pure solvent* (instead of the reagent solution) and the 'blank titration' carried out by noting the change in weight. The corrected values of w are then plotted against the moles of the reagent added. A change in slope (Fig. 48) indicates the formation of the compound having different number of unpaired electrons and thereby having different magnetic moment compared to the original compound which has been titrated magnetically with the reagent.

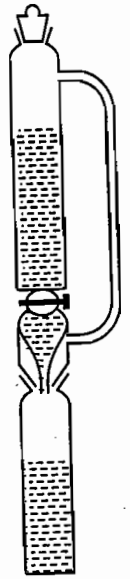


Fig. 47. Magnetic titration apparatus which is attached with Guey balance.

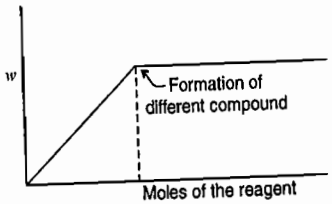


Fig. 48. Plot of w (the difference in weight) *vs* moles of the reagent.

It may be mentioned in passing that it is possible to calculate the formation constants of complexes by magnetic titrations involving reactants and products having different magnetic moments in solution.

3. Ferromagnetism and Antiferromagnetism

In magnetically dilute substances, *i.e.*, substances in which the metal ions containing unpaired electrons are isolated from one another by a cluster of ligands, each paramagnetic metal ion will act independent of other such ions because the distance between the metal ions is too large to allow the paramagnetic spin (*i.e.*, the total electron spin of the metal ion which is responsible for paramagnetism) of one ion to interact with that of the other ion. But, this is not the case in magnetically concentrated substances, *i.e.*, substances in which the paramagnetic metal ions allow their total electron spins to interact with one another through exchange interaction.

If we neglect the contribution of orbital magnetic moment and assume that only the spin magnetic moment contributes towards μ_{eff} of a magnetically concentrated substance, then ΔE, the energy of spin interaction of paramagnetic ions in such a substance is given by

$$\Delta E = 2J(S)_i(S)_k \qquad ...(44)$$

where $(S)_i$ and $(S)_k$ are the total electron spins of the ith and kth metal ion of the substance. J is known as exchange coupling constant (it is not to be confused with spin–orbital coupling constant). J is a measure of the strength of interaction between the total electron spins of the metal ions.

If J is positive, then the total electron spins, *i.e.*, $(S)_s$ of all the paramagnetic ions in the magnetically concentrated substance in the ground state *get aligned in the same direction*. This phenomenon is called **ferromagnetism.**

If J is negative, then the total electron spins, *i.e.*, $(S)_s$ of all the paramagnetic ions in the magnetically concentrated substance in ground state are *paired up*. This is called **antiferromagnetism.**

The ferromagnetic alignments of spins produce χ greatly in excess of that produced by normal paramagnetic alignments below a particular temperature. Unlike in normal paramagnetic substances, χ in ferromagnetic substances is dependent on the strength of the magnetic field applied. Fig. 49 shows the variation of χ with temperature for a ferromagnetic substance. The χ vs T graph for a paramagnetic substance is also given for the sake of comparison.

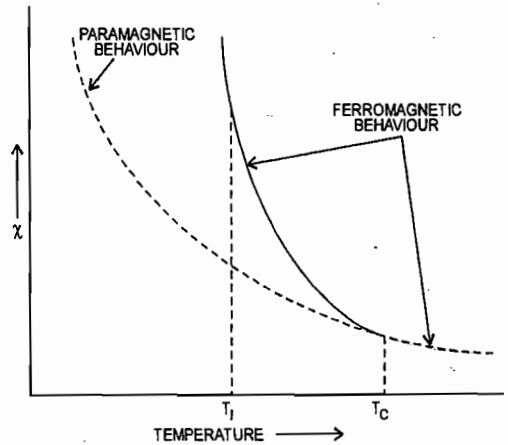


Fig. 49. Variation of χ with temperature for a ferromagnetic substance.

The ferromagnetic behaviour of a substance exists upto a particular temperature, known as Curie temperature or **Curie point,** T_c. Above this temperature, the substance starts behaving as a normal paramagnetic substance. It can be seen from the graph that below T_c, say, at T_1, χ for a ferromagnetic substance is much higher than χ for a normal paramagnetic substance. It does not obey Curie-Weiss law (Eq. 18) in this range. But, above this temperature, the ferromagnetic substance obeys Curie-Weiss law.

The total electron spin vectors $(S)_s$ of atoms or ions in a ferromagnetic material are all coupled parallel to one another in groups or domains. There are many domains of this type in a ferromagnetic material. The magnetic moments of these domains are oriented in different directions in the absence of an external magnetic field with the result that these magnetic moments average out to be zero. When, however, the substance is placed in a magnetic field, the magnetic moments of all the domains start aligning parallel to the direction of the applied field. The magnetic moments of more and more domains align as we go on increasing the strength of the applied field till at a particular strength of the field, the magnetic moments of almost all the domains get aligned parallel to the direction of the field. Beyond this field strength, χ of the substance will not increase with increase in the strength of the field.

The tendency of magnetic moments of domains to align in the presence of an external magnetic field is opposed by thermal agitation which tends to randomise the magnetic moments of domains. However, the thermal energy is not always able to randomise the magnetic moments once these have been aligned. This results in the retention of magnetic moments of domains in a ferromagnetic substance even after the external field has been switched off. This phenomenon is known as **hysteresis.**

Antiferromagnetic spin exchange interactions cause a lowering of χ. *In cases where total electron spins* of neighbouring metal ions interact directly without any intervening diamagnetic ions, the pairing of total electron spins occurs through the overlapping of orbitals of metal ions leading to the formation of normal covalent bonds. In extreme cases, it results in total electron spin pairing as in $[Fe_2(CO)_9]$, $[W_2Cl_9]^{3+}$, etc. However, in most of the antiferromagnetic substances, the electron spin interactions leading to the pairing of total electron spins of neighbouring metal ions occurs through the intervening diamagnetic atoms or ions even if the paramagnetic metal ions of antiferromagnetic substances are very close. This type of

total electron spin exchange occurs through linear O^{2-} or F^- bridges lying in between the paramagnetic metal ions of a ferromagnetic substance. This is illustrated in Fig. 50.

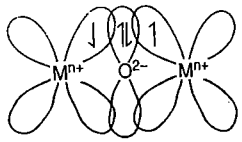


Fig. 50. Exchange of electron spin.

If we do not take into consideration the intervening diamagnetic ions, each paramagnetic ion is surrounded from all sides by similar paramagnetic ions of opposite electron spins each of which, in turn, is surrounded by paramagnetic ions having the same electron spin as that of the first ion and so on (Fig. 51). Such a system is thus said to consist of interpenetrating ferromagnetic lattices. Examples of this type of antiferromagnetic materials are MnO, NiO and KMF_3 where M is a bivalent paramagnetic metal ion

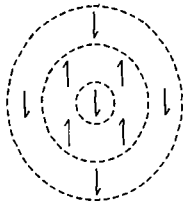


Fig. 51. A system of interpenetrating ferromagnetic lattices.

The possible mechanism of pairing of total electron spins in neighbouring Mn^{2+} ions in MnO may now be considered. As shown in Fig. 52, each Mn^{2+} ion has all the *d* orbitals half-filled. Maximum stability will be attained if the spins of all the five electrons in one Mn^{2+} ion are parallel while those in the other Mn^{2+} ion are antiparallel, as shown. One of the *d* orbitals of Mn^{2+} ion (state I) containing one electron overlaps with a similar *d* orbital of Mn^{2+} ion (state II) but in which the electron has opposite spin, through an O^{2-} bridge (*i.e.*, through an electron pair of O^{2-}) to yield stable MnO.

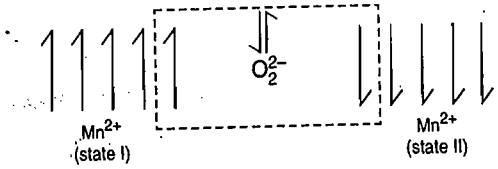


Fig. 52. Mechanism of pairing of total electron spins in Mn^{2+} ions in MnO.

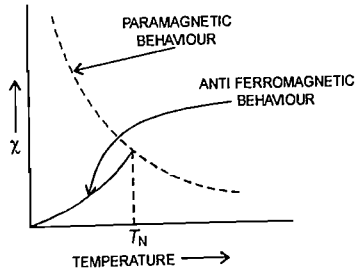


Fig. 53. Variation of χ with temperature for an antiferromagnetic substance.

The above type of antiferromagnetism can be decreased by dissolving the substance in a solvent in which the intervening diamagnetic ions get replaced by bulkier solvent molecules due to solvation. Alternatively, antiferromagnetism of a substance may be diluted by adding a diamagnetic isomorphous solid.

Antiferromagnetism is very much temperature-dependent. The variation of χ with temperature for an antiferromagnetic substance is shown in Fig. 53. The χ vs *T* graph for a paramagnetic substance is also shown in the figure for the sake of comparison.

For antiferromagnetic substances also, there is a characteristic temperature, known as **Neel temperature** or **Neel point, T_N** above which the antiferromagnetic substance behaves as a normal paramagnetic substance. But, below the Neel point, χ decreases with decrease in temperature, as shown in the figure. The reason for this type of behaviour is discussed below.

As is clear from earlier discussion on antiferromagnetism, the coupling of total electron spins (called electron spin pair interactions) of atoms or ions of a substance are responsible for its antiferromagnetic behaviour. But, the thermal energy tends to decouple and randomise these coupled total electron spins.

At the Neel point, the thermal energy available to the antiferromagnetic system is comparable to the energy of electron spin pair interaction (the two energies have opposite signs). Electron spin pair interactions decrease the energy of the system. Therefore, at the Neel point, both the coupled total

electron spins and the uncoupled and randomised total electron spins of atoms or ions of the substance, are equally probable.

Above the Neel point, no coupling of total electron spins (or no electron spin pair interactions) are possible and only the uncoupled and completely randomised total electron spins of atoms or ions exist, as happens in the case of a paramagnetic substance. Therefore, at temperatures above the Neel point, the antiferromagnetic substances behave as paramagnetic substances because the randomly oriented total electron spins tend to align along the applied magnetic field. Like other paramagnetic substances, χ in these substances is also inversely proportional to temperature measured above the Neel point.

Below the Neel point, the thermal energy available to an antiferromagnetic system is less than the energy of electron spin pair interactions. Therefore, below the Neel point as we go on decreasing thetemperature, the uncoupling and randomisation of total electron spins goes on decreasing and the extent of coupling of total electron spins goes on increasing. As a result, below the Neel point, the antiferromagnetic character of a substance which is directly related to the extent of electron spin pair interactions (or to the extent of coupling of total electron spins) goes on increasing with decrease in temperature. In other words, below the Neel point, χ decreases with decrease in temperature (*i.e.*, $\chi \propto T$) in antiferromagnetic substances.

Intramolecular antiferromagnetism occurs when the electron spins of the metal ions belonging to the same molecule of a polynuclear chemical species get coupled. An example of this type of antiferromagnetic material is provided by copper acetate, $Cu_2(OOCCH_3)_4.2H_2O$ (Fig. 54)

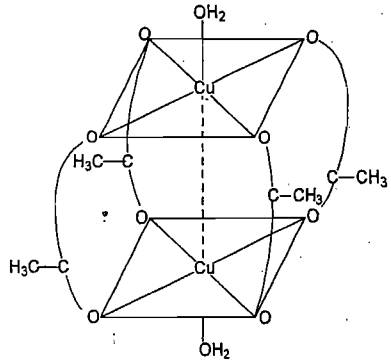


Fig. 54. Origin of antiferromagnetism.

The various types of magnetism and their characteristics are summed up in Table 6.

TABLE 6

Types of Magnetism and Their Characteristics

Type of magnetism	Approximate magnitude of χ in $cm^3\ mol^{-1}$	Sign of χ	Dependence on applied magnetic field	Origin of magnetism
Diamagnetism	10^{-6}	Negative	Independent	Field induced, paired electron circulations
Paramagnetism	$0–10^{-4}$	Positive	Independent	Angular momentum of electron
Ferromagnetism	$10^{-2}–10^{-4}$	Positive	Dependent	Electron spin exchange ⇅ (*J* is positive)
Antiferromagnetism	$0–10^{-4}$	Positive	May depend	Electron spin exchange ⇅ (*J* is negative)

MAGNETIC BEHAVIOUR OF TRANSITION METAL COMPLEXES

The various aspects of magnetic behaviour of transition metal complexes such as theoretical background, valence bond approach and crystal field approach would now be discussed in some details.

I. Theoretical Background

The magnetic moment originating from the spin of a free electron, μ_s, is given by

$$\mu_s = g\sqrt{s(s+1)} \quad \text{B.M.} \qquad \ldots(45)$$

where *s* is the spin of the free electron and *g* is magnetogyric ratio or Lande splitting factor. As is obvious from Eq. 45, *g* is the ratio of magnetic moment to the spin angular momentum. (Since there is no orbital

angular momentum associated with free electron, g for free electron is the ratio of magnetic moment to spin angular momentum given by $\sqrt{s(s+)}$.

The Lande splitting factor for any chemical species containing unpaired electrons can be calculated with the help of the relation

$$g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \quad \ldots (46)$$

where L and J are, respectively, the resultant orbital angular momentum quantum number and overall angular momentum quantum number.

Since a free electron has no orbital angular momentum, hence $L=0$. Therefore,

$$g = 1 + \frac{S(S+1) + J(J+1)}{2J(J+1)}$$

$$= 1 + \frac{S(S+1) + S(S+1)}{2S(S+1)} \qquad (\because J = S \text{ if } L = 0)$$

$$= 1 + 1 = 2$$

Therefore, $\mu_{s.o.}$ for a free electron is equal to $2\sqrt{1/2(1/2+1)} = 1{\cdot}73$ B.M.

If, however, the electron is not free and is a part of a chemical unit, *i.e.*, if it is present on a metal ion of a complex, the magnetic moment μ may depend on the orbital angular momentum in addition to the spin angular momentum depending upon the nature of the metal ion and its environment.

The paramagnetic properties of metal ions may be divided into the following categories :

1. When energy separations (ΔE) between J states are greater than kT. When the unpaired electrons of a metal ion are well shielded from the outer influence, the resultant orbital angular momentum (L) of electrons is retained or L of the metal ion is a good quantum number. Therefore, the coupling of (L) and (S) yielding overall spin angular momentum (J) is quite significant. If the lowest energy state of such a metal ion is considerably separated from the adjacent excited state so that the energy difference ΔE between the two states is greater than kT at room temperature, then only the lowest energy state of the metal ion will be occupied. The magnetic moment for such an atom is given by

$$\mu_{eff} = g\sqrt{J(J+1)} \quad \ldots (47)$$

where g, as mentioned before, is Lande splitting factor and J is the overall angular momentum quantum number corresponding to overall angular momentum (J) of the lowest energy state. J is a good quantum number because of significant (L)–(S) coupling. This type of paramagnetism (or μ_{eff}) is independent of the geometry or environment around the metal ion and the extent of magnetic dilution. Magnetic dilution means increasing the distance between paramagnetic metal ions by incorporating diamagnetic atoms, molecules or ions in between them, as, for example, by dissolving the material in a solvent or by doping the metal ion salt with isomorphous diamagnetic material.

This category of paramagnetism is found in lanthanide ions in which electrons in incomplete d or f shells are well shielded by other electrons present in outer shells and the separation (ΔE) between the adjacent J states of lanthanide ions are comparable to separation between adjacent energy terms arising due to interelectronic repulsion energies (~ 1000 cm^{-1}). The J states in such cases are well separated from one another so that at ordinary temperatures, only the lowest J state is occupied by such metal ions, that is, ΔE in such cases is larger than kT. The magnetic moments, μ_{eff}, obtained for lanthanide ions are in close agreement with μ_{eff} calculated by the relation, $\mu_{eff} = g\sqrt{J(J+1)}$ except for Sm^{3+} and Eu^{3+} in which cases the ground state is close to the excited state so that $\Delta E \simeq kT$. Therefore, a fraction of these ions will be present in higher J states also at room temperature according to Boltzmann's distribution law. In such cases, μ_{eff} calculated only by taking J of the ground state (*i.e.*, by assuming that all the ions occupy only the ground J state) will not give the correct magnetic moment of the system.

The μ_{eff} values calculated and actually observed in the case of lanthanide ions are shown in Table 7.

TABLE 7

Calculated and Experimentally Observed Values of μ_{eff} for Lanthanide Ions

Number of f electrons	Lanthanide Ions M^{3+}	Ground state	Lande splitting factor, g	Magnetic Moments, μ_{eff} (B.M.)	
				Calculated	Experimentally observed
0	La	$^1S_0$	–	0	diamagnetic
1	Ce	$^2F_{5/2}$	6/7	2·54	2·3–2·5
2	Pr	$^3H_4$	4/5	3·58	3·4–3·6
3	Nd	$^4I_{9/2}$	8/11	3·62	3·5–3·6
4	Pm	$^5I_4$	3/5	2·68	–
5	Sm	$^6H_{5/2}$	2/7	0·84	1·5–1·6
6	Eu	$^7F_0$	–	0	3·4–3·6
7	Gd	$^8S_{7/2}$	2	7·94	7·8–8·0
8	Tb	$^7F_6$	3/2	9·72	9·4–9·6
9	Dy	$^6H_{15/2}$	4/3	10·63	10·4–10·5
10	Ho	$^5I_8$	5/4	10· 60	10·3–10·5
11	Er	$^4I_{15/2}$	6/5	9·57	9·4–9·6
12	Tm	$^3H_6$	7/6	7·63	7·1–7·4
13	Yb	$^2F_{7/2}$	8/7	4·50	4·4–4·9
14	Lu	$^1S_0$	–	0	diamagnetic

2. When energy separations (ΔE) between J states are very small compared to kT. For such systems, the energy gaps between various J states are so small (compared to kT) that all the J states of ground terms are almost equally occupied by the metal ions at room temperature. By way of illustration, the J states of ^3F ground term of a metal ion beloging to the First transition series with d^2 configuration are shown in Fig. 55.

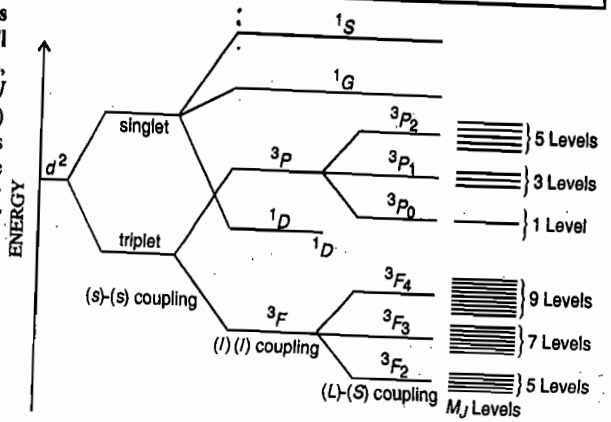


Fig. 55. The J states of ^3F ground term of a metal ion of First transition series with d^2 configuration.

The energy of metal ions which are almost equally distributed in all the J states of the ground term is equivalent to the energy when all the metal ions occupy the ground term for which the spin-orbit coupling is not operative. In such a case, (L) and (S) appear to interact separately with the external magnetic field and magnetic moment μ_{eff} is given by

$$\mu_{eff} = \sqrt{4S(S+1) + L(L+1)} \quad \ldots (48)$$

This equation is applicable in those paramagnetic metal ions of the First transition series where orbital angular momentum is not quenched (the quenching of orbital angular momentum will be discussed shortly). However, for several metal ions of the First transition series (particularly in the first half of the series), the

orbital angular momentum is almost completely quenched (*i.e.*, $L \approx 0$) in which case, the magnetic moment is given by

$$\mu_{eff} = \sqrt{4S(S+1)+0\times 1} = 2\sqrt{S(S+1)} \quad \ldots(49)$$

where S is the total spin of electrons in the metal ion.

Eq. 49 can also be written in the form

$$\mu_{eff} = 2\sqrt{n/2(n/2+1)} = \sqrt{n(n+2)} \quad \ldots(50)$$

where n, the number of unpaired electrons present in the metal is obviously equal to twice the total spin of electrons in the metal ion.

3. When energy separations (ΔE) between J states are comparable to kT. This situation is a mixture of two extremes 1 and 2, discussed above. The average magnetic susceptibility of a sample is the result of 'weighted' contributions from each J state of the multiplet obtained from spin–orbit coupling in the ground term. In such cases, magnetic susceptibility is given by the relation

$$\chi = (N/3kT)\sum g^2\beta^2 J(J+1)(2J+1)e^{-\Delta E/kT}\sum(2J+1)e^{-\Delta E/kT} \quad \ldots(51)$$

As is evident from the above relation, χ is not directly proportional to $1/T$. Such systems, therefore, do not obey the Curie law.

4. The situation in the case of heavy atoms. In the case of metal ions of Second and particularly Third transition series, the complexes are mainly spin paired. The metal ions with odd number of electrons will, therefore, exhibit paramagnetism which is equivalent to roughly one unpaired electron and the metal ions with even number of electrons would show diamagnetism. This could be due to the following reasons :

1. Smaller size of $3d$ orbitals makes the occupancy of two electrons in the same $3d$ orbital energetically less favourable than when the two electrons are present in $4d$ or $5d$ orbitals of comparatively bigger size.

2. The separation in energy terms of the metal ion caused by the ligand fields are considerably higher in $4d$ and $5d$ orbitals compared to $3d$ orbitals.

Both these factors favour a low spin complex.

II. Valence Bond Approach to Explain Magnetic Behaviour

As discussed in earlier pages, three different expressions are available for calculating the overall magnetic moments of substances depending upon the particular situation. These expressions are :

1. $\mu_{eff} = \sqrt{4S(S+1)+L(L+1)}$ when the J energy levels of the ground state are very close to one another (cf. Eq. 48) so that all of these J levels are almost equally populated at room temperature.

2. $\mu_{eff} = g\sqrt{J(J+1)}$ when the J energy levels of the ground state are well separated from one another (cf. Eq. 47) so that the energy gaps between the adjacent J levels of the ground state $> kT$.

3. $\mu_{eff} = \sqrt{4S(S+1)}$ when the orbital angular momentum is almost completely quenched so that its contribution to μ_{eff} is practically zero (cf. Eq. 49).

Since the valence bond theory does not envisage the splitting of energy terms (which arise because of interelectronic repulsions amongst the d electrons of a configuration) due to electrostatic crystal field potential of the ligands on the d electrons of the complexed metal ion, the theory presumes *that the ground and other energy states of the metal ion remain unsplit or unaltered when the metal ion is complexed.* Thus, according to the valence bond theory, the μ_{eff} of a complex can be calculated by using L, S and J of the ground state of its metal ion in its free state.

The overall magnetic moments (μ_{eff} values) calculated for complexed transition metal ions of the First transition series using different expressions are given in Table 8. The experimental values are also given for the sake of comparison.

TABLE 8

μ_{eff} Values Calculated (Using different expressions) and Determined Experimentally

Ions	Ground states	μ_{eff} calculated using the expression :			
		$\mu_{eff} = \sqrt{4S(S+1)+L(L+1)}$	$\mu_{eff} = g\sqrt{J(J+1)}$	$\mu_{eff} = \sqrt{4S(S+1)}$	μ_{eff} (Experimental)
$Ti^{3+}(d^1)$	$^2D_{3/2}$	3·00	1·55	1·73	1·7–1·8
Ti^{2+}, $V^{3+}(d^2)$	$^3F_2$	4·47	1·65	2·85	2·7–2·9
V^{2+}, $Cr^{3+}(d^3)$	$^4F_{3/2}$	5·20	0·70	3·87	3·7–3·9
Cr^{2+}, $Mn^{2+}(d^4)$	$^5D_0$	5·48	0	4·90	4·8–4·9
Mn^{2+}, $Fe^{3+}(d^5)$	$^6S_{5/2}$	5·92	5·92	5·92	5·7–6·0
Fe^{2+}, $Co^{3+}(d^6)$	$^5D_4$	5·48	6·71	4·90	5·0–5·6
$Co^{2+}(d^7)$	$^4F_{9/2}$	5·20	6·63	3·87	4·3–5·2
$Ni^{2+}(d^8)$	$^3F_4$	4·47	5·59	2·87	2·9–3·5
$Cu^{2+}(d^9)$	$^2D_{5/2}$	3·0	3·55	1·73	1·8–2·1

As can be seen from the above table, the values of μ_{eff} calculated by using all the three expressions differ considerably from the values determined experimentally. The values closest to experimental values are those calculated by using the relation $\mu_{eff} = \sqrt{4S(S+1)}$ involving only the spin of the electrons. This implies that the orbital angular momentum makes negligible contribution to μ_{eff} in the case of the complexes of metal ions belonging to the First transition series. The valence bond theory does not suggest any *precise mechanism* for the quenching of orbital angular momentum. It vaguely suggests that the orbital angular momentum of electrons in the complexed metal ion may be partly or completely destroyed or quenched due to the surrounding of the metal ion by the ligands. In such a case, the orbital motion of the d electrons of the metal ion will be severely disturbed by the electrons of the ligands. However, this qualitative explanation of quenching of orbital angular momentum does not give us any idea about the extent to which the orbital motion of electrons is disturbed or the extent to which the orbital angular momentum is quenched. Whenever the experimentally observed μ_{eff} exceeds $\mu_{s.o.}$, it is believed that some orbital angular momentum is retained or the orbital angular momentum is not completely quenched. Similarly, whenever the experimentally observed μ_{eff} is the same as $\mu_{s.o.}$, it is believed that the orbital motion of electrons is completely disturbed and, therefore, the orbital angular momentum is completely quenched.

We shall now apply VB approach to explain the observed magnetic moments (μ_{eff} values) of some complexes. Magnetic measurements show that sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ is diamagnetic in nature. This suggests +2 oxidation state for the complexed metal ion in which all the six d electrons are paired. According to VB approach, this can happen only if Fe(II) metal ion rearranges its six electrons in such a manner that it vacates two of the five d orbitals for the formation of $3d^24sp^3$ hybrid orbitals which can accommodate the six ligand electron pairs. In other words, sodium nitroprusside is an **inner orbital complex** of Fe(II).

The magnetic moment of $[Fe(H_2O)_5NO]^{2+}$ is 3·9 B.M. which indicates the presence of *three* unpaired electrons on the Fe atom in this complex. The valence bond approach suggests the presence of Fe in +1 oxidation state whose sole electron in $4s$ orbital shifts to $3d$ orbitals to make the $4s$ orbital available for $4sp^35d^2$ hybridisation so that the resulting six hybrid orbitals accommodate the six ligand electron pairs. In other words, $[Fe(H_2O)_5NO]^{2+}$ in an **outer orbital complex** of Fe(I).

It has been observed experimentally that **tetrahedral complexes** of Ni(II) in which the nickel orbitals are sp^3 hybridised, have μ_{eff} in the range of 3·2–4·0 B.M., the values which are higher than the $\mu_{s.o.}$ value for two unpaired electrons. (The $\mu_{s.o.}$ value for two unpaired electrons is 2·83 B.M.). On the other hand, the **square planar complexes** of Ni(II), involving dsp^2 hybridisation of nickel orbitals, are diamagnetic. But some Ni(II) complexes in solution phase have μ_{eff} values which are even lower than 2·83 B.M. The above observations are explained on the ground that tetrahedral as well as square planar complexes coexist in equilibrium with each other in the solution phase.

Magnetic moments of various complexes of metal ions of the First transition series are given in Table 9 along with some other relevant data.

TABLE 9

Magnetic Moments of Complexes of Metal Ions of First Transition Series

Complexes	Stereochemistry	Hybridisation involved	Number of unpaired electrons(n)	μ_{eff} (B.M.)	
				Experimental	Calculated $\mu_{s.o.}$
$K_3[TiF_6]$	octahedral	d^2sp^3	1	1·70	1·73
$V(acac)_3$	octahedral	d^2sp^3	2	2·80	2·83
$[Cr(NH_3)_6]Br_3$	octahedral	d^2sp^3	3	3·77	3·88
$[Cr(H_2O)_6](ClO_4)_2$	octahedral	sp^3d^2	4	4·97	4·90
$[Cr(dipy)_3]Br_2.4H_2O$	octahedral	d^2sp^3	2	3·27	2·83
$[Mn(py)_6]Br_2$	octahedral	sp^3d^2	5	6·00	5·92
$K_4[Mn(CN)_6].3H_2O$	octahedral	d^2sp^3	1	2·18	1·73
$(Et_4N)_2[MnCl_4]$	tetrahedral	sp^3	5	5·94	5·92
$Na_3[FeF_6]$	octahedral	sp^3d^2	5	5·85	5·92
$K_3[Fe(CN)_6]$	octahedral	d^2sp^3	1	2·25	1·73
$[Fe(NH_3)_6]Cl_2$	octahedral	d^2sp^3	4	5·45	4·90
$K_4[Fe(CN)_6]$	octahedral	d^2sp^3	0	0	0
$[Fe(Ph_3P)_2]I_2$	tetrahedral	sp^3	4	5·10	4·90
Fe(II)phthalocyanine	planar	dsp^2	2	3·96	2·83
$Na_3[CoF_6]$	octahedral	sp^3d^2	4	5·39	4·90
$[Co(NH_3)_6]Cl_3$	octahedral	d^2sp^3	0	0	0
$[Co(en)_6]SO_4$	octahedral	sp^3d^2	3	4·56	3·88
$K_2Ba[C_4(NO_2)_6]$	octahedral	d^2sp^3	1	1·88	1·73
$[Co\ py_4Cl_2]$ violet	octahedral	sp^3d^2	3	5·15	3·88
$[Co\ py_2Cl_2]$ blue	tetrahedral	sp^3	3	4·42	3·88
Co(II)phthalocyanine	planar	dsp^2	1	2·73	1·73
$[Ni(NH_3)_6]Cl_2$	octahedral	sp^3d^2	2	3·32	2·83
$[Ni(diarl)_3](ClO_4)_2$	octahedral	d^2sp^3	0	0	0
$(Et_4N)_2[NiCl_4]$	tetrahedral	sp^3	2	3·89	2·83
$[Ni(Et_3P)_2Cl_2]$	planar	dsp^2	0	0	0
$[Cu(phen)_3](ClO_4)_2$	octahedral	sp^3d^2	1	1·96	1·73

Limitations of Valence Bond Approach. 1. The explanation for the magnetic behaviour of complexes offered by VB approach is purely qualitative. The theory fails to explain why in some cases the observed μ_{eff} values are higher and in other cases lower than the $\mu_{s.o.}$ values.

2. The valence bond theory fails to explain why μ_{eff} values of tetrahedral complexes of a metal ion are different from the μ_{eff} values of octahedral complexes of the same metal ion containing the same number of unpaired electrons. For instance, the μ_{eff} values for tetrahedral complexes of Co(II) containing three unpaired electrons range between 4·4–4·8 B.M. whereas for octahedral outer orbital complexes of Co(II), also containing three unpaired electrons, range from 4·8–5·2 B.M. Similarly, μ_{eff} for tetrahedral Ni(II) complexes containing two unpaired electrons ranges between 3·2–4·0 B.M. whereas μ_{eff} for octahedral Ni(II) complexes, also containing two unpaired electrons, ranges between 2·9–3·3 B.M.

3. According to the valence bond theory, the formation of inner orbital complexes of metal ions with d^7, d^8 and d^9 configurations requires promotion of electrons to higher orbitals which is sometimes energetically unfavourable.

III. Crystal Field Approach to Explain Magnetic Behaviour

The application of crystal field theory to explain the magnetic behaviour of transition metal complexes meets with much greater success than the application of the valence bond theory. Unlike the valence bond theory, the crystal field theory does not have to assume the energetically unfavourable excitation of electrons from lower energy *d* orbitals to higher energy *d*, *s* or *p* orbitals in octahedral complexes of metal ions with d^7, d^8 and d^9 configurations. Nor does the crystal field theory have to assume the same ground state for the free and the complexed metal ion as is done in the case of the valence bond theory. Apart from this, the crystal field theory satisfactorily explains all those features of magnetochemistry of transition metal complexes which the valence bond theory fails to explain.

The explanation of quenching of orbital angular momentum based on the crystal field concept is highly logical. One can even predict the *extent* of quenching of orbital angular momentum from the calculations based on the crystal field theory and as such one can calculate the contribution of $\mu_{orbital}$ to the observed μ_{eff} of transition metal complexes.

Although a quantitative treatment of quenching of orbital angular momentum based on crystal field concept is beyond the scope of the book, yet a qualitative description of the subject is given below.

Quenching of Orbital Angular Momentum. The quenching of orbital angular momentum may be explained as follows.

An electron will possess angular momentum along a given axis if it is possible, by rotation around this axis, to transform the orbital that it occupies into another orbital which is equivalent to it in shape, size and energy. The orbital angular momentum along the given axis possessed by the electron in such an orbital will be numerically equal to the number of times the orbital gets transformed into the equivalent orbital during a rotation of 90° around that axis. Let us consider a free metal ion in which all the *d* orbitals are degenerate, *i.e.*, are of equal energy. An electron in $d_{x^2-y^2}$ orbital will contribute to orbital angular momentum equal to 2 in units of $h/2\pi$ along the Z axis since a rotation of $d_{x^2-y^2}$ orbital by 45° around the Z axis will carry it into an equivalent d_{xy} orbital or since a rotation of $d_{x^2-y^2}$ orbital by 90° around Z axis will carry it into d_{xy} orbital ***twice***. Using similar arguments, an electron in d_{xy} orbital will contribute to orbital angular momentum of 2 in units of $h/2\pi$ along Z axis. Likewise, an electron in d_{xz} orbital will have an orbital angular momentum equal to 1 in units of $h/2\pi$ along Z axis since the d_{xz} orbital gets transformed into an equivalent d_{yz} orbital by rotating the former around Z axis by an angle of 90°. Using similar arguments, an electron in d_{yz} orbital will have an orbital angular momentum of 1 in units of $h/2\pi$ around Z axis. The d_{z^2} orbital does not carry itself into any other equivalent orbital by its rotation around the Z axis. Therefore, it has zero orbital angular momentum along Z axis.

When the metal ion is surrounded octahedrally by six or tetrahedrally by four ligands, the degeneracy of *d* orbitals is lifted. The d_{xy} and $d_{x^2-y^2}$ orbitals become of different energy and are thus non-equivalent. Therefore, an electron in $d_{x^2-y^2}$ orbital can no longer be equated with an electron in d_{xy} orbital. In other words, the $d_{x^2-y^2}$ orbital cannot be transformed into d_{xy} orbital and vice versa by the rotation of the orbital along the Z axis. Hence, an electron in $d_{x^2-y^2}$ orbital will now have zero orbital angular momentum along the Z axis.

However, some orbital angular momentum along Z direction will be retained since d_{xz} and d_{yz} orbitals are still equivalent energywise, shapewise and sizewise. Therefore, an electron in d_{xz} or d_{yz} orbital will contribute an orbital angular momentum of 1 in units of $h/2\pi$ along the Z axis.

Thus, a metal ion with electrons in t_{2g} orbitals (in the case of octahedral complexes) or t_2 orbitals (in the case of tetrahedral complexes) would make some orbital magnetic moment contribution along the Z direction to the overall μ_{eff} of the complex. The direction of the magnetic field applied is also taken as the Z

direction by convention. But if t_{2g} or t_2 orbitals are half or fully filled so that the electrons in these orbitals have a spherical distribution of charge around the nucleus, the orbital angular momentum will obviously have zero value and the orbital magnetic momentum will not make any contribution to overall μ_{eff} in such cases.

Thus, μ_{eff} for metal ions with the following configurations in their octahedral complexes will have no contribution from orbital magnetic moment :

Spin free or high spin :

t_{2g}^3 (ground state $^4A_{2g}$) ; $t_{2g}^3 e_g^1$ (ground state ^5E_g) ; $t_{2g}^3 e_g^2$ (ground state $^6A_{1g}$) ;

$t_{2g}^6 e_g^2$ (ground state $^3A_{2g}$) ; $t_{2g}^6 e_g^3$ (ground state ^2E_g)

Spin paired or low spin :

t_{2g}^6 (ground state $^1A_{1g}$) ; $t_{2g}^6 e_g^1$ (ground state ^2E_g)

However, μ_{eff} for metal ions with the following configurations in their octahedral complexes will have non-zero contribution from orbital angular moment :

t_{2g}^1 (ground state $^2T_{2g}$) ; t_{2g}^2 (ground state $^3T_{1g}$) low spin ;

t_{2g}^4 (ground state $^3T_{1g}$) ; t_{2g}^5 (ground state $^2T_{2g}$).

This is due to the fact that all these configurations have electronic arrangements which contain electrons in d_{xz} and/or d_{yz} orbital and which generate non-uniform distribution of electronic charge around the nucleus.

Thus, we observe that all configurations of metal ions in **octahedral complexes** which have no orbital angular momentum along the direction of the applied magnetic field and hence have no orbital magnetic moment contribution to make to the overall magnetic moment μ_{eff}, have either an A or E ground state. Similarly, all configurations which have some orbital angular momentum retained and hence make some orbital magnetic moment contribution to overall μ_{eff}, have T ground states.

Similar conclusions can be drawn for metal ions in tetrahedral or tetragonal ligand environments. For instance, μ_{eff} for metal ions having configurations e^1, $e^3t_2^3$ (ground state E) and e^2, $e^4t_2^3$ (ground state A_2) in their tetrahedral complexes have no contribution from orbital angular momentum and for metal ions having configurations $e^2t_2^2$, $e^4t_2^5$ (ground state T_2) and $e^2t_2^1$, $e^4t_2^4$ (ground state T_1) will have non-zero contribution from orbital angular momentum.

We can thus generalise that the orbital angular momentum is completely quenched when the metal ion in its complexes has A or E as the ground state and is partially quenched when the metal ion in its complexes has T as the ground state.

Although in most of the ions with A or E as ground state, the experimentally observed μ_{eff} is very close to $\mu_{s.o.}$ and is temperature–independent, yet some ions show a slight departure from this. In the latter cases, a low lying excited T state (of the same spin multiplicity as the ground state) mixes up due to spin-orbit coupling with A or E ground state as a result of which the excited T state will have some character of A or E ground state and A or E will have some character of T state. In other words, the ground state A or E in such cases will retain some orbital angular momentum. Such systems having ground states with orbital angular momentum or $L = 0$ but having low lying excited T states of some multiplicity as the ground states will have observed μ_{eff} different from $\mu_{s.o.}$. The contribution of orbital magnetic moment to overall μ_{eff} in such cases depends upon the extent of mixing of ground state with the excited state and is, therefore, inversely proportional to Δ, the energy difference between ground and excited states. Taking this into account, the following equation has been suggested for μ_{eff} :

$$\mu_{eff} = \mu_{s.o.}(1 - \alpha\lambda/\Delta) \quad \ldots(52)$$

where α is a constant depending upon the spectroscopic ground term and the number of d electrons (being 2 for ^2D and ^5D terms, 4 for ^3F and ^4F terms and zero for ^6S term). λ is the spin–orbit coupling parameter

which is positive for d^n configurations with $n < 5$ and negative for d^n configurations with $n > 5$.

For d^3 and d^8 metal ions in octahedral ligand environments, the ground state A_2 arises from the splitting of the F term as already discussed. Also, the energy gap between A_2 and the excited state T_{2g} is 10 Dq. Eq. 52, therefore, takes the form

$$\mu_{eff} = \mu_{s.o.}(1 - 4|\lambda|/10Dq) \quad \ldots(53)$$

for d^3 metal ions in its octahedral complexes and

$$\mu_{eff} = \mu_{s.o.}(1 + 4|\lambda|/10Dq) \quad \ldots(54)$$

for d^8 metal ions in their octahedral complexes. $|\lambda|$ in the above expressions is the absolute magnitude of spin-orbit coupling parameter without considering its sign.

For d^4 and d^9 metal ions in their octahedral complexes, the ground term E_g arises from the splitting of the D term, as discussed earlier. Hence, α is 2. Also the energy gap between the ground state E_g and the excited state T_{2g} is 10 Dq again. Therefore, Eq. 52 is written as

$$\mu_{eff} = \mu_{s.o.}(1 - 2|\lambda|/10Dq) \quad \ldots(55)$$

for d^4 metal ions in octahedral complexes and as

$$\mu_{eff} = \mu_{s.o.}(1 + 2|\lambda|/10Dq) \quad \ldots(56)$$

for d^9 metal ions in their octahedral complexes.

It is evident from above that whereas for A or E terms of metal ions with d^3 and d^4 configurations in their octahedral complexes with weak field ligands, μ_{eff} would be lower than $\mu_{s.o}$, it would be higher than $\mu_{s.o.}$ for d^8 and d^9 metal ions. Secondly, since the energy gap between electronic ground state A or E and the excited state T in these cases is far greater than kT, hence μ_{eff} is independent of temperature.

Weak field octahedral complexes of metal ions with d^5 configuration (ground state $^6A_{1g}$) has no excited state of the same multiplicity as the ground state (why ?). Therefore, mixing of ground state with any of the excited states due to spin–orbit coupling is not possible. Thus, there cannot be any orbital contribution to μ_{eff} due to mixing of the ground state with the excited state due to spin-orbit coupling. Apart from this, the gap between any of the excited T states and the ground $^6A_{1g}$ state is so high that none of the molecules of octahedrally complexed d^5 ion in high spin state can be present in any excited T state. Such weak field octahedral complexes of d^5 ion, therefore, show μ_{eff} equal to $\mu_{s.o.}$. In a system with five unpaired electrons, magnetic moment is equal to 5·92 B.M. which is independent of temperature.

Alternatively, since the ground state $^6A_{1g}$ arises from the S term for which α is zero, hence μ_{eff} is the same as $\mu_{s.o.}$ (cf. Eq. 52).

A low spin d^6 metal ion in octahedral complexes, also has A_{1g} ground state but all the electrons in it are paired up and hence its complexes are diamagnetic.

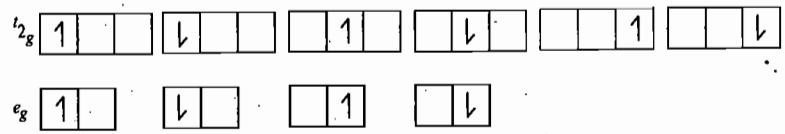
As already stated, the T ground states retain orbital angular momentum. Therefore, there may be appreciable orbital magnetic moment contribution to μ_{eff} in systems which have T ground states. However, spin–orbit coupling can remove the degeneracy of some of the levels contained in the T states and a quantitative estimation of the contribution to μ_{eff} due to the retained orbital angular momentum of T ground state is possible only if the exact magnitude of the splitting of the energy levels of T state due to spin-orbit coupling is known. This involves complicated calculations the discussion of which is beyond the scope of the book. These calculations, however, establish that overall magnetic moments (μ_{eff}) in such cases are functions of λ and T (temperature). Thus, while in molecules in which the ground states are A or E, μ_{eff} is independent of temperature, it varies with temperature in molecules in which the ground state is T. The temperature-dependent studies of μ_{eff} are thus a more reliable guide to judging the presence or absence of orbital contribution to μ_{eff} than the studies of μ_{eff} at room temperature alone. Since a given metal ion can have T ground state either in its octahedral or in its tetrahedral complex (but not in both geometries), the temperature-dependent studies of μ_{eff} can also predict whether the geometry of the complex is tetrahedral or octahedral.

Energy Terms in Strong Field Octahedral Complexes

We briefly discussed in the chapter on Molecular Symmetry and Group Theory, the procedure for deriving the energy terms in the case of strong field octahedral complexes of transition metal ions. We shall elaborate this procedure further at this stage.

In the strong field octahedral complexes, V_{oct} > interelectronic repulsions amongst *d* electrons >> spin-orbit coupling interaction. Therefore, in such complexes, the weaker interelectronic repulsions are considered as perturbations over the stronger V_{oct} effects for deriving the energy terms (the much weaker spin-orbit coupling interactions are ignored in this derivation). Accordingly, the effect of strong V_{oct} on a d^n system is considered first and the terms thus obtained are subjected to perturbations due to electrostatic interactions amongst the *d* electrons.

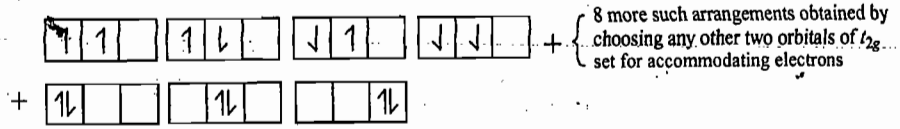
Consider a strong octahedral electrostatic crystal field potential of ligands (V_{oct}) experienced by a d^1 system. Since there is only one *d* electron, there is no question of any interelectronic repulsions amongst the *d* electrons. The strong V_{oct} will split the *d* orbitals into the t_{2g} and e_g sets. If the electron is present in the lower energy t_{2g} set (t_{2g}^1 configuration), the corresponding wave function $\psi_{t_{2g}}$ transforms as T_{2g} representation of O_h point group. If, on the other hand, the single *d* electron is present in e_g set (e_g^1 configuration), the corresponding wave function ψ_{e_g} transforms as E_g representation of O_h point group. Thus, d^1 configuration in strong V_{oct} generates T_{2g} and E_g terms. Since the total spin of the configuration with only one *d* electron is 1/2, the spin multiplicity is 2×1/2 + 1, *i.e.*, 2. Thus, the terms which arise in this case are $^2T_{2g}$ and ^2E_g. The sum of total degeneracies of these terms is (2×3 + 2×2) = 10 which is also the number of electronic arrangements possible for both the configurations, as shown below :



Now consider a d^2 system in a strong octahedral crystal field generated by ligands. The configurations that arise from the system (ignoring the electrostatic *d* electron interactions in the first instance) are t_{2g}^2, $t_{2g}^1 e_g^1$ and e_g^2.

The first strong field configuration t_{2g}^2 can be considered as t_{2g}^1 configuration to which one more electron in t_{2g} set of orbitals has been added so that the configuration can be written as $t_{2g}^1\ t_{2g}^1$ and the wave function for this configuration can be written as $\psi_{t_{2g}}^1\ \psi_{t_{2g}}^1$ (since the interaction between the electrons has been ignored in the first step). This wave function forms the basis of (or transforms as) the reducible representation obtained from the direct product $T_{2g}\times T_{2g}$ in octahedral symmetry group as explained in the chapter on Molecular Symmetry and Group Theory. This direct product reduces to $T_{1g} + T_{2g} + E_g + A_{1g}$. (The student is advised to check it by using the octahedral character table). The possible total spin that each term can have is either 1/2 + 1/2, *i.e.*, 1 or 1/2 − 1/2, *i.e.*, 0. Therefore, the possible spin multiplicities of the terms are 3 (*i.e.*, 2 × 1 + 1) and 1 (*i.e.*, 2 × 0 + 1) and the possible terms are $^3T_{1g}$, $^3T_{2g}$, ^3E_g, $^3A_{1g}$, $^1T_{1g}$, $^1T_{2g}$, ^1E_g, $^1A_{1g}$. However, all these terms do not actually exist for the t_{2g}^2 configuration. The terms which actually exist would be those for which the sum of the total degeneracies is equal to the total number of electronic arrangements (involving both the spin and the space factors) for the particular configuration.

It can be easily seen that, in all, fifteen electronic arrangnements exist for t_{2g}^2 configuration, as shown below :



Therefore, the sum of total degeneracies of the set of the terms for t_{2g}^2 configuration must be fifteen. If the terms are written as $^aT_{1g}+{}^bT_{2g}+{}^cA_{1g}+{}^dE_g$ (where *a*, *b*, *c*, *d* are spin multiplicities). the sum of total degeneracies in this set of terms would be given by $3\times a + 3\times b + 1\times c + 2d$, which must be equal to 15. Therefore, the possible sets of terms would be,

$$^3T_{1g} + {}^1T_{2g} + {}^1E_g + {}^1A_{1g}\ (3\times3 + 1\times3 + 1\times2 + 1\times1 = 15)$$

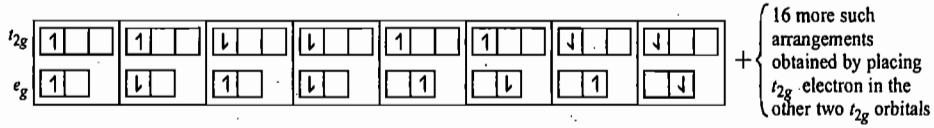
$$^1T_{1g} + {}^3T_{2g} + {}^1E_g + {}^1A_{1g}\ (1\times3 + 3\times3 + 1\times2 + 1\times1 = 15)$$

$$^1T_{1g} + {}^1T_{2g} + {}^3E_g + {}^3A_{1g}\ (1\times3 + 1\times3 + 3\times2 + 3\times1 = 15)$$

Out of the above three sets, it can be shown (by following a complicated procedure) that the set of terms which actually exists is the first set, *viz.*, $^3T_{1g}$, $^1T_{2g}$, ^1E_g, $^1A_{1g}$. The relative energies of these terms have also been calculated by following a complicated procedure which involves interelectronic repulsions as perturbations, the discussion of which, however, is beyond the scope of the book.

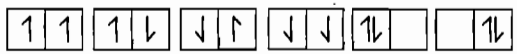
Consider now the configuration $t_{2g}^1 e_g^1$. The wave function for this configuration; ignoring the interelectronic interaction, can be written as $\psi_{t_{2g}}\psi_{e_g}$ which forms the basis of (or transforms as) the reducible representation obtained from the direct product $T_{2g}\times E_g$ in octahedral symmetry point group as explained in the chapter on Molecular Symmetry and Group Theory. The direct product $T_{2g}\times E_g$ reduces to T_{1g} and T_{2g} irreducible representations of the octahedral group. Suppose the spin multiplicities of the terms are *a* and *b*. The set of terms for $t_{2g}^1 e_g^1$ configuration would thus be $^aT_{1g}+{}^bT_{2g}$.

As discussed above, the sum of total degeneracies of these terms must be equal to the total number of electronic arrangements of the configuration. As can be seen, the following 24 electronic arrangements are possible for this configuration :



Thus, $(a\times3 + b\times3) = 24$ or $a + b = 8$ or $a = b = 4$ or 3 + 1 (it has to be kept in mind that the spin multiplicity *a* or *b* of a two-electron system cannot be 4 ; it has to be 3+1). Thus, the terms which arise out of $t_{2g}^1 e_g^1$ configuration are $^3T_{1g}$, $^1T_{1g}$, $^3T_{2g}$, $^1T_{2g}$. The relative energies of these terms have also been calculated (by followig a complicated procedure) which involves interelectronic repulsions as perturbations.

Consider finally the configuration e_g^2, the wave function for which can be written as $\psi_{e_g^1}\psi_{e_g^1}$ (ignoring the interelectronic interactions). This wave function forms the basis of (or transforms as) the reduciable representation obtained from the direct product $E_g \times E_g$ of octahedral symmetry group which reduces to $A_{1g} + E_g + A_{2g}$. Since only the following 6 arrangements of electrons are possible in this case,



$^aA_{1g} + {}^bE_g + {}^cA_{2g}$ must have the sum of their total degeneracies as 6 (*a* and *b* are spin multiplicities having a value of 3 or 1). Therefore, the possible sets of energy terms are :

$$^1E_g + {}^3A_{2g} + {}^1A_{1g}\ (1\times2 + 3\times1 + 1\times1 = 6)$$

$$^1E_g + {}^1A_{2g} + {}^3A_{1g}\ (1\times2 + 1\times1 + 3\times1 = 6)$$

It can be shown, as mentioned above, that it is the first set, *viz.*, $^1E_g + {}^3A_{2g} + {}^1A_{1g}$ which actually exists for e_g^2 configuration. Again, the relative energies of terms can also be calculated (by following a complicated procedure) which includes interelectronic repulsions as perturbations.

The terms for d^3 metal ion configuration under strong V_{oct} can be derived in a similar manner. The strong field configurations t_{2g}^3, $t_{2g}^2e_g^1$, $t_{2g}^1e_g^2$, e_g^3 can be assumed to be derived from t_{2g}^2, $t_{2g}^1e_g^1$, $t_{2g}^1e_g^1$, e_g^2 configurations to which one electron has been added either to a t_{2g} or an e_g orbital. Ignoring the interelectronic repulsions, the corresponding wave functions of the configurations can be written as $\psi_{t_{2g}^1}\psi_{t_{2g}^1}\psi_{t_{2g}^1}$, $\psi_{t_{2g}^1}\psi_{t_{2g}^1}\psi_{e_g^1}$, etc.

The wave function $\psi_{t_{2g}^1}\psi_{t_{2g}^1}\psi_{t_{2g}^1}$ forms the basis of the reducible representation given by the direct product $T_{2g}\times T_{2g}\times T_{2g}$ of octahedral character table which reduces to $4\times T_{1g}+3\times T_{2g}+2\times E_g+A_{2g}+A_{1g}$. Considering the spin multiplicities also, which for a three-electron system can be 4 or 2, the possible terms are $4\times{}^4T_{1g}$, $4\times{}^2T_{1g}$, $3\times{}^4T_{2g}$, $3\times{}^2T_{2g}$, $2\times{}^4E_g$, $2\times{}^2E_g$, ${}^4A_{2g}$, ${}^2A_{2g}$, ${}^4A_{1g}$, ${}^2A_{1g}$. Again, all these terms do not exist for t_{2g} configuration. The terms that actually exist are those for which the sum of total degeneracies is equal to the number of electronic arrangements for this configuration. The derivation of multiplicities of the existing terms in this case is much more complicated and is beyond the scope of the book. Suffice it to say that the terms for the configuration t_{2g}^3 that actually exist come out to be ${}^4A_{2g}$, ${}^2E_g$, ${}^2T_{1g}$, ${}^2T_{2g}$ for which the sum of total degeneracies come out to be 20 as required. The existing energy terms for the other configurations of the d^3 system are derived by following the same procedure. The energy terms for d^4 and d^5 metal ion configurations are also dervied in a similar manner.

The procedure for deriving energy terms for configurations containing more than half-filled t_{2g} or e_g subshell can be simplified as discussed below.

The terms for a t_{2g} or e_g subshell which is more than half full can be obtained by considering such configurations as containing positive holes or 'positive electrons' (the positive hole formalism has been discussed adequately earlier in this chapter). The positive electrons behave amongst themselves exactly as the negative electrons do amongst themselves and give rise to energy terms identical to those given by electronic configurations containing the same number of electrons. As can be seen, only one symmetric electronic arrangement containing all paired electrons is possible for t_{2g}^6 configuration and also for e_g^4 configuration and has the symmetry label ${}^1A_{1g}$ in octahedral symmetry. A t_{2g}^4 configuration is equivalent to t_{2g}^6 configuration containing two 'positive holes' or 'positive electrons' and will thus give rise to the same energy terms as given by normal t_{2g}^2 electronic configuration. Similarly, t_{2g}^5 configuration is equivalent to fully occupied t_{2g}^6 configuration containing one 'positive electron' and will give rise to the same energy terms as given by t_{2g}^1 normal electronic configuration. In a similar manner, the e_g^3 configuration will be equivalent to e_g^4 configuration containing one positive electron and will give rise to the same energy terms as given by e_g^1 normal electronic configuration.

Terms Correlation Diagrams

Let us qualitatively draw the variation in the energies of terms of a d^n metal ion starting from free metal ion (zero crystal field) on extreme left hand side and finishing with the metal ion in the strong crystal field (of infinite strength) on extreme right hand side. While drawing these correlation diagrams, the following points are to be kept in mind :

1. For a metal ion with a particular d^n configuration in free state, the total number of electronic energy levels remains the same whether under the influence of a weak crystal field potential or under the influence of a strong crystal field potential.

2. There is one to one correspondence between energy levels of the same symmetry in a weak crystal field and a strong crystal field.

3. In these correlation diagrams, the **non-crossing rule** is observed, that is, the energy levels of same symmetry never cross each other and each energy level of a *particular symmetry* has contribution from all other energy levels of the *same symmetry*.

4. While all energy levels are shown in d^1, d^9, d^2, d^8 correlation diagrams, only the lower energy levels out of a large number of energy levels are shown in d^3 to d^7 correlation diagrams.

5. According to positive hole formalism, d^9, d^8, d^7, d^6 electronic configurations of free metal ions give rise to terms that are identical to those given by d^1, d^2, d^3, d^4 electronic configurations. The 'positive electrons experience the same magnitude of crystal field potential from ligands as is done by negative electrons but of opposite sign (why ?). Therefore, the terms arising due to interelectronic repulsions in free metal ions with d^n and d^{10-n} configurations split up in opposite manner in weak V_{oct}. (Weaker V_{oct} is considered as perturbation over the stronger interelectronic repulsions responsible for giving rise to the terms).

6. Because of the positive hole formalism. strong field configurations $t_{2g}^5, t_{2g}^4, e_g^3$ give rise to the same terms as given by strong field configurations $t_{2g}^1, t_{2g}^2, e_g^1$. (Here the weaker interelectronic repulsion is considered as perturbation over the stronger V_{oct}).

7. Although the correlation diagrams are drawn for octahedral crystal field, these can be used for tetrahedral crystal field also, remembering that there is no centre of symmetry in a tetrahedron so that no term can have a g or u subscript. Also V_{tet} experienced by a particular d^n system is of opposite sign to the sign of V_{oct} experienced by the same system. Since V_{tet} is *less than half* of V_{oct}, the former is always weaker than the interelectronic repulsion.

The qualitatively drawn correlation diagrams for various d^n systems are given below (Figs. 56–64).

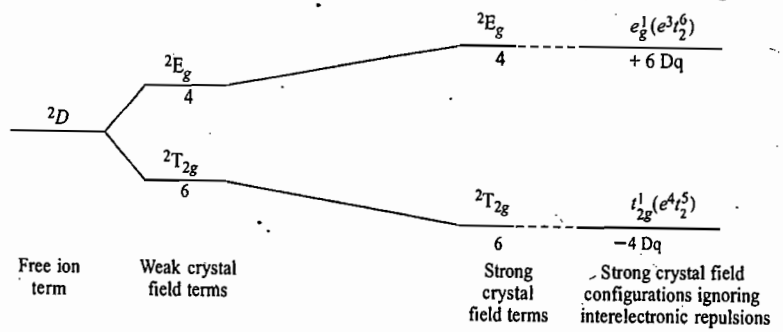


Fig. 56. Qualitative correlation diagram for d^1 octahedral and d^9 tetrahedral system. The subscript g is not used for tetrahedral system. The number below each term indicates its total degeneracy. The strong field configurations of tetrahedral system are given in parentheses alongwith strong field configurations of octahedral system. Examples are : complexes of Ti^{3+} (octahedral) and Cu^{2+} (tetrahedral). The strength of crystal field does not alter the ground state.

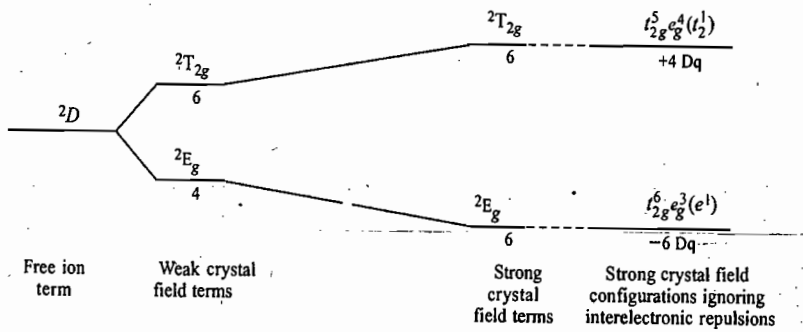


Fig. 57. Qualitative correlation diagram for d^9 octahedral and d^1 tetrahedral system. The subscript g is not used for tetrahedral system. The number below each term indicates its total degeneracy. The strong field configurations of tetrahedral system are given in parentheses alongwith strong field configurations of octahedral system. Examples are : Cu^{2+} (octahedral) and Ti^{3+} (tetrahedral). The strength of crystal field does not alter the ground state.

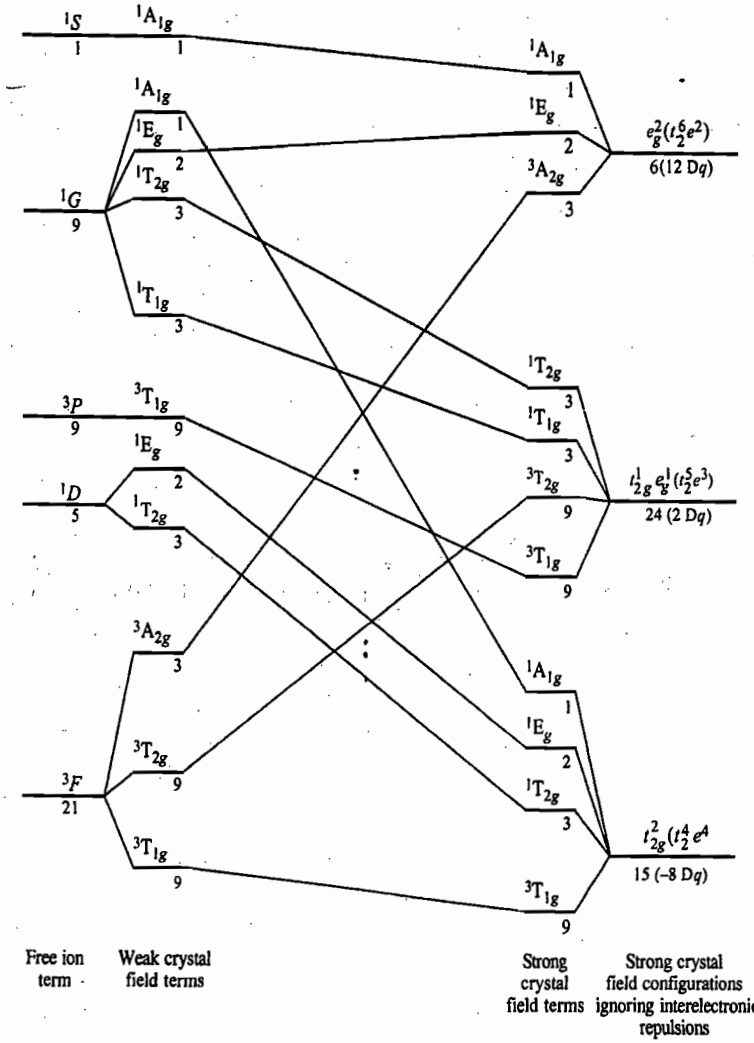


Fig. 58. Qualitative correlation diagram for d^2 octahedral and d^8 tetrahedral system. The subscript g is not used for tetrahedral system. The number below each term indicates its total degeneracy. The strong field configurations of tetrahedral system are given in parentheses along with strong field configurations of octahedral system. Examples are : complexes of V^{3+} (octahedral) and Ni^{2+} (tetrahedral). The strength of crystal field does not alter the ground state.

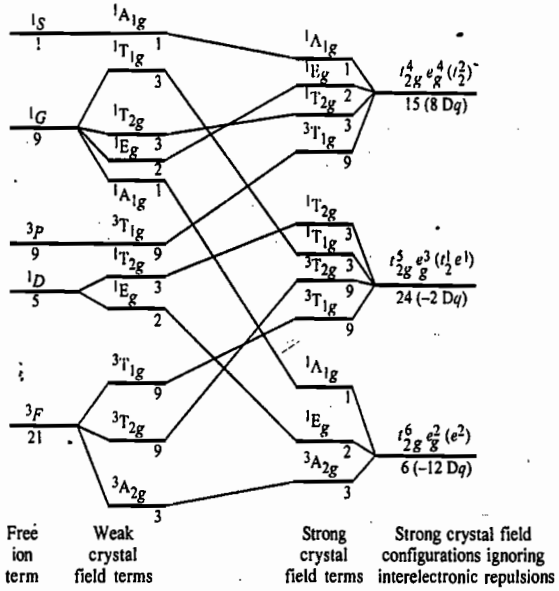


Fig.59. Qualitative correlation diagram for d^8 octahedral and d^2 tetrahedral system. The subscript g is not used for tetrahedral system. The number below the term indicates its total degeneracy. The strong field configurations of tetrahedral system are given in parentheses along with strong field configurations of octahedral system. Examples are : Ni^{2+} (octahedral) and V^{3+} (tetrahedral). The strength of the crystal field does not alter the ground state.

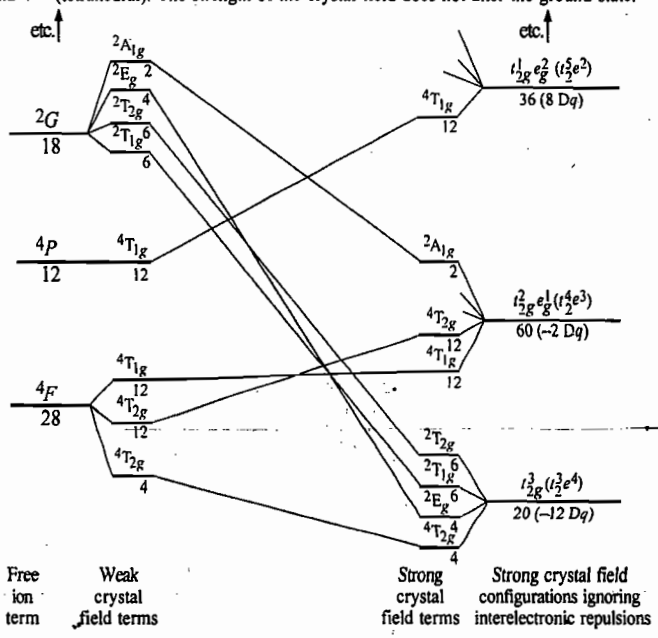


Fig. 60. Qualitative correlation diagram for d^3 octahedral and d^7 tetrahedral system. The subscript g is not used for tetrahedral system. The number below the term indicates its total degeneracy. The strong field configurations of tetrahedral system are given in parentheses alongwith strong field configurations of octahedral system. Examples are : complexes of Cr^{3+} (octahedral) and Co^{2+} (tetrahedral). The strength of the crystal field does not alter the groud state.

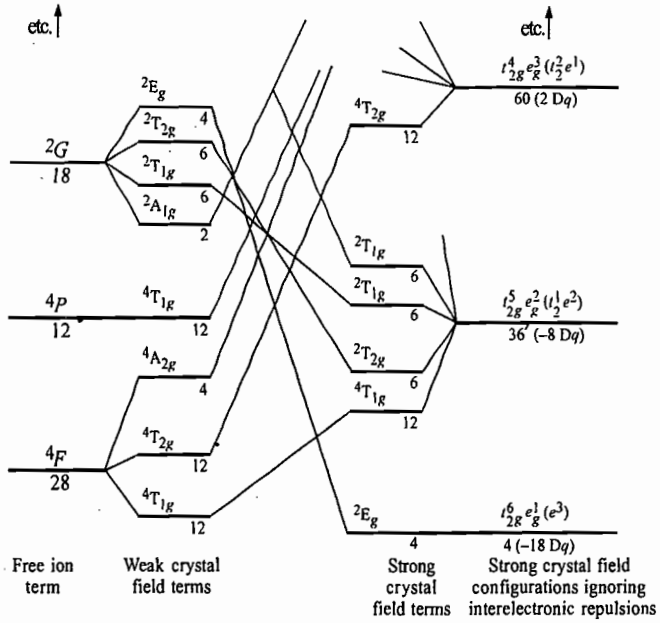


Fig. 61. Qualitative correlation diagram for d^7 octahedral and d^3 tetrahedral system. The subsricpt g is not used for tetrahedral system. The number below the term indicates its total degeneracy. The strong field configurations of tetreahedral system are written in parentheses along with strong field configurations of octahedral system. Examples are : Co^{2+} (octahedral) and Cr^{3+} (tetrahedral). The strength of the crystal field can alter the ground state and can cause pairing of electrons.

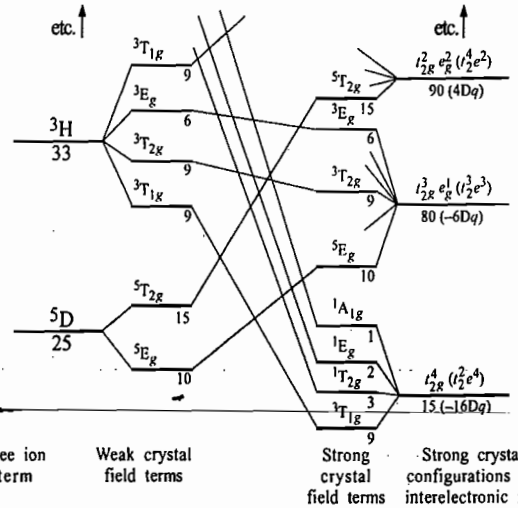


Fig. 62. Qualitative correlation diagram for d^4 octahedral and d^6 tetrahedral system. The subscript g is not used for tetrahedral system. The number below the term indicates its total degeneracy. The strong field configurations of tetrahedral system are given in parentheses alongwith strong field configurations of octahedral system. Examples are : Mn^{3+} (octahedral) and Fe^{2+} (tetrahedral). The strength of the crystal field can alter the ground state and can cause pairing of electrons.

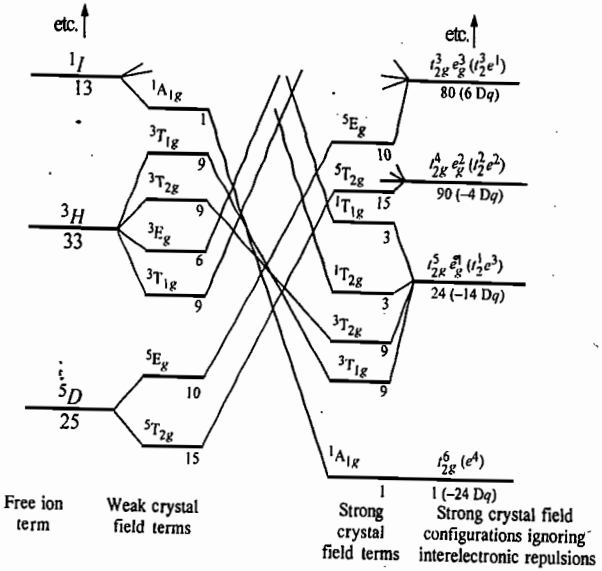


Fig. 63. Qualitative correlation diagram for d^6 octahedral and d^4 tetrahedral system. The subscript g is not used for tetrahedral system. The number below the term indicates its total degeneracy. The strong field configurations of tetrahedral system are given in parentheses alongwith strong field configurations of octahedral system. Examples are : complexes of Fe^{2+} (octahedral) and Mn^{2+} (tetrahedral). The strength of the crystal field can alter the ground state and can cause pairing of electrons.

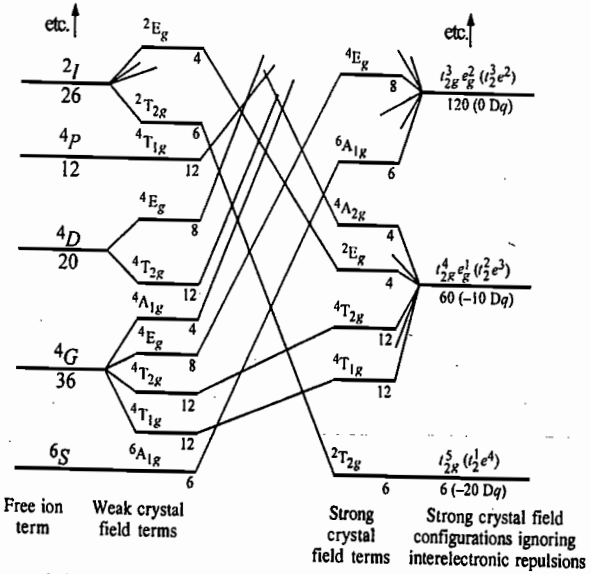


Fig. 64. Qualitative correlation diagram for d^5 octahedral and d^5 tetrahedral system. The subscipt g is not used for tetrahedral system. The number below the term indicates its total degeneracy. The strong field configurations of tetrahedral complex are given in parentheses alongwith strong field configuration of octahedral complex. Examples are : complexes of Mn^{3+}, Fe^{3+} (octahedral, tetrahedral). The strength of the cyrstal field can alter the ground state and can cause pairing of electrons.

Spin Pairing Energies And Correlation Diagram

The interelectronic repulsion energies of d electrons when present in a complex ion are not only different but also extremely difficult to determine than when these electrons are present in a free ion. However, energies of strong field **configurations** can be determined conveniently. Since in the case of strong field configurations of complexed ions we can ignore interelectronic repulsions of d electrons, we can write down the energy changes that occur in going from free ions to strong field configurations.

As can be seen, in the correlation diagrams of octahedral d^1, d^9, d^2, d^8, d^3 systems (Figs. 56 to 60), the ground term of free ion correlates with the *lowest* strong field configuration indicating that whatever be the strength of the crystal field, no lowering of energy occurs on attaining octahedral complexation of these metal ions.

In the correlation diagrams for octahedral d^4 and d^7 systems (Figs. 62 and 61), the free ion ground term correlates with the strog field configuration which lies 10 Dq higher than the lowest strong field configuration. In other words, the strong field ground term lies lower in energy by 10 Dq compared to the free ion ground term. Similarly, it is clear from the correlation diagrams of octahedral d^5 and d^6 systems (Figs. 64 and 63) that their free ion ground term correlates with the strong field configuration that lies 20 Dq higher than the lowest strong field configuration. In other words, the ground strong field configuration lies lower in energy by 20 Dq compared to the free ion ground term.

We can now qualitatively argue about the magnitude of d interelectronic repulsion. It can be seen from the correlation diagram of d^4 octahedral system that the ground strong field configuration correlates with free ion term ^3H lying next above the free ion ground term ^5D (Fig. 62). Similarly, correlation diagram of d^7 octahedral system shows that the ground strong field configuration correlates with the free ion term which is one term further removed from the free ion ground term (Fig. 61). In the correlation diagram for d^5, d^6 octahedral systems, the ground strong field configuration correlates with a free ion term which lies many terms above the free ion ground term. Thus, during the pairing of electrons in the strong field, the extent of interelectronic repulsion encountered in going from free ion to strong field configuration changes in the order :

$$d^4 < d^7 < d^5 \sim d^6$$

A little reflection shows that it should be possible to ascertain whether the octahedral complexes of $d^4 - d^7$ metal ions would be strong field complexes or weak field complexes provided we know the magnitudes of interelectronic repulsions and CFSEs involved in going from the free ions to strong field configurations obtained by pairing of d electrons. Since, however, the exact d interelectronic repulsion energies involved in pairing of electrons in complexes are rarely known and also since the assumption that crystal field interactions are purely electrostatic with no covalent contributions at all, is not correct, hence no conclusion can be drawn visa-vis the nature of octahedral complexes. Experimentally, it has been obseved that whereas strong field or spin paired complexes of Co^{3+}, Fe^{2+} (d^6) are quite common, those of Mn^{2+} (d^5) and Co^{2+} (d^7), though known, are not that common. The spin paired or strong field complexes of d^4 ions are rarely known.

Tanabe–Sugano Diagrams (T–S Diagrams)

The terms correlation diagrams, described above, are drawn only qualitatively. The quantitatively drawn diagrams showing the change in the energies of levels of a d^n system accompanying the change : a free metal ion ⟶ weak octahedral field ⟶ strong octahedral field environments are known as **Tanabe–Sugano diagrams**. These diagrams, which are essential for interpretting electronic absorption spectra of complexes, make use of two parameters B and C (known as **Racah parameters**) to describe the interelectronic repulsions of d electrons of the systems. Since it is usually not possible to calculate energies of all energy levels of a d^n system in the presence of both the d interelectronic repulsions and crystal fields, the calculations of energies of the energy levels have been carried out only for certain relationships (or C/B ratios) of Racah interelectronic repulsion parameters C and B. In these diagrams,

the variation of crystal field strength, in units of Dq/B is represented by the horizontal axis and the variation of energy, in units of E/B, is represented by the vertical axis. The zero of energy in T–S diagrams is taken as the energy of the lowest term. In other words, the ground term is always located on the horizontal axis. Whenever, there is a change in the ground term, the plot of Dq/B versus E/B shows a sharp bend in the plotted energy levels.

The T–S diagram for d^2 to d^8 systems in *octahedral environment* are shown in Figs. 65 to 71.

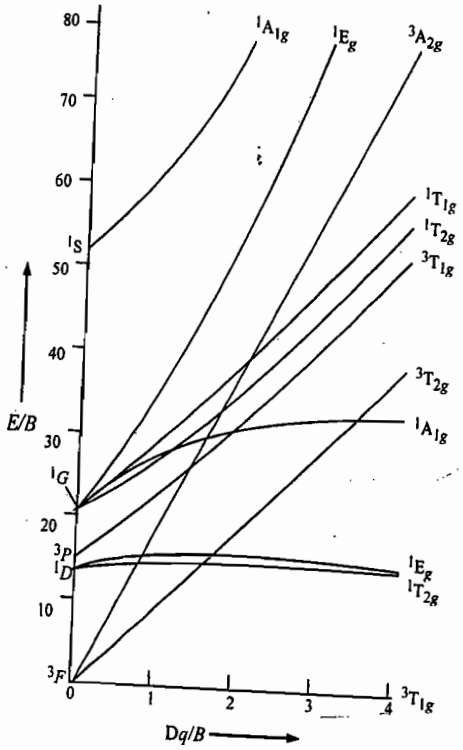


Fig. 65. Tanabe–Sugano diagram for d^2 system drawn for $C/B = 4{\cdot}40$

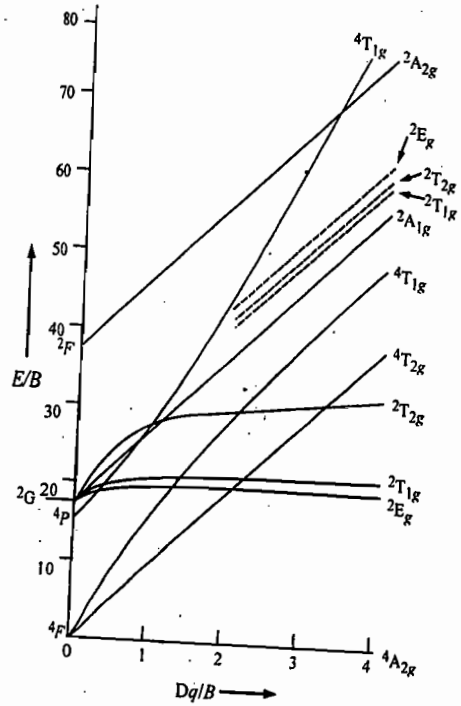


Fig. 66. Tanabe–Sugano diagram for d^3 system drawn for $C/B = 4{\cdot}50$

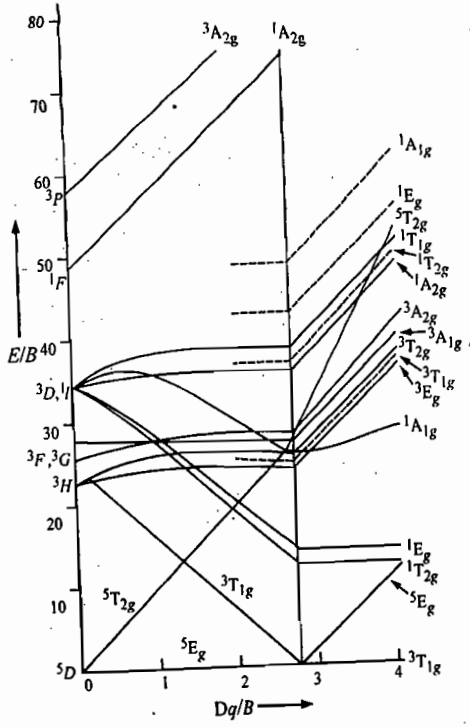


Fig. 67. Tanabe–Sugano diagram for d^4 system drawn for $C/B = 4{\cdot}6$

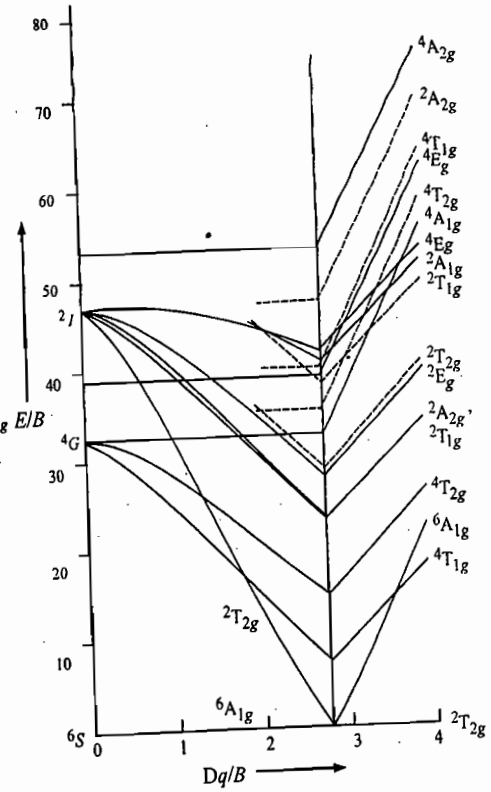


Fig. 68. Tanabe–Sugano diagram for d^5 system drawn for $C/B = 4{\cdot}5$

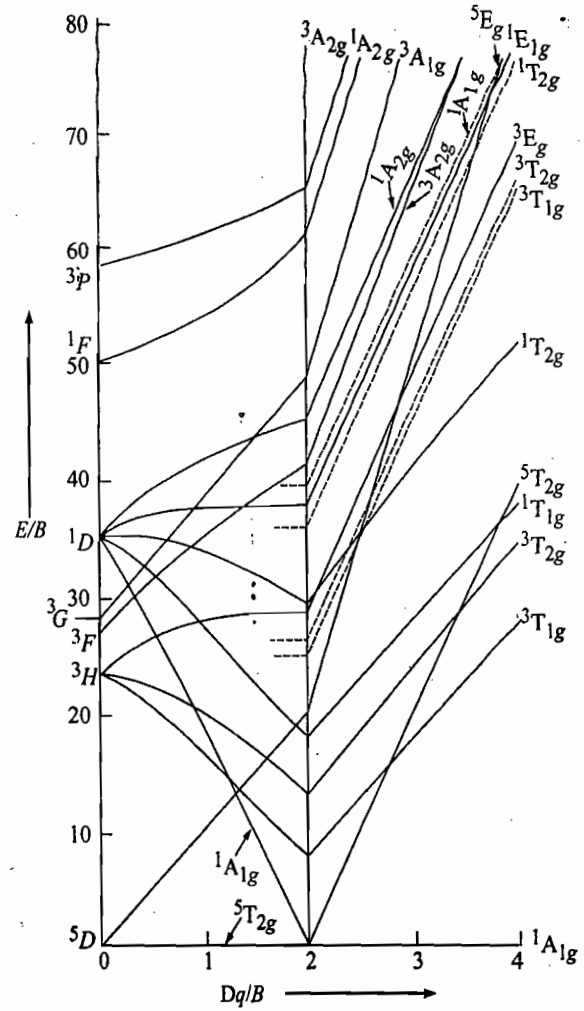


Fig. 69. Tanabe–Sugano diagram for d^6 system drawn for $C/B = 4{\cdot}5$

The energy of any level at a particular Dq/B value depends upon both the parameters B and C. But the energy *difference*, ΔE, between any two energy levels of the same multiplicity (which always have the same value of parameter C) is a function of parameter B only. However, the energy difference ΔE between two energy levels having different multiplicities is a function of both the parameters B and C (such levels have different values of B and C). Although the T–S diagrams are drawn for octahedral complexes of metal ions of the First transition series, these can be also applied to tetrahedral complexes of the series with some modification and remembering that d^{10-n} (octahedral weak field) $\equiv d^n$ (tetrahedral).

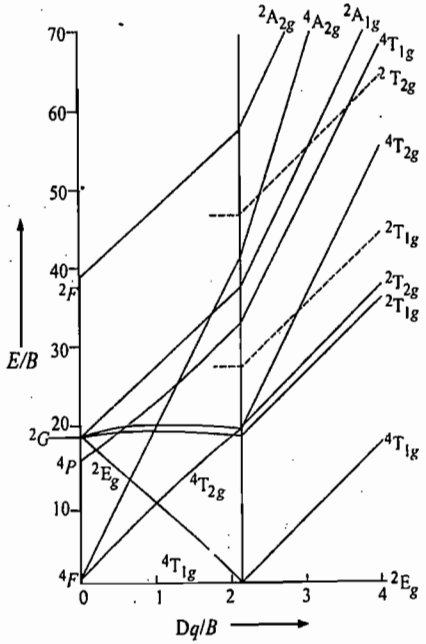


Fig. 70. Tanabe–Sugano diagram for d^7 system drawn for $C/B = 4{\cdot}65$

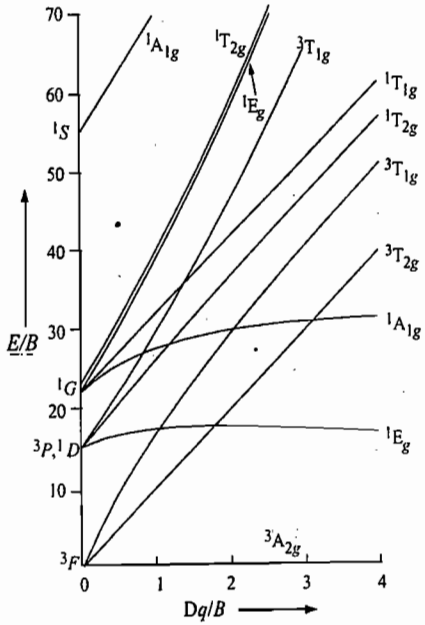


Fig. 71. Tanabe–Sugano diagram for d^8 system drawn for $C/B = 4{\cdot}70$

As can be seen from Figs. 67, 68, 69, 70, for d^4, d^5, d^6, d^7 metal ions, respectively, in octahedral environment, there is a certain break point in the plot of Dq/*B* vs *E*/*B* where at a certain Dq/*B*, the high spin ground states (having higher spin multiplicity) of the system starts increasing in energy and becomes the excited states *after* crossing this point whereas an excited state of lower spin multiplicity becomes the ground state *after* this point. Obviously, at the break point, the *d* interelectronic repulsion is equal to the CFSE of the system (CFSE is measured in terms of Dq/*B*). In other words, in the narrow range on either side of this point, there is a possibility of octahedral complex occurring either in the high spin state or in the low spin state or in both the states in equilibrium (in solution phase). Hence, this point is called **high spin–low spin crossover point**. It is this point where the spin pairing *just* starts occurring. On the left of this point, the complex will occur as a high spin complex and on the right of this point, it will occur as a low spin complex.

As can be seen from the T–S diagrams for d^4, d^5, d^6, d^7 systems, the high spin–low spin crossover points occur at 2·7 Dq/*B*, 2·8 Dq/*B*, 2·0 Dq/*B* and 2·2 Dq/*B*, repectively. Remembering that the parameter *B* for the metal ions of the First transition series does not vary much, it appears from the T–S diagrams that spin pairing should occur more easily in the case of d^6 (Fe^{2+}) and d^7 (Co^{2+}) and less easily in the case of d^4 (Cr^{2+}, Mn^{3+}) and d^5 (Mn^{2+}, Fe^{3+}) ions. These conclusions are largely in agreement with experimental observations.

By observing the energy positions of electronic absorption bands in the spectra of octahedral complexes, it is possible to calculate the values of parameters Dq, *B* and *C* with the help of T–S diagrams.

It is pertinent to add that the Orgel diagrams are nothing but the simplified qualitatively drawn T–S diagrams pertaining only to those energy levels which have the same spin multiplicity as that of the ground state energy level.

Although Tanabe–Sugano diagrams are drawn primarily for quantitative interpretation of the properties of d^n metal ions in the octahedral ligand environments, it is possible to use these diagrams for the metal ions in the tetrahedral ligand environments also. For this, we have to remember that d^n(octahedral) $\equiv d^{10-n}$(tetrahedral).

Evaluation of 10 Dq and *B* from Tanabe Sugano Diagrams

For the evaluation of 10 Dq and the Racah parameter *B*, we shall confine ourselves to the spin allowed transitions. It is, therefore, convenient to use simplified Tanabe-Sugano diagrams that contain only the terms which have the same spin multiplicity as the ground state. Out of these simplified diagrams, Fig. 72 is applicable to d^2, d^7 octahedral systems (weak field) and d^3, d^8 tetrahedral systems whereas Fig. 73 is applicable to d^3, d^8 octahedral systems (weak field) and d^2, d^7 tetrahedral systems. The subscript *g* is dropped from the terms of Figs. 72 and 73 if these figures are used for tetrahedral systems.

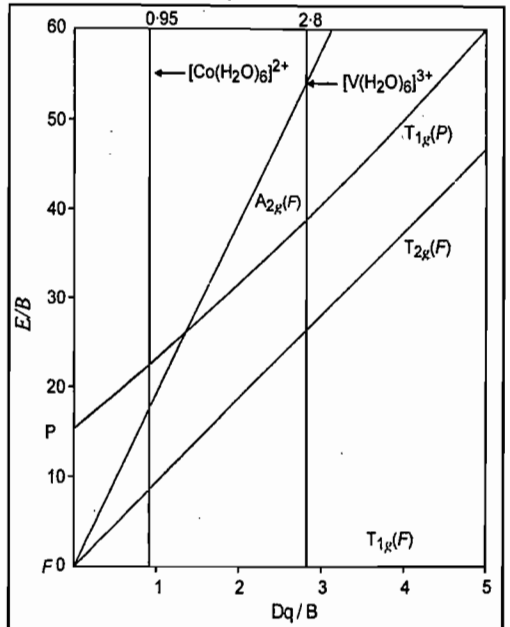


Fig. 72. Simplified T–S diagram for d^2, d^7 octahedral and d^3, d^8 tetrahedral systems.

The utility of these figures will be shown by considering a few weak field hexaaquametal ions. (These figures can be equally utilised for other weak field octahedral complexes as well).

1. As already stated, the electronic spectra of $V(H_2O)_6^{3+}$ complex ion in aqueous medium shows two transitions, *viz.*, E_1 at 17000 cm^{-1} [$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$] and E_2 at 25600 cm^{-1} ($^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$], respectively. The ratio of these two energies is given by

$$\frac{E_2/B}{E_1/B} = \frac{E_2}{E_1} = \frac{25600}{17200} \simeq 1{\cdot}5$$

It is clear from Fig. 72 that this ratio of energy gaps, *i.e.*, $\frac{E_2/B}{E_1/B}$, is obtained only at Dq/*B* value of 2·8. If we draw a vertical line at Dq/*B* value of 2·8, then E_2/B and E_1/B gaps come out to be 39 and 26, respectively, so that their ratio is 1·5.

Since E_1/B (*i.e.* lower energy gap) $= 26 = \frac{17200\ \text{cm}^{-1}}{B}$, hence $B \simeq 660$ cm^{-1}.

The position of the third electronic transition $E_3[^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)]$ can also be calculated by noting E_3/B from the figure at Dq/*B* value of 2·8. E_3/B is 55 so that E_3 is 660 × 55 = 36000 cm^{-1}. The E_3 transition corresponds to simultaneous excitation of two electrons and is thus forbidden, apart from being Leporte forbidden also. The value of $B_{V(H_2O)_6^{3+}}$ (660 cm^{-1}) obtained by this procedure is less than the $B_{V^{3+}}$ (free ion) value of 860 cm^{-1}. This is as expected. The value of 10Dq is 10 × 2·8 × 660 cm^{-1} ≃ 18500 cm^{-1}.

2. The electronic absorption spectrum of $[Co(H_2O)_6]^{2+}$ (*aq*) shows three electronic transitions at 8000 cm^{-1} [$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$], 19600 cm^{-1}[$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$] and 21600 cm^{-1}[$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$].

The ratio $\frac{E_3/B}{E_1/B} = \frac{E_3}{E_1} = \frac{21600\ \text{cm}^{-1}}{8000\ \text{cm}^{-1}} = 2{\cdot}7$

This ratio is achieved in Fig. 72 only where Dq/*B* is 0·95. If we draw a vertical line at Dq/*B* value of 0·95 in the figure, the energy gap E_1/B is observed to be 8·2, that is, $E_1/B = \frac{8000\ \text{cm}^{-1}}{B} = 8{\cdot}2$

or $$B = \frac{8000\ \text{cm}^{-1}}{8{\cdot}2} = 980\ \text{cm}^{-1}$$

which is smaller than $B_{Co^{3+}}$ (free ion) value of 1120 cm^{-1}.

The value of 10 Dq is, therefore, $10 \times 0{\cdot}95 \times 980\ \text{cm}^{-1} = 9300\ \text{cm}^{-1}$. The position of second transition E_2 can also be calculated from Fig. 72. It can be seen from this figure that $E_2/B \simeq 18{\cdot}5$ which gives E_2 as $18{\cdot}5 \times 980\ \text{cm}^{-1} = 18{,}100$ which is quite close to the actual transition observed at 19,100 cm^{-1}.

3. The three crystal field transitions observed in the electronic spectrum of $Ni(H_2O)_6^{2+}(aq)$ are $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ at 8700 cm^{-1}, 14500 cm^{-1} and 25300 cm^{-1}, respectively. It can be easily verified from Fig. 73 that the ratio of energy gaps which is most sensitive to changes in $Dq/B = \frac{E_3/B}{E_2/B} = E_3/E_2 \equiv \frac{25300\ \text{cm}^{-1}}{14700\ \text{cm}^{-1}} \equiv 1{\cdot}72$. The corresponding Dq/B at which the above ratio fits in the figure is 1.0. If a vertical line is drawn at Dq/B value of 1·0, it can be seen that E_3/B is 28.

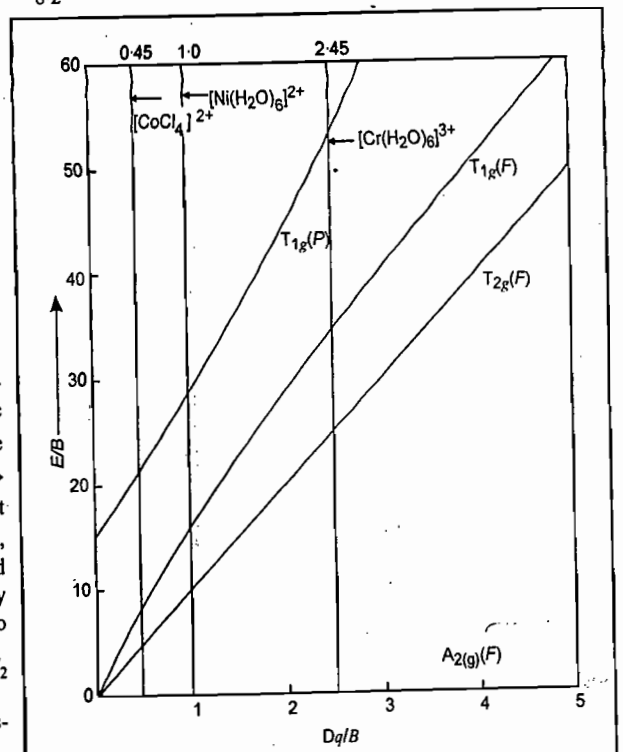


Fig. 73. Simplified T–S diagram for d^3, d^8 octahedral and d^2, d^7 tetrahedral systems.

Thus, E_3/B or $\frac{25300\ \text{cm}^{-1}}{B}$ is 28 or $B = \frac{25300\ \text{cm}^{-1}}{28} \approx 900\ \text{cm}^{-1}$ which is, as expected, less than $B_{Ni^{2+}}$ (free ion) value of 1040 cm^{-1}. The value of 10 Dq is $10 \times 1{\cdot}0 \times 900\ \text{cm}^{-1} = 9000\ \text{cm}^{-1}$.

4. The electronic spectrum of $Cr(H_2O)_6^{3+}(aq)$ shows three electronic transitions E_1 [$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$], E_2[$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$] and E_3[$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$] at 17000 cm^{-1}, 24,000 cm^{-1} and 37000 cm^{-1}, respectively. The last transition appears as a shoulder on the tail of intense charge transfer transition. The ratio of energy gap $\frac{E_2/B}{E_1/B}$, *i.e.*, $\frac{E_2}{E_1}$ is $\frac{24000\ \text{cm}^{-1}}{17000\ \text{cm}^{-1}}$, *i.e.*, 1·41. It can be seen from Fig. 73 that this ratio is achieved when Dq/B is 2·45. If a vertical line is drawn at this value of Dq/B, E_2/B comes out to be ~ 35. Thus, E_2/B or $\frac{24000\ \text{cm}^{-1}}{B} = 35$ and B is $\frac{24000\ \text{cm}^{-1}}{35} \simeq 690\ \text{cm}^{-1}$ which is less than $B_{Cr^{3+}}$ (free ion) value of 1030 cm^{-1}.

Also, since Dq/B is 2·45, 10 Dq is $10 \times 2{\cdot}45 \times 690$, *i.e.*, 16900 cm^{-1}. The E_3/B gap at Dq/B value of 2·45 is 53 so that the position of the third transition should be $53 \times 690\ \text{cm}^{-1}$, *i.e.*, 36600 cm^{-1} which confirms that the shoulder appearing on the tail of charge transfer transition is indeed due $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$.

5. Although the evaluation of 10 Dq and B is difficult from the electronic spectra of spin paired complexes due to masking of crystal field absorption bands by the high intensity, low energy charge transfer bands, it is possible in a few cases to evaluate these quantities by using Tanabe–Sugano diagrams.

The electronic spectra of $[Co(en)_3]^{3+}$ in aqueous medium is clearly interpretable. The two crystal field absorption bands occur at 21400 cm^{-1} ($^1A_{1g} \rightarrow {}^1T_{1g}$) and at 29400 cm^{-1} ($^1A_{1g} \rightarrow {}^1T_{2g}$). The right side of simplified Tanabe–Sugano diagram (Fig. 74) is used for evaluating 10 Dq and B. The ratio $\frac{E_2/B}{E_1/B}$, *i.e.*, $\frac{E_2}{E_1}$ is $\frac{29400}{21400}$ or 1·37 which fits in the figure at Dq/B value of 4·0. If a vertical line is drawn at this Dq/B, E_2/B is seen to be 52. Accordingly, $E_2/B = \frac{29400\ \text{cm}^{-1}}{B} = 52\ \text{cm}^{-1}$ or $B = \frac{29400\ \text{cm}^{-1}}{52}$ or 565 cm^{-1} which is very much reduced compared to $B_{Co^{3+}}$ (free ion) value of 1400 cm^{-1}.

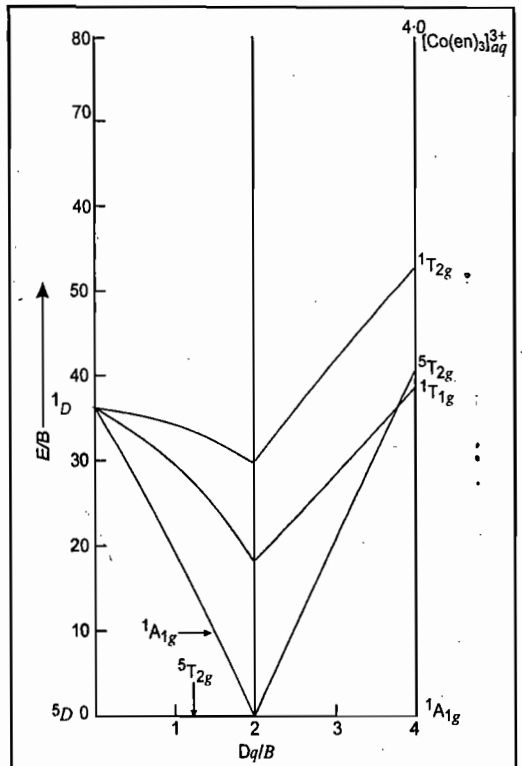


Fig. 74. Simplified Tanabe–Sugano diagram for d^6 octahedral system.

Also $10\ Dq = 10 \times \frac{Dq}{B} \times B = 10 \times 4 \times 565\ \text{cm}^{-1}$
$= 22600\ \text{cm}^{-1}$

6. Tanabe–Sugano diagrams can also be utilised to evaluate 10 Dq and B in tetrahedral complexes provided crystal field absorption bands in their electronic spectra are clearly identifiable. The electronic spectrum of $[CoCl_4]^{2-}$ in > 10 N HCl contains the absorption bands at 5800 cm^{-1} [$^4A_2(F) \rightarrow {}^4T_1(F)$] and at 15000 cm^{-1} [$^4A_2(F) \rightarrow {}^4T_1(P)$]. The lowest energy absorption band $^4A_2(F) \rightarrow {}^4T_2(F)$ is not observable in the visible region.

The ratio $\frac{E_3/B}{E_2/B}$, *i.e.*, $\frac{E_3}{E_2} = \frac{15000}{5800} \simeq 2{\cdot}6$.

This ratio fits in Fig. 73 at Dq/B value of 0·45. If a vertical line is drawn at this Dq/B, the energy gap E_3/B is found to be 21·0. Thus, E_3/B or $\frac{15000\ \text{cm}^{-1}}{B} = 21$ or $B = \frac{15000\ \text{cm}^{-1}}{21} = 715\ \text{cm}^{-1}$ and 10 Dq is $10 \times 0{\cdot}45 \times 715\ \text{cm}^{-1}$, *i.e.*, 3220 cm^{-1}.

7. No simplified Tanabe–Sugano diagram similar to those shown in Figs. 72 and 73 can be drawn for weak field octahedral systems because there is no excited term which has the same multiplicity as that of the ground state of the d^5 weak field system. Therefore, the left side (before the spin cross-over point) of the complete Tanabe–Sugano diagram (Fig. 68) is utilized to evaluate 10 Dq and B. The electronic spectrum of ($Mn(H_2O)_6^{2+}$ in aqueous medium is given in Fig. 75.

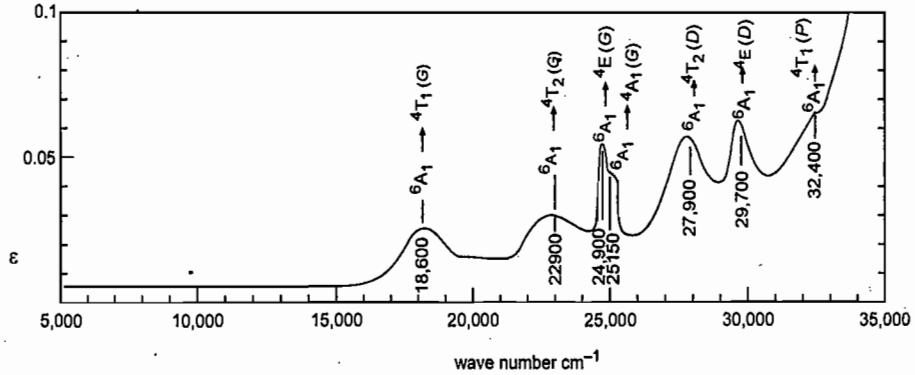


Fig. 75. Electronic spectrum of $[Mn(H_2O)_6]^{2+}$ in aqueous medium.

Since all crystal field transitions in the electronic spectrum are spin forbidden, their extinction coefficients are very low.

The ratio $\frac{E_2/B}{E_1/B}$, *i.e.*, $\frac{E_2}{E_1} = \frac{{}^6A_{1g} \rightarrow {}^4T_{2g}(G)}{{}^6A_{1g} \rightarrow {}^4T_{1g}(G)} = \frac{22900}{18600} \simeq 1{\cdot}2$

The ratio fits in Fig. 68 only at Dq/B value of 1·1. If a vertical line is drawn at this Dq/B value, we observe that

$$\frac{{}^6A_{1g} \rightarrow {}^4T_{2g}}{B} = 29 \qquad \text{or } B = \frac{22900\ \text{cm}^{-1}}{29} \simeq 790\ \text{cm}^{-1}$$

The $B_{Mn(H_2O)_6^{2+}}$ value of 790 cm^{-1} is less than the free ion value of 960 cm^{-1}, as expected.

Also, since Dq/B is 1·1, 10 Dq is 10 × 1·1 × 790 cm^{-1}, *i.e.*, 8700 cm^{-1}.

QUESTIONS

1. Discuss (l) – (l), (s) – (s) and (l) – (s) coupling of electrons occurring in a free gaseous atom.
2. Write down all the energy terms that are possible for a free gaseous atom having the configurations : (*i*) $3d^24s^2$ (*ii*) $2s^22p^1$
3. Write down all the possible electronic arrangements for $2s^2p^3$ configuration of free N atom.
4. Write down all the splittings, in proper order, of the following energy terms due to spin–orbit coupling : (*i*) ^6S of free Mn^{2+} (*ii*) ^3F of free Fe^{2+} (*iii*) ^5D of free Fe^{2+} (*iv*) ^4P of free Cr^{2+}
5. Discuss the splitting of D and F terms under the influence of weak V_{oct} and V_{tet}.
6. Discuss Leporte selection rule and spin selection rule of electron absoption spectroscopy. Under what conditions are these rules relaxed ?
7. What factors contribute to the width of absorption bands ? It has been observed that some absorption bands are sharper that the others in the electronic absorption spectrum of a transition metal complex. What do you think can be the reason ?

8. Discuss the utitility of Orgel diagrams. What are their limitations ? Draw Orgel diagrams for d^n configurations of metal ions in their transition metal complexes.
9. Discuss the electronic spectra of transition metal ions, Ti^{3+}, V^{3+}, Cr^{3+} and Mn^{2+} in their aqueous solutions.
10. (*a*) Why do electronic spectra of $[V(H_2O)_6]^{3+}$ show only two absorption bands against three predicted for the system?
    (*b*) Discuss the electronic spectra of $[Ni(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[FeCl_4]^{2-}$ and $[CoCl_4]^{2-}$.
11. Find out the energies of ground term configurations d^1 to d^{10}.
12. Write notes on :
    (*a*) Electron absorption spectra of low spin complexes
    (*b*) Charge transfer spectra
    (*c*) Spectrochemical and nephelauxetic series.
13. Write short notes on diamagnetism, para magnetism, ferromagnetism and antiferromagnetism.
14. What is quenching of orbital angular momentum and what are its consequences on the μ_{eff} of transition metal complexes ?
15. Discuss crystal field and VB approach to explain magnetic behaviour of transition metal complexes.
16. Discuss the magnetic behaviour of transition metal complexes in which ΔE between J states are (*i*) less than kT (*ii*) higher than kT (*iii*) comparable to kT.
17. Describe in details how you would derive the energy terms in the case of strong field octahedral complexes of transition metal ions with d^1, d^2 and d^3 configurations.
18. Work out the number of electronic arrangements for the following strong field configurations : e_g^1, e_g^2, t_{2g}^2, $t_{2g}^1e_g^1$.
19. What are terms correlation diagrams ? To what use are they put ?
20. Draw and discuss the qualitative correlation diagrams for the following systems :
    (*i*) d^1 octahedral and d^9 tetrahedral
    (*ii*) d^9 octahedral and d^1 tetrahedral
    (*iii*) d^2 octahedral and d^8 tetrahedral
    (*iii*) d^8 octahedral and d^2 tetrahedral
21. What are Tanabe-Sugano (T–S) diagrams ? To what use are they put ?

31 COORDINATION COMPOUNDS. PART VI

REACTION MECHANISM

Most of the reactions in inorganic chemistry are ionic in nature. As such they take place almost instantaneously and hence no mechanism is involved in their occurrence. Reactions of coordination compounds, however, are slow and proceed via definite pathways. The mechanisms involved in some of the reactions of coordination compounds, notably substitution reactions and electron transfer reactions, have been discussed in this chapter in some details.

Substitution Reactions in Octahedral Complexes. Substitution reactions involve the replacement of one ligand by another. This is called **nucleophilic substitution (S_N)** since ligands are all nucleophiles. In some reactions, the central metal ion may also get replaced by other metal ions. This is named as **electrophilic substitution (S_E)** since metal ions are all electrophiles.

Let us consider the substitution reaction in which one of the ligands X is replaced by another ligand Y :

$$[MX_6] + Y \longrightarrow [MX_5Y] + X$$

There are several mechanisms by which this type of reactions may occur but we shall consider only two main types of mechanisms. These are :

1. *Unimolecular Nucleophilic Substitution (S_N^1) Mechanism*
2. *Bimolecular Nucleophilic Substitution (S_N^2) Mechanism.*

1. Unimolecular Nucleophilic Substitution (S_N^1) or Dissociative S_N^1 Mechanism. According to this mechanism, the complex first undergoes dissociation losing the ligand to be replaced and changes into a 5-coordinated, *viz.*, square pyramidal intermediate complex, which then readily adds the new ligand Y. This may be illustrated as follows :

$$[MX_6] \xrightarrow{\text{slow}} \underset{\text{Five-coordinated intermediate complex}}{[MX_5]} + X$$

$$[MX_5] + Y \xrightarrow{\text{fast}} [MX_5Y]$$

The first step in which a ligand is lost is slow and the second step in which the intermediate complex formed reacts with the new ligand is fast. From our knowledge of chemical kinetics we know that the rate of a multi-step reaction depends only on the slowest step. This means that the rate of the above reaction depends only on the concentration of one species, *viz.*, the complex MX_6. The rate law for such a reaction may thus be represented as :

$$\text{Rate} = k[MX_6]$$

Since the rate of the reaction depends only upon the concentration of one species, the mechanism is referred to as **unimolecular nucleophilic substitution, *i.e.*, S_N^1 mechanism**. Since in this mechanism the complex first gets dissociated, it is also termed as **dissociative S_N^1 mechanism.**

2. Bimolecular Nucleophilic Substitution (S_N^2) or Associative S_N^2 Mechanism. According to this mechanism, the new ligand first adds on to the complex to form a seven-coordinated activated or intermediate

complex which then readily undergoes dissociaton to yield the final product. This may be illustrated as below :

$$[MX_6] + Y \xrightarrow{\text{slow}} \underset{\text{Seven-coordinated activated or intermediate complex}}{[MX_6Y]}$$

$$[MX_6Y] \xrightarrow{\text{fast}} [MX_5Y] + X$$

In this case, the reaction rate depends upon the first step, *i.e.*, upon the concentration of the complex as well as the concentration of the incoming ligand Y. The rate law may, therefore, be expressed as

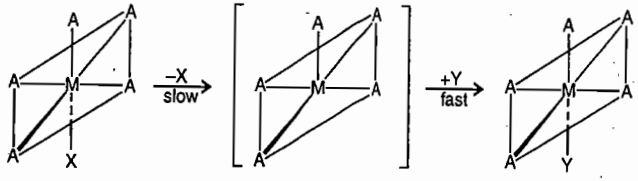
$$\text{Rate} = k[MX_6][Y]$$

Since the rate of the reaction depends upon the concentration of two species, the mechanism is referred to as **bimolecular nucleophilic substitution, *i.e.*, S_N^2 mechanism.** Since in this mechanism the incoming ligand first gets associated with the complex, it is also named as **associative S_N^2 mechanism.**

Types of Intermediates formed during S_N^1 and S_N^2 Reactions

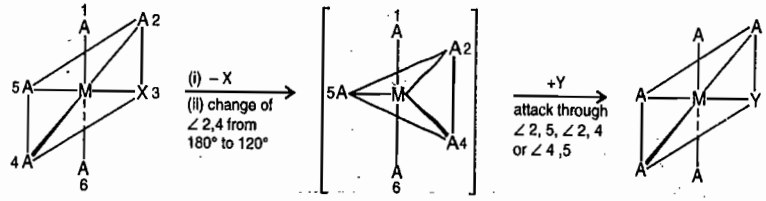
Consider an octahedral complex MA_5X being attacked by a nucleophile Y. If the reaction proceeds through a dissociative S_N^1 mechanism, two types of intermediates can be formed :

1. In the first type, the bond M–X dissociates causing least disturbance to the remaining MA_5 intermediate which has a *square pyramidal* geometry. The intermediate MA_5 is then attacked by Y to produce MA_5Y, as shown below :



Square pyramidal (SP) intermediate

2. In the second type, the bond M–X dissociates and the remaining MA_5 specie immediately adjusts the bond angles to produce a *trigonal bipyramidal* intermediate which is then attacked by Y to produce MA_5Y, as illustrated below :



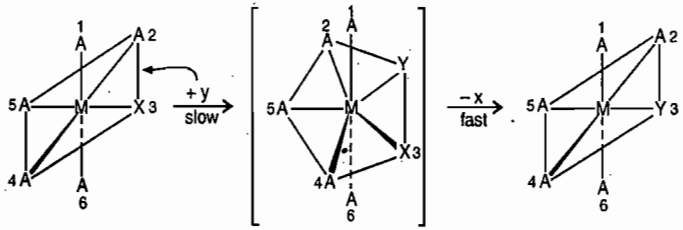
Trigonal bipyramidal (TBP) intermediate

It is evident that the formation of a trigonal bipyramidal (TBP) intermediate involves the movement of at least two metal-ligand bonds whereas no such movement is required during the formation of a square pyramidal (SP) intermediate. The S_N^1 reactions thus proceed normally through the more stable SP intermediate unless a TBP intermediate is so much stabilised by pi bonding that it becomes more stable than the SP intermediate. In that case, the S_N^1 reaction proceeds through a TBP intermediate.

If the reaction proceeds through an associative S_N^2 mechanism, there are again two types of intermediates :

1. The first type of intermediate is formed if the nucleophile Y attacks through one of the edges of the

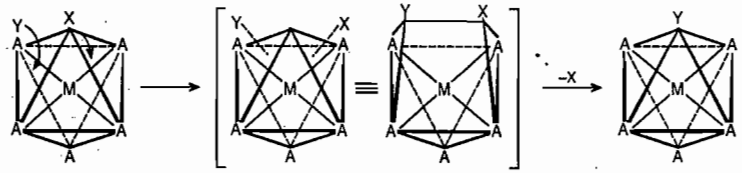
octahedron which leads to the formation of a *pentagonal bipyramidal* (PBP) intermediate, as shown below :



Pentagonal bipyramidal (PBP) intermediate

The formation of a PBP intermediate requires the movement of at least four ligands to adjust the nucleophile Y. The ligand–ligand repulsions also increase the energy of PBP intermediate because the decrease in A–M–A bond angles brings the electron pairs of metal–ligand bonds nearer to one another in this intermediate.

2. The second type of intermediate is formed if the nucleophile Y attacks through the middle of one of the triangular faces of the octahedron. As soon as Y starts approaching M, the outgoing ligand X starts moving towards the middle of another triangular face so that the '*octahedral wedge*' *intermediate* formed has both X and Y ligands in equivalent positions. The formation of an octahedral wedge (OW) intermediate is shown below :



Octahedral wedge (OW) intermediate

The formation of an OW intermediate requires minimum movement of ligands and the ligand–ligand repulsions are less than such repulsions in PBP intermediate. The M–X and M–Y distances are a little longer than the M–A distances in this intermediate. The OW intermediate requires less energy for its formation than the PBP intermediate. The S_N^2 reaction, therefore, would preferably proceed through an OW intermediate rather than a PBP intermediate. While writing the intermediates of S_N^2 reactions, the **principle of microscopic reversibility** should not be violated. This principle states that the outgoing and the incoming groups in the intermediates should occupy equivalent positions.

LABILITY AND INERTNESS OF OCTAHEDRAL COMPLEXES

Labile and Inert Complexes. *Complexes which permit quick exchange of one or more ligands from their coordination sphere by other ligands are called* **labile complexes.** On the other hand, *complexes which either do not permit exchange of ligands or in which the exchange of ligands is slow are known as* **inert complexes.** It should be clearly understood that, in general, inertness of a complex has nothing to do with its thermodynamic stability. For instance, the complex $[Ni(CN)_4]^{2-}$ is *thermodynamically stable* but *kinetically* it is *labile*. This is evident from the following ligand exchange reaction :

$$[Ni(CN)_4]^{2-} + (^{14}CN)^- \xrightarrow[\text{in aqueous medium}]{\text{very fast}} [Ni(CN)_3(^{14}CN)]^{2-} + (CN)^-$$

On the other hand, the complex $[Co(NH_3)_6]^{3+}$ is *thermodynamically unstable* but *kinetically* it is *inert*. The complex in aqueous solution remains undecomposed even over a period of several days, there being no exchange of the ligand NH_3 by the ligand H_2O.

Interpretation of Lability and Inertness of Transition Metal Complexes

Attempts have been made to explain lability and inertness of transition metal complexes on the basis of valence bond as well as crystal field theory. The valence bond theory is simple in approach but offers only a partial explanation for the lability and inertness of complexes. The crystal field theory, however, explains the phenomenon more satisfactorily.

The Valence Bond Theory. According to the valence bond theory, transition metal complexes undergoing substitution reactions through the dissociative S_N^1 mechanism would be *labile* if the bonds holding the ligands with the central metal ion are comparatively *weak* and would be *inert* if such bonds are comparatively *strong*. Since the outer n*d* orbitals are associated with higher energy than the inner (n−1)*d* orbitals, the metal–ligand bonds utilising metal hybrid orbitals containing contributions from outer n*d* orbitals would be less stable than the metal–ligand bonds utilising metal hybrid orbitals containing contributions from inner (n−1)*d* orbitals. This implies that outer orbital octahedral complexes in which the metal ion utilises $nsnp^3nd^2$ hybridised orbitals for metal–ligand bonding would permit relatively easier delinking of the outgoing ligand compared to the inner-orbital octahedral complexes in which the metal ion utilises $(n-1)d^2ns\,np^3$ hybrid orbitals for metal–ligand bonding. Thus, according to the **valence bond theory,** *all outer orbital complexes would be labile and all inner orbital complexes would be inert if substitution reaction proceeds through S_N^1 mechanism.*

It may be noted, however, that since the metal–ligand bonds in inner orbital complexes are quite *strong* and hence require considerable energy for their dissociation, *the inner orbital complexes would prefer to follow an associative S_N^2 mechanism rather than a dissociative S_N^1 mechanism in their substitution reactions.* It follows from above that the *outer orbital complexes would follow the dissociative S_N^1 mechanism in their substitution reactions.* The dissociative S_N^1 mechanism is also preferred for outer orbital complexes because these would need to utilise an additional higher energy n*d* orbital for the formation of seven-coordinated intermediate in the S_N^2 mechanism.

Some inner orbital complexes containing metal ions *with at least one empty* (n−1)*d orbital* which can accommodate electrons from the incoming nucleophile would facilitate the formation of seven-coordinated intermediates. Such complexes would, therefore, be *labile*. Examples of such labile inner orbital octahedral complexes are :

1. Octahedral complexes of Sc^{3+}, Y^{3+}, Zr^{4+}, Ce^{4+} (all d^0 systems)
2. Octahedral complexes of Ti^{3+}, V^{4+}, Mo^{5+} (all d^1 systems)
3. Octahedral complexes of Ti^{2+}, V^{3+}, Nb^{3+}, Mo^{4+} (all d^2 systems)

Some inner orbital complexes in which the metal ions have at least one electron in each of the three (n−1)*d* orbitals (which are left out of hybridisation) will have to accommodate electrons from the incoming nucleophile into an outer higher energy n*d* orbital. Such complexes would, therefore, form seven-coordinated intermediates with *difficulty* and would thus be *inert*. Examples of inert inner orbital complexes are the octahedral complexes with d^3, d^4, d^5 and d^6 metal ion configurations.

Metal ion configurations of labile and inert inner orbital octahedral complexes are shown in Table 1

TABLE 1

Metal Ion Configurations of Labile and Inert Octahedral Inner Orbital Compelxes

Metal Ion Configurations	Reactivity	Remarks
(n−1)*d* *ns* *np*		
d^0	*Labile*	*Three vacant (n−1)d orbitals*
d^1	Labile	Two vacant (n−1)*d* orbitals
d^3	Inert	No vacant (n−1)*d* orbital
d^6	Inert	No vacant (n−1)*d* orbital

Some exceptions to the above generalisations are also known. For example, octahedral complexes of Ni(II) with d^8 configuration are predicted by VB theory to be *labile* because according to this theory, Ni(II) will utilise $nsnp^3nd^2$ hybrid metal orbitals for metal–ligand bonding but experimentally they are found to be *inert*. This and some other exceptions are, however, well explained by the crystal field theory.

Crystal Field Theory. Before we discuss the crystal field theory to explain the inertness and lability of octahedral complexes, it would be worthwhile to differentiate between *activation energy* and *crystal field activation energy*.

Activation Energy. Activation energy is defined as *the energy required to transform the reacting complex into the transition state* (*i.e.*, the intermediate). The activation energy is made up of energy changes due to changes in metal–ligand bond lengths, bond angles, ligand–ligand repulsions, crystal field stabilization energies (cf. Chapter 27), etc.

Crystal Field Activation Energy (CFAE). Crystal field activation energy is defined *as the change in the crystal field stabilisation energy (CFSE) when the reacting complex is transformed into the transition state* (*i.e.*, the intermediate). Thus,

$$\text{CFAE} = \text{CFSE of intermediate} - \text{CFSE of reacting complex}$$

The crystal field activation energy is only a part of the overall activation energy. Since the geometries of the reacting complex and the intermediate are different, *the order and extent of splitting of d orbitals of the metal ion in the two species would be different.* Hence, CFSE of the reacting complex would be different from the CFSE of the intermediate.

Evaluation of CFAE. The following assumptions are made for calculating CFSEs from which CFAEs are easily calculated :

1. The geometry of the reacting complex is assumed to be octahedral even if all the six ligands are not identical.

2. Inter-electronic repulsions amongst the *d* electrons are assumed to be negligible.

3. The Dq for the reacting complex is assumed to be the same as Dq for its intermediate. Actually, the two Dqs are quite different due to different geometries of the complex and the intermediate.

4. The Jahn-Tellar effect which causes distortions in octahedral geometries, is assumed to be negligible. Actually the Jahn–Tellar distortions are quite appreciable in some 6-coordinated complexes.

Because of the above drastic assumptions, some of the calculated CFAEs come out to be negative as is evident from Tables 2 and 3. However, such CFAEs, when calculated by employing more exact but very tedius calculations, come out to be either zero or small but are never negative. Therefore, for determining the reactivity of a complex by this over-simplified crystal field approach, the negative CFAEs can be roughly taken as zero.

According to the crystal field theory,

1. If the calculated CFAE is negative or zero or low, the reacting complex would require less energy for its transformation into the intermediate.

2. If the calculated CFAE is high, the reacting complex would require more energy for its transformation into the intermediate.

It should be kept in mind that since CFAE is only a part of total activation energy, a valid comparison of lability on the basis of CFAE can be made only if all other factors which contribute to the activation energy are more or less the same. This implies that the complexes should be more or less identical except for the configuration of the metal ions and these should be involved in similar type of reactions.

CFAE and S_N^1 Reactions. Let us now interpret the lability of octahedral complexes involved in reactions proceeding through S_N^1 mechanism. We have already established that, under normal conditions, the S_N^1 reactions proceed through the lower energy SP intermediates instead of higher energy TBP intermediates.

CFAEs of octahedral complexes undergoing S_N^1 substitution reactions through SP intermediates are

given in Table 2. The configurations of metal ions are shown to vary from d^0 to d^{10}.

TABLE 2

Crystal Field Activation Energies (in Dq) of Octahedral Complexes undergoing S_N^1 Reactions through the formation of Square Pyramidal Complexes as intermediates

System	Weak Field Complexes			Strong Field Complexes		
	CFSE for :		CFAE	CFSE for :		CFAE
	Octahedral complexes	Square pyramidal complexes		Octahedral complexes	Square pyramidal complexes	
d^0	0	0	0	0	0	0
d^1	− 4	− 4·57	− 0·57	− 4	− 4·57	− 0·57
d^2	− 8	− 9·14	− 1·14	− 8	− 9·14	− 1·14
d^3	− 12	− 10·00	2·00	− 12	− 10·00	2·00
d^4	− 6	− 9·14	− 3·14	− 16	− 14·57	1·43
d^5	0	0	0	− 20	− 19·14	0·86
d^6	− 4	− 4·57	− 0·57	− 24	− 20·00	4·00
d^7	− 8	− 9·14	− 1·14	− 18	− 19·14	− 1·14
d^8	− 12	− 10·00	2·00	− 12	− 10·00	2·00
d^9	− 6	− 9·14	− 3·14	− 6	− 9·14	− 3·14
d^{10}	0	0	0	0	0	0

From Table 2, we draw the following conclusions :

1. Amongst the **weak field octahedral complexes**, those containing metal ions with d^0, d^1, d^2, d^4, d^5, d^6, d^7, d^9 and d^{10} configurations, have negative or zero CFAEs and would, therefore, be labile whereas those containing d^3 and d^8 configurations of metal ions have positive CFAEs and would, therefore, be slow to react.

2. Amongst the **strong field complexes**, those containing metal ions with d^0, d^1, d^2, d^7, d^9 and d^{10} configurations, have negative or zero CFAEs and would, therefore, be labile whereas those containing d^3, d^4, d^5, d^6 and d^8 configurations of metal ions have positive CFAEs and would, therefore, be slow to react. Amongst these complexes, the order of reactivity on the basis of CFAEs is $d^6 < d^3 \sim d^8 < d^4 < d^5$.

CFAEs and S_N^2 Reactions. As discussed earlier, an OW intermediate requires less energy for its formation than the PBP intermediate. The S_N^2 reactions, therefore, proceed through lower energy OW intermediates rather than PBP intermediates. The CFAEs of octahedral complexes with metal ions having d^0 to d^{10} configuations undergoing S_N^2 substitution reactions through OW intermediates are shown in Table 3 :

TABLE 3

Crystal Field Activation Energies (in Dq) of Octahedral Complexes undergoing S_N^2 Reactions through the formation of Octahedral Wedge Complexes as Intermediates

System	Weak Field Complexes			Strong Field Complexes		
	CFSE for :		CFAE	CFSE for :		CFAE
	Octahedral complexes	Octahedral wedge complexes		Octahedral complexes	Octahedral wedge complexes	
d^0	0	0	0	0	0	0
d^1	− 4	− 6·08	− 2·08	− 4	− 6·08	− 2·08
d^2	− 8	− 8·68	− 0·68	− 8	− 8·68	− 0·68
d^3	− 12	− 10·20	1·80	− 12	− 10·20	1·80
d^4	− 6	− 8·79	− 2·79	− 16	− 16·26	− 0·26
d^5	0	0	0	− 20	− 18·86	1·14
d^6	− 4	− 6·08	− 2·08	− 24	− 20·37	3·63
d^7	− 8	− 8·68	− 0·68	− 18	− 18·98	− 0·98
d^8	− 12	− 10·20	1·80	− 12	− 10.20	1·80
d^9	− 6	− 8·79	− 2·79	− 6	− 8·79	− 2·79
d^{10}	0	0	0	0	0	0

We draw the following conclusions from Table 3 :

1. Amongst the **weak field octahedral complexes**, those containing metal ions with d^0, d^1, d^2, d^4, d^5, d^6, d^7, d^9 and d^{10} configurations, have either negative or zero CFAEs. Such complexes would, therefore, be labile. The complexes with metal ion configurations of d^3 and d^8 have positive CFAEs. They would, therefore, be slow to react.

2. Amongst the **strong field octahedral complexes,** those containing metal ions with d^0, d^1, d^2, d^4, d^7, d^9 and d^{10} configurations, have either negative or zero CFAEs. Such complexes would, therefore, be labile. The complexes with metal ion configurations of d^3, d^5, d^6 and d^8 have positive CFAEs. These complexes would, therefore, be slow to react. The order of reactivity amongst these complexes is $d^6 < d^3 \sim d^8 < d^5$.

From the combined data given in Tables 2 and 3, we conclude that

1. Octahedral complexes with metal ion configurations of d^3 and spin-paired d^5 and d^6 (and to some extent d^4) would be slow to react by S_N^1 or S_N^2 mechanism (strong ligand field causes pairing of electron spins). Similarly, octahedral complexes with metal ion configuration of d^8 (*e.g.*, complexes of Ni(II) would be slow to react whatever be the strength of the ligand field and whatever be the mechanism of their substitution reactions.

2. Octahderal complexes with metal ion configurations of d^0, d^1, d^2, spin-free d^4, d^5, d^6, d^7, d^9 and d^{10}, would be labile by either of the two mechanisms.

It is evident from the above discussion that both the VB and CF theories are in complete agreement to predict the lability of d^0, d^1, d^2, spin-free d^4, d^5, d^6, d^7, d^9 and d^{10} systems and inertness of d^3 and spin-paired d^4, d^5 and d^6 systems. But the two theories are in disagreement for predicting the character of d^8 system. While the VB theory predicts that complexes with d^8 configuration of metal ions would be *labile*, the CF theory predicts them to be *inert*. The experimental evidence is in favour of the prediction made by the CF theory. For example, the rate of substitution in weak field octahedral Ni(II) (d^8) complexes is found to be much slower than in similar weak field (or spin-free) Fe (II) (d^6) and Co (II) (d^7) complexes.

Lability of Non-transition Metal Complexes

According to VB theory, all non-transition metal octahedral complexes are outer orbital complexes and are, therefore, labile. They react through dissociative S_N^1 mechanism. The CF theory also predicts that all non-transition metal octahedral complexes would be labile since the CFAEs in these cases are zero irrespective of whether the reaction proceeds through S_N^1 or S_N^2 mechanism.

Factors controlling Lability of Non-transition Metal Complexes. The relative lability of non-transition metal complexes depends upon the following factors :

1. Charge on the central metal atom. The greater the positive charge on the central metal atom, the lesser is the lability of the complex. For example, the lability of $[AlF_6]^{3-}$, $[SiF_6]^{2-}$ and $[PF_6]^-$ (the oxidation number of Al, Si and P being +3, +4 and +5, respectively), *decreases* in the order of their mention. Thus, the complex $[PF_6]^-$, in which the oxidation number of the central metal atom is *highest*, is the *least* labile.

2. Size of the central metal ion. *The smaller the size of the central metal ion, the lesser is the lability of the complex.* This is easily understandable if we assume that the bonding in non-transition metal complexes is predominantly ionic. The smaller the size of the metal ion for a particular ligand, the smaller would be the metal–ligand bond length and the greater would be the metal–ligand attraction. Thus, amongst the aqua complexes $[Mg(H_2O)_6]^{2+}$, $[Ca(H_2O)_6]^{2+}$ and $[Sr(H_2O)_6]^{2+}$, the Mg-complex is the *least labile* and lability increases as we move from Mg-complex to Ca-complex and from Ca-complex to Sr-complex.

3. Charge to ionic size ratio. *The greater the ratio of the charge on the complex to the size of the central metal ion, the lesser would be the lability of the complex.* Thus, for the reaction involving the [illegible] O* (O* is ^{18}O). [illegible] $(H_2O)_5H_2O^*]^{n+} + H_2O$,

the lability of complexes $[Na(H_2O)_6]^+$, $[Mg(H_2O)_6]^{2+}$ and $[Al(H_2O)_6]^{3+}$, *decreases* in the order of their mention. Thus, amongst the three complexes, $[Al(H_2O)_6]^{3+}$ with largest charge/radius ratio of 6·0 is the least labile whereas $[Na(H_2O)_6]^+$, with smallest charge/radius ratio of 1·05 is the most labile. The radii of Na^+, Mg^{2+} and Al^{3+} ions are 0·95, 0·60 and 0·50 Å, respectively.

4. Geometry of the complex. Tetrahedral and square planar complexes, compared to octahedral complexes, offer better sites for the attack of an incoming ligand. Hence, *for the same set of the metal ion and the ligands, the square planar and tetrahedral complexes are more labile than the octahedral complexes.*

SUBSTITUTION REACTIONS OF OCTAHEDRAL COMPLEXES

Most of the kinetic studies on the substitution reactions of octahedral complexes have been carried out in aqueous medium. Consider a substitution reaction of octahedral complex $[MA_5X]^{n+}$ in the presence of a ligand Y^- in aqueous medium. Since water also acts as a ligand and is much more abundant than Y^-, it is always the *aquation* of the complex $[MA_5X]^{n+}$ that occurs first (reaction 1) :

$$[MA_5X]^{n+} + H_2O \longrightarrow [MA_5(H_2O)]^{(n+1)+} + X^- \quad \text{... (1)}$$

The ligand Y^- would then replace the coordinated H_2O to give $[MA_5Y]^{n+}$ provided Y^- is present in appreciable amount (reaction 2) :

$$[MA_5(H_2O)]^{(n+1)+} + Y^- \longrightarrow [MA_5Y]^{n+} + H_2O \quad \text{... (2)}$$

Since all substitution reactions in aqueous medium proceed through the reaction of the complex with water, it is imperative to study the mechanism of substitution in reactions of complexes with water. The reaction in aqueous medium in which *a water molecule replaces a coordinated ligand from the complex species is termed as* **aquation reaction** or **acid hydrolysis** (reaction 1). The reaction in aqueous medium in which *the anion of water, i.e, OH^- ion, replaces a coordinated ligand from the complex species is known* as **base hydrolysis :**

$$[MA_5X]^{n+} + OH^- \longrightarrow [MA_5OH]^{n+} + X^- \quad \text{... (3)}$$

Since some OH^- ions are always present due to auto-ionization of H_2O, some $[MA_5OH]^{n+}$ is always formed alongwith $[MA_5(H_2O)]^{(n+1)+}$ during the hydrolysis of $[MA_5X]^{n+}$ even in neutral aqueous medium.

Mechanistic studies on the hydrolysis of a number of octahedral complexes of Co(III) and other metal ions are reported in literature. We shall, however, deal with only a few typical cases.

ACID HYDROLYSIS OF OCTAHEDRAL COMPLEXES

A. Mechanism of Acid Hydrolysis When No Inert Ligand* in the Complex is a pi Donor or a pi Acceptor

In **S_N^1 mechanism** of aquation, the slow, that is, the rate-determining step is that in which the bond M–X dissociates to produce a five-coordinated complex as an intermediate which then quickly reacts with water, as shown below :

$$[MA_5X]^{n+} \xrightarrow{\text{slow}} [MA_5]^{(n+1)+} + X^- \quad \text{... (4)}$$

$$[MA_5]^{(n+1)+} + H_2O \xrightarrow{\text{fast}} [MA_5(H_2O)]^{(n+1)+} \quad \text{... (5)}$$

$\therefore$ Rate of aquation = k_1 (concentration of $[MA_5X]^{n+}$

In **S_N^2 mechanism** of aquation, the slow, *i.e.*, the rate-determining step is that in which a seven-coordinated intermediate is formed which then readily gives up the leaving group X^- to yield the aquated product, as shown below :

$$[MA_5X]^{n+} + H_2O \xrightarrow{\text{slow}} [MA_5X(H_2O)]^{n+} \quad \text{... (6)}$$

$$[MA_5X(H_2O)]^{n+} \xrightarrow{\text{fast}} [MA_5(H_2O)]^{(n+1)+} + X^- \quad \text{... (7)}$$

* An inert ligand in the reacting complex is the one which remains attached to the metal ion in the product also.

$\therefore$ Rate of aquation $= k_2$ (concentration of $[MA_5X]^{n+} \times [H_2O]$)

Since H_2O is present in large abundance, its concentration, *viz.*, $[H_2O]$, remains constant. Hence,

$$\text{Rate of aquation} = k_2 \text{ (concentration of } [MA_5X]^{n+} \times \text{constant)}$$
$$= k_2' \text{ (concentration of } [MA_5X]^{n+})$$

Thus, both S_N1 and S_N2 pathways of aquation predict that the rate of the reaction would be dependent only on the concentration of the complex $[MA_5X]^{n+}$. This fact has been verified experimentally.

It follows from the above discussion that kinetic measurements of the aquation process would fail to establish whether the aquation reaction follows S_N1 or S_N2 mechanism. We shall have to look to some other factors which can help. These factors are : *1. Charge on the Substrate 2. Strength of Metal–Leaving Group Bond 3. Inductive Effects of Inert Ligands 4. Stability Constants 5. Solvation Effects* and *6. Steric Effects*. The role of each factor in establishing the pathway of the aquation process has been discussed below.

1. Charge on the Substrate. It has been observed during the aquation of several octahedral complexes of Co(III) and some other metal ions that *an increase in the positive charge on the reacting species decreases its rate of aquation.* For instance, the rate of aquation of cis $[Co(en)_2Cl_2]^+$ is some hundred times faster than the rate of aquation of cis $[Co(en)_2Cl(H_2O)]^{2+}$, as shown below :

$$\text{cis } [Co(en)_2Cl_2]^+ + H_2O \xrightarrow{\text{fast}} \text{cis } [Co(en)_2Cl(H_2O)]^{2+} + Cl^-$$

$$\text{cis } [Co(en)_2Cl(H_2O)]^{2+} + H_2O \xrightarrow{\text{slow}} \text{cis } [Co(en)_2(H_2O)_2]^{3+} + Cl^-$$

Similarly, the rate constants for the aquation of complexes $[RuCl_6]^{3-}$, $[RuCl_3(H_2O)_3]^0$ and $[Ru(H_2O)_5Cl]^{2+}$ decrease regularly with increase in the positive charge, the rate constants being $1{\cdot}0\ s^{-1}$, $2{\cdot}1\times10^{-6}\ s^{-1}$ and $\sim10^{-8}\ s^{-1}$, respectively.

The above ovservations favour a dissociative S_N1 path for the aquation process since the increase in positive charge on the substrate would obviously render the dissociation of the leaving group from metal M more difficult, resulting in the slower reaction by this mechanism.

Had the aquation occurred through S_N2 path, the increased positive charge on the substrate would not have made any significant impact on the rate of the aquation process. This is because the increase in charge would not only make the breaking of the M–X bond more difficult but would also make the formation of the M–H_2O bond more easy. In other words, the two processes involved in the formation of the 7-coordinated intermediate from the octahedral complex are kinetically affected in opposite directions with the result that the rate of the overall aquation process, if it takes place through S_N2 mechanism, would remain practically unchanged with any change in the charge on the substrate.

2. Strength of M–X, *i.e*, Metal–Leaving Group Bond. The observed rate constants for the aquation, *viz.*, acid hydrolysis of $[Co(NH_3)_5X]^{2+}$ are given in Table 4.

It is evident from the data given in Table 4 that the rate of aquation goes on decreasing with increase in the basicity of the leaving group X^-. Since the strength of the M–X bond is directly proportional to the basicity of the group X^-, we can also say that the rate of aquation goes on decreasing with increase in the strength of the M–X bond. This indicates that the rate-determining step in the aquation process does involve the dissociation of the M–X bond. The data thus clearly support a dissociative S_N1 mechanism for the aquation reaction of the octahedral complex.

TABLE 4

Rate Constants for the Acid Hydrolysis of $[Co(NH_3)_5X]^{2+}$

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

Leaving Group X^-	Dissociation constant for X^- (k_d)	$k_{aquation}$
CF_3COO^-	$2{\cdot}0 \times 10^{-14}$	$5{\cdot}5 \times 10^{-3}$
CCl_3COO^-	$5{\cdot}0 \times 10^{-14}$	$5{\cdot}4 \times 10^{-3}$
$CHCl_2COO^-$	$2{\cdot}0 \times 10^{-13}$	$1{\cdot}6 \times 10^{-3}$
CH_2ClCOO^-	$7{\cdot}1 \times 10^{-12}$	$0{\cdot}6 \times 10^{-3}$
$CH_3CH_2COO^-$	$6{\cdot}6 \times 10^{-10}$	$0{\cdot}3 \times 10^{-3}$

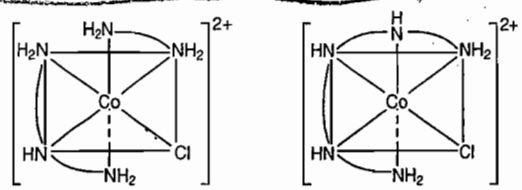
3. Inductive Effects of Inert Ligands. As already mentioned, the ligands which remain coordinated to the metal ion during the substitution reactions of the complex are referred to as inert ligands. It has been observed that the rate of the aquation reaction

$$[Co(en)_2(\text{subtd. py})Cl]^{2+} + H_2O \longrightarrow [\ Co(en)_2(\text{subtd. py})H_2O]^{3+} + Cl^- \quad ...(8)$$

varies with the basicity of the inert ligand. (subtd. py stands for substituted pyridine, *i.e.*, pyridine in which one of the H atoms is replaced by any other substituent). This again points towards a dissociative S_N1 mechanism for reaction (8). This is because the greater the basicity or electron-donating power of the inert ligand, the greater would be the accumulation of negative charge on Co which would result in easier heterolytic dissociation of Co–Cl bond.

4. Stability Constants. A study of stability constants of $[Co(NH_3)_5X]^{2+}$ with different leaving groups, reveals that during the aquation of the complex, the leaving group X^- is present in the product as well as in the intermediate in the form of a solvated anion. This means that X^- and the intermediate are formed by the dissociation of the Co–X bond which get solvated immediately. Thus, the aquation of $[Co(NH_3)_5X]^{2+}$ occurs through a solvation-assisted dissociation mechanism. (Solvation lowers the energy of the intermediate and thus makes the reaction more facile).

5. Solvation Effects. It is observed that the rate of aquation of $[Co(NH_3)_5Cl]^{2+}$, $[Co(en)(NH_3)_3Cl]^{2+}$, $[Co(en)(diene)Cl]^{2+}$ and $[Co(tetraene)Cl]^{2+}$ complexes *decreases in the order of their mention.* In these complexes, en is ethylene diamine, diene is diethylenetriamine and tetraene is tetraethylenepentamine. It is apparent from the above order that the rate of aquation goes on decreasing as the extent of chelation in the reacting complex goes on increasing. Although the above order can, to some extent, be explained by S_N2 (trans) attack of water on the complex, yet it cannot explain satisfactorily the relative rates of aquation of highly chelated species such as $[Co(en)(diene)Cl]^{2+}$ and $[Co(tetraene)Cl]^{2+}$ whose structures are as shown :



However, the solvation theory explains the relative rates of aquation of *all* the chelated complexes mentioned above in a satisfactory manner. According to the **solvation theory,**

1. In aqueous medium, the reacting species, the intermediates and the products are all present in the hydrated state.

2. The hydration of any species decreases its energy and thus stabilises it. The extent of stabilisation is related to the extent of hydration of the species.

3. The greater the charge and the smaller the size of the specie, the greater would be the extent of its hydration and hence the extent of its stabilisation.

The five-coordinated intermediate formed during aquation through S_N1 mechanism is smaller in size than the seven-coordinated intermediate formed through S_N2 mechanism. The five-coordinated intermediate being smaller in size, would get hydrated and thus get stabilised to a greater extent than the seven-coordinated intermediate. The greater stability of five-coordinated intermediate makes the S_N1 mechanism more feasible than the S_N2 mechanism for the aquation of the octahedral complexes. The presence of chelating agents such as en, diene, tetraene, etc., in place of unidentate ligands like NH_3, causes an increase in the size of the complex ion without causing any appreciable increase in the steric overcrowding around the central Co(III) ion (refer to the structures shown above).

Let us consider the aquation of the complexes $[Co(NH_3)_5Cl]^{2+}$ (smaller size) and $[Co(en)(NH_3)_3Cl]^{2+}$ (bigger size). Assuming that the process involves S_N1 mechanism, the aquation reactions can be represented as follows :

$$[CO(NH_3)_5Cl]^{2+}_{hydrated} \xrightarrow{\text{slow}} [Co(NH_3)_5]^{3+}_{hydrated} + Cl^-_{hydrated}$$

$$[Co(NH_3)_5]^{3+}_{hydrated} \xrightarrow[\text{fast}]{+H_2O} [Co(NH_3)_5H_2O]^{3+}_{hydrated} \quad ...(9)$$

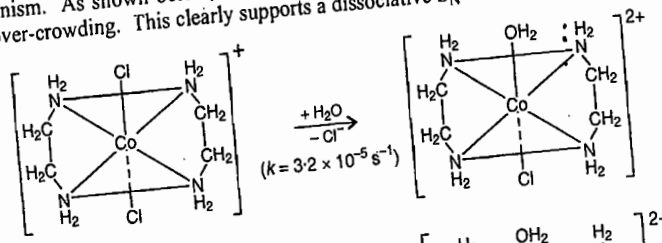
$$[CO(en)(NH_3)_3Cl]^{2+}_{hydrated} \xrightarrow{slow} [Co(en)(NH_3)_3]^{3+}_{hydrated} + Cl^-_{hydrated}$$

$$[Co(en)(NH_3)_3]^{3+}_{hydrated} \xrightarrow[fast]{+H_2O} [Co(en)(NH_3)_3H_2O]^{3+}_{hydrated} \quad \ldots(10)$$

The intermediate $[Co(en)(NH_3)_3]^{3+}$ of the chelated complex is bigger in size than the intermediate $[Co(NH_3)_5]^{3+}$ of the complex containing unidentate ligands. The former is, therefore, stabilised by hydration to *a lesser extent* and thus requires more energy for its formation than the latter. As a result, the rate-determining step in the aquation of the chelated complex $[Co(en)(NH_3)_3Cl]^{2+}$ would be *slower* than that in the complex containing no chelate, *i.e.*, $[Co(NH_3)_5Cl]^{2+}$. Similarly, it can be deduced that a chelate complex of a bigger size would be aquated at a slower rate than a chelate complex of a smaller size provided the chelate rings which increase the sizes of the chelate complexes do not bring about any appreciable change in the steric environments around the central metal ions.

6. Steric Effects. As is well known, an increase in the bulk of the ligands which can cause *an increase in the steric overcrowding around the metal ion favours a dissociative S_N^1 mechanism* and *disfavours an associative S_N^2 mechanism.* This places at our disposal a convenient means of predicting the mechanism of aquation by varying the bulk of the ligands and studying the rates of aquation.

Let us consider the rates of aquation of some chelate complexes in which there is increasing overcrowding around the metal ion due to an increase in the bulk of chelating agents proceeding through a dissociative S_N^1 mechanism. As shown below, the rate constants of the aquation reaction increase with increase in the steric over-crowding. This clearly supports a dissociative S_N^1 mechanism for the aquation reaction.



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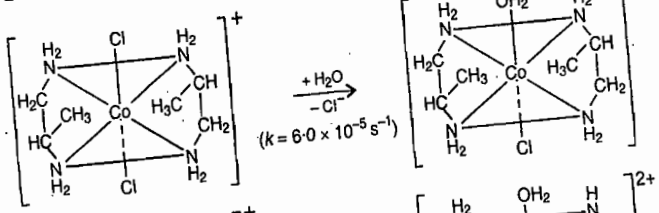

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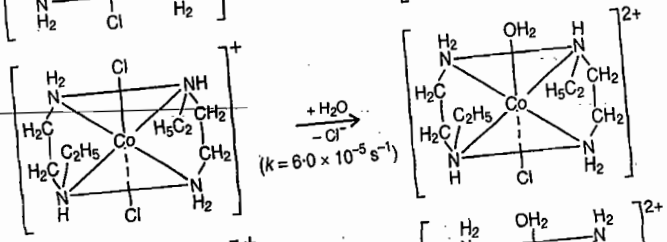

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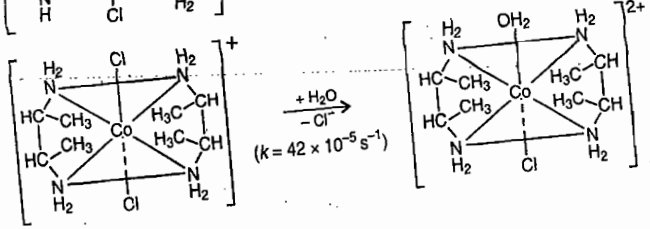
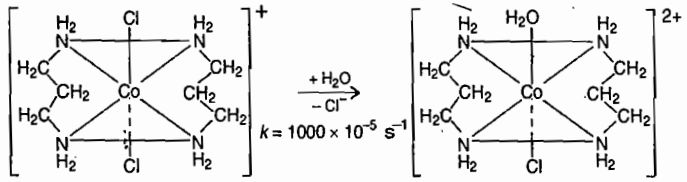


...(14)

It is well known that a six-membered chelate ring produces more steric strain in the complex than a five-membered ring. Therefore, a complex containing a six-membered chelate ring should be aquated faster than a complex containing a five-membered chelate ring provided the reaction proceeds through a dissociative S_N^1 mechanism. This has been found to be so experimentally. For example, the aquation reaction represented by Eq. 15, proceeds much faster than the aquation reactions represented by Eqs. 11–14. This is due to the fact that propylenediamine ligand forms a six-membered ring compared to ethylenediamine which forms a five-membered ring.



...(15)

It must be remembered that for similar types of complexes in which the coordinated ligands differ in size but do not produce any appreciable change in steric environment around the central metal ion, *the solvation effects are more important than the steric effects* and as such the rates of aquation should be interpreted on the basis of solvation effects. For instance, the rate of aquation of $[Co(NH_3)_4Cl_2]^+$ is much faster ($k = 180\times10^{-3}\ s^{-1}$) than the rate of aquation of $[Co(en)_2Cl_2]^+$ ($k = 3{\cdot}2\times10^{-5}\ s^{-1}$) due to solvation effect. Steric enviornments around the metal ion in both the complexes are similar.

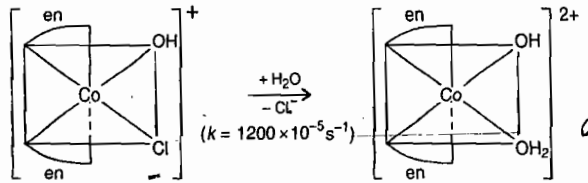
On the other hand, if the substitution of the ligands causes considerable steric overcrowding around the central metal ion, it is the steric effect which becomes more important than the solvation effect, as happens in aquation reactions represented by Eqs. 11–14.

In the case of complexes in which the substitution of ligands causes *moderate increase* in steric overcrowding around the central metal ion, both effects (*i.e.*, solvation and steric) determine the rate of aquation.

It clearly follows from the above discussion that a dissociative mechanism in which breaking of bond is much more important than making of bond is operative during the acid hydrolysis of octahedral complexes in which no ligand is a pi donor or a pi acceptor. A dissociative S_N^1 mechanism involving the formation of a square pyramidal intermediate is apparently closest to the actual mechanism of acid hydrolysis of these complexes and explains satisfactorily most of the experimental observations.

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

Let us consider aquation reactions of cis complexes $[Co(en)_2(OH)Cl]^+$ and $[Co(en)_2(NH_3)Cl]^{2+}$, represented as follows :



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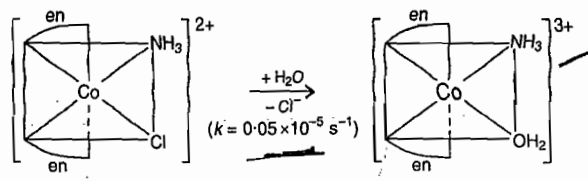
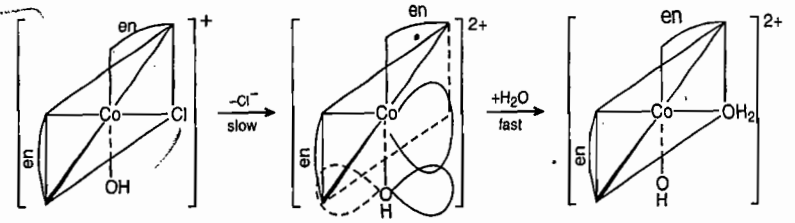


...(17)

As can be seen, the rate constants of reactions 16 and 17 are widely different, the rate of aquation of cis $[Co(en)_2(OH)Cl]^+$ being much faster than that of the other complex. Even if we take into account the

difference in the basicities of OH^- and NH_3 ligands and the difference in the charges on the two complexes, it is still difficult to explain such a wide difference in the rates of aquation of these complexes unless we take into consideration the pi bonding capability of the OH^- ligand.

The coordinated OH^- ligand has filled p orbitals which are capable of forming pi bond with the empty orbitals of the central metal ion. The coordinated NH_3 ligand, however, has no such orbital ; the only lone pair in NH_3 is already used up in coordination. The SP intermediate formed during the aquation of cis $[Co(en)_2(OH)Cl]^+$ has an empty d^2sp^3 hybrid orbital of the central metal ion which can overlap with a filled *p* orbital of coordinated OH^- ligand forming a pi bond. This pi bond stabilises the SP intermediate as shown below :

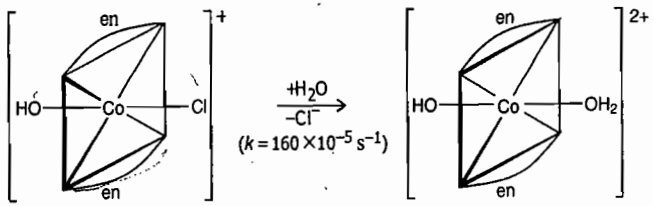


...(18)

SP intermediate stabilised by pi bonding

Stabilisation of SP intermediate through pi bonding makes the aquation of cis $[Co(en)_2(OH)Cl]^+$ complex much easier than the aquation of cis $[Co(en)_2(NH_3)Cl]^{2+}$ whose SP intermediate cannot be stabilised by pi bond.

Let us now consider aquation reactions of trans complexes $[Co(en)_2(OH)Cl]^+$ and $[Co(en)_2(NH_3)Cl]^{2+}$, represented as follows :



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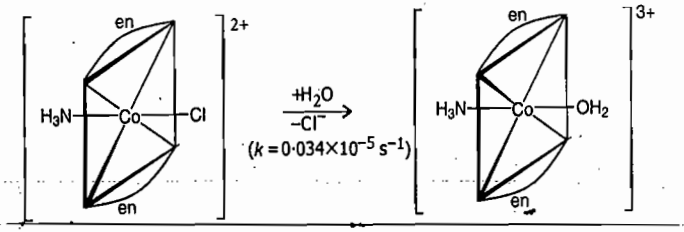
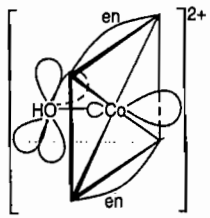


...(20)

The rate constants of reactions 19 and 20 show that aquation of trans $[Co(en)_2Cl(OH)]^+$ complex is also much faster than the aquation of trans $[Co(en)_2(NH_3)Cl]^{2+}$ complex. However, the empty d^2sp^3 hybrid orbital of the central metal ion in SP intermediate is incapable of forming pi bond with the filled *p* orbital of coordinated OH^- ligand because of lack of symmetry, as shown. This rules out the possibility of the formation of an SP intermediate during the aquation of trans $[Co(en)_2Cl(OH)]^+$ complex. The fact, however, remains that the aquation of hydroxy trans complex $[Co(en)_2Cl(OH)]^+$ is much faster than that of the ammonia complex $[Co(en)_2Cl(NH_3)]^{2+}$. This points out that the aquation



of the hydroxy trans complex proceeds through the formation of some other intermediate which can be stabilised by pi bonding. A TBP intermediate can be one such intermediate because it can be stabilised by pi bonding involving the overlapping of the empty *d* orbital of the metal with the filled *p* orbital of the coordinated OH^- ligand in the TBP intermediate, as illustrated in Fig. 1, in which the aquation of trans complex $[Co(en)_2Cl(OH)]^+$ through S_N1 *mechanism involving the formation of a TBP intermediate is depicted.*

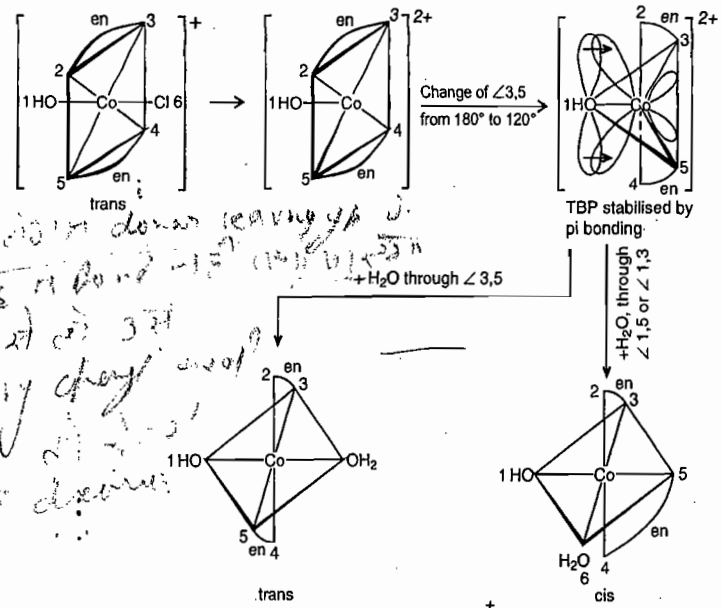


Fig. 1. Depiction of aquation of trans $[Co(en)_2Cl(OH)]^+$ complex through S_N1 mechanism involving the formation of a TBP intermediate.

The formation of a TBP intermediate from an SP intermediate requires some energy since some bond angles have to change from 90° to 120°. However, this extra energy required is more than compensated by the energy released as a result of the pi bonding. Thus, a pi bonded TBP intermediate formed during the aquation of trans $[Co(en)_2Cl(OH)]^+$ complex is more stable than an SP intermediate. This explains the faster rate of aquation of trans $[Co(en)_2Cl(OH)]^+$ complex compared to that of trans $[Co(en)_2(NH_3)Cl]^{2+}$ complex. It also explains the formation of a mixture of cis and trans products during aquation of trans $[Co(en)_2Cl(OH)]^+$. The attack of water through angles 1,5 and 1,3 of TBP intermediate leads to cis product and through angle 3,5 to trans product. An SP intermediate would have given a product having the same geometry as that of the reacting complex. For instance, trans $[Co(en)_2(NH_3)Cl]^{2+}$ complex on aquation through the formation of an SP intermediate gives only the trans product $[Co(en)_2(NH_3)(H_2O)]^{3+}$ complex.

The various observations made above may thus be **summed up** as follows :

1. In the absence of a pi bonding inert ligand, both cis and trans isomers aquate through the formation of an SP intermediate giving products which have the same geometries as those of the reacting complexes.

2. In the presence of a pi bonding inert ligand, cis isomers aquate through the formation of a pi bonded SP intermediate whereas the trans isomers aquate through the formation of a pi bonded TBP intermediate.

3. Aquation of comlexes through the formation of a TBP intermediate always produces a mixture of cis and trans products whereas aquation through an SP intermediate always leads to the retention of geometry.

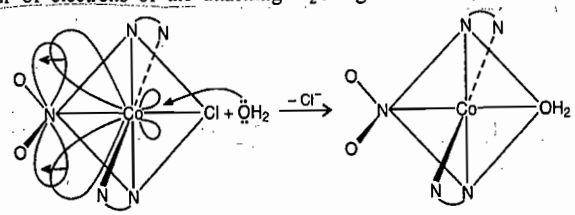
4. In all cases, aquation involves a dissociative S_N1 mechanism and not an associative S_N2 mechanism.

Some other pi bonding inert ligands containing filled *p* orbitals are NH_2^-, Cl^-, Br^-, etc. The mechanism of aquation of complexes containing these ligands is the same as of complexes containing OH^- ligand. The rates of aquation of such complexes are directly related to the pi bonding capability of the inert ligand.

C. Mechanism of Acid Hydrolysis When the Inert Ligand is a pi Acceptor

The mechanism of aquation of complexes having an inert pi acceptor ligand lying cis or trans to the leaving group is *different* from the mechanism of aquation when the inert ligands are either pi donors or are capable of forming pi bonding.

1. Mechanism When Inert pi Acceptor Ligand is Trans to the Leaving Group. Consider the aquation of trans $[O_2NCo(en)_2Cl]^+$. In this complex, one of the filled t_{2g} orbitals of Co can overlap with an empty *p* orbital of NO_2 group to form pi bond. The electron charge of t_{2g} orbital would shift more towards NO_2 group to maximise pi overlap. This results in a decrease of the electron charge from around the leaving Cl^- group. The lone pair of electrons of the attacking H_2O ligands would, therefore, experience lesser repulsion from t_{2g} electrons from the direction cis to the leaving group (or ***trans to the NO_2 group***). As a result, the attack of H_2O on the central Co atom from a position cis to the leaving group becomes easier in the presence of such pi bonding, as shown.



The presence of a pi acceptor ligand like NO_2 in the complex would make the formation of the Co–OH_2 bond easier and *would thus favour an associative S_N2 mechanism for aquation.* A dissociative S_N1 path for the aquation of trans $[O_2NCo(en)_2Cl]^+$ complex is unlikely because due to the electron-withdrawing inductive effect of NO_2 group, the bonding electrons of Co–Cl bond are pulled towards Co making the dissociation of the Co–Cl bond to release Cl^- ion difficult.

2. Mechanism When Inert pi Acceptor Ligand is Cis to the Leaving Group. The extent of pi overlap when NO_2 group is cis to the leaving group is less than when it is trans to the leaving group. Hence, the withdrawl of t_{2g} electron charge from around the leaving Cl^- group would be less and, therefore, the formation of Co–OH_2 bond would not be as easy in the cis as it is in the trans complex. Consequently, the aquation of cis $[O_2NCo(en)_2Cl]^+$ would be slower than the aquation of the trans isomer. But, it would still be faster than the aquation of, say, cis or trans $[H_3NCo(en)_2Cl]^{2+}$ isomer in which the inert ligands are incapable of forming pi bonds with the filled t_{2g} orbitals of the central metal ion. These facts are illustrated clearly by the data given in Table 5.

TABLE 5

Rate of Aquation of Complexes Containing pi Acceptor Inert Ligands

(Rates of aquation of cis and trans isomers of $[H_3NCo(en)_2Cl]^{2+}$ are given for comparison).

Complex	Rate constant k (s^{-1})
trans $[O_2NCo(en)_2Cl]^+$	98×10^{-5}
trans $[H_3NCo(en)_2Cl]^{2+}$	0.034×10^{-5}
cis $[O_2NCo(en)_2Cl]^+$	11.0×10^{-5}
cis $[H_3NCo(en)_2Cl]^{2+}$	0.05×10^{-5}

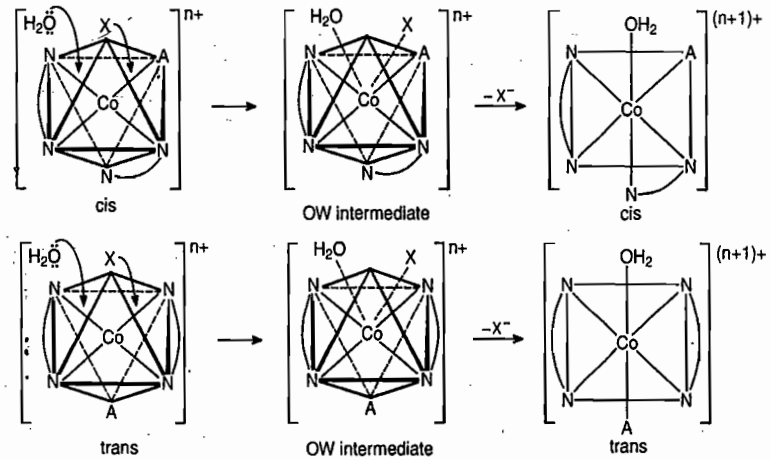
Aquation of other complexes containing inert pi acceptor ligands such as CO, CN^-, etc., also proceeds through an associative S_N2 rather than a dissociative S_N1 path.

Intermediates formed during aquation of complexes containing inert pi acceptor ligands. It is fully borne by experiment that aquation of cis $[ACo(en)_2X]^{n+}$ complex always yields 100% cis $[ACo(en)_2(H_2O)]^{(n+1)+}$ complex where A is an inert pi acceptor ligand such as NO_2, CO, CN^-, etc. Similarly, aquation of trans $[ACo(en)_2X]^{n+}$ complex always yields 100% trans $[ACo(en)_2(H_2O)]^{(n+1)+}$ complex. This observation can be explained by assuming that H_2O attacks the reacting species from a position cis to the leaving group (or trans to the inert pi acceptor ligand) resulting in the formation of a **pentagonal bipyramidal**

(PBP) intermediate. However, the formation of this intermediate is *energetically unfavourable* because it requires the readjustment of four metal–ligand bonds to accommodate the incoming H_2O ligand.

An alternative intermediate requiring lesser energy for its formation and having incoming H_2O and leaving X^- groups in equivalent positions is the **octahedral wedge (OW) intermediate** which has been described earlier. The formation of such a symmetric intermediate in which the leaving group X^- and incoming group H_2O occupy equivalent sites, requires minimum movement of ligands and is of lower energy compared to the energy of PBP intermediate.

The experimental observation that aquation of complexes containing pi acceptor ligands proceeds with the retention of geometry can also be explained satisfactorily, as illustrated below :



BASE HYDROLYSIS OF OCTAHEDRAL COMPLEXES

Hydrolysis of octahedral complexes in the presence of OH^- ions is known as the **base hydrolysis.** The base hydrolysis is known to proceed with a faster rate compared to the acid hydrolysis of octahedral complexes. Base hydrolysis is a second-order reaction, being first-order with respect to OH^- and first-order with respect to the complex ion. The rate of base hydrolysis (r) is thus represented as

$$r = k\,[\text{complex}][OH^-]$$

We shall discuss the mechanism of the base hydrolysis by taking into consideration the octahedral ammine complexes of Co(III) since the base hydrolysis of these complexes has been very well studied.

Mechanism of Base Hydrolysis

Two mechanisms have been given in literature to explain the base hydrolysis of octahedral ammine complexes. These are S_N2 and S_N1(CB) mechanisms.

S_N2 Mechanism for Base Hydrolysis. According to this mechanism, the ligand OH^-, being a strong nucleophile, attacks the ammine complex, as shown below :

$$[Co(NH_3)_5X]^{2+} + OH^- \xrightarrow{slow} [Co(NH_3)_5X(OH)]^+$$

$$[Co(NH_3)_5X(OH)]^+ \xrightarrow{fast} [Co(NH_3)_5(OH)]^{2+} + X^-$$

Accordingly, the rate of hydrolysis (r) is represented as

$$r = k\,[\text{complex ion}]\,[OH^-]$$

However, the above mechanism fails to explain some of the experimental observations, two important

of which are as follows :

1. At high concentration of OH^-, the reaction rate becomes *almost independent of OH^- concentration* and appears to be first-order with respect to the complex ion only. This observation cannot be explained by a simple S_N2 mechanism.

2. According to a simple S_N2 mechanism, the rate of base hydrolysis should be directly related to the strength of the nucleophilic character of the attacking ligand. However, there are several equally strong nucleophiles other than OH^-, such as $[NCS]^-$, NO_2^-, N_3^-, whose concentrations do not affect the rate of hydrolysis of the ammine complexes. In other words, the rates of hydrolysis of ammine complexes are independent of the concentrations of these nucleophiles and are dependent only on the concentration of the complex ion. The fact why OH^- alone and no other strong nucleophile should influence the rate of base hydrolysis cannot be explained by a simple S_N2 mechanism.

S_N1(CB) Mecahnism for Base Hydrolysis. The above mentioned and several other observations can be explained satisfactorily by the **S_N1(CB) mechanism** proposed by Garrik. S_N1(CB) stands for substitution, nucleophilic, unimolecular, conjugate base. The main features of this mechanism are discussed below.

1. In organic chemistry, there are several instances in which OH^- acts as a catalyst but the rates of these reactions depend upon the concentration of the OH^- added. Such reactions generally involve the following acid-base equilibrium :

$$AH + OH^- \rightleftharpoons A^- + H_2O \quad \ldots(i)$$

where AH is an organic compound with a removable hydrogen and A^- is its conjugate base (CB).

Since the ammine complexes of Co(III) also have removable hydrogens, occurrence of an acid-base equilibrium similar to (*i*) was proposed by Garrik as the first step in their base hydrolysis :

$$\underset{\text{Ammine complex}}{[Co(NH_3)_5Cl]^{2+}} + OH^- \overset{K}{\rightleftharpoons} \underset{\text{CB of ammine complex}}{[Co(NH_3)_4NH_2Cl]^+} + H_2O \quad \ldots(ii)$$

2. Because the conjugate base (CB) produced in (*ii*) contains a coordinated $\ddot{N}H_2^-$ ligand which, being a pi acceptor, is also capable of forming pi bond with Co(III) in the five-coordinated intermediate more efficiently than in seven-coordinated intermediate, the better pi-stabilised five-coordinated intermediate was proposed to be formed from the conjugate base in the second step :

$$\underset{\text{CB of ammine complex}}{[Co(NH_3)_4NH_2Cl]^+} \xrightarrow[\text{slow}]{k} \underset{\text{Five-coordinated intermediate}}{[Co(NH_3)_4NH_2]^{2+}} + Cl^- \quad \ldots(iii)$$

The pi-bonding $\ddot{N}H_2^-$ ligand also helps in the dissociation of Cl^- from Co(III). The effect of pi bonding on the stability of intermediates has already been discussed in the section dealing with acid hydrolysis of octahedral complexes.

3. The five-coordinated intermediate $[Co(NH_3)_4NH_2]^{2+}$ then quickly reacts with H_2O to give the final product of hydration :

$$[Co(NH_3)_4NH_2]^{2+} + HOH \longrightarrow [Co(NH_3)_5OH]^{2+} \quad \ldots(iv)$$

Explanation for the Observed Reaction Rates in Different Cases

1. Experimentally observed second-order kinetics (as also some other features) can be explained satisfactorily by S_N1(CB) mechanism provided the equilibrium (*ii*) is established quickly and the amount of the conjugate base (CB) present at equilibrium is small, *i.e.*, *K* is small.

Since reaction (*iii*) involves the dissociation of Cl^- from the conjugate base, it is supposed to be *slower* than reactions (*ii*) and (*iv*). The reaction (*iii*) thus constitutes the rate-determining step of the overall reaction. Reaction (*iv*) involves the acceptance of a proton from H_2O by the basic $-\ddot{N}H_2$ group. This reaction is assumed to be the fastest. The rate of hydrolysis (*r*) is, therefore, given by the rate of step (*iii*). Thus

$$r = k\,(\text{concentration of } [Co(NH_3)_4NH_2Cl]^+) \quad \ldots(v)$$

From reaction (*ii*),

$$K = \frac{\text{Concn. of } [Co(NH_3)_4NH_2Cl]^+}{\text{Concn. of } [Co(NH_3)_5Cl]^{2+} \times [OH^-]} \quad \ldots(vi)$$

$$\therefore \text{Concn. of } [Co(NH_3)_4NH_2Cl]^+ = K(\text{Concn. of } [Co(NH_3)_5Cl]^{2+} \times [OH^-])$$

$$\therefore \text{Rate of hydrolysis, } r = kK\,(\text{Concn. of } [Co(NH_3)_5Cl]^{2+} \times [OH^-])$$

$$= k'\,(\text{Concn. of } [Co(NH_3)_5Cl]^{2+} \times [OH^-]) \quad \ldots(vii)$$

2. As mentioned earlier, the rate of base hydrolysis tends to be almost independent of $[OH^-]$ at very high concentration of OH^- ions. This observation can be explained by S_N1(CB) mechanism as follows : If the amount of OH^- added is very large, there would be very little change in the concentration of OH^- as a result of the acid-base equilibrium reaction (*ii*). In other words, the concentration of OH^- can be taken as constant so that the rate of hydrolysis, as given by reaction (*vii*), becomes

$$r = k'\,(\text{Concn. of } [Co(NH_3)_5Cl]^{2+} \times \text{constant})$$

$$= k''\,(\text{Concn. of } [Co(NH_3)_5Cl]^{2+}) \quad \ldots(viii)$$

Thus, at very high concentration of OH^-, the rate of hydrolysis would depend only upon the concentration of the complex ion.

3. Ligands such as NO_2^-, $[NCS]^-$, N_3^-, etc., are as strong nucleophiles as OH^- but they do not influence the rate of hydrolysis of ammine complexes. This observation can be explained as follows : Although the anions mentioned above are as strong nucleophiles as the OH^-, yet they are not as strong bases as the OH^-. In fact, these anions are much weaker bases than OH^- and hence none of them is able to extract a proton from the ammine complex to yield a conjugate base of the complex by reaction (*ii*). In the absence of the formation of a conjugate base (CB), the hydrolysis of the complex cannot proceed through S_N1(CB) mechanism.

Hydrolysis of ammine complexes brought about by NO_2^-, $[NCS]^-$, N_3^-, etc., can, however, be explained by the conventional associative S_N2 or dissociative S_N1 mechanism as follows : Since during the hydrolysis, water molecules are present in much more abundance than the anion NO_2^-, N_3^- or $[NCS]^-$, it is the H_2O molecule rather than the N_3^-, NO_2^- or $[NCS]^-$ anion which would have the chance to attack the complex ion or its intermediate through an S_N2 or S_N1 mechanism. The product of hydrolysis, in general, is, therefore, the aquated species, as illustrated below :

S_N2 *Path* :

$$[Co(NH_3)_5X]^{2+} + H_2O \xrightarrow[\text{slow}]{N_3^-,\ NO_2^- \text{ or } [NCS]^-} [Co(NH_3)_5X(H_2O)]^{2+} \xrightarrow{\text{fast}} [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

S_N1 *Path* :

$$[Co(NH_3)_5X]^{2+} + H_2O \xrightarrow[\text{slow}]{N_3^-,\ NO_2^- \text{ or } [NCS]^-} [Co(NH_3)_5]^{3+} + X^- \xrightarrow[\text{fast}]{H_2O} [Co(NH_3)_5(H_2O)]^{3+} \quad \ldots(x)$$

The rate of hydrolysis (*r*) according to both the mechanisms is given by

$$r = k\,(\text{concn. of } [Co(NH_3)_5X]^{2+}) \quad \ldots(xi)$$

and is, evidently, independent of the concentration of N_3^-, NO_2^- or $[NCS]^-$ present.

4. It has been verified by NMR spectroscopy that the ammine hydrogens trans to Cl^- are 100 times more acidic than those cis to Cl^- in the $[M(en)_2Cl_2]^+$ complexes of Co(III) and Rh(III). Both the metal ions have the same configuration, t_{2g}^6. Therefore, the removal of a proton from NH_2 group trans to Cl^- is easier than its removal from NH_2 group cis to Cl^-. Thus, the formation of CB of cis $[M(en)_2Cl_2]^+$ isomer (which contains NH_2 groups trans to Cl^-) should be easier than the formation of CB of trans $[M(en)_2Cl_2]^+$ isomer (which contains NH_2 groups cis to Cl^-) and, therefore, the base hydrolysis of cis $[M(en)_2Cl_2]^+$ isomer should be quicker than that of trans $[M(en)_2Cl_2]^+$ isomer (M = Rh(III) or Co(III). This has been found to be so experimentally.

5. For any complex to hydrolyse through an S_N1(CB) mechanism, the formation of its conjugate base

(CB) is a must. But this is possible only if the complex contains at least one acidic hydrogen. This means that any complex not containing any acidic hydrogen would hydrolyse through a mechanism other than S_N1(CB) mechanism. This is found to be so experimentally. For example, the complexes $[Co(CN)_5Br]^{3-}$ and $[Co(CN)_5I]^{3-}$ hydrolyse slowly to yield $[Co(CN)_5OH]^{3-}$, their rates of hydrolysis being *independent of OH^- concentration* indicating thereby that their hydrolyses do not proceed through S_N1(CB) mechanism. Neither of these complexes contains any acidic hydrogen. To quote another example, the rates of hydrolysis of $[Co(py)_4Cl_2]^+$ and $[Co(dipy)_2(OAc)_2]^+$ (where py is pyridyl and dipy is dipyridyl) are *independent of OH^- concentration* in the *p*H range of 6 to 12 indicating that their hydrolyses do not occur through S_N1(CB) mechanism. Neither pyridyl nor dipyridyl complex has any acidic hydrogen.

Even those complexes which do contain removable hydrogens but *which are difficult to be removed due to high negative charge on the complex ion* (*e.g.*, $[Fe(CN)_5NH_3]^{3-}$, would find it extremely difficult to form their conjugate bases. Hence the hydrolyses of such complexes also would not proceed through S_N1(CB) mechanism and the rates of their hydrolyses would be independent of OH^- concentration. This has been found to be so experimentally.

6. The reaction of $[Co(en)_2(NO_2)Cl]^+$ with NO_2^- produces $[Co(en)_2(NO_2)_2]^+$ in non-aqueous dimethyl sulphoxide (DMSO) medium. The rate of reaction is slow ($t_{1/2}$ = 5 – 6 hours) and is independent of the concentration of NO_2^-. The following mechanism has been proposed for the reaction :

$$[Co(en)_2(NO_2)Cl]^+ \xrightarrow[DMSO]{slow} [Co(en)_2(NO_2)]^{2+} + Cl^- \quad ...(xii)$$

$$[Co(en)_2(NO_2)]^{2+} + NO_2^- \xrightarrow[DMSO]{fast} [Co(en)_2(NO_2)_2]^+ \quad ...(xiii)$$

The addition of a small amount of OH^- reduces the $t_{1/2}$ to a few seconds, *i.e.*, it increases the reaction rate appreciably. This catalytic action of OH^- in *non-aqueous medium* can be explained satisfactorily by S_N1(CB) mechanism, as illustrated below :

$$[Co(en)_2NO_2Cl]^+ + OH^- \xrightarrow[DMSO]{fast} \underset{\text{Conjugate Base}}{[Co(en)(en\text{-}H)NO_2Cl]} + H_2O \quad ...(xiv)$$

(en-H is ethylene diamine from which one H^+ has been removed)

$$\underset{\text{Conjugate Base}}{[Co(en)(en\text{-}H)NO_2Cl]} \xrightarrow[DMSO]{fast} [Co(en)(en\text{-}H)NO_2]^+ + Cl^- \quad ...(xv)$$

$$[Co(en)(en\text{-}H)NO_2]^+ + NO_2^- \xrightarrow[DMSO]{fast} [Co(en)(en\text{-}H)(NO_2)_2] \quad ...(xvi)$$

$$[Co(en)(en\text{-}H)(NO_2)_2] + H_2O \xrightarrow[DMSO]{fast} [Co(en)_2(NO_2)_2]^+ + OH^- \quad ...(xvii)$$

The dissociation of Co–Cl bond in the conjugate base $[Co(en)(en\text{-}H)NO_2Cl]$ is easier due to the presence of pi bonding $\ddot{N}H^-$ group compared to the dissociation of Co–Cl bond in the complex $[Co(en)_2NO_2Cl]^+$ *in the absence of* OH^-. This explains why the rate-determining step (*xii*) is comparatively slower with $t_{1/2}$ = 5–6 hours than the step (*xv*), with $t_{1/2}$ = a few seconds although both of them are kinetically slow steps. Also, the OH^- consumed in step (*xiv*) is regenerated in step (*xvii*), thus, explaining that the action of OH^- is catalytic.

Some other bases (such as piperidine) also act as catalysts for the above reaction in non-aquous medium, yielding the same product. Their catalytic action can be similarly explained on the basis of S_N1(CB) mechanism. The reactions involving the consumption and regeneration of the base (B) are as follows :

$$[Co(en)_2NO_2Cl]^+ + B \overset{fast}{\rightleftharpoons} [Co(en)(en\text{-}H)NO_2Cl] + BH^+ \quad ...(xviii)$$

$$[Co(en)(en\text{-}H)NO_2Cl] + BH^+ + NO_2^- \xrightarrow[-HCl]{fast} [Co(en)_2(NO_2)_2]^+ + B \quad ...(xix)$$

A simple S_N1 or S_N2 mechanism is incapable of explaining the catalytic action of OH^- or any other base (B) in the above reaction in non-aqueous medium.

7. If base hydrolysis of an ammine complex occurs through an associative S_N2 mechanism, then the conversion of OH^- to a better nucleophile (but a weaker base) would obviously increase the reaction rate. If, on the other hand, base hydrolysis occurs through an S_N1(CB) mechanism for which the presence of OH^- is a must, then the conversion of OH^- to a better nucleophile (but a weaker base) would retard the reaction.

It has been observed that for all reactions occurring through S_N2 path, HO_2^- is a better nucleophile than OH^-. The anion HO_2^- can be generated by the action of H_2O_2 on OH^- :

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HO_2^- \quad (K > 150)$$

Therefore, if the rate of base hydroysis *increases* with the addition of H_2O_2, an S_N2 mechanism would be operative because H_2O_2 converts OH^- to a better nucleophile. However, if the rate of base hydrolysis *decreases* with the addition of H_2O_2, an S_N1(CB) mechanism would be operative because the concentration of OH^- necessary for the production of the conjugate base would decrease since OH^- gets converted to HO_2^-.

Experimentally, it has been observed that the addition of H_2O_2 actually *decreases* the rate of base hydrolysis of ammine complexes of Co(III). This observation strongly favours an S_N1(CB) mechanism for these complexes.

8. The isotopic exchange studies on base hydrolysis using $^{18}OH^-$ unambiguously support the S_N1(CB) mechanism for base hydrolysis of ammine complexes of Co(III) and not a pure S_N1 or S_N2 mechanism.

Stereochemistry of Intermediates of Base Hydrolysis

Let us consider the base hydrolysis of the complex ion $[Co(en)_2AX]^+$. Assuming that the hydrolysis occurs through an S_N1(CB) mechanism, the rate-determining step yields a five-coordinated intermediate $[Co(en)_2(en\text{-}H)A]^+$, as shown below :

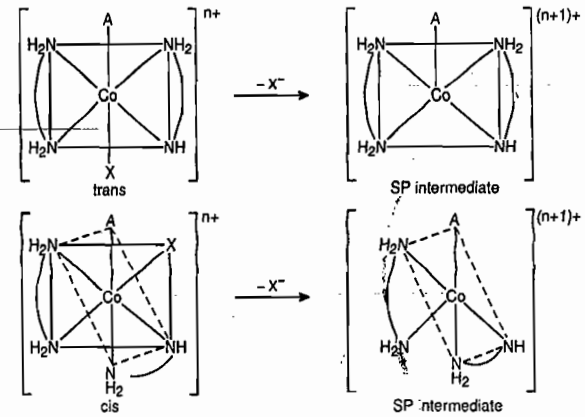
$$[Co(en)_2AX]^+ + OH^- \rightleftharpoons \underset{\text{Conjugate base}}{[Co(en)(en\text{-}H)AX]} + H_2O \quad ...(xx)$$

$$\underset{\text{(CB)}}{[Co(en)(en\text{-}H)AX]} \xrightarrow{Slow} \underset{\text{Five-coordinated intermediate}}{[Co(cn)(en\text{-}H)A]^+} + X^- \quad ...(xxi)$$

$$[Co(en)(en\text{-}H)A]^+ \xrightarrow[fast]{H_2O} [Co(en)_2A(OH)]^+ \quad ...(xxii)$$

The five-coordinated intermediate can, in principle, have the following two geometries :

1. Square Pyramidal (SP). The formation of a five-coordinated square pyramidal intermediate requires no movement of ligands which remain attached with Co(III) after the dissociation of X^- from the conjugate base. Therefore, under normal conditions (*i.e.*, in the absence of pi bonding), the square pyramidal intermediate is more stable than the other possible trigonal bipyramidal (TBP) intermediate. The formation of a square pyramidal intermedaite from the conjugate base is illustrated below :



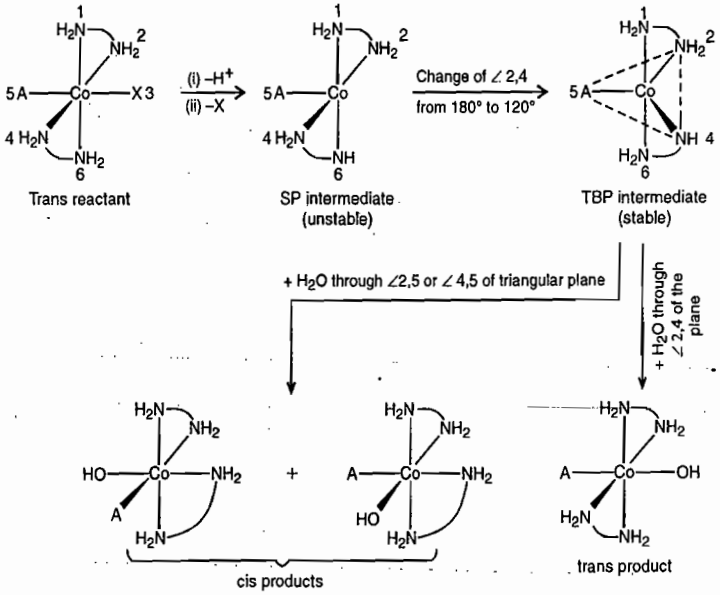
Evidently, if the base hydrolysis proceeds through the formation of a square pyramidal intermediate, the geometry of the product and of the reacting ammine complex would remain the same since the attacking water molecule would preferentially approach the metal through the site vacated by the leaving group.

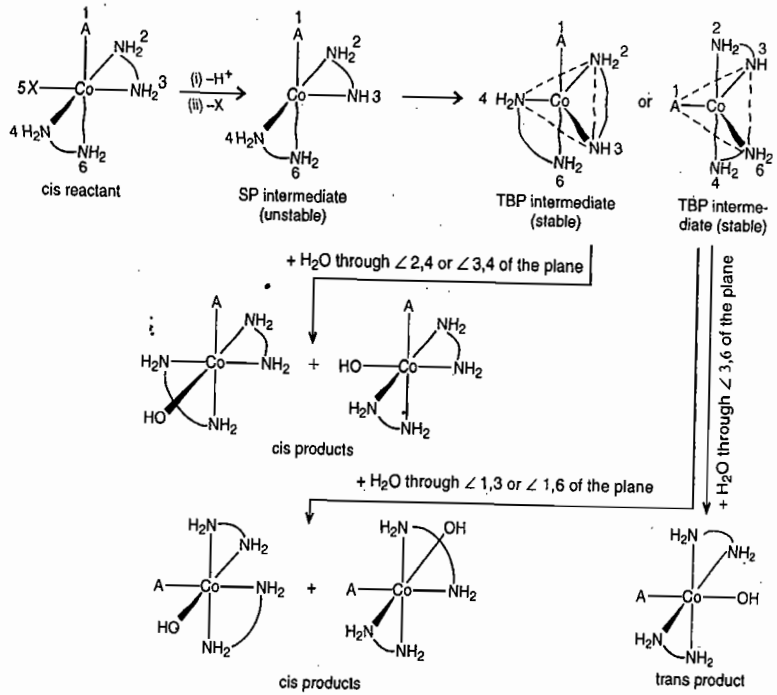
2. Trigonal Bipyramidal (TBP). The formation of a five-coordinated trigonal bipyramidal intermediate requires movement of some of the Co–ligand bonds. This obviously requires some energy. Hence, under normal conditions, a trigonal bipyramidal intermediate is less likely to form. However, in the presence of a coordinated ligand such as $-\ddot{N}H_2^-$ or $>\ddot{N}H^-$ in the intermediate which is capable of forming pi bond with the central Co(III) ion, the TBP intermediate becomes more stable than the SP intermediate. This is because the amount of energy released due to pi bonding far exceeds the energy required for the formation of TBP intermediate.

Since the intermediates formed during base hydrolysis of ammine complexes of Co(III), contain pi bonding ligands such as $-\ddot{N}H_2^-$ or $>\ddot{N}H^-$, a TBP intermediate is expected to be more stable than an SP intermediate.

A trigonal bipyramidal intermediate gives a mixture of cis and trans products irrespective of the fact whether the reacting complex has a cis or a trans geometry. We can, therefore, predict the geometry of the intermediate formed during base hydrolysis of a complex proceeding through an S_N^1(CB) mechanism. If the product has the *same geometry* as that of the reacting complex, the intermediate formed would be *square pyramidal*. On the other hand, if the product is *a mixture* of *cis and trans forms*, irrespective of the type of the geometry of the reacting complex, the intermediate formed would be *trigonal bipyramidal*. Experimental studies on the geometries of the products formed during base hydrolyses of ammine complexes of Co(III) reveal that the product formed in each case is a *mixture* of *cis and trans* forms irrespective of the geometry (cis or trans) of the reacting complexes. This observation clearly proves that the five-coordinated intermediate formed during the base hydrolyses of ammine complexes of Co(III) through an S_N^1(CB) mechanism is trigonal bipyramidal.

The stereochemistry of the base hydrolysis of $[Co(en)_2AX]^+$ complex is shown below :





The sterochemistry of the base hydrolysis of any other ammine complex can be presented in a similar manner.

SUBSTITUTION REACTIONS OF SQUARE PLANAR COMPLEXES

As regards substitution reactions of square planar (SPL) complexes, exhaustive studies have been made only on square planar complexes of Pt(II). This is because these complexes are slow towards substitution and are thus easier to study.

The mechanism of substitution reactions of square planar complexes appears to be associative S_N^2 rather than dissociative S_N^1. This may be inferred from the following observations :

1. In the case of square planar complexes of Ni(II), Pd(II) and Pt(II), five empty metal orbitals (one *d*, one *s* and three *p*) of comparable energies can be made available for sigma bonding. Since only four ligands are to be sigma-bonded with the metal ion, only four of the five orbitals of the metal ion are used up for this purpose. The fifth orbital can easily accommodate electrons from the attacking ligand. In other words, a five-coordinated intermediate or an "activated complex" gets formed from a four-coordinated SPL complex through an associative S_N^2 mechanism.

2. The rates of substitution reactions of SPL complexes are sensitive to the nature of the reacting complex. For example, amongst the following reactions :

$$\text{trans } [NiCl(o\text{-tolyl})(PEt_3)_2]^+ + py \longrightarrow \text{trans } [Ni(py)(o\text{-tolyl})(PEt_3)_2]^{2+} + Cl^- \quad ....(1)$$

$$\text{trans } [PdCl(o\text{-tolyl})(PEt_3)_2]^+ + py \longrightarrow \text{trans } [Pd(py)(o\text{-tolyl})(PEt_3)_2]^{2+} + Cl^- \quad ....(2)$$

$$\text{trans } [PtCl(o\text{-tolyl})(PEt_3)_2]^+ + py \longrightarrow \text{trans } [Pt(o\text{-tolyl})(PEt_3)_2]^{2+} + Cl^- \quad ....(3)$$

reaction (1) is 50 times faster than reaction (2), which, in turn, is about 100,000 times faster than reaction (3).

It is known that the square planar Ni(II) expands its coordination number with greater ease than the square planar Pd(II) and the square planar Pd(II) expands its coordination number with much greater ease

than the square planar Pt(II). Thus, *there exists a parallelism between the reactivity of the square planar complexes of these metal ions and the ease with which these ions expand their coordination number.* Such a relationship clearly indicates the formation of an intermediate or an "activated complex" with a higher coordination number during the substitution reactions of SPL complexes of Ni(II), Pd(II) and Pt(II). This type of intermediate or "activated complex" is formed in such reactions only through an associative S_N^2 mechanism.

3. Consider reactions of the type

$$[PtL_nCl_{4-n}] + Y \xrightarrow{H_2O} [PtL_nCl_{3-n}Y] + Cl^- \quad ...(4)$$

Here L is a unidentate ligand and n can vary from 0 to 3. The complexes $[PtL_nCl_{4-n}]$ and $[PtL_nCl_{3-n}Y]$ can be *neutral* or *charged* species depending upon the nature of L.

The rate of reaction (r) in such cases is found to be represented by the expression :

$$r = k_1 \text{ (concn. of } [PtL_nCl_{4-n}] \times [Y]) + k_2 \text{ (concn. of } [PtL_nCl_{4-n}]) \quad ...(5)$$

The above rate law suggests that substitution of Cl^- by Y in reaction (4) follows *two independent pathways*. The reaction rate for the **first reaction path** is given by

$$r = k_1 \text{ (concn. of } [PtL_nCl_{4-n}] \times [Y]) \quad ...(6)$$

indicating that the rate-determining step is bimolecular and the mechanism involved is associative S_N^2.

The reaction rate for the **second reaction path** is given by

$$r = k_2 \text{ (concn. of } [PtL_nCl_{4-n}])$$

which indicates that the mechanism of the second reaction path is such that the step involving the attack of the ligand Y is fast and does not constitute the rate-determining step of the reaction. The second reaction path is believed to consist of a slow aquation reaction, *viz.*,

$$[PtL_nCl_{4-n}] + H_2O \xrightarrow{slow} [PtL_nCl_{3-n}(H_2O)] + Cl^- \quad ...(7)$$

followed by a fast replacement of coordinated H_2O by the ligand, as shown below :

$$[PtL_nCl_{3-n}(H_2O)] + Y \xrightarrow{fast} [PtL_nCl_{3-n}Y] + H_2O \quad ...(8)$$

Reaction (7), being slow, is the rate-determining step of the second reaction path. We shall now discuss the mechanism of this step.

S_N^1 ***mechanism.*** Suppose the mechanism for step (7) is S_N^1 involving the following reactions :

$$[PtL_nCl_{4-n}] \xrightarrow{slow} [PtL_nCl_{3-n}] + Cl^- \quad ...(9)$$

$$[PtL_nCl_{3-n}] + H_2O \xrightarrow{fast} [PtL_nCl_{3-n}(H_2O)] \quad ...(10)$$

In that case, the rate of reaction (r) would be given by

$$r = k_2 \text{ (Concn. of } [PtL_nCl_{4-n}]) \quad ...(11)$$

S_N^2 ***mechanism.*** Suppose the mechanism for step (7) is S_N^2 involving the reactions :

$$[PtL_nCl_{4-n}] + H_2O \xrightarrow{slow} [PtL_nCl_{4-n}(H_2O)] \xrightarrow{fast} [PtL_nCl_{3-n}(H_2O)] + Cl^- \quad ...(12)$$

In that case, the rate of reaction (r) would be given by

$$r = k_2 \text{ (Concn. of } [PtL_nCl_{4-n}] \times [H_2O]) \quad ...(13)$$

Since water is present in large excess, its concentration remains practically constant. Hence the rate of reaction is represented as

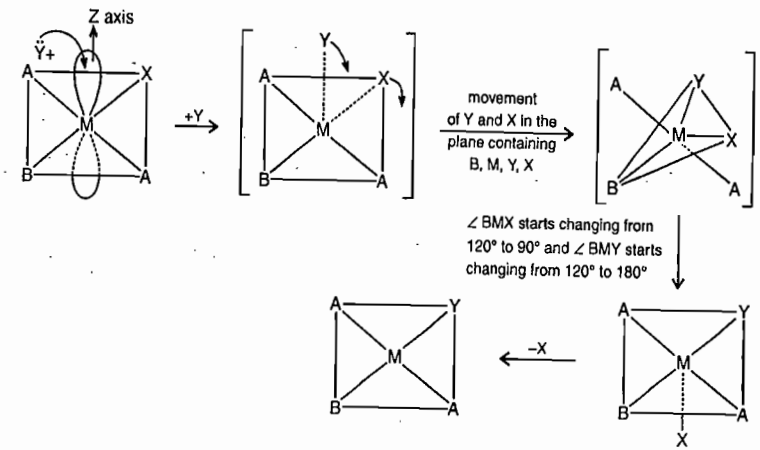
$$r = k_2 \text{ (Concn. of } [PtL_nCl_{4-n}]) \quad ...(14)$$

Thus, both S_N^1 and S_N^2 mechanisms for reaction (7) yield the same expression for the rate constant, *viz.*, $r = k_2$ (Concn. of $[PtL_nCl_{4-n}]$), as given in the rate law equations (11) and (14).

It has been observed that there is *very little variation* in the rates of aquation (*i.e.*, rates of replacement of Cl^- by H_2O) of complexes such as $[PtCl_4]^{2-}$, $[PtCl_3(NH_3)]^-$, $[PtCl_2(NH_3)_2]$ and $[PtCl(NH_3)_3]^+$. If aquation of these complexes proceeds through an S_N^1 mechanism, it would involve breaking of Pt–Cl bond which becomes increasingly difficult in going from $[PtCl_4]^{2-}$ to $[Pt(NH_3)_3Cl]^+$. This would happen because of the increase in the positive charge on the complexes from –2 to +1. Therefore, the rates of aquation *should decrease considerably* in going from a complex of lower positive charge to a complex of higher positive charge (or from a complex of higher negative charge to a complex of lower negative charge). Since this is *contrary to experimental observations, an S_N^1 mechanism is ruled out* in the aquation reactions of square planar complexes of Pt(II).

The increase in positive charge on the complex would make the breaking of Pt–Cl bond more difficult but it would make the formation of Pt–OH_2 bond easier. In an S_N^2 mechanism, the two effects are equally important. As a result, the reaction rate for the aquation of the above mentioned complexes via S_N^2 mechanism should be *virtually the same* irrespective of the charge on the complex, as is actually the case. The above observations clearly indicate that the aquation reaction (7) and the general substitution reaction (4) follow the S_N^2 mechanism.

The S_N^2 mechanism for the substitution reaction of square planar complexes may be illustrated as follows :



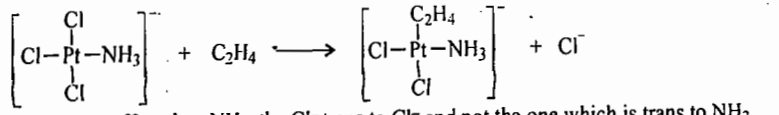
The ligand Y attacks M from +Z direction (probably by utilising the empty p_z orbital of the metal) to form a five-coordinated square pyramidal intermediate which then transforms into a more stable trigonal bipyramidal intermediate. This again gets converted to another square pyramidal intermediate containing the leaving group X along –Z direction. The removal of X from this intermediate yields the substituted square planar complex. Although the trigonal bipyramidal intermediate should be more stable than the two square pyramidal intermediates proposed in the above mechanism, the energy of conversion of the square pyramidal intermediate to trigonal bipyramidal intermediate and vice-versa shoud be very small for this mechanism to be operative.

Since in reaction (4), the concentration of the ligand, *viz.*, [Y], is much less than the concentration of water which acts both as a medium for the reaction and as a ligand, the fraction of molecules of the substrate $[PtL_nCl_{4-n}]$ reacting through the first reaction path is far less than the fraction of molecules reacting through the second path in which water also acts as a ligand.

Trans Effect

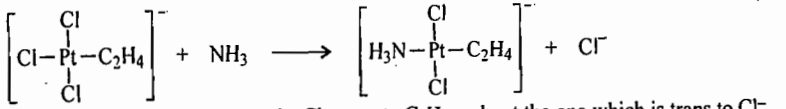
The ability of an attached group to direct substitution into a position trans (*i.e.*, opposite) *to itself is called the* **trans effect.** Such a group has a marked influence on the rate of a reaction. Consider the

substitution reaction :



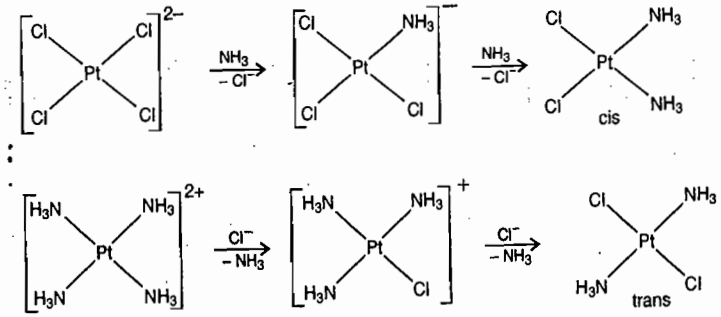
Since Cl^- has greater trans effect than NH_3, the Cl^- trans to Cl^- and not the one which is trans to NH_3, is replaced by C_2H_4.

Now, consider the substitution reaction :



Since C_2H_4 has greater trans effect than Cl^-, the Cl^- trans to C_2H_4 and not the one which is trans to Cl^-, is replaced by NH_3.

The trans effect has been made use of in synthesising certain specific (cis or trans) complexes. For instance, the cis and trans diamminedichloroplatinum (II) complexes have been synthesised separately, keeping in view the trans effects of Cl^- and NH_3, as illustrated below :



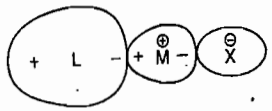
The order of ligands for the increasing trans effect is roughly as :

$$H_2O < OH^- < NH_3 < RNH_2 < py < Cl^- < Br^- < SCN^- \simeq I^- \simeq NO_2^- \simeq [SO_3H]^- \simeq PR_3 \simeq SC(NH_2)_2 < NO \simeq CO \simeq C_2H_4 \simeq CN^-$$

The ligands showing high trans effect are those which can form pi bonds by accepting *d* orbital electrons from Pt(II).

Theories of Trans Effect. The trans effect is a kinetic pheonomenon affecting the magnitude of activation energy of a reaction. The stability of both the ground state (*i.e.*, square planar complex before substitution) and of the activated complex can, in principle, affect the activation energy required for the substitution reaction. Therefore, any factor that changes the stability of the ground state and/or which changes the stability of activated complex would be a contributor to the trans effect shown by the attached ligand. There are two theories of trans effect of which one relates to the ground state and the other to the activated complex. These are briefly discussed below.

1. The Polarization Theory. This theory is primarily concerned with the effects on the ground state. Let us consider two bonds L–M and M–X trans to each other in a square planar complex. Suppose the ligand L is more polarizable than the ligand X. The primary charge on the metal ion polarizes the electron charge cloud on L and thus induces a dipole in L. The dipole in L, in turn, induces a dipole in M, as shown.



The orientation of this dipole on the metal ion is such that it repels the negative charge in the ligand X which is trans to L. Hence, the ligand X would be less attracted by the metal ion because of the presence of L. According to this theory, the polarization of a ligand should be directly related to its trans effect. This is largely true for ligands which do not form pi bonds with the metal ions. The theory makes no mention of the trans effect of ligands present in the activated complex.

2. The pi Bonding Theory. This theory satisfactorily explains the trans effect of those attached ligands which are pi acceptors or pi acids like phosphine, CO, olefins, etc. Consider a square planar complex in which an attached ligand L is a pi acid whose trans effect we want to investigate. The ligand X is situated trans to L. According to pi bonding theory, there is a correlation between the tendency of a ligand to remove the *d* orbital electrons from the metal ion by pi bonding and the magnitude of their trans effect. The transition state in the substitution reaction of a square planar complex is proposed to have a trigonal bipyramidal geometry (Fig. 2).

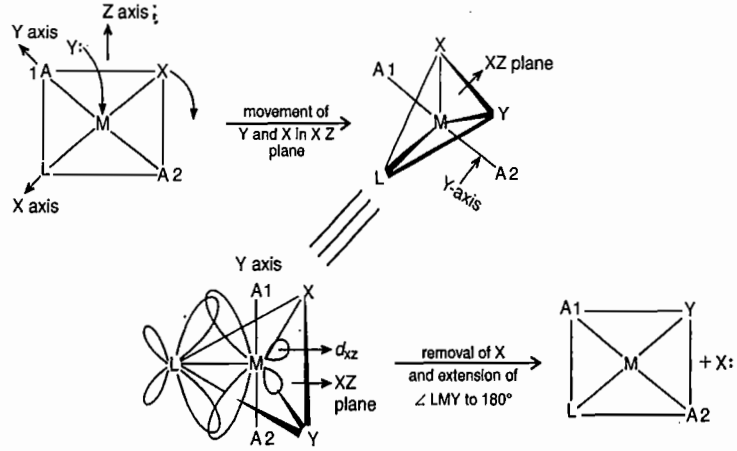


Fig. 2. Illustration of pi bonding theory of trans effect.

The trigonal bipyramidal transition state can be stabilised if the empty pi orbital (*p*, *d* or π*) of ligand L overlaps with a non-bonding filled dπ orbital of the metal to form a pi bond. In Fig. 2, the square planar complex is shown to be in XY plane and the pi bonding is shown between the empty pi bonding orbital (say, *d* orbital) of the ligand L and filled d_{xz} orbital of the metal. It is clear from the figure that electrons from d_{xz} orbital are withdrawn away from the incoming nucleophile Y during M–L pi bonding thus stabilising the trigonal bipyramidal transition state.

Although the pi bonding theory proposes stabilisation of the trigonal bipyramidal state, there is evidence that the M–X bonds are longer when they are placed trans to a ligand with a strong trans effect than when they are placed cis to such a group even in the ground state. Therefore, a ligand with a strong trans effect, affects the ground state as well as the transition state. The present view, therefore, is that both the effects, namely, polarization which weakens the bonds in the ground state and pi bonding which stabilises trigonal bipyramidal transition state contribute towards the trans effect shown by an attached ligand. The extent of contribution by each depends upon the nature of the ligand.

OXIDATION–REDUCTION REACTIONS

Oxidation-reduction reactions can occur either through atom or group transfer or through electron transfer. Reactions of both the categories are discussed below.

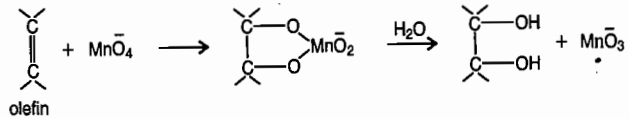
1. Oxidation-Reduction Reactions Through Atom or Group Transfer

In several cases, oxidation-reduction reactions can be explained in terms of atom or group transfer.

For example, MnO_4^- acts as an oxidant through atom transfer while oxidising organic compounds. Thus,

$$(i)\ RH + MnO_4^- \longrightarrow R^- + (HMnO_4) \quad \text{(transfer of H atom)}$$

$$R_2CHO + MnO_4^- \longrightarrow R_2CO + (HMnO_4) \quad \text{(transfer of H atom)}$$

(ii) 

(atom transfer)

olefin

$Fe^{2+}(aq)$ acts as a *reducing agent* if it transfers an H atom from its inner hydration shell to an organic free radical whereas $Fe^{3+}(aq)$ acts as an *oxidising agent* if it transfers OH from its inner hydration shell to an organic free radical. Thus,

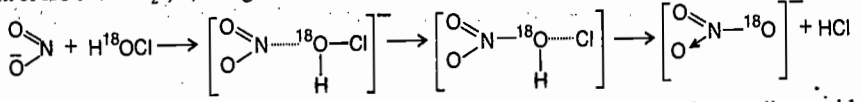
$$[Fe(H_2O)_6]^{2+} + R\cdot \longrightarrow RH + [Fe(H_2O)_5OH]^{2+}$$

(Transfer of H atom from $Fe^{2+}(aq)$)

$$[Fe(H_2O)_6]^{3+} + R\cdot \longrightarrow ROH + H^+ + [Fe(H_2O)_5]^{2+}$$

(Transfer of OH from $Fe^{3+}(aq)$)

The atom or group transfer reactions have been studied by NMR and Isotopic Exchange Techniques. For example, the oxidation of NO_2^- by HOCl has been shown to occur through the transfer of oxygen atom of HOCl to NO_2^-, by using ^{18}O exchange.



Atom or group transfer reactions generally proceed through *inner sphere mechanism* discussed later in this chapter. In this mechanism, the atom or group under transfer first forms a bridge between the two reacting species which then breaks to affect the transfer of the atom or group from one reacting species to the other. The oxidation-reduction in such atom or group transfer reactions does not, necessarily, require the transfer of electrons other than those which were already present with the atom or group being transferred.

Many electron transfer reactions which proceed through inner sphere mechanism also yield products associated with transferred atoms or groups. Such examples are discussed separately under category (2).

2. Oxidation-Reduction Reactions Through Electron Transfer

The quantum mechanical picture of an electron in an orbital is of a charge with charge density falling off with distance from the nucleus and the probability of the existence of electron even far away from the nucleus being not zero. This means that the electron may be occasionally found even far from the nucleus. In other words, the electron may momentarily extend its orbital and come very close to another nucleus which may accept that electron subject to certain conditions.

Consider atom A and ion A^+ of a monoatomic *gas*. Since the range of extension of electron orbital is more than the accepted diameters of A and A^+, the electron from A may get transferred to A^+ even before the actual collision for electron transfer occurs between A and A^+ (all the collisions, however, do not lead to electron transfer).

The situation for electron transfer from a metal ion in solution is more difficult. In the first place, the extension of orbitals is likely to be hindered by the molecules of the solvent. Secondly, the ligands of the complex would tend to insulate the electron of the metal ion and thus inhibit the extension of orbitals of metal ions.

Electron Transfer and the Law of Conservation of Energy. Consider the reaction

$$\underbrace{[Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}}_{\substack{\text{Complex ions in ground state}\\ \text{(stable state)}}} \longrightarrow \underbrace{[Fe^*(H_2O)_6]^{2+} + [Fe^*(H_2O)_6]^{3+}}_{\substack{\text{Complex ions in excited state}\\ \text{(higher energy state)}}}$$

The reacting complex ion $[Fe(H_2O)_6]^{3+}$ in its ground state (or stable state) has an equilibrium Fe–O distance of 2·05 Å. Any *change* in this distance would *increase* the energy of the complex ion. Similarly, the equilibrium Fe–O distance in $[Fe(H_2O)_6]^{2+}$ in its ground state is 2·21 Å. Any *change* in this distance would *increase* the energy of the complex ion. According to Frank-Condon principle, the nuclear positions and hence the internuclear distances in a molecule remain unchanged during electron transfer. This is because the electrons move too much faster than the nuclei in the specie. Therefore, the Fe–O distance in $[Fe^*(H_2O)_6]^{2+}$ produced from $[Fe(H_2O)_6]^{3+}$ by electron transfer would, at first, be 2·05Å, *i.e.*, the same as the Fe–O distance in $[Fe(H_2O)_6]^{3+}$ complex. This distance is shorter than the Fe–O distance of 2·21 Å in $[Fe(H_2O)_6]^{2+}$ in its stable or ground state. Thus, $[Fe^*(H_2O)_6]^{2+}$ produced would be in the higher energy or excited state. It would come to the lower energy or stable state by re-adjusting the Fe–O distance to 2·21 Å. While doing so, it has to lose the excess energy to the system. Likewise, $[Fe^*(H_2O)_6]^{3+}$ produced from $[Fe(H_2O)_6]^{2+}$ by electon transfer would, at first, have the Fe–O distance of 2·05 Å in its stable state. Therefore, $[Fe^*(H_2O)_6]^{2+}$ produced would also be in an excited state and would come to the ground state by re-adjusting the Fe–O distance to 2·05Å. While doing so, it also loses the excess energy to the system. After the products come to the stable states, these are in no way different from reacting species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$. Hence they can *again* participate in electron transfer and can *again* liberate energy. Thus, electron transfer between two ions of the same metal in aqueous solution would lead to *constant generation of energy*. But, this is contrary to the law of conservation of energy. However, the law is *not violated* if the metal-ligand distances in both the complex ions are, somehow, made the same prior to electron transfer between them.

In the above example, the ions $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ can have the *same* Fe–O distance falling in between 2·05 Å and 2·21Å. It has been calculated that minimum energy is required to bring Fe–O distance in both the species to the same value of 2·09 Å. Let E_a be the energy required to produce $[Fe^{\#}(H_2O)_6]^{2+}$ and $[Fe^{\#}(H_2O)_6]^{3+}$ species having the *same* distance of 2·09 Å in each. Then

$$E_a = \text{Energy of } \{[Fe^{\#}(H_2O)_6]^{2+} + [Fe^{\#}(H_2O)_6]^{3+}\} - \text{Energy of } \{[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+}\}$$

The electron transfer process when all the four species have the same Fe–O distance of 2·09 Å may thus be represented as

$$[Fe^{\#}(H_2O)_6]^{2+} + [Fe^{\#}(H_2O)_6]^{3+} \longrightarrow [Fe^{\#}(H_2O)_6]^{3+} + [Fe^{\#}(H_2O)_6]^{2+}$$

After the electron transfer, $[Fe^{\#}(H_2O)_6]^{2+}$ and $[Fe^{\#}(H_2O)_6]^{3+}$ species produced would come to the ground states by releasing energy exactly *equal* to the energy E_a which was required for the formation of the reacting species $[Fe^{\#}(H_2O)_6]^{2+}$ and $[Fe^{\#}(H_2O)_6]^{3+}$. In this way no net energy change would occur during electron transfer between the ions to yield different oxidation states of the same metal.

In the case of electron transfer between ions of *different metals* M and M′, the probability of electron transfer from M^{2+} to $(M')^{3+}$ may be *different*, say, *more* than the probability of electron transfer from $(M')^{3+}$ to M^{2+}. In that event the backward reaction may not occur. This case is thus different from the one involving electron transfer between the ions of the same metal in which there is equal probability of electron transfer between the forward and the backward reactions. Thus, electron transfer between ions of different metals does not violate the law of conservation of energy.

Electron Transfer and Spin States of Metal Ions. Another restriction placed on electron transfer between ions of the same metal in solution phase is that, leaving aside the electrons that are to be transferred, the two ions should have essentially the same electron spin. Let us consider the case of $[Co(NH_3)_6]^{2+}$—$[Co(NH_3)_6]^{3+}$ system. The ammonia ligand is of a moderate crystal field strength. It causes electron spin pairing in $[Co(NH_3)_6]^{3+}$ but cannot do so in $[Co(NH_3)_6]^{2+}$ with the result that Co in the former complex is in the *low spin* state (t_{2g}^6) and in the latter complex, it is in the *high spin* state ($t_{2g}^5e_g^2$). As such, the electron transfer from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ is not allowed if both the ions are in their ground spin states. In order that electron transfer occurs, the excitation of one or both the ions is required to such an extent that the electron spins of both the ions become the same (barring the spin of electron being transferred). This would obviously require considerable energy. Thus, the electron transfer

from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ is more difficult than, say, the electron transfer from $[Fe(H_2O)_6]^{2+}$ to $[Fe(H_2O)_6]^{3+}$. Both Fe(II) and Fe(III) are in high spin state in these complexes.

Mechanism of Electron Transfer Reactions in Solution Phase

The probability of an electron leaking through a potential energy barrier (that would be impenetrable according to classical mechanics) is a well known phenomenon. As already mentioned, electron can be transferred from distances which are considerably larger than the distances essential for actual collision of the reactants. Thus, "electron tunneling effect" is directly related to the phenomenon of extension of electronic orbitals in space.

Electron transfer reactions are generally quicker than those involving the exchange of ligands on the metal ions. These, however, can be conveniently studied by Radioactive Exchange as well as by NMR techniques.

Two types of transition states or intermediates are generally formed during electron transfer reactions. These are : *Outer Sphere Transition States* and *Inner Sphere Transition States.*

Outer Sphere Transition States. *When the inner coordination spheres of two reacting complex ions remain intact in the transition state (i.e., intermediate) of an electron transfer reaction,* it is called an **outer sphere transition state.** The mechanism of electron transfer through such a transition state is called **outer sphere mechanism.**

Inner Sphere Transition State. *When the coordinated ligand of one complex ion forms a bridge with the other complex ion in the transition state of an electron transfer reaction,* it is called **inner sphere transition state.** The mechanism of electron transfer through such a transition state is called **inner sphere mechanism.**

Both the mechanisms of electron transfer have been discussed below in some details.

1. Outer Sphere Mechanism. If the reductant and the oxidant complex ions are both inert and if their inner coordination shells are saturated, the rate of ligand exchange would be very small and *the possibility of the formation of* a **ligand bridge** *would be negligible.* However, the observed rate of electron transfer between such pairs of complex ions is quite fast. This cannot be explained by any mechanism involving the dissociation of an atom or a group, or exchange of a coordinated ligand, since both the complex ions are inert. Such electron transfer reactions would obviously occur through outer sphere mechanism. We shall now consider some examples of electron transfer reactions occurring through this mechanism.

1. $[Co(NH_3)_6]^{2+} - [Co(NH_3)_6]^{3+}$ System. Consider the reacion

$$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

Since the reacting $[Co(NH_3)_6]^{3+}$ ion is an inert complex and Co(III) has in it a saturated inner coordination shell, the exchange of coordinated ammonia ligands between the two complexes is found to be exceedingly slow. The coordinated NH_3 ligands do not have any other lone pair through which they can form a bridge between the two cobalt ions. Hence, an inner sphere transition state of the type $[(NH_3)_5Co-(NH_3)-Co(NH_3)_5]^{5+}$ is not possible. Therefore, electron transfer from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ must occur through *outer sphere mechanism* in which inner coordination shells of the reductant, *i.e.*, $[Co(NH_3)_6]^{2+}$ and the oxidant, *i.e.*, $[Co(NH_3)_6]^{3+}$, *in the transition state* remain intact.

The outer sphere electron transfer process is *slow* because of the following reasons :

(*i*) Since the Co–N distances in the oxidant and the reductant complex ions are *appreciably different, considerable energy of activation* is required to excite the two ions to have identical Co–N distances (because only then the electron transfer between these two ions would occur).

(*ii*) The electron being transferred from $[Co(NH_3)_6]^{2+}$ occupies an e_g orbital which is already engaged in M–L sigma bonding** (the configuration of Co(II) in the complex ion is $t^5_{2g}\,e^2_g$). The delinking of this electron from Co(II) would, therefore, require more energy.

**d_{z^2} and $d_{x^2-y^2}$ orbitals alongwith *s* and *p* orbitals of M are involved in M–L sigma bonding

(*iii*) The spin states of Co(II) and Co(III) in the reacting complex ions are different.

2. $[Fe(CN)_6]^{4-} - [Fe(CN)_6]^{3-}$ System. Consider the reaction

$$[Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

Both the reacting complex ions are inert towards substitution and their coordination shells are fully saturated.

The isotopic exchange studies confirm that the coordinated CN^- ligands of both the complex ions are *not exchangeable.* Therefore, the formation of an inner sphere bridged transition state is ruled out. The electron transfer in the above reaction, therefore, proceeds through *outer sphere mechanism.*

The observed rate of electron transfer is *fast.* This may be due to the following reasons :

(*i*) The Fe–C distances in both the complex ions are almost the same. Hence, very little energy is required to make the Fe–C distances in the two complex ions identical so that electron transfer may occur.

(*ii*) Leaving aside the electrons that are to be transferred, both the metal ions have the same electron spin. This facilitates the transfer of electrons.

(*iii*) The electron under transfer is in t_{2g} orbital (electronic configuration of Fe(II) in $[Fe(CN)_6]^{4-}$ is t^6_{2g}) which is not engaged in M–L sigma bonding. Therefore, the delinking of this electron from Fe(II) is easy.

(*iv*) The ligand CN^- is unsaturated and the presence of unsaturated and/or conjugate ligands on the reductant facilitates the electron tunnelling.

(*v*) CN^- is a pi acceptor ligand, *i.e.*, it can form pi bond by accepting electrons from the t_{2g} orbitals of the metal ion. Such ligands always stabilise the lower valency of the metal ion which implies that such ligands stabilise the product formed due to acceptance of electrons.

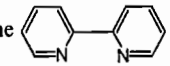
3. $[Os(dipy)_3]^{2+} - [Os(dipy)_3]^{3+}$ System. The reaction

$$[Os(dipy)_3]^{2+} + [Os(dipy)_3]^{3+} \longrightarrow [Os(dipy)_3]^{3+} + [Os(dipy)_3]^{2+}$$

cannot occur through inner sphere mechanism because both the complex ions are inert and their coordination shells are fully saturated.

The observed reaction rate is *fast* due to the following reasons :

(*i*) The Os–N distances in both the complexes are almost the same. Hence very little energy is required to make the Os–N distances in the two complexes identical.

(*ii*) The ligand dipyridine  is a pi acceptor and is highly conjugated. This facilitates electron tunneling.

(*iii*) The electron under transference is present in t_{2g} orbital which is not engaged in M–L sigma bonding. Hence, this electron can be easily detached from the metal ion.

(*iv*) Except for the electron which is being transferred, the two metal ions have the same electron spin.

Let us now summarise the **main characteristics of electron transfer reactions occurring through outer sphere mechanism :**

1. Electron transfer reactions occur between those metal ions which are either both inert with their coordination shells saturated or one of the complex ions is inert with its coordination shell saturated. In the latter case, none of the coordinated ligands would be a bridging ligand.

2. Electron transfer between ions of the same metal is fast if M–L distances in the reductant and the oxidant are very nearly the same.

3. Electron transfer is fast if the electrons are able to reach the surface of the complex either through unsaturation or through conjugation.

4. The rate of electron transfer depends upon the polarising power of the central metal ion.

5. Electron transfer is fast if the electron being transferred is present in a t_{2g} orbital and is slow if it is present in an e_g orbital.

6. Electron transfer is fast if the coordinated ligands present on the system are pi acceptors.

7. Electron transfer is fast if the electron spins of the two complex ions (leaving aside the electrons being transferred) are the same.

2. Inner Sphere Mechanism. Electron transfer reactions proceeding through inner sphere mechanism generally have one inert and one labile reactant. The inert reactant has a coordinated ligand which is capable of forming a bridge. A few examples of electron transfer reactions proceeding through inner sphere transition states (*i.e.*, intermediates) are discussed below in Examples 1–4.

Example 1. Consider the following reactions :

(*a*) $[Cr(H_2O)_6]^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow [Cr(H_2O)_6]^{3+} + [Co(NH_3)_6]^{2+}$

(*b*) $[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5(H_2O)]^{3+} \longrightarrow [Cr(H_2O)_6]^{3+} + [Co(NH_3)_5(H_2O)]^{2+}$

(*c*) $[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5(OH)]^{2+} \longrightarrow [Cr(H_2O)_5(OH)]^{2+} + [Co(NH_3)_5(H_2O)]^{2+}$

The reductant in all these reactions is $[Cr(H_2O)_6]^{2+}$ which is a very labile complex ion and can easily lose a H_2O molecule. The order of the rate of electron transfer in the above reactions is (*a*) << (*b*) < (*c*).

In reaction (*a*), the oxidant $[Co(NH_3)_6]^{3+}$ is an inert complex ion with no coordinated ligand capable of forming a bridge with the reductant. Electron transfer in this reaction, therefore, cannot occur through inner sphere mechanism and the rate of electron transfer would be slow.

In reaction (*b*), the oxidant $[Co(NH_3)_5(H_2O)]^{3+}$ is again inert but the coordinated H_2O is capable of forming a bridge, though a very weak one, with the reductant leading to the formation of the intermediate bridged complex $[(H_2O)_5Cr-(H_2O)-Co(NH_3)_5]^{5+}$. The oxygen of the coordinated H_2O has one un-engaged lone pair of electrons through which it can associate with the reductant. The formation of an aqua bridge has been established by H_2O^{18} exchange studies. The reaction (*b*) thus proceeds through inner sphere mechanism and is much faster than the reaction (*a*).

In reaction (*c*), the inert oxidant $[Co(NH_3)_5(OH)]^{2+}$ has a co-ordinated OH^- ligand which is capable of forming a fairly strong bridge with the reductant leading to the formation of the bridged intermediate $\left[(H_2O)_5Cr-\overset{H}{O}-Co(NH_3)_5X\right]^{4+}$. Since OH bridge is stronger (*i.e.*, stabler) than aqua bridge, the energy of activation required to form OH–bridged intermediate would be less than required for the formation of aqua-bridged intermediate. Reaction (*c*), therefore, proceeds through inner sphere mechanism and is *more facile* than reaction (*b*).

Example 2. Consider the reaction :

(*d*) $[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5X]^{2+} \xrightarrow{\text{Water}} [Cr(H_2O)_5X]^{2+} + [Co(NH_3)_5(H_2O)]^{2+}$

which has been studied in aqueous phase in the presence of radioactive free X^- ligand (where X^- is F^-, Cl^-, Br^- or I^-) and it has been observed that the product $[Cr(H_2O)_5X]^{2+}$ shows an almost complete absence of radioactivity. This observation confirms that it is the X^- ligand initially attached to the inert oxidant $[Co(NH_3)_5X]^{2+}$ which gets transferred to the reductant. This cannot happen if X^- completely dissociates from the oxidant and becomes free. Therefore, the intermediate or the transition state must have X^- associated with both the oxidant and the reductant. This observation provides an indirect proof for the formation of inner sphere or bridged complex in the transition state. The mechanism of reaction (*d*) may thus be represented as follows :

(*i*) $[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5X]^{2+} \xrightarrow{\text{slow}} [(H_2O)_5Cr-X-Co(NH_3)_5]^{4+} + H_2O$

(*ii*) $[(H_2O)_5Cr-X-Co(NH_3)_5]^{4+} \xrightarrow[\text{fast}]{\text{hydrolysis}} [Cr(H_2O)_5X]^{2+} + [Co(NH_3)_5(H_2O)]^{2+}$

The rate of reaction (*d*) is thus given by

$$r = k\,(\text{Concn. of } [Cr(H_2O)_6]^{2+}) \times (\text{Concn. of } [Co(NH_3)_5X]^{2+})$$

It has also been observed that the rate of electron transfer in the reaction depends upon the nucleophilic character (and *not* the basicity) of the halide ion X^-. The rates are thus in the order $I^- > Br^- > Cl^- > F^-$. It is obvious that the stronger the nucleophilic character of the halide ion, the greater would be its capability to form a Cr–X–Co bridge.

Example 3. Consider the reaction given below :

(*e*) (*i*) $[R-\overset{O}{\overset{\|}{C}}-O-Co(NH_3)_5]^{2+}$ (Oxidant) + $[Cr(H_2O)_6]^{2+}$ (Reductant) $\longrightarrow$ $[(H_2O)_5Cr-O-\underset{R}{\underset{|}{C}}-O-Co(NH_3)_5]^{4+}$

(*ii*) $[(H_2O)_5Cr-O-\underset{R}{\underset{|}{C}}-O-Co(NH_3)_5]^{4+} \xrightarrow{\text{hydrolysis}} [Co(NH_3)_5(H_2O)]^{2+} + [(H_2O)_5-Cr-O-\overset{O}{\overset{\|}{C}}-R]^{2+}$

Evidently, the COOR group forms a bridge between the oxidant and the reductant so that the above reaction proceeds through inner sphere mechanism. This readily explains why the rate of electron transfer in reaction (*e*) is fast compared to reaction (*a*). The rate of reaction is further increased if R is unsaturated or conjugated since this factor is known to facilitate electron transfer.

Example 4. Consider the reactions given below :

(*f*) (*i*) $[Cr(NH_3)_5(NCS)]^{2+}$ (Oxidant) + $[Cr(H_2O)_6]^{2+}$ (Reducant) $\longrightarrow [(H_3N)_5Cr-NCS-Cr(H_2O)_5)]^{4+}$

(*ii*) $[(H_3N)_5Cr-NCS-Cr(H_2O)_5]^{4+} \xrightarrow{\text{hydrolysis}} [Cr(NH_3)_5(H_2O)]^{2+} + [Cr(H_2O)_5(NCS)]^{2+}$

(*g*) (*i*) $[Cr(NH_3)_5N_3]^{2+}$ (Oxidant) + $[Cr(H_2O)_6]^{2+}$ (Reducant) $\longrightarrow [(H_3N)_5Cr-N=N=N-Cr(H_2O_5)]^{4+}$

(*ii*) $[(H_3N)_5Cr-N=N-N=Cr(H_2O_5]^{4+} \xrightarrow{\text{hydrolysis}} [Cr(NH_3)_5(H_2O)]^{2+} + [Cr(H_2O)_5N_3]^{2+}$

The electron transfer reaction (*g*) is found to be faster than (*f*). This can be explained if we assume inner sphere mechanism for both these reactions.

The bridged transition state of reaction (*f*) is less stable and hence would require more energy for its formation compared to the energy required for the formation of the bridged transition state of reaction (*g*). As a result, the electron transfer reaction (*g*) is faster than (*f*). The Cr–NCS–Cr bridge is less stable because S–Cr linkage is weaker than N–Cr linkage whereas Cr–N–N–N–Cr bridge is more stable as it acquires greater stability through resonance.

The observed energy of activation (E_a) for all the above mentioned electron transfer reactions is found to be very low (about 3–4 kcal mol^{-1}) and the entropy change (ΔS) is found to be negative.

If a dissociative step, like the one shown below :

$$[Cr(NH_3)X]^{2+} \longrightarrow [Co(NH)_5]^{3+} + X^-$$

were the rate-determining step in these reactions, the energy of activation would have been considerably high and ΔS (= $S_{Products} - S_{Reactants}$) would have been positive.

It is clear from above that in electron transfer reactions occurring through inner sphere mechanism, an atom or a group is also transferred from one complex ion to another. However, the transfer of electron is

not caused by the atom or the group which is transferred. In the electron transfer process, the oxidant and the reductant first form a bridged intermediate and the electron is transferred from the reductant to the oxidant in this bridged intermediate which then breaks up to give the products. The *transfer* or *non-transfer* of the bridging atom or group would depend upon the *relative stabilities of the products* that are possible from the bridged intermediate. To illustrate this point, let us consider the following reaction :

(*h*) (*i*) $[IrCl_6]^{2-} + [Cr(H_2O)_6]^{2+} \longrightarrow \underset{\text{Bridged intermediate}}{[Cl_5Ir-Cl-Cr(H_2O)_5]^0}$

(*ii*) $[Cl_5Ir-Cl-Cr(H_2O)_5]^0 \xrightarrow[\text{2. Hydrolysis}]{\text{1. Electron transfer}} [IrCl_6]^{3-} + [Cr(H_2O)_6]^{3+}$

In the above reaction, no transfer of bridging Cl atom has occurred although an electron has been transferred from the reductant $[Cr(H_2O)_6]^{2+}$ to the oxidant $[IrCl_6]^{2-}$. The electron transfer obviously occurs prior to the breaking of the bridge in the intermediate. Since the final products of reaction, *viz.*, $[IrCl_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$ are more stable than $[IrCl_5(H_2O)]^{2-}$ and $[Cr(H_2O)_5Cl]^{2+}$, the other possible products of the bridged intermediate, the latter readily breaks up in a manner shown in *h* (*ii*) to give these products.

Let us now summarise **the main characteristics of electron transfer reactions occurring through inner sphere mechanism :**

1. In order that electron transfer occurs through inner sphere mechanism, one of the complexes should be *inert* and the other one *labile*. The inert complex ion should have a ligand *capable of bridging both the complex ions* during the formation of the intermediate.

2. Electron transfer reactions occurring through inner sphere mechanism are *faster* than similar reactions occurring through outer sphere mechanism.

3. The rate of electron transfer increases if the bridging ligand has unsaturation or extended conjugation in its structure.

4. The rate of electron transfer also increases with increase in the nucleophilic character of the bridging ligand.

5. Alongwith the transfer of electron, the bridging ligand is also transferred from one complex ion to another. But it is not always necessary. The transfer or non-transfer of the bridging ligand depends upon the relative stabilities of the products that are possible from the bridged intermediate.

TWO-ELECTRON TRANSFER REACTIONS

As is well known, the oxidation states of some post-transition elements change by *two* units. It is, therefore, expected that a two-electron transfer would occur in the electron transfer reactions of the ions of these elements. The 2-electron transfer reactions are further categorised into *complimentary* and *non-complimentary reactions.*

Complimentary reactions are those in which reductant loses and the oxidant gains two electrons. For instance, in the Tl^+-Tl^{3+} system in aqueous medium containing ClO_4^- ions, the two electrons are transferred from $Tl^+(aq)$ to $Tl^{3+}(aq)$. The observed rate of the two-electron transfer reaction is given by

$$r = k_1[Tl^+][Tl^{3+}] + k_2[Tl^+][TlOH]^{2+}$$

The above rate law can be explained if we assume the following two reactions occurring *independently*:

(*a*) $[Tl(H_2O)_n]^+ + [Tl(H_2O)_n]^{3+} \longrightarrow [Tl(H_2O)_n]^{3+} + [Tl(H_2O)_n]^+$

(*b*) $[Tl(H_2O)_n]^+ + \underset{\text{(Present in small quantity)}}{[Tl(H_2O)_{n-1}(OH)]^{2+}} \longrightarrow [Tl(H_2O)_n]^{3+} + [Tl(H_2O)_{n-1}(OH)]^0$

There are several other 2-electron transfer reactions. Some of these are :

$Sn^{2+} + Tl^{3+} \longrightarrow Sn^{4+} + Tl^+$

$Sn^{2+} + Hg^{2+} \longrightarrow Sn^{4+} + Hg^0$

$V^{2+} + Tl^{3+} \longrightarrow V^{4+} + Tl^+$

Non-complimentary reactions are those in which the number of electrons released by the reductant is not equal to the number of electrons accepted by the oxidant. Such reactions generally proceed through a multi-step path. For example, the reduction of Tl^{3+} with Fe^{2+} is believed to involve the following steps :

$Fe^{2+}(aq) + Tl^{3+}(aq) \longrightarrow Fe^{3+}(aq) + Tl^{2+}(aq)$

$Fe^{2+}(aq) + Tl^{2+}(aq) \longrightarrow Fe^{3+}(aq) + Tl^+(aq)$

$2Fe^{2+}(aq) + Tl^{3+}(aq) \longrightarrow 2Fe^{3+}(aq) + Tl^+(aq)$

QUESTIONS

1. What is meant by the terms : Inert and Labile complexes ? Show that inertness of a complex is different from its thermodynamic stability ?
2. (*a*) What do you understand by nucleophilic substitution reactions for octahedral complexes? Discuss S_N^1 and S_N^2 mechanisms for octahedral complexes.

   (*b*) Discuss briefly S_N^1(CB) mechanism for the reaction :

   $$[Co(en)_2NH_3Cl]^{2+} + OH^- \longrightarrow [Co(en)_2NH_3OH]^{2+} + Cl^-$$
3. (*a*) Explain what is meant by S_N^1, S_N^2 and S_N^1(CB) mechanisms. Give examples.

   (*b*) Explain on the basis of valence bond theory, the cause of lability and inertness of octahedral complexes.
4. (*a*) What do you understand by labile and inert complexes ? (*b*) Explain on the basis of crystal field theory, the cause of lability and inertness of octahedral complexes.
5. Discuss in details the mechanism involved in the base hydrolysis of $[Co(en)_2NH_3Cl]^{2+}$.
6. Discuss the mechanism involved in electron transfer reactions. Give suitable examples.
7. What do you understand by S_N^1(CB) mechanism ? Discuss with a suitable example.
8. Discuss the lability of octahedral complexes of Ni(II) on the basis of crystal field and valence bond theories. In your opinion, which theory explains the reactivity of these complexes more satisfactorily and why ?
9. Discuss, giving suitable examples, the types of intermediates that are formed in S_N^1, S_N^2 and S_N^1(CB) mechanisms.
10. What type of octahedral complexes undergo acid hydrolysis by S_N^2 mechanism ? What type of intermediates and productes would be formed ? Illustrate giving suitable examples.
11. Discuss the factors which determine the lability of complexes formed by non-transition elements.
12. What is an inert ligand ? What type of intermediates and products are formed if the inert ligand is (*a*) pi acceptor (*b*) pi donor ?
13. Comment on the role of pi bonding in determining the geometry of the product formed during the acid hydrolysis of octahedral complexes.
14. Discuss what type of mechanism for acid hydrolysis of octahedral complexes is suggested by the following factors :

    (*i*) Charge on the substrate (*ii*) Strength of the metal–leaving group bond (*iii*) Inductive effect of ligands.
15. Explain the following order of the rates of aquation of complexes on the basis of the solvation effect :

    $[Co(NH_3)_5Cl]^{2+} > [Co(en)(NH_3)Cl]^{2+} > [Co(en)_2(NH_3)_5Cl]^{2+} > [Co(en)(diene)Cl]^{2+} > [Co(tetraene)Cl]^{2+}$
16. Can the above order be explained by S_N^1(trans) mechanism ? Explain the order if your answer is yes or give reasons why the order cannot be explained if your answer is no. (*Hint* : build your arguments on rate constants of aquation given in the text)
17. Explain why

    (*i*) $[(NH_2)(CH_2)_2(NH_2)_2CoCl_2]^+$ is slower to aquate than $[(NH_2(CH_2)_3(NH_2)_2CoCl_2]^+$

    (*ii*) $[(NH_2(CH_2)_2NH_2)_2CoCl_2]^+$ is slower to aquate than $[(NH_2CH(CH_3)CH(CH_3)_3NH_2)_2CoCl_2]^+$
18. Discuss the mechanism of aquation of cis and trans $[Co(en)_2Cl(OH)]^+$ complexes.

19. Explain in what way the acid hydrolysis of cis $[Co(en)_2Cl(OH)]^+$ complex differs from that of trans $[Co(en)_2Cl(NO_2)]^+$ complex.

20. Give at least two arguments against the S_N2 mechanism for the base hydrolysis of octahedral ammine complexes of Co(III).

21. List all points of evidence to establish that base hydrolysis of octahedral complexes proceeds through S_N1(CB) mechanism.

22. Discuss the stereochemistry of the intermediates formed during the base hydrolysis ofoctahedral ammine complexes of Co(III).

23. Give examples of oxidation-reduction reactions occurring through the transfer of atoms or groups of atoms.

24. What are the conditions for the transfer of an electron from M^{2+} to M^{3+} in aqueous medium ?

25. Discuss the outer sphere and inner sphere mechanisms of electron transfer reactions. Why is the electron transfer in the system $[Co(NH_3)_6]^{2+}$–$[Co(NH_3)_6]^{3+}$ slower than that in the system $[Fe(CN)_6]^{4-}$–$[Fe(CN)_6]^{3-}$?

26. Give at least one example of an electron transfer reaction which occurs through inner sphere mechanism and also involves transfer of atom or group.

27. Give at least one example of an electron transfer reaction which occurs through the inner sphere mechanism but does not involve the transfer of atom or group.

28. Explain why

(*i*) The transfer of electron from $[Cr(H_2O)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ in aqueous medium isslower than the transfer from $[Cr(H_2O)_6]^{2+}$ to $[Co(NH_3)_5OH]^{2+}$.

(*ii*) The transfer of electron from $[Cr(H_2O)_6]^{2+}$ to $[Cr(NH_3)_3(NCS)]^{2+}$ is slower than the transfer from $[Cr(H_2O)_6]^{2+}$ to $[Cr(NH_3)_5N_3]^{2+}$.

29. Give evidence to suggest that the substitution in square planar complexes proceeds through an S_N2 mechanism. Why are Ni(II) and Pd(II) square planar complexes more labile than square planar complexes of Pt(II) ?

30. What is trans effect ? Which theory of trans effect satisfactorily explains the following order of trans effect of inert ligands :

$$F^- < Cl^- < Br^- < I^-$$

31. Discuss the theories of trans effect. Which theory explains better the trans effect of CO compared to that of pyridine ?

32. Discuss the complimentary and the non-complimentary two-electron transfer reactions giving suitable examples.

MONONUCLEAR COMPLEXES OF Pi ACCEPTOR LIGANDS

32

Pi Acceptor Ligands. The pi acceptor ligands are those which *possess vacant pi orbitals in addition to the lone pairs of electrons.* These ligands *donate* their lone pairs to the metal to form a normal σ bond with the latter. In addition to it, the vacant orbitals *accept* electrons from the filled metal orbitals to form a type of pi bond which suppliments the σ bond. These ligands are thus called **pi acid* ligands** (since they *accept* pi electron charge due to their vacant pi orbitals) or **pi acceptor ligands** or **pi bonding ligands.** Common examples are CO, CNR, PR_3, NO, etc. In many of the complexes, formed by pi acceptor ligands, the atoms are in *low positive, zero* or *negative* oxidation states, *i.e.,* these ligands stabilise lower oxidation states. This is because of the fact that there is higher electron charge density on the metal in its lower oxidation state than in its higher oxidation state. Therefore, the metal, being electopositive in nature, would feel more comfortable if some of the excess electronic charge gets transferred to the vacant orbitals of the ligand by pi bonding.

Some of the common pi acceptor ligands and their mononuclear complexes are discussed below.

MONONUCLEAR METAL CARBONYLS

Metal carbonyls are regarded as the coordination compounds formed between the electron donor CO groups and the transition metals such as Ni, Fe and Co. The formation of the first metal carbonyl, $Ni(CO)_4$, was reported by L. Mond in 1889 and the formation of the second metal carbonyl, $Fe(CO)_5$, was reported independently by L. Mond and Berthelot shortly after the discovery of $Ni(CO)_4$. The metals Ni, Fe and Co react directly with CO gas to form the metal carbonyls. Carbonyls of other metals are produced by the reduction of appropriate salts or complexes of these metals in the presence of CO gas.

The preparation and properties of metal carbonyls have already been described in details in Chapter 16.

Bonding in Mononuclear Metal Carbonyls

In order to understand properly the nature of bonding in mononuclear metal carbonyls, the students would need to refer to the molecular orbital energy level diagram of CO molecule discussed earlier in Chapter 4. For convenience of reference, this diagram has been reproduced here (Fig. 1).

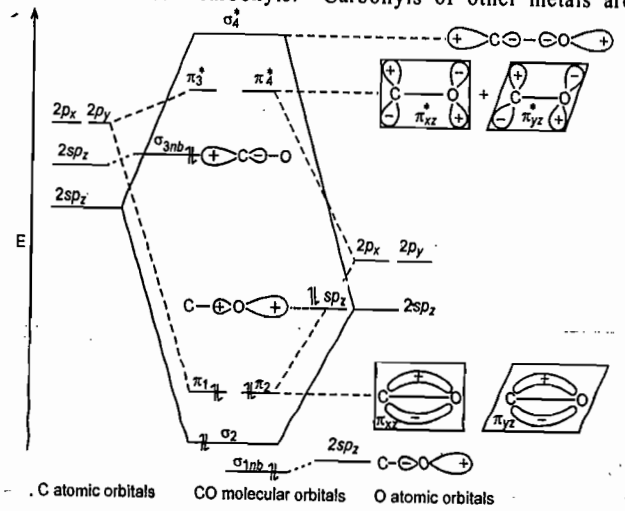


Fig. 1. MOEL diagram of CO molecule; shapes of molecular orbitals are also shown. Positions of pure 2*s* and 2p_z orbitals of C and O atoms are not shown.

* According to Lewis concept, a substance which accepts electrons is called an **acid.**

Since $\sigma_{3(nb)}$ is the highest occupied nonbonding orbital localised on C atom (having more directional characteristics than the lowest energy $\sigma_{1(nb)}$ localised on O atom), its electron pair can easily be donated for forming dative (or coordinate) bond.

As is the case in other metal complexes, the overlap of a lone pair in $\sigma_{3(nb)}$ molecular orbital on the C atom with the empty hybrid metal orbital (the hybridisation may involve $(n-1)d$, ns, np orbitals) forms a metal-to-carbon σ bond, as shown in Fig. 2. Apart from this, the transition metal atom in a metal carbonyl has filled non-bonding d orbitals (called $d\pi$ orbitals) which are of proper symmetry to overlap with the low lying antibonding molecular orbitals of CO. This type of overlapping results in an additional π bond between the metal M and the ligand CO (cf. Fig. 2). The $d\pi$–π^* overlap is shown in the figure in one plane (*i.e.*, *XZ* plane) only. A similar $d\pi$–π^* overlap occurs in the other, *i.e.*, the *YZ* plane (not shown in the figure).

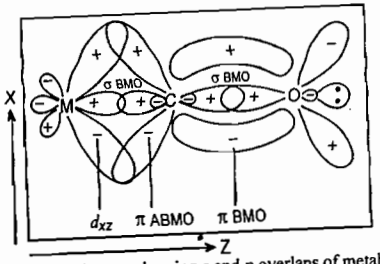


Fig. 2. Diagram showing *s* and *p* overlaps of metal and CO orbitals of proper symmetry in XZ plane. The pi back bonding is shown involving d_{zx} orbital of the metal.

The $d\pi$–π^* overlap, apart from providing an additonal bond (pi bond) between M and C, stabilises or strengthens the M–C bond by removing the excess negative charge which gets accumulated on the metal as a result of the coordination of CO with it. The stronger M–C bond brings the two atoms closer to each other thus bringing about a better π overlap. In other words, one type of bonding strengthens the other type. Such an effect in bonding is known as **synergic effect**. During the fomation of the above type of π bonds, electronic charge is transferred from the filled non-bonding orbitals of the metal to the π^* orbitals of the ligand CO. This reduces the bond order of CO. Thus, *while the π back bonding strengthens the M–C bond, it weakens the* CO *bond.* This means that M–C and CO bond orders in carbonyls are roughly complementary to each other and any factor that increases the metal π-electron transfer to CO would increase the M—C bond order and decrease the CO bond order simultaneously.

Since the bond order between M and C is generally *higher* than a normal σ bond due to additional π back bonding, the single line in M–C bond simply represents a metal–carbon bond *without any reference to the actual bond order in this bond.*

Let us consider the following isoelectronic and isostructural species :

$$[Ni(CO)_4],\ [Co(CO)_4]^-\ \text{and}\ [Fe(CO)_4]^{2-}$$

The overall negative charge in the case of the last two species is assumed to reside on the metal. The greater the negative charge on the metal, the greater would be the ease of the electron transfer from the metal to the π^* orbitals of CO. Accordingly, the M–C bond order increases in the order :

$$Ni-C < Co-C < Fe-C$$

Simultaneously, the C–O bond order decreases in the order :

$$Ni(CO)_4 > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$$

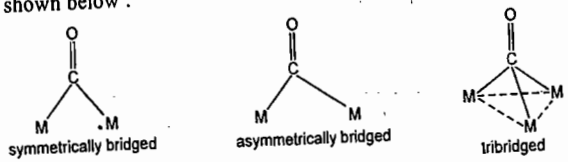
The actual bond orders as determined from spectroscopic data are given in Table 1.

TABLE 1

Bond Orders in Metal Carbonyls Determined from Spectroscopic Data

Metal Carbonyl	M–C Bond order	C–O Bond order	M–C + C–O Bond order
$Ni(CO)_4$	1·33	2·64	3·97
$[Co(CO)_4]^-$	1·89	2·14	4·03
$[Fe(CO)_4]^{2-}$	2·16	1·85	4·01

In several metal carbonyls, the CO groups are bonded or 'bridged' to two or more metal atoms in the manner shown below :



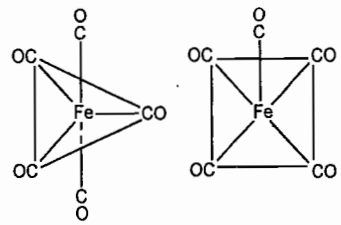
As a simple picture it is assumed that the bridging CO group contributes only one electron to each of the metal atoms. The picture of M–C π bonding in a bridging carbonyl group is rather complicated. It is more extensive and different from the one in a terminal carbonyl group. It is probably because of this reason that the CO bond order in a bridging carbonyl group is found to be lower than in a terminal carbonyl group.

Most of the metal carbonyls obey th **inert gas rule** which states that the compounds in which the central metal atom appears to have attained the configuration of a noble gas either by the sharing or by the transference of electrons tend to be more stable. The total number of electrons which the metal atom in its compound appears to have around itself is called the effective atomic number (EAN) of the metal in that compound. The obeyance of the EAN or the inert gas rule could be attributed to the capability of ligand CO, in some way, to force the metal atom to have as many filled non-bonding electron pairs in the *d* shell as possible. This would increase the tendency of the metal atom to form π bond by transferring the charge from the $d\pi$ orbitals of the metal to the π^* orbitals of ligand CO.

Infrared Absorption Spectra of Mononuclear Metal Carbonyls

The most extensively studied property of metal carbonyls is their **IR absorption spectra**. These spectra have been used for various determinations as discussed below.

1. Determination of Geometry of Mononuclear Metal Carbonyls. If there is a possibility for a metal carbonyl to have more than one geometry, we can calculate the number of IR-active together with Raman-active vibrational bands for each geometry. The next step is then to run the IR and Raman spectra and tally the number of bands observed with the number of bands predicted theoretically (*i.e*, by calculations) for each geometry. For example, the metal carbonyl $Fe(CO)_5$ can, in principle, have two geometries, *viz.*, triangular bipyramidal (TBP) and square pyramidal (SP), as shown :



The IR and Raman bands actually observed tally with the number of such bands calculated for a TBP geometry, thus confirming that the metal carbonyl $Fe(CO)_5$ exists in the form of a trigonal bipyramid.

2. Determination of Bond Order of CO Bond. The vibrational stretching frequency of the CO bond ν_{CO} is directly related to its bond order. (The vibrational stretching frequency of a group is written as ν_{group}). Any factor which increases the electron charge density in π^* orbitals of the ligated CO would decrease the bond order as also the vibrational frequency of the CO bond. Similarly, any factor which decreases the electron charge density in π^* orbitals of ligated CO would increase the bond order of CO and, therefore, increase the vibrational frequency of the CO bond. In other words, the IR absorption band due to the stretching vibration of ligated CO with a higher bond order would occur at a higher ferquency than the similar IR absorption band of ligated CO with a lower bond order. Thus, the IR spectra can serve as an excellent tool to determine the bond order of CO bond and thereby study the π back bonding in metal carbonyls. Infrared absorption for free CO occurs at about 2250 cm^{-1} whereas the absoption for ligated CO occurs at a considerably lower frequency between 2220–1700 cm^{-1}. This establishes a lower bond order for ligated CO. The lower bond order is due to the transfer of electronic charge from metal to π^* orbitals of CO. Thus, IR evidence lends full support to the concept of π bonding in metal carbonyls.

The presence of a positive charge on the metal carbonyl would resist the flow of the metal electron charge to π^* orbitals of CO. This would increase the CO bond order and hence CO in a metal carbonyl cation would absorb at a higher frequency compared to its absorption in a neutral metal carbonyl.

The following IR absorption data support the above arguments :

$$\left.\begin{array}{l}\text{Metal Carbonyls}\\ \text{Absorption frequency}\\ \text{for CO, } viz.,\ \nu_{CO}\end{array}\right\}\begin{array}{l}\longrightarrow\ [V(CO)_6]^-\ \ [Cr(CO)_6]\ \ [Mn(CO)_6]^+\\ \longrightarrow\ 1860\ cm^{-1}\ \ 1980\ cm^{-1}\ \ 2090\ cm^{-1}\end{array}$$

In the case of a **mixed carbonyl,** if a ligand other than CO is electron-donating, it would facilitate the flow of metal $d\pi$ electrons into the π^* orbitals of CO and would thus decrease the CO bond order and also the ν_{CO}. If, in the mixed carbonyl, the other ligand is also pi acceptor, it would compete with the ligated COs for gaining the metal $d\pi$ electron charge. If that ligand is a better pi acceptor than CO ligand, most of the metal $d\pi$ electron charge would be utilised for π back bonding with that ligand and very little $d\pi$ electron charge would get transferred to π^* orbitals of CO. This would result in an increase of CO bond order and hence of ν_{CO}. The reverse would happen if the 'other' ligand is a poorer pi acceptor than CO ligand. Let us consider an example : Me_3P in $[Me_3PNi(CO)_3]$ is a weaker π acceptor than F_3P in $[F_3PNi(CO)_3]$. Accordingly, ν_{CO} in $[F_3PNi(CO)_3]$ is higher (1990 cm^{-1}) than in $[Me_3PNi(CO)_3]$ (1980 cm^{-1}).

3. Differentiating Between Terminal CO and Bridging CO. The CO bond in terminal carbonyl group (–C≡O) is stronger than the CO bond in a bridging carbonyl group (>CO). Hence, infrared absorption for a terminal CO would occur at a higher frequency than for a bridging CO. It is established that if the CO group in a neutral binary carbonyl absorbs between 2050–1900 cm^{-1}, the CO group is terminally bonded and if the absorption occurs at a lower frequency, *i.e.*, between 1900–1800 cm^{-1}, the CO group is a bridging carbonyl group.

4. Study of Reaction Rates. Rates of substitution reactions of metal carbonyls can be studied conveniently by measuring the rates of decrease of the intensity of CO absorption bands in the infrared spectra of the carbonyls.

Radio Isotope Exchange Studies of Mononuclear Metal Carbonyls

These studies are carried out to determine the rate of exchange of free ^{14}CO with ligated ^{12}CO. In other words, the radio isotope exchange studies are employed to determine the lability of M–C bond. For example, the formation of $Fe_2(CO)_9$ from photolysis of $Fe(CO)_5$ is possible via two routes :

Route 1. Dissociation of $Fe(CO)_5$ to give $Fe(CO)_4$ intermediate which then combines with another molecule of $Fe(CO)_5$ to yield $Fe_2(CO)_9$:

$$Fe(CO)_5 + h\nu \rightleftharpoons Fe(CO)_4 + CO$$
$$^{14}CO + Fe(CO)_4 \rightleftharpoons Fe(CO)_4(^{14}CO)$$
$$Fe(CO)_4(^{14}CO) \rightleftharpoons Fe(CO)_3(^{14}CO) + CO$$
$$Fe(CO)_5 + Fe(CO)_3(^{14}CO) \longrightarrow Fe_2(CO)_8(^{14}CO)$$

Route 2. Activation of $Fe(CO)_5$ and the combination of another molecule of $Fe(CO)_5$ to give $Fe_2(CO)_9$:

$$Fe(CO)_5 + h\nu \rightleftharpoons Fe(CO)_5^*$$
$$Fe(CO)_5^* + Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO$$

Experimentally, the introduction of free ^{14}CO in the reaction mixture does not result in the exchange of ^{14}CO with CO of $Fe(CO)_5$ even after a prolonged time indicating thereby that the formation of $Fe_2(CO)_9$ does not occur through the dissociation of Fe–CO bond and that route 1 for the formation of $Fe_2(CO)_9$ is ruled out. The carbonyl $Fe_2(CO)_9$ is thus formed from $Fe(CO)_5$ through route 2.

The exchange reaction

$$V(CO)_6 + {}^{14}CO \rightleftharpoons [(^{14}CO)V(CO)_5] + CO$$

is, however, quite rapid. This is probably because the d^5 system obtained after rearragnement of d^3s^2 system is *more labile* than a d^8 system obtained after rearrangement of d^6s^2 system.

$Ni(CO)_4$ is known to be quite stable thermodynamically. However, kinetically it is unstable and undergoes exchange with ^{14}CO rapidly following a dissociative mechanism :

$$Ni(CO)_4 + {}^{14}CO \longrightarrow Ni(CO)_3(^{14}CO) + CO$$

Structures of Some Mononuclear Metal Carbonyls

Structures of some common binary metal carbonyls are discussed below.

Structure of $V(CO)_6$. In this carbonyl, the metal atom is octahedrally surrounded by six CO ligands. It is paramagnetic as the central vanadium metal is apparently one electron short of inert gas configuration. It is, therefore, unstable. In species $[V(CO)_6]^-$, the metal atom has an effective atomic number of 36 (23 e^- from V + 1 e^- from negative charge + 2×6 = 12 e^- from 6 terminal COs = 36 e^-) and thus obeys the inert gas rule. It is, therefore, more stable than $V(CO)_6$ and is diamagnetic.

Structures of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$. All these carbonyls have octahedral structure. All of them obey the inert gas rule, *i.e.*, the central metal atoms appear to have inert gas configuration. The anionic metal carbonylates such as $[Cr(CO)_5]^{2-}$, $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ are also known. These species also obey the inert gas rule and are thus stable.

Structure of $Fe(CO)_5$. This carbonyl has trigonal bipyramidal structure as shown earlier. This structure has been confirmed by infrared spectra and X-ray studies. But strangely enough, ^{13}C-nmr gives only one type of signal for axial as well as equatorial CO groups. This is probably because of the "fluxionality" in the structure which means that the axial and the equatorial M–CO bonds *exchange their positions very fast* so that an average ^{13}C resonance signal is obtained for all the five ^{13}COs attached with Fe atom.

Polynuclear Metal Carbonyls

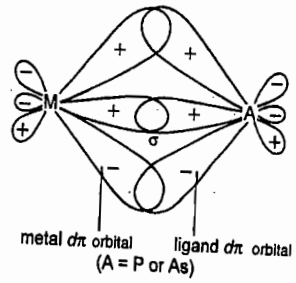
Metals such as Fe, Mn, Co, Tc, etc., form a number of polynuclear carbonyls in which the metal atoms are either linked directly through metal–metal bonds as in $Mn_2(CO)_{10}$ or through bridging carbonyl groups as in $Co_2(CO)_8$. Other examples of polynuclear carbonyls are $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$, $[Fe_5(CO)_{15}C]$, etc. By definition, these carbonyls fall under the category of **metal clusters** and would thus be discussed separately in the next chapter on 'Metal Clusters'.

Carbonyls of Ni, Pd and Pt

Amongst the carbonyls of Ni, Pd and Pt, $Ni(CO)_4$ is the only neutral mononuclear carbonyl which is easier to form. It has a tetrahedral structure.

Compounds of Phosphorus and Arsenic as Pi Acceptor Ligands

There are several compounds of trivalent phosphorus and arsenic which can act as pi acceptor ligands. This is because both P and As have vacant *d* orbitals which are of proper symmetry to overlap with the *d* orbitals of the central metal atom. The overlap facilitates shifting of the electron charge from the metal to the ligand through π back bonding, as shown.



The availability of *d* orbitals of P or As atom to the *d* orbitals of the metal is, however, influenced by the electronegativity of the group attached to P or As atom. For example, in PF_3, F atom, being highly electronegative, would polarise the sigma electron charge cloud from P towards F thereby reducing σ donor character of P atom. But, this shifting of the electron charge from P would, at the same time, increase the π-acceptor character of the 3*d* orbitals of P atom. In the case of $P(C_2H_5)_3$, the effect is just the opposite. This implies that PF_3 would behave as a better pi acceptor ligand than $P(C_2H_5)_3$. As a result, while we can easily get $Ni(PF_3)_4$, $Ni(PF_3)_3CO$, $Ni(PF_3)_2(CO)_2$, ---------- $Ni(CO)_4$, it is not possible to go beyond the isolation of $Ni[P(C_2H_5)_3]_2(CO)_2$, It is assumed that, in general, the pi acceptor character of ligands containing P or As atom is less than that of CO. Let us now consider metal carbonyls in which some of the CO groups are replaced by ligands containing P or As atom. For these studies, we would need, for the sake of comparison, IR absorption data on mixed metal carbonyls containing ligands which are incapable of forming π bonds with metals. Ligands containing N and O atoms are examples of such

ligands. The infrared absorption frequencies of a few relevant mixed carbonyls are given in Table 2.

As can be seen from Table 2, the unsubstituted $Mo(CO)_6$ absorbs around 2050 and 1900 cm^{-1}. Replacement of three CO groups by a better σ donor ligand diene, *i.e*, ($H_2NCH_2CH_2NHCH_2CH_2NH_2$) which is incapable of forming π bonds with the metal because of the absence of *d* orbitals in N atoms, places greater negative charge on the metal which facilitates the transfer of π electron charge from the metal to the remaining CO groups. Also, the same amount of π electron charge of the metal is now distributed over only three COs in [Mo(diene)$(CO)_3$] compared to six COs in $Mo(CO)_6$. As a result, the extent of π back bonding in M–C is more in [Mo(diene)$(CO)_3$] than in $Mo(CO)_6$. The bond order of M–C is, therefore, higher and the bond order of CO bond is lower in the former than in the latter carbonyl.

TABLE 2**

Infrared Absorption Frequencies of Some Mixed Carbonyls

Metal Carbonyls	IR Absorption Frequency ν_{CO} (cm^{-1})
$Mo(CO)_6$	2050, 1900
Cis (diene) $Mo(CO)_3$	1883, 1723
Cis $(py)_3Mo(CO)_3$	1890, 1730
Cis $(Ph_3P)_3Mo(CO)_3$	1934, 1835
Cis $(Ph_3As)_3Mo(CO)_3$	1936, 1840
Cis $(Ph_2PCl)_3Mo(CO)_3$	1980, 1880
Cis $(PhPCl_2)_3Mo(CO)_3$	2010, 1890
Cis $(PCl_3)_3Mo(CO)_3$	2030, 1910

Pyridine (py) is a weaker σ donor than diene and has π^* orbitals to accept *dπ* electron charge from the metal. Therefore, although the M–C bond order is higher in [$Mopy_3(CO)_3$] than in $Mo(CO)_6$, it is lower than the bond order of M–C bond in [Mo(diene)$(CO)_3$]. Similarly, the CO bond order is lower in [$Mopy_3(CO)_3$] than in $Mo(CO)_6$ but is higher than the bond order of CO in [Mo(diene)$(CO)_3$]. The above arguments are supported by the IR absorption frequencies of COs in [$Mopy_3(CO)_3$], $Mo(CO)_6$ and [Mo(diene)$(CO)_3$].

Phosphines and arsines having the same groups attached to P and As, cause approximately the same extent of increase in M–C bond order and similar extent of decrease in CO bond order indicating that π acceptor capabilities of these ligands are of a similar magnitude.

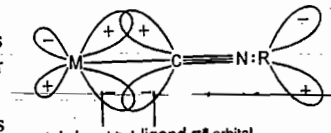
If a ligand such as Ph_3P (triphenylphosphine), which is a weaker π acceptor than CO, partially replaces the COs from a binary carbonyl complex, the remaining COs present in the carbonyl get more *dπ* electron charge density in their π^* orbitals. Hence, the CO bond order in such mixed carbonyls would be lower than in the corresponding pure carbonyls. This is evident from the relative positions of ν_{CO} observed for such mixed carbonyls (Table 2).

If we go on replacing the Ph of Ph_3P ligand by more electron-attracting Cl groups, the ν_{CO} in the resulting mixed carbonyls goes on increasing (Table 2). This is due to the fact that the presence of electron-attracting groups in the phosphine ligand would facilitate the transfer of *dπ* electrons from the metal to P atom so that more and more of *dπ* electron charge is used up in M–P back bonding and less and less of *dπ* electron charge is available for M–C back bonding in the mixed carbonyl with each replacement of Ph of triphenyl phosphine with Cl. Thus, the CO bond order in mixed phosphine carbonyls varies in the order :

$$[(Ph_3P)_3Mo(CO)_3] < [(Ph_2PCl)_3Mo(CO)_3] < [(PhPCl_2)_2Mo(CO)_3] < [(PCl_3)_3Mo(CO)_3]$$

Isocyanide Complexes

Isocyanide (RNC) group is similar to CO group since N:R is isoelectronic with O atom. Thus, an isocyanide can enter into similar type of σ–π synergic bonding as is done by CO, as shown :

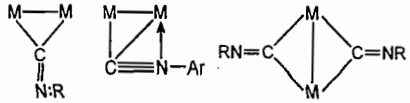


However, the extent of π bonding is less in isocyanide complexes than in metal carbonyls. Infrared absorption spectra prove beyond doubt that there is M→CNR π back bonding in isocyanide complexes, the evidence being provided by the fact that ν_{NC} decreases upto about 100 cm^{-1} in going from free isocyanides to ligated isocyanides.

Isocyanides are stronger σ donors than CO and in several isocyanide complexes, the π bonding is of minor importance compared to σ bonding, as in $[Ag(CNR)_4]^+$, $[Fe(CNR)_6]^{2+}$ and $[Mn(CNR)_6]^{3+}$. However,

**While making use of these data, we should remember that ν_{CO} is proportional to the CO bond order and that any *increase* in M–C bond order due to π bonding would lead to an equivalent *decrease* in the CO bond order and vice versa.

the isocyanide ligands are capable of extensive back acceptance of π electrons from the metal atoms in their low oxidation states. This is indicated by their ability to form complexes such as $Cr(CNR)_6$ and. $Ni(CNR)_4$ in which both Cr and Ni atoms are in zero oxidation state. The above observations have been confirmed by their infrared absorption spectra as well as X-ray studies.



There are several compounds containing isocyanide groups of the type shown :

Geometric isomers of the above type of bridged isocyanides have also been isolated.

Complexes of Nitric Oxide

The NO molecule (bond order 2·5) is very similar to CO molecule in forming complexes with transition metals. However, there is one major difference in the structures of NO and CO molecules. The difference is that NO molecule contains one additional electron in its π molecular orbital as compared to CO molecule. The molecular orbital energy level diagram of NO molecule is shown in Fig. 3.

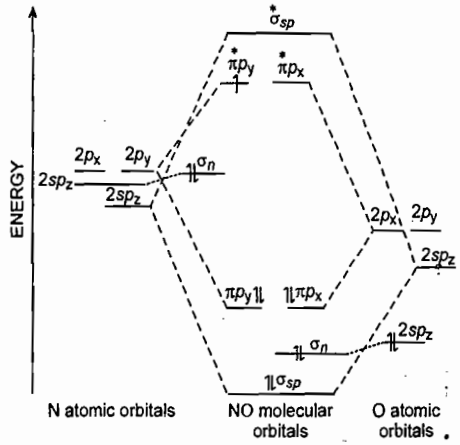


Fig. 3. Molecular orbital energy level diagram of NO. Positions of pure 2*s* and $2p_z$ orbitals of N and O atoms are not shown.

The following categories of NO complexes are known :

1. Complexes Derived from NO^+ Ion. The odd electron in π^* molecular orbital of NO molecule (bond order 2·5) is quite readily lost to produce stable NO^+ specie (bond order 3). This fact receives confirmation from the comparison of the IR absorption spectra of free NO (ν_{NO} ~ 1880 cm^{-1}) with those of salts containing NO^+ ion (ν_{NO^+} = 2200 – 2300 cm^{-1}). As already stated, the IR vibrational frequency of a bond is directly related to its bond order. The complexes of nitric oxide would prefer to have NO^+ as the ligand provided no other electronic factor is operative. In fact, a large number of complexes of nitric oxide are reported to have NO^+ ion (nitrosonium ion) as the ligand which appears to act as a 3-electron donor. Most of such complexes obey EAN or inert gas rule if we assume that NO ligand is a 3-electron donor. For example, the effective atomic number (EAN) of Fe in $[Fe(NO)_2(CO)_2]$ is 26 + 2×3 + 2×2 = 36 which is the atomic number of the next inert gas. Similarly, the EAN of Mn in $[Mn(CO)(NO)_3]$ is 25 + 1×2 + 3×3 = 36.

The ligation of NO^+ to the metal in such complexes can be envisaged to be taking place in the following steps :

1. Initially, during its complexation with the metal, NO loses one π^* electron to the metal reducing its valence by one unit and getting itself converted to NO^+ :

$$M + NO \longrightarrow M^- + :N\equiv\overset{+}{O}:$$

2. In the second step, NO^+, which is isoelectronic with CO, donates a pair of electrons to the metal to get coordinated to the metal :

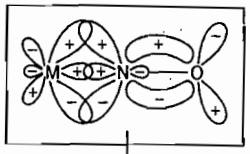
$$\overset{-}{M} + :N\equiv\overset{+}{O}: \longrightarrow \overset{2-}{M}\leftarrow\overset{+}{N}\equiv\overset{+}{O}$$

In this way, NO in its nitrosonium complexes acts as a 3-electron donor.

The $\overset{2-}{M}\leftarrow\overset{+}{N}\equiv\overset{+}{O}$ bond would, evidently, be highly polar. Hence, the electron charge from the filled *dπ* orbitals of the metal would get transferred to π^* molecular orbital of NO^+ :

$$\overset{2-}{M}\leftarrow\overset{+}{N}\equiv\overset{+}{O} \xleftrightarrow[\text{bonding}]{\pi\text{ back}} \overset{-}{M}\rightleftarrows\overset{+}{N}=\overset{+}{O}$$

The above transference is pictorially represented as shown :



XZ
Plane

The IR absorption frequency of NO^+ in nitrosonium complexes (in which NO^+ is present as a coordinated cation) falls between 1600 – 1900 cm^{-1} which is much lower than the absorption frequency of NO^+ in its ionic salts (containing NO^+ as a free cation) which falls between 2200 – 2300 cm^{-1}. The extent of lowering of absorption frequency of NO^+ is much greater compared to similar lowering of ν_{CO} in case of metal carbonyls estabilishing therby that π back bonding in nitrosonium complexes is much greater than in metal carbonyls.

As in metal carbonyls, the residence of negative charge on the nitrosonium complexes increases the extent of π back bonding, as is obvious from the IR absorption data shown :

Complex	Absorption frequency of NO^+ group
$[Fe(NO)(CN)_5]^{2-}$	1944 cm^{-1}
$[Mn(NO)(CN)_5]^{3-}$	1730 cm^{-1}
$[V(NO)(CN)_5]^{3-}$	1530 cm^{-1}

The complex formed between NO and Fe^{2+} (*aq*) which is dark brown (the colour of the complex is employed as 'ring test' for the detection of NO_3^- ion) has finally been estabilished to be a nitrosonium complex. The magnetic moments and spectral studies reveal that the complex is a d^7 spin-free iron (I) specie with the structure $[(NO)Fe(H_2O)_5]^{2+}$. The brown colour is due to the charge transfer bands occurring in the visible region.

2. Complexes Derived from NO. If the π^* electron of NO remains localised on NO itself and is not transferred to M, the ligand would act as a 2-electron σ donor through its nitrogen atom and the metal complex formed would be paramagnetic. Several complexes such as $[Mn(NO)(CN)_5]^{2-}$ and $[Cr(NO)(CN)_5]^{3-}$ are paramagnetic and at one time these were thought to be derived from NO. But it has now been established that the unpaired electron in most of such complexes is localised on the metal rather than on the ligand NO.

3. Complexes Derived from NO^-. In these complexes, nitric oxide is bound to the metal atom in such a manner that it appears to have accepted one electron from M^{n+} to get converted into $(NO)^-$. The $(NO)^-$ then donates two electrons through its N atom to the resulting $M^{(n+1)+}$ to form a σ coordinate bond ($\bar{M}\leftarrow:\overset{+}{N}\bar{O}:$). In this way nitric oxide in these complexes acts effectively as 1-electron donor. Examples of such complexes are the well known complexes $[Co(NH_3)_5(NO)]^{2+}$ and $[Co(CN)_5(NO)]^{3-}$ which are synthesised by passing nitric oxide gas through aqueous solutions of Co^{2+} salts containing NH_3 or CN^- ions. These complexes are analogous to $[Co(NH_3)_5Cl]^{2+}$ and $[Co(CN)_5Br]^{3-}$, respectively, of Co(III) with respect to their charges and magnetic properties. The complexes $[Co(CN)_5(NO)]^{3-}$ and $[Co(NH_3)_5(NO)]^{2+}$ contain spin-paired Co(III) with t_{2g}^6 configuration. During the conversion of NO to NO^- it can be assumed that one electron from $d\pi$ orbital of Co(II) gets transferred to π^* molecular orbital of the ligand transforming Co(II) to Co(III). It is, therefore, expected that IR absorption frequency and bond order of NO^- in the complexes of NO^- should be lower than those in free NO. Experimentally it is found to be so. The absorption frequency of NO^- in Co complexes mentioned above is much lower falling in the range of 1100–1200 cm^{-1}.

Apart from the above categories, there are some complexes in which NO exists in both the forms. For example, the complex $Fe(NO)_4$ is considered to be $[(NO^+)_3Fe(NO^-)]$ since the NO group absorbs in both the regions, *i.e.*, 1600–1900 cm^{-1} and 1100–1200 cm^{-1}.

Complexes of nitric oxide can be prepared in a number of ways. Some typical syntheses are shown below.

$$Fe(CO)_5 + NO \longrightarrow Fe(NO)_4 + 5CO$$
$$Co_2(CO)_8 + 2NO \longrightarrow 2[Co(NO)(CO)_3] + 2CO$$
$$[Ni(Ph_3P)_2(CO)_2] + 2NO \longrightarrow [Ni(Ph_3P)_2(NO)_2] + 2CO$$
$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [(NO)Fe(H_2O)_5]^{2+} + H_2O$$
$$[Co(NH_3)_5(H_2O)]^{2+}(aq) + NO \longrightarrow [Co(NH_3)_5(NO)]^{2+} + aq$$

QUESTIONS

1. What are π-acceptor ligands ? Discuss in details the nature of bonding involved in metal carbonyls.
2. Discuss in details how the spectral studies carried out on metal carbonyls have helped in (*i*) determination of geometries of metal carbonyls (*ii*) determination of bond order of CO (*iii*) Differntiating between terminal CO and bridging CO and (*iv*) studying rates of substitution reactions.
3. Discuss the structures of $Cr(CO)_6$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. Show that the metal atoms in these carbonyls obey the inert gas rule.
4. Explain why carbonyls $Pd(CO)_4$ and $Pt(CO)_4$ do not exist whereas $Ni(CO)_4$ exists as a stable metal carbonyl. Also explain why $Ni(CO)_2Cl_2$ does not exist whereas carbonyls $Pd(CO)_2X_2$ do exist (X is a halide ion).
5. Arrange the following carbonyls in the order of increasing CO bond order : $Mo(CO)_6$, $[(PPh_3)_3Mo(CO)_3]$, $[(PCl_3)_3Mo(CO)_3]$, $[(diene)Mo(CO)_3]$, $[(PPhCl_2)_3Mo(CO)_3]$. Give resons in support of your answer.
6. Discuss the type of bonding involved in isocyanide complexes.
7. Give the molecular orbital energy level diagram of NO molecule. Give a brief description of the various categories of complexes of nitric oxide.

33 METAL CLUSTERS

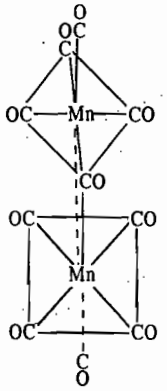
Metal Clusters. A metal cluster may be defined as a group of two or more metal atoms that are directly linked to one another through metal–metal bonds. Metal clusters can be broadly divided into two categories :

1. **Carbonyl clusters** in which the metal atoms are in low oxidation states (–1, 0, +1). The carbonyl groups in these clusters tend to stabilise the low oxidation states. Carbonyl clusters are formed mainly by the last few members of each of the First, Second and Third transition series, *viz.*, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt.

2. **Halide type of clusters** in which the metal atoms are in relatively higher oxidation states (+2, +3). These clusters are formed by the first few members of each of the Second and Third transition series, *viz.*, Nb, Ta, Mo, W, Re. Many clusters of this type contain multiple, *i.e.*, double and triple, metal–metal bonds.

1. CARBONYL CLUSTERS

The carbonyl clusters which we shall discuss here include neutral carbonyls, carbonyl anions and hydrido carbonyls. The relationship between the three types of carbonyls is based on the fact that one CO group can be replaced either by two H atoms or by one H atom and one negative charge or by two negative charges. The carbonyl clusters can be further subdivided into two categories, *viz.*, *(a) Low Nuclearity Carbonyl Clusters (LNCC)* and *(b) High Nuclearity Carbonyl Clusters (HNCC)*.



$Mn_2(CO)_{10}$

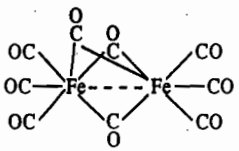
(I)

a. Low Nuclearity Carbonyl Clusters (LNCC). These clusters contain comparatively small number of metal atoms, *viz.*, 2, 3 or 4, in their structures. Accordingly we come across dinuclear, trinuclear and tetranuclear carbonyl clusters

A number of **dinuclear carbonyl clusters** are known. Common examples are $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ and $Co_2(CO)_8$.

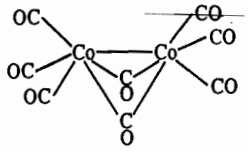
In $Mn_2(CO)_{10}$, each metal atom has an octahedral environment and the two $Mn(CO)_5$ units are joined solely by Mn—Mn bond, as shown (Structure I). The carbonyl obeys the inert gas rule, each Mn atom having 36 electrons around itself (25 e^- from Mn + 1 e^- from Mn—Mn bond + 2×5 = 10 e^- from five terminal CO groups = 36 e^-)

In the case of the carbonyl $Fe_2(CO)_9$, the two atoms of Fe are linked through three bridging carbonyl groups, as shown (Structure II). There are three terminal CO groups on each Fe atom. The carbonyl obeys the inert gas rule, each Fe atom having 36 electrons around itself (26 e^- from Fe + 3 e^- from 3 bridging CO groups + 6 e^- from 3 terminal CO groups + 1 e^- from Fe–Fe bond). The dinuclear carbonyl $Co_2(CO)_8$ contains three terminal CO groups on each metal atom, two bridging carbonyl groups and a Co—Co bond in its structure, as shown (Structure III).



$Fe_2(CO)_9$

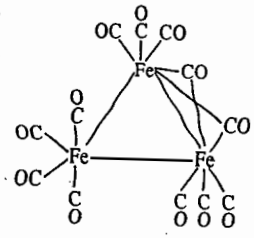
(II)



$Co_2(CO)_8$

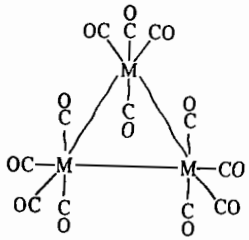
(III)

The majority of M_3 clusters present in **trinuclear carbonyls** have a triangular geometry. The carbonyl clusters with the formula $M_3(CO)_{12}$, where M=Ru, Os, Fe, have sufficient number of electrons to enable each metal atom to obey the inert gas rule, that is, to have 36 electrons around each atom. This situation is also expressed by saying that each metal atom has an 18-electron closed shell configuration. $Fe_3(CO)_{12}$ has structure IV which contains two bridging CO groups whereas $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have structure V containing all carbonyl groups as terminal CO groups.



$Fe_3(CO)_{12}$

(IV)

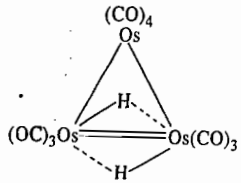


$M_3(CO)_{12}$ (M=Ru,Os)

(V)

The CO group in $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ can be replaced by CH_3CN. The mixed carbonyls, thus obtained, are quite reactive.

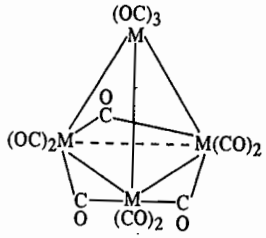
Generally, in polynuclear carbonyl clusters, the metal atoms are bonded through metal—metal single bonds. In the hydrido carbonyl cluster, $H_2Os_3(CO)_{10}$, however, the metal atoms are bonded with each other through a double bond, as shown in structure VI.



$H_2Os_3(CO)_{10}$

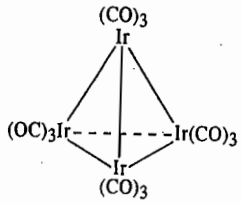
(VI)

Many homonuclear and heteronuclear **tetranuclear carbonyl clusters** containing four metal atoms are also known. Most of them display tetrahedral cluster structures. The structures of $M_4(CO)_{12}$ where M=Co, Rh, Ir, are shown below (Structures VII, VIII). In these carbonyls also, each metal atom has an 18-electron closed shell configuration.



$M_4(CO)_{12}$ (M=Co, Rh)

(VII)



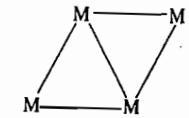
$Ir_4(CO)_{12}$

(VIII)

Some tetranuclear carbonyl clusters also exhibit butterfly and planar cluster structures of the type shown (Structures IX and X).

Butterfly cluster structure

(IX)



Planar cluster structure

(X)

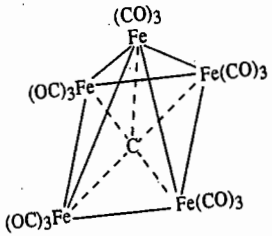
It may be noted that the procedure of electron counting in LNCCs is the same as used for electron counting in mononuclear carbonyls discussed in the last chapter.

b. High Nuclearity Carbonyl Clusters (HNCC). These clusters contain five or more than five metal atoms directly bonded to one another. A large number of such carbonyl clusters have recently been isolated. Examples are $Rh_6(CO)_{16}$, $Ru_6(CO)_{18}H_2$ and $\{(Ni_3(CO)_6\}_n^{2-}$. Many mixed carbonyl clusters containing encapsulated carbon atom are also known. Many of these carbido carbonyl clusters can be prepared either by pyrolysis or by refluxing metal carbonyls for long periods in solvents such as $CHCl_3$,

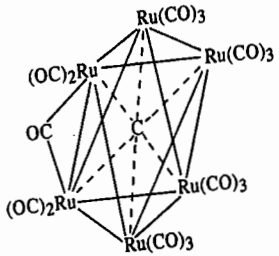
CCl_4, etc. Examples of carbido carbonyl clusters are :

$Fe_5(CO)_{15}C$, $Ru_6C(CO)_{17}$, $[Os_{10}C(CO)_{24})]^{2-}$ and $Fe_4C(CO)_{13}$.

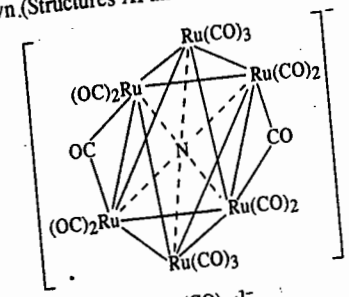
Structures of the first two carbido carbonyl clusters are as shown (Structures XI and XII).



$Fe_5C(CO)_{15}$
(XI)



$Ru_6C(CO)_{17}$
(XII)



$[Ru_6N(CO)_{16}]^-$
(XIII)

Many nitrido carbonyl clusters in which nitrogen atom is encapsulated in the structure have also been synthesised. Examples are $[Ru_6N(Co)_{16}]^-$ and $[Fe_4N(CO)_{12}]^-$. The structure of $[Ru_6N(CO)_{16}]^-$ is as shown (Structure XIII).

A few common routes for the synthesis of nitrodo carbonyl clusters are given below :

$$2[H_3Ru_4(CO)_{12}]^- + 2NO^+ \longrightarrow HRu_4N(CO)_{12} + H_2O + H_3Ru_4N(CO)_{11} + CO_2$$

$$2[Fe(CO)_3NO]^- + 3Fe_3(CO)_{12} \longrightarrow 2[Fe_4N(CO)_{12}]^- + 3Fe(CO)_5 + 2CO_2 + CO$$

$$2Ru_3(CO)_{12} + N_3^- \longrightarrow [Ru_6N(CO)_{16}]^- + 8CO + N_2.$$

Other elements that can appear as encapsulated atoms are H as in $[HCo_6(CO)_{15}]^-$, P as in $[Rh_6P(CO)_{22}]^{3-}$, S as in $[Rh_{17}S_2(CO)_{32}]^{2-}$ and As as in $[Rh_6As(CO)_{22}]^{3-}$.

Electron Counting Scheme for HNCCs. Wade suggested that the same rules as are applicable for determining frame work or skeletal bonding in polyhedral closo, nido and arachno boranes are also applicable to the corresponding polynuclear carbonyl clusters (see Chapter 15). Thus, the $(m+1)$ electron pairs rule which is applicable to closo boranes, is also applicable for closo carbonyl clusters. Similarly, the $(m+2)$ and $(m+3)$ electron pairs rules which are applicable to nido and arachno boranes, respectively, also apply for nido and arachno carbonyl clusters. The structural aspects of closo, nido and arachno boranes have already been discussed in details in Chapter 15). A closo frame work or skeletal structure of a polyhedral metal carbonyl cluster containing m metal atoms consists of a closed m-vertex polyhedron of m metal atoms. The nido and arachno skeletal structures of polyhedral metal carbonyl clusters containing m metal atoms each are derived from $(m+1)$- and $(m+2)$-vertex polyhedra, respectively, from which one and two vertices, respectively, have been removed.

Wade's Rules. In order to obtain the total electron count from which the framework or skeletal electron pairs available for binding the metal atoms of a cluster can be calculated, Wade suggested to proceed as follows :

1. Add all the valence electrons of all the metal atoms in the carbonyl cluster.
2. Add two electrons for each CO group, whether terminal or bridged, to the total valence electrons obtained in step 1.
3. Add one electron for each negative charge, if any, to the total electrons obtained in steps 1 and 2.
4. ... to the number of electrons obtained upto step 3, the number of valence electrons of each ... that is, add 1, 4, 5 and 5 electrons, respectively, for encapsulated

5. Keep in mind the important assumption that in addition to electrons necessary for skeletal bonding, each metal atom utilises 12 electrons for non-skeletal bonding with carbonyl groups.

The total electron count and the number of skeletal electron pairs for a few HNCCs calculated with the help of **Wades' rules** mentioned as above are given in Table 1. The geometrical shapes of polyhedral carbonyl clusters, as predicted from Wades' rules, are also given in Table 1.

TABLE 1

Total Electron Count, the Skeletal Electron Pairs and the Skeletal Structures of Some High Nuclearity Carbonyl Clusters

Carbonyl cluster	Valence electrons of metal atoms	Total electron count (TEC)	Electrons used for non-skeletal bonding	Skeletal electron pairs	Metal cluster 'frame work' or skeletal structure
$Rh_6(CO)_{16}$	$6\times9=54$	$54+32=86$	$6\times12=72$	$\frac{(86-72)}{2}=7$ (*i.e.*, 6+1)	Closo six-vertex polyhedron (*i.e.*, octahedron)
$Os_5(CO)_{16}$	$5\times8=40$	$40+32=72$	$5\times12=60$	$\frac{72-60}{2}=6$ (*i.e.*, 5+1)	Closo five-vertex polyhedron (*i.e.*, trigonal bipyramidal)
$Os_5C(CO)_{15}$	$5\times8=40$	$40+30+4=74$	$5\times12=60$	$\frac{74-60}{2}=7$ (*i.e.*, 5+2)	Nido (derived from (5+1)-vertex polyhedron, *i.e.*, octahedron whose one vertex is removed)
$[Fe_4C(CO)_{12}]^{2-}$	$4\times8=32$	$32+24+4+2=62$	$4\times12=48$	$\frac{62-48}{2}=7$ (*i.e.*, 4+3)	Arachno (derived from (4+2)-vertex polyhedron, *i.e.*, octahedron whose two adjacent vertices are removed.
$[H_3Ru_4(CO)_{12}]^-$	$4\times8=32$	$32+24+3+1=60$	$4\times12=48$	$\frac{60-48}{2}=6$ (*i.e.*, 4+2)	Nido (derived from (4+1)-vertex polyhedron, *i.e.*, trigonal biyramid whose one vertex is removed
$[Ru_5N(CO)_{14}]^-$	$5\times8=40$	$40+28+5+1=74$	$5\times12=60$	$\frac{74-60}{2}=7$ (*i.e.*, 5+2)	Nido (derived from (5+1)-vertex polyhedron, *i.e.*, octahedron whose one vertex is removed
$[Fe_4N(CO)_{12}]^-$	$4\times8=32$	$32+24+5+1=62$	$4\times12=48$	$\frac{62-48}{2}=7$ (*i.e.*, 4+3)	Arachno (derived from (4+2)-vertex polyhedron, *i.e.*, octahedron whose two adjacent vertices are removed.

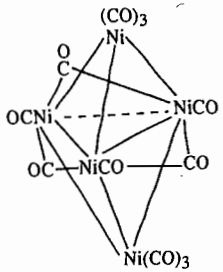
Many carbonyl clusters consist of a central polyhedron to which one or more atoms are appended by their placement over one or more of the triangular faces of the polyhedron. These appended atoms are called capping atoms. The electron counting rules can be extended to cover such structures. For instance, consider $Os_7(CO)_{21}$ in which the total electron count is 98. Vide rule 5, the number of electrons used by the metal atoms for non-skeletal bonding with carbonyl groups $= 12\times7 = 84$. Therefore, the number of skeletal electron pairs available for frame work bonding is $1/2(98-84) = 7$ (*i.e.*, 6+1). This predicts a closo octahedron of Os_6 in the structure. The seventh Os atom is capped on one of the eight triangular faces of Os_6 octahedron. A capping atom does not increase the number of skeletal electron pairs. *It simply increases the total electron count by 12.*

As rightly predicted by Wade's rules, the carbonyl $[Os_8(CO)_{22}]^{2-}$ contains an Os_6 octahedron whose two triangular faces are capped by the two Os atoms. Similarly, the carbonyl $[Os_{10}C(CO)_{24}]^{2-}$ contains an O_6 octahedron whose four triangular faces are capped by the four Os atoms. The carbon atom lies at the centre of the O_6 octahedron.

As can be seen from Table 1, Wade's rules can be applied to predict the skeletal structures of LNCCs also containing four metal atoms. In fact, the rules apply even in the case of trinuclear LNCCs. For

example, consider the carbonyl $Fe_3(CO)_{12}$. The total electron count in this case is 48 and the skeletal electron pairs available for framework bonding are 1/2(48—36)=6, *i.e.*, 3+3. The Fe_3 cluster in $Fe_3(CO)_{12}$ thus has an arachno structure derived from (3+2)-vertex polyhydron (*i.e.*, trigonal bipyramid) whose two axial vertices are removed leaving an effectively triangular geometry for the Fe_3 cluster in this carbonyl.

Similarly, the structure of $Co_4(CO)_{12}$ is rightly predicted by Wade's rules to have been derived from a (4+1)-vertex polyhydron (*i.e.*, trigonal bipyramid) whose one axial vertex is removed to give an effectively tetrahedral geometry for the Co_4 cluster in this carbonyl. It is worth remembering that a trinuclear LNCC generally has a total electron count of 48 and a tetranuclear LNCC generally has a total electron count of 60.



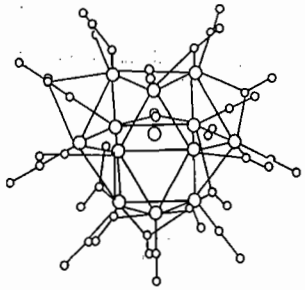
$[Ni_5(CO)_{12}]^{2-}$
(XIV)

It will not be out of place to mention that although Wade's rules can predict the structures of a majority of polyhedral carbonyl clusters yet there are a few exceptions to these rules as well.

For example, the structure of $[Ni_5(CO)_{12}]^{2-}$ is predicted (by Wade's rules) to be arachno whereas actually it is found to be closo trigonal bipyramidal (Structure XIV).

We have so far discussed carbonyl clusters of mostly Fe, Ru and Os. A few of the carbonyl clusters of Co, Rh and Ir will also be discussed briefly. Of the latter, Rh forms the largest number of carbonyl clusters followed by Co. The number of Ir carbonyl clusters is limited.

Rhodium carbonyl clusters consisting of 5 to 22 Rh atoms often adopt structures that have an interstitial Rh atom within a polyhedron of Rh atoms as in $[Rh_{13}(CO)_{24}H_2]^{3-}$, in which the arrangement of Rh atoms is a fragment of hexagonal closed packed array as shown (Structure XV).



$[Rh_{13}(CO)_{24}H_2]^{3-}$
(XV)

Rh also forms mixed metal clusters, especially with Pt. An example is furnished by $[PtRh_8(CO)_{19}]^{2-}$.

Co forms high nuclearity carbonyl clusters with metal atoms ranging between 5–16.

Apart from the above, high nuclearity carbonyl clusters of some other metals are also known. Examples are carbonyl clusters of Ni, Pd and Pt.

Nickel carbonyl clusters can be synthesised by reacting $Ni(CO)_4$ with an alkali metal in THF.

$$Ni(CO)_4 \xrightarrow[\text{THF}]{\text{Alkali metal}} [Ni_5(CO)_{12}]^{2-} + [Ni_6(CO)_{12}]^{2-}$$

$$[Ni_6(CO)_{12}]^{2-} \xrightarrow{FeCl_3} [Ni_9(CO)_{18}]^{2-}$$

The carbonyl cluster $[Ni_6(CO)_{12}]^{2-}$, when refluxed in CCl_4, gives a number of carbido carbonyl clusters such as $[Ni_8C(CO)_{16}]^{2-}$, $[Ni_9C(CO)_{17}]^{2-}$ and $[Ni_{10}C(CO)_{18}]^{2-}$.

A number of mixed carbonyl-trimethyl phosphine clusters of Pd are known. These have the formulae. $Pd_7(CO)_7(PMe_3)_7$ and $Pd_{10}(CO)_{18-n}(PMe_3)_n$ where n ranges from 1 to 17. Both these structures contain a Pd_6 octahedron which is capped by one and four Pd atoms, respectively.

The platinum carbonyl clusters, that have been discovered only recently, can be divided into the following two categories :

1. Columnar platinum clusters with the general formula $[(Pt_3(CO)_6]_n^{2-}$ (n varies from 2 to 5) whose structures are built up by stacking planar $Pt_3(CO)_6$ units one above the other. The stacking is essentially prismatic.

2. Large platinum cluster anions such as $[Pt_{19}(CO)_{22}]^{4-}$, $[Pt_{26}(CO)_{32}]^{3-}$ and $[Pt_{38}(CO)_{44}H_m]^{2-}$ (the value of m is uncertain). The first cluster anion has D_{5h} symmetry and the last two have approximately cubic close packed array of Pt atoms and seem to have properties bordering between those of molecules and bulk metals.

Recently some mixed Ni–Pt clusters have also been synthesised.

2. HALIDES TYPE CLUSTERS

The best known **dinuclear clusters** of this type have the general formula $[Re_2X_8]^{2-}$ (X=Cl, Br, I, NCS, etc.). These clusters possess the following typical structural features :

a. They have short Re—Re distance of 2·20 Å compared with Re—Re distance of 2·75 Å in bulk metal.

b. They possess eclipsed conformation which seems to be rather surprising. Since the sum of the van der Waals radii of two Cl atoms is more than the experimentally observed distance between the two chlorine atoms attached to the two separate Re atoms, one would have expected a less sterically crowded staggered conformation to be more stable. Both the conformations are shown in Fig. 1.

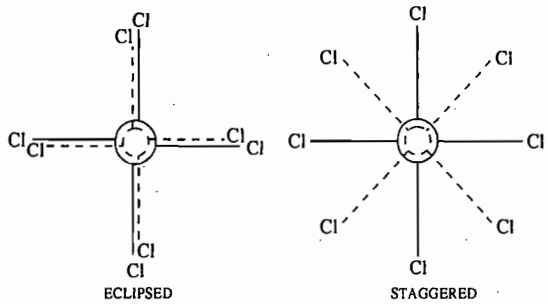
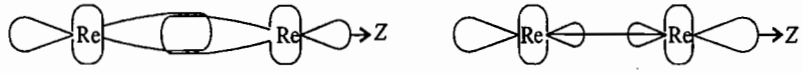


Fig. 1. Eclipsed and staggered conformations of $[Re_2Cl_8]^{2-}$.

A plausible explanation for both the above mentioned observations is given below.

1. The $d_{x^2-y^2}$, s, p_x and p_y orbitals of each Re atom hybridise to give four dsp^2 hybrid orbitals on each Re atom. These hybrid orbitals accommodate 8 electrons donated by the four chloride ions attached to each Re.

2. The d_{z^2} and p_z orbitals of each Re atom hybridise to give two *dp* hybrid orbitals on each Re atom. A *dp* hybrid orbital of one Re atom overlaps with a similar orbital on the other Re atom to yield a σ (bonding) and a σ* (antibonding) molecular orbital. Each Re atom is thus left with a nonbonding *dp* hybrid orbital. This is diagrammatically shown in Fig. 2 (σ* orbital is not shown) :



dp hybrid σ bonding molecular orbital.

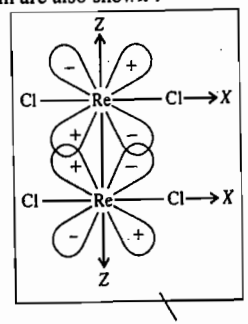
The two *dp* hybrid nonbonding molecular orbitals, one on each Re atom

Fig. 2. σ bonding and nonbonding molecular orbitals of Re_2 unit of $[Re_2X_8]^{2-}$

The d_{xz} orbitals of the two Re atoms of the eclipsed form are in the same *XZ* plane. These orbitals, therefore, overlap with each other to give π_{xz} (bonding) and π^*_{xz} (antibonding) molecular orbitals.

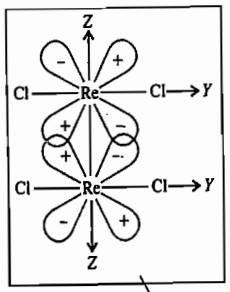
Similarly, the d_{yz} orbitals of the two Re atoms of the eclipsed form, being in the same *YZ* plane, overlap with each other to give π_{yz} (bonding) and π^*_{yz} (antibonding) molecular orbitals. The lobes of d_{xy} orbitals of the two Re atoms of the eclipsed form are of proper symmetry to give positive overlap yielding δ (bonding) and δ* (antibonding) molecular orbitals. The π and δ bonding molecular orbitals

of the eclipsed form of $[Re_2Cl_8]^{2-}$ are shown in Fig. 3. The d_{xy} orbitals of the two Re atoms of the staggered form are also shown :



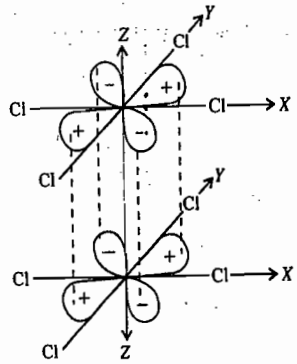
XZ plane

π_{xz} bonding molecular orbital of eclipsed form
(The Cl atoms along Y-axis direction are not shown)

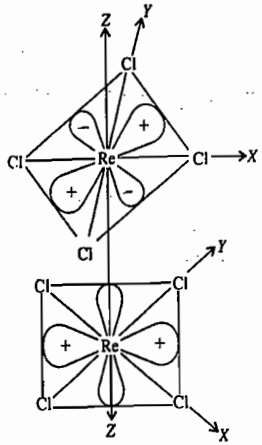


YZ plane

π_{yz} bonding molecular orbital of eclipsed form.
(The Cl atoms along X-axis are not shown)



The δ bonding molecular orbital formed from overlapping of d_{xy} orbitals in the eclipsed form.



The orientation of d_{xy} orbitals on Re atoms of the staggered form.

Fig. 3. Molecular orbitals of the eclipsed form of $[Re_2Cl_8]^{2-}$ and orientation of d_{xy} orbitals of the staggered form.

It can be easily visualised that the π overlap between the two d_{xz} or the two d_{yz} orbitals of the two Re atoms of the staggered form of $[Re_2Cl_8]^{2-}$ is not possible since neither the two d_{xz} orbitals are in the same plane nor are the two d_{yz} orbitals so. Also, as is clear from the figure given above, the lobes of the two d_{xy} orbitals on Re atoms of the staggered form are not properly placed for a δ overlap.

The qualitatively drawn molecular orbital energy level diagram for Re—Re bonding in the eclipsed form of $[Re_2Cl_8]^{2-}$ is shown in Fig. 4.

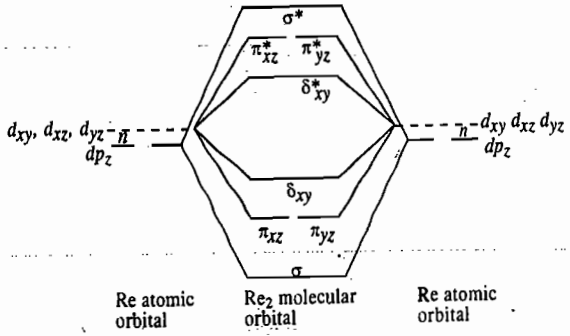


Fig. 4. Molecular orbital energy level diagram for Re—Re bonding in the eclipsed form of $[Re_2Cl_8]^{2-}$.

The oxidation state of Re in $[Re_2Cl_8]^{2-}$ is +3 and hence Re in this anion has d^4 configuration. The eight electrons of the two Re atoms would occupy one σ, two π and one δ bonding molecular orbitals. There is thus a quadruple bond between the two Re atoms. This explains both the observations *a* and *b*, mentioned above, *i.e.*, the short Re—Re distance and the existence of eclipsed form only for $[Re_2Cl_8]^{2-}$.

There are a number of other dinuclear compounds which have eclipsed form and have short M—M distances due to the existence of multiple bonds between the metal atoms. Examples are the carboxylate complexes of the general formulae $Re_2(RCOO)_4X_2$ and $Mo_2(RCOO)_4$. The metal ions in these complexes have d^4 configuration. Their skeletal structures are shown in Fig. 5. (The lines between the atoms do not show the exact bond order).

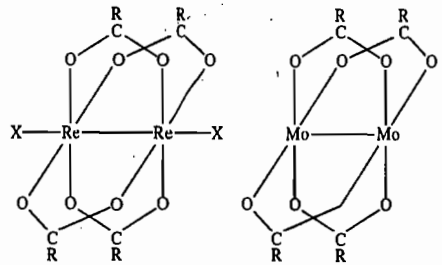
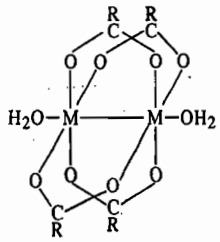


Fig. 5. The skeletal structures of $Re_2(RCOO)_4X_2$ and $Mo_2(RCOO)_4$

In both the above compounds the eight electrons from four oxygen atoms coordinated to each metal atom occupy $d_{x^2-y^2}\,sp^2$ hybrid orbitals of each metal atom. The two ligands X^- in $Re_2(RCOO)_4X_2$ donate two pairs of electrons to the two vacant nonbonding *dp* hybrid orbitals localised on each Re atom. Thus, the configuration of Re_2 in $Re_2(RCOO)_4X_2$ is $\sigma^2\pi^4\delta^2n^4$ and of Mo_2 in $Mo_2(RCOO)_4$ is $\sigma^2\pi^4\delta^2$. This results in a quadruple metal-metal bond in both the compounds leading to shortening of the metal-metal bonds compared to the metal-metal distances in the bulk metals.

The presence of quadruple bonds (specially π and δ bonds) in the above mentioned dinuclear complexes of Re and Mo favours the formation of the eclipsed form.

Calculations show that the energies of δ molecular orbital (bonding), *dp* hybrid orbital (non bonding) and δ* molecular orbital (antibonding) of the dinuclear metal clusters discussed above are very close to one another. Also the π and δ overlaps between the *d* orbitals of metals in these compounds lead to very weak bonds compared to bonds formed due to π overlap between *p* orbitals in the compounds of lighter metals.



$M_2(RCOO)_4 \cdot 2H_2O$
(M = Cu, Cr)
(XVI)

Cupric carboxylates have also an eclipsed structure like the carboxylates of Re and Mo discussed above. However, the Cu—Cu distance in cupric carboxylate is longer than in the copper metal. This is probably due to the fact that the electron spins of the odd electrons of the two Cu^{2+} ions, each of which is a d^9 system, get mutually paired up leading to a single Cu—Cu bond. The structure of $Cu_2(RCOO)_4.2H_2O$ is as shown (Structure XVI). It is difficult to explain the eclipsed conformation of the cupric carboxylates.

The carboxylate $Cr_2(COO)_4.2H_2O$ has a similar structure but the bond order of Cr—Cr bond is uncertain.

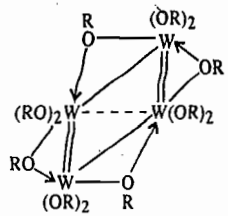
Another important class of dinuclear complexes are metal alkoxides with the formula $M_2(OR)_6$ (M = Mo, W).

The metal-metal multiple bonds in such compounds can be easily saturated as is obvious from the reaction given below :

$$(RO)_3W{\equiv}W(OR)_3 + 2X_2 \longrightarrow X_2(RO)_3W{-}W(OR)_3X_2$$

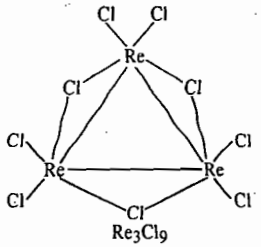
(R = *i*Pr, *t* Bu ; X_2 is halogen)

The compound $W_2(O\,iPr)_6$ can be dimerised. The dimer is a fluxional molecule in which double bonds and single bonds keep on exchanging places in the W_4 ring at room temperature. The alkoxy groups O*i*Pr also keep on exchanging places between the bridged and the terminal positions. The instant structure of $W_4(OR)_{12}$ is as shown (Structure XVII).



$W_4(OR)_{12}$
(XVII)

The **trinuclear halide type clusters** have the general formula Re_3X_9 (X=Cl, Br, I). The structure of Re_3Cl_9 is as shown (Structure XVIII). The lines do not show the exact bond order.

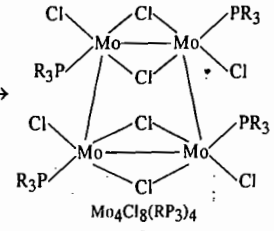


Re_3Cl_9
(XVIII)

Since the Re–Re distance in this trinuclear cluster is shorter than the distance in Re metal, the bond order between the Re atoms appears to be more than one. Of the two terminal chlorines on each Re atom, one is above and the other is below the triangular plane containing the three Re atoms. In the solid state, the trinuclear cluster retains the basic triangular structure but further bridging through chloro ligands occurs resulting in the formation of a polymeric structure. Re_3Cl_9 reacts with a number of ligands (L) to give $Re_3Cl_9L_3$. The solid Re_3Cl_9 dissolves in HCl to give $[Re_3Cl_{12}]^{3-}$. Both $Re_3Cl_9L_3$ and $[Re_3Cl_{12}]^{3-}$ have triangular structures.

The **tetranuclear halide type metal clusters** are also known. We have already mentioned the dimerisation of dinuclear metal clusters containing metal–metal double bonds. For instance, the dinuclear alkoxide of $W_2(OR)_6$ dimerises to give a tetranuclear metal cluster $W_4(OR)_{12}$ whose structure has already been discussed above. The W=W bond in $W_4(OR)_{12}$ can be saturated to give $W_4(OR)_{16}$. Similarly, the dinuclear metal cluster $[Mo_2Cl_8]^{4-}$ containing Mo–Mo bond polymerises to give a tetranuclear metal cluster $Mo_4Cl_8(PR_3)_4$ (Structure XIX).

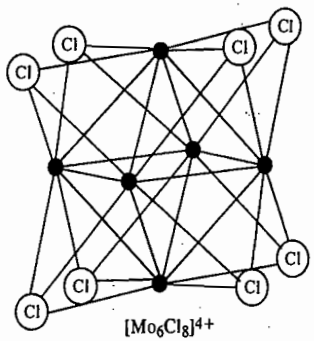
$$2K_4Mo_2Cl_8 \xrightarrow{R_3P} Mo_4Cl_8(RP_3)_4 + 8KCl$$



$Mo_4Cl_8(RP_3)_4$
(IX)

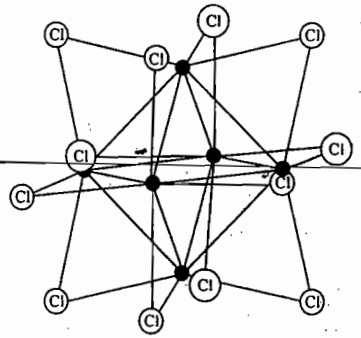
The lines in the above structure of the polymer do not show the exact bond order. Experimental evidence shows that there are alternate single and triple bonds in the Mo_4 ring in the above structure.

Mo, W and Ta form **hexanuclear metal clusters** of the type M_6X_8 and M_6X_{12}. In M_6X_8 type of clusters, each of the eight faces of M_6 octahedron is capped by a μ_3–X atom. A typical example is the metal cluster $[Mo_6Cl_8]^{4+}$ in which each Mo atom has d^4 configuration. The structure of $[Mo_6Cl_8]^{4+}$ is as shown (Structure XX).



$[Mo_6Cl_8]^{4+}$
Solid circles represent Mo atoms
(XX)

There are 12 Mo–Mo bonds in the Mo_6 octahedron and there are 6×4 =24 valence electrons to form these 12 Mo—Mo bonds in $[Mo_6Cl_8]^{4+}$. Therefore, each Mo—Mo bond utilises one electron pair and is thus a normal single bond. Another hexanuclear metal cluster having similar structure is $[Mo_6S_8]^{4+}$. In the M_6X_{12} type of hexanuclear metal clusters, each of the 12 edges of M_6 octahedron is bridged by a μ_2–X atom. A typical example of this type is the cluster $[Nb_6Cl_{12}]^{2+}$ whose structure is as shown (Structure XXI).



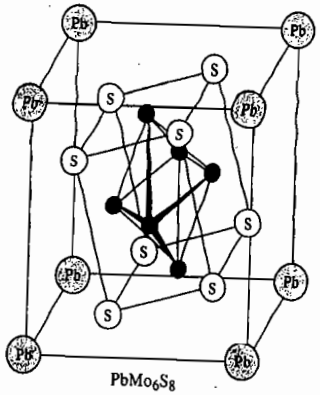
$[Nb_6Cl_{12}]^{2+}$
Solid circles represent Nb atoms
(XXI)

There are 16 valence electrons (*i.e.*, 6×5 – 12 – 2) with Nb_6 octahedron which are used up to form 12 Nb—Nb bonds in Nb_6 octahedron. Thus, there are only 8 valence electron pairs for 12 Nb—Nb bonds of the metal cluster. Therefore, each Nb—Nb bond has a bond order of 8/12 or 2/3.

Some newly discovered metal clusters. Apart from the above two main categories of metal clusters (*i.e.*, carbonyl type and halide type), two new types of metal clusters have been discovered recently. These are named as *Chevrel phases* and *'Naked' Clusters* (or clusters without ligands). The 'naked' clusters are also called *Zintl ions*. A brief description of these newly discovered clusters is given below.

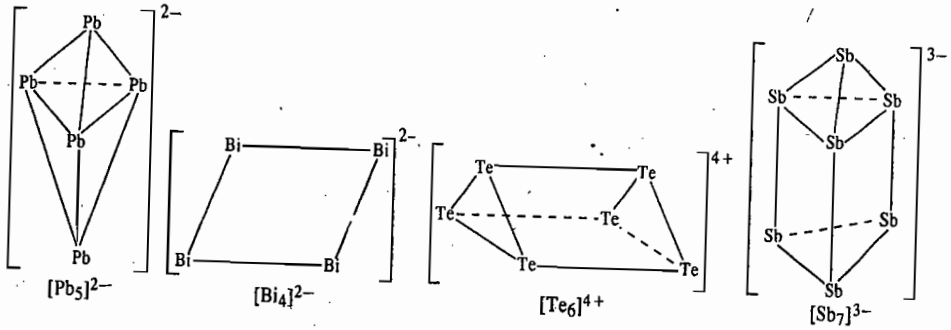
1. Chevrel Phases. These are mixed Mo clusters having the general formula $M_xMo_6X_8$ where M represents a metal such as Pb, Sn, Cu, Co and Fe and X represents S, Se and Te. These clusters are named after their discoverer Roger Chevrel. The arrangement of atoms in one such compounds, namely, $PbMo_6S_8$ is as shown (Structure XXII).

The structure may be considered as an octahedral cluster of Mo atoms surrounded by a cubic cluster of eight S atoms which, in turn, is surrounded by a cubic lattice of Pb atoms. The Chevrel compound $PbMo_6S_8$ is a super conductor below 13·3° K.



$PbMo_6S_8$
Solid circles represent Mo atoms
(XXII)

2. Zintl Ions or 'Naked' Clusters or Clusters Without Ligands. Some post transition metal alloys with sodium (known as Zintl alloys) dissolve in liquid ammonia to give highly coloured ions such as Sn_9^{4-}, Sb_7^{3-}, Bi_4^{2-}, Pb_5^{2-}, Bi_9^{5+}, Te_6^{4+}, etc. Such polyatomic ions are referred to as **Zintl ions** or **'naked' clusters.** The cluster structures of some of the Zintl ions are shown in Fig. 6.



$[Pb_5]^{2-}$ $[Bi_4]^{2-}$ $[Te_6]^{4+}$ $[Sb_7]^{3-}$

Fig. 6. Cluster structures of some Zinlt ions

QUESTIONS

1. What is a metal cluster ? Illustrate giving suitable examples.
2. What are low nuclearity and high nuclearity carbonyl clusters ? Taking suitable examples discuss the structure and bonding in low nuclearity and high nuclearity carbonyl clusters.
3. Describe the procedure for predicting the skeletal structures of high nuclearity and low nuclearity carbonyl clusters. Are there any exceptions to the Wade's rules used in the above procedure ?
4. Discuss the structures of the following :
   $Os_7(CO)_{12}$, $[Os_{10}C(CO)_{24}]^{2-}$, $[Ru_6N(CO)_{16}]^-$ and $H_2Os_3(CO)_{10}$.
5. Discuss the structures of $Mo_4Cl_8(R_3P)_4$, Re_3Cl_9, $[Mo_6Cl_8]^{4+}$.
6. Discuss, on the basis of molecular orbital theory, the structure of $[Re_2Cl_8]^{2-}$.
7. Taking suitable examples, discuss the structures of trinuclear, tetranuclear and hexanuclear halide type of metal clusters.
8. Discuss the structures of $W_2(OiPr)_6$ and its dimer.
9. Discuss the structure and bonding in $[Nb_6Cl_{12}]^{2+}$.
10. What are Chevrel phases and Zintl ions ? Discuss their structures.

34 ORGANOMETALLIC COMPOUNDS

Organometallic Compounds. Organometallic compounds are those *in which the central metal atoms are bonded directly to carbon atoms of hydrocarbon radicals or molecules.* The term metal generally stands for elements less electronegative than carbon, as, for example, boron, arsenic, silicon, etc. Compounds such as carbides, cyanides and carbonyls, though they contain metal-carbon bonds, are excluded from the family of organometallic compounds, by convention. Organometallic compounds containing either the hydrocarbon radicals attached to the metal such as $(C_2H_5)_4Pb$ or containing hydrocarbon radicals alongwith H atoms attached to the metal such as $(CH_3)_3SnH$, are called **simple organometallic compounds** whereas those containing at least one hydrocarbon radical alongwith some other groups attached to the metal such as R-Mg-X and $(C_4H_9)_2SnCl_2$, are called **mixed organometallic compounds.**

CLASSIFICATION OF ORGANOMETALLIC COMPOUNDS BASED ON THE NATURE OF METAL–CARBON BOND

The following five types of organometallic compounds can be distinguished depending upon the nature of the metal–carbon bond.

I. IONIC ORGANOMETALLIC COMPOUNDS

Most of the organometallic compounds of alkali metals (with the exception of lithium compounds which are largely covalent) fall in this category. Such compounds are colourless salt-like solids which are soluble in polar solvents. The ionic organometallic compounds are quite reactive and are, therefore, kinetically unstable. Most of the ionic organometallic compounds have a short life. The compounds with *maximum ionic character* are those which have *large cations* (*i.e.*, cations having small polarising power) and *small carbanions* (*i.e.*, carbanions having small polarisability). A common example is $\overset{+}{C}s\overset{-}{C}H_3$. Hydrocarbons containing *sp* hybridised carbon atoms would give carbanions easily to form stable organometallic compounds with alkali metals. Such hydrocarbons, as, for example, R–C≡CH, are sufficiently acidic to easily release the acetylenic hydrogen as H^+ and get converted into acetylenic anions. Similarly, carbanions having an extended conjugated system or a delocalised pi system, as in

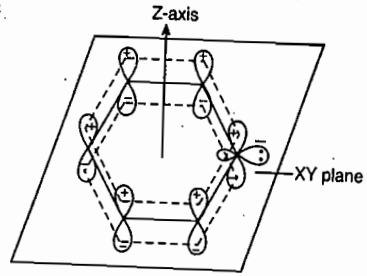
$$H_2C{=}CH{-}\overset{-}{C}H_2 \longleftrightarrow \overset{-}{C}H_2{-}CH{=}CH_2 \longleftrightarrow H_2\dot{C}{-}\overset{-}{C}H{-}\dot{C}H_2,$$

form more stable ionic compounds than those formed by simple unconjugated carbanions. In carbanions having extended conjugation, the unit negative charge is spread over several carbon atoms, as shown above in the case of the allyl anion, with the result that the net charge on each carbon atom is *less than unity.* Such anions are, therefore, *poor nucleophiles* and consequently *less reactive.* Apart from this, these anions are also resonance-stabilised. The organometallic compounds of these anions are *coloured* due to excitation of their π molecular orbital electrons to π* molecular orbitals, the absorption for which occurs in the visible region. Unlike the anions of conjugated hydrocarbons, the anions of unconjugated hydrocarbons have their entire negative charge localised on one of their carbon atoms. These anions are, therefore, *better nucleophiles* and consequently *more reactive.*

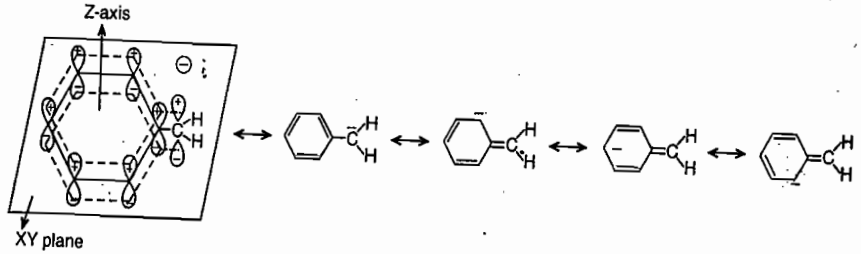
Problem 1. ***Why is*** $Na^+(CH_2C_6H_5)^-$ ***less reactive than*** $Na^+(C_6H_5)^-$**?**

Answer. In $(C_6H_5)^-$, the negative charge is localised in a doubly occupied σ type sp^2 hybrid orbital

which has a *different symmetry* than the six π bonding orbitals of the benzene ring, as shown. Hence this doubly occupied sp^2 hybrid orbital cannot overlap with the six $p\pi$ orbitals of the ring. In other words, charge remains localised in this orbital and consequently the anion is *unstable* so that the compound $Na^+(C_6H_5)^-$ is highly *reactive.*



The anion $(C_6H_5CH_2)^-$ is more stable because the negative charge is placed at the doubly occupied orbital of CH_2 which is now of *proper symmetry* to overlap with the six $p\pi$ orbitals of benzene. As a result, the negative charge now gets distributed over all the carbon atoms, as shown below :



This decreases the negative charge on the CH_2 group. The nucleophilic character of the group, therefore, *decreases* and *so does its reactivity.* The compound $Na^+(CH_2C_6H_5)^-$ is, therefore, less reactive than $Na^+(C_6H_5)^-$.

Problem 2. ***Why is*** $Na^+(C_5H_5)^-$ ***more stable than*** $Na^+(C_5H_{11})^-$**?**

Answer. C_5H_5 readily accepts an electron to become a 6-electron *aromatic system*, $C_5H_5^-$, which obeys the 4n+2 rule (see the section on Aromaticity of Cyclic C_nH_n Ligands). The negative charge is, therefore, evenly distributed over all the carbon atoms of the ring through π-electron delocalisation. This type of electron delocalisation leading to a distribution of charge does not occur in the case of $C_5H_{11}^-$ and the charge remains localised only on one carbon atom of the anion. Hence, $C_5H_{11}^-$ is a better nucleophile and, therefore, *more reactive* than $C_5H_5^-$. In other words, $Na^+(C_5H_5)^-$ is **more stable** than $Na^+(C_5H_{11})^-$.

II. COMPOUNDS CONTAINING METAL–CARBON SIGMA BONDS

Metallic elements of Groups 2, 13, 14 and 15 as well as the transition metals with fully filled *d* orbitals such as Zn, Cd and Hg form organometallic compounds in which the metal atoms are bonded to carbon atoms by σ bonds. A groupwise discussion of organometallic compounds of this category is given below.

1. Organometallic Compounds of Group 2 Elements*

All the elements of Group 2 form organometallic compounds. These are discussed below.

Organometallic compounds of beryllium. Beryllium forms a variety of organometallic compounds. The dialkyl beryllium compounds can be conveniently prepared in the following manner :

$$2LiR + BeCl_2 \xrightarrow[\text{ether}]{\text{Solvent}} BeR_2 + 2\,LiCl$$

$$Be + HgR_2 \xrightarrow{\Delta} BeR_2 + Hg$$

In the above reactions, R is an alkyl group. These dialkyl compounds are colourless solids or viscous liquids. Dimethyl beryllium is polymeric and contains Be – CH_3 – Be bridges in its structure.

A detailed discussion of the structure of dimethyl beryllium is given in a subsequent section.

*Organometallic compounds of Group 1 elements have been discussed in Chapter 13 which is the right place for such a discussion.

It readily reacts with Lewis bases as shown below :

$$Be(CH_3)_2 + N(CH_3)_3 \longrightarrow (CH_3)_2BeN(CH_3)_3$$

The extent of polymerisation of other dialkyl beryllium compounds decreases with increase in the bulk of the alkyl group, so much so that di-*t*-butyl beryllium is monomeric. The alkyl beryllium alkoxide (RBeOR′) can be prepared by reacting BeR_2 with R′OH but excess of alcohol in the reaction leads to the formation of alkoxide $Be(OR')_2$.

Beryllium also forms complexes with cyclopentadiene. The cyclopentadienly group is linked with the metal through a sigma or a pi bond as in [$Be(\eta^5\text{-}C_5H_5)X$] (where X is Cl, Br or I) and in [$Be(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)$], respectively.

Organometallic compounds of magnesium. The dialkyl and diaryl magnesium compounds can be prepared in the following manner :

$$LiR + R\text{–}Mg\text{–}X \xrightarrow[\text{ether}]{\text{Solvent}} MgR_2 + LiX$$

$$HgR_2 + Mg \xrightarrow[\text{ether}]{\text{Solvent}} MgR_2 + Hg$$

$$2C_2H_4 + H_2 + Mg \xrightarrow[\text{pressure}]{\text{Under}} Mg(C_2H_5)_2$$

These dialkyl magnesium compounds are highly susceptible to hydrolysis to yield alkanes and $Mg(OH)_2$. Thus,

$$Mg(C_2H_5)_2 + 2HOH \longrightarrow 2C_2H_6 + Mg(OH)_2$$

Dimethyl magnesium is polymeric. It contains Mg – CH_3 – Mg bridges in its structure. Diphenyl magnesium dissolves in ether to yield $Ph_2Mg(OC_2H_5)$ where Ph is phenyl group. Diphenyl magnesium reacts with phenyl lithium to give $Li[MgPh_3]$, as shown below :

$$LiPh + MgPh_2 \longrightarrow Li[MgPh_3]$$

Another class of organometallic compounds of magnesium, called **Grignard reagents,** can be synthesised by refluxing alkyl or aryl halides with magnesium in dry solvent ether.

$$RBr + Mg \xrightarrow[\text{ether(dry)}]{\text{Solvent}} RMgBr$$

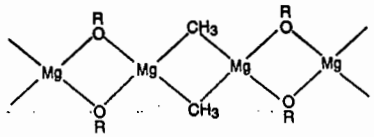
Grignard reagents are of great synthetic value in organic chemistry.

Organometallic compounds containing one alkyl and the other alkoxy group attached with Mg can also be easily synthesised by reacting dialkyl magnesium compounds with alcohols in the following manner :

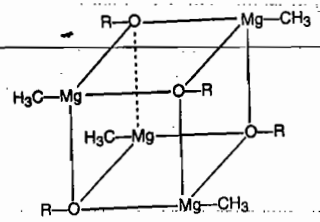
$$MgR_2 + R'OH \longrightarrow R\text{–}Mg\text{–}OR' + ROH$$

These compounds are polymeric and contain alkyl and alkoxy bridges between Mg atoms. The degree of polymerisation depends upon the bulk of the alkyl and alkoxy groups.

CH_3 – Mg – OR (R is CH_3 or C_2H_5) exists in two polymeric forms whose structures are given below :



Chain Polymer



Three-dimensional Polymer

It is to be noted that the lines between Mg and the alkyl or alkoxy groups in organometallic compounds do not depict the exact bond order.

Organometallic compounds of calcium, strontium and barium. Organometallic compounds of these elements are much more reactive than those of beryllium and magnesium. Because of their easy decomposition, these compounds have not been studied in details. The compound CaR_2 has been synthesised by reacting HgR_2 with calcium at low temperatures. It is quite unstable. The compound RCaI can be prepared by methods similar to those employed for the synthesis of RMgI. The cyclopentadienyl complexes of calcium, strontium and barium have complicated structures in which C_5H_5 rings are linked with the metal through sigma and/or pi bonds.

Organometallic compounds of Group 12 elements are distinctly defferent from organometallic compounds of other transition elements and resemble orgametallic compounds of Be and Mg of Group 2. The elements, Zn, Cd, Hg of Group 12 and their cations have fully filled (n – 1)*d* orbitals unlike the (n – 1)*d* orbitals of other transition elements and their ions which are only partially filled. That is why the properties of organometallic compounds of Zn, Cd and Hg are different from the properties of organometallic compounds of the remaining transition elements (*d* block elements). The organometallic compounds of Group 12 elements are, therefore, discussed along with the organometallic compounds of Group 2 elements (*e.g.*, Be, Mg) and **not** along with organometallic compounds of transition elements.

2. Organometallic Compounds of Group 12 Elements (Hg, Cd, Zn)

A large number of organometallic compounds of mercury are known. The compounds RHgX and R_2Hg (R = alkyl or aryl group) can be easily prepared from Grignard reagents, as follow :

$$HgCl_2 + RMgCl \longrightarrow RHgCl + MgCl_2$$

$$RHgCl + RMgCl \longrightarrow R_2Hg + MgCl_2$$

Organometallic compounds of mercury are used in the preparation of organometallic compounds of other metals. For example,

$$R_2Hg + 2Na \longrightarrow 2RNa + Hg$$

RHgX compounds are extremely toxic and hence are used for treating seeds and also as pesticides and fungicides.

Organometallic compounds of cadmium can be synthesised in a manner similar to the synthesis of organometallic compounds of mercury. The properties of organometallic compounds of cadmium are similar to those of organometallic compounds of mercury.

Zinc, like magnesium, forms addition compounds with alkyl halides.

$$Zn + C_2H_5I \longrightarrow ZnC_2H_5I$$

The compound decomposes on heating.

$$2ZnC_2H_5I \longrightarrow \underset{\text{Zinc diethyl}}{Zn(C_2H_5)_2} + ZnI_2$$

*Hg, Cd and Zn are *d* block elements, *i.e.*, transition elements. However, since they have fully filled *d* orbitals having the [noble gas]$(n-1)d^{10}ns^2$ configurations, they are discussed here along with Group 2 Elements and not with the other transition elements.

Organometallic compounds described above are used in the synthesis of a number of organic compounds.

The reactivity of alkyls and aryls of Group 2 and Group 12 metals is influenced by the electronegativities of the metals. As compared to carbon (2·5), electronegativities of Hg, Cd, Zn and Mg are 1·9, 1·7, 1·6 and 1·3, respectively (Pauling's values). The rates of hydrolysis of the compounds R_2M where R is CH_3 and M is the metal of Group 2 or Group 12 are as shown in the table.

Compounds R_2M (R is CH_3)	Elecronegativity of M, E_M	$E_C - E_M$ ($E_C = 2{\cdot}5$)	Relative rate of hydrolysis of R_2M
R_2Hg	1·9	0·6	Very slow
R_2Cd	1·7	0·8	Slow
R_2Zn	1·6	0·9	Very fast
R_2Mg	1·3	1·3	Very Very fast

As can be seen, the reactivity of R_2M towards hydrolysis increases with decrease in the electronegativity of the metal or an increase in the difference in the electronegativities of the metal and the carbon atom. The reactivity difference may be explained as follows :

The hydrolysis reaction takes place as

$$R_2M + H_2O \longrightarrow MO + 2RH$$

For example,

$$(CH_3)_2Hg + H_2O \longrightarrow HgO + 2CH_4$$

$$(CH_3)_2Zn + 2H_2O \longrightarrow Zn(OH)_2 + 2CH_4$$

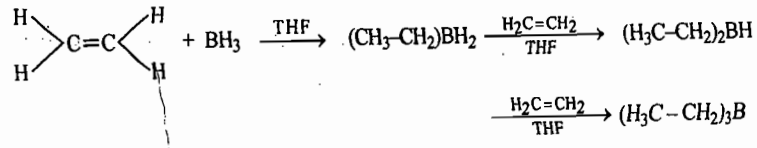
Since the coordination number of the metal M in R_2M is not saturated, it can add on to it more nucleophiles such as H_2O. Therefore, the transition state of the hydrolysis reaction is the one in which H_2O (as a nucleophile or as a ligand) gets coordinated to R_2M as $R_2M \leftarrow OH_2$. The stability of this transition state depends upon the electrophilic nature of M which, in turn, depends upon the polarity of the M–C bond. Since carbon has a higher elecronegativity than that of the metal M, a partial positive charge (+δ) would be created on M and a partial negative charge (–δ) would be created on the carbon atom. The magnitude of +δ would, obviously, depend upon the electronegativity difference. The lesser the electronegativity of the metal, the greater would be the magnitude of +δ, the stronger would be the electrophilic character of the metal M and the stabler would be the transition state formed during hydrolysis. This is the reason why the rate of hydrolysis of $(CH_3)_2Zn$ is much faster than that of $(CH_3)_2Hg$.

3. Organometallic Compounds of Group 13 Elements

Organometallic compounds of boron. Organometallic borons containing alkyl or aryl groups can be prepared by the following reactions :

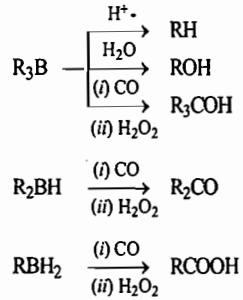
1. $$BX_3 + 2LiR \longrightarrow BR_3 + 3LiX$$ (R is alkyl or aryl group)

Actually, in this reaction we get a mixture of BRX_2, BR_2X and BR_3.

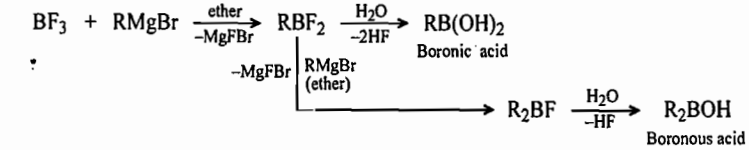
2. 

Lower alkyl borons are quite unstable and catch fire when brought in contact with air.

Alkyl and aryl borons are of great synthetic value. These are employed in the synthesis of hydrocarbons, alcohols, phenols, carbonyl compounds and carboxylic acids, as shown below :



Another class of organometallic borons is **boronic** and **boronous acids** which are prepared as follows.



The strength of these acids depends upon the nature of group R.

Boronic acid is stable in water but on warming it polymerises into a cyclic trimer.

$$3RB(OH)_2 \xrightarrow{\Delta} (RBO)_3 + 3H_2O$$

Organometallic boron anion, $[BR_4]^-$ can be prepared by the action of BX_3 with RLi in non-aqueous medium.

$$BX_3 + 4RLi \longrightarrow 3LiX + [BR_4]^- + Li^+$$

The organometallic boron compound $Na[B(C_6H_5)_4]$ is soluble in water whereas its potassium and rubidium analogues are not. Therefore, this compound is employed for the gravimetric estimation of K^+ and Rb^+.

Organometallic compounds of aluminium. The organometallic aluminium compounds containing alkyl or aryl groups can be prepared by any of the following procedures :

1. $$2Al + 3R_2Hg \longrightarrow (R_3Al)_2 + 3Hg$$

2. $$AlCl_3 + RMgCl \xrightarrow{-MgCl_2} \underbrace{RAlCl_2,\ R_2AlCl \text{ and } R_3Al}_{\text{(mixture)}}$$

3. $$AlH_3 + 3C_2H_4 \longrightarrow Al(C_2H_5)_3$$

The trialkyl aluminium compounds are generally dimeric and contain Al – R – Al bridges and R – Al bonds in their structures. The terminal alkly and the bridging alkyl groups in such dimeric compounds are in a process of very fast exchange at room temperature.

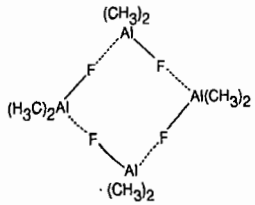
The trialkyl aluminium compounds are efficient Lewis acids and combine with Lewis bases such as amines, phosphines, etc., to form adducts of the type $R_3Al.Base$.

The trialkyl aluminium compounds react with alkyl lithium to produce alkyl derivatives of $LiAlH_4$.

$$R_3Al + RLi \longrightarrow Li[AlR_4]$$

Triphenyl aluminium and dimethyl phenyl aluminium are dimeric containing Al–phenyl–Al bridges.

The alkyl chlorides, bromides and iodides of aluminium are also dimeric but they contain Al–halogen–Al bridges instead of Al–alkyl radical–Al bridges in their structures. Alkyl fluorides of aluminium have cyclic tetrameric structures having Al–F–Al bridges. The structure of tetramer of $(CH_3)_2AlF_4$ is as shown.



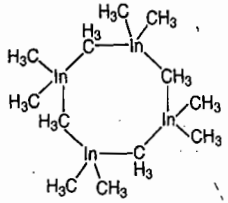
Structure of tetramer $[CH_3)_3AlF]_4$

The structures of organometallic compounds containing Al–alkyl radical–Al or Al–aryl radical–Al bridges are discussed in a subsequent section.

Organometallic compounds of gallium, indium and thallium. Amongst the organometallic compounds of Group 13 elements, trimethyl gallium $(CH_3)_3Ga$ is monomeric in vapour as well as in solid phase whereas the corresponding aluminium compound, containing bridged CH_3 groups, is dimeric. Trimethyl gallium has a planar trigonal structure. Gallium and aluminium have similar electronegativities (1·8 and 1·6) and the terminal M–CH_3 bond lengths are also the same. Then why should the Al analogue exist as a dimer is not clear. $(C_6H_5)_3Ga$ and other trialkyl and triaryl gallium compunds are monomers in the solid phase, vapour phase and solution phase.

All the trialkyl indium compounds, except $(CH_3)_3In$, are monomeric in vapour, solid and solution phase.

Trimethyl indium, $(CH_3)_3In$, is monomeric in vapour phase and in solution but it is a weakly associated tetramer in the crystalline state. The structure of the tetramer is as shown.



Structure of tetramer $[CH_3)_3In]_4$

All the trialkyl thalium compounds, with the exception of trimethyl thalium, are monomeric

Trimethyl thalium, $(CH_3)_3Tl$, has a crystal structure similar to $(CH_3)_3In$ although in solution this and the other trialkyls, as also the triaryls, are monomeric.

The triaryl of Ga, In and Tl are monomeric and there is concrete evidence that *p* electrons of the alkyl group participate in bonding in these compounds. Gallium, indium and thallium also form organometallic cations of the type $(CH_3)_2Ga(NH_3)_2]^+$ and $[(CH_3)_2Tl]^+$. These cations are quite stable in solid phase.

In and Tl also form compounds such as $(\eta^5\text{–}C_5H_5)In$ and $(\eta^5\text{–}C_5H_5)Tl$ which are monomeric in gas phase and polymeric in solid phase.

4. Organometallic Compounds of Group 14 Elements

Organometallic compounds of silicon (silicones), have already been discussed in sufficient details in Chapter 16 as also in Chapter 35 on Inorganic Polymers.

Organometallic compounds of germanium. These compounds are mainly of the general formula R_nGeX_{4-x} where R is alkyl or aryl group and n = 1, 2, 3 or 4. These compounds can be prepared as follows:

$$GeCl_4 + 4RLi \longrightarrow R_4Ge + 4LiCl$$

$$2RCl + Ge \longrightarrow R_2GeCl_2$$

Actually, in both the above reactions, a mixture of R_4Ge, R_3GeCl, R_2GeCl_2, $RGeCl_3$ is obtained.

The extent of catenation in organogermanium compounds is much less than in the compounds of carbon and silicon. Nevertheless, quite a few organometallic compounds with Ge–Ge bonds have been synthesised as follows :

$$2C_6H_5GeBr + 2Na \xrightarrow[\text{xylene}]{\text{Boiling}} 2NaBr + C_6H_5Ge-GeC_6H_5$$

$$2(CH_3)_3GeBr + 2K \xrightarrow{\text{Reflux}} 2KBr + (CH_3)_3Ge-Ge(CH_3)_3$$

$$(C_2H_5)_3GeBr + NaGe(C_6H_4CH_3)_3 \xrightarrow[\text{ammonia}]{\text{Liquid}} NaBr + (C_2H_5)_3Ge-Ge(C_6H_4CH_3)_3$$

These compounds are known to be fairly stable.

Some crystalline cyclic polymers of the general formula $[Ge(C_6H_5)_2]_n$, where *n* = 4, 5 or 6, are also known.

Organometallic compounds of tin. Organometallic compounds of tin are better studied than those of germanium and lead due to their utility in industry. These compounds can be prepared by methods similar to those employed for the preparation of organometallic compounds of silicon and germanium. Thus, some of the organotin compounds can be prepared as follows :

$$SnCl_4 + 4CH_3MgCl \longrightarrow Sn(CH_3)_4 + 4MgCl_2$$

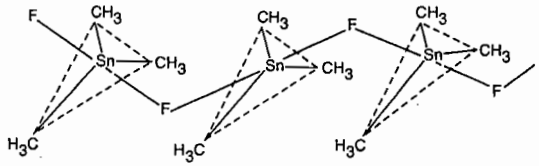
$$3SnCl_4 + 4Al(CH_3)_3 \longrightarrow 3Sn(CH_3)_4 + 4AlCl_3$$

$$Sn + 2C_2H_5X \longrightarrow (C_2H_5)_2SnX_2$$

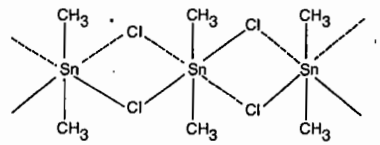
Here also, in all the above reactions a mixture of organotin compounds, *viz.*, R_4SnX_{4-n} (n = 1, 2, 3 or 4) is actually formed.

The aryl tin compounds can be prepared in a similar manner.

Tetraalkyl and tetraaryl compounds of tin, *i.e.*, SnR_4, are monomeric, colourless and volatile liquids or solids whereas R_3SnX, R_2SnX_2 and $RSnX_3$ (X = halogen) exist as strongly associated species. The association of the molecules occurs through halogen bridges as shown below in the structures of trimethyl tin fluoride and dimethyl tin chloride.



Structure of trimethyl tin fluoride



Structure of dimethyl tin chloride

There are several compounds of tin containing the Sn–Sn bonds. The synthesis of some of these compounds is shown below :

$$3Ar_3SnLi + SnCl_2 \longrightarrow (Ar_3Sn)_3SnLi + 2LiCl$$

$$(Ar_3Sn)_3SnLi + Ar_3SnCl \longrightarrow (Ar_3Sn)_4Sn$$

(Ar in these reactions is the aryl group)

$$2(CH_3)_3SnBr + Na(CH_3)_2Sn-Sn(CH_3)_2Na \xrightarrow[\text{ammonia}]{\text{Liquid}} (CH_3)_3Sn(CH_3)_2Sn-Sn(CH_3)_2Sn(CH_3)_3 + 2NaBr$$

Some cyclic organotin compounds such as $[Sn(CH_3)_2]_6$, $[Sn(C_2H_5)_2]_{6\,or\,7}$, $[Sn(Phenyl)_2]_6$ are also known.

Recently, organometallic compounds of Ge and Sn, in which the metal is doubly bonded to the metal or carbon, have been synthesised. Some examples are $R_2Ge{=}CR_2$, $R_2Sn{=}CR_2$, $R_2Ge{=}GeR_2$ and $R_2Sn{=}SnR_2$ which are named as germenes, stannenes, digermenes, and distannens, respectively.

Dialkyl tin laurate and dialkyl tin maleate are used as stabilisers of PVC. Without the addition of these organotin compounds, the PVC loses its plastic properties and becomes brittle. The stabilising action of dialkyl tin laurate and maleate may be due to the following reasons :

With the passage of time, PVC slowly degrades and produces traces of HCl. The HCl thus produced

catalyses further decomposition of PVC. However, the organotin compounds added to PVC react with the HCl produced and thus inhibit the catalytic degradation of PVC.

The organotin compounds act as antioxidants and thus prevent the changes which occur in PVC due to atmospheric oxygen.

Organometallic compounds of lead. The tetralkyl or tetraaryl lead can be prepared by any one of the following reactions :

$$4LiR + 2PbCl_2 \longrightarrow PbR_4 + Pb + 4LiCl$$

$$4AlR_3 + 6PbCl_2 \longrightarrow 3PbR_4 + 4AlCl_3 + 3Pb$$

$$4RMgX + 2PbCl_2 \longrightarrow PbR_4 + 4Mg(X)Cl + Pb$$

$$4RX \xrightarrow[\text{alloy}]{Pb-Na} PbR_4 + 4NaX$$

Tetraalkyl and tetraaryl compounds of lead are monomeric volatile liquids which are quite stable. Tetraethyl lead is the most widely used organolead compound. It is mixed in petrol and serves as an excellent antiknock in automobile engines.

Although the extent of catenation in organometallic compounds of lead is very small as compared to the compounds of Si and Sn, yet quite a few dimeric compounds of lead such as Pb_2R_6 are well known.

It is pertinent to add here and that no matter whether we take Pb(II) or Pb(IV) compounds for the preparation of organolead compounds, we almost always end up with organolead compounds of Pb(IV).

The only well defined organometallic compounds of Pb(II) are $Pb[CH(SiMe_3)_2]_2$ and $Pb(\eta^5 - C_5H_5)_2$.

The metallic elements of Group 14, *i.e.*, Si, Ge, Sn and Pb, have approximately the same electronegativity (~1·8). Therefore, the polarity of the M–C bond and the magnitude of the resulting +δ charge created at M would be nearly the same in all cases. It is, therefore, expected that the rate of hydrolysis of all the compounds of the type R_4M should be practically the same. But, actually it is not so. The rate of hydrolysis of R_4M varies in the order : $R_4Si < R_4Ge < R_4Sn < R_4Pb$. This may be attributed to variation in the strength of the M–C bond. The M–C bonds involving smaller M atoms are stronger than those involving bigger M atoms. This is because σ overlap is better in M–C bonds involving smaller M atoms. The stronger the M–C bond, the lesser it is prone to hydrolytic attack.

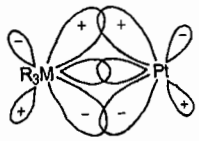
The bond energies of M–C bonds decrease as we move down the group. This is evident from the data given in the table .

Compound (Me = methyl)	Bond energy (kJ mol^{-1}) of M—C bond)
Me_4Si	290
Me_4Ge	240
Me_4Sn	220
Me_4Pb	160

These values also indicate that M–C bond in Me_4Si is the strongest while that in Me_4Pb is the weakest. This explains why Me_4Si is resistant towards hydrolysis whereas Me_4Pb undergoes hydrolysis most readily.

5. Organometallic Compounds of Group 15 Elements

Elements of Group 15 form organometallic compounds of the general formula R_3M where R is an alkyl or an aryl radical and M is P, As, Sb or Bi. These elements have an empty set of *d* orbitals which can form π bonds with filled *dπ* orbitals of a transition metal such as platinum, apart from donating their lone pairs of electrons to the element M through σ type of overlap, as shown.



(M = P, As, Sb, Bi)

Trialkyl and triaryl phosphines, arsines, stibines and bismuthines all react with alkyl and aryl halides to yield phosphonium, arsonium, stibonium and bismuthonium halides. Thus,

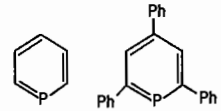
$$R_3M + RX \longrightarrow R_4M^+X^-$$

Some other organometallic compounds of Groups 15 elements are given below.

Organometallic compounds of phosphorus. There are many naturally occurring organophosphorus compounds which play a vital role in biological systems. The complete discussion of such organophosphorus compounds is beyond the scope of the book. We shall, however, discuss very briefly some of the synthetically prepared organometallic compounds of phosphorus.

Of the organophosphorus compounds in which P is attached to one other atom only, H–C≡P is the most important. This is a colourless reactive gas which can be prepared by passing an electric arc through PH_3 using graphite electrodes. Other compounds of this category such as F–C≡P and H_3C–C≡P can be synthesised from H–C≡P by appropriate reactions.

Important organophosphorus compounds in which P is attached with two other atoms are H_3C–P=PCF_3 and the two pyridine analogues shown :



Organophosphorus compounds in which P is attached with three or four other atoms are most common. These include $[PMe_4]^+$, $[PPh_4]^+$, tertiary phosphines, PR_3 and ylides, $Ph_3P = CH_2$. Phosphines behave as sigma donor pi acceptor unidentate ligands towards several metal ions.

The ylides are highly reactive compounds which serve as the starting material for the synthesis of a variety of other organophosphorus compounds. The ylides can be prepared as follows :

$$[Ph_3PCH_3]^+Br^- \xrightarrow{LiBu} Ph_3P = CH_2$$

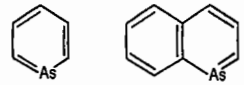
$$[(CH_3)_4P]^+Br^- + NaNH_2 \xrightarrow[< 0°C]{THF} (CH_3)_3P = CH_2$$

Pentaorganophosphorus compounds are rare. A few such compounds which have been synthesised are PPh_5, $P(CF_3)_3(CH_3)_2$ and $P(CF_3)_2(CH_3)_3$. PPh_5 has a trigonal pyramidal structure like PF_5.

Many organophosphorus compounds are highly toxic and paralyse the nervous system. Some of the organophosphorus compounds have been developed as herbicides, pesticides and nerve gases.

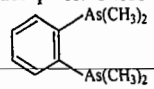
Organometallic compounds of arsenic. A number of organoarsenic(III) and organoarsenic(V) compounds are known. Some of the important compounds are described below.

The compounds in which As (III) is attached to two other atoms are **arsabenzene** and **arsanaphthalene** whose structures are as shown :



arsabenzene arsanaphthalene

Arsabenzene is a colourless liquid which is thermally stable. Arsanaphthalene is a deep yellow liquid which is thermally unstable.

There are a large number of organoarsenic compounds in which As (III) is attached with three other atoms. **Trialkyl** and **triaryl arsines** are very well studied unidentate ligands which act as sigma donors and pi acceptors. These compounds have pyramidal structure as expected. Orthophenylenebisdimethyl arsine. 

is a bidentate ligand chelating with the metals through two arsenic atoms.

Dialkyl (or diaryl) arsine halides and alkyl (or aryl) arsine dihalides can be prepared, alongwith AsR_3, in the following manner :

$$AsCl_3 \xrightarrow{RMgCl} AsR_3 + R_2AsCl + RAsCl_2$$

Arsine monohalides, R_2AsX, are hydrolysed to R_2AsOH and the dihalides, $RAsX_2$ to $RAs(OH)_2$. These halides also act as unidentate ligands like AsR_3.

Quaternary arsonium salts such as $[Ph_3AsCH_3]Cl$ are also known. They react with $NaNH_2$ to give

reactive and rather unstable ylides.

$$[Ph_3AsCH_3]Cl + NaNH_2 \longrightarrow Ph_3As{=}CH_2 + NaBr + NH_3$$

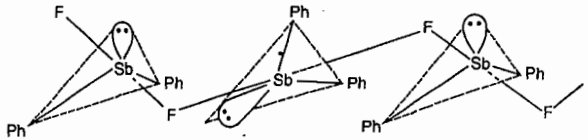
A few organoarsenic(V) compounds are also known. Well known compound is $As(CH_3)_5$. This compound can be prepared as follows :

$$(CH_3)_3AsCl_2 \xrightarrow[(CH_3)_2O]{LiCH_3} [As(CH_3)]_4^+Cl^- \xrightarrow[(CH_3)_2O]{LiCH_3} As(CH_3)_5$$

It is an unstable compound and decomposes to C_2H_6, $As(CH_3)_3$ and cyclic $(CH_2)_n$ (n = 4 or 5).

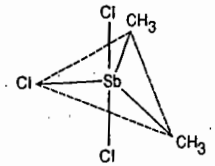
Organometallic compounds of antimony and bismuth. These compounds are not so well studied as are organoarsenic compounds. The compounds MR_3 (M = Sb or Bi ; R = alkyl or aryl group) are colourless volatile liquids or solids. These are weaker ligands than phosphines (PR_3) or arsines (AsR_3). As expected, bismuthines (BiR_3) and stibines (SbR_3) have pyramidal structures like NR_3, PR_3 and AsR_3.

Halo and dihalo stibines, R_2SbX and $RSbX_2$ can be prepared by methods similar to those used for the preparation of R_2AsX and $RAsX_2$. Stibine, in these halides, has a tendency to increase its coordination number by dimersing or polymerising as shown in the case of Ph_2SbF in which F forms bridges between Sb atoms.

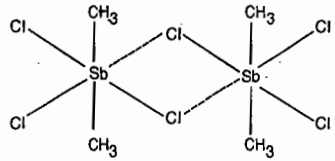


Polymerisation of PhSbF

The compound $(CH_3)_3SbCl_3$ is monomeric in solution in $CHCl_3$ and CH_2Cl_2 but it is dimeric in the solid state. The structures of the compound in solution and in the solid state are given below :



Structure of monomer of $(CH_3)_3SbCl_3$



Structure of dimer

The Sb(V) compounds are prepared by the oxidation of Sb(III) compounds with chlorine.

$$SbPh_3 + Cl_2 \longrightarrow Ph_3SbCl_2 \xrightarrow[-2LiCl]{3LiPh} Li^+[SbPh_6]^- \xrightarrow[-LiOH,\ -C_6H_6]{H_2O} SbPh_5$$

The compound pentaphenylstibine ($SbPh_5$) has a **square pyramidal** structure whereas PPh_5 and $AsPh_5$ are **trigonal bipyramidal.** The reason for the difference in the structures of $SbPh_5$ compared to PPh_5 and $AsPh_5$ is not known.

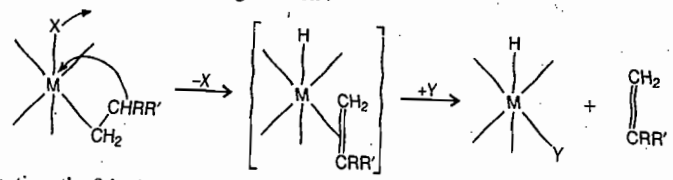
Organobismuth(V) compounds, are, in general, similar to their As and Sb analogues but are less stable.

BiR_4X and R_3BiX_2 are known whereas no pentaalkylbismuth (BiR_5) has been prepared so far. Although $BiPh_5$ has been prepared, yet it is found to be quite unstable.

6. Organometallic Compounds of Transition Metals

Very few exmples of **alkyl compounds** of transition metals are known. Wherever such compounds are known to exist, the oxidation state of the metal is very low and the metal generally lies near the end of the transition series. The rarity of alkyl compounds of transition metals appears to be quite strange since the M–C bonds in these compounds are comparable in strength to the M–C bonds in compounds of the main

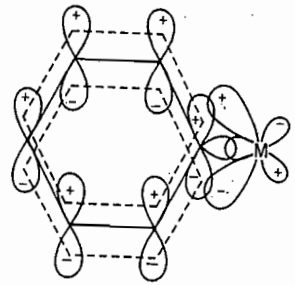
group elements. The reason perhaps lies in comparatively greater chemical reactivity exhibited by these compounds as illustrated by the following reaction :



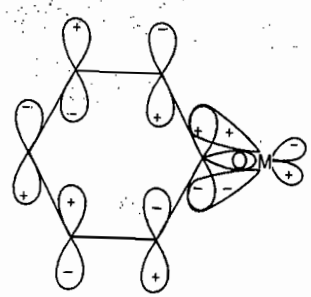
In this reaction, the β hydrogen shifts from the alkyl chain and occupies one of the coordination sites of the metal replacing one of the already coordinated ligands. The intermediate thus formed is unstable and decomposes to give an alkene, as shown above. *This explains the reactivity of the alkyl complexes of transition metals.*

If, however, the organic ligand does not contain any β hydrogen (as in $-CH_2Ph$) or if the other ligands already attached to the metal are held firmly in their coordination sites as in $[CH_3{-}CH_2{-}Rh(NH_3)_5]$ so as to inhibit the accommodation of β hydrogen in any of the coordination sites, then the alkyl complexes would *be quite stable.*

In alkyl compounds of transition metals there is practically no contribution from π bonding to the M–C bonds since all the orbitals of ligands are used up in C–C bonding. However, there is slight possibility of electron donation from π bonding molecular orbitals of the aryl ligands to the vacant metal orbitals of the same symmetry. There is also some possibility of transfer of electronic charge from filled $d\pi$ orbitals of the metals to empty π antibonding molecular orbitals of aryl ligands. This is illustrated below :



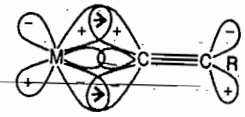
Overlap between the empty $d\pi$ orbital of the metal with π bonding molecular orbital of the aryl ligand



Overlap between the filled $d\pi$ orbital of the metal with empty π antibonding molecular orbital of the aryl ligand

Because of the factors mentioned above, *aryls of transition metals are slightly more stable than the alkyls of transition metals.*

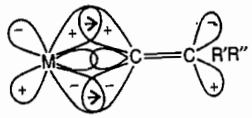
The **alkynyl compounds** of transition metals, *viz.*, M–C≡CR *are more stable than alkyl or aryl compounds.* The reason is that the alkynyl group (–C≡CR) acts as a σ donor as well as a π acceptor like the carbonyl group (see Mononuclear Complexes of pi Acceptor Ligands, Chapter 32). The extent of M to C π bonding is much higher in metal alkynyls compared to metal aryls and alkyls. The type of bonding involved in alkynyl compounds is as shown.



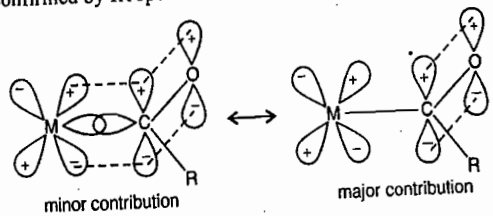
Overlap between $d\pi$ orbital of the metal and π* molecular orbital of the ligand in alkynyl compounds

The above type of π bonding would increase the bond order of M–C bond and decrease the bond order of C≡CR bond. This is confirmed by a decrease in the IR absorption frequency of C≡CR band from about 2260—2190 cm^{-1} in free alkynes to about 2100 cm^{-1} in metallated C≡CR in alkynyl compounds.

In the case of alkenyl compounds of transition metals, apart from the M–C σ bond, there is a possibility of overlap between the filled $d\pi$ orbitals of metal and the π^* antibonding molecular orbitals of the alkene. This would enhance the bond order of M–C bond and decrease the double bond character of metallated alkene, as shown. This is confirmed by IR spectra.



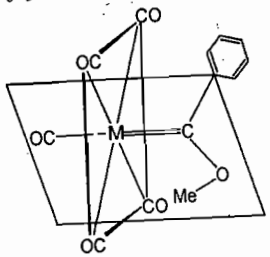
A fractional double bond character is also exhibited by the M–C bond of **acyl** compounds of transition metals. This is because of the overlapping of the $d\pi$ orbitals of the metal with the π bonding molecular orbitals of the acyl group, as shown.



Some other compounds containing M–C σ bond are cyclopentadienyl complexes containing η^1-M–C_5H_5 linkage and fluorocarbon alkyl or aryl complexes containing M–C_6F_5 or M–C_nF_{2n+1} linkages.

III. YLIDES

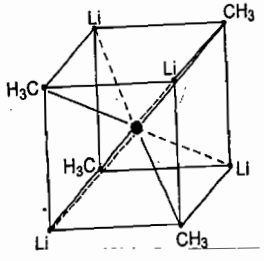
Ylides are the compounds in which the metal is *doubly bonded* with the carbon atom of the ligand. Such compounds are formed by the main group elements as well as by the transition elements. Examples are (*i*) the Wittig reagent, $Ph_3P{=}CH_2$ and (*ii*) the compounds having the structure as shown where M = Cr, Mo, W, Fe, etc. The CO bond order in these compounds is quite high indicating that these compounds are stabilised by the withdrawal of electron density from the M=C bond.



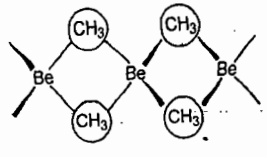
IV. ORGANOMETALLIC COMPOUNDS WITH MULTICENTRE BONDS

Organometallic compounds which are loosely called electron-deficient and occur in polymeric forms fall under this category. Examples are : $(LiCH_3)_4$, $[Be(CH_3)_2]_n$, $[Al(CH_3)_3]_2$, etc. These compounds can be considered as intermediates between ionic organometallic compounds of alkali metals and σ bonded organometallic compounds of Si, Sn, Pb, etc. Elements which have the highest tendency to form multicentre organic compounds are Li, Be, Mg, B and Al. In none of these compounds, the bonding can be explained by the classical concepts of chemical bonding (*i.e.*, by ionic or normal covalent bonding). This is the reason why such multicentre organometallic compounds are sometimes designated as non-classically bonded compounds.

The **structure of $(LiCH_3)_4$** can be considered as derived from a cube in which the two tetrahedra, one of $(CH_3)_4$ and the other of Li_4, having a common centre are interlinked as shown. Each Li atom in $Li(CH_3)_4$ appears to be associated with three CH_3 groups and each CH_3 group is associated with three Li atoms. The conventional concepts of bonding cannot explain the type of linkage that exists in $Li(CH_3)_4$.

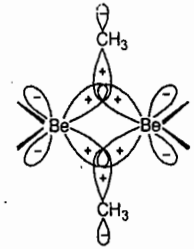


The **structure of polymeric $[Be(CH_3)_2]_n$** is as shown :



As can be seen, the Be atoms are linked together through the CH_3 bridges. The geometry of each Be atom in this compound is tetrahedral. The bonding in $[Be(CH_3)_2]_n$ cannot be explained with the help of the conventional two centre–two electron bonds. It can, however, be successfully explained by the concept involving the formation of molecular orbitals by the overlapping of two sp^3 hybrid orbitals of the two Be atoms and one sp^3 hybrid orbital of the bridging CH_3 group.

The overlapping of the three orbitals gives rise to three molecular orbitals, one of which is bonding and out of the remaining two, one is non-bonding and the other antibonding. The bonding molecular orbital contains in it two electrons resulting in the formation of a three centre–two electron (3c–2e) bond, as shown.

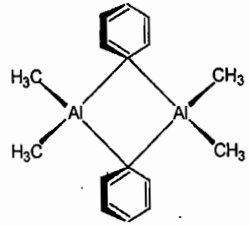


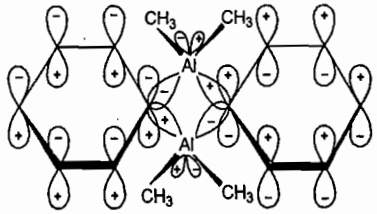
Aluminium trimethyl is dimeric in benzene solution as well as in vapour phase whereas aluminium triethyl and **aluminium tripropyl** are dimeric in benzene solution but monomeric in vapour phase.

Thus, the bulk of the alkyl group appears to determine the extent of polymerisation in aluminium trialkyls. The bridging by CH_3 groups in $Al_2(CH_3)_6$ involves three centre–two electron bonds.

Aluminium triphenyl is also dimeric in solution and in vapour phase. Although phenyl group is bulkier than CH_3 group yet it is capable of forming a bridge between the two Al atoms leading to the formation of a dimeric species. Some mixed methyl aryls of aluminium also have a dimeric structure.

The structure of dimer **$[Al(CH_3)_2Ph]_2$** and the type of bonding involved in this dimer are shown below.





Each C_6H_5 group forms a bridge between two Al atoms by overlapping one of its $p\pi$ orbital with two sp^3 hybrid orbitals of the two Al atoms, thereby forming a 3c–2e bond. The bonding between the terminal CH_3 and Al is a normal 2c–2e covalent bond. The geometry of each Al is tetrahedral.

It may be noted that Ga, In and Tl alkyls and aryls do not form dimers and the bonding in these cases can be explained by the simple 2c–2e covalent bonds*. The reason for the non-existence of dimers is probably *steric*. The angle M–C–M of the bridge has to be quite small to permit a good overlap of the three orbitals of the three atoms, M, C (of alkyl or aryl) and M. For this the bulky metal atoms (*i.e.*, Ga, In, Tl, etc.) should be brought very close to one another. But, this would introduce large electrostatic repulsions between electrons of these metal atoms. Consequently, the dimeric forms of the alkyls or aryls of Ga, In and Tl would be unstable as compared to the alkyls or aryls of Al. But the above reasoning fails to explain why $B(CH_3)_3$ does not dimerise while BH_3 does.

V. ORGANOMETALLIC COMPOUNDS WITH PI BONDED LIGANDS

This category includes organometallic compounds of alkenes, alkynes and some other carbon-containing compounds having electrons in their π molecular orbitals. Overlapping of these π molecular orbitals with the vacant orbitals of the metal atom gives rise to an arrangement in which the metal atom gets bound to all the C atoms over which the π molecular orbital of the organic ligand is spread. The bonding in these complexes also cannot be explained by the classical concepts, *i.e.*, by ionic or normal covalent bonding.

The most important compound of this category is ***ferrocene***, *viz.*, bis(cyclopentadienyl) iron which was synthesised in 1951 as follows :

$$\underset{\substack{\text{Cyclopentadiene}\\ \text{(in excess)}}}{2C_5H_6} + 2N(Et)_2H + FeCl_2 \longrightarrow \underset{\text{Ferrocene}}{Fe(C_5H_5)_2} + 2[N(Et)_2H_2]^+Cl^-$$

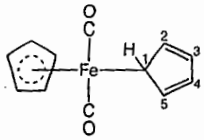
* Indium and thalium form very loosely bonded tetramers $[In(CH_3)_3]_4$ and $[Tl(CH_3)_3]_4$ in the solid state. These tetramers, however, revert to their monomeric form very easily when heated to vapour state or when brought in solution state.

The synthesis of ferrocene marked the beginning of the discovery of a large number of organometallic compounds containing π bonded ligands with interesting structural features. Ferrocene is known to have a 'sandwitch' structure with D_{5d} symmetry as shown.

The delocalised π molecular orbitals of each cyclopentadienyl ring overlap with the orbitals of the metal. The structure thus comprises of two parallel cyclopentadienyl rings which are staggered at room temperature, as shown.

Preparation, properties and the type of bonding involved in ferrocene have been discussed in details in a subsequent section.

Several compounds have been reported in literature in which one molecule of the ligand is π bonded and the other is σ bonded. One such example is the compound shown.



In this case, one of the C_5H_5 rings is π bonded with the metal whereas the other ring is σ bonded through one of its carbon atoms to iron atom. This Fe–C σ bond goes on exchanging its positions very rapidly through 1,2 shifts at (or even below) the room temperature. Thus, at one instant, the bond is between Fe and C_1 and at the next instant it shifts between Fe and C_2 and then between Fe and C_3 and so on. The molecule in which this type of M–C bond exchanges sites by choosing different carbon atoms at different times is called a **fluxional molecule** and this property is known as **fluxionality**. Several other fluxional organometallic compounds of transition metals are also known.

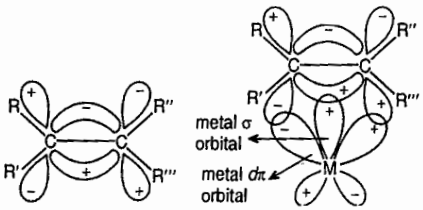
Ruthacene is another well known compound which has a similar sandwitch structure. But, in ruthacene, the two C_5H_5 rings are *exactly parallel* (edge by edge) to each other so that the symmetry of the molecule is D_{5h} and not D_{5d}.

Since the discovery of ferrocene and similar compounds, a large number of organometallic compounds containing π bonded ligands have been isolated and their structures studied. The structures and the type of bonding involved in π-metal alkenyl compounds, π-metal alkynyl compounds and ferrocene have been discussed below at some length.

BONDING IN Pi METAL ORGANOMETALLIC COMPLEXES

1. Bonding in π-Metal Olefin or Alkenyl Complexes

A traditional representation of a metal-olefin bond is as shown :

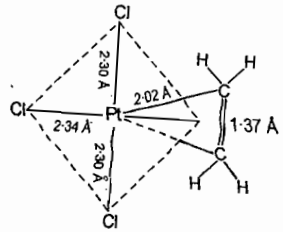


In the olefin ligand, in addition to a σ bond formed due to the overlapping of sp^2 hybrid orbitals of the two carbon atoms, the p_z orbitals of the two carbon atoms overlap to form a π bonding and a π* antibonding molecular orbital. The π bonding molecular orbital is occupied whereas π* antibonding molecular orbital is vacant.

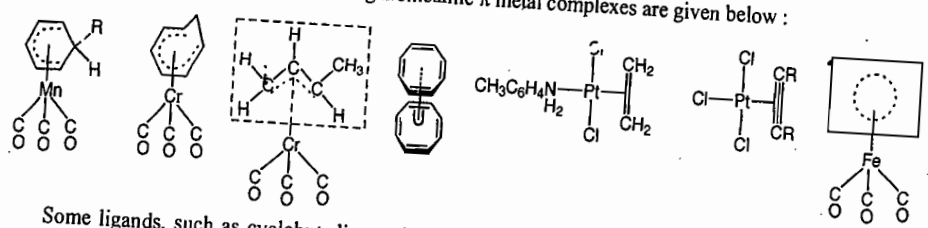
The occupied π bonding molecular orbital of alkene then overlaps with empty σ orbital of the metal while one of the filled $d\pi$ orbitals of the metal interacts with the empty π* antibonding molecular orbital of alkene resulting in a bond with π symmetry about the Z-axis. Thus, the metal-alkene bond consists of two components, *viz.*, σ donation from ligand to metal and simultaneous π donation from metal to ligand. The metal–carbon bond is, thus, similar to the metal–carbon bond in metal carbonyls. Both alkene and CO are very weak σ donors but the presence of low energy empty π* molecular orbitals on these ligands makes the $d\pi$–π* bonding possible. The transfer of electrons from ligand to metal during the formation of σ bond is enhanced by simultaneous removal of charge from the metal through $d\pi$–π* back donation. This effect, known as **synergic effect**, would strengthen the M–C bond. It is very difficult to assess the relative extent of σ and π bonding in such cases. However, there is evidence to suggest that, in general, π

bonding makes greater contribution to M–C bond in these alkenyl complexes.

The structure of the alkenyl complex $K^+[PtCl_3(C_2H_4)]^-$ has been established to be approximately square planar as shown. The olefin-metal bond lies perpendicular to the plane containing Pt and the three Cl atoms. *In this compound, the dsp^2 hybridised σ orbital of Pt overlaps with π bonding molecular orbital of ethene. Simultaneously, the filled* $d\pi$ orbital of Pt overlaps with π* orbital of C_2H_4. The two carbon atoms of C_2H_4 are equidistant from Pt. The ethene group lies perpendicular to the Pt–Cl bond which is trans to the C_2H_4 ligand.



Structures of some other common organometallic π metal complexes are given below :

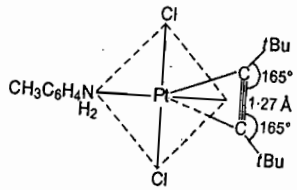


Some ligands, such as cyclobutadiene which are incapable of independent existence, are known to exist in their π bonded complexes. An example is the mixed carbonyl cyclobutadiene complex of iron whose structure is as shown above.

2. Bonding in π-Metal Alkynyl Complexes

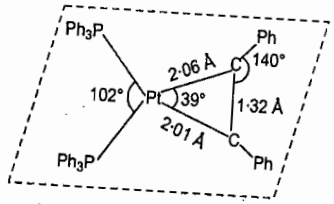
The alkynyl complexes have been studied to a lesser extent. However, they are similar to alkenyl complexes.

In most of the cases, as shown in $CH_3C_6H_4NH_2PtCl_2C_2(t\text{-}Bu)_2$ complex, the C≡C bond remains short and the alkyne group is perpendicular to the plane of coordination.



The alkynyl group occupies one coordination site and Pt in this complex has coordination number 4.

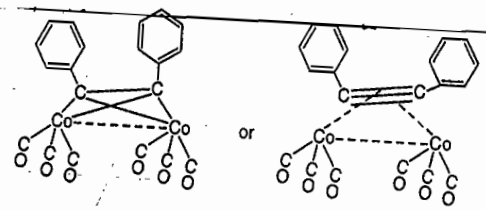
In some complexes, the alkynyl group lies almost in the plane of the complex. Thus, the structure of $[C_2Ph_2Pt(PPh_3)_2]$ is planar in which the ligand C_2Ph_2 appears to occupy two coordination sites instead of one, as shown. (The lines between the atoms do not show exact bond order)



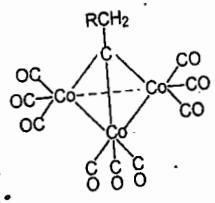
The infrared spectral studies reveal that the $\nu_{C\equiv C}$ in the complex appears at ~1750 cm^{-1} whereas $\nu_{C\equiv C}$ in free $C_2(Ph)_2$ appears at ~2100 cm^{-1}. This indicates a decrease in the bond order in the complexed $C_2(Ph)_2$ which can happen only when the $d\pi \rightarrow \pi^*$ back bonding is considerably significant..

Alkynyl group also forms a bridge between two metals as in $[C_2(C_6H_5)_2Co_2(CO)_6]$, whose structure is as shown.

It can be argued that each carbon atom of alkynyl group has become essentially sp^3 hybridised and forms two σ bonds with two Co atoms.



Alternatively, each filled BMO of bridged alkynyl group may interact with an orbital of one Co atom. The treatment of the complex with HCl yields the complex $RCH_2C(Co)_3(CO)_9$ in which the RCH_2C residue is tri-bridged as shown.



3. Bonding in Ferrocene

Bonding in ferrocene can be best understood if we consider its formation from Fe^{2+} and two cyclopentadienyl anions, $C_5H_5^-$, since it is the *anion* $C_5H_5^-$ *containing six π electrons which obeys* the 4n+2 *rule of aromaticity* and not the radical $\cdot C_5H_5$. The carbon atoms in $C_5H_5^-$ ring are sp^2 hybridised, the hybridised orbitals being completely utilised in forming C—C and C—H bonds. Each carbon atom of the ring has a $p\pi$ (or p_z) orbital. The various bonding aspects are as follows.

1. The five $p\pi$ atomic orbitals of the ring combine linearly to give an equal number of molecular orbitals having symmetry *a* (*i.e.*, one molecular orbital with no planar node), symmetry e_1 (*i.e.*, two degenerate molecular orbitals having one planar node) and symmetry e_2 (*i.e.*, two degenerate molecular orbitals having two planar nodes). The wave functions (ψs) of these five molecular orbitals are written as five linear combinations of the five $p\pi$ atomic orbitals wave functions (ϕs) of the $C_5H_5^-$ ring. The (+) sign is given to ϕ in the combination if its positive lobe points towards +Z axis and a (–) sign if its positive lobe points towards –Z axis. The five molecular orbitals of $C_5H_5^-$ system and their wave functions are presented in Fig. 1.

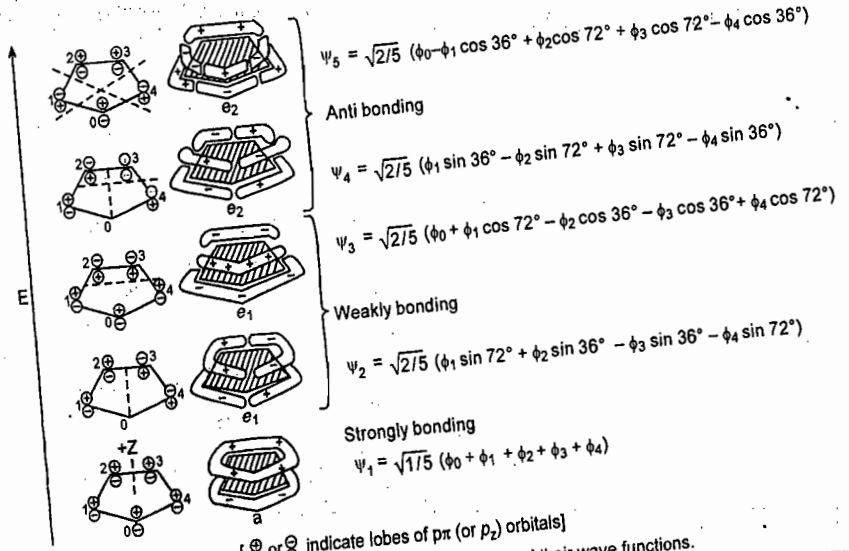


Fig. 1. The five molecular orbitals of $C_5H_5^-$ system and their wave functions.

The coefficients of ϕs in a ψ are chosen according to the contribution of each ϕ to the molecular orbital wave function. All the ψs are normalised.

2. The molecular orbitals, *i.e.*, ψ_1, ψ_2, etc., of one (*i.e.*, upper) $C_5H_5^-$ ring then linearly combine with molecular orbitals of the same symmetry, *i.e.*, ψ'_1, ψ'_2, etc., of the other (*i.e.*, lower) $C_5H_5^-$ ring to give 10 molecular orbitals of the resulting two-$C_5H_5^-$ ring system, *i.e.*, ψ_1 combines with ψ'_1 to give two molecular orbitals $1/\sqrt{2}\,(\psi_1+\psi'_1)$ and $1/\sqrt{2}\,(\psi_1-\psi'_1)$ of the 'two-$C_5H_5^-$ ring' ligand. Similarly, ψ_2 combines with ψ'_2 to give two molecular orbitals $1/\sqrt{2}(\psi_2+\psi'_2)$ and $1/\sqrt{2}(\psi_2-\psi'_2)$ of the two-$C_5H_5^-$ ring ligand and so on. The +Z direction of the upper ring is taken to be pointing downwards while the +Z direction of the lower ring is

taken to be pointing upwards. This means that the +Z directions of the upper and the lower rings are pointing towards the centre of the two-$C_5H_5^-$ ring ligand system. If, in any molecular orbital of the two-$C_5H_5^-$ ring ligand system, the orientations of the lobes of all the p_z orbitals of a $C_5H_5^-$ ring are *identical* with the one given for a particular ψ of free $C_5H_5^-$ ring, then that ψ appears in the molecular orbital wave function of the two-$C_5H_5^-$ ring system with a + sign. If, on the other hand, the orientations of the lobes of all the p_z orbitals of a $C_5H_5^-$ ring belonging to such a ligand system are *opposite* to the ones given for a particular ψ of free $C_5H_5^-$ ring, then that ψ appears with a – sign in the molecular orbital wave function (all the five ψs of free $C_5H_5^-$ are given in Fig. 1.)

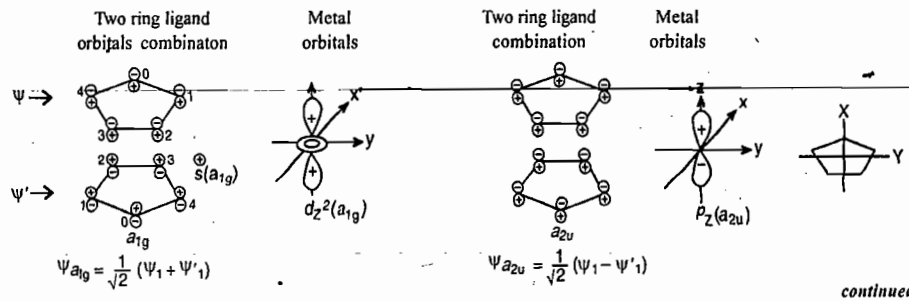
We shall use the above sign convention to write the wave functions in the form of linear combinations of ψs and ψ's for two of the ten molecular orbitals of the two-$C_5H_5^-$ ring ligand system. The pictorial representations of all the ten molecular orbitals of this ligand system are shown in Fig. 2. We may again emphasize that while writing the molecular orbital wave functions, one must keep in mind that the +Z axis of the upper ring of this ligand system is taken to be pointing downwards and of the lower ring is taken to be pointing upwards.

Let us first consider a_{1g} molecular orbital of the two-$C_5H_5^-$ ring ligand system represented in Fig. 2. We observe from the pictorial representations of this molecular orbital that the + lobes of all the p_z orbitals of the upper ring are pointing towards +Z direction so that the normalised linear combination of the p_z orbital wave functions of the upper $C_5H_5^-$ ring is $+\sqrt{1/5}\,(\phi_0+\phi_1+\phi_2+\phi_3+\phi_4)$, *i.e.*, $+\psi_1$. A similar situation is observed for the lower $C_5H_5^-$ ring in which the + lobes of all the p_z orbitals are again pointing towards +Z axis. Therefore, the normalised linear combination of p_z orbital wave functions of the lower ring is $+\sqrt{1/5}\,(\phi'_0+\phi'_1+\phi'_2+\phi'_3+\phi'_4)$, *i.e.*, $+\psi'_1$. (The prime (') is used to denote ϕ_s and ψs of the lower ring). Thus, the molecular orbital a_{1g} of the two-$C_5H_5^-$ ring ligand system can be represented as the linear combination $\psi_1+\psi'_1$ or more correctly as $1/\sqrt{2}\,(\psi_1+\psi'_1)$ where $1/\sqrt{2}$ is the normalising constant.

Now consider a_{2u} molecular orbital of the two-$C_5H_5^-$ ring ligand system which is also shown in Fig. 2. As can be seen, the + lobes of all the p_z orbitals of the upper ring are pointing towards the +Z direction. Therefore, the normalised linear combination of the p_z orbital wave function of the upper ring is $+\sqrt{1/5}\,(\phi_0+\phi_1+\phi_2+\phi_3+\phi_4)$, , *i.e.*, $+\psi_1$. However, in the lower ring, the –lobes of all the p_z orbitals are now pointing towards the +Z axis so that the normalised linear combination of the p_z orbital wave functions of the lower ring is $-\sqrt{1/5}\,(\phi'_0+\phi'_1+\phi'_2+\phi'_3+\phi'_4)$, *i.e.*, $-\psi'_1$. Thus, the molecular orbital a_{2u} can be represented by the linear combination $\psi_1-\psi'_1$ or more correctly as $1/\sqrt{2}\,(\psi_1-\psi'_1)$ where $1/\sqrt{2}$ is the normalising constant.

The wave functions of the rest of the eight molecular orbitals of the two-$C_5H_5^-$ ring ligand system can be written in a similar manner as linear combinations of ψs and ψ's.

3. The ten molecular orbitals which are linear combinations of ligand orbitals ($\psi \pm \psi'$) of the two-$C_5H_5^-$ ring ligand system then combine with orbitals of the metal of the same symmetry to give bonding and antibonding MOs of ferrocene. The ten MOs obtained from the combination of ligand orbitals of the two rings alongwith the orbitals of the metal with which they combine are shown in Fig. 2.



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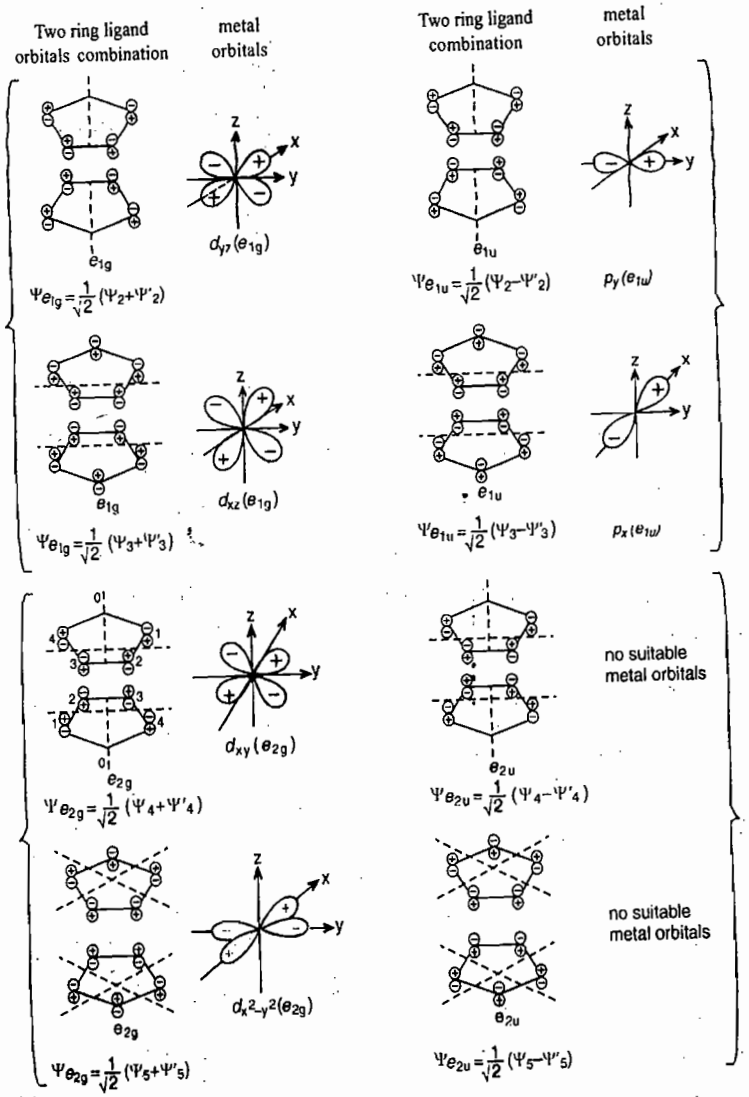


Fig. 2. The molecular orbitals of the 'to-C_5H_5– ring ligand systems' in ferrocenes. The dotted lines indicate the regions of nodes.

The a_{1g} BMO of ferrocene is mainly based on the ligand system, there being only a minor contribution from the 4s and $3d_{z^2}$ orbitals of iron to this molecular orbital. The a_{2u} BMO also has a minor contribution from the $4p_z$ orbital of iron and is thus mainly based on the ligand system. The e_{1g} BMOs arise from a combination of e_{1g} molecular orbitals of the ligand system and $3d_{xz}$ and $3d_{yz}$ orbitals of iron. The e_{1u} BMOs arise from a combination of e_{1u} molecular orbitals of the ligand and $4p_x$ and $4p_y$ orbitals of iron. Both the e_{1g} and e_{1u} types of BMOs are again based mainly on the ligand system since they have only

minor contributions from the metal orbitals. The a^*_{1g} MO has only a minor contribution from the a_{1g} MO of the ligand and can be considered mainly as a nonbonding molecular orbital (NBMO) of the metal. Its energy is approximately the same as that of the d_{z^2} orbital of the metal.

The molecular orbital energy level diagram for ferrocene is shown in Fig. 3. As can be seen from this figure, there is room for 18 electrons in BMOs and NBMOs of ferrocene. In terms of electron counting, these 18 electrons come from Fe^{II} ion (6 electrons) and two $C_5H_5^-$ anions (2×6=12 electrons).

The stability of $Fe(C_5H_5)_2$ with 18 electrons compared to $Co(C_5H_5)_2$ with 19 electrons and $Ni(C_5H_5)_2$ with 20 electrons can be explained as follows :

Cobaltocene and nickelocene have one and two electrons, respectively, in their ABMO whereas ferrocene has none. The electrons in ABMO are easier to remove (why ?) so that cobaltocene and nickelocene are easily oxidisable compared to ferrocene.

Similarly, chromocene, $Cr(C_5H_5)_2$, with 16 electrons and vanadocene, $V(C_5H_5)_2$, with 15 electrons have unfilled BMO–NBMO set with the result that these systems can easily get reduced by accepting two and three electrons, respectively.

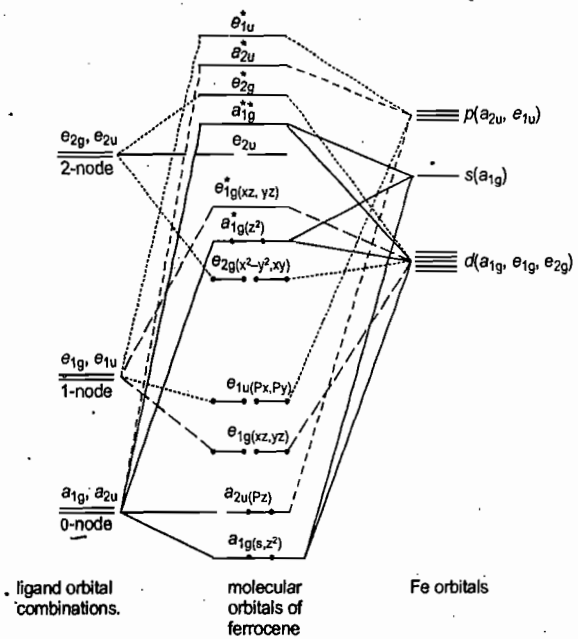


Fig. 3. The molecular orbital energy level diagram of ferrocene.

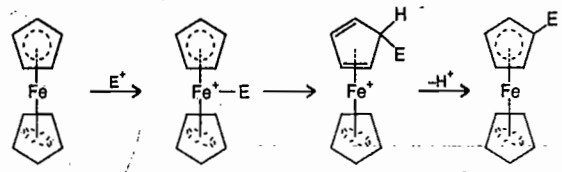
Aromatic Character of Ferrocene. Ferrocene cannot be hydrogenated under normal conditions nor does it undergo the Diels–Alder reaction which is a characteristic property of conjugated dienes. This shows that the $C_5H_5^-$ rings in ferrocene behave as aromatic systems. This is supported by the fact that ferrocene has π delocalised MOs similar to the ones in aromatic systems. Ferrocene, therefore, gives almost all the reactions which are typical of aromatic systems.

Reactions of Ferrocene. Reactions of ferrocene can be divided into two groups : ***A.*** *Reactions of the C_5H_5 rings.* ***B.*** *Reactions involving interaction of Fe atom with ring substituents.*

A. Reactions of C_5H_5 Rings. Aromatic Properties. These include ***electrophilic substitution reactions*** (such as nitration, halogenation and other related reactions) and **Friedel-Crafts reactions** (such as acylation, alkylation and other related reactions).

Electrophilic Substitution Reactions. The mechanism of electrophilic substitution reactions in ferrocene is illustrated below.

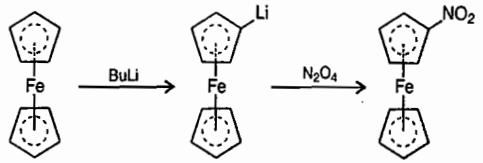
The attacking electrophile E^+ first interacts with Fe atom to give a π diene cationic intermediate which then loses a proton to give the final product, as shown:



This mechanism explains why the rate of electrophilic substitution in ferrocene derivatives is proportional to the ease of oxidation of Fe atom.

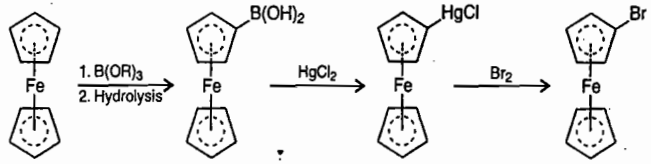
Nitration and Halogenation. Direct nitration and halogenation leads to the decomposition of ferrocene. The processes are, therefore, carried out indirectly as described below :

Nitration :

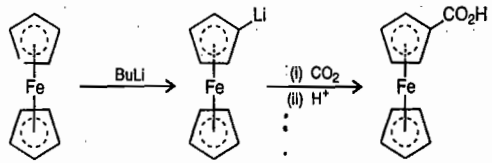


Nitroferrocene on reduction with Pd/HCl gives amino ferrocene.

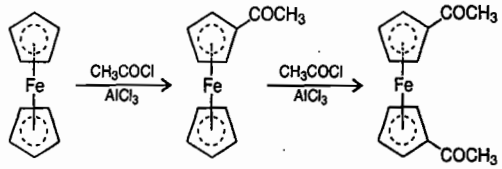
Bromination :



Carboxyllation. Ferrocene can also be carboxyllated as shown below :

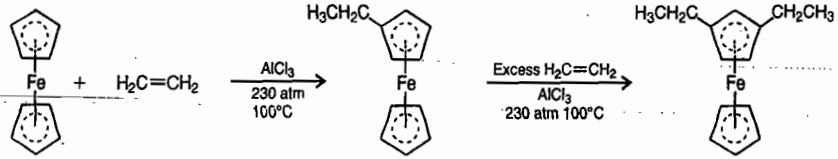


Friedel-Crafts Reaction. Ferrocene readily undergoes acylation as illustrated below :



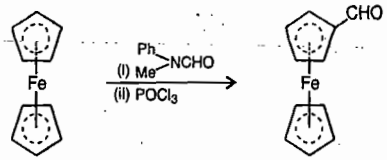
Ferrocene can also be **alkylated** in a similar manner.

Alkylation of ferrocene can also be carried out as shown below :

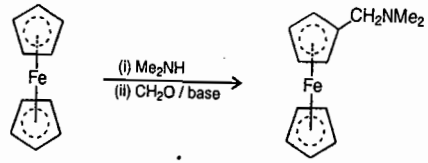


Since the presence of an alkyl group increases the electron density on the $C_5H_5^-$ ring, hence, in the presence of excess of the ligand, the disubstitution of alkyl group also occurs in the same ring, as shown above.

Vilsmeir Reaction. Ferrocene undergoes Vilsmeir reaction to yield ferrocene carboxyaldehyde which is a useful starting material for the preparation of other ferrocene derivatives.

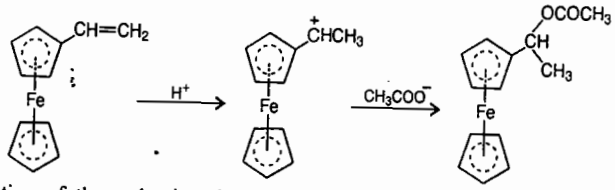


Mannich condensation. Ferrocene also undergoes Mannich condensation as shown.

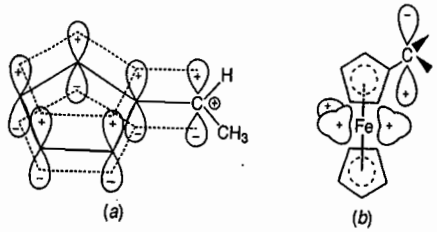


The Vilsmeir reaction and the Mannich condensation are reactions which are shown by those aromatic systems that are more reactive than benzene. It follows, therefore, that ferrocene is more aromatic than benzene.

B. Interaction of Fe Atom with Ring Substituents. α-Carbonium Ion Stabilisation. Ring substituted ferrocene reacts with acetic acid through the formation of a stable α-carbonium ion (intermediate) as shown :



The stabilisation of the carbonium ion can be attributed to either the delocalisation of the ring π electrons upto the vacant *p* orbital of the α-carbonium ion of the same symmetry, as shown in (*a*) or to a direct interaction between lone orbitals of iron of proper symmetry and the *p* orbital of the carbonium ion, as shown in (*b*). According to one view, both the above factors contribute towards the stabilisation of the carbonium ion.



Preparation. Ferrocene can be prepared by several methods, some of which are described below.

1. By the reaction of Fe (III) salts with appropriate Grignard reagent. Fe (III) is first reduced by the Grignard reagent to Fe (II) which then reacts to form ferrocene.

2. By the reaction of iron with cyclopentadiene in the presence of R_3NH^+Cl.

(*i*) $Fe + 2R_3NH^+Cl^- \longrightarrow FeCl_2 + 2R_3N + H_2$

(*ii*) $FeCl_2 + \underset{\text{Cyclopentadiene}}{2C_5H_6} + 2R_3N \longrightarrow Fe(C_5H_5)_2 + 2R_3NH^+Cl^-$

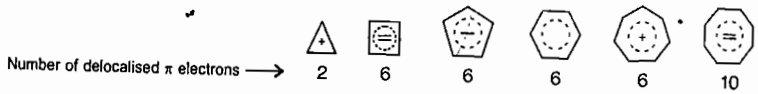
Net reaction : $Fe + 2C_5H_6 \longrightarrow Fe(C_5H_5)_2 + H_2$

Ferrocene forms orange red crystals which melt at 174°C. The compound is thermally stable upto 500°C.

Aromaticity of Cyclic C_nH_n Ligands

As discussed above, ferrocene exhibits a distinct aromatic character. In fact, not only ferrocene but all compounds containing carbocyclic ligands which obey **Huckel rule,** exhibit aromatic character. According to this rule, a carbocyclic species would *exhibit aromatic character if it contains* (4n + 2) *π electrons in a delocalised state.* This is also known as **4n + 2 rule** (n being zero or any integer like 1, 2, etc).

Thus, according to **4n + 2 rule,** the carbocyclic species which contains 4×0 + 2, *i.e.,* 2 ; 4×1 + 2, *i.e.,* 6 or 4×2 + 2, *i.e.,* 10 π electrons in the delocalised state will exhibit aromatic character. Accordingly, all the cyclic species given below exhibit aromaticity since they obey the 4n + 2 rule.



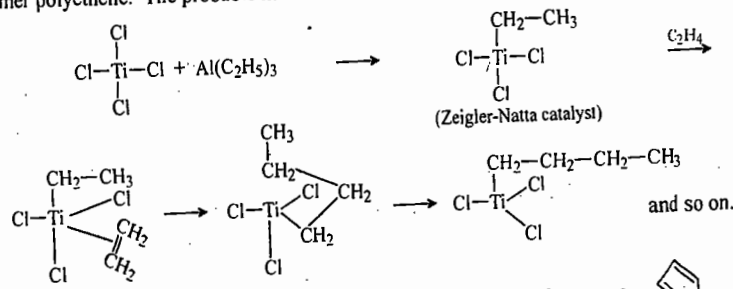
Another essential condition for species to exhibit aromatic character is that they should have *planar structures* which should be retained in the complexes derived from these species. In ferrocene, the two C_5H_5 rings have planar structures and they obey the Huckel rule. Ferrocene, therefore, exhibits distinct aromatic character like benzene.

Since the number of delocalised electrons in ferrocene, consisting of the delocalised electrons of the two C_5H_5 rings and the valence electrons of iron (II), is much larger than in benzene, the former is much more reactive towards electrophilic substitutions than the latter.

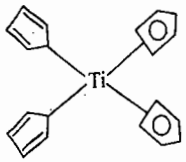
VI. SOME OTHER ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS

In addition to the organometallic compounds of transition metals already discussed above, some other organometallic compounds are also of interest. These are described below.

Organometallic Compounds of Titanium. When $TiCl_4$ is added to $Al(C_2H_5)_3$ in hexane, it yields a brown solid known as **Ziegler–Natta catalyst** which is employed in the conversion of ethene to straight chain polymer polyethene. The probable mechanism is as follows :

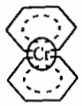


Several stable cyclopentadienyls, such as $[Ti(\eta^5\text{-}(C_5H_5)_2(CO)_2]$, $Ti(\eta^5\text{-}C_5H_5)_2]$, etc., are known. More interesting are the compounds in which Ti is attached to four C_5H_5 rings, as shown:



Some alkyls and aryls of Ti are also known but these are quite unstable.

Organometallic Compounds of Chromium. An important organometallic compound of chromium is dibenzene chromium, $Cr(C_6H_6)_2$, which is a 'sandwich' compound like ferrocene. The Cr atom in this compound is sandwiched between the two parallel benzene rings as shown:



In $Cr(CO)_6$, the metal is present in zero oxidation state. Similarly, in dibenzene chromium, $Cr(C_6H_6)_2$, the metal is present in zero oxidation state. This compound is prepared as follows :

$$3CrCl_3 + 6C_6H_6 + 2Al + AlCl_3 \longrightarrow 3[Cr(\eta^6\text{-}C_6H_6)_2]^+[AlCl_4]^-$$

$$2[Cr(\eta^6\text{-}C_6H_6)_2]^+[AlCl_4]^- + Na_2S_2O_4 + 4NaOH \longrightarrow 2[Cr(\eta^6\text{-}C_6H_6)_2] + 2Na_2SO_3 + 2NaCl + 2AlCl_3 + 2H_2O$$

A similar $\eta^5\text{-}C_5H_5$ complex of Cr(0) is also known.

Organometallic Compounds of Nioblum and Tantalum. Nb and Ta form a number of organometallic compounds with cyclopentadienyl group. Some of these compounds are $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)_2]$, $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$, $[Nb(\eta^5\text{-}C_5H_5)_2Cl_3]$ and $[Ta(\eta^5\text{-}C_5H_5)_2Cl_2]$.

Organometallic Compounds of Molybdenum. A number of organometallic compounds of Mo are known, of which dibenzene molybdenum cation $[(C_6H_6)_2Mo]^+$, having Mo in +1 oxidation state, is important from structural point of view. It is also a 'sandwich' cation having structure similar to dibenzene chromium.

Organometallic Compounds of Palladium. $PdCl_2$ and K_2PdCl_4 react with alkenes to produce complexes of the type $[PdCl_3(C_2H_4)]^-$, $Pd[Cl_2(C_2H_4)_2]$, etc. The Pd–alkene bonding in these complexes is unique in the

sense that alkene acts both as s donor through its filled pi bonding orbitals and pi acceptor through its vacant pi antibonding orbital, the structure of $[PdCl_3(C_2H_4)]^-$ being similar to that of $[PtCl_3(C_2H_4)]^-$. The reactions involving $PdCl_2$ and alkenes are of great commercial importance, as is evident from the following reactions :

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow \underset{\text{Ethanal}}{CH_3CHO} + Pd + 2HCl$$

$$C_2H_4 + CO + H_2 \xrightarrow{PdCl_2} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

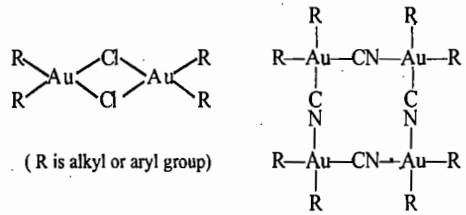
These reactions proceed through the organometallic intermediates which contain Pd–alkene bond.

Organometallic Compounds of Silver. When an alkene is made to react with heated AgCl, it forms an organometallic compound.

$$AgCl + C_2H_4 \xrightarrow{\Delta} Ag(C_2H_4)Cl$$

The structure contains a Ag–alkene bond which is similar to Pd – olefin bond in $[PdCl_2(C_2H_4)_2]$ and $[PdCl_3(C_2H_4)]^-$.

Organometallic Compounds of Platinum. Platinum forms a number of organometallic compounds. The first organometallic compound was reported way back in 1825. It is known as **Zeis's salt** and has the formula $K[Pt(C_2H_4)Cl_3].H_2O$. In this compound, C_2H_4 acts as σ donor and pi acceptor to Pt(II) with the result that C_2H_4 ligates perpendicularly to the plane containing Pt^{2+} and three Cl^- ions. The Zeis's salt is commercially employed as a catalyst in the synthesis of a number of organic compounds.



(R is alkyl or aryl group)

Organometallic Compounds of Gold. A number of organometallic compounds of gold are also known. These contain strong Au–C bonds in their structures. The structures of two of these compounds are as shown :

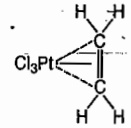
Classification of Ligands in Organometallic Compounds

The ligands in organometallic compounds can be classified in two ways :

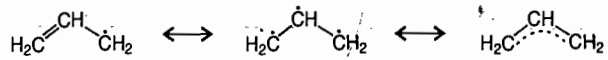
A. Classification based on the number of carbon atoms through which the ligand is attached to the metal atom. Most of the organometallic compounds can be considered as a special class of coordination compounds containing M—C bonds. The organic groups attached with the metal atom can thus be referred to as **organic ligands** as well. *The number of carbon atoms through which an organic ligand is attached or associated with a metal atom is known as the* **hapticity** *of that ligand.* It is represented by the symbol η^n where n is the number of carbon atoms of the ligand attached with the metal. The ligands may thus be classified as follows.

1. Monohapto ligands (designated as η^1). The organic ligands which are attached with the metal through *one carbon atom only* are called monohapto ligands. Examples are : C_2H_5-Mg-X, $(CH_3)_4Pb$ and $(C_6H_5)_3P$ in which C_2H_5, CH_3 and C_6H_5 act as monohapto ligands.

2. Dihapto ligands (designated as η^2). The ligands which are attached to the metal through *two carbon atoms* are called **dihapto ligands**. For example, in the complex shown, C_2H_4 acts as a dihapto ligand. The two dotted lines represent association of the two carbon atoms with the metal (platinum).

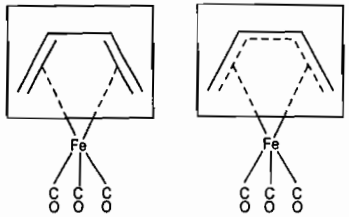


3. Trihapto ligands (designated as η^3). The allylic radical has three π electrons which are completely delocalised over all the three carbon atoms, as shown below :



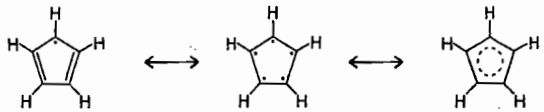
The allylic group is bound with the metal through a completely delocalised π bonding molecular orbital meaning thereby that all the three carbon atoms are equally associated with the metal, as happens in the case of bis(allyl) nickel.

It may, however, be remembered that allylic group can also act as a monohapto (η^1) ligand as in allyl magnesium bromide ($CH_2{=}CH{-}CH_2{-}Mg{-}Br$).

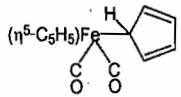


4. Tetrahapto ligands (designated as η^4). The conjugated dienes such as butadiene and alkyl substituted butadienes act as tetrahapto ligands as in butadiene tricarbonyl iron. The bonding between diene and Fe occurs through the delocalized π molecular orbitals of the ligand and the orbitals of iron. Thus the iron atom gets equally associated with the four carbon atoms of the ligand, as shown.

5. Pentahapto ligands (designated as η^5). The cyclopentadienyl radical represented by the structure

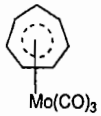


can combine with the metal through its π bonding molecular orbitals which are completely delocalised over all the carbon atoms of the 5-membered ring. In this way, the C_5H_5 group acts as a pentahapto group. The best example is provided by ferrocene. In this compound, as already discussed, the two C_5H_5 rings are parallel to each other with iron atom 'sandwiched' between the two rings. The overall symmetry is D_{5d} since the two parallel rings are present in the staggered conformation. All the carbon atoms of the C_5H_5 ring are equally associated with iron atom. It may be noted, however, that the C_5H_5 ligand can also act as a monohapto (η^1) ligand as it does in the compound shown.



6. Hexahapto ligands (designated as η^6). The benzene ring in dibenzene chromium, $(C_6H_6)_2Cr$, acts as a hexahapto ligand. The two benzene rings are parallel and in the eclipsed form. The bonding occurs through the metal orbital and the completely delocalised π bonding molecular orbitals of benzene rings as shown. Evidently, all the carbon atoms are equally associated with the metal atom.

7. Heptahapto ligands (designated as η^7). Cycloheptatrienyl group (tropilium group) acts as a η^7 ligand in tricarbonyl cycloheptatrienyl molybdenum. All the seven carbon atoms are equally associated with Mo since the bonding of the ligand occurs through the completely delocalised π molecular orbitals of the ligand.



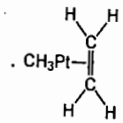
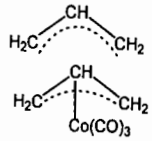
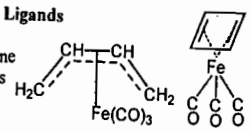
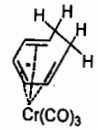
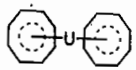
8. Octahapto ligands (designated as η^8). Cyclooctatetraene forms organometallic compounds with uranium metal. As in other polyhapto closed ring ligands, all the eight carbon atoms of the ligand are equally associated with the metal.

As already illustrated, a polyhapto ligand may have a particular hapiticity in one organometallic compound while it may have a different hapiticity in some other organometallic compound. Therefore, while specifying the hapiticity of a particular ligand, it is essential to mention the organometallic compound in which that ligand is present.

B. Classification based on the number of electrons contributed by the ligand for carbon–ligand bonding. Table 1 presents examples of different classes of ligands based on this classification.

TABLE 1

Classification of Ligands on the Basis of the Number of Electrons Contributed by the Ligand for the Metal-Carbon Bond.

Classes of Ligands with Examples	
1. One-electron Ligands CH_3 in $CH_3{-}Mg{-}Br$; C_6H_5 in $(C_6H_5)_3As$; $CH_2{=}CH{-}CH_2$ in $CH_2{=}CH{-}CH_2{-}Mg{-}Br$	**2. Two-electron Ligands** Alkanes in para alkenyl organometallics such as 
3. Three-electron Ligands Allyl group in  and para allylic organometallics such as	**4. Four-electron Ligands** Butadiene in para butadiene organometallics such as 
5. Five-electron Ligands Cyclopentadienyl group in para cyclo pentadienyl organometallics such as	**6. Six-electron Ligands** Cyclooctatriene in para cyclooctatriene organometallics such as 
7. Seven-electron Ligands Tropilium (or cyclo heptatrienyl) group in para tropilium organometallics such as	**8. Eight-electron Ligands** Cyclooctatetraene in para cyclo-octatetraene organometallics such as 

It may, however, be kept in mind that the number of electrons contributed by a polyelectron ligand to form an M–C bond in a particular case may be *less than the maximum number of electrons* which that ligand can contribute.

Inert Gas Rule or 18-Electron Rule. *A complex in which the central metal atom appears to have acquired the configuration of an inert gas by transference or by sharing of electrons tends to be* **more stable.** This generalisation is known as **inert gas rule**. The total number of electrons which the metal atom appears to have around itself in the complex, is called the **effective atomic number** (EAN) of the metal in that complex.

According to the inert gas rule (also called **EAN rule**), the effective number of electrons in the (n–1)*d*, n*s* and n*p* orbitals of a transition metal in its complex compound should be equal to 10 + 2 + 6 = 18. This implies that the total number of electrons acquired by the metal through covalent or coordinate bonding with the ligands plus the number of original electrons in (n–1)*d*, n*s* and n*p* orbitals of the metal prior to its complexation should be equal to 18 in any of the stable complexes of the metal. This statement derived from the inert gas rule is known as **18–electron rule**. In transition metal complexes, the inner (n–1)*d* orbitals also actively participate in chemical bonding. Thus, these orbitals alongwith n*s* and n*p* orbitals constitute the valence shell of a transition metal.

It is to be kept in mind that the EAN or 18–electron rule is not universally valid. If it were so, then each metal in any particular oxidation state would always have a unique coordination number. This is contrary to experimental observations. Nevertheless, the rule is still helpful in rationalising coordination numbers and studying structures of simple metal carbonyls and organometallic compounds, as would be shown a little later in this chapter.

Counting of the effective number of electrons. *The effective number of electrons in the valency shell (i.e., in (n–1)d, ns and np orbitals) of the metal in a given complex are counted by following the procedure given below.*

1. Count the number of electrons in the valency shell of the free metal atom (the valency shell includes the (n–1)*d* orbitals as well). Add or subtract electrons according as the charge on the metal in the complex is positive or negative.

2. Check the number of electrons which the organic ligands formally contribute to the valency shell of the atom in accordance with the classification of ligands already given (cf. Table 1). CO is treated as a special ligand. Each terminal CO contributes *two* electrons and each bridging CO contributes *only one* electron to the valency shell of the metal atom.

3. Check the number of electrons donated to the valency shell of the atom by the conventional ligands present in the complex.

4. Check the number of electrons formally contributed to the valency shell of the metal by the metal–metal bonds. Each metal–metal bond contributes *one* electron to the valency shell of the metal in the complex.

Summation of the number of electrons checked in steps 1, 2, 3 and 4 would give the effective number of electrons in the valency shell of the atom in its complex.

The application of the above rules is illustrated in the case of various carbonyls in Table 2 and in the case of some mixed organometallic transition metal complexes in Table 3.

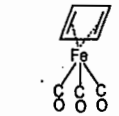
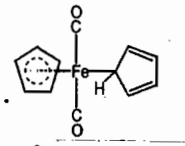
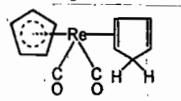
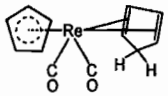
TABLE 2

Effective Number of Electrons in the Valency Shell of Central Metal in Various Metal Carbonyls

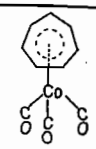
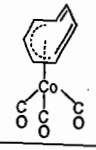
Metal Carbonyls	Number of electrons in valency shell of the free metal atom	Number of electrons contributed by the ligands	Number of electrons contributed by metal–metal bonds	Effective number of electron in valency shell of the metal
$Fe(CO)_5$	8	2×5 = 10	–	18
$Fe_2(CO)_9$ (contains 3 CO bridges and one M–M bond)	8	2×3 + 1×3 = 9	1	18
$Mo(CO)_6$	6	2×6 = 12	–	18
$V(CO)_6$ (paramagnetic)	5	2×6 = 12	–	17
$Mn_2(CO)_{10}$ (contains one M–M bond)	7	2×5 = 10	1	18

TABLE 3

Effective Number of Electrons in the Valency Shell of Central Metal Atom in Some Mixed Organometallic Compounds

Sr. No.	Organometallic compounds	No. of electrons in the valency shell of the free metal atom	No. of electrons contributed by the organic ligands	No. of electrons contributed by other ligands	Effective number of electrons in valency shell of the metal
1		8	4	2 × 3 = 6	18
2		8	5 + 1 = 6	2 × 2 = 4	18
3		7	5 + 2 = 7	2 × 2 = 4	18
4		7	5 + 4 = 9	2 × 2 = 4	20

(continued)

5		9	7	2 × 3 = 6	22
6		9	3	2 × 3 = 6	18

Assuming that the 18-electron rule is strictly obeyed, we can predict the structure of a complex from the effective number of electrons. For example, the complex η^5-C_5H_5-$Re(CO)_2C_5H_5$ can have two structures shown at serial numbers 3 and 4 in Table 3. Structure at serial number 3 which obeys the 18 electron rule should be the correct structure. This is actually so, as confirmed by the X-ray studies. Similarly, the structure of the complex $(\pi\text{-}C_7H_7)Co(CO)_3$ shown at serial number 6 should be the correct structure for this complex. This is actually so, as confirmed by the X-ray studies.

It may be noted that the 18-electron rule is specifically observed when the metal as well as the ligands have π bonding orbitals and the metal has more than half-filled *d* orbitals in its configuration.

The 18-electron rule is, however, not without exceptions. Thus, while the majority of metal carbonyls obey the rule, $V(CO)_6$ does not.

The Basis for the 18-Electron Rule. The 18-electron rule arises from the kinetic stability of a species which is associated with filled electron shells. The maximum use of valence orbitals which include (n–1)*d*, n*s* and n*p* orbitals of transition metals, also implies maximum number of bonding electrons and hence maximum stability. Fig 4 (*a*) shows a qualitative molecular orbital diagram for an octahedral complex of a transition metal considering only σ bonding between the metal and the ligand in *X*, *X'*; *Y*, *Y* and *Z*, *Z* directions.

The overlap of e_g orbitals (*viz.*, d_{z^2}, $d_{z^2-y^2}$ orbitals) of the metal with the σ orbital combinations of the same symmetry of the ligand gives e_g and e_g^* molecular orbitals. Similarly, p_x, p_y, p_z orbitals of the metal of t_{1u} symmetry overlap with σ orbital combination of the same symmetry of the ligands to give t_{1u} and t_{1u}^* molecular orbitals and *s* orbital of the metal of a_{1g} symmetry overlaps with σ orbital combination of a_{1g} symmetry of the ligands to give a_{1g} and a_{1g}^* molecular orbitals. The t_{2g} orbitals of the metal (*i.e.*, d_{xy}, d_{yz}, d_{xz}) do not combine with the orbitals of the ligand since there are no σ orbital combinations of the ligands having t_{2g} symmetry. Therefore, these t_{2g} orbitals would remain non-bonding.

It can be seen that, in all, 18 electrons are required to fill up all the bonding and non-bonding molecular orbitals (upto t_{2g} level) and the extent of bonding would be maximum when there are, in all, 18 electrons in the molecular orbitals including those present with the metal prior to its combining with the ligands. In case there are more than 18 electrons, some of them are bound to occupy antibonding molecular orbitals thereby reducing the bond order and destablising the complex.

If all the nine bonding and non-bonding molecular orbitals of a molecule are fully occupied and if there is a large energy gap (Δ) between the non-bonding (t^n_{2g}) molecular orbitals and the lowest energy antibonding molecular orbital (e_g^*), then the kinetic stability of such a molecule would be very high because (*i*) electrons from t^n_{2g} orbitals cannot be easily excited to e_g^* orbitals to initiate thermal decomposition of the complex (*ii*) the electrons of an attacking nucleophile cannot be accommodated easily in the high energy e_g^* molecular orbital.

It should be kept in mind that unless the energy gap (Δ) for the $t_{2g} \rightarrow e_g^*$ transition is high, the compound with even 18 effective electrons in the valency shell of the central metal atom would not be stable.

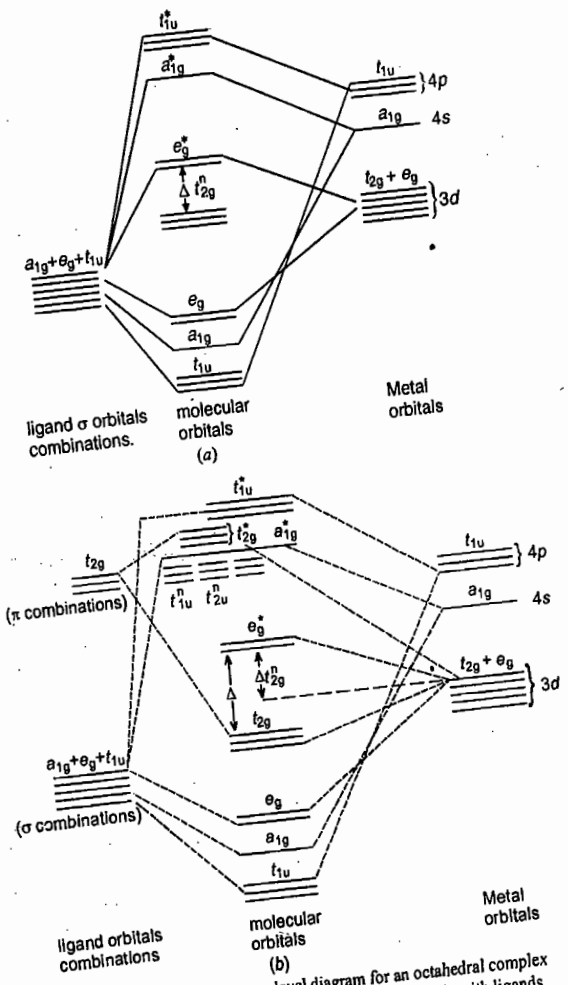


Fig. 4. Molecular orbital energy level diagram for an octahedral complex involving(*a*) only σ bonds (*b*) σ as well as π bonds with ligands having empty π orbitals.

Role of Pi Bonding Ligands in Stabilising the Complexes. Majority of complexes which obey 18-electron rule contain ligands such as CO, R_3P, alkenes, etc., which can get π bonded to the metal by back donation of electrons from the metal. This type of back donation removes the excess negative charge which gets accumulated on the metal due to σ donation of lone pairs of electrons of these ligands to the metal. Secondly, the π bonding ligands of this type, *i.e.*, the π-acceptor ligands, increase the energy gap (Δ) for $t_{2g} \rightarrow e_g^*$ transition so that neither the electron excitation from t_{2g} to e_g^* nor the accommodation of electrons from the attacking nucleophile in t_{2g} or e_g^* are favoured. In other words, the π bonding increases the kinetic as well as the thermal stability of the complexes (see Fig. 4*b*).

Explanation for exceptions to the 18-electron rule. As already mentioned, the 18-electron rule is not without exceptions. Thus, the d^8 square planar complexes have 16 effective electrons in their valency shells but they are stable. Similarly, the d^3 and d^6 octahedral complexes do not have effective 18 electrons

in their valency shells, yet they are stable. A probable explanation for these exceptions is discussed below.

1. d^8 square planar complexes. For a square planar complex, the splitting of *d* orbitals is as shown in Fig. 5.

The maximum bonding in d^8 square planar complexes occurs when the central metal has 8 electrons which can be accommodated in low energy d_{z^2}, d_{xz}, d_{yz} and d_{xy} orbitals.

The 9th electron shall have to be accommodated in the higher energy antibonding $d_{x^2-y^2}$ orbital. As is evident from Fig. 5, energy gap (Δ) for $d_{xy} \rightarrow d_{x^2-y^2}$ transition is quite large. Hence, accommodation of electrons from the attacking nucleophile in the antibonding $d_{x^2-y^2}$ orbital is energetically unfavourable. Consequently, the d^8 square planar complexes would be quite stable. In such complexes, the effective number of electrons = 8 + 2×4 = 16.

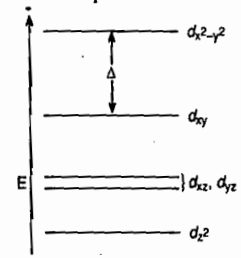


Fig. 5. The splitting of *d* orbitals in a square planar complex.

2. d^3 and d^6 octahedral complexes. In octahedral complexes of the metal with d^3 (or t_{2g}^3) configuration the charge distribution is spherically symmetrical around the metal atom so that there is no favoured direction of attack by a polar nucleophile. A similar situation exists for the octahedral complexes of the metal with d^6 (or t_{2g}^6) configuration. Both the types of octahedral complexes containing metals with t_{2g}^3 or t_{2g}^6 configuration are, therefore, quite stable although the effective number of electrons in the case of the metal having d^3 configuration in its octahedral complexes is 15 (*i.e.*, 3 + 2 × 6) and, therefore, the octahedral complexes of this metal do not observe the 18-electron or inert gas rule. The octahedral complexes of d^6 metal, however, do obey the 18-electron rule. This factor further enhances their stability. Important examples of d^3 and d^6 octahedral complexes are vitamin B_{12} and certain alkyl and aryl derivatives of Cr(III), Co(III), etc.

3. Metal carbonyls. As mentioned earlier, the paramagnetic $V(CO)_6$ complex does not obey the 18-electron rule whereas other paramagnetic species such as $Co(CO)_4$ dimerise to obey the 18-electron rule. This is probably because of the fact that the maximum coordination number of V atom is 6. It would have to change its coordination number from 6 to 7 for dimerisation into the species $(CO)_6V-V(CO)_6$ through the formation of a V—V bond. Since only six ligands can be accommodated comfortably around V atom, this type of increase in coordination number of V atom would put lot of steric strain on the $V(CO)_6$ moity and would thus make the dimer unstable. In contrast, coordination number of Co in $Co(CO)_4$ moity is 4 whereas its normal coordination number is 6. Hence, no additional strain would be created by increasing the coordination number of Co from 4 to 5 during the dimerisation of this moity through a Co—Co bond. Therefore, the dimer $[Co(CO)_4]_2$ would be stable.

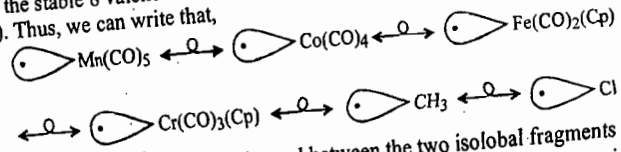
Concept of Isolobality and Isolobal Analogies

The concept of isolobality is the outcome of the attempts to draw an anology between the Lewis octet rule applicable to main group chemistry (specially organic chemistry) and the 18-electron rule applicable to transition metal organometallic chemistry. The concept was developed by Dahl, Mingos, Hoffman and coworkers. According to the isolobality concept, *if the two sets of frontier orbitals belonging to two different molecular fragments are the same in number, symmetry and shapes, the two molecular fragments are called* **isolobal fragments**. *The orbitals whose similarity is important in determining the isolobality of the molecular fragment are called* **frontier orbitals.**

Let us consider a few examples of isolobal organometallic and main group fragments.

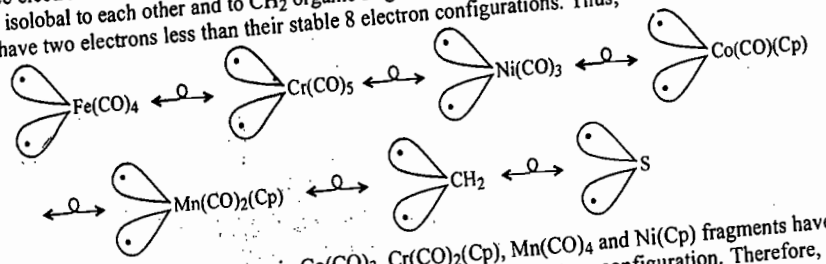
1. It can be easily calculated that Mn in $Mn(CO)_5$, Co in $Co(CO)_4$, Fe in $Fe(CO)_2Cp$ and Cr in $Cr(CO)_3Cp$ have a 17 valence electron configuration which is one electron short of the stable 18 valence electron configuration of the transition metal atoms in their organometallic compounds. Cp designates pentavalent carbon fragment implying that the fragment contributes five electrons towards the valence shell configuration of the metal ion. All the above mentioned organometallic fragments are isolobal with CH_3 fragment and Cl. Both C in CH_3 and Cl have seven valence electron configurations having one

electron less than the stable 8 valence electron configuration of the main group elements in their compounds (Lewis octet rule). Thus, we can write that,

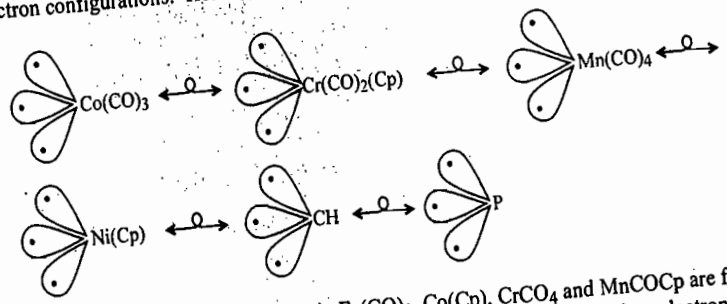


(In some of the books, the sign ↔ is used between the two isolobal fragments instead of the sign ↔ used in this book). The lobes of main group fragments are shown by considering the full sp^3 hybridisation of the valence orbitals of the main group element. All the above mentioned isolobal fragments have one unpaired electron in the hybrid orbital of central atom.

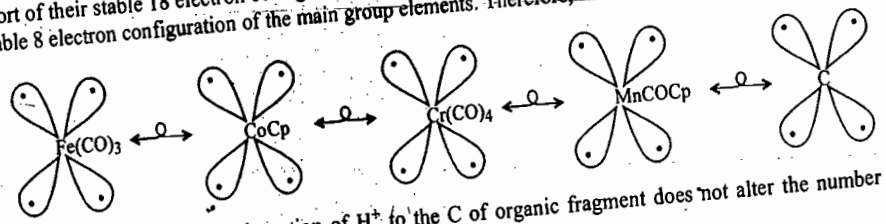
2. Each transition metal atom in $Fe(CO)_4$, $Cr(CO)_5$, $Ni(CO)_3$, $Co(CO)(Cp)$ and $Mn(CO)_2(Cp)$ has 16 valence electrons which is two electrons less than its stable 18 valence electron configuration. So, these are all isolobal to each other and to CH_2 organic fragment as well as S atom. Both C in CH_2 fragment and S atom have two electrons less than their stable 8 electron configurations. Thus,



3. Each transition metal atom in $Co(CO)_3$, $Cr(CO)_2(Cp)$, $Mn(CO)_4$ and $Ni(Cp)$ fragments have three electrons less in its valence orbitals than the stable 18 valence electron configuration. Therefore, all the above mentioned fragments are isolobal with each other and with CH fragment as well as with P atom. Both C in CH fragment and the P atom have also three electrons less in their valence orbital than their stable 8 electron configurations. Hence,

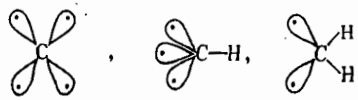


4. Similarly, the transition metal atoms in $Fe(CO)_3$, $Co(Cp)$, $CrCO_4$ and $MnCOCp$ are four electrons short of their stable 18 electron configurations. The uncombined C atom is also four electrons short of the stable 8 electron configuration of the main group elements. Therefore,

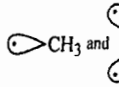


Since the addition or subtraction of H^+ to the C of organic fragment does not alter the number of

valence electrons with the C, the species CH^+, CH_2^+, CH_3^+ are considered to be the same as



fragments, respectively. Similarly, CH_2^- and CH^- are considered to be the same as



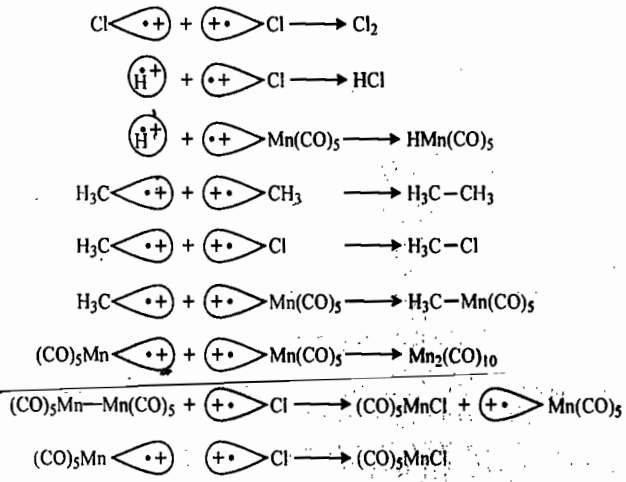
, respectively.

The isolability also occurs within the molecular fragments of the main group elements. For example, BH and CH fragments are isolobal, each containing three frontier sp^3 hybrid orbitals as shown

Three frontier sp^3 hybrid orbitals containing three unpaired electrons | Three frontier sp^3 hybrid orbitals containing two unpaired electrons

(+ and – are the geometric signs of the lobes)

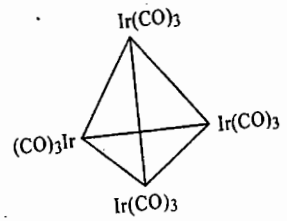
This is the reason why BH fragments are replacable with C–H fragments in polymeric boranes to give isostructural carboranes. This, in general, is true of the other isolobal fragments also. Apart from this, the two isolobal fragments combine with each other to give stable molecules. Some of the reactions of isolobal fragments are given below.

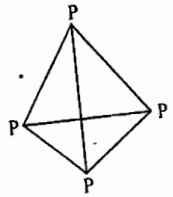


It is not necessary that the properties of the products obtained by combining isolobal fragments of main group fragments should be similar to the properties of the products obtained by combining transition metal fragments. Thus, $HMn(CO)_5$ is only weakly acidic compared to HCl although H, $Mn(CO)_5$ and Cl are all isolobal fragments. The chemical properties of the products, in fact, depend on the electronegativity difference of the combining isolobal fragments in the two cases mentioned above.

The isolobal fragments, upon polymerisation, generally give isostructural molecules.

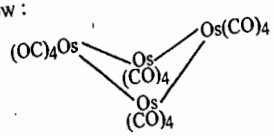
The structures of $Ir_4(CO)_{12}$ and P_4 are given below :

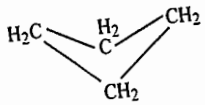




We observe that in the first structure, each $Ir(CO)_3$ group is tetrahedrally linked to three other similar groups. The same is true of the second structure where each P atom is tetrahedrally linked with three other P atoms. This is because $Ir(CO)_3$ group, in which valence orbitals of Ir are three electrons short of the stable 18 electron configuration of transition metals, is isolobal with P atom which is also three electrons short of the stable 8 electron configuration, of main group elements. Since both $Ir(CO)_3$ and P are isolobal with each other, these polymerise in a similar manner to give isostructural $[Ir(CO)_3]_4$ or $Ir_4(CO)_{12}$ and P_4

Similarly, CH_2 fragment and $Os(CO)_4$ fragment are isolobal with each other because the C in former fragment is two electrons short of the stable 8 electron configuration of main group elements and the Os in the latter fragment is also 2 electron short of the stable 18 electron configuration of the transition elements. Therefore, the polymerisation of the two fragments give isostructural $(CH_2)_4$ and $[Os(CO)_4]_4$ whose structures are given below :





The concept of isolobality is also important in rationalising the reactions of organometallic compounds.

Nomenclature of Organometallic Compounds

Most of the organometallic compounds are coordination compounds containing one or more ligands attached to the metal M through M—C bonds. The rules governing their nomenclature are, therefore, similar to those used for naming the coordination compounds described in Chapter 26. In the case of organometallic compounds, the following **additional rules** are also observed :

1. The ligands (without the prefixes, mono, di, tri, etc.) are named in the alphabetical order irrespective of the charge on them.

2. The presence of hydrocarbon ligands in the coordination sphere is customarily indicated by the names of their radicals (such as methyl, ethyl, phenyl, etc.) although these are known to behave as anions in several cases. Thus, according to this rule :

$K[B(C_6H_5)_4]$ is named as potassium tetraphenylborate (III)

$K[SbCl_5(C_6H_5)]$ is named as potassium pentachloro(phenyl)antimonate (V)

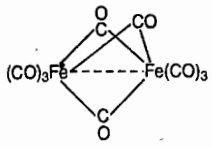
$K_3[Fe(CN)_5CO]$ is named as potassium carbonylpentacyanoferrate (II)

$K[PtCl_3C_2H_4]$, is named as potassium trichloro(ethene) platinate (II).

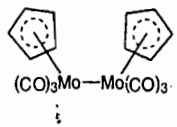
3. In the case of unsaturated molecules or groups (*i.e.*, those containing more than one, generally

conjugated double bond), the ligand is named with the prefix η^n where η^n is the number of carbon atoms in the organic ligand attached to the metal). When some (but not all) ligand atoms involved in double bonds or some (but not all) ligand atoms in a chain or ring are bound to the central atom, numerals indicating these ligand atoms are inserted preceding η^n. Some common examples are given below :

Structures :



(1)



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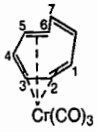

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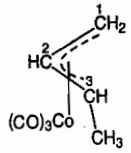

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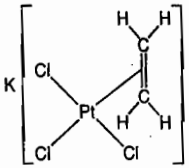
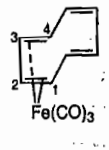


(5)



(6)

Names :

(1) Tri(μ carbonyl)bis(tricarbonyl) diiron.

(2) Bis[tricarbonyl)(η^5-cyclopentadienyl)]dimolybdenum

(3) Tricarbonyl(1-6η^6-cyclooctatetraene)chromium

(4) Tricarbonyl(1-3η^3-2-butenyl)cobalt

(5) Potassium trichloro(η^2-ethene)platinate(II)

(6) Tricarbonyl(1-4η^4-cyclooctatetraene) iron

QUESTIONS

1. (*a*) What are organometallic compounds ? How are they classified ?

   (*b*) What does the term 'metal' signify in organometallic compounds ? What are simple and mixed organometallic compounds ? Which of the following can be categorised as organometallic compounds and why :

   Metal cyanides, metal carbonates, metal aryls, metal carbonyls, metal cyclopentadienyls, metal thiocyanates.

2. Discuss the main features of ionic organometallic compounds. What type of organometllic compounds would have the maximum ionic character ? Why are the alkali metal alkyls more reactive than the alkali metal alkynyls and allyls ?

3. What type of transition state is formed during the hydrolysis of $(CH_3)_2Zn$? Comment on the relative rates of hydrolysis of $(CH_3)_2Mg$, $(CH_3)_2Zn$ and $(CH_3)_2Hg$.

4. Discuss the structures of $(CH_3)_3Ga$, $(CH_3)_3In$ and $(CH_3)_3Al$. What factors are possibly responsible for the difference in the structures of these compounds.

5. 'Si, Ge, Sn and Pb have nearly the same value of electronegativity *viz.*, 1·8. However, the rates of hydrolysis of their tetraalkyls are not the same.' why is it so ?

6. 'Although trialkyl phosphines, arsines and stibines are weak σ donors, yet they form kinetically stable complexes with transition metal ions.' Why is it so ?

7. Why are the alkyls of transition metals kinctically less stable than the alkyls of main group elements ?

8. Predict which would be more stable and why ?

   (*a*) $[Ph\text{-}CH_2\text{-}Rh(NH_3)_4Cl]^+$ or $[CH_3CH_2Rh(NH_3)_4Cl]^+$ (*b*) $[(NH_3)_5RhCH_2CH_2Ph]_2^+$ or $[(NH_3)_4ClRhCH_2CH_3]^+$.

9. (*a*) Why are the transition metal aryls more stable than the transition metal alkyls ?

   (*b*) Why are the transition metal alkyls less stable than transition metal alkynyls ?

10. (*a*) What spectroscopic evidence in your opinion is the best to demonstrate π back bonding in transition metal alkenyls and alkynyls ?

    (*b*) What are ylides ? Discuss the structure of $Ph(OCH_3)C{=}M(CO)_5$.

11. Why are multi centre organometallic compounds sometimes called non-classically bonded compounds ? Discuss the structures of $Li(CH_3)_4$ and $[Be(CH_3)_2]_n$
12. Explain the following observations :
    (a) Aluminium trimethyl is dimeric in solution as well as in vapour phase.
    (b) Aluminium tripropyl is dimeric in solution but monomeric in vapour phase.
    (c) Aluminium triphenyl is dimeric in solution as well as in vapour phase.
13. How would an alkyl and an aryl group form a bridge between two aluminium atoms in dimeric aluminium trialkyls and dimeric aluminium triaryls ?
14. What is a fluxional molecule ? Discuss the structure of one such molecule.
15. Discuss the bonding in π–metal olefin and π–metal acetylene complexes. How is the bonding in these complexes different from the one in σ–metal olefin and σ–metal acetylene complexes ?
16. Give an example in which a highly unstable cyclic hydrocarbon is stabilised by π bonding with the metal.
17. Discuss the bonding in ferrocene. Explain on the basis of the molecular orbital energy level diagram the cause for kinetic stability of ferrocene.
18. Check the signs of ψs and ψ's in all the ten ligand orbital combinations of the two–$C_5H_5^-$ ring ligand system' on the basis of the sign convention given in the text.
19. Describe various reactions of ferrocene which establish its aromatic character. How can you say that aromaticity of ferrocene is more even than that of benzene.
20. Discuss in details the properties of ferrocene which can be ascribed to the presence of (i) $C_5H_5^-$ rings and (ii) iron atom in the structure of ferrocene.
21. What is meant by hapticity of a ligand ? How is it designated ? Show clearly that the hapticity of a ligand varies from one organometallic compound to another.
22. Give examples where cyclopentadienyl group acts as a one-electron as well as a five electron ligand.
23. Discuss the 18–Electron Rule. Apply this rule to calculate effective atomic number of the metal in each of the following complexes :
    $[(C_2H_4)Fe(CO)_3]$, $[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)_2]$, $[\eta^5\text{-}C_5H_5Re\ \eta^2C_5H_5]$
24. Discuss carefully the theoretical basis of the 18–Electron Rule. Does this rule apply for high-spin organometallic octahedral complexes ? If not, why ?
25. How does the presence of π–acceptor ligands increase the stability of octahedral complexes ?
26. Explain why square planar Ni(II) organometallic complexes are stable although they do not obey the 18–Electron Rule.
27. Why are Cr(III) octahedral organometallic complexes more stable than the similar Mn(III) and V(III) complexes.
28. How does the electronegativity of metal M influence the rate of hydrolysis of M—C bond in organometallic compounds ? Explain giving examples. Why does $Si(CH_3)_4$ undergo hydrolysis easily whereas $C(CH_3)_4$ does not ?
29. Name the following organometallic compounds :
    $[PtClBr(NH_3)(C_2H_4)]$, $Na[AsCl_5(CH_3)]$, $[ReH(C_5H_5)(CH_3)_2]$, $[C_8H_6Cl_2Fe(CO)(NO)_2]$, $[Mo(CO)_3C_5H_5]_2$.
30. Illustrate the concept of isolobality. What is the significance of this concept ? What are isolobal fragments and frontier orbitals?

35 INORGANIC POLYMERS

Inorganic polymers are giant molecules composed of atoms other than carbon. These atoms are linked together mainly by covalent bonds. Some common examples of inorganic polymers are :

Polyphosphazines, $\left(-\underset{R}{\overset{R}{P}}=N-\right)_n$; Polyphosphates, $\left(-\overset{O}{\overset{\|}{P}}(OR)-O-\overset{O}{\overset{\|}{P}}(OR)-O-\right)_n$; Polymeric sulphur nitride, $(SN)_n$; Polycarboranes, $\left(-\underset{R}{\overset{R}{Si}}-C(B_{10}H_{10})C-\underset{R}{\overset{R}{Si}}-\right)_n$; Silicones, $\left(-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\right)_n$ and a majority of silicate minerals.

General Properties of Inorganic Polymers

1. With a few exceptions (such as sulphur), inorganic polymers do not burn. They only soften or melt at high temperatures.

2. Inorganic polymers which have cross-linked structures with a high density of covalent bonds are generally stiffer and harder than the organic polymers.

3. The chain segments between cross links in polymers having cross-linked structures, are usually short and stiff. Consequently, these structures are not flexible enough to permit intercalation of solvent molecules. As a result there are very few inorganic polymers which swell reversibly imbibing solvent molecules.

4. Most of the inorganic polymers are built up of highly polar repeat units. These polymers would, therefore, dissolve only in polar solvents. Most of these polymers, however, react with the solvents. There are thus only a few inorganic polymers which actually dissolve in appropriate solvents.

5. Inorganic polymers are generally much less ductile than the organic polymers. Thus, while organic polymers such as polyethylene can extend by about 20 per cent or more before fracture, inorganic polymers break even when extended by about 10 per cent.

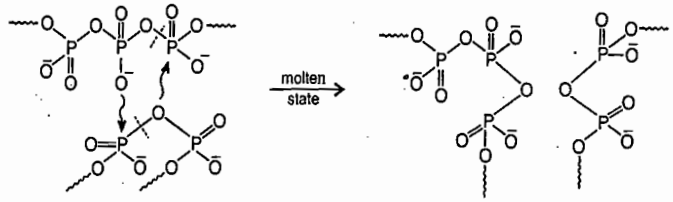
6. Inorganic polymers can usually be obtained in pure crystalline as well as in pure amorphous forms. Organic polymers, on the other hand, have structures which are partly crystalline and partly amorphous.

7. Inorganic polymers, in general, are stronger, harder and more brittle than the organic polymers.

Glass Transition Temperature, T_g. The glass transition temperature is defined as the temperature at which the internal energy of polymer molecules increases to such an extent that the chain segments of the polymer molecules are just ready to leave their lattice positions. At this temperature, the chain segments start moving past one another even if an infinitesimally small strain is applied to the polymer.

The glass transition temperature depends upon the chain length and the degree of cross-linking. It also depends upon the barrier restricting internal rotation round the chain links. Below the glass transition temperature, the chain segments of the polymer are 'frozen' on the lattice sites. The polymer in this condition is hard, invariably brittle and hence breakable like glass. Above the glass transition temperature,

the segments of the polymer begin to exhibit diffusional motion as do the molecules of a liquid. At temperatures sufficiently higher than T_g, the polymer is present in the molten state. In this state there is exchange of bonds between the atoms, as shown below in the case of a polyphosphate.



As can be seen, the above exchange reaction involves breaking of P–O bonds at some places and the formation of new P–O bonds at other places. This gives sufficient mobility to the chain segments of the polymer in the molten state.

The cross-linked inorganic polymers show a wide range in their glass transition temperatures. In this temperature range, they change from rigid solids to leathery solids, from leathery solids to rubbery solids and finally to highly viscous liquids.

The glass transition temperature of a linear polymer is fairly sharp. This is because the movement of chain segments from one site to another does not involve the exchange of bonds as happens in the case of cross linked inorganic polymers. The chains in a linear polymer are held together by weak van der Waals forces which are overcome by the supply of even a small amount of energy. Therefore, the energy required for the movement of chains in such polymers is small. Consequently, the glass transition temperature of a linear polymer is lower than that of a cross-linked polymer in which the movement of chain segments requires the breaking of bonds.

IMPORTANT INORGANIC POLYMERS

There is a very wide variety of inorganic polymers important amongst which are :

I. Phosphorus-based Polymers *II. Sulphur-based Polymers*

III. Boron-based Polymers *IV. Silicon-based Polymers* and

V. Coordination Polymers

The various types of polymers mentioned above have been described below in some details. But before this, it is important to mention that the type and the extent of association between the atoms in one polymer may be totally different from those in the other polymer. Therefore, the lines between the atoms in the structures of polymers signify only the association between the atoms and not the exact bond types or the bond orders.

I. PHOSPHORUS-BASED POLYMERS

The phosphorus-based polymers can be divided into two categories, *viz., the chain polymers* and *the network polymers,* depending upon the type of linkage involved between their atoms.

A. Phosphorus-Based Chain Polymers

These include polyphosphazines, polyphosphoryl halides, vitreous polyphosphates, crystalline polymetaphosphates, plasticised and flexible polyphosphates and polyphosphoric acids.

1. Polyphosphazines. These polymers have the general structure $\left(\begin{array}{c}R\\|\\P=N\\|\\R\end{array}\right)_n$ where R usually stands for Cl, OCH_3 and OC_2H_5. The polymers with R as Cl are known as polyphosphonitrilic chlorides and those

with R as OCH_3 and OC_2H_5 are, respectively, known as polydimethoxy and polydiethoxyphosphazines. These are discussed below.

Polyphosphonitrilic chlorides, $\left(\begin{array}{c}Cl\\|\\P=N\\|\\Cl\end{array}\right)_n$. These polymers constitute what is known as inorganic rubber. They exhibit high elasticity and can be stretched several-fold with almost complete recovery. However, they undergo degradation under normal atmospheric conditions more rapidly than do the organic rubbers. Hence these polymers do not find much commercial use.

Polyphosphonitrilic chlorides can be prepared as follows :

$$nPCl_5 + nNH_4Cl \xrightarrow{C_2H_2Cl_4} H\left(\begin{array}{c}Cl\\|\\P=N\\|\\Cl\end{array}\right)_{n-7}Cl + \underset{\text{Cyclic trimer}}{(PCl_2N)_3} + \underset{\text{Cyclic tetramer}}{(PCl_2N)_4} + (4n-1)HCl$$

The above reaction yields a mixture of cyclic trimers and tetramers along with a series of linear polymers. The linear polymerisation is terminated by H and Cl atoms.

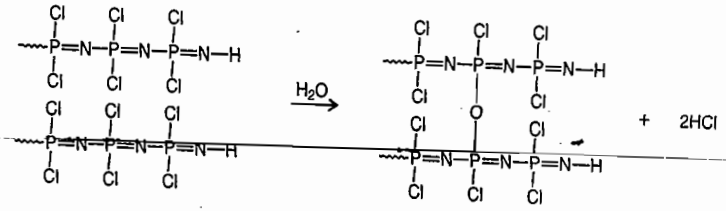
The cyclic trimer or tetramer when heated in vacuum at 250° C, changes into a chain polymer :

$$\underset{\text{Cyclic tetramer}}{n(PCl_2N)_4} \longrightarrow \underset{\text{Chain polymer}}{Cl\left(\begin{array}{c}Cl\\|\\P=N\\|\\Cl\end{array}\right)_{4n-4}Cl} + P_4 + 2N_2 + 3Cl_2$$

The resulting chain polymer is somewhat cross-linked and hence has limited solubility in inorganic solvents. Polyphosphonitrilic chloride is at least as good an elastomer as vulcanised rubber.

The freshly prepared polyphosphonitrilic chlorides are soluble in chloroform but insoluble in petroleum ether. When the solutions are allowed to stand, the polymers get cross-linked and slowly gel.

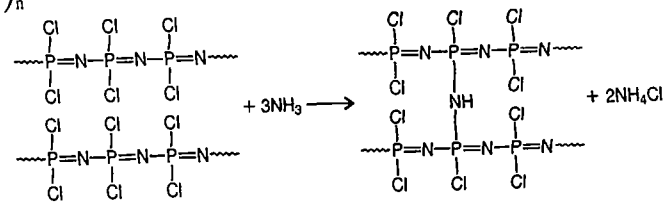
When samples of highly elastic inorganic rubber are stored in absence of air, there is no change in their elastic properties. However, storage in air makes the material brittle. This is due to the action of water in forming oxygen bridges between the chains so that there is reduction in average length of chain segments at lattice sites, as shown below.



The Cl atoms of the *polymerising units of chain polymers* $\left(\begin{array}{c}Cl\\|\\P=N\\|\\Cl\end{array}\right)_n^*$ *can be replaced by other substituents* such as OCH_3, OC_2H_5, etc. These substituted polyphosphazines are generally chain polymers. But,

*Chain terminating atoms are often omitted while writing the formulae of chain polymers.

when $\left(\begin{matrix}Cl\\|\\P=N\\|\\Cl\end{matrix}\right)_n$ reacts with ammonia it produces cross-linked polymers, as shown below :



Polydimethoxy and polydiethoxyphosphazines, $\left(\begin{matrix}OCH_3\\|\\P=N\\|\\OCH_3\end{matrix}\right)_n$, $\left(\begin{matrix}OC_2H_5\\|\\P=N\\|\\OC_2H_5\end{matrix}\right)_n$. Polydimethoxy and polydiethoxyphosphazines can be prepared by reacting phosphonitrilic chloride with sodium methoxide and sodium ethoxide, respectively, when the chlorine atoms get replaced by the alkoxy groups.

Polydimethoxy and polydiethoxyphosphazines are colourless, transparent film-forming thermoplasts. They are, however, unstable and when heated above 100°C, they slowly get converted into cyclic $[P(OR)_2N]_3$ and $[P(OR)_2N]_4$ polymers where R is CH_3 or C_2H_5.

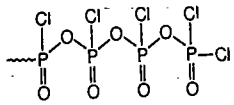
The polymer, $\left(\begin{matrix}OCH_2CF_3\\|\\P=N\\|\\OCH_2CF_3\end{matrix}\right)_n$, *viz.*, polydi(trifluoroethoxy) phosphazine, can be transformed into inflexible films and can also be spun into fibres. This polymer is crystalline upto its melting point, *i.e.*, 240°C. It is soluble in acetone, tetrahydrofuran, ethyl acetate, dimethyl ether, etc. It does not burn in air but starts decomposing at 150°C.

Polydiaryloxyphosphazines are more stable than the polydialkoxy phosphazines. Thus, polyphenylphenoxyphosphazine $\left(\begin{matrix}C_6H_5\\|\\P=N\\|\\OC_6H_5\end{matrix}\right)_n$ can be spun into fibres from melts at 225°C. The Young's modulus of the fibre is similar in magnitude to that of nylon.

All the polyphosphazines have a much lower electrical conductivity than the analogous carbon-based unsaturated polymers suggesting that pi bonds are not as delocalised in polyphosphazines as are the double bonds in carbon-based unsaturated polymers.

X-ray analysis of polyphosphazines depicts patterns which are typical of semicrystalline polymers. The chain repeat distance in these polymers is 4·9 Å which is hardly affected by the type or the size of the substituents present on P atoms.

Polyphosphoryl Chlorides. These polymers have the general formula $P_nO_{2n-1}Cl_{n+2}$ and have the general structure as shown.



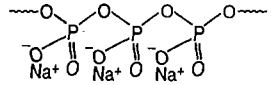
Preparation. Polyphosphoryl chlorides are prepared by reacting phosphorus oxychloride with phosphorus pentoxide.

$$(n+2)POCl_3 + (n-1)P_2O_5 \longrightarrow 3P_nO_{2n-1}Cl_{n+2}$$

The nature of the product depends upon the Cl/P ratio. The polymer obtained at Cl/P ratio of 1·1 is a clear amorphous mass exhibiting considerable elasticity. It can be flexed to a large extent without breaking.

Polyphosphoryl chlorides are strongly acidic being similar in properties to acid chlorides. In air, they give fumes of HCl due to their interaction with moisture. They act as good chlorinating agents in organic reactions.

Vitreous Polyphosphates (Phosphate Glasses). In vitreous polyphosphates, the charges on polyphosphate anions are neutralised by the charges on cations like Na^+, K^+, etc., as shown.



Vitreous sodium polyphosphate can be readily obtained by heating $Na_4P_2O_7$ or Na_3PO_4 with P_2O_5.

The polyphosphate anions in these polymers have long straight chains. But, on an average, one P atom out of every thousand P atoms is a part of a branching unit thereby forming a cross link between the chains. These cross links, however, disappear within 12 hours when the polymer is dissolved in water or in a neutral aqueous salt solution.

Crystalline Polymetaphosphates. Insoluble crystalline poly-metaphosphates of alkali metals have been known for over 100 years. These have been synthesised by the selective condensation of disodium hydrogen pyrophosphate or its potassium analogue. By varying the experimental conditions of condensation, a number of polymetaphosphates, designated as Na(or K)PO_3-II, Na(or K)PO_3-III and Na(or K)PO_3-IV, having the same general formula ($NaPO_3$) but different properties, are isolated. The various metaphosphates, though conventionally written as monomers, are actually polymeric with the general formula $(NaPO_3)_n$.

Maddrell's Salts. Sodium polymetaphosphates $NaPO_3$-II and $NaPO_3$-III are known as Maddrell's salts. These salts are negligibly soluble in water and in saline solutions at room temperature. However, at elevated temperatures and in the presence of salts of alkali metal ions (other than Na^+ ions) and ammonium ions in solution, these metaphosphates dissolve at a higher rate. Also $NaPO_3$-II dissolves more readily than $NaPO_3$-III under the conditions mentioned above. The potassium Maddrells' salts KPO_3-II and KPO_3-III behave in a similar manner.

The X-ray studies on Maddrell's salt, $NaPO_3$-II, reveal that the polymer consists of long –P–O–P– chains made up of interconnected PO_4 groups. However, the pattern repeats itself after every three units and the chains do not spiral.

Kuroll's Salts. The polymetaphosphates Na(or K)PO_3-IV are known as Kuroll's salts. These are somewhat more soluble than the corresponding Maddrell's salts in pure water. If a Kuroll's salt is kept in ice-cold distilled water for a few days or in hot water for a few hours, its crystals swell and become gummy. Eventually they dissolve completely to give a highly viscous solution. The dissolution of sodium Kuroll's salt is greatly speeded up by the presence of salts having cations other than Na^+ ions. The potassium Kuroll's salt behaves in a similar manner.

Properties and Structures of Crystalline Polymetaphosphates. The process of dissolution of Kuroll's and Maddrell's salts in solutions of simple salts containing cations other than those appearing in the polymetaphosphate which is being dissolved, is an exchange process between cations of the salt and the cations of polymetaphosphates.

The dissolution of long chain polymeric metaphosphates in the presence of salts is due to the introduction of cations of different sizes of the salt in place of cations present in the crystal lattice of difficultly soluble metaphosphates so that the long chains of these polymers are now loosely held at their lattice positions and can be effectively removed from these positions in the aqueous medium. However, a salt containing the same cation as the one contained in the polymeric metaphosphate will not be able to cause such 'loosening' of long chains because the exchange of cations of the salt now occurs with the identical cations of the polymer. Therefore, in such a case, or in a case where no salt is added for dissolving the polymer, the latter is insoluble.

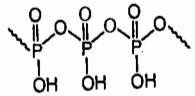
The chain phosphates exhibit optical bifringence and anisotropic electrical conductivity and both these properties increase with increase in the chain length of the polymers. The molar masses of chain polymers are extremely high (250000 to several million).

X-ray studies on rubidium Kuroll's salt reveal that its structure consists of –P–O–P– chains running in the direction of fibrous cleavage and consisting of interconnected PO_4 groups. Each unit cell contains

a portion of two different chains which spiral in opposite directions around the screw axis of the crystal. The pattern repeats itself after every two P atoms in the chains. Thus there are four units of $RbPO_3$ per unit cell. The P–O distances within the chains are $1{\cdot}62 \pm 0{\cdot}03$ Å and the angles O–P–O and P–O–P in the chains are 99·5° and 129°, respectively.

When potassium Kuroll's salt is dissolved in sodium chloride solution, a gummy mass is readily precipitated by the addition of alcohol to the solution. By warming the mass in alcohol-water mixture, a rubber-like solid is produced. The material bounces when dropped on a hard surface. If this material is allowed to remain in a container for some time, it flows out and adheres to the surface of the container in the form of a flexible mass called **plasticised polyphosphate**. The exposure of this mass to moist air results in the formation of powder crust due to the hydrolysis of the plasticised polyphosphate.

Polyphosphoric Acids. The polyphosphoric acids consist of long straight chains of –P–O–P– units, as shown.



The H_2O/P_2O_5 molar ratio of these amorphous solids is 1. These polyacids when put in sealed containers start flowing slowly after a few days and assume the shape of the container. The amorphous polyacids are tough and not rubber-like because of hydrogen bonding in the chains. They are highly hygroscopic and hydrolyse rapidly.

B. Phosphorus-Based Network Polymers

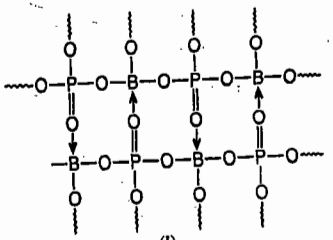
These include polymeric phosphorus pentoxide, polymeric orthophosphates of boron, aluminium and iron, sulphur-phosphorus polymers, ultraphosphate glasses, borophosphate glasses, etc.

Polymeric Phosphorus Pentoxide. Polymeric phosphorus pentoxide exists in three crystalline forms, two of which are sheet polymers and the third is a glassy material having a three-dimensional network structure. All the three forms contain P–O–P linkages. One sheet form consists of large rings containing ten P and ten O atoms each while the other sheet form consists of rings containing six P and six O atoms each.

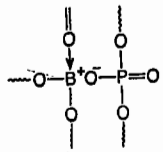
In all the three forms of polyphosphorus pentoxide, each P atom is tetrahedrally surrounded by four oxygen atoms, three oxygens being shared with adjacent PO_4 tetrahedra.

Polymeric Boron Orthophosphate, $(BPO_4)_n$. The crystal structure of boron polyphosphate is similar to that of silica. The P–O distance is 1·55 Å and B–O distance is 1·44 Å. A simplified picture of the structure (in two dimensions) is as shown.

However, the P–O and B–O distances reported above are shorter than the corresponding normal sigma bonds. Since a number of covalent structures of type I and ionic structures of type II are possible, the actual structure appears to be a resonance hybrid of the covalent structure I and the ionic structure II. Ionic structure II explains the shortening of the P–O bond due to fractional pi bond and a slight shortening of the B–O bond due to partial ionic bond.



(I)



(II)

Because of its rigid three-dimensional network structure resembling that of $(SiO_2)_x$, boron polyphosphate is unusually stable.

Polymeric aluminium orthophosphate, $(AlPO_4)_n$. Polymeric aluminium orthophosphate is similar in structure to polymeric boron orthophosphate. Like SiO_2, the polymeric aluminium phosphate also exists in several crystalline modifications.

Polymeric silver phosphate, $(Ag_3PO_4)_n$. Polymeric silver phosphate is a yellow crystalline substance in which each Ag is surrounded by four O atoms (Ag–O distance is 2·34 Å). In addition to these O atoms, each Ag atom has two other Ag atoms as its neighbours (Ag–Ag distance is 3·00 Å compared to the

distance of 2·88 Å in silver metal). As in $(BPO_4)_n$, there appears to be a fractional pi bond character in P–O bonds of PO_4 units in this case.

Polymeric ferrous phosphate, $[Fe_3(PO_4)_2.8H_2O]_n$.** In this polymer, P atoms are tetrahedrally surrounded by O atoms and Fe atoms are octahedrally surrounded by O atoms, PO_4 units and H_2O molecules. There are complex bonds of interconnected P tetrahedra and Fe octahedra extending throughout the crystal with the individual bonds apparently held together by hydrogen bonds between H_2O molecules.

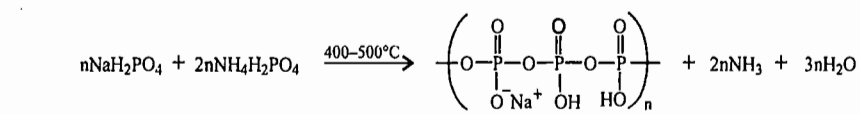
Sulphur–Phosphorus Polymers. The liquid sulphur at 160–250°C, when rapidly cooled, gets transformed into highly elastomeric form S_μ. This form contains long chains of S atoms. The S atom chains terminate into free radicals, *viz.*, $\dot{S}–S_x–S$. It is known from ESR that there are, on the average, 10^5 S atoms in the chains.

The elastic properties of S_μ can be changed by the addition of a small percentage of P. The Young's modulus decreases rapidly with increasing P content. It appears that P vulcanises elastic S_μ in about the same way as S vulcanises natural rubber, *i.e.*, through cross-linking. The incorporation of ten or higher percentage of P increases the cross-linking of S_μ to such an extent that the resulting material loses elastomeric properties almost completely.

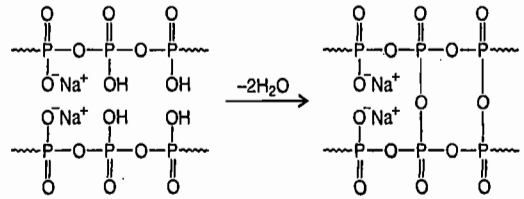
Ultraphosphate Glasses. These are amorphous polyphosphates in which the molar ratio of phosphate anion/metal cation is greater than unity. They can be considered to be derived from P_2O_5 polymer by interruption of a portion of P–O–P bonds by metal cations and hydroxy groups or from linear metaphosphates $(MPO_3)_n$ by successive substitution of pairs of M^+ ions by an oxygen cross link.

The ultraphosphtate glasses resemble the glassy organic plastics in processability.

Amongst the alkali metal ultraphosphates, sodium ultraphosphate is prepared by heating a mixture of NaH_2PO_4 and H_3PO_4 or a mixture of NaH_2PO_4 and $NH_4H_2PO_4$, the molar ratio depending upon the cross link density of the polymer required. Thus, when NaH_2PO_4 and $NH_4H_2PO_4$ are heated together, polycondensation occurs to form linear polyphosphate.



Further heating of $(NaH_2P_3O_9)_n$ formed to still higher temperatures produces cross links by removing H_2O molecules from hydroxy groups of different polyphosphate chains to yield sodium ultraphosphate, as shown.



Simple alkali metal ultraphosphates are rapidly attacked and dissolved by water. The rate of attack increases as we move from lithium to sodium and from sodium to potassium ultraphosphate. The ultraphosphate of alkaline earth metal cations are much more resistant to hydrolysis. The durability of ultraphosphates increases with cross link density. The more tightly bound the network, the more resistant is the ultraphosphate to hydrolytic attack. The durability of ultraphosphates is also strongly *p*H dependent. At lower *p*H, the rate of attack decreases as *n* increases while at higher *p*H, the reverse is true. Ultraphosphates of lithium and sodium have higher Young's modulus than the ultraphosphates of bulkier cations.

The surface of an ultraphosphate glass in normal atmosphere gets covered with a very thin layer of partially hydrolysed glass and adsorbed water at an equilibrium concentration that depends upon humidity.

**Normally, round brackets ( ) are used in the formulae of polymers to denote polymerising units. But, in the formulae of certain polymers, it becomes necessary to use square brackets [ ] alongwith the round brackets. In such formulae, the square brackets are employed to denote the polymerising units. These square brackets do not indicate coordination sphere.

This layer makes the surface non-misting, that is, when a cold glass is brought into a warmer humid atmosphere, the water vapours which condense on the glass surface form a uniform thin layer instead of discrete droplets (as happens in the case of ordinary glass) so that the vision through the ultraphosphate glass remains un-impaired.

Borophosphate Glasses. The borophosphate glasses are readily produced by melting together H_3PO_4, boric oxide and appropriate quantities of alkali metal carbonates or oxides. The optimum temperature for polycondensation is around 700°C.

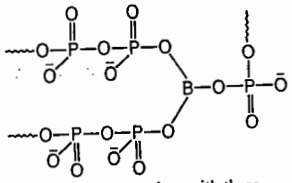
Borophosphate glasses fall in three distinct categories :

1. Those in which there is stoichiometric excess of alkali over phosphoric oxide. In this category of glasses, practically all the boron atoms are present as trigonal BO_3 groups. The fraction of four-coordinated boron atoms is less than 0·1.

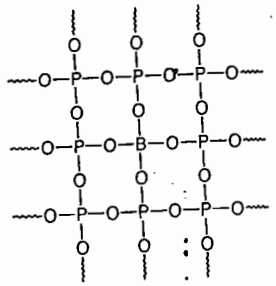
2. Those in which there is excess of phosphoric oxide over alkali. In this class, if there is less than 10 mole percentage of boric oxide, practically all the boron atoms are four-coordinated. As the proportion of boric oxide goes above 10 mole per cent, the fraction of four-coordinated boron atoms decreases rapidly and becomes one third at 33 mole per cent of B_2O_3.

3. Those in which alkali and phosphoric oxide are present in equivalent proportions (in moles). The fraction of four-coordinated boron atoms decreases steadily with increase in the content of B_2O_3, this being about one-third at low concentration of B_2O_3 and almost zero at about 47 mole per cent of B_2O_3.

The structure of borophosphate glasses with boron atoms occupying three coordination sites and four coordination sites are as shown.



Borophosphate glass with three-coordinated boron atoms.



Borophosphate glass with four-coordinated boron atoms.

For acidic borophosphate glasses, *i.e.*, when there is excess of P_2O_5 over alkali, the glass transition temperature of any chosen composition increases with continued condensation and removal of OH groups in the same way as it does with simple ultraphosphate glasses. Also there is a direct relationship between cross link density in the polymer and the glass transition temperature between 0–10 mole percentage of boric oxide.

The simple alkali borophosphates with composition around 80 mole per cent P_2O_5 and 5 mole per cent B_2O_3 dissolve fairly easily in water. The solubility, however, decreases with increase in the fraction of four-coordinated boron atoms. Borophosphate glasses containing both alkali and alkaline earth metal cations are considerably more durable than simple ultraphosphate glasses of similar compositions. The addition of 5 mole per cent B_2O_3 to an ultraphosphate polymer with composition : Li_2O 10 mole %, Na_2O 10 mole % and BaO 5 mole %, increases the durability of the resulting polymer towards running water. A number of multicomponent borophosphate glasses have been prepared which are as durable as ordinary silica glass at similar temperatures. For instance, the rate of dissolution in running water of borophosphate glass with composition : P_2O_5 55 mole %, B_2O_3 5 mole %, MgO 9 mole %, CaO 9 mole %, Li_2O 7 mole % and Na_2O 15 mole %, is as low as 5×10^{-6} mole per year at 20°C. This rate is the same as that of a reasonably durable silica glass. However, the rate of attack by water on borophosphate glasses increases with increase in temperature much more rapidly than on silica glass.

As happens in the case of ultraphosphate glasses, the water vapours on borophosphate glasses condense in the form of a thin layer and not in the form of minute water droplets. The visibility through borophosphate glasses is thus not impaired. This is the reason why these glasses are ideal for the manufacture of spectacles and other lenses.

Applications of Phosphorus-Based Polymers. 1. The long chain vitreous sodium phosphate polymers are employed in food processing industry. Their use in this industry is based on the interaction of phosphates with proteins.

2. The short chain vitreous phosphate polymers are used for deflocculation of proteins.
3. The potassium Kuroll's salt is employed in the manufacture of sausages to prevent water loss.
4. The sodium Maddrell's salt is used as a polishing agent in dental surgery.
5. The borophosphate glasses are used for manufacturing optical lenses.

II. SULPHUR-BASED POLYMERS

A large number of sulphur-based polymers are now known. These include linear chain polymers as well as network polymers. The most important linear chain polymers are polymeric sulphur and polymeric sulphur nitride. The important network polymers comprise of chalcogenide glasses.

Polymeric Sulphur

It is prepared by heating rhombic sulphur (S_8) to 165–180°C and then suddenly cooling the melt in ice bath. The cyclic S_8 structure of rhombic sulphur opens up to produce $\cdot S-(S)_6-S\cdot$ radical which recombines with S_8 unit to produce $\cdot S-(S)_{14}-S\cdot$ radical which further combines with S_8 unit and so on, as illustrated below :

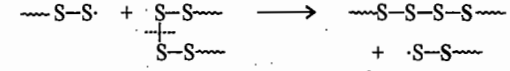
$$\cdot S-(S)_6-S\cdot + S_8 \xrightleftharpoons{165-180^\circ C} \cdot S-(S)_{14}-S\cdot$$

$$\cdot S-(S)_{14}-S\cdot + S_8 \rightleftharpoons \cdot S-(S)_{22}-S\cdot \text{ and so on}$$

{$(S)_6$, $(S)_{14}$, $(S)_{22}$, etc., are actually zigzag chains of 6, 14, 22, etc., of sulphur atoms, respectively.}

The final product is washed with carbon disulphide to remove the traces of S_8 rhombic sulphur.

The pure polymeric sulphur has a glass transition temperature of 75°C. Above this temperature, the sulphur chains undergo dissociation and re-association, as shown below :



At temperatures below the melting point of sulphur, *viz.*, 114°C, the polymeric sulphur is unstable and reverts back to rhombic sulphur, S_8. The transition from polymeric sulphur to rhombic sulphur is facilitated by the presence of S_8 in the polymer. The removal of S_8 by washing the polymer with carbon disulphide slows down the transition.

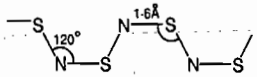
Polymeric Sulphur Nitride, $(SN)_n$

Polymeric sulphur nitride was first prepared in 1910 by Burt by passing vapours of S_4N_4 over silver gauze or silica wool at 100–300° C . In 1973, Labes and coworkers synthesised crystalline polymeric sulphur nitride in the form of bundles of fibres and found that the material possesses metallic conductivity in a direction parallel to the length of the fibre.

Pure $(SN)_n$ can be prepared by passing S_4N_4 vapour over silver wool at 220° C. The gaseous S_2N_2 formed is condensed to solid state by passing through a liquid nitrogen-cooled trap. It is then sublimed into an ice-cooled trap from which it is slowly allowed to warm upto the room temperature. The S_2N_2 during this process of slow warming, gets polymerised to $(SN)_n$.

Polymeric sulphur nitride consists of layers of fibres stacked parallel to one another. The polymer shows metallic conductivity and metallic ductility. It is soft and malleable. The polymer is slowly attacked by moisture when exposed to it for several months. It decomposes in vacuum at 140° C to give sulphur and nitrogen.

The structure of the polymer comprises of nearly planar chains of S—N bonds of approximately the same length (1·6 Å). The structure of a portion of the polymer is as shown.



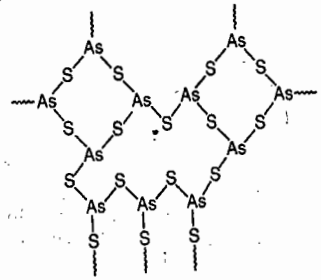
The electrical conductivity of the polymer $(SN)_n$ is in the range of 1200–3700 S cm^{-1} and increases 50–200 times when the temperature is lowered to 4·2 K. It has been found recently that the polymer becomes a superconductor at 0·26 K. The polymer is the first example of a non-metallic superconductor.

Chalcogenide Glasses

The chalcogenide glasses are a family of amorphous cross-linked polymers formed by compounds of chalcogens (S, Se, Te) with one or more of the polyvalent elements such as antimony, arsenic, bismuth, germanium, indium, phosphorus, tin and thalium. While the best known two-component chalcogenide glass is $(As_2S_3)_n$, there are many multicomponent chalcogenide systems like Si–P–Te, Si–Sb–Te, Ge–P–Se, Si–Sb–S and As–Ge–Si–Te. The chalcogenide glass $(As_2Pb_3S_8)_n$ occurs as such in nature.

Chalcogenide polymers are generally prepared by the fusion of the elements under conditions selected for minimising oxidation and loss of volatilisation of the components.

The X-ray studies reveal that chalcogenide glasses consist of short chains of chalcogen atoms linked together by polyvalent atoms which serve as branching and cross-linking sites. Thus, the parent network of As, Sb, P chalcogenides, is a triple-connected assembly of As, Sb or P atoms linked through S, Se or Te atoms. A typical As–S polymer network is as shown.



These polymers resemble organic polymers. Compared to inorganic polymers such as ultraphosphate and borophosphate glasses, these polymers have lower softening points, higher refractive indices and lower tensile strengths.

Chalcogenide glasses are fairly stable to acids but are attacked by concentrated alkalies. Most of the polymers begin to oxidise in air at about 3000° C. But some of these polymers can be distilled in vacuum without showing any sign of decomposition – a property most unlikely of polymers. This happens because of the dissociation of polymeric network into small fragments in vapour phase in vacuum which recombine spontaneously when the vapours condense. The glass transition temperatures of As and Ge chalcogenides increase linearly with As or Ge content of the glass. In the range of 5–15 mole % As and 3–8 mole % Ge, the chalcogenide glasses show distinct rubbery properties although over a small range of temperature. In this respect the chalcogenide polymers differ markedly from the oxide glasses (*e.g.*, borate, phosphate and silica glasses) which do not exhibit rubber-like properties in any temperature range.

Chalcogenide glasses are deeply coloured. However, most of them are good infrared transmitting materials and have been used for the fabrication of IR windows for army and civil optical devices.

Switching Phenomenon in Chalcogenide Glasses. The chalcogenide glasses undergo reversible change from low conductivity to high conductivity state under applied voltage. This phenomenon is known as **'switching.'** It can occur in two forms, *viz.*, threshold switching and memory switching.

In **threshold switching**, the chalcogenide glass maintains a high resistance until a certain threshold voltage gradient (*i.e.*, 10^4 volts/cm) is reached. At this voltage gradient the chalcogenide glass changes suddenly into a low resistance state which has about a thousand-fold greater conductivity than the state prior to the application of threshold voltage. The chalcogenide glass continues to remain in this high conductivity state as long as a certain minimum current (called 'holding current') is maintained. If the current falls below the holding current value, the chalcogenide glass returns to the high resistance state once again.

In the **memory switching**, the chalcogenide glass exhibits a high resistance until a threshold voltage gradient is exceeded. At this stage, the chalcogenide glass suddenly changes into a high conductivity state. The material then remains in this condition even after the current is switched off. It can, however, return to high resistance state by passing a short current pulse that exceeds the original threshold voltage gradient.

The switching phenomenon is probably due to the fact that the current of high voltage causes decomposition of bonds in the chalcogenide glass so that when the voltage gradient becomes high

enough, a conducting path within the glass is produced. A detailed discussion of switching is, however, beyond the scope of the book.

Some of the chalcogenide glasses are used for infrared transparent windows in civil and military devices.

The chalcogenide glasses have a great potential for their use in ultrasonic delay lines, high energy particle detector multipliers, memory devices for computers, electroluminiscent displays, etc.

III. BORON-BASED POLYMERS

Boron-based polymers constitute an important class of inorganic polymers. Amongst these the most important ones are polycarboranes and polymeric boron nitride.

1. Polycarboranes

These are mainly linear polymers in which meta or para carboranes are linked through a variety of hetero atom bridges such as P–O–P.

When acetylene is added to decacarborane, $B_{10}H_{10}$, it forms a closed icosahedral molecule $C_2B_{10}H_{12}$ with a diameter of about 4·0 Å in which the two carbon atoms are adjacent to each other. This product is named ortho (or 1,2)-dicarbaclosododecacarborane.

$$\underset{\text{Decaborane}}{B_{10}H_{10}} + C_2H_2 \longrightarrow \underset{\text{Ortho dicarbocloso dodecacarborane}}{C_2B_{10}H_{12}}$$

When the ortho product is heated to 475°C, it undergoes an intramolecular rearrangement to give the isomeric meta carborane in which the two carbon atoms are separated by one boron atom. On further heating above 630° C, the material isomerises to para carborane in which the carbon atoms lie at opposite vertices of the cage. The skeletal structures of ortho, meta and para carboranes are shown in Fig 1.

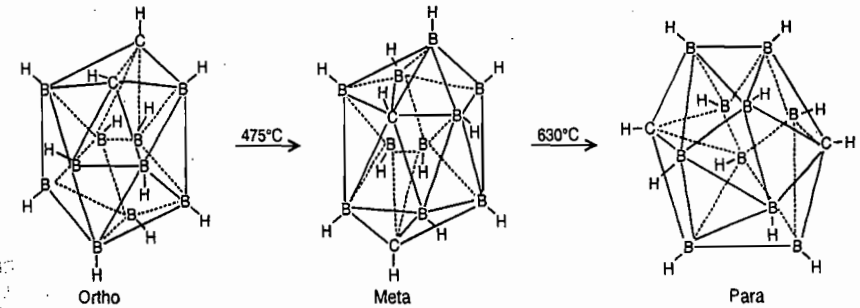
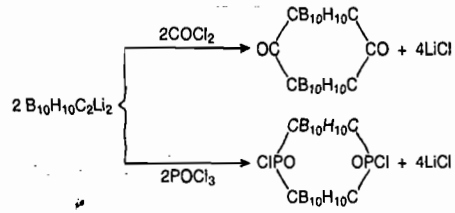


Fig. 1. The skeletal structures of ortho, meta and pera dicarbaclosododeca carboranes.

In these compounds, the H atoms attached to C atoms can be easily replaced by Li atoms :

$$C_2B_{10}H_{12} + 2Li \longrightarrow C_2B_{10}H_{10}Li_2 + H_2$$

The dilithium salts of ortho, meta and para carboranes then easily react with halogen-containing compounds such as $COCl_2$, $POCl_3$, etc., to give cyclic or linear polycarboranes.



The main products in the reaction of ortho $C_2B_{10}H_{10}Li_2$ with halogen compounds are cyclic polymers, as shown.

The lithium derivatives of meta and para carboranes give rise to linear polycarboranes which, however, do not contain more than five repeat units. In other words, these polycarboranes are only low molar mass polymers.

The lithium derivatives of meta and para carboranes react with $(CH_3)_2SnCl_2$ to give crystalline polymers of reasonable chain lengths containing 20–30 repeat units.

$$nLi_2C_2B_{10}H_{10} + n(CH_3)_2SnCl_2 \longrightarrow \left(CB_{10}H_{10}CSn(CH_3)_2\right)_n + 2nLiCl$$

The most interesting polycarboranes are those in which the carboranes are bound by **polysiloxane bridges**. If meta $Li_2C_2B_{10}H_{10}$ is made to react with $(CH_3)_2SiCl_2$, it produces $ClSi(CH_3)_2C(B_{10}H_{10}CSi(CH_3)_2Cl$, as shown below :

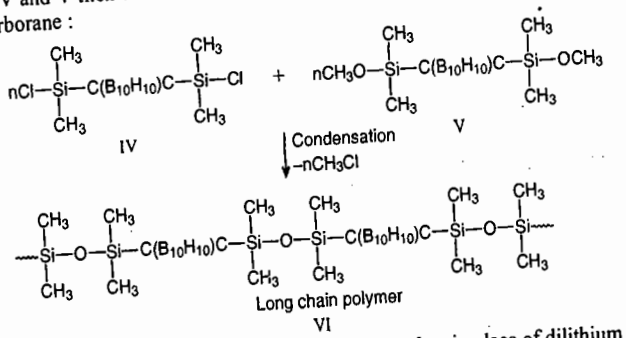
$$\underset{\text{(meta)}}{LiCB_{10}H_{10}CLi} + 2(CH_3)_2SiCl_2 \longrightarrow \underset{\text{(meta)}}{ClSi(CH_3)_2C(B_{10}H_{10})CSi(CH_3)_2Cl} + 2LiCl$$

III IV

The product IV is then reacted with methanol to give the methoxy derivative :

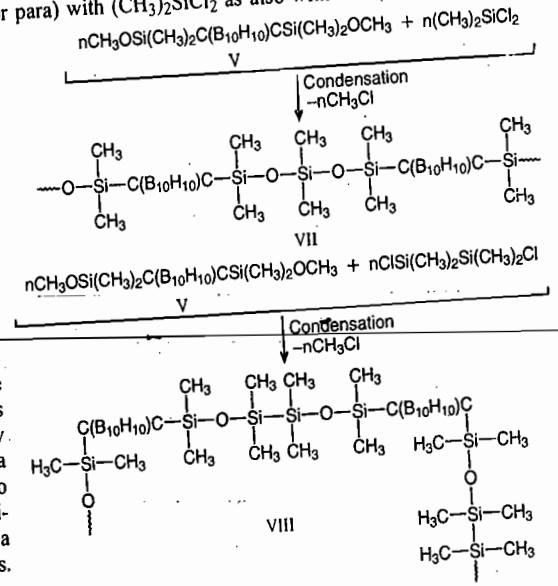
$$\text{IV (meta)} + CH_3OH \longrightarrow \underset{\text{V (meta)}}{CH_3OSi(CH_3)_2C(B_{10}H_{10})CSi(CH_3)_2OCH_3}$$

Compounds IV and V then condense at 140°C in the presence of ferric chloride (catalyst) to yield the long chain polycarborane :



A similar polymer is obtained if dilithium para carborane is taken in place of dilithium meta carborane.

The reactions of compound V (meta or para) with $(CH_3)_2SiCl_2$ as also with $ClSi(CH_3)_2Si(CH_3)_2Cl$ produce long chain polymers VII and VIII having structures similar to that of VI, as shown.



All polycarboranes containing Si–O–Si linkages are partially crystalline elastomers whose glass transition temperatures decrease with increasing number of Si atoms in the linking groups. To make these elastomers useful as rubbers, a small quantity of 1-venyl 2-methyldichloro 1,2 dicarbaclosododecacarborane is added to the condensation reaction. The resulting elastomer is cross-linked with peroxide initiators. The properties of the cross-linked material as rubber can be further improved by compounding it with finely divided silica fillers. The final product is stable upto 260°C. However, its oxidative decomposition begins at about 300° C. This puts a limitation to their use at high temperatures.

Polymeric Boron Nitride

The polymeric boron nitride, $(BN)_n$, exists in two forms, *i.e.*, as a layer polymer and as a three-dimensional network polymer.

The Layer Polymer. This form resembles graphite and was first discovered by Balmain in 1842. It can be obtained by a variety of methods. A common method involves heating of boric acid with urea in an atmosphere of nitrogen at 600° C followed by the treatment of the product with ammonia at 950° C. The final product is an amorphous powder.

The structure of boron nitride resembles that of graphite. It thus consists of infinite sheets of six-membered rings of alternating boron and nitrogen atoms stacked in layers. There is, however, an important difference between the structure of polymeric boron nitride and graphite. In boron nitride, the sheets are stacked over one another in such a manner that the atoms in each successive layer are directly superimposed whereas in graphite, the atoms in one layer lie opposite to the centres of the six-membered rings in the next layer, as shown in Fig. 2.

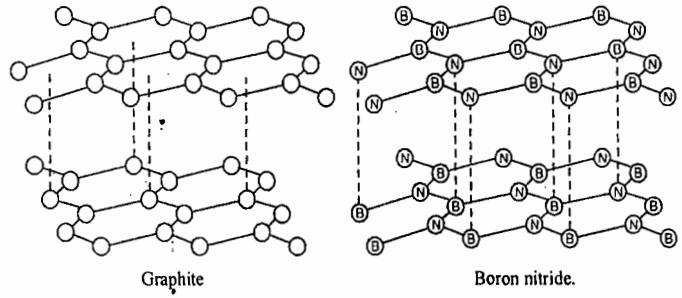


Fig. 2. Layer structures of graphite and boron nitride.

The crystallographic unit cell constants of boron nitride are very similar to those of graphite, the B–N distance in $(BN)_n$ being 1·45 Å compared to C–C distance of 1·42 Å in graphite. The interlayer separation in $(BN)_n$ is 3·3 Å compared to 3·5 Å in graphite.

There is, however, a distinct difference between the two polymers. Unlike graphite, the polymeric boron nitride is an electrical insulator. This is because the nitrogen atom in one layer of $(BN)_n$ is always adjacent to a boron atom so that the lone pair of electrons on each N atom in a layer is bound to the electron-deficient B atom of the adjacent layer. In other words, the electrons in boron nitride are highly localised making the polymer non-conducting.

Boron nitride is soft like graphite and can be easily machined. The articles fabricated from this polymer, either by sintering or by machining, can be safely exposed to atmosphere upto a temperature of about 800°C. The melting point of polymeric boron nitride (under an atmosphere of nitrogen) is about 3000° C.

The Three-Dimensional Network Polymer. If the layer form of polymeric $(BN)_n$ is heated at 1500–2000°C under extremely high pressure in the presence of a catalyst, it gets converted into a three-dimensional network polymeric form. This form is isomorphic with diamond and is comparable with the latter in hardness. It is, therefore, used as a substitute for diamond in jewellery as also for the fabrication of cutting tools. It shows signs of surface oxidation in air around 200°C.

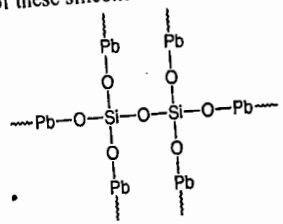
IV. SILICON-BASED POLYMERS

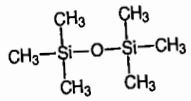
Silicon-based polymers constitute the most important class of inorganic polymers. These include organopolysiloxanes, commonly known as **silicones**.

Organosilicones or Organopolysiloxanes

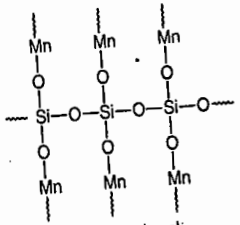
Organosilicon polymers have been described briefly in Chapter 16. However, since these polymers constitute an important class of inorganic polymers, it would be pertinent to describe them in some more details alongwith other inorganic polymers.

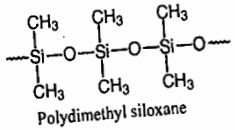
The chemical constitution of organosilicones can be represented as $(R_xSiO_{2-x/2})_n$ where n is very large while x varies from 0 to 4. On one extreme of these silicones is silica (x=0) which is an inorganic polymer and on the other extreme is tetraorganosilane (x=4) which is an organometallic compound and is monomeric, *e.g.*, $(CH_3)_4Si$. In between x=0 and x=4 are the polymeric silicones which can be categorised both as organic as well as inorganic polymers. These polymers resemble inorganic polymers in having a high percentage of ionic character of Si–O bonds and they resemble organic polymers in having organic groups on silicon atoms.


Barysilite mineral

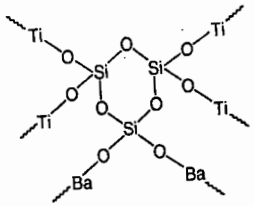

Hexamethyl disiloxane

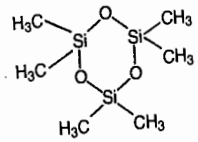
Organosilicon polymers contain chains or network of alternating silicon and oxygen atoms in their structures, that is, they have polysiloxane structure exhibited by some natural silicon minerals such as barysilite, rhodonite, benitoite, as shown.


Rhodonite mineral


Polydimethyl siloxane

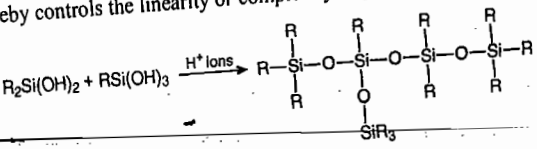
But, whereas the polysiloxane structures in natural silicon minerals are cross linked through metaloxy groups, the polysiloxane structures of the corresponding siloxanes contain non-bridging alkyl (*e.g.*, CH_3) groups on silicon atoms. There is thus no cross linking. The polymeric molecules in silicones are held together by weak van der Waals forces with the result that the silicones are either liquids of varying viscosity or gums or solids containing polymeric molecules which are generally soluble in organic media.

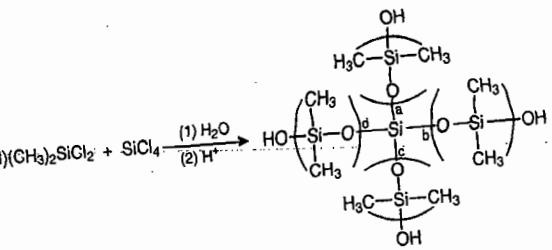

Benitoite mineral


Hexamethylcyclotrisiloxane

The physical properties and, therefore, the usefulness of organopolysiloxanes (silicones) are determined by the kind and the number of organic groups present on each silicon atom as well as by the manner in which the silane units are hooked together. For example, whereas CH_3 groups on silicon promote fluidity, low viscosity, low melting point and high liquid compressibility, the phenyl groups on silicon induce the contrasting properties in the silicones. The number of organic groups on silicon establishes the functionality of individual siloxane building units and thereby controls the linearity or complexity of polysiloxanes.

Preparation of Silicones. The preparation of organosilicones by the condensation of silanols has already been described in Chapter 16. The condensation of dihydroxysilanes (which are obtained by the hydrolysis of dichlorosilanes) yields linear polymers. Chain branching in silicones is introduced by condensation of tri and/or tetrafunctional silanols with other silanols in the catalytic presence of H^+ ions, as shown.

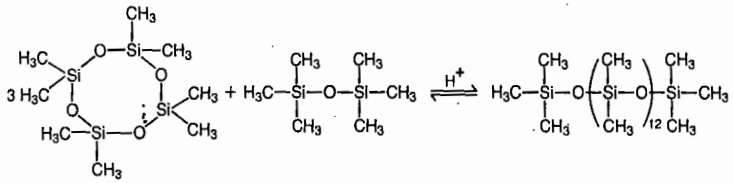




A general method for preparing straight chain silicones involves the opening up of appropriate cyclic polysiloxanes by heating them alone or with di or trisilanes in the catalytic presence of an acid or a base. The process ends in a thermodynamic equilibrium between the reactants and the products which consist of simple or mixed siloxanes depending upon the nature of the reactants. This process is known as **equilibration of cyclopolysiloxanes.**

A brief description of various types of silicones is given below.

1. Fluid or Liquid Polysiloxanes. These are low molar mass straight chain polymers which are obtained by the equilibration of cyclopolysiloxanes with a disiloxane, as shown below :



These polysiloxanes can also be prepared by the hydrolysis of dichlorosilanes, as already discussed in Chapter 16.

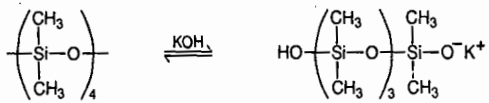
Uses. Liquid polysiloxanes are used as insulators in electrical appliances. They are also used as lubricants since they do not become viscous even at very low temperatures. Because of their adequate stability and high boiling points, they are used in vacuum pumps and high temperature oil baths.

2. High Polymer Organosiloxanes or Polysiloxane Gums. Polysiloxane gums which are high molar mass organosiloxanes can be prepared by equilibration of cyclic siloxanes in the absence of monofunctional groups. The resulting straight chain polymers are end-blocked by the catalyst, as shown.

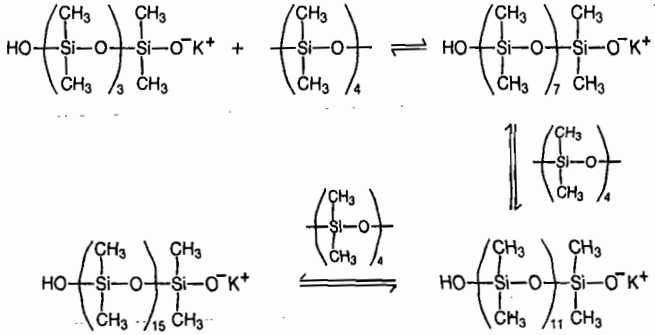
Cyclic tetramer — Straight chain polymer

The above reaction is supposed to take place through the following steps :

Initial step **:**



Condesation **:**



The rate of the polymerisation reaction increases with increase in temperature and is related to the square root of the concentration of the cyclic tetramer. It is also related to the ring strain in the cyclic polymer taken for equilibration. Thus, cyclic hexamer is more easily equilibrated than cyclic tetramer.

The average molar mass of the polymer obtained is independent of temperature and varies inversely with the concentration of the catalyst. The molar mass of hydroxy end-blocked gums can be increased further by azeotropic removal of water with toluene or by heating the polymer under vacuum. Catalysts such as amine salts or some metal salts also increase the average molar mass.

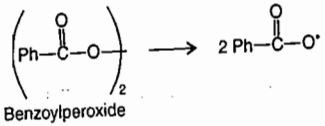
Polysiloxane gums are used as lubricants and as antifoams. They are also used in textile finishing.

3. Silicone Rubber or Elastomers. Preparation of silicon rubbers involves two steps, *viz., compounding* and *cross linking.*

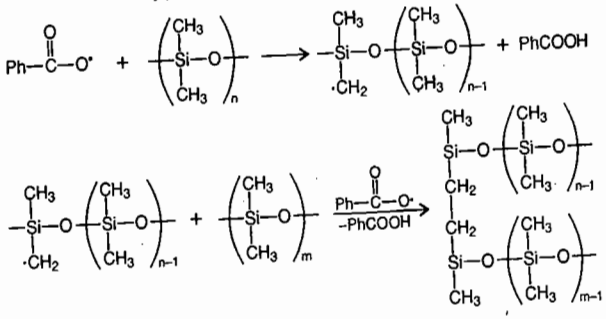
Compounding. It consists of milling (or mixing under high pressure) of polysiloxane gum, a filler and a cross-linking agent together with certain additives to obtain desired physical properties. A typical formulation comprises of 100 parts of benzene-soluble polysiloxane gum, 20–50 parts of SiO_2 as filler, 6 parts of benzoyl peroxide as vulcanising agent and suitable amounts of additives.

Cross Linking. This step involves the cross-linking and curing processes which connect polymer molecules with one another so that it becomes an elastomer of desired properties.

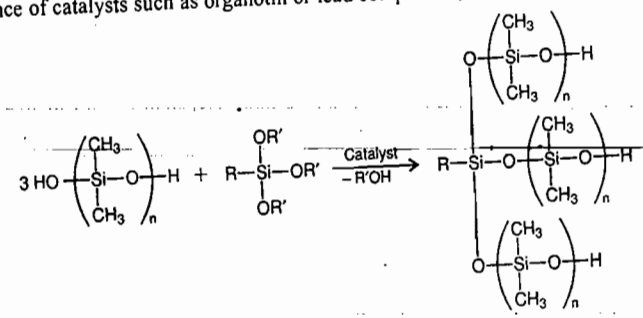
The polysiloxane gum required for making silicone rubber should be a linear polymer of high molar mass since the tensile strength of the elastomer increases with increase in the size of the gum polymer. Fillers are added to reinforce the polysiloxane gum which, in itself, is soft and weak. Silica, which is used as a filler, is in a very fine state of subdivision. It is prepared by the action of HCl on Na_2SiO_3 or by the hydrolysis of $SiCl_4$.



Cross linking is achieved by the addition of several reagents, the most common of which are benzoyl peroxide, 2,4-dichlorobenzoylperoxide or tertiary butyl perbenzoate. The vulcanising temperature ranges between 120° and 130° C when the cross-linking agent is benzoyl peroxide. The mechanism of cross linking step is as shown.



Cross linking or vulcanisation can be affected even at room temperature if the process is carried out in the presence of catalysts such as organotin or lead compounds, as shown below :



Silicone rubbers are extremely useful materials on account of their high thermal stability, low temperature performance, reluctance towards oxidation, chemical stability, water repelling power and flexibility.

4. Silicon Resins. Silicone resins contain ring structures and have a much higher cross link density than is found is silicone elastomers. In a stretched elastomer, the molecular chains uncoil through rotation about the –Si–O– bonds. In a resin, such rotation is highly restricted and the response to stress occurs largely through bending and stretching of bonds. The properties of resins are a function of R/Si ratio where R is alkyl group. As the R/Si ratio is lowered from 2·0 to 1·0, the polymers become progressively *less fluid, less soluble and less fusible. Most of the resins have R/Si ratio between 1·00 and 1·6 and their* properties are intermediate between those of fluid silicones and those expected of a highly cross linked structure with R/Si ratio equal to 1·00.

For the preparation of silicone resins, a mixture of chlorosilanes such as CH_3SiCl_3, $(CH_3)_2SiCl_2$, $C_6H_5SiCl_3$, $(C_6H_5)_2SiCl_2$, $C_6H_5(CH_3)SiCl_2$ are first hydrolysed. During hydrolytic reaction, about 90 per cent of silanol groups (*i.e.*, Si–OH groups) condense to form siloxane linkages. In this process of random condensation, some ring closure invariably occurs because of extreme flexibility of Si–O–Si chains. The remaining 10 per cent of silanol groups condense more slowly and with increasing difficulty because fewer fruitful molecular collisions can now occur since the increasing viscosity renders molecular motion slow. Also, with the growing size of the polymer, the remaining hydroxy groups get fixed in the network too far apart to get condensed with one another.

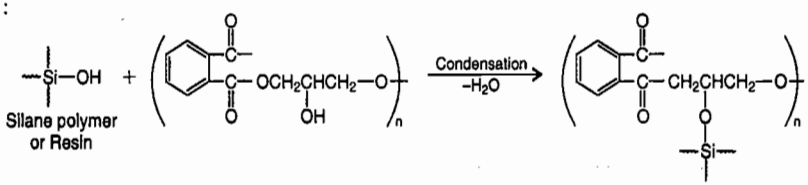
After hydrolysis the product is shaken with an organic solvent and the organic layer is separated. This organic layer is then washed thoroughly to remove the Cl^- ions in order to check the reversibility of the hydrolytic reaction.

The silanol groups (*i.e.*, Si–OH) left uncondensed in the finished resin impart typical properties to the resin. These groups contribute towards viscosity of the product which is an important property that determines the usefulness of a resin. For instance, the viscosity of resin used for laminating purposes should be relatively low so that it may impregnate the glass fibres better. The silanol groups also determine the shelf life of the resin. The resins, on storage, constantly go on condensing and cross-linking depending upon temperature. This type of condensation is extremely slow in solid resins, slow in concentrated solutions and fast in dilute solutions.

Final curing of the resin involves further reaction of the residual silanol groups. The ultimate condensation of these silanol groups occurs after the resin is applied. This process can be hastened by heating the resin in the presence of a suitable catalyst. The most common catalysts are metal salts of organic acids such as naphthalates of cobalt, zinc, lead and tin.

The nature of the substituents on Si alters the characteristics of the resin. For example, while CH_3 groups give flexibility, C_2H_5, C_3H_7, etc., groups make the resin softer, increase its solubility in organic solvents and increase its water-repellence. The phenyl groups increase resistance towards heat and so on.

Copolymeric resins of desired properties can be obtained by condensing two polymers, as shown below :



The silicon resins can be copolymerised with phenolic polyester, epoxy cellulosic or other functional resins. The properties of these copolymeric resins depend upon the nature of the condensing polymers and the degree of condensation.

Uses. Silicon resins are used as electrical insulators. They are also used for coatings on metals, for lamination purposes and for coating cooking pans, etc.

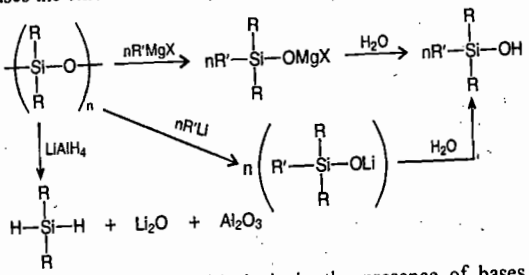
Properties of Silicones. Some characteristic properties of silicones are discussed below.

1. Thermal stability. The Si–O–Si bond in siloxanes is shorter than the expected Si–O–Si bond as calculated from their radii. This indicates that there is some ionic character and/or partial double bond

character in Si–O bond due to which it becomes quite stable. This is the reason why polysiloxanes are thermally stable and do not decompose even upto 350–400° C.

2. Chemical stability. Highly polar character of Si–O bond and the ability of Si to expand its valency shell by utilising its *d* orbitals renders polysiloxanes susceptible to attack by several reagents. Strong bases and concentrated acids may cause depolymerisation. Similarly, some electron-deficient salts may cause the cleavage of Si–O as well as the Si–C bonds. Dry chlorine attacks silicones resulting in chlorination of alkyl groups. Except for the above reactions, polysiloxanes are chemically inert. Common chemical reagents such as dilute acids and bases, metal salts, water at room temperature, H_2O_2, NH_4OH, etc., have little effect on polysiloxanes. Polysiloxanes are quite resistant to attack by oxygen. However, minor oxidation does occur above 200° C. At higher temperatures, oxidation becomes considerable when fluid polysiloxanes get cross linked through oxygen atoms to yield a rubber-like gel in a few hours. Silicon resins, being already cross linked, show much less change in viscosity with change in temperature. The presence of aromatic groups on Si atom increases the oxidative stability of the polysiloxanes.

3. Chemical reactivity. Siloxane bond can be cleaved by Grignard reagents, alkyl lithium as also by lithium aluminium hydride, as shown.



The siloxanes may undergo hydrolysis and alcoholysis at elevated temperatures in the presence of strong acids and bases to give silanols and alkoxysilanes. In general, the greater the extent of substitution on Si atom, the greater is the ease of hydrolysis in the presence of acids and the greater is the difficulty of hydrolysis in the presence of bases.

4. Properties dependent on molecular structure. Many of the observed physical properties of polysiloxanes such as compressibility, small temperature coefficient of viscosity and surface properties have been attributed largely to almost regularly coiled structure (helical structure) of polysiloxanes and weak intermolecular forces. The molecules have pronounced kinked and coiled structures at low temperatures. With increase in temperature, the kinked structure opens out which results in a greater interaction and entanglement of polymer molecules. This results in an increase in viscosity which partly compensates the normal decrease in viscosity caused by greater thermal motion of molecules due to increase in temperature. The net result of these two opposite factors is that the viscosity of polysiloxanes does not change appreciably with change in temperature.

The ability of polysiloxanes to coil, in contrast to analogous linear organic polymers or other types of polymers possessing relatively rigid structures may be attributed, to larger size of silicon atom compared to that of carbon atom. The coiling may also be facilitated by flexibility in the magnitude of Si–O–Si bond angle which can have values varying from 104° to 180° in different polysiloxanes.

Polysiloxanes are water-repellent. When glass is coated with polysiloxanes, the oxygen atoms of polysiloxanes adhere to the glass surface while the R groups on Si are directed outwards, *i.e.*, towards the air.

5. Other properties. Polysiloxanes are electrical insulators. They are transparent to visible light but absorb considerable amount of ultraviolet light, especially of shorter wave lengths.

V. COORDINATION POLYMERS

The development of coordination polymers as useful materials is still at a very primitive stage. The characterisation of these polymers is quite troublesome because of solubility problems which also hinder determination of the degree of polymerisation.

Any macromolecular species which contains coordinate covalent bonds between the metal and the ligands is termed as a **coordination polymer**. The coordination polymers are classified as inorganic polymers although a large number of ligands employed are of organic origin. If the metal to ligand distances are less than the sum of the radii of metal cation and ligand anions, it is taken as a proof of the presence of a coordinate covalent bond in the polymer.

Coordination polymers can be classified into two main categories, *viz.*,

1. *Natural Coordination Polymers* 2. *Synthetic Coordination Polymers*

Inorganic polymers belonging to both the categories have been discussed here in some details. As already mentioned, the square brackets, [ ], denote the polymerising unit and not the coordination sphere.

1. Natural Coordination Polymers

The word 'natural' does not mean that these polymers occur in nature. The term 'natural coordination polymers' is used for those polymers which were not synthesised as polymers but were found to be polymeric in later course of their characterisation. Therefore, it is still quite common to refer to these natural polymers by their monomeric names and formulae. For example, polymeric gold (I) and polymeric silver (I) cyanides are commonly written as AuCN and AgCN although these should be written as $(AuCN)_n$ and $(AgCN)_n$ where *n*, here and in the ensuing discussion, is the number of monomeric units which get associated and, therefore, denotes the degree of polymerisation. Similarly, polymeric potassium dicyanocuperate(II) is commonly written as $K[Cu(CN)_2]$ whereas it should actually be represented as $K_n[Cu(CN)_2]_n$.

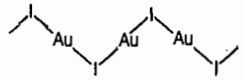
The natural coordination polymers have been further subdivided into three categories :

A. Chain Polymers B. Two-Dimensional Polymers and *C. Three-Dimensional Network Polymers.*

A. Chain Polymers

There is a large number of natural coordination polymers which have chain structure. Some typical chain polymers with typical types of chains have been described below.

Polymeric Gold (I) Iodide. The sum of the radii of Au^+ and I^- ions is 3·2 Å whereas the Au–I distance in $(AuI)_n$ polymer is 2·60 Å. This indicates that the Au–I bond in gold (I) iodide is fairly covalent in character and that the compound is not an ionic compound but a coordination polymer with a coordination number of 2 for Au (I). The polymer has a *zig-zag chain structure*, as shown.



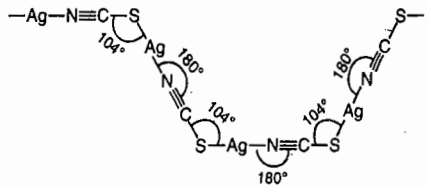
Polymeric Cyanides of Gold (I) and Silver (I). The polymeric cyanides of gold (I) and silver (I) contain *straight chain rods* of the type shown below :

$$-C \equiv N \cdots\cdots M - C \equiv N \cdots\cdots M - C \equiv N \cdots\cdots$$

where M stands for Au or Ag.

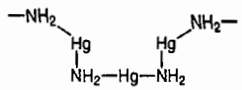
The bonding of the ligand with the metal is largely covalent. The cause of rigidity, *i.e.*, of rod-like structure, is that the angles between the lone pairs on carbon and nitrogen atoms are 180° each and these are the lone pairs which form bonds with the metal.

Polymeric Sulphocyanides of Gold (I) and Silver (I). If we consider polymers of Au(I) and Ag (I) with SCN^- ligand, we get coordination polymers with *zig-zig chain structures* as the one shown for silver sulphocyanide polymer :



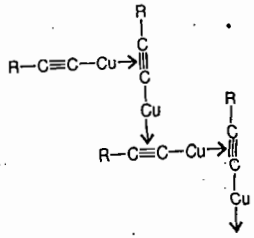
The reason for this zig-zag structure is that the angles between the lone pairs on S and N atoms of SCN^- ligand are not 180° each. Instead, the angle between the lone pairs on S is 104°. The coordinate bonds of S and N with Ag are formed through the lone pairs on these atoms. The coordination number of Ag(I) in the polymer is evidently 2.

Polymeric $[Hg(NH_2)]_nX_n$. The polymeric cation $[Hg(NH_2)]_n^{n+}$ in this polymer has also a *zig-zag chain structure* in which NH_2 forms a bridge between the two Hg atoms as shown.



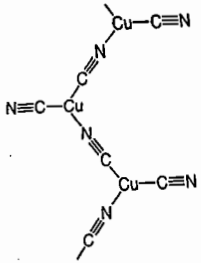
The coordination number of Hg in this polymeric cation is 2.

Polymeric Copper (I) Acetylide. The structure of this polymer is as shown.



There is considerable back coordination from *d* orbitals of Cu atom to π^* orbitals of acetylene group.

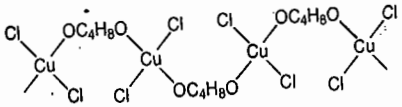
Silver (I) acelylide is also polymeric and has a similar structure. The metal in these acetylides has a coordination number 2.



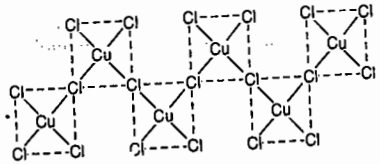
Polymeric $[Cu(CN)_2)]_n^{n-}$ Anion. The polymer commonly written as $K[Cu(CN)_2]$ actually contains a polymeric anion $[Cu(CN)_2)]_n^{n-}$ which has a chain structure of the type as shown.

Cu metal in this polymeric anion has coordination number 3. The polymer should actually be written as $K_n[Cu(CN)_2]_n$.

Polymeric $(CuCl_2.dioxane)_n$. This polymer contains bridging chains of dioxane. The Cu metal has a coordination number 4 and the geometry around each Cu atom is square planar, as shown.

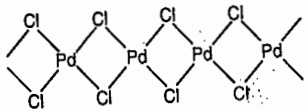


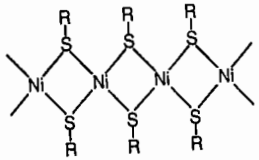
Polymeric $(CuCl_3)_n^{n-}$ Anion. The polymer commonly represented as $Cs[CuCl_3]$ contains a polymeric anion $(CuCl_3)_n^{n-}$ which is formed by sharing of two adjacent Cl^- ions of the square planar $CuCl_4$ units. The resulting chain is arranged in a spiral in the crystal lattice in a manner as shown.



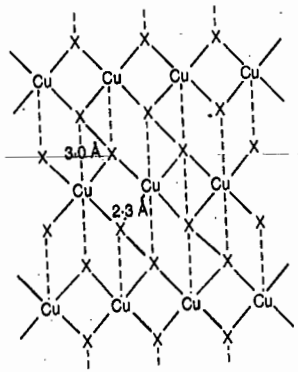
The coordination number of Cu in the square planar arrangement is 4.

The compounds commonly written as $PdCl_2$ and $Ni(SR)_2$ have structures in which each ligand forms a bridge between two metal ions. In these polymers also, the metal ion, which is in square planar environment as shown, has coordination number 4.

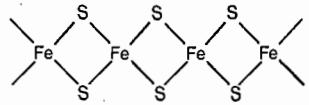




Polymeric Cupric Halides. Cupric halides are also polymeric in nature and should actually be represented as $(CuX_2)_n$. Each Cu(II) ion has a coordination number 4. Each halide ion forms a bridge between the two Cu(II) ions. There also appears to be a weak association between Cu(II) ion of one chain and halide ion of the adjacent chain, as shown.

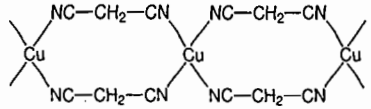


$K_n(FeS_2)_n$. There are several coordination polymers in which the geometry around the metal ion is tetrahedral. One such polymer is $K_n(FeS_2)_n$, the structure of whose anion, *viz.*, $(FeS_2)_n^{n-}$, is as shown.

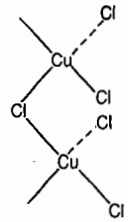


The Fe–S bond is predominantly covalent and the S^{2-} ligands form double bridges. The geometry around Fe is tetrahedral.

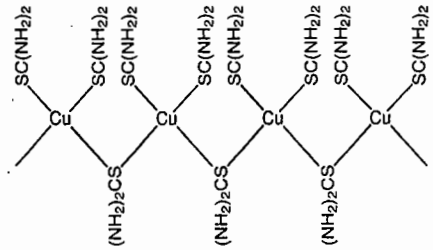
The polymeric cation $[Cu(NCCH_2CN)_2]_n^{n-}$ also contains the metal cation Cu^{2+} in tetrahedral environment in which both the ligands are involved in bridging, as shown.



Polymeric $M'_{2n}(MX_3)_n$. There are several polymers in which the geometry around the metal ion is tetrahedral but there is only a single bridge beween the metal ions. Examples are the polymers $M'_{2n}(MX_3)_n$ in which $M' = K^+$ or NH_4^+ ; $M = Cu^+$ or Ag^+ and X = Cl, Br or I. The structure of the anion of one such polymer is as shown.



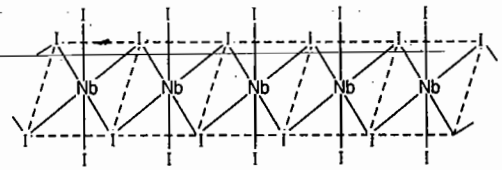
Thiourea Complex of Copper. Till now this complex was considered to be a monomer having the formula $[Cu(H_2NCSNH_2)_3]X$ with Cu(I) having a coordination number 3. However, X-ray studies on this complex of copper reveal that it is not a monomer with coordination number 3 for Cu but, instead, it is a polymer in which Cu has a coordination number 4 with a tetrahedral environment, as shown below :



Polymeric $(MX_3)_n$. There are several inorgnic compounds of the general formula $(MX_3)_n$ in which all the ligands are involved in forming bridges with the metal ion. Examples are $(MoI_3)_n$, $(MoBr_3)_n$, $[Co(NH_2)_2OH]_n$, $[Cr(NH_2)_3]_n$ and $(PbX_3)_n$. The structure of $(MoX_3)_n$ is as shown (X is a halogen atom).

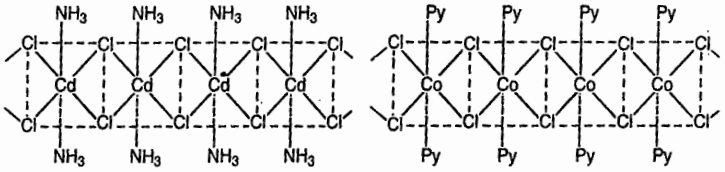
As can be seen, each Mo atom has an octahedral environment and its coordination number is 6. Each halogen atom is a bridging ligand. All other polymers have similar structures.

Polymeric $(NbI_4)_n$. There are several coordination polymers in which the coordination ~~number of metal ion is 6 and the environment~~ around the ion is octahedral but in which only four of the six ligands around each metal atom form bridges leading to formation of double-bridged chains in their structures. $(NbI_4)_n$ is one such polymer whose structure is as shown.



As can be seen, there are four bridging iodine atoms and two terminal iodine atoms around each Nb atom which, evidently, has octahedral environment.

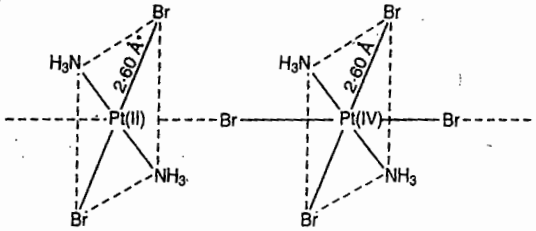
Polymeric $[Cd(NH_3)_2Cl_2]_n$ and $[Co(C_5H_5N)_2Cl_2]_n$. These polymers have the structures in which the four chlorines around each metal atom are the bridging ligands, as shown below :



As can be seen, each of the above polymers has four bridging chlorine atoms. Ammonia molecules in the first polymer and pyridine (py) molecules in the second polymer form the terminal groups.

The octahedral violet polymer $[Co(py)_2Cl_2]_n$ can be reversibly converted into the blue coloured monomer $Co[py]_2Cl_2$ which has a tetrahedral structure.

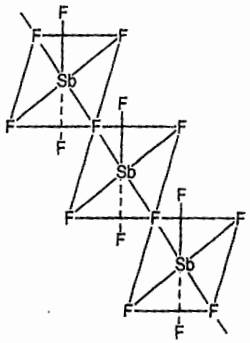
Polymeric $[Pt(NH_3)_2Br_3]_n$. There are many polymers in which only two of the six ligands around each octahedrally coordinated metal ion form bridges between the metal ions. Well known examples are $[Pt(NH_3)_2Br_3]_n$ and $[Pt(en)_2Br_3]_n$. The structure of $[Pt(NH_3)_2Br_3]_n$ polymer is as shown.



As can be seen, the polymer has a chain structure containing alternating bromine bridged units, $Pt(II)(NH_3)_2Br_2$ and $Pt(IV)(NH_3)_2Br_4$.

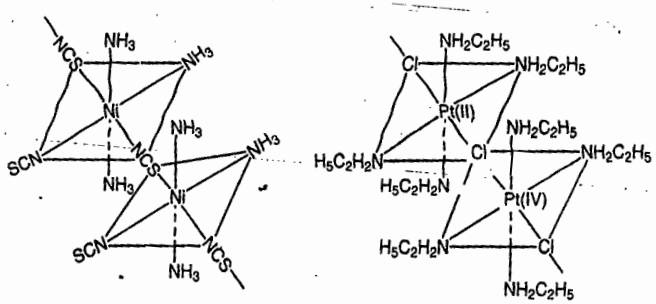
The polymer $[Pt(en)_2Br_3]_n$ has similar structure.

Polymeric $[SbF_5]_n$. Antimony pentafluoride has recently been found to be polymeric in naure. ^{19}F NMR shows three types of fluorines in the ratio of 1 : 2 : 2, thus supporting the structure as shown.

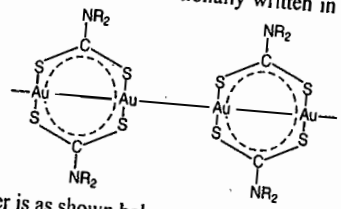


As can be seen, the structure has two fluorines in equivalent axial positions and two fluorines in equivalent equitorial positions around each Sb atom. There are two bridging fluorines in equivalent equatorial positions around each Sb atom but the number of bridging flourines per antimony atom is one, as can be seen from the structure.

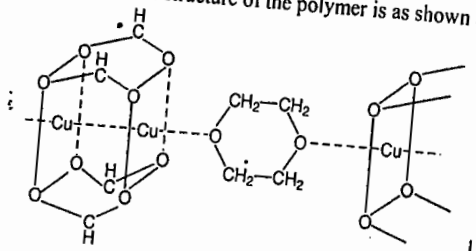
Polymeric $[Ni(NH_3)_3(NCS)_2]_n$ and the Wolfram's Red Salt, $[Pt(C_2H_5NH_2)_4Cl_2]$–$[Pt(C_2H_5NH_2)_4]Cl_4$. The polymeric $[Ni(NH_3)_3(NCS)_2]_n$ has the structure as shown below in which two NCS groups around each Ni atom are the bridging ligands. Wolfram's red salt has a structure with chains of Pt(II)Cl–Pt(IV)Cl, as shown.



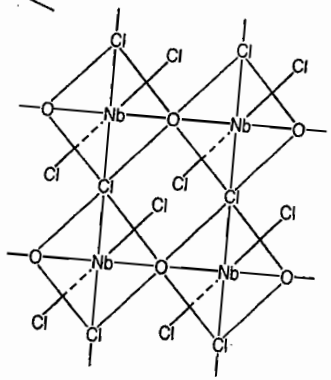
Polymeric Thiocarbamates of Gold. The thiocarbamates of gold are conventionally written in the monomeric form $(R_2NCS_2)Au$. Actually these are polymeric and should be represented as $[(R_2NCS_2)Au]_n$. These polymers have the structure as shown.



Polymeric Adduct of Copper(II) Formate with Dioxane. This adduct has a polymeric structure in which each Cu atom is present in octahedral environment and is bridged to another Cu atom by dioxane. There is a weak Cu·····Cu association in the polymer. The structure of the polymer is as shown below :



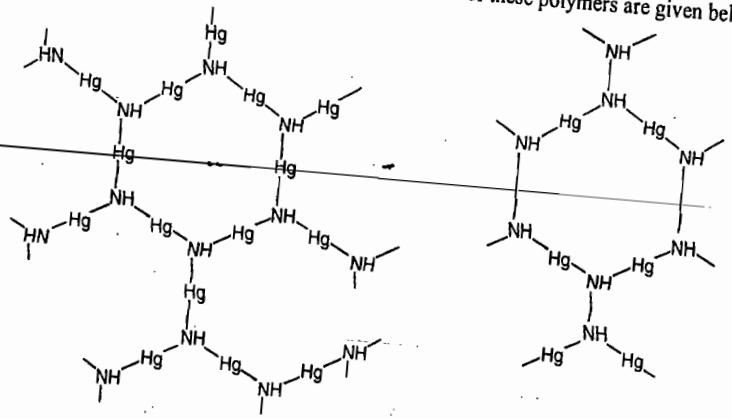
Polymeric $(NbOCl_3)_n$. Each Nb in this polymeric compound has octahedral environment consisting of four chlorine and two oxygen atoms. The bridging Cl and O atoms constitute a double chain as shown.



B. Two-Dimensional Polymers

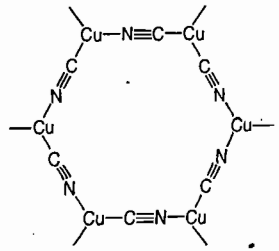
The commonly known two-dimensional polymers are **$[Hg_2(NH)Br_2]_n$ and $[Hg_2(N_2H_2)Cl_2]_n$.**

These polymers containing metal ions with a coordintaion number 2 form a 'planar' network structure with the help of a bridging ligand. The structure of the cations of these polymers are given below :

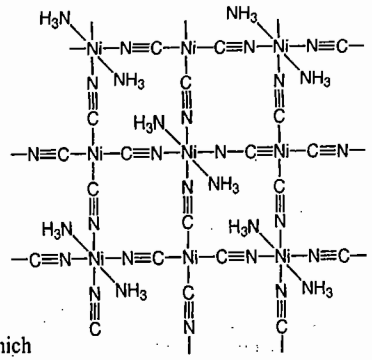


Polymeric $K_n[Cu(CN)_3H_2O]_n$. The structure of this polymer contains puckered hexagons of $Cu_6(CN)_6$. Water molecules fill the voids in the lattice. Each Cu atom has a coordination number 3.

The hexagonal structure of the anion of $[Cu(CN)_3H_2O]^-_n$ is as shown.



Polymeric $[Ni(NH_3)(CN)_2]_n$. The structure of polymeric $[Ni(NH_3)(CN)_2]_n$ consists of alternating square planar and octahedral Ni(II)s bridged by CN groups as shown. The octahedral Ni(II) has two NH_3 molecules trans to each other.

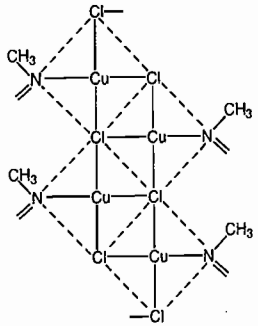


Polymeric $[Cu_2Br(OH)_3]_n$. This is a polymeric complex of Cu(II) having layer structure in which each Cu atom has 4 oxygen atoms around it in a square planar fashion.

Polymeric $(HgI_2)_n$. In this red coloured compound, the sheets are composed of two layers of iodine atoms with Hg atoms placed between them in such a manner that two iodine atoms from the upper layer and two from the lower layer occupy tetrahedral sites around each Hg atom.

Polymeric $(2HgO.HgCl_2)_n$. It has a layer structure in which three bridging oxygens and one terminal chlorine occupy tetrahedral sites around each Hg atom.

Polymeric $(Cu_2Cl_2.CH_3N_2CH_3)_n$. This compound has the structure as shown in which each Cu atom is tetrahedrally surrounded by three Cl atoms and one N atom.



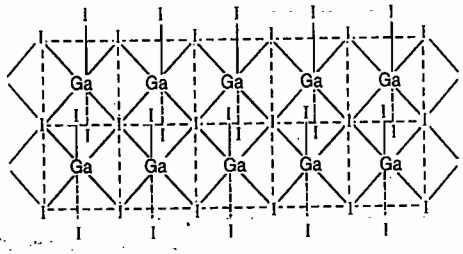
Polymeric Dihalides of Cadmium. $(CdI_2)_n$ and $(CdCl_2)_n$ are also polymeric. These are sheet polymers based on octahedral centres. In $(CdI_2)_n$, the I atoms are hexagonally close packed and Cd atoms occupy the octahedral sites formed by the two layers of I atoms. In $(CdCl_2)_n$, the Cl atoms are cubic closed packed and Cd atoms again occupy the octahedral sites between the two layers of Cl atoms.

Polymeric Trihalides. Polymeric trihalides are of the following three types :

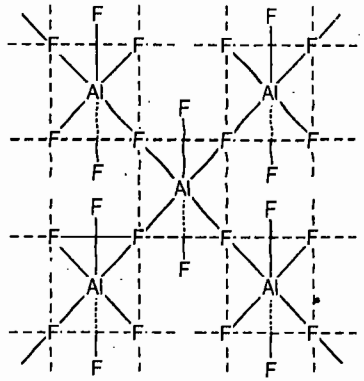
1. $(CrCl_3)_n$ Type. In this type, chlorine atoms are cubic close packed and 2/3rd of octahedral sites between two adjacent layers of chlorine atoms are occupied by the metal atoms M(III) where M = Cr, Ru.

2. $(BiX_3)_n$ Type. In this type, the halogen atoms are hexagonally close packed and 2/3rd of octahedral sites between two adjacent layers of the halogen atoms are occupied by the metal atom M(III). Examples are BiI_3 and $CrBr_3$.

3. $(GaI_3)_n$ Type. In this type, the metal atom is coordinated to four I atoms of the layer and to two I atoms trans to the layer. The structure of the well knwon polymer $(GaI_3)_n$ is as shown.



Polymeric Sheet Anions. Polymeric sheet anions based on octahedral coordination are also known. There are, for example, many tetrafluoaluminates in which $(AlF_6)^{3-}$ units share four equatorial corners as shown.



The same arrangement exists in tetrafluoanions of Ni(II), Cu(II), Zn(II), etc.

C. Polymers with Three-Dimensional Network

Several compounds containing the polymeric cation $(Hg_2N)^{n+}_n$, in whihc Hg orbitals are *sp* hybridised and N orbitals are sp^3 hybridised, are known. Their structure is *inverse trydmite* with Hg replacing O and N replacing Si in it. Tetrahedral N in Hg_2N^+ unit is responsible for forming three-dimensional network. Hg in this cation has a coordination number 2.

Zinc cyanide is also polymeric and has a three-dimensional network based on tetrahedral coordination of Zn in $Zn(CN)_4$ units which are linked together through linear CN bridges between Zn atoms.

Silver chloride is also polymeric in which Ag and Cl atoms have coordination number of 6 each. The bond between Ag and Cl atoms is predominantly covalent.

Apart from the above mentioned examples of natural polymers, there are millions of synthesised inorganic compounds which were earlier thought to be monomeric but have now been found to be polymeric. It is not possible to give a list of all such compounds in this book.

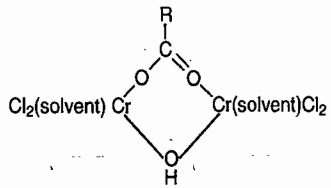
2. Synthetic Coordination Polymers

The coordination polymers which were intentionally synthesised as polymeric compounds are known as **synthetic coordination polymers.** Very few of the synthetic coordination polymers have inorganic back bones and even in those having inorganic back bones, the ligands involved are of organic origin.

The thermal stability of synthetic coordination polymers is not very much different from that of organic polymers since both types of polymers contain bonds involving carbon atoms.

A brief description of important synthetic coordination polymers is given below.

Volan and Quilon Polymers. Volan and quilon are coordination polymers of chromium. A typical process for synthesizing these polymers involves the reduction of CrO_2Cl_2 by methanol or ethanol in the presence of an appropriate carboxylic acid. This yields a solution of a coordination polymer with the structure as shown.

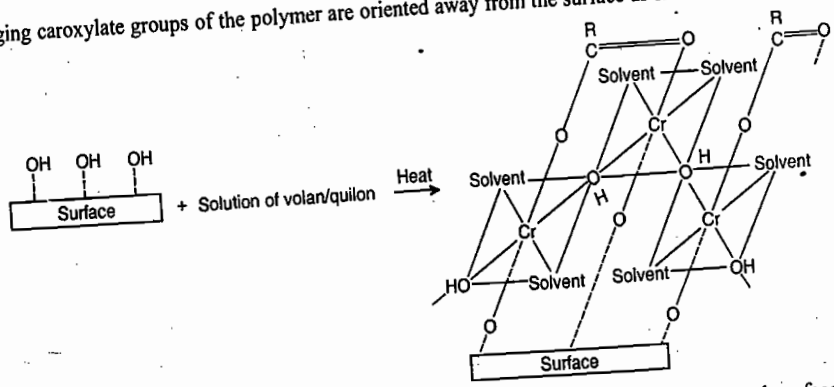


If R comprises of methacrylate groups, the polymer is called **volan** and if it comprises of stearate and myristate groups, the polymer is called **quilon.**

The dilution of the solution of volan or quilon in the presence of a base leads to ionisation of chlorine and a further bridging of Cr atoms by OH^- groups.

If a glass surface containing functional groups such as OH, NH_2, COOH, O^-, $CONH_2$, etc., is treated with the above solution and heated, further polymerisation occurs giving an insoluble coating which is attached firmly to the surface. The polymer adheres to the treated surface in such a manner that the

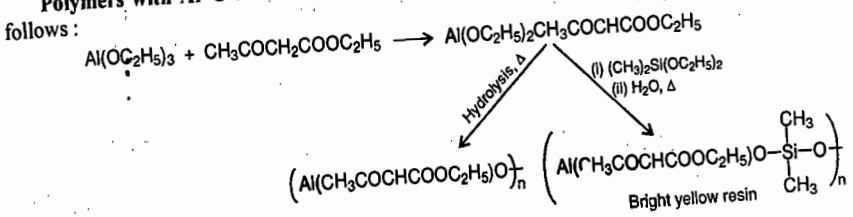
bridging caroxylate groups of the polymer are oriented away from the surface as shown :



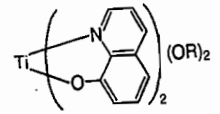
The methacrylate, stearate and myristate groups are oriented away from the treated surface. The carboxylate groups of volan or quilon impart water-repellence and non-adhesiveness to the treated surface.

Carboxylate group containing fluorocarbons, when used in the preparation of the coordination polymers, produces a coating on treated surface which makes it both water and oil-repellent.

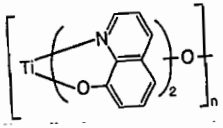
Polymers with Al–O Back Bone. Some polymers with Al–O back bone have been synthesised as follows :



Polymers with Ti–O Back Bone. Monomers, such as the one shown, can be easily prepared by interaction of 8-hydroxy quinoline with tetraalkoxy titanium.

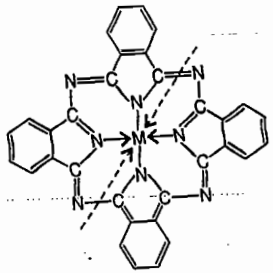


The hydrolysis and subsequent heating produces polymers of the type as shown with Ti–O back bone. This particular polymer is stable upto 400° C. It is infusible and sparingly soluble in organic solvents.

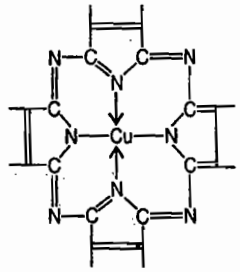


A copolymer with Ti–O–Si–O back bone can also be prepared by reacting the monomer with $(C_6H_5)_2Si(OH)_2$. The copolymer has the composition $[Ti(C_9H_6NO)_2OSi(C_6H_5)_2O]_n$. It is stable upto 275° C.

Polymers having Pthalocyanine and Related Structures. One of the most thermally stable systems of coordination compounds is the one which contains the pthalocyanine structure, as shown.



Two types of procedures have been adopted for the preparation of polymeric compounds containing pthalocyanine structure :

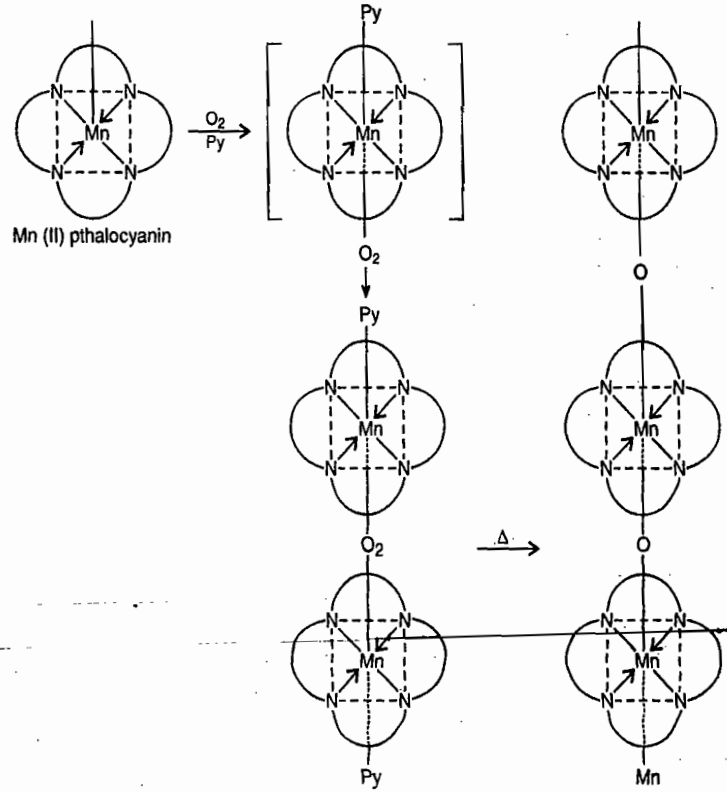


1. Polymerisation through pthalocyanine units. The reaction of 3, 3, 4, 4- tetracyanodiphenyl ether and a copper salt yields a cross-linked pthalocyanine.

In general, a tetranitrile or pyromellitic anhydride reacts with a metal salt to produce a pthalocyanine polymer.

The reaction of bis (β-diketonato) Cu(II), *i.e.*, $Cu(CH_3COCHCOCH_3)_2$ with $C_2(CN)_4$ results in pthalocyanine-like polymers having the structure as shown.

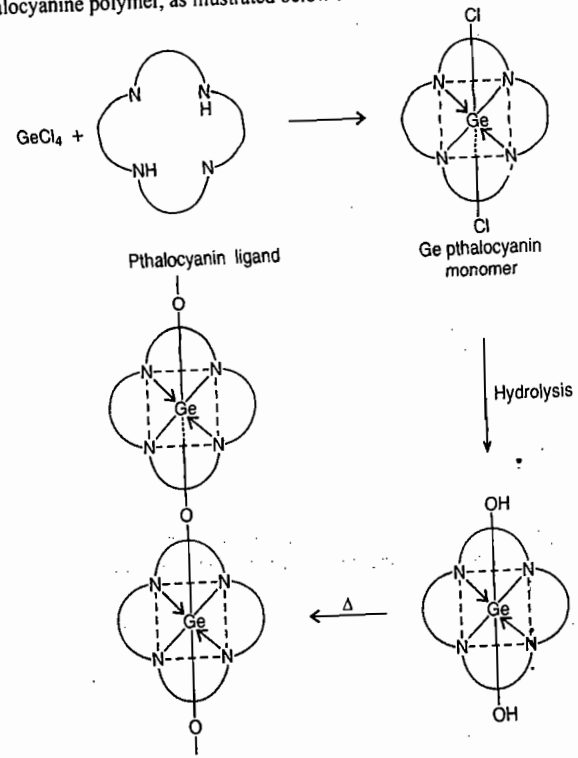
2. Increasing the coordination number of the central metal ion in pthalocyanine. Mn(II) pthalocyanine produces a dimer when the aerial oxygen is passed through its pyridine solution. This dimer containing hexa-coordinated Mn(II) then loses pyridine to yield a long chain polymer containing several pthalocyanine units as shown :



The polymer obtained has the formula $[Mn(C_{32}H_{16}N_8)O]_n$. It is a thermally stable polymer.

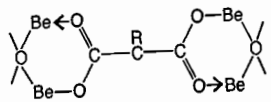
Similarly, Ge increases its coordination number from 4 to 6 when it changes from the Ge-pthalocyanine

monomer to Ge-pthalocyanine polymer, as illustrated below :



The polymer $[Cr(C_{32}H_{16}N_8)OAc]$ has a similar structure except for the fact that this polymer has acetato bridge instead of the oxo bridge.

Polymers derived from Basic Beryllium Carboxylates. Basic beryllium acetate itself is polymeric and its structure has already been described in Chapter 14. Replacement of monocarboxylate group with dicarboxylate group yields the type of polymer shown.

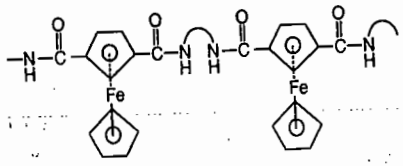


The polymer is unstable and decomposes to give $Be_4O(OOCRCOO)_3$.

The basic beryllium acetate $Be_4O(OAc)_6$ reacts with C_4H_9OH to give a low molar mass polymer :

$$Be_4O(OAc)_6 \xrightarrow{C_4H_9OH} [Be(OH)(OOCCH_3)Be(OC_4H_9)(OOCCH_3)]_n$$

Polymers with Cyclopentadienyl Rings. The –COCl derivative of ferrocene reacts with diamines and dihydroxy compounds to yield polymeric product of the formula



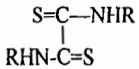
Similarly, ferrocene, in the presence of free radicals, gets polymerised to $(C_5H_4FeC_5H_4)_n$.

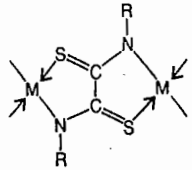
Dichlorodicyclopentadienyl titanium reacts with $TiCl_4$, followed by hydrolysis to give polymeric product $[Ti(C_5H_5)ClO]_n$, as shown below :

$$Ti(C_5H_5)_2Cl_2 + TiCl_4 \longrightarrow 2Ti(C_5H_5)Cl_3 \xrightarrow{\text{hydrolysis}} [Ti(C_5H_5)ClO]_n$$

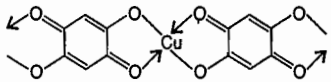
This polymer is thermodynamically stable upto 260°C.

Polymers with bis Chelating Agents. A number of organic ligands can act as bis chelating agents, that is, one part of such ligands coordinates to one metal ion and the other part to another metal ion leading to chains of ligands and the metal ions. There are many ligands of this type which form polymers when reacted with the metal salts. Some of these systems are discussed below.

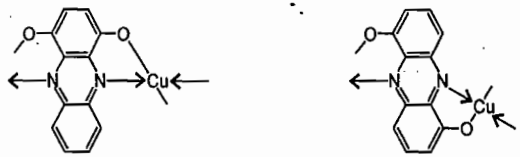
1. Dithiooxamides such as rubeanic acid  react with a number of cations such as Cu^{2+}, Ni^{2+}, etc., to yield polymeric products of the type shown.



2. Dihydroxy quinones such as 2,5 dihydroxy p-benzoquinone also act as bis chelating agents with Cu^{2+}, Ni^{2+}, Cd^{2+}, etc., to give polymeric products of the following type :

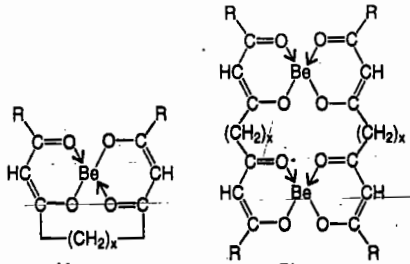


3. The chelating reagents 1,4 and 1,6 dihydroxyphenazines act as catenating groups to yield the following types of polymers :



These polymers are solids at room temperature.

4. Bis β-diketonates such as $C_6H_5CO(CH_2)_8COCH_2COC_6H_5$ yield low melting fibre-forming polymers with metal ions such as Be^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc. The polymers formed are of low molar mass. The low solubility of the monomer is perhaps the cause of insufficient extent of polymerisation. This view is supported by the fact that the degree of polymerisation in vapour phase is greater than in solution phase. Thus when Be polymers of low molar mass, obtained by reacting Be^{2+} with bis β-diketonates in solution phase, are sublimed, they, first of all, degrade to give monomers and dimers of the type as shown. When these monomers or dimers further react in vapour phase, they yield high molar mass polymers which are amorphous solids with intrinsic viscosity varying between 0·1–2·7.



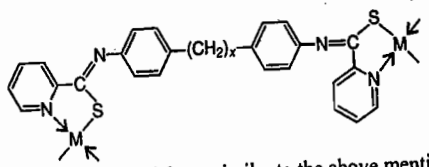
5. Diols can also act as bis chelating agents. For example, pyrocatechol when reacted with $Al(OR)_3$ yields a polymer of the type $(Al(OR)OC_6H_4O)_n$.

6. Some Schiff's bases and related ligands containing –CH=N– groups also act as bis chelating agents. The salicyladimine made from aromatic diamines and salicylaldehyde react with Cu(II) salts to give a mixture of soluble and insoluble copper derivatives. The soluble derivatives are dimeric whereas the

insoluble derivatives are polymeric. Similarily,

$$C_6H_5-COCH_2-\underset{CH_3}{C}=N(CH_2)_5N=\underset{CH_3}{C}-CH_2COC_6H_5$$

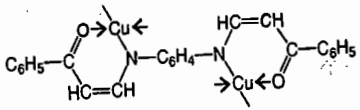
reacts with Cu(II) to give tarry products which are believed to be polymeric. Thiopicolinamides form polymers with Cu(II), Ni(II), Zn(II) with a molar mass around 4000. These polymers have the following structure :



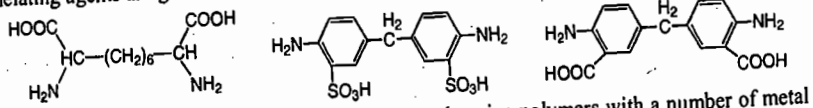
Another series of bis chelating agents, which are similar to the above mentioned ligands, are ketoimidies of the type

$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH=CH-NH-C_6H_4-NH-CH=CH-\overset{O}{\overset{\|}{C}}-C_6H_5$$

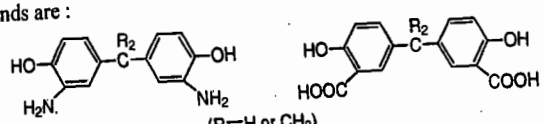
which, with Cu (II), form polymers of the type :



7. There are several bis amino acids which act as chelating as well as catenating agents when they react with a number of metal ions such as Cu(II), Ni(II), etc., to give insoluble polymeric products. Some such chelating agents are given below :

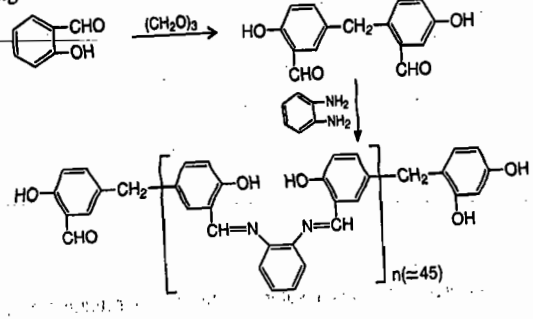


Many other structurally similar bis chelating agents also give polymers with a number of metal ions. Examples of such ligands are :

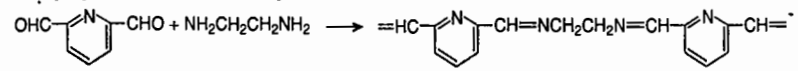


(R=H or CH_3)

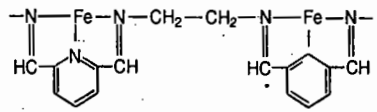
Polymers of Polymeric Ligands. Polymeric Schiff's bases constitute an important class of polymeric ligands. One of these ligands can be prepared in the following manner :



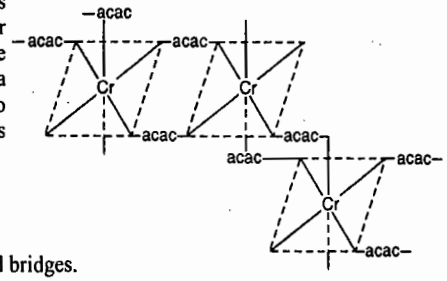
Another polymeric ligand can be synthesised as follows :



The metal ions are accommodated by these ligands in chelation sites to produce the coordination polymer. For example, the polymeric ligand II reacts with $FeSO_4$ to give Fe (II) polymer having the structure as shown.



Double Bridged Polymers. When the chromium complex tris(acetylacetonato)Cr(III) reacts with diphenylphosphoric acid, a polymer $[Cr(CH_3COCH_2COCH_3)_2OP(C_6H_5)_2O_2]_n$ results whose molar mass varies between 5000 and 11000. It has a structure in which each Cr atom is doubly bridged to another Cr atom by acetylacetonato (acac) bridges, as shown.

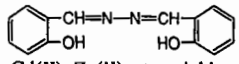


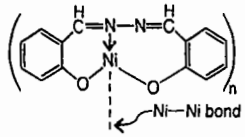
It has been possible to make fibres and films from low molar mass soluble fractions of the polymer which indicates that double bridges are flexible. The flexibility and the spiral nature of back bone is due to 8-membered bridges.

Miscellaneous Polymers. Besides the polymers discussed above, there are some other coordination polymers which do not fall under any one category. For instance, the reaction of ferrocene with diazotised p-amino salicylaldehyde gives tetrasalicyl derivative of ferrocene which acts as a bis chelating agent with various metal salts to give coordination polymers.

Venyl ferrocene can be polymerised by acid catalysis to produce polymeric oils. Also azo diisobutylnitrite converts venyl ferrocene into a solid polymer whereas chloroprene converts venyl ferrocene into an elastomer. A mixture of venyl ferrocene and cinnamoyl ferrocene can be polymerised with dienes or azodiisobutyl nitrite.

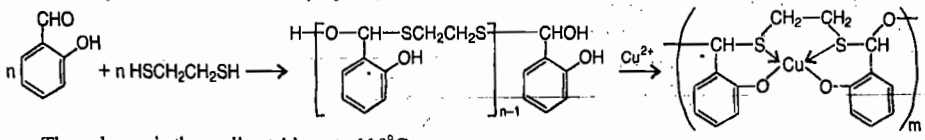
Bis(methylsalicylate)Be on mixing with polyallkylacetoacetate gives a polymer which when baked at 120°C, yields a hard product.

The compound  when treated with salts of Co(II), Cu(II), Ni(II), Cd(II), Zn(II), etc., yield a polymer with intermolecular coordination of the type shown.



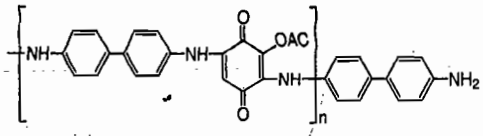
The polymer formed with Ni(II) is diamagnetic which does not melt or decompose upto 350°C.

Salicylaldehyde reacts with dithiols to give a polymeric ligand which then reacts with a metal ion such as Cu(II) to produce a coordination polymer, as illustrated below :



The polymer is thermally stable upto 110°C.

The polymeric ligand, polyaminoquinone having the structure



reacts with metal ions such as Cu(II) to yield an insoluble, infusible coordination polymer.

Polyacrylic acid can react with bivalent metal ions to give coordination polymers. Likewise, polyacrylhydroxamic acid reacts with a number of metal ions to yield coordination polymers. The 1:1 complexes of tris (2-hydroxyphenyl)–S–triazine are polymeric in nature.

The existence of a large number of purely inorganic coordination systems with polymeric character leaves no doubt that purely inorganic polymers can be made and used. But, at present, most of the coordination polymers prepared are rather poorly characterised and are semi-organic in nature. Such polymers generally have low molar mass and decompose in 250–350° C range. As such, these semi-organic polymers have been put to a very limited use.

Isopoly and Heteropoly Acids and Anions

The polymerisation of simple monomeric oxide anions of Cr, Mo, W, V, Nb and Ta occurs when their alkaline solutions are gradually acidified. The polymerisation of CrO_4^{2-} ion yields polymeric anions which are structurally different from the polymeric anions of Mo, W, V, Nb and Ta. Therefore, polymerisation of CrO_4^{2-} anion is discussed first.

1. Polymerisation of CrO_4^{2-} Anion

Only CrO_4^{2-} ion exists in aqueous solutions above *p*H 8. On gradually decreasing the *p*H of the solution, the ions $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ are formed by the corner sharing of tetrahedral CrO_4^{2-} units. These polymeric anions are isolated from their solutions as sodium and potassium salts. Their structures are given in Fig. 1.

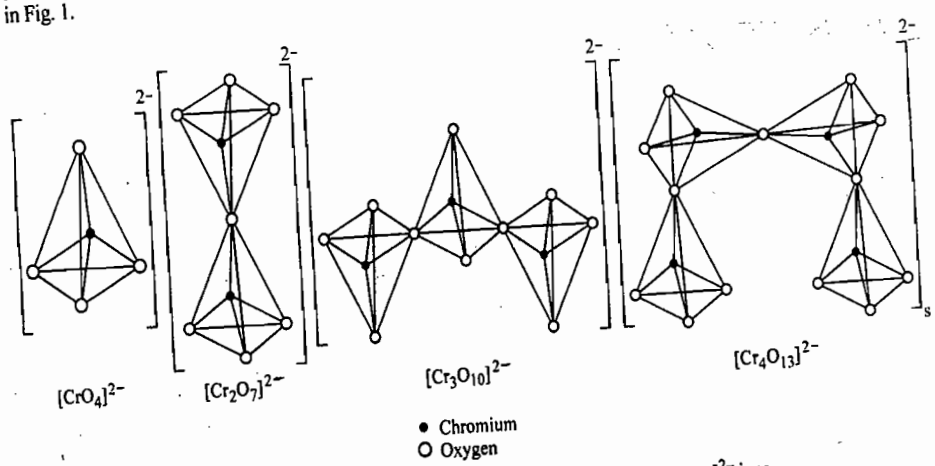


Fig.1. The structures of $[CrO_4]^{2-}$, $[Cr_2O_7]^{2-}$, $[Cr_3O_{10}]^{2-}$ and $[Cr_4O_{13}]^{2-}$ ions.

Out of the isopolyanions of Cr^{6+}, Mo^{6+}, W^{6+}, V^{5+}, Nb^{5+} and Ta^{5+}, only the isopolyanions of Cr^{6+} are formed by sharing the corners of CrO_4^{2-} tetrahedra. The isopolyanions of V^{5+}, Nb^{5+}, Ta^{5+}, Mo^{6+} and W^{6+} are formed by sharing the corners and/or edges (but not faces) of MO_6 octahedra (M = V^{5+}, Nb^{5+}, Ta^{5+}, Mo^{6+}, W^{6+}). This is probably due to the small size of Cr^{6+} ion which comfortably accommodates four O^{2-} anions tetrahedrally around itself. The surrounding six O^{2-} anions around the small-sized Cr^{6+} cation increase the electrostatic repulsion amongst the six similarly charged O^{2-} ions making octahedral CrO_6^{6-} ion unstable in spite of two additional Cr–O bonds formed in going from CrO_4^{2-} to CrO_6^{6-}. The bigger-sized V^{5+}, Nb^{5+}, Ta^{5+}, Mo^{6+} and W^{6+} can accommodate six O^{2-} anions octahedrally around themselves in their isopolyanions without being destabilised.

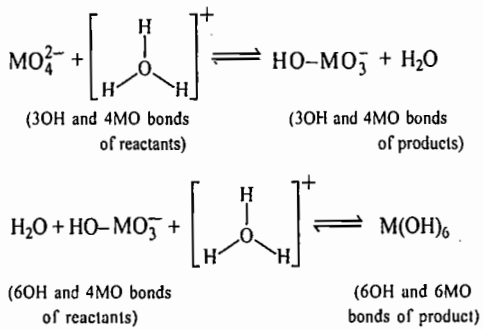
2. Polymerisation of Molybdates, Tungstates, Vanadates, Niobates and Tantalates

The acidification of basic solutions of vandate ion $[VO_4^{3-}]$, niobate ion $[NbO_4^{3-}]$, tantalate ion $[TaO_4^{3-}]$, molybdate ion $[MO_4^{2-}]$ and tungstate ion $[WO_4^{2-}]$ leads to their polymerisation yielding polyacids and polyanions. These polyacids and polyanions are of the following two types :

(*a*) Isopoly acids and their anions which contain Mo^{6+}, W^{6+}, V^{5+}, Nb^{5+} or Ta^{5+}, apart from O and H.

(*b*) Heteropoly acids and anions which contain O, H, any one of Mo^{6+}, W^{6+}, V^{5+}, Nb^{5+}, Ta^{5+} and one or two atoms of another element in addition to the already present metal ion.

(*a*) Isopoly Anions and Isopoly Acids of Mo^{6+} and W^{6+}. In strongly basic solutions, only simple molybdate (MoO_4^{2-}) and tungstate (WO_4^{2-}) ions exist. On acidification of their solutions, the following equilibria are established. :



In spite of the unfavourable ΔS in the second reaction, it is found to be as facile as the first reaction. This is because the enthalpy of the second reaction is large and negative and it more than compensates unfavourable ΔS of their reaction. (The large negative enthalpy of the second reaction results from the formation of two additional MO bonds in going from the reactants to the product.)

The $M(OH)_6$ formed in the second reaction reacts with HMO_4^- ion present in the acidic medium in the following manner :

$$M(OH)_6 \underset{-H_2O}{\overset{HMO_4^-}{\rightleftharpoons}} [(HO)_5MOMO_3]^- \underset{-H_2O}{\overset{HMO_4^-}{\rightleftharpoons}} [(HO)_4M(OMO_3)_2]^{2-} \underset{-H_2O}{\overset{HMO_4^-}{\rightleftharpoons}} [(HO)_3M(OMO_3)_3]^{3-}$$

$$\Big\Updownarrow HMO_4^- \; -H_2O$$

$$\underset{\text{(contains condensing } MO_6 \text{ octahedral units)}}{[M_7O_{24}]^{6-}} \underset{}{\overset{\text{isomerisation}}{\rightleftharpoons}} \underset{\text{(contains } MO_4 \text{ tetrahedral units)}}{[M(OMO_3)_6]^{6-}} \underset{-H_2O}{\overset{HMO_4^-}{\rightleftharpoons}} [(HO)M(OMO_3)_5]^{5-} \quad [(HO)_2M(OMO_3)_4]^{4-}$$

The rearrangement of isopolyanions containing tetrahedral MO_4 units to the isopolyanions containing octahedral MO_6 units may occur either in the last step (as shown above) or in any of the earlier steps. During the rearrangement, the coordination number of metal changes from 4 to 6 and the basic building unit of isopolyanion becomes MO_6 octahedron. The MO_6 octahedra link with each other by sharing an edge or a vertex (*but not a face*).

In the condensing MO_6 octahedra present in the isopolyanions and isopolyacids, the terminal MO bond lengths are shorter than bridged MO bond lengths. The presence of longer bridged M–O–M bonds formed due to edge sharing of MO_6 octahedra in the isopoly acids and anions increase the distance r between the edge sharing MO_6 octahedra and thereby decrease the inter-metal ion repulsions, as shown below in Fig.2.

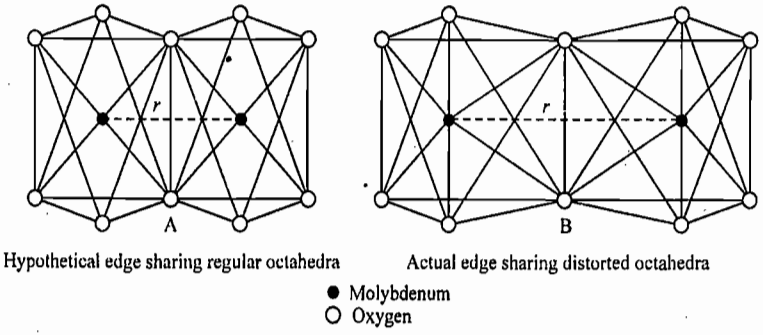


Fig. 2. The structures of regular edge sharing MO_6 octahedra and the distorted edge sharing MO_6 octahedra.

Thus, the distortion of MO_6 octahedra by edge sharing stabilises the structures of isopoly anions and isopolyacids. Considering that electrostatic repulsion among the metal ions is a dominant factor in rationalising structures of polyanions, the corner sharing which increases the distance between the metal ions of the condensing octahedra to a large extent should be more common than edge sharing in the structures of isopolyanions and acids.

Actually, however, edge sharing of MO_6 octahedra is prefered over the corner sharing in the structures of isopolyanions and acids. This is because the edge sharing reduces the number of O^{2-} ions in the structures of isopolyanions and isopolyacids to a greater extent than does the corner sharing. The edge sharing, therefore, reduces the unfavourable high O^{2-} anionic charges around the metal ion of the condensing MO_6 octahedra to a greater extent than does their corner sharing. In other words, the edge sharing stabilises the structure containing condensing MO_6 octahedra to a greater extent than does the corner sharing. The face sharing of MO_6 octahedra in isopolyanion does not occur although it should reduce the unfavourable O^{2-} anionic charge on their condensing MO_6 octahedral structure most effectively. This is because the condensation of MO_6 octahedra by face sharing brings metal ions *closest* to each other and thus causes the highest metal ion–metal ion repulsions compared to condensation of MO_6 octahedra by edge sharing or corner sharing.

The edge sharing of MO_6 octahedra and the subsequent metal ion–metal ion repulsions distort the condensing MO_6 octahedra in the structures of isopolyanions. The distorted MO_6 octahedra in the structures of isopolyanion become increasingly difficult to be accommodated as the size of the isopolyanion increases. Ultimately a stage is reached when edge sharing is no longer possible. Further condensation of MO_6 octahedra to produce bigger-sized isopolyanions then occurs by vertex (or apex) sharing of distored MO_6 octahedra.

The stage of saturation of edge sharing of MO_6 octahedra is reached earlier by isopolyanions of relatively

bigger metal ions because less number of bigger-sized edge sharing distored MO_6 octahedra can be accommodated in the isopolyanions of such metal ions. Thus, edge sharing of MO_6 octahedra can occur to a greater extent in the isopolyanions of smaller-sized Mo^{6+} ion than in the isopolyanions of the bigger-sized W^{6+} ion.

In addition to the electrostatic repulsion between the metal ions of the condensing distorted MO_6 octahedra of isopolyanions, there is another factor which also determines their structure. This is discussed below.

In the isopolyanions of Mo^{6+}, W^{6+}, V^{5+}, Nb^{5+} and Ta^{5+}, the terminal oxygens are strongly π bonded to the metal ion through its π bonding t_{2g} orbitals. The strongly π bonded oxygen atoms in isopolyanions are never trans to each other because they do not compete for the same π bonding t_{2g} orbital. Instead, they are always located opposite to a σ bonding bridging oxygen. The metal ions in the condensed MO_6 octahedra of isoprophyl anions are obviously pulled more in the direction of the shorter terminal M = O bond.

Thus, both the factors, the longer σ MO bonds of the M–O–M bridge and the shorter terminal M=O bond opposite to the bridging oxygens distort the condensed octahedra in the isopolyanions and isopolyacids to increase the distance between the metal ions of the adjacent condensing MO_6 octahedra and thus to decrease the metal ion–metal ion repulsions and to stabilise the structure of isopolyanion.

It is known that the metal ions like Al^{3+}, Ga^{3+}, In^{3+}, etc. do not form stable isopolyanions by sharing edges of condensing MO_6 octahedra. This is probably due to the fact that these metal ions are poor pi acceptors and do not form M = O bonds (M = Al^{3+}, Ga^{3+}, In^{3+}). Therefore, the necessary distortion of their MO_6 octahedra to increase metal ion–metal ion distance and to decrease metal ion–metal ion repulsion does not occur. This will make the isopoly anion structures of Al^{3+}, Ga^{3+} and In^{3+} based on condensing edge shared octahedra highly unstable and unlikely to occur.

From the above discussion, it can be inferred that there should be a larger number of edge sharing condensing MO_6 octahedra (M is the metal ion having M–O–M σ bonding and π bonding capability with O) in the isopoly anions of smaller metal ions. This appears to be true. For instance, the ionic radii of V^{5+}, Mo^{6+}, W^{6+}, Nb^{5+} and Ta^{5+} are 54 pm, 59 pm, 61 pm, 64 pm and 64 pm, respectively and their most common edge sharing polyanions are $[V_{10}O_{28}]^{6-}$, $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$, $[W_6O_{19}]^{2-}$ and $[W_7O_{24}]^{6-}$, $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ respectively.

The following four major molybdate species exist in solution :

(*a*) Simple MoO_4^{2-} ions which are stable at high *p*H, *i.e.*, in alkaline solutions.

(*b*) Heptapolymolybdate or paramolybdate $[Mo_7O_{24}]^{6-}$ which exists in solution at *p*H ~ 5.

(*c*) Octamolybdate $[\beta\text{-}Mo_8O_{26}]^{4-}$ formed in more acidic solutions.

(*d*) $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, the largest polymolybdate known till recently. However, even a larger anion, is formed at *p*H 1·8.

In very strong acidic solutions *p*H << 1·8, the hydrated oxide MoO_3 is obtained.

Apart from the above mentioned major isopolymolybdate species, other isopolymolybdates formed in solution by acidification of MoO_4^{2-} ion are $Mo_2O_7^{2-}$, $[Mo_6O_{19}]^{2-}$ and $[Mo_{10}O_{34}]^{8-}$.

In some of the structures, $[MoO_4]^{2-}$ tetrahedra are also present along with MoO_6 octahedra. The structures of some isopolymolybdate ions are shown in Figs. 3*a*, *b*, *c*, *d*, *e* and *f*.

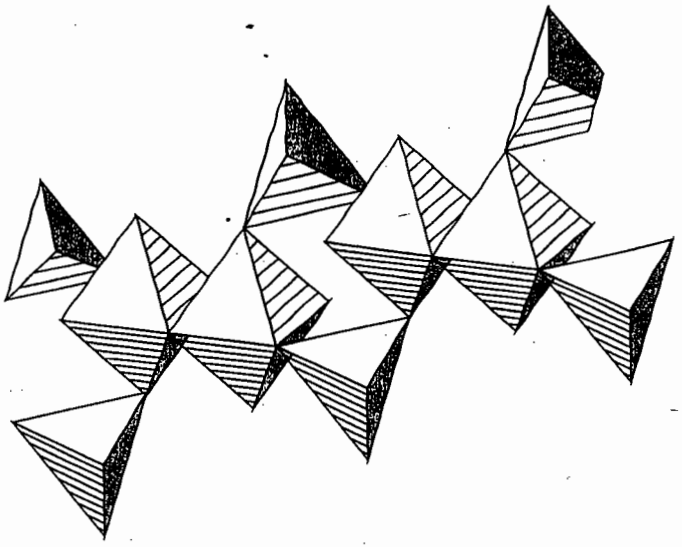


Fig. 3 (*a*). The polymeric structure of $[Mo_2O_7]_n^{2-}$ in which the edge shared MoO_6 octahedra are linked through MoO_4 tetrahedra.

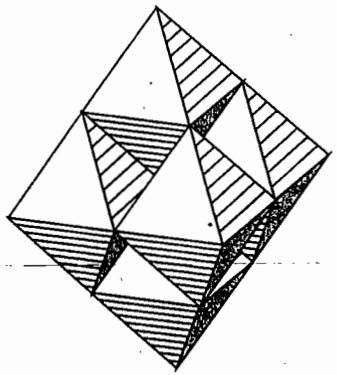


Fig. 3 (*b*). The structure of $[Mo_6O_{19}]^{2-}$ in which the sixth octahedron is hidden

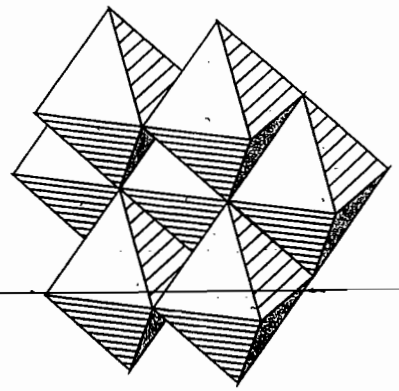


Fig. 3 (*c*). The structure of para molybdate $[Mo_7O_{24}]^{6-}$

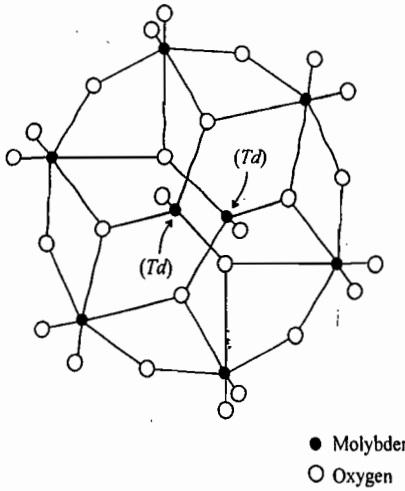


Fig. 3 (*d*). The structure of α-$[Mo_8O_{26}]^{4-}$ ion in which a ring of six MoO_6 octahedra is capped with two MoO_4 tetrahedra

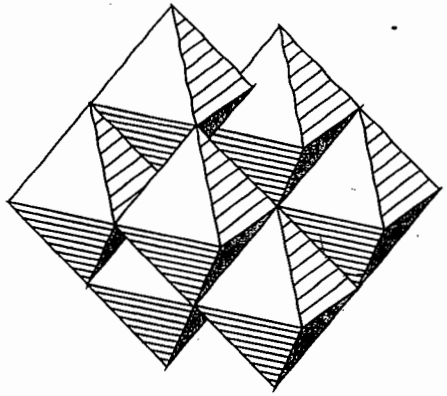


Fig. 3 (*e*). The structure of β-$[Mo_8O_{26}]^{4-}$ ion in which one MoO_6 unit is obscured

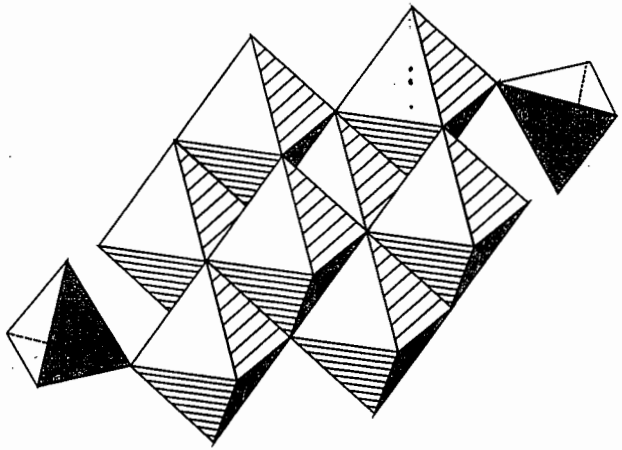


Fig. 3 (*f*). The structure of an isopolymolybdate $[Mo_{10}O_{34}]^{8-}$ ion

Both α and β forms of $[Mo_8O_{26}]^{4-}$ can coexist in solution in equilibrium with each other. The structure of α-$[Mo_8O_{26}]^{4-}$ consists of a central ring of six edge sharing distorted octahedra capped by a tetrahedral MoO_4 unit on each side of this ring. The capped tetrahedral MoO_4^{2-} units in $[Mo_8O_{26}]^{4-}$ can be replaced by isostructural $[PhAsO_3]^-$. The structure of β isomer consists entirely of condensing MoO_6^{6-} octahedra. Both α and β $[Mo_8O_{26}]^{4-}$ can coexist in solultion in equilibrium with each other.

Gradual acidification of strongly alkaline Na_2WO_4 solution produces $[W_6O_{19}]^{2-}$, $[W_7O_{24}]^{6-}$ (para tungstate A) and its protonated form $[HW_7O_{24}]^{5-}$, the dodecameric $[H_2W_{12}O_{40}]^{6-}$ (meta tungstate ion) and $[H_2W_{12}O_{42}]^{10-}$ (para tungstate B). The structures of $[W_6O_{19}]^{2-}$ and $[W_7O_{24}]^{6-}$ are similar to $[Mo_6O_{19}]^{2-}$

and $[Mo_7O_{24}]^{6-}$. The structures of the other isopolytungstate ions are given in Figures 4, 5, 6, and 7.

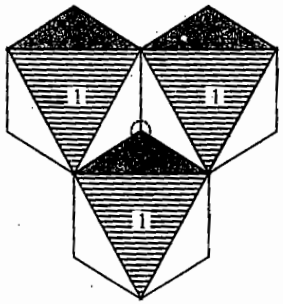


Fig. 4 (*a*). A 'tritungstate' group made up of three edge-sharing WO_6 octahedra. Four such 'tritungstate' groups are present in metatungstate ion

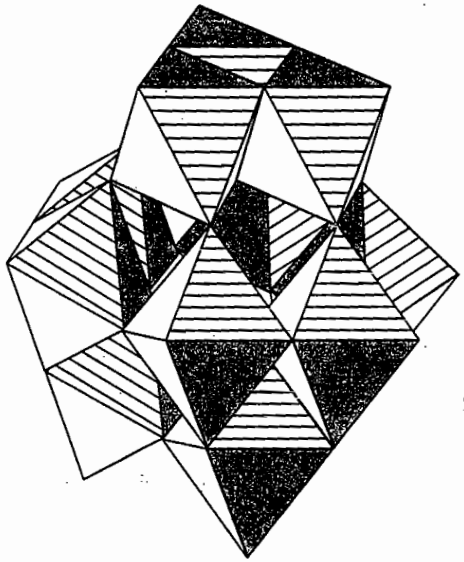


Fig. 4 (*b*). The structure of meta tungstate ion $[H_2W_{12}O_{40}]^{6-}$. The two protons (H^+) are present in the inner cavity formed by four 'tritungstate' groups of the ion.

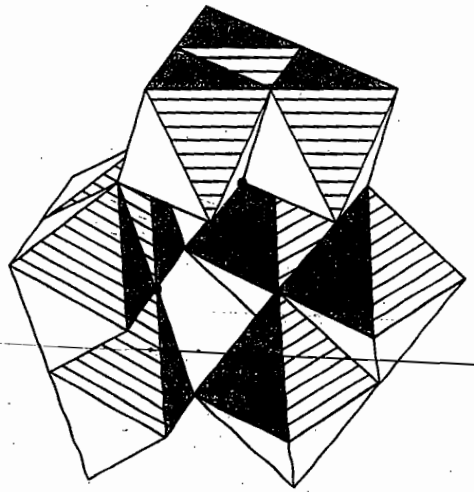


Fig. 4 (*c*). The inner tetrahedral cavity in the meta tungstate ion shown after removing (1,1,1) tritungstategroup of meta teungstate ion whose struture is shown in Fig. 4(*b*) the fourth point of tetrahedral cavity is shown in Fig 4(*a*) by ◌ which indicates that the fourth point lies on the other side of the tritungstate group (1, 1, 1).

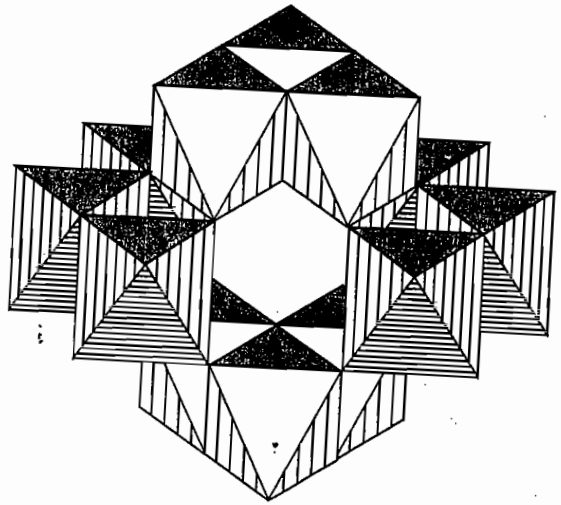


Fig. 5. The structure of para tungstate B ion $[H_2W_{12}O_{42}]^{10-}$

The structure of meta tungstate ion $[H_2W_{12}O_{40}]^{6-}$ consist of four identical tritungstate groups, each such group made of three WO_6 edge sharing octahedra as shown in Fig. 4*a*. The four tritungstate groups are fused with each other through corner sharing to give a structure of perfect tetrahedral symmetry (Fig. 4*b*). Such a structure is called "Keggin structure". The two protons (H^+) occupy the inner tetrahedral cavity of Keggin structure which is more clearly shown in Fig. 4*c* where one tritungstate group (1, 1, 1) of Keggin structure (Fig. 4*b*) has been 'removed'. The structure of para tungstate B ion $[H_2W_{12}O_{42}]^{10-}$ is shown in Fig. 5. The top and bottom tritungstate groups are similarly placed as in meta tungstate ion $[H_2W_{12}O_{40}]^{6-}$ (Fig. 4*b*). But the other two tritungstate groups of middle layer are of different type. The three edge shared WO_6 octahedra of each tritungstate group of the middle layer form a chain. The structure of $[W_{10}O_{32}]^{4-}$ can be derived from the structure of $[M_6O_{19}]^{2-}$ (M = W) shown in Fig. 3*b*. If one WO_6 octahedron of this structure is removed and the two remaining parts, each of formula (W_5O_{16}), are fused through vertices, the structure of $[W_{10}O_{32}]^{4-}$ is obtained (Fig. 6). The structure of $[W_4O_{16}]^{8-}$ is shown in Fig. 7.

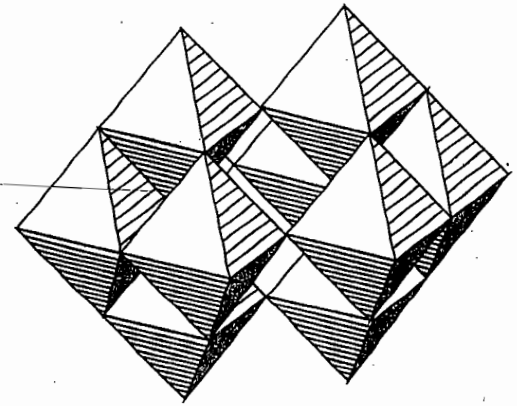


Fig.6. The structure of $[W_{10}O_{32}]^{4-}$ ion which is composed of two fused identical (W_5O_{16}) groups

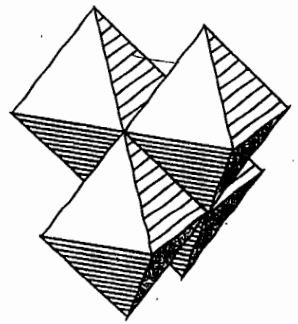


Fig.7. The structure of $[W_4O_{16}]^{8-}$ ion.

(b) Isopoly Vanadates, Isopoly Niobates and Isopoly Tantalates. When V_2O_5 is dissolved in strong alkaline solutions, monovanadate ion, VO_4^{3-} (also called orthovanadate ion), is predominantly formed. The gradual acidification of the alkaline solution of monovanadate ions, till neutralisation, produces pyrovanadate $V_2O_7^{4-}$ and metavanadate $[VO_3]_n^{n-}$. The structure of pyrovanadate ion contains two VO_4^{3-} tetrahedra linked through a vertex. The structures of $[VO_4]^{3-}$, $[V_2O_7]^{4-}$ and polymeric meta vanadate are shown in Figures 8*a*, 8*b* and 8*c*. The lines between V and O do not show the exact bond order.

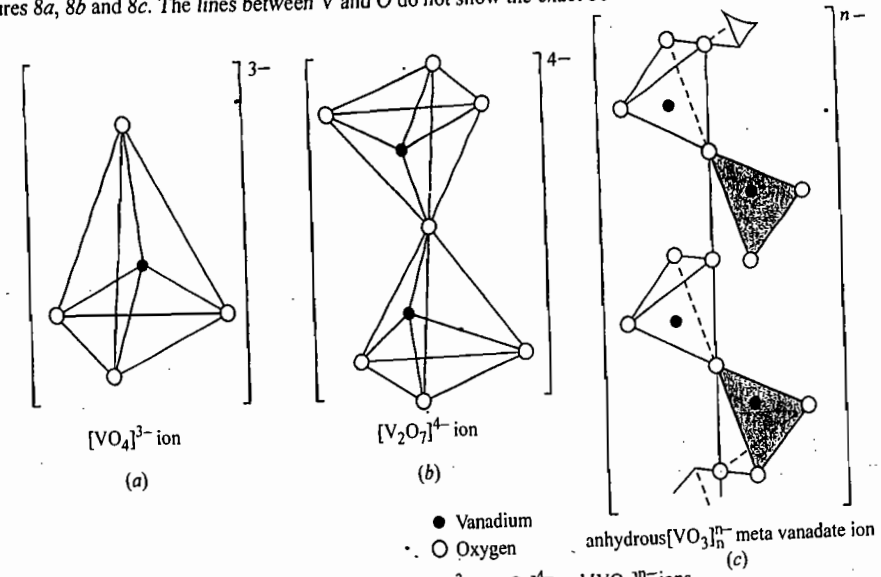


Fig. 8. The structures of $[VO_4]^{3-}$, $[V_2O_7]^{4-}$ and $[VO_3]_n^{n-}$ ions

The meta vanadate ions do not involve the discrete VO_3^- ions. The anhydrous meta vanadate such as NH_4VO_3 contains infinite chains of corner-linked VO_4 tetrahedra (Fig. 8*c*).

The ortho, pyro and meta vanadates are all based on tetrahedral VO_4 units in which the coordination number of V remains 4.

Further acidification of the vanadate solution, after the neutralisation, produces $[V_{10}O_{28}]^{6-}$.

The structure of $[V_{10}O_{28}]^{6-}$ is made up of ten edge sharing VO_6 octahedra in which vanadium aquires a coordination number of 6. Its structure is shown in Fig. 9.

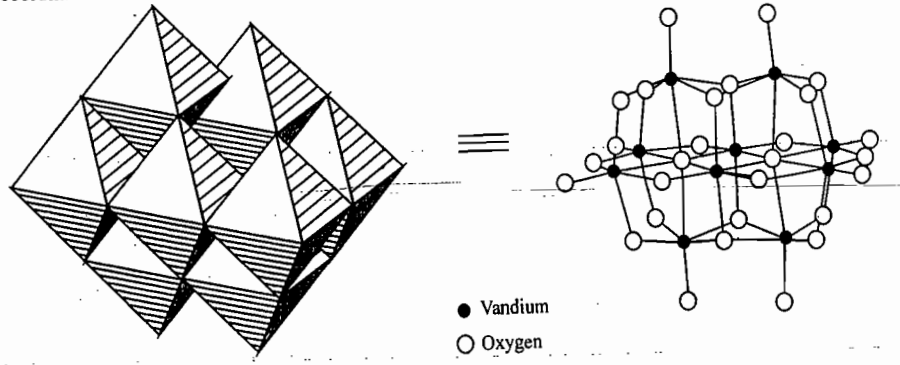


Fig. 9. The structure of $[V_{10}O_{28}]^{6-}$ ion

When $[n\text{-}Bu_4N]_3[H_3V_{10}O_{28}]$ is dissolved in acetonitrile, the tetrabutyl ammonium salt of $[V_5O_{14}]^{3-}$ anion is formed. This anion is the first example of the transition metal polyoxyanion which has a cage structure that is built entirely from corner shared MO_4 tetrahedra instead of edge shared or corner shared MO_6 octahedra. (Fig. 10)

The same isopolyvanadate ion $[V_5O_{14}]^{3-}$ is also formed when n Bu_4NOH and $[H_3V_{10}O_{28}]^{3-}$ are dissolved in a non-aqueous solvent. Thus,

$$[H_3V_{10}O_{28}]^{3-} + 3OH^- \longrightarrow 2[V_5O_{14}]^{3-} + 3H_2O$$

When the tetrabutyl ammonium salt of $[H_2V_{10}O_{28}]^{4-}$ is refluxed in acetonitrile, the anion $[CH_3CNV_{12}O_{32}]$ is obtained in small quantity in which CH_3CN is suspended in the basket-like structure of $[V_{12}O_{32}]^{4-}$ ion.

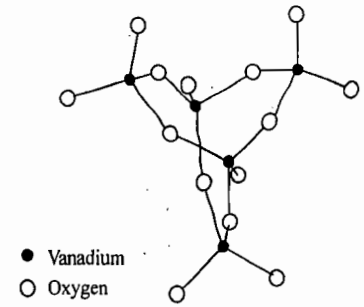


Fig.10. The structure of $[V_5O_{14}]^{3-}$ made from corner sharing of VO_4 tetrahedra

Fusing Nb_2O_5 and Ta_2O_5 with excess of alkali hydroxide followed by dissolution in water produces solutions of their isopolyanions. The isopolyanion $[M_6O_{19}]^{8-}$ (M = Nb and Ta) predominantly exist in solution upto pH 11. These polyanions have edge sharing distorted MO_6 octahedra as the structure building unit and have the same structure as $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$ already discussed. Below pH 11, the protonation of this anion starts giving $[HM_6O_{19}]^{7-}$, $[H_2M_6O_{19}]^{6-}$ and $[H_3M_6O_{19}]^{5-}$ (M = Nb and Ta). If the pH is lowered to less than 10, the hydrous oxides $V_2O_5\,xH_2O$ and $Nb_2O_5\,xH_2O$ start precipitating.

3. Heteropoly Anions and Heteropoly Acids. The first heteropolyanion, $[PMo_{12}O_{40}]^{3-}$, was reported by J. J. Berzelius. This anion is now used for the quantitative estimation of PO_4^{3-} in its solutions. Since then, a large number of heteropolyanions of Mo and W have been prepared with a large number of heteroatoms of both metals and non-metals. The salts of hetropolyanions are thermally more stable than the corresponding salts of isopolyanions. The heteropoly anions are extensively used as catalysts in petrochemical industry, as precipitants for dyes with which they form lakes and as flame retardants. The heteroatoms in heteropolyanions are situated inside the "cavities" formed by MO_6 octahedra (M = Mo, W) and are bonded to O atoms of MO_6 units of condensing MO_6 octahedra.

Heteropolyanions can be prepared by acidifying the solutions of simple monomeric anions.

$$HPO_4^{2-} + 12MoO_4^{2-} + 23H^+ \longrightarrow [PMo_{12}O_{40}]^{3-} + 12H_2O$$

Many of the heteropolyanions are quite stable in acidic solutions.

Some important categories of heteropolyanions are given below.

a. 1 : 12 (Tetrahedral Heteroatom) Polyanions. In this category of heteropolyanions, the heteroatom is relatively small in size and is situated in a tetrahedral inner cavity of the polyanion. In other words, the heteroatom inside the polyanion is tetrahedrally surrounded by four oxygen atoms of different MO_6 edge sharing units of the heteropolyanion. Common heteroatoms are P, As, Si, Ti, Ge, etc. The general formula for such heteropolyanions is $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ (M = Mo, W; X = heteroatom). The structure of this category of heteropolyanions has either full tetrahedral (Td) symmetry (Keggin structure) (Fig. 11) or has a structure which can be derived from Keggin structure by rotating one of the four sets of three condensed MO_6 octahedra of Keggin structure by 60°. The resulting structure no more has a fully tetrahedral symmetry as it contains only one three-fold axis of symmetery against four three-fold axes of symmetry of tetrahedral Keggin structure. This 'isomeric Keggin structure' is as stable as regular Keggin structure of this

category of heteropolyanions. For example $[XW_{12}O_{40}]^{4-}$ ($X = Si^{4+}, Ge^{4+}$) exist in both the isomeric forms. An interesting 1:12 heteropolyanion is $[Co^{2+}W_{12}O_{40}]^{6-}$ in which Co^{2+} is present in a tetrahedral hole, *i.e.*, the Co^{2+} ion in the heteropolyanion is surrounded tetrahedrally by four oxygen atoms of different condensing Mo_6 units of the heteropolyanion. The oxidation of this hetropolyanion yields $[Co^{3+}W_{12}O_{40}]^{5-}$ in which the high spin Co^{3+} ion is tetrahedrally surrounded by four oxygen atoms as shown in Fig. 11.

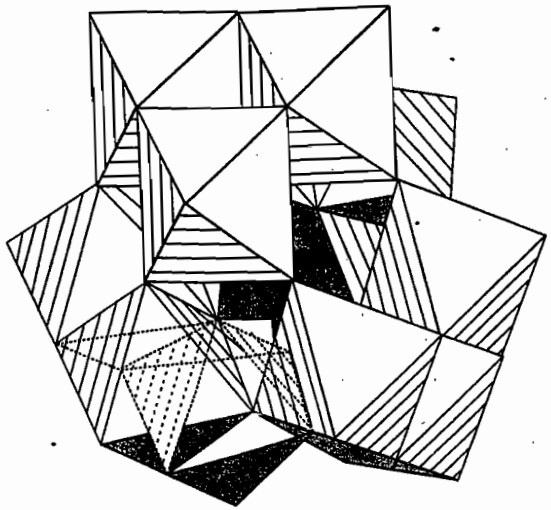


Fig.11. The 'Keggin' structure of $[X^{n+}M_{12}O_{40}]^{(8-n)-}$. The obscured triangular faces of the MO_6 octahedron are shown in dotted lines.

b. 2:18 (Tetrahedral Heteroatom) Polyanions. When the solutions of the salts of 1:12 heteropolyanions $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ are allowed to stand, the salts of 2:18 heteropolyanions can be crystallised. The general formula of this catergory of heteropolyanions is $[X_2^{5+}M_{18}O_{62}]^{6-}$ (M = Mo, W; X = P, As). The structure of this heteropolyanion is called 'Dawson structure'. If the three corner linked MO_6 octahedra are removed from the Keggin structure to leave a structure with a set of three octahedra over a ring of six octahedra, one half of $[X_2^{5+}M_{18}O_{62}]^{6-}$ anion is produced. If two such halves are fused together by corner sharing of their MO_6 octahedra, the Dawson structure of this anion results (Fig.12).

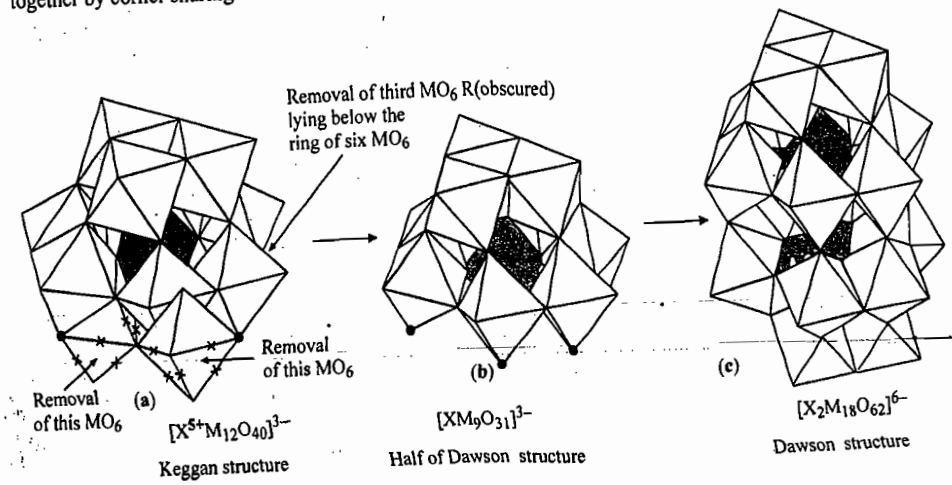


Fig.12. Formation of Dawson structure from Keggin structure .

c. 1:6 (Octahedral Heteroatom) Polyanions. Such heteropolyanions are formed by larger-sized heteroatoms like Te, I, Co, Al, etc. which are octahedrally coordinated to six oxygens of six edge sharing MO_6 octahedra. Mo forms this type of heteropolyanions more frequently than W. This again indicates that Mo has a greater tendency to form large heteropolyanion structures slowly by edge sharing rather than corner sharing of MO_6 octahedra. The example of this type is the heteropolyanion $[X^{n+}M_6O_{24}]^{(12-n)-}$ (Fig. 13).

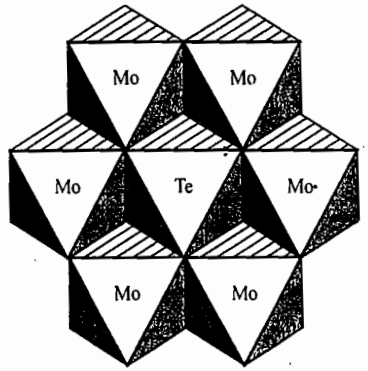


Fig.13. The structure of $[Te^{n+}Mo_6O_{24}]^{(12-n)-}$ ion

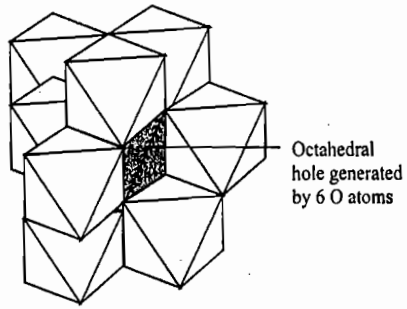


Fig.14. The structure of $[X^{n+}Mo_9O_{32}]^{(10-n)-}$ ($X = Ni^{4+}, Mn^{4+}$)

d. 1:9 (Octahedral Heteroatom) Polyanions. The general formula of such heteropolyanions is $[X^{n+}Mo_9O_{32}]^{(10-n)-}$ and their structure is also based on edge sharing MoO_6 octahedra. The heteroatom is octahedrally surrounded by six oxygen atoms of MoO_6 octahedra Fig. 14. The examples are $[MnMo_9O_{32}]^{6-}$ and $[NiMo_9O_{32}]^{6-}$. The Ni and Mn in these heteropolyanions are present in their unusual oxidation state of +4.

e. 1:12 (Icosahedral Heteroatom) Polyanions. These heteropolyanions of the general formula $[X^{n+}M_{12}O_{42}]^{(12-n)-}$ contain the heteroatom Ce, Th or U, which is icosahedrally surrounded by 12 oxygen atoms of MO_6 octahedra (Fig. 15.)

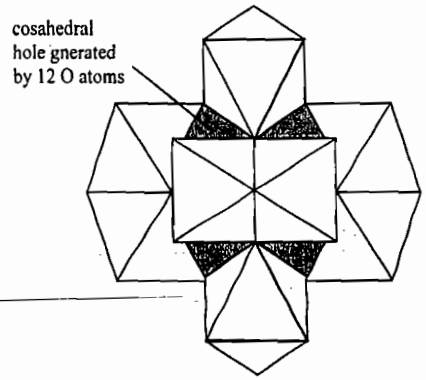


Fig.15. The structure of $[X^{+n}Mo_{12}O_{42}]^{(12-n)-}$ ion ($X = Ce^{4+}, U^{4+}, Th^{4+}$)

Recently, a number of other heteropolyanions such as $[NaP_5W_{30}O_{110}]^{14-}$, $[H_7P_8W_{48}O_{184}]^{33-}$ (both having double crown structure involving both edge sharing and corner sharing WO_6 octahedra) and $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}]$ (also having crown structure) have been prepared.

A huge-sized heteropolyanion $[Mo_{154}(NO)_{14}O_{420}(OH_{28})(H_2O)_7]^{(25\pm5)-}$ has also been reported recently.

Important Reactions of Isopolyanions and Heteropolyanions. Only two important reactions of heteropolyanions and isopolyanions will be described here.

1. Reactions with Isocyanides. Isocyanides react with heteropolyanions and isopolyanions to convert a terminal M = O to M = NR.

$$\overset{|}{\underset{|}{M}} = O + OCNR \longrightarrow M = NR + CO_2$$

For example, $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$ react with RNCO to yield products like $[W_6O_{18}NAr]^{2-}$, $[Mo_6O_{17}(NPh)_2]^{2-}$; $[Mo_6O_{15}(NAr)_4]^{2-}$, etc.

2. Reduction : Formation of Heteropolyblues. The reduction of isopoly and heteropoly molybdates and tungstates yield blue species. The reductions are reversible and the structural features of the species are retained during reduction. The reduction of $[Mo_6O_{19}]^{2-}$ yields $[Mo_6O_{19}]^{3-}$. The added electron is weakly localised on one Mo atom but it gets delocalised on all the Mo atoms when $[Mo_6O_{19}]^{3-}$ is subjected to heat. The reduction of Keggin ion $[PW_{12}O_{40}]^{3-}$ yields $[PW_{12}O_{40}]^{7-}$. The four added electrons in the product appear to be distributed in such a way that each sub-unit, having three edge shared WO_6 octahedra, of the structure has one added electron. In the $[H_2W_{12}O_{40}]^{12-}$, which is obtained by reducing $[H_2W_{12}O_{40}]^{6-}$, the six added electrons due to reduction appear to be localised on one sub-unit of three edge sharing WO_6 octahedra. The Keggin ion $[PMo_{12}O_{40}]^{3-}$ can be reduced to give a number of products of the general formula $[PMo_{12}O_{40}]^{4-, 5-, 6-, 7-}$.

The Dawson ion $[X_2Mo_{18}O_{62}]^{6-}$ (X = P, As) can also be reversibly reduced to yield blue species.

The question of the extent of delocalisation of the added electrons in all the blue species obtained by the reduction of isopoly and heteropoly molybdates is not finally settled as yet. Some chemists maintain that during the reduction of a heteropolyanion, the added electron gets **localised** on only some of the atoms converting them from M^{6+} to M^{5+} oxidation state (M = Mo, W). The transfer of electrons from these M^{5+} to M^{6+} of the heteropoly anions is responsible for the **intense** charge transfer absorption in the visible region and hence for the deep colour shown by these ions.

QUESTIONS

1. What are inorganic polymers ? Discuss their general properties and clearly indicate the manner in which they differ from organic polymers.
2. (*a*) What is glass transition temperature of a polymer ? Why is it so called ?
   (*b*) Discuss in details the various types of phosphorus-based chain polymers.
3. What are ultraphosphate glasses and borophosphate glases ? Discuss their structures, properties and uscs.
4. Name one nonmetallic polymer which exhibits super conductance at low temperatures. Discuss the preparation and structure of this polymer.
5. What are chalcogenide glasses ? Explain clearly how these glasses change from a state of low conductivity to a state of high conductivity. Give the probable mechanism of this phenomenon.
6. How do carboranes produce polymeric elastomers ? How can the preperties of such elastomers be modified to make these elastomers behave as inorganic rubbers ?
7. Give the strucuture of polymeric boron nitride. Why is it a poorer electrical conductor than graphite ?
8. Discuss the structures, properties and uses of various typcs of silicon polymers.
9. Distinguish between natural and synthetic polymers. Discuss the structures of some important natural chain polymers.
10. Discuss the structures of polymeric $[Hg_2(NH)Br_2]_n$, $[KCu(CN)_3]_n$, $[NiNH_3(CN)_2]_n$ and $(Cu_2Cl_2CH_3N_2CH_3)_n$.
11. What are synthetic coordination polymers ? Discuss the structures and uses of volan, quilon and related compounds.
12. Discuss the structure of inorganic polymers having pthalocyanine and similar structural units.
13. Discuss the synthesis and structures of some inorganic polymers of bis chelating agents.
14. (*a*) Discuss the structure of an inorganic polymer in which acetylacetone forms a double bridge.
    (*b*) Which polymer is obtained when salicylaldehyde reacts with dithiols in the presence of a cupric salt ?
    (*c*) What happens when pyridine 2, 6 dialdehyde reacts with ethylene diamine in the presence of iron (II) sulphide ?

36 INORGANIC NOMENCLATURE

In the recent past, inorganic compounds not only increased in number but also in complexity. New compounds were assigned unsystematic and adhoc names which varied considerably from one text book to another. This caused great inconvenience and confusion to the student. The International Union of Pure and Applied Chemists (IUPAC), therefor, framed a set of rules for naming the various inorganic compounds. With these rules, most of the ambiguities in the naming of inorganic compounds have been removed. However, in certain cases, the trivial names are still being preferred because of their simplicity and long usage. Examples are water, ammonia, hydrazine, phosphine, arsine, etc.

Based on the rules framed by the IUPAC, the nomenclature of inorganic compounds has been discussed in this chapter in some details.

Before discussing the subject, we shall briefly describe how the symbols of elements and formulae of inorganic species are written.

Writing Symbols of Elements and Formulae of Inorganic Species

The upper left superscript on the symbol of an element gives the mass number while the lower left subscript gives the atomic number of the element. In the case of an ion of the element, while the upper right superscript gives the ionic charge, the lower right subscript gives the number of atoms of the element. For example, ${}^{16}_{8}O_2^{2-}$ signifies that two atoms of oxygen each with a mass number of 16 and atomic number of 8 are grouped together to form the dinegative peroxo anion.

Till now, the word 'proton' was used to signify cation derived from the naturally occurring mixture of isotopes of hydrogen. But, the latest IUPAC convention recommended the use of the word 'proton' for the cation derived from the isotope ${}^{1}_{1}H$ of hydrogen only. The word 'hydron' is now recommended to signify cation derived from the naturally occurring mixture of isotopes of hydrogen. Thus, while previously we used to say that all Bronsted acids release protons, now we should say that all Bronsted acids release hydrons. However, the new terminology has yet to become popular.

While writing the formula of an ionic compound, the electropositive constituent (cation) is written first followed by the electronegative constituent (anion). Examples are NaCl, $BaCO_3$, $ZnSO_4$, etc. In Bronsted acids, the replaceable hydrogen is always considered a positive constituent and is written first.

In the formula of an oxoacid, the replaceable hydrogen is followed by the central atom, the oxygen atom or atoms and the negative ligands in the order of their mention. If there are more than one negative ligands attached with the central atom of the oxo acid, they are written in the alphabetical order of the first symbols of their formulae. Examples are : HClO, $HClO_3$, H_2SO_4, HSO_3F, etc.

In the formula of a polyatomic ion, the central atom is written first, followed by oxygen (if any) and the negative ligands, respectively. If there are more than one negative ligands, they are written in alphabetical order of the first symbols of their formulae. Examples are : $[ICl_4]^-$, $[IBr_2Cl_2]^-$, $[Mo_6O_{18}]^{2-}$, $[P_2W_{18}O_{62}]^{2-}$, etc. There are two central atoms in the last anion which are also written in the alphabetical order.

In some compounds, oxygen is a part of a well recognised cationic group as in VO^{2+}, VO^{3+}, NbO^{3+}, etc. In such compounds, oxygen comes just after the metal. The other atoms or groups are listed in alphabetical order after oxygen.

In polyatomic inorganic compounds which do not contain cations and anions, the central atom is listed first followed by the other atoms in alphabetical order. Examples are : $PBrClI$, $SbCl_2F$, $PbBrCl_2$, etc. When parts of such molecules are themselves recognised as distinct groups such as P=O, S=O, Se=O, etc., then these groups are treated as positive part of the compound and are listed first. Examples are : $POCl_3$, $SOCl_2$, etc.

In the formulae of addition compounds, the component molecules are cited in the order of increasing number. If they occur in equal numbers, they are listed in alphabetical order of their first symbols. Water and boron compound components of the addition compounds are written last. Examples are : $Na_2CO_3.10H_2O$, $Al_2(SO_4)_3.K_2SO_4.24H_2O$, $2CH_3OH.BF_3$, etc.

The formulae of free radicals are represented by putting dots as superscripts on the right of the symbols or the formulae of the species, the number of dots being equal to the number of unpaired electrons contained by each species. Examples are : $Cl^{\cdot}$, $O^{\cdot\cdot}$, $H^{\cdot}$, $(CN^{\cdot})$, $(CH_3^{\cdot})$, $(SnCl_3^{\cdot})$, etc.

The name of a molecule containing a single element is written by applying to it a suitable multiplying prefix which signifies the number of atoms of the element present in the molecule. Examples are :

H	Monohydrogen	S_6	Hexasulphur	O_2	Dioxygen	P_4	Tetraphosphorus
S_μ	Polysulphur	O_3	Trioxygen	S_8	Octasulphur	N_2	Dinitrogen

INORGANIC NOMENCLATURE

Before we discuss the naming of inorganic compounds it would be useful to familiarise the student with various affixes, numbers, enclosing marks, etc., which are commonly used in inorganic nomenclature.

Multiplying Affixes. The simple multiplying affixes, such as mono, di, tri, tetra, penta, hexa, hepta, octa, nona (9), deca (10), undeca (11), dodeca (12), nonadeca (19), icosa (20), henicosa (21), triaconta (30), hentriaconta (31), tetraconta (40), hecta (100) are used to indicate stoichiometric proportions, extent of substitution, number of identical coordinated groups, number of identical central atoms in condensed acids and their characteristic ions, number of atoms of the same element forming the skeleton of a molecule or an ion, etc. Examples are :

a. Stoichiometric Proportions.

CO	Carbon monoxide	N_2O	Dinitrogen oxide	CO_2	Carbon dioxide
N_2O_4	Dinitrogen tetraoxide	SO_2	Sulphur dioxide	Fe_3O_4	Triiron tetraoxide
SO_3	Sulphur trioxide				

When the oxidation states of the elements are normally invariant, the stoichiometric proportions need not be specified. Thus, Na_2SO_4 is named as sodium sulphate and not as disodium sulphate. Similarly, $CaCl_2$ is named as calcium chloride and not as calcium dichloride.

b. Extent of Substitution

$SiCl_2H_2$	Dichlorosilane	$PO_2S_2^{3-}$	Dithiophosphate ion

c. Number of Identical Coordinated Groups.

$[CoCl_2(NH_3)_4]^+$	Tetraamminedichlorocobalt(III) ion
$[CrBr_2(H_2O)_4]^+$	Tetraaquadibromochromium(III) ion

d. Number of Identical Atoms in Condensed Acids

H_3PO_4	Monophosphoric acid (mono can be omitted)
$H_4P_2O_7$	Diphosphoric acid
$H_5P_3O_{10}$	Triphosphoric acid
$H_2S_3O_{10}$	Trisulphuric acid

e. Number of Atoms of the Same Element forming the Skeleton of Molecules or Ions.

Si_2H_6	Disilane	B_4H_{10}	Tetraborane	$S_4O_6^{2-}$	Tetrathionate ion

The multiplying affixes such as *bis, tris, tetrakis, pentakis,* etc., are used with enclosing marks to indicate a set of identical organic radicals or groups which themselves contain the multiplying affixes such as di, tri, tetra, etc. Examples are :

$(ClCH_2CH_2)_2NH$	Bis(2-chloroethyl)amine
$P(C_{10}H_{21})_3$	Tris(decyl) phosphine
$Tl(I_3)_3$	Thalium tris(triiodide)
$[P(CH_2OH)_4]^+$	Tetrakis(hydroxymethyl)phosphonium ion

However, simple affixes di, tri, tetra, etc., are used if the organic radicals or groups do not contain any multiplying affixes. Examples are :

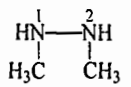
$[Cr(C_2O_4)_3]^{3-}$	Trioxalatochromate(III)	$[P(CH_3)_4]^+$	Tetramethylphosphonium ion

Structural Affixes. These affixes indicate different types of structures of inorganic compounds. These affixes are italicised and separated from the rest of the name by hyphens. The various structural affixes and the structures which they signify are given below.

Structural Affixes	Structures Signified
antiprismo	8 atoms bound into a rectangular antiprism
asym	Asymmetric
catena	A chain structure
cis	2 groups occupying adjacent positions
closo	A ring structure
dodecahedro	8 atoms bound into a dodecahedron with triangular faces
fac	3 groups occupying the corners of the same face of an octahedron
hexahedro	8 atoms bound into a hexahedron (*e.g.*, a cube)
hexaprismo	12 atoms bound into a hexagonal prism
icosahedro	12 atoms bound into a triangular icosahedron
mer (*meridional*)	3 groups on an octahedron in such a relationship that one is cis to the two others which are themselves trans
nido	a nestlike structure
octahedro	6 atoms bound into a pentagonal prism
pentaprismo	10 atoms bound into a pentagonal prism
quadro	4 atoms bound into a quadrangle (*e.g.*, a square)
sym	symmetric
tetrahedro	4 atoms bound into a tetrahedron
trans	2 groups directly across a central atom from each other
triangulo	3 atoms bound into a triangle
triprismo	6 atoms bound into a triangular prism
η	signifies the number of contiguous atoms of the group that are attached to a metal
μ	signifies that the group so designated bridges to centres of coordination
σ	signifies that one atom of the group is attached to a metal.

Numbers. Arabic numerals are used in inorganic nomenclature to indicate the atoms at which there is a substituent or addition in a chain. Examples are :

$\overset{1}{H_3Si}-\overset{2}{ClSiH}-\overset{3}{SiH_2}-\overset{4}{SiH_3}$ 2-chlorotetrasilane



1, 2 dimethylhydraizne

Arabic numerals are also used sometimes in place of multiplying affixes. Examples are :

B_6H_{10}	Hexaborane(10) (in place of hexaborondecahydride)
$MgSO_4.7H_2O$	Magnesium sulphate 7-water (in place of magnesium sulphate heptahydrate)
$AlK(SO_4)_2.12H_2O$	Aluminium potassium sulphate 12-water (in place of aluminium potassium sulphate dodecahydrate).

Arabic numerals followed by + and – are used to indicate the charge on a free or coordinated ion. Examples are :

$$Al^{3+},\ CO_3^{2-},\ [Cu(CN)_6]^{4-},\ [Co(NH_3)_6]^{3+}$$

Enclosing Marks. Enclosing marks are used in formulae to enclose sets of identical groups of atoms, as already illustrated. Examples are :

$$Ca_3(PO_4)_2,\ B[N(CH_3)_2]_3,\ [Fe(CN)_6]^{3-}$$

Enclosing marks are invariably used following the affixes bis, tris, etc., to avoid any possibility of ambiguity.

Enclosing marks in the form of square brackets are generally used to enclose a complex ion or a neutral complex. Examples are :

$$[Co(C_2O_4)_3]^{3-},\ [Co(NH_3)_3(NO_2)_3]$$

Italic Letters. The symbols of elements, printed in italics, are used to designate

1. The element in a heteroatomic chain or ring at which there is substitution. For example,

CH_3ONH_2	*O*-methylhydroxylamine	$[Hg(SCN)_4]^{2-}$	*S*-tetrathiocyanatomercurate(II) ion.
$HONHCH_3$	*N*-methylhydroxylamine	$[Zn(NCS)_4]^{2-}$	*N*-tetrathiocyanatozincate(II) ion.

2. The point of attachment in some addition compounds. For example,

$CH_3ONH_2.BH_3$, *O*-methylhydroxylamine (*N–B*) borane.

Names of Compounds in General

For ionic compounds, the electropositive constituent (cation) is named first followed by the name of the electronegative constituent (anion).

If the electronegative constituent is monoatomic element whose name ends in –en, –ese, –ine, –ium, –ogen, –on, –orus, –um, –ur or –ygen, its name would end in *–ide*. Examples are sodium chloride (NaCl), sodium oxide (Na_2O), silicon carbide (SiC), etc.

If the electronegative constituent is homopolyatomic, its name is similar to the name of the monoatomic parent qualified by mutliplicative prefix. Examples are : tetrasodium nonastannide Na_4Sn_9, thalium triiodide TlI_3, disodium disulphide Na_2S_2, etc.

If the electronegative constituent is heteropolyatomic, it is designated by the termination *–ate*. Examples are : potassium chlorate or potassium trioxochlorate ($KClO_3$), sodium arsenate or sodium tetraoxoarsenate (Na_3AsO_4), calcium phosphate or calcium tetraoxophosphate $[Ca_3(PO_4)_2]$.

Name of Ions

The **monoatomic cations** are named as the corresponding elements, with their oxidation states mentioned in parenthesis. Examples are :

Cu^+	Copper(I) cation	or	Copper(1+) ion	Sn^{2+}	Tin(II) cation	or	Tin(2+) ion
Cu^{2+}	Copper(II) cation	or	Copper(2+) ion	Sn^{4+}	Tin(IV) cation	or	Tin(4+) ion
Fe^{2+}	Iron(II) cation	or	Iron(2+) ion	I^+	Iodine(I) cation	or	Iodine(1+) ion
Fe^{3+}	Iron(III) cation	or	Iron(3+) ion	Cr^{3+}	Chromium(III)cation	or	Chromium(3+) ion

It is clear from the above examples that if oxidation state is written in Roman numeral in parenthesis, no sign of charge is written. If the oxidation state is written in Arabic numeral, it is followed by the sign of charge.

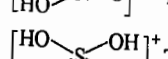
If to the anions such as I^-, S^{2-}, O^{2-}, P^{3-} and As^{3-}, we add 1, 2, 2, 3 and 3 protons, respectively, we get neutral molecules, *viz.*, HI, H_2S, H_2O, PH_3 and AsH_3, respectively. If we add one more proton to each of these neutral molecules, we get polyatomic cations, *viz.*, IH_2^+, SH_3^+, OH_3^+, PH_4^+ and AsH_4^+, respectively. These **polyatomic cations** are named by adding the ending *–onium* to the root of the name of the anion element. Thus, IH_2^+, SH_3^+, OH_3^+, PH_4^+ and AsH_4^+ are named as iodonium ion, sulphonium ion, oxonium ion, phosphonium ion and arsonium ion, respectively.

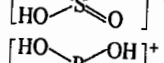
However, some common polyatomic cations such as NH_4^+, H_3O^+, NH_2OH^+, NO^+, OH^+, NO^{2+}, PO_2^+, UO^{2+}, VO^{3+} are not named in accordance with the above procedure. These cations continue to be designated by their trivial names, *viz.*, ammonium cation, hydronium cation, hydroxylammonium cation, nitrosyl cation, hydroxyllium cation, nitryl cation, phosphoryl cation, uranyl cation and vanadyl cation, respectively.

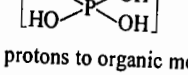
The cations obtained by adding a proton to organic acids are named by adding the suffix *–ium* to the names of such acids. Examples are :

$(CH_3COOH_2)^+$ Acetic acidium $(CH_3CH_2COOH_2)^+$ Propionic acidium

The cations obtained by adding a proton to inorganic oxoacids are named as if these were complex cations. Examples are :

$(H_2NO_3)^+$ or  Dihydroxooxonitrogen(V) cation

$(H_3SO_4)^+$ or  Trihydroxooxosulphur(VI) cation

$(H_4PO_4)^+$ or  Tetrahydroxophosphorus(V) cation

The cations obtained by adding protons to organic molecules are named by adding the suffix *–ium* to the parent name. Examples are :

$C_5H_5NH^+$	Pyridinium	$N_2H_5^+$	Hydrazinium
$(CH_3)_2COH^+$	Acetonium	$N_2H_6^{2+}$	Hydrazinium (2+)

The cations which result due to the loss of a H^- from a neutral molecule are named by using the suffix *–ylium*. Examples are :

CH_3^+ Methylium ; SiH_3^+ Silylium

The name of substituted cations are derived from the parent cations. Examples are :

$[PCl_4]^+$	Tetrachlorophosphonium ion	$[SCl_3]^+$	Trichlorosulphonium ion
$[N(C_2H_5)_4]^+$	Tetraethylammonium ion		

The **homopolyatomic cations** are named by applying multiplying prefixes to the names of the elements followed by the oxidation states of the cations in Arabic numerals put in parenthesis. Examples are :

$(O_2)^+$ Dioxygen(1+) ion $[Hg_2]^{2+}$ Dimercury(2+) ion $(S_4)^{2+}$ Tetrasulphur(2+) ion

The coordination complex cations are named as per the nomenclature of Coordination Compounds already discussed in Chapter 26.

The names for **monoatomic anions** consist of the names of the elements with the termination *–ide*. Examples are : H^-, hydride(1–) ion. F^-, fluoride (1–) ion, O^{2-}, oxide (2–) ion, N^{3-}, nitride (3–) ion.

The names of certain **polyatomic anions** also end in *–ide*. This is followed by the charge in parenthesis. The charge may be omitted if it is only one unit. Examples are :

I_3^-	Triiodide(1–) ion	I_5^-	Pentaiodide(1–) ion	O_2^{2-}	Peroxide(2–) ion
N_3^-	Azide or trinitride(1–) ion	S_2^{2-}	Disulphide(2–) ion	S_4^{2-}	Tetrasulphide(2–) ion

It may be noted that **homopolyatomic anions** also contain charge number in parenthesis after their names.

Heteropolyatomic anions of oxoacids whose names end in *–ous* and in which the central atom has an oxidation state which is lower than its maximum oxidation state, may be designated by their trivial names. These names end in *–ite*. The termination *–ite* denotes a lower state of oxidation for the central atom. However, according to the IUPAC nomenclature, heteropolyatomic anions may be considered as coordination complex species in which central atom is coordinated to a number of ligands. The trivial as well as the IUPAC names of some common heteropolyatomic anions are gives below :

Anion	Trivial Name	IUPAC Name	Anion	Trivial Name	IUPAC Name
NO_2^-	Nitrite	Dioxonitrate(1–)	$S_2O_4^{2-}$	Dithionite	Tetraoxodisulphate(2–)
$N_2O_2^{2-}$	Hyponitrite	Dioxodinitrate(2–)	SeO_3^{2-}	Selenite	Tetraoxoselenate(2–)
AsO_3^{3-}	Arsenite	Trioxoarsenate(3–)	ClO_2^-	Chlorite	Dioxochlorate(1–)
SO_3^{2-}	Sulphite	Trioxosulphate(2–)	ClO^-	Hypochlorite	Monooxochlorate(1–)
$S_2O_6^{2-}$	Disulphite	Hexaoxodisulphate(2–)	IO^-	Hypoiodite	Monooxoiodate(1–)

Heteropolyatomic anions obtained by removing H^+ of a hydroxy group of an oxoacid whose name ends in *–ic* are named by replacing *–ic* of the acid by *–ate*. Examples are :

Anion	Trivial Name	IUPAC Name	Anion	Trivial Name	IUPAC Name
SO_4^{2-}	Sulphate	Tetraoxosulphate(2–)	SO_3F^-	Fluorosulphate	Fluorotrioxosulphate(1–)
NO_3^-	Nitrate	Trioxonitrate(1–)			

If all the removable protons are not removed from an oxoacid, the name of the resulting anion is derived by adding hydrogen or dihydrogen to indicate the number of protons which are still present in the anion. Examples are :

Anion	Trivial Name	IUPAC Name
HSO_4^-	Hydrogen sulphate	Hydrogen tetraoxosulphate(1–)
HCO_3^-	Hydrogen carbonate	Hydrogen trioxocarbonate(1–)
$H_2PO_4^-$	Dihydrogen phosphate	Dihydrogen tetraoxophosphate(1–)

Polyatomic anions derived from neutral molecules by the loss of one or more protons are named by adding *–ide* after the names of their parent compounds. Examples are :

H_3C^- Methanide $H_5C_6^-$ Benzenide $H_5C_5^-$ Cyclopentadienide

Anions derived formally by the addition of H^- ions to mononuclear hydrides are named using the nomenclature of coordination compounds. Examples are :

BH_4^- Tetrahydroborate(1–) PH_6^- Hexahydrophosphate(1–)

Heteropolyatomic anions which do not fall in any of the above mentioned categories, are named according to the nomenclature of coordination compounds, that is, the groups attached to the central atom are treated as ligands. Examples are :

PF_6^- Hexafluorophosphate(V) anion or Hexafluorophosphate(1–) anion

$[Zn(OH)_4]^{2-}$ Tetrahydroxozincate(II) anion or Tetrahydroxozincate(2–) anion

HF_2^- Difluorohydrogenate(1–) anion

In the case of the following anions, trivial names are still in use :

OH^-	Hydroxide	CN^-	Cyanide	HS^-	Hydrogen sulphide	$NHOH^-$	Hydroxamide
NH_2^-	Amide	AsO_3^{3-}	Arsenite	NCS^-	Thiocyanate–N	$N_2H_3^-$	Hydrazide
NH^{2-}	Imide	NO_2^-	Nitrite	SCN^-	Thiocyanate–S	N_3^-	Azide

The trivial names of some anions ending in *–ate* have become very common although their names do not conform to IUPAC nomenclature. The trivial names of such ions are allowed. Examples are : cyanate, dichromate, diphosphate, disulphate, metaborate, metaphosphate, metasilicate, orthosilicate, permanganate, phosphinate, phosphonate, hypophosphate, etc.

Names of Radicals

A radical is a group of atoms which occurs repeatedly in a number of different compounds. Certain neutral and cationic radicals containing oxygen or other chalcogens (*viz.*, S, Se and Te) have special names ending in *–yl*, irrespective of the charge. Examples are :

HO	Hydroxyl	SO	Sulphinyl (Thionyl)	PO	Phosphoryl	SeO_2	Selenonyl
CO	Carbonyl	SO_2	Sulphonyl (Sulphuryl)	ClO	Chlorosyl	CrO_2	Chromyl
NO	Nitrosyl	S_2O_5	Disulphuryl	ClO_2	Chloryl	UO_2	Uranyl
NO_2	Nitryl	SeO	Seleninyl	ClO_3	Perchloryl	NpO_2	Neptunyl

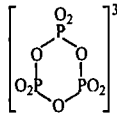
Radicals analogous to the above containing other chalcogens in place of oxygen are named by adding the prefixes *thio*, *seleno*, etc. Accordingly, while $POCl_3$ is named as phosphoryl chloride, $PSCl_3$ is named as thiophosphoryl chloride. Similarly, while $COCl_2$ is named as carbonyl chloride, $CSeCl_2$ is named as selenocarbonyl chloride and so on.

Names of Isopolyanions

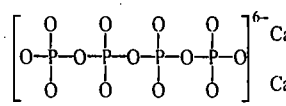
Anions of polyacids derived by condensation of molecules of the same acid are known as **isopolyanions**. These are named by indicating the number of atoms of the characteristic element with Greek number prefixes. Alternatively, they may be named according to the nomenclature of coordination compounds in which the central atoms are assumed to be coordinated with oxygen or other groups which act as ligands. The bridging group is written first. Both the nomenclatures are in use. Examples are :

Anion	Trivial Name	IUPAC Name
$S_2O_7^{2-}$	Disulphate	μ-oxo-hexaoxodisulphate(2–)
$P_3O_{10}^{5-}$	Triphosphate	di-μ-oxo-octaoxotriphosphate(5–)

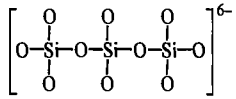
Cyclic and straight-chain structures of polyanions are distinguished by using the prefixes *cyclo* and *catena*. The latter prefix, however, is usually omitted. Examples are :



Cyclotriphosphate ion
or
Cyclotri-μ-oxo-hexaoxotriphosphate(3–)



Catenatetraphosphate ion
or
Catenatri-μ-oxodecaoxotetraphosphate(6–)



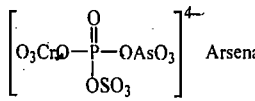
Catenatrisilicate ion
or
Catenadi-μ-oxooctaoxotrisilicate(6–)

Names of Heteropolyanions

Dinuclear anions are named by considering the anion which occurs first in alphabetical order as the ligand on the atoms of the second anion. Examples are :

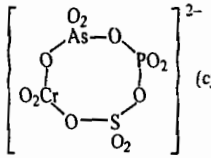
$[O_3P–O–SO_3]^{3-}$ Phosphatosulphate(3–) $[O_3As–O–PO_3]^{4-}$ Arsenatophosphate(4–)

In **polyanions** with an obvious central atom, the peripheral anions are named as ligands on the central atom and cited in alphabetical order. A well known example is :

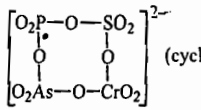


Arsenatochromatosulphatophosphate(4–)

Cyclic heteropolyanions are named in a manner similar to the naming of chain structures, the starting point and the direction of citation of various units being taken in alphabetical order. Examples are :



(cycloarsenatochromatosulphatophosphate(2–)



(cycloarsenatochromatosulphatophosphate(2–)

Condensed heteropolyanions comprising of three-dimensional frameworks of polyhedra of linked MoO_6, WO_6, etc., surrounding a central atom are designated by prefixes molybdo, tungsto, phospho, etc. Examples are :

$[P_2Mo_{18}O_{62}]^{6-}$(Octadecamolybdodiphosphate (6–) $[PW_{12}O_{40}]^{3-}$(Phosphododecatungstate(3–)

If the structure of the heteropolyanion is known, it may also be named according to its structure. For example, $[SiW_{20}O_{40})^{4-}$ may be named as hexatriacontaoxo(tetraoxosilicato)dodecatungstate (4–) since its structure contains an SiO_4 unit. Alternatively, it may be named as silicoicosatungstate (4–).

Names of Acids

Acids yielding *–ide* anions are named as binary and pseudobinary compounds of hydrogen. Examples are : hydrogen chloride, hydrogen sulphide, hydrogen cyanide.

For **oxo acids**, the old as well as the new IUPAC nomenclatures are equally valid. According to the old nomenclature, different oxidation states are distinguished by using the notation *ous* and *ic* and by using the prefix *hypo* and *per*. The *–ous* names are used for acids corresponding to the *–ite* anions and *–ic* names are used for acids corresponding to *–ate* anions. Examples are :

$HClO$	Hypochlorous acid	H_2SO_3	Sulphurous acid	$H_2S_2O_3$	Thiosulphuric acid
HNO_2	Nitrous acid	$H_2N_2O_2$	Hyponitrous acid	H_3PO_4	Phosphoric acid
$HClO_2$	Chlorous acid	H_2SO_4	Sulphuric acid	$H_2S_2O_4$	Dithionous acid
HNO_3	Nitric acid	H_2SO_5	Permonosulphuric acid	$H_4P_2O_6$	Hypophosphoric acid
$HClO_3$	Chloric acid	H_2PO_2	Hypophosphorous acid	$H_2S_2O_6$	Dithionic acid
HNO_4	Pernitric acid	$H_2S_2O_8$	Perdisulphuric acid	$H_5P_3O_{10}$	Triphosphoric acid
$HClO_4$	Perchloric acid	H_3PO_3	Phosphorous acid	$H_2S_2O_7$	Disulphuric acid

It is worth mentioning here that while writing the formula of an oxoacid, the hydrogen atoms which are responsible for the acidic properties of the acid, are written first. This is followed by the central atom and then the oxgen atoms that are bound to the central atom.

The prefix hypo is used to denote very low oxidation state of the central element as in naming H_3PO_2. Similarly, the term per is used to designate the highest oxidation state of the central element as, for example, of the halogens in their oxoacids $HClO_4$, $HBrO_4$ and HIO_4. These acids are thus named as perchloric acid, perbromic acid and periodic acid, respectively. It may be noted that the prefix per is not to be used for any oxo acid of the halogens other than those in their highest oxidation states.

In the case of oxo acids, prefixes ortho and meta are used to distinguish acids differing in their water content. Examples are :

H_3BO_3	Orthoboric acid	$(H_2SiO_3)_n$	Metasilicic acid	H_4SiO_4	Orthosilicic acid
$(HBO_3)_n$	Metaboric acid	H_3PO_4	Orthophosphoric acid	$(HPO_3)_n$	Metaphosphoric acid

It is to be noted that the decrease in water content results in polymerisation to form chains or rings.

According to the IUPAC nomenclature, the oxoacids may be named according to ***acid nomenclature*** or according to ***hydrogen nomenclature***.

The **acid nomenclature** of some of the oxoacids is given below.

H_3BO_3	Trioxoboric acid	$HClO_3$	Trioxochloric acid
H_4SiO_4	Tetraoxosilicic acid	$HClO_4$	Tetraoxochloric acid
$(H_2SiO_3)_n$	Polytrioxosilicic acid	$H_2N_2O_2$	Dioxodinitric acid
H_2CO_3	Trioxocarbonic acid	$H_2S_2O_7$	μ-oxohexaoxodisulphuric acid
$HOCN$	Nitridooxocarbonic acid	$H_2S_2O_6$	Hexaoxodisulphuric acid (S–S)
HNO_3	Trioxonitric acid	H_2IO_6	Hexaoxoiodic acid
HNO_2	Dioxonitric acid	$(HO)_2OPPO(OH)_2$	Hexaoxodiphosphoric acid

In **hydrogen nomenclature**, the acid is considered as an ionic compound of H^+ cation and is named as per the nomenclature of such compounds. Examples are :

H_2CrO_4	Dihydrogen tetraoxochromate (2–)
$H_2Cr_2O_7$	Dihydrogen μ–oxohexaoxodichromate (2–)
H_5IO_6	Pentahydrogen hexaoxoiodate (5–)
H_3AsO_3	Trihydrogen trioxoarsenate (3–)
H_3AsO_4	Trihydrogen tetraoxoarsenate (3–)
$(HPO_3)_n$	Poly(hydrogen trioxophosphate(1–))
$H_4P_2O_7$	Tetrahydrogen μ–oxohexaoxodiphosphate(4–)
$H_2S_2O_6$	Dihydrogen hexaoxodisulphate(S–S)
$HClO_2$	Hydrogen dioxochlorate (1–)
H_3PO_3	Trihydrogen trioxophosphate (3–)
HPH_2O_2	Hydrogen dihydridodioxophosphate (1–)
HNO_2	Hydrogen dioxonitrate (1–)
HNO_3	Hydrogen trioxonitrate (1–)
H_2SO_4	Dihydrogen tetraoxosulphate (2–)
$(H_2SiO_3)_n$	Poly(dihydrogen trioxosilicate)
H_3BO_3	Trihydrogen trioxoborate
$(HBO_2)_n$	Poly[hydrogen dioxoborate(1–)]

As can be seen from the above examples, if the central element is capable of existing in more than one oxidation states, it is advisable to put the charge of the anion in parenthesis after the name of the acid.

Names of Salts and Salt-like Compounds

Simple salts are named just as the binary compounds are named in general, as already discussed.

Salt containing acid hydrogen are named by placing the word 'hydrogen' immediately before the name of the anion. The numerical prefixes indicate the number of replaceable hydrogen atoms.

Examples are :

$NaHCO_3$	Sodium hydrogen carbonate	or	Sodium hydrogen trioxocarbonate
KHS	Potassium hydrogen sulphide		
LiH_2PO_4	Lithium dihydrogen phosphate	or	Lithium dihydrogen tetraoxophosphate
Na_2HPO_4	Disodium hydrogen phosphate	or	Disodium hydrogen tetraoxophosphate

Names of Addition Compounds

Addition compounds are named by connecting the names of the individual compounds by hyphens and indicating the number of molecules after the name of the addition compounds by Arabic numerals seperated by solid lines and enclosed in brackets. Examples are :

$Na_2CO_3.10H_2O$	Sodium carbonate-water (1/10)
$CaCl_2.8NH_3$	Calcium choride-ammonia (1/8)
$3CdSO_4.8H_2O$	Cadmium sulphate-water (3/8)
$AlCl_3.4C_2H_5OH$	Aluminium chloride-ethanol (1/4)
$FeSO_4.(NH_4)_2SO_4.6H_2O$	Ammonium sulphate ferrous sulphate-water (1/1/6)
$Al_2(SO_4)_3.K_2SO_4.24H_2O$	Aluminium sulphate potassium sulphate-water (1/1/24)
$NH_3.BF_3$	Ammonia-boron trifluoride(1/1)
$8H_2S.46H_2O$	Hydrogen sulphide-water (8/46)
$2CH_3OH.BF_3$	Methanol-boron trifluoride (2/1)

Names of Neutral Hydrides

The names of neutral hydrides end in *–ane*. If the mononuclear hydrides have the number of H atoms equal to the standard bonding number of the atom to which they are attached, no other prefix is required otherwise a prefix λ^n is written before their names (n is the number of H atoms attached). Examples are :

$H_2P–PH_2$	Diphosphane	PH_5	λ^5–Phosphane
$H_3Si–SiH_2–SiH_2–SiH_3$	Tetrasilane	SH_6	λ^6–Sulphane

Names of Boron Hydrides

The boron hydrides are designated as **boranes**. The simplest hydride BH_3 is named as borane and the higher hydrides are named by indicating the number of boron atoms by Greek numerical prefixes and the number of hydrogen atoms by Arabic numerals placed in parenthesis after the name of the boranes. Examples are :

B_2H_6	Nidodiborane (6)	$B_{10}H_{14}$	Nidodecaborane (14)
B_4H_{10}	Arachnotetraborane (10)	$B_6H_6^{2-}$	Closohexaborane (6) anion
B_5H_9	Nidopentaborane (9)	$B_8H_8^{2-}$	Closooctaborane (8) anion
B_5H_{11}	Arachnopentaborane (11)	B_8H_{16}	Hyphooctaborane (16)
B_6H_{10}	Nidohexaborane (10)	$B_{10}H_{18}$	Hyphodecaborane (18)
B_9H_{15}	Arachnononaborane (15)		

(1) **Closoboranes** have closed structures in which all the corners of a polyhedron are occupied by boron atoms. They have the general formula $B_nH_n^{2-}$.

(2) **Nidoboranes** have more open nest-like structures in which n corners of $(n+1)$-cornered polyhedrons are occupied by B atoms. They have the general formula B_nH_{n+4}.

(3) **Arachnoboranes** have still more open structure in which n corners of $(n+2)$-cornered polyhedrons are occupied by boron atoms. They have the general formula B_nH_{n+6}.

(4) **Hyphoboranes** have the most open net-like structures in which n corners of $(n+3)$-cornered polyhedrons are occupied by boron atoms. They have the general formula B_nH_{n+8}.

Names of Coordination Compounds

Nomenclature of **coordination compounds** has already been discussed comprehensively in Chapter 26.

QUESTIONS

1. Illustrate giving examples, how the formulae of inorganic compounds are written according to IUPAC rules.
2. Name the various multiplying affixes used in inorganic nomenclature. What do they indicate ? Give examples.
3. Name at least ten structural affixes used in inorganic nomenclature. Specify the structures which they signify.
4. Discuss the use of the following in inorganic nomenclature, giving suitable examples :
   Multiplying affixes, Enclosing marks, Arabic numerals, Italic letters.
5. Illustrate with suitable examples, how the inorganic compounds are named in general.
6. Discuss with examples the IUPAC nomenclature for monocations, monoatomic anions and radicals, polyatomic anions, isopolyanions, heteropolyanions, cyclic heteropolyanions and condensed heteropolyanions. Give examples.
7. Name the following species according to IUPAC nomenclature :
   IH_2^+, PH_4^+, SH_3^+, AsH_4^+, S_2^{2-}, $N_2H_3^-$, C_2^{2-}, N_3^-, SeO_3^{2-}, NO, NO_2, SeO_2^+, UP_2, ClO_3^-, $S_2O_5^-$, $S_2O_7^{2-}$, $Mo_7O_{25}^{5-}$, $Cr_4O_{18}^{2-}$, $[O_3P-O-SO_3]^{3-}$, $[O_3As-O-PO_3]^{4-}$, $[P_2Mo_{18}O_{62}]^{6-}$, $[PW_{12}O_{40}]^{3-}$.
8. Discuss, giving suitable examples, the IUPAC nomenclature for inorganic acids.
9. Discuss in details the IUPAC nomeclature for oxoacids, illustrating the acid nomenclature and the hydrogen nomenclature.
10. Discuss how the addition compounds, neutral hydrides and boron hydrides are named according to IUPAC guidelines. Give examples.
11. Name the following compounds according to IUPAC nomenclature :
    H_2SO_5, $H_2S_2O_8$, $H_2S_2O_6$, $H_5P_3O_{10}$, $H_4P_2O_6$, H_4SiO_4. $CaCl_2.8NH_3$, $3CdSO_4.8H_2O$, $AlCl_3.4C_2H_5OH$, $Na_2CO_3.10H_2O$, $FeSO_4.(NH_4)_2SO_4.6H_2O$, NH_3BF_3, $8H_2S.46H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, B_2H_6, B_4H_{10}, B_5H_9, B_6H_{10}, $B_{10}H_{14}$, $B_{20}H_{16}$.

37 BIOINORGANIC CHEMISTRY

Bioinorganic chemistry is a fast developing branch of chemistry which explores the role of metallic (and some non-metallic) elements in biological systems. We shall, however, confine our discussion to the role of only the metallic elements. Metals such as Na, K, Ca, Mg, whose ions are present in biological systems in bulk quantities, are called **bulk metals** and metals such as Fe, Cu, Co, Zn, Cr, Mn, Mo, W, Ni, etc., whose ions are present in trace amounts, are called **trace metals**. Both the categories of metals are essential for sustaining life. There is a large number of biochemicals containing metal ions which play a significant role in biological systems. The most important amongst these are myoglobin and hemoglobin, the compounds containing iron.

MYOGLOBIN AND HEMOGLOBIN

Both myoglobin and hemoglobin are *metal porphyrins* which contain the 'heme' group in their structure. The heme group consists of an iron atom which is coordinated to four nitrogen atoms of porphyrin-IX, as shown in Fig. 1.

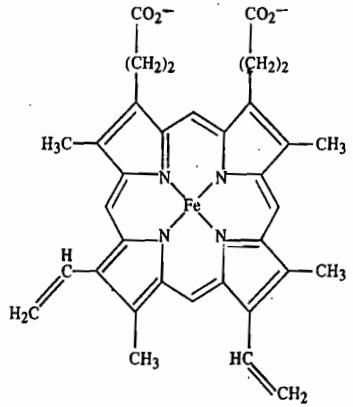


Fig. 1. Structure of the heme group present in myoglobin and hemoglobin.

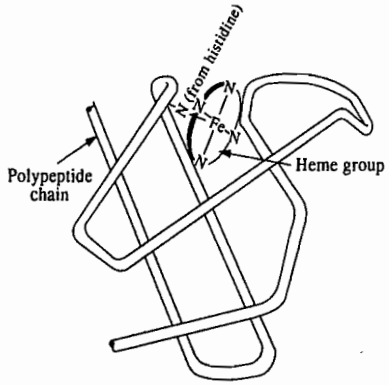


Fig. 2. Coordination of coiled polypeptide chain with the heme group.

In myoglobin, the heme group is embedded in a crevice formed by the coiling of its polypeptide chain containing 150–160 amino acid residues. The polypeptide chain is coordinated to iron atom of the heme group through the N atom of one of its histidine groups, as shown in Fig. 2.

The molar mass of myoglobin is about 17000. Myoglobin which has not taken up oxygen is called *deoxymyoglobin* or simply myoglobin.

Hemoglobin, which has a molar mass of about 64500, comprises of four myoglobin-like (not myoglobin) sub units. None of the polypeptide chains of these sub units has exactly the same sequence of groups as are present in the polypeptide of myoglobin. Nevertheless, the polypeptide chains of both hemoglobin

and myoglobin coil in a similar manner to produce crevices for accommodating the heme group. Each sub unit of hemoglobin contains a polypeptide chain and a heme group coordinated through the N atom of the histidine group of its polypeptide chain. The four sub units of hemoglobin are linked with one another through salt bridges present between the four polypeptide chains. These salt bridges are formed due to electrostatic interaction between the $-NH_3^+$ and $-COO^-$ groups present on all the four polypeptide chains of hemoglobin. Each polypeptide chain consists of a peptide backbone with various side chains having a number of cationic groups (such as $-NH_3^+$), anionic groups (such as $-COO^-$) and nonpolar aliphatic and aryl groups. It is now believed that these salt bridges between the polypeptide chains of hemoglobin introduce **strain** in the molecule.

The oxygenated hemoglobin is called *oxyhemoglobin*. Hemoglobin which has not taken up oxygen is called *deoxyhemoglobin* or simply hemoglobin.

The five-coordinated high spin Fe(II) present in myoglobin and hemoglobin lies about 0·5 Å above the plane containing the four coordinated nitrogens of the porphyrin ring and the coordinated N atom of the histidine group.

The approach to the sixth coordination site of Fe(II) is sterically overcrowded by groups from the side chains attached with the main coiled polypeptide chain surrounding the heme group. The probable structure of the heme group present in hemoglobin and myoglobin is shown in Fig. 3.

Both myoglobin and hemoglobin are paramagnetic due to the presence of unpaired electrons in Fe(II).

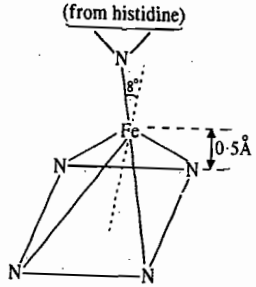


Fig. 3. Probable structure of the heme unit present in myoglobin and hemoglobin.

Role of Myoglobin and Hemoglobin in Biological Systems

Oxygenation. Hemoglobin picks up oxygen from the lungs and carries it to the muscle tissues via the circulatory system. The oxygenated hemoglobin then transfers this oxygen to the myoglobin present in the muscle tissues where it remains stored as such till it is transferred to other oxygen acceptors for performing metabolic actions in the biological system. Apart from acting as oxygen carrier, hemoglobin has an additional function of carrying CO_2 from worked up muscle tissues to the lungs. This is done by certain side chains present on the polypeptide chains of hemoglobin. The heme groups of hemoglobin are not involved in flushing out CO_2 from the muscles.

Oxygenation of myoglobin may be represented as

$$\underset{\text{Myoglobin}}{Mb} + O_2 \rightleftharpoons \underset{\text{Oxymyoglobin}}{MbO_2}$$

so that

$$K = \frac{[MbO_2]}{[Mb][O_2]} \quad \ldots(1)$$

If f is the fraction of myoglobin molecules bearing oxygen and p is the equilibrium partial pressure of oxygen, then, Eq. 1 may be written as

$$K = \frac{f}{(1-f)p} \quad \ldots(2)$$

or

$$f = \frac{Kp}{1+Kp} \quad \ldots(3)$$

The constant K is called the **binding constant** of myoglobin for oxygen.

Hemoglobin, with its four myoglobin-like sub units, exhibits more complex behaviour. It approximately follows Eq. 4 :

$$K = \frac{[Hb(O_2)_4]}{[Hb][O_2]^n} \quad \ldots(4)$$

so that

$$f = \frac{Kp^n}{1+Kp^n} \quad \ldots(5)$$

The exponent n is called the **Hill constant**. Its exact value depends upon the pH of the biological system. If the value of n is 1, it would mean that the oxygen intake by one heme group of hemoglobin is totally independent of the oxygen intake of its other three heme groups.

If the value of n is 4, it would imply that only Hb and $Hb(O_2)_4$ remain as the ultimate participants in the oxygenation of hemoglobin. The value of n ranging between 1 and 4 means that the attachment of oxygen to one heme group of hemoglobin progressively increases its tendency to bind with the subsequent heme groups of hemoglobin.

The phenomenon where the addition of oxygen to one heme group facilitates its addition to the other heme groups of hemoglobin is known as **cooperativity effect**. Thus, a value of 4 for n would represent the maximum cooperativity effect.

A graph showing percent oxygen saturation of myoglobin and hemoglobin as a function of partial pressure of oxygen is given in Fig. 4.

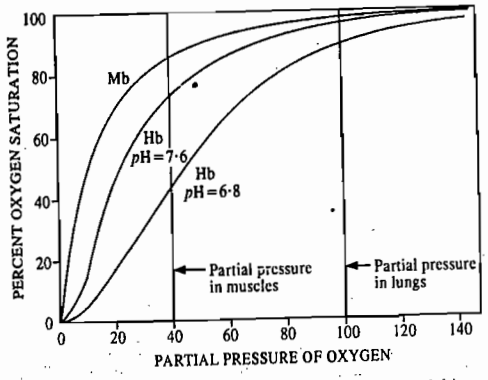


Fig. 4. A plot of percent oxygen saturation of myoglobin and hemoglobin vs partial pressure of oxygen.

It can be seen from the graph that at the partial pressure of oxygen prevailing in the lungs (which is around 100–120 mm Hg), both hemoglobin and myoglobin are almost completely saturated with oxygen. However, at the low partial pressure of oxygen prevailing in the muscles (20–40 mm Hg), hemoglobin is a much poorer oxygen binder compared to myoglobin. Hence in the muscle tissues where myoglobin is already present, oxygenated hemoglobin passes on its oxygen to myoglobin. The working muscles consume this oxygen to produce energy and carbon dioxide.

The binding power of hemoglobin with oxygen is pH-dependent. This is called **Bohr effect.** The binding power of hemoglobin decreases with decrease in pH. Hence, the transfer of oxygen from oxygenated hemoglobin to myoglobin is more efficient in the working muscles where the CO_2 concentration is higher than in the resting muscles. CO_2 being acidic, decreases the pH.

Explanation for Cooperativity Effect in Hemoglobin

The following explanation is generally offered for the cooperativity effect in hemoglobin.

In hemoglobin, the heme group is dome shaped having the iron atom about 0·5 Å out of the porphyrin plane and the Fe—N bond of histidine residue of polypeptide chain about 8° off the perpendicular to the porphyrin plane, as shown above in Fig. 3.

When an oxygen molecule binds to the iron atom of a heme group through its vacant sixth coordination site, the iron atom becomes low spin and, therefore, becomes smaller in radius (the low spin Fe(II) as well as Fe(III) have smaller radii than that of the high spin Fe(II)). As a result, the low spin iron moves towards the porphyrin plane and just fits in the hole generated by the four coordinating nitrogens of the porphyrin plane. This automatically pulls the coordinated histidine to move by about 0·5 Å towards the plane thereby making the Fe—N (histidine) bond vertical. These changes in the heme unit due to its coordination with O_2 form the trigger of cooperativity phenomenon.

The movement of iron atom and the coordinated histidine towards the porphyrin plane results in the movement of the whole polypeptide chain of which the histidine group is a part. This results in the breaking of some of the interpolypeptide salt bridges. As already mentioned, the presence of salt bridges introduces strain in the hemoglobin molecules. Hence the rupture of these salt bridges relaxes the constrained hemoglobin molecule. Conformational changes that subsequently occur in the polypeptide chains of the relaxed molecule increase the sizes of the crevices engulfing the remaining heme groups

with the result that the sixth coordination sites of the iron atoms in the other heme groups become more approachable to the attacking oxygen molecules. There is thus a progressive increase in the binding constants of the successive oxygenation reactions of hemoglobin that follow the first oxygenation reaction, as shown below :

$$Hb + O_2 \overset{K_1}{\rightleftharpoons} HbO_2$$
$$HbO_2 + O_2 \overset{K_2}{\rightleftharpoons} Hb(O_2)_2$$
$$Hb(O_2)_2 + O_2 \overset{K_3}{\rightleftharpoons} Hb(O_2)_3$$
$$Hb(O_2)_3 + O_2 \overset{K_4}{\rightleftharpoons} Hb(O_2)_4$$
$$K_4 > K_3 > K_2 > K_1$$

The above explanation of cooperativity effect is called **trigger mechanism.**

It may be of interest to know that the Fe—O_2 bond in both oxyhemoglobin and oxymyoglobin is bent, as shown in Fig. 5. This is due to the fact that the sixth coordination site of iron, being sterically overcrowded as discussed earlier, does not have enough space for a straight Fe—O—O link.

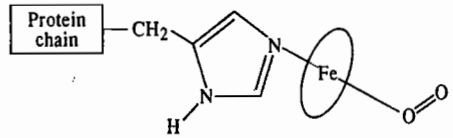


Fig. 5. Structure of oxyhemoglobin and oxymyoglobin.

Both oxygenated hemoglobin [$Hb(O_2)_4$] and oxygenated myoglobin [MbO_2] are diamagnetic in character. This observation can be explained either by formulating that in the heme group of both oxyhemoglobin and oxymyoglobin, a singlet oxygen is bound to low spin iron(II) or by assuming that each heme group in these compounds contains an Fe^{III}—O_2^- link in which the only unpaired electron of low spin Fe(III) and odd electron on O_2^- are strongly coupled antiferromagnetically. However, none of the two explanations are universally accepted.

It is interesting to note that a heme group, which is without a polypeptide chain, takes up an oxygen molecule to finally yield a stable μ-oxoproduct, as shown in Fig. 6.

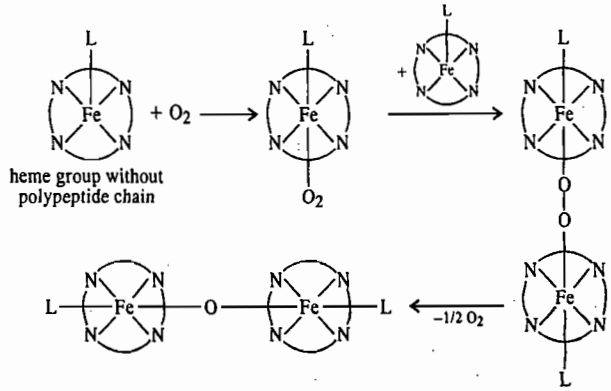


Fig. 6. Formation of μ-oxoproduct from a heme group which is without a polypeptide chain

This reaction is irreversible. The essential condition for the formation of the μ-oxoproduct is that the two reacting heme groups should be able to come in contact with each other. Nature, however, avoids such irreversible oxidation process by surrounding the heme groups in hemoglobin and myoglobin by bulky polypeptide chains so that the direct contact between the heme groups becomes impossible. This explains why the oxygen intake by hemoglobin and myoglobin is completely reversible.

METALLO-ENZYMES

Enzymes are catalysts for biological systems. Their basic structure is built of proteins. Enzymes which are of interest to inorganic chemists are those which are composed of a protein structure called **epoenzyme** and a small **prosthetic group** which may be a simple or a complexed metal ion. A group that combines reversibly with an enzyme for a particular reaction and is then released to combine with another enzyme, is termed as **coenzyme**. The prosthetic groups and the coenzymes are also called **cofactors**.

More than 1500 metallo-enzymes have so far been identified. Their names are derived by adding the suffix 'ase' to the name of the process catalysed or to the name of the molecules on which the enzyme acts. The molecule on which the enzyme acts is called the **substrate**.

Some important metallo-enzymes are listed below.

1. *Phosphohydrolases* and *phosphotransferases*, all containing magnesium.
2. *Cytochromes*, *peroxidases*, *catalases* and *ferridoxine*, containing iron.
3. *Tyrosinase, amine oxidase, cytochrome oxidase, ascorbate oxidase* and *galactose oxidase*, all containing copper.
4. *Arginase and oxaloacetate decarboxylase* all containing manganese.
5. *Alcohol dehydrogenase*, *alkaline phosphatase*, *carbonic anhydrase* and *carboxy peptidase*, all containing zinc.
6. *Nitrogenase* containing both iron and molybdenum.

Although it is beyond the scope of the book to discuss all these enzymes in any details yet it is pertinent to say a few words about the structures and functions of some of these enzymes to illustrate how essential these metallo-enzymes are to biological systems.

1. Carbonic anhydrase. Carbonic anhydrase, as mentioned above, is a zinc enzyme that catalyses the hydration of CO_2 and dehydration of carbonic acid (HCO_3^- to be more precise). This enzyme can hydrate 10^6 molecules of CO_2 per second at 37°C which is about 10^7 times faster than the uncatalysed rate of hydration of CO_2. Carbonic anhydrase, with a molar mass of about 30,000, occurs in animals as well as in plants. The zinc ion lies in a deep pocket created by the coiled epoenzyme and is coordinated with the three nitrogen atoms of the three imidazole rings of histidine groups of the epoenzyme. The fourth coordination site is perhaps occupied by a water molecule when the enzyme is at rest. The stereochemistry of zinc in the enzyme is tetrahedral, as shown in Fig. 7.

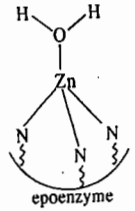


Fig. 7. Stereochemistry of Zn in carbonic anhydrase

The Lewis acidity of Zn^{2+} ion in carbonic anhydrase polarizes the coordinated H_2O molecule to the point of loss of H^+ ion to form coordinated OH group. It is the hydroxy form of the enzyme which is believed to reversibly hydrate CO_2 to HCO_3^-. The probable mechanism illustrating the role of the enzyme in the process is shown in Fig. 8.

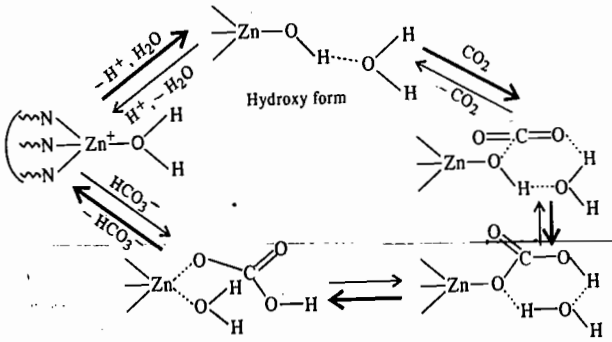
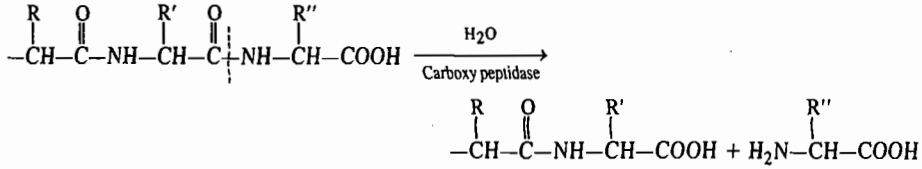


Fig. 8. The probable mechanism for reversible hydration of CO_2

Like all truly catalytic reactions, catalytic reversible hydration of CO_2 is a close loop. The clockwise cycle shows the hydration of CO_2 to HCO_3^- and the anticlockwise cycle shows the release of CO_2 from HCO_3^-. The cycle may proceed either way depending upon the concentrations of the reactants in the biological system.

2. Carboxy peptidase. It is also a zinc enzyme which hydrolyses the terminal peptide (amide) bond of the peptide chain from the side of its carboxy end, as shown below :



The enzyme is selective. It hydrolyses those polypeptides in which the terminal amino acid segment has an aromatic or a branched chain aliphatic substituent R″.

In this enzyme, the metal ion is bonded to two imidazoles of histidine group and a glutamic acid residue of the epoenzyme. A water molecule is weakly bonded to the fourth coordination site of the Zn^{2+} ion when the enzyme is at rest (Fig. 9).

The active Zn^{2+} ion is located in a depression formed on the surface of the coiled epoenzyme. Close to this depression there is an empty pocket formed by the coiled epoenzyme for accommodating the substrate (Fig. 9).

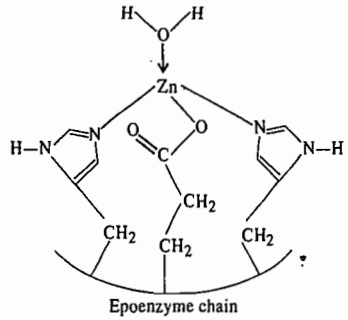


Fig. 9. Structure of the zinc enzyme carboxy peptidase.

The enzyme is believed to act through the displacement of the coordinated water by the C=O group of the terminal amide linkage of the substrate, as shown in Fig. 10.

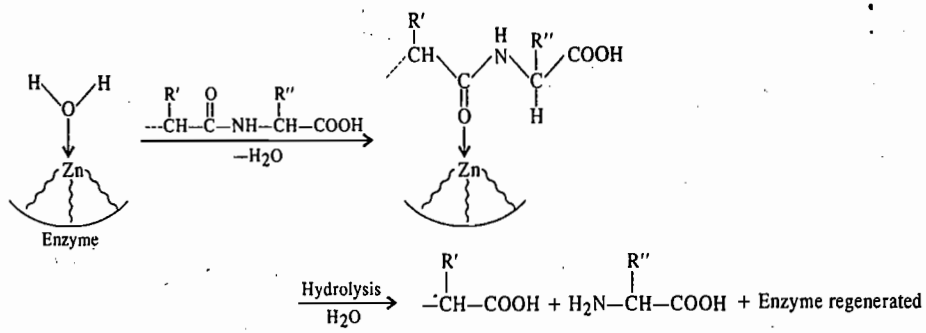


Fig. 10. Mechanism for the hydrolysis of the peptide (amide) bond carried out by the enzyme carboxy peptidase.

It has been established that the Zn^{2+} ions can be replaced by Co^{2+} ions with full retention of enzyme activity. Advantage is taken of this fact for getting information about the metal ion environment in the zinc enzyme. Since Zn^{2+} ion is a d^{10} system, the zinc enzyme does not give *d–d* electron absorption bands in the visible region. Zinc is, therefore, replaced by cobalt in the enzyme. The cobalt enzyme would show absorption bands in the visible region due to *d–d* transitions from which valuable information about metal ion environment in the enzyme can be obtained.

3. Peroxidases. Peroxidases are a class of enzymes which catalyse the oxidation of substrates by H_2O_2. The heme group containing high spin Fe(III) is the prosthetic group present in peroxidases. The heme group of a peroxidase is lodged deeply in a rather large protein molecule with a histidine nitrogen coordinating to the fifth position of Fe(III). The sixth coordination site of Fe(III) of the heme group of the peroxidase can be occupied by a water molecule when the enzyme is at rest or by the substrate when it is in function.

We shall abbreviate a peroxidase enzyme as RFe(III) in the ensuing discussion where R symbolises porphyrin ring part containing Fe(III). There is strong evidence for the presence of the oxidised peroxidase containing $R^{\bullet+}$ and $Fe^{IV}=O$ in the peroxidase catalysed oxidation of the substrate by H_2O_2. ($R^{\bullet+}$ is the cation radical formed by removal of a π electron from porphyrin part). The oxidised peroxidase then oxidises the substrate :

$$H_2O_2 + RFe^{III} \longrightarrow R^{\bullet+}Fe^{IV}=O + H_2O$$

$$R^{\bullet+}Fe^{IV}=O + \underset{\text{(Substrate containing two removable hydrogens)}}{AH_2} \longrightarrow RFe^{III} + \underset{\text{(Oxidised substrate)}}{A} + H_2O$$

4. Catalases. Catalase enzymes have molar mass of about 24000. Every catalase molecule has four high spin Fe(III) heme groups. Each heme group has a separate peptide chain which is coordinated to Fe(III). The catalase catalyses the disproportionation of H_2O_2.

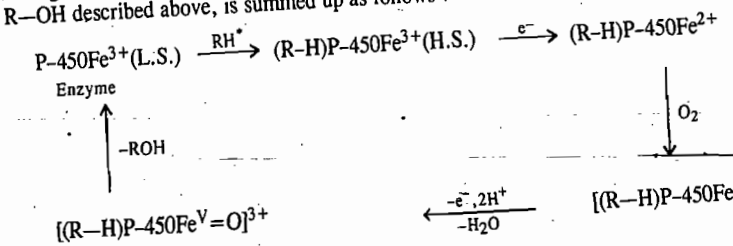
$$H_2O_2 + H_2O_2 \xrightarrow{\text{Catalase}} 2H_2O + O_2$$

The heme groups of a catalase are located in deep pockets made by coiled peptide chains. Such pockets presumably check the escape of reactive intermediates, such as $\dot{O}H$, O_2^-, etc., formed during the catalytic disproportionation reaction. Catalases can also catalyse the oxidation of substrate by H_2O_2.

5. Cytochrome P-450. The membrane-bound cytochrome P-450 enzyme, which occurs in animals, bacteria and plants, catalyses the introduction of oxygen atom from O_2 into the substrate. Of the many possible substrates, the most important are molecules in which the C—H groups can get converted to C—OH groups. The enzyme performs a very important function in humans. It catalyses hydroxylation of drugs, steroids, pesticides, etc. The hydroxylated compounds are water-soluble and thus get excreted through urine.

The enzyme contains low spin Fe(III) in the heme group. The fifth coordination site of Fe(III) is occupied by a coordinated S atom belonging to the side chain of the eponezyme. It is not certain whether the sixth coordination site is occupied by a water molecule or is lying vacant when the enzyme is at rest.

The cytochrome P-450 containing low spin Fe(III) is abbreviated as $P\text{-}450Fe^{3+}$(L.S). When it binds a substrate (R—H), it gives a high spin intermediate $(R\text{—}H)P\text{-}450Fe^{3+}$(H.S.). A one-electron transfer reduces this intermediate to $(R\text{—}H)P\text{-}450Fe^{2+}$ which then binds O_2 molecule to yield $[(R\text{—}H)P\text{-}450FeO_2]^{2+}$. On the addition of another electron and two H^+ ions and simultaneous elimination of a water molecule, this intermediate changes to $[(R\text{—}H)P\text{-}450Fe^{V}=O]^{3+}$. This species containing $Fe^{V}=O$ converts R—H to R—OH and regenerates the original enzyme. The mechanism involving the catalytic oxidation of substrate R—H to R—OH described above, is summed up as follows :



Inhibition and Poisoning of Enzymes

Ligands that can occupy an active site** in an enzyme and can also coordinate strongly to the metal ion of prosthetic group of that enzyme would naturally resist their detachment from the enzyme and would

* RH stands for the substrate.

**An active site is a pocket usually close to the metal ion of the enzyme where the substrate gets accommodated *immediately before* the reaction.

thus oppose the attachment of the substrate with the metal ion of the enzyme. This would inhibit the action of that enzyme. For example, if azide ion is added to the enzyme carbonic anhydrase, it would occupy an active site close to the Zn^{2+} ion of the enzyme. The azide ion would coordinate with the Zn^{2+} ion replacing the $Zn^{2}\leftarrow OH_2$ bond with a stronger Zn←azide bond. Consequently, the enzyme carbonic anhydrase would not get converted into the hydroxy form which is the active form of the catalyst for the reversible hydration of CO_2, as illustrated earlier. In other words, *the addition of azide ion would inhibit the catalytic action of carbonic anhydrase.* Similarly, addition of small amounts of CN^- ion or H_2S would inhibit the enzymatic activity of carbonic anhydrase.

Sometimes heavier metal ions such as Cd^{2+}, Hg^{2+}, As^{3+}, replace the metal ion of the prosthetic group of an enzyme. This deactivates the enzyme. Apart froms this, the heavier metal ions (soft acids) form extremely stable complexes with the S-containing amino acid units (soft bases) of the epoenzyme. This soft acid—soft base interaction brings about very significant changes in the conformation of the enzyme as a result of which the enzyme loses its activity as a catalyst. This is known as **poisoning of the catalyst.**

The poisoning effect of heavy metal ions can sometimes be reversed by adding S-containing ligands such as cysteine, glutathione and 2,3 dimercaptopropanol (popularly known as British Anti Lewisite, **BAL**) to the biological system containing the poisoned enzyme. These compounds bind more strongly with the heavy metal ions than do the thio groups present in the epozymes.

Nature has devised its own mechanism for inhibiting the heavy metal ion poisoning. As soon as the metallo-enzyme is under attack of heavy metal ions, the concentration of *thioneins* (a group of protein of high molar mass) increases in the liver, kidneys and spleen. The exact mechanism for detection of the presence of the heavy metal ion by the body and the reason for the over production of thioneins is not yet known. These thioneins are built up from about 60 condensed amino acid units, one third of which are S-containing amino acid units having several free SH groups. These free SH groups have a strong tendency to bind (or chelate) with heavy metal ions (soft acid-soft base interaction). The thioneins, therefore, bind with the heavy metal ions (like Cd^{2+}, As^{3+}, Hg^{2+}) more strongly compared with the enzymes and thus protect the metallo-enzymes from being poisoned by heavy ions.

ROLE OF ALKALI AND ALKALINE EARTH METAL IONS IN BIOLOGICAL SYSTEMS

We have discussed above the role of some biochemicals containing iron and zinc ions in biological systems. We shall now discuss briefly the role played by the bulk metal ions, *viz.*, Na^+, K^+, Ca^{2+} and Mg^{2+} in biological systems.

Role of Na^+ and K^+ ions. Sodium cation is a major cation of extracellular fluids of animals including human beings which is known to activate certain enzymes in the animal body. Sodium ions are relatively harmless except when present in excess amounts in which case they may cause hypertension. The saline water containing excessive amounts of NaCl is harmful to plant and aquatic life because of the toxicity of Na^+ ions.

The potassium ion is essential to all organisms with the possible exception of blue green algae. It is a major cation of intracellular fluids of animal cells. It is moderately toxic to mammals but only when injected intravenously.

The sodium and potassium ions, taken together, constitute what is known as **Na^+—K^+ pump** or simply as **'sodium pump'**. The functioning of this pump is actually a biological process which goes on occurring in each and every cell of all animals. Although the discussion of the exact mechanism of the functioning of this pump is beyond the scope of the book yet it may suffice to say that it transfers Na^+ ions from the intracellular fluids to the extracellular fluids with the help of 'carrier proteins'. Simultaneously it transfers K^+ ions from the extracellular fluids to the intracellular fluids. Since each operation of the pump (*i.e.*, each cycle of this biological process) pumps out larger number of sodium ions from the cell than the number of K^+ ions that it pumps into the cell, the *interior of the cell acquires an excess negative* charge and the exterior of the cell acquires an excess positive charge. This results in the development of electrical potential gradient across the cell membrane which is responsible for the transmission of nerve signals in animals. The Na^+—K^+ pump also maintains the volume of the cell. Without the existence of the Na^+—K^+ pump in the cell, the latter would have swelled in volume and ultimately bursted.

Role of Mg^{2+} and Ca^{2+} Ions. Magnesium is an important constituent of chlorophyll which initiates the process of photosynthesis in green plants.

Magnesium ions are concentrated more in intracellular than in extracellular fluids in animal bodies. The presence of Mg^{2+} ions is a necessary requirement for the activation of phosphate transfer enzymes which participate in the energy releasing biochemical process occurring in animal body. Magnesium ions are also required for carbohydrate metabolism.

Mg^{2+} and Ca^{2+} ions are also responsible for the transmission of electrical *impulses* along the nerve fibre and for the contraction of muscles.

Calcium ions are essential for the formation of bones and teeth and for maintaining rythem of heart and for clotting of blood. The enamel on teeth is also a double salt of calcium, $3Ca_3(PO_4)_2.CaF_2$.

Calcium ions are normally maintained at extremely low concentration in the intracellular fluids. Their concentration in the intracellular fluids is 10000 times less than their concentration in the extracellular fluids. The maintenance of low calcium ion concentration in the intracellular fluids is carried out by two biochemical processes known as **'calcium pumps'**. One of these processes pumps Ca^{2+} ions out of the muscle cells and the other pumps Ca^{2+} ions into the muscle cells.

BIOLOGICAL FUNCTIONS AND TOXICITY OF SOME ELEMENTS

Apart from the metal ions mentioned above, there are several other elements which, in large quantities, are harmful but, in trace amounts, are useful for biological systems. Some of these elements are listed below.

Chromium. It is an essential trace element which is involved in glucose metabolism. Cr(III) and insulin both maintain the correct level of glucose in the blood. However, it is highly toxic as Cr(VI) in which state it is carcinogenic. If Cr(III) is totally absent in the body, the removal of glucose from the blood would occur at lesser rates than normal.

Manganese. It is an essential trace element for almost all organisms. The Mn(II) enzyme produced in the liver converts nitrogenous waste products into urea which is carried by the blood to kidneys which excrete it out into the urine. It activates several enzymes. Its deficiency in soil inhibits plant growth and leads to infertility in mammals which consume such plants. Manganese is an essential element for plant growth. It, alongwith fertilizers, enriches the soil.

Cobalt. It is an essential trace element for many organisms. It is a constituent of vitamin B_{12} and activates a number of enzymes. However, it is highly toxic to plants and moderately toxic to mammals when injected intravenously. Deficiency of cobalt in soil adversely affects the health of grazing animals. Cobalt in traces is essential for the healthy growth of animals.

Nickel. It is an essential trace element for several hydrogenases and ureases (both are classes of enzymes). Its deficiency in food slows down the functioning of the liver in chicks.

It is highly toxic to plants and moderately toxic to mammals. It is carcinogenic if present in higher concentrations in biological systems. Its use in industry (particularly electroplating) causes severe water pollution.

Copper. It is an essential trace element for all organisms. It is an important constituent of hemocyanin which supplies oxygen to certain aquatic creatures and redox enzymes. Copper-containing enzymes play an important role in the pigmentation of skin, functioning of brain and in iron metabolism in human body. The deficiency of copper in human system results in its inability to utilise iron stored in the liver.

The excess of copper in human body is, however, harmful. A disease known as Wilson disease upsets the copper metabolism of human system in such a way that it gets deposited in excess in the liver, kidneys and brain. Patients suffering from this disease are treated with controlled doses of EDTA which forms a water soluble complex with Cu^{2+} ion. The water soluble copper complex gets excreted through urine.

It is highly toxic to invertibrates and moderately toxic to other mammals also when present in higher concentrations.

Arsenic. It is an essential ultratrace element in red algae, chicks and some mammals including humans. Its deficiency in chicks results in depressed growth. It is moderately toxic to plants and highly toxic to mammals when present in more than ultratrace quantities. Mining operations, burning of coal, use of insecticides and herbicides containing arsenic are the chief sources of arsenic pollution in air and water.

Selenium. It is an essential trace element for mammals and some plants. It is an essential constituent of some enzymes and protects biological systems from free radical oxidants. Its deficiency in soil leads to white muscle disease in grazing sheep. In higher concentrations it is moderately toxic to plants but highly toxic to mammals.

Molybdenum. It is an essential trace element for all organisms. It is a constituent of several enzymes which are used by nature for nitrogen fixation and nitrate reduction. It is moderately toxic. Excess of molybdenum in biological systems may cause deficiency of copper.

Cadmium. This element has practically no use in living organisms. It is toxic to all organisms. It is a cumulative poison for mammals causing kidney failure, hypertension, anaemia and disorder of bone marrow. Since zinc is generally contaminated with cadmium, hence its use in galvanizing industry is the chief source of cadmium pollution.

Iodine. It is an essential element for many organisms. It is an important constituent of thyroxine. Its deficiency causes goitre. Although iodide ions are not toxic, yet I_2 is toxic like other halogens in elemental form.

Mercury. It has practically no biological function. It is highly toxic to fungi, plants and animals. It is a cumulative poison for mammals. Fungicides of organomercurial category cause air, water and soil pollution.

Lead. It has no known biological function. It is highly toxic to plants and is a cumulative poison for mammals. It inhibits the synthesis of hemoglobin in mammals and is highly toxic for central nervous system. Lead tetraethyl used in gasoline as an antiknock and lead pigments are serious health hazards.

Iron. The role of biochemicals containing iron (hemoglobin and myoglobin) in biological systems has already been discussed. Although iron is essential to all form of life yet its excessive intake can cause siderosis and damage organs. Iron is also present in plants and bacteria in the form of cytochromes and ferridoxin which are responsible for electron transfer reactions in biological systems. Apart from this, iron is an important constituent of nitrogenase (a nitrogen-fixing enzyme) and a number of other important enzymes in biological systems.

Zinc. The role of biochemicals of zinc in the form of zinc enzymes has already been discussed. It is an essential element for almost all organisms. It is present in a large number of essential enzymes. Its deficiency may cause loss of appetite. It is only slightly toxic in macro doses. However, excess oral doses may cause diarrhea and vomitting.

Radioactive Elements. They have no biological function. Their accumulation in biological systems is harmful due to radioactivity. They are potential pollutants of air and water in the form of nuclear wastes.

BIOLOGICAL FIXATION OF NITROGEN

The nitrogen atoms constituting biomolecules such as amino acids, pyrimidines, etc., come from NH_4^+ ions which, in turn, come from atmospheric nitrogen by its chemical or biochemical reduction. The process of conversion of atmospheric nitrogen into NH_4^+ ions is known as **fixation of nitrogen.** Biological fixation of nitrogen is carried out by blue green algae and a family of bacteria known as *rhizobium bacteria*. These bacteria invade the roots of leguminous plants such as peas, beans, alfalfa, cloves, etc., and form root nodules in which nitrogen fixation takes place.

Since the bond energy of the N≡N bond is quite high (~950 kJ mol^{-1}), the nitrogen bond is highly resistant to chemical attack. That is why the chemical process of nitrogen fixation (*viz.*, the Haber process) takes place at high pressure and temperature. The biological process of nitrogen fixation, though less efficient, takes place under ordinary conditions of pressure and temperature. The biological process essentially occurs under anaerobic conditions.

The enzyme present in the nitrogen fixing bacteria is the *nitrogenase complex* which, in fact, is a family of enzymes varying slightly from one bacterial species to another in which they are present. The nitrogenase complex is composed of two kinds of protein components : one kind of component is known as the *reductase* and the other kind of component is known as the *nitrogenase*. The reductase supplies electrons which are used by the nitrogenase to reduce the nitrogen to NH_4^+. The reductase is an Fe–S protein while the nitrogenase is an Fe–Mo–S protein.

The stoichiometry of the reaction catalysed by the nitrogenase complex is :

$$N_2 + 6e^- + \underset{\text{(adenotriphosphate)}}{12\,ATP} \longrightarrow \underset{\text{(adenodiphosphate)}}{2NH_4^+} + 12\,ADP + 4H^+$$

Recent studies suggest the folowing reaction sequence :

(i) The reduced ferridoxine (which is the real source of electrons in the reaction given above) transfers its electrons to the reductase component of the nitrogenase complex.

(ii) ATP then binds to the reductase and thereby alters its comformation in such a way that it causes a shift in the reduction potential of the reductase from −0·30 V to −0·40 V. The greater the magnitude of the negative value of the reduction potential, the greater is the tendency to lose electrons and hence the greater is the reducing power of the reductase.

(iii) The increased reducing power of the reductase enables it to tranasfer its electrons to the nitrogenase component of the nitrogenase complex which contains the bound nitrogen.

(iv) The ATP then gets hydrolysed and the nitrogen bound to the nitrogenase component gets reduced to NH_4^+.

Since the sources of energy required for chemical fixation of nitrogen to ammonia are becoming more and more costly, efforts are being made by bioscientists to carry out nitrogen fixation by micro-organisms.

QUESTIONS

1. Illustrate the structure of myoglobin and hemoglobin. Describe in details the role played by these bio-inorganic compounds in biological systems.
2. What is Hill constant ? What is the significance of this parameter ?
3. Explain the terms cooperativity effect and Bohr effect. What explanation is offered for the cooperativity effect in hemoglobin ?
4. Discuss the mechanism of the intake of oxygen by myoglobin and hemoglobin. How would you account for the diamagnetic character of oxygenated myoglobin and oxygenated hemoglobin ?
5. What are metallo-enzymes ? Explain the terms epoenzymes, prosthetic groups, coenzymes and cofactors as used in the context of the structures of metallo-enzymes
6. Describe the role of the following metalloenzymes in biological systems :
   (i) Carbonic anhydrase *(ii)* Carboxy peptidase *(iii)* Peroxidases
   (iv) Cytochrome P-450 and *(v)* Catalases.
7. What is meant by poisoning of enzymes ? Describe briefly the causes of the poisoning of enzyme catalysts. Discuss the mechanism which is used by Nature to counteract the poisoning of enzyme catalysts.
8. Discuss the role played by bulk metal ions in biological systems. What are sodium pump and calcium pump ?
9. Discuss briefly the biological functions and toxicity of the following elements :
   Chromium, manganese, cobalt, nickel, copper, arsenic, selenium, molybdenum, cadmium, iodine, mercury, lead, iron and zinc.
10. Write a note on biological fixation of nitrogen.

38 ENVIRONMENTAL CHEMISTRY

Environment, in general, comprises of *(i)* the atmosphere *(ii)* the hydrosphere *(iii)* the lithosphere and *(iv)* the biosphere.

(i) **Atmosphere.** It is the layer of gases surrounding the earth. It filters harmful radiations and allows only near UV, visible and other longer wave length radiations to pass through it.

(ii) **Hydrosphere.** It includes all types of water bodies like rivers, ponds, lakes, oceans, glaciers, polar ice caps, etc.

(iii) **Lithosphere.** It is the outer crust of earth consisting of minerals and soil.

(iv) **Biosphere.** It includes all living organisms and their interaction with the atmosphere, hydrosphere and lithosphere.

All the constituents of environment influence one another.

Environmental chemistry is a science which deals with various chemical phenomena occurring in the environment. It includes the study of sources and effects of certain specific chemical species, called *pollutants*, on air, water and soil. By definition, ***pollutant** is a substance produced either by a natural source or by human activity which has an adverse effect on the environment, that is, which causes* **environmental pollution.**

Environmental pollution can affect humans, animals, plants and also materials. While it may cause illness or even death in case of humans and animals, it may reduce the growth of desirable plants and in some cases may cause them severe injury. The effect on materials includes corrosion of metals and marble as well as discolouring of paints. An idea about the adverse effect of environmental pollution can be had from the facts that nearly 4000 persons died of respiratory diseases in London in 1852, hundreds of Japanese suffered from disease and death on eating polluted fish from Minimata Bay during 1953–60, nearly 500 Iraqis died after consuming polluted wheat in 1972 and so on.

Long Distance Movement of Pollutants. There is sufficient evidence to establish that many types of pollutants get distributed over the entire earth in short periods. Radioactive fallout from atmospheric nuclear tests conducted in any part of the world becomes detectable in all parts of the world within days or weeks and from the analysis of the fallout the scientists can easily learn a great deal about the type of the tests carried out. Even the polar regions are not immune from the fallout. Chlorinated hydrocarbons such as DDT and its metabolites get distributed throughout the world having been transported by air or by some other means not yet fully understood. Thus, DDT at the level of 100 ppb has been detected in the liver and fat of animals living in Antarctica, thousands of kilometres away from the sites where the pesticides are actually used.

There is now growing evidence that many chronic diseases such as asthma, emphysema and bronchitis are *environmentally induced*. The alergy problem being induced by *parthenium* (congress grass) whose seed was inadvertently brought into the country from USA alongwith the imported wheat during the period in which India had a shortage of food grains, is a source of immense worry for the country. The World Health Organization has estimated that 80–90 per cent of all human cancers are environmentally related or induced.

The inordinate population growth, rapid industrialisation, fast urbanisation and modified agricultural operations have intensified the interaction of man with the environment. As a result there is alarming

increase in the pollution of air, water and soil. Human health is seriously affected by environmental and ecological disorders. The situation, if not controlled, would be a big threat to the very survival of mankind on this earth.

The developed countries where the pollution problems have been more severe, started taking effective remedial measures since early sixties. In 1970, they celebrated the 'Earth Day' under the auspices of the United Nations. In 1972, the United Nations held a conference on Human Environment. Since then the developing countries including India have also become conscious about protecting their environment. The setting up of the Central Ganga Authority for complete depollution of the pious Ganga water is a consequence of that very consciousness. The Government of India have now a full fledged Ministry of Environment which seriously looks after the conservation and protection of environment.

Mankind is faced with several types of pollution such as air pollution, water pollution, soil pollution, thermal pollution, metal pollution, noise pollution, etc. In this chapter, we shall deal with only three types of pollution, *viz.*, air pollution, water pollution and soil pollution.

AIR POLLUTION

The problem of air pollution is not a new one. It has been around for centuries. More than three centuries ago, John Evenlyn, a noted scientist and diarist complained about severe air pollution around London. He described with great accuracy, the effects of air pollution resulting from combustion of coal. Extensive studies in this context, however, have been carried out only during the last few decades. When we talk of pollution of air, we mean generally the pollution of that part of the atmosphere which is **nearest** to the earth's surface extending to a height of about 80 km. This is known as **homosphere** since it is composed of a *homogeneous mixture* of various constituents.

Air Pollutants. The air in nature is never clean. It is invariably polluted. The common gaseous pollutants are CO, CO_2, SO_2, H_2S, NO, NO_2 and common solid pollutants, called **particulates**, are carbon and dust particles, pollens, aerosols of lead, etc. The gaseous pollutants are released into the atmosphere as a result of volcanic activity, vegetation decay, forest fires, coal refuse fires, etc. (natural activities) as well as by combustion of coal and oil, burning of gasoline in automobiles, agricultural and slash burning, etc. (human activities). The particulates are produced by volcanic eruptions, high velocity winds and biological processes (natural activities) as well as by smelting and mining operations, stone crushing and grinding, incomplete combustion, etc. (human activities)

In addition to the above common pollutants, some specific pollutants such as chlorine, hydrocarbons, chlorofluorocarbons, pesticides, etc., are also ejected into the atomshpere from specific industrial units and industrial processes.

The various air polutants and the sources from which they originate, are given in Table 1.

TABLE 1

Air Pollutants and Their Sources

Pollutants	Major Sources	Maximum permissible exposure in ppm during an average period of 8 hours per day
CO	Incomplete combustion of carbonaceous matter in automobile engines and defective furnaces, incomplete combustion of agricultural & slash matter, volcanic eruptions, forest fires.	50
SO_2	Combustion of sulphur-bearing fuels such as coal and oil, volcanic eruptions.	5
NO, NO_2	Combustion of fuel, interaction of N_2 and O_2 of the atmosphere at high temperatures.	5
H_2S	Biological decay of organic matter, oil refineries.	20
Cl_2	Industrial units producing paper, plastics, chlorinated hydrocarbons, dyes, chlorochemicals, etc.	1

Pollutants	Major Sources	Maximum permissible exposure in ppm during an average period of 8 hours per day
Hydrocarbons	Combustion of fuel in automobiles, refineries, anaerobic bacterial decomposition of organic matter, natural gas.	1000
Chlorofluoro-carbons	Industrial units manufacturing refrigerants, fire fighting agents, their use as solvents.	1030
Pesticides	Application of pesticides and their volatilization from soil, water, treated surfaces and industrial units producing pesticides.	–
Particulates	Volcanic eruptions, fly ash, smelting and mining operations, smoke from incomplete combustion, dust from crushers and grinders.	–
$PbCl_2$, $PbBr_2$	Addition of $(C_2H_5)_4Pb + C_2H_4Cl_2 + C_2H_4Br_2$ to gasoline to improve its antiknock property.	–
CO_2*	Combustion of carbonaceous matter, biological decay, lime kilns	5000

*Normally, CO_2 is *not* considered as an air pollutant.

We shall now discuss at length the adverse effects of various pollutants, the maximum limits of their tolerance and methods of their detection and control.

Carbon Monoxide. As mentioned above, carbon monoxide originates from incomplete combustion of carbonaceous matter in automobile engines and defective furnaces, incomplete combustion of agricultural and slash matter and also by the interaction of carbon dioxide with coke at high temperature in industrial furnaces such as blast furnaces. Some natural processes such as forest fires, volcanic activity, seed germination, lightning discharge during thunder storms, etc., also release carbon monoxide in small amounts. Major proportion of the gas is, of course, contributed by human activity. Thus, of the total amount of CO present in the atmosphere, about 73 per cent is contributed by vehicular exhausts and about 17 pet cent by forest fires and agricultural and slash burning. Industrial processes involved in steel, paper and petroleum industries contribute about 9·5 per cent of CO. The contribution by natural phenomena is thus very very small.

Although considerable amount of CO is being emitted continuously by human activity, its concentration in the atmosphere does not increase to any significant extent. This is because some factors operate in nature which eliminate carbon monoxide. Recent researches have shown that soil is capable of removing large amounts of CO from the atmosphere by virtue of the action of some soil microorganisms. Technically, *the elements or organisms which consume a pollutant are known as a* **sink.** Thus, soil microorganisms act as a *sink* for CO.

In thickly populated urban areas, the concentration of CO is considerably high because of heavy vehicular traffic and insufficent availability of soil to act as sink. On the country side, the concentration of the gas is comparatively small.

Toxic effects of carbon monoxide. The toxic effects of CO on human beings and animals arise from its reversible combination with haemoglobin (Hb) present in the red cells of the blood to form Hb.CO.

$$Hb + CO \rightleftharpoons Hb.CO$$

Normally, haemoglobin of the blood combines with oxygen of the atmosphere present in the lungs to form oxyhaemoglobin, $Hb.O_2$ which undergoes dissociation to release the oxygen to the body muscles. Thus, $Hb.O_2$ *acts as an oxygen-carrier for blood.* Since Hb has much greater affinity for CO than for O_2, the haemoglobin is more readily attacked by CO to form Hb.CO, as shown above. The combination of haemoglobin with CO inhibits its oxygen-carrying capacity in the blood thereby reducing the availability of oxygen for the body cells resulting in *anoxia* (oxygen starvation). Hb contains 5-coordinated Fe (II) atoms. The sixth coordination site of each of these Fe (II) atoms is unoccupied. The molecular oxygen present in the lungs adds to the Fe (II) atoms through the sixth coordination site and gets detached easily

at the cells of the muscles. If, instead of O_2, the stronger CO ligand occupies the sixth coordination site of the metal atoms, Hb would not be able to take up O_2 from the lungs and deliver it to the body cells.

The maximum permissible concentration of CO in the atmosphere is 40 ppm for an exposure of 8 hours. If the concentration is higher or the exposure is longer, adverse effects start.

There is some medical evidence that even as low a concentration as 10 ppm of CO in the atmosphere may produce increased mortality amongst hospitalised heart patients. The higher rate of heart disease in smokers is also believed to be due to CO which the smoker inhales from the cigarette smoke. It has been estimated that a person who smokes a pack of cigarettes daily inhales smoke which may raise the level of blood Hb.CO to about 5% or more. This results in impairment of mental performance, visual activity and other body functions.

The most effective treatment for CO poisoning is to confine the victim in a chamber having oxygen at 2 to 2·5 atm pressure. This accelerates elimination of carbon monoxide from the haemoglobin ($Hb.CO + O_2 \rightleftharpoons Hb.O_2 + CO$). Exposure to oxygen under high pressure also corrects *anoxia* by making available large amounts of dissolved oxygen for blood *directly* thus enabling the body to bypass the uptake of oxygen through haemoglobin.

Carbon Dioxide. Usually, carbon dioxide is not considered as an air pollutant. However, release of vast quantities of the gas into the atmosphere by the combustion of fossil fuels, decomposition of carbonates and biological decay are likely to bring about significant changes in climate.

As we know, a large amount of heat is received by the earth from the sun. About 66% of this energy is absorbed by the earth and the remaining 34% is reflected or scattered back into the space. There is growing spectroscopic evidence that earth absorbs radiation mostly in the visible region and reflects (or scatters) radiation in the infrared region.

CO_2 transmits (*i.e.*, allows to pass) the short wave length radiations (*viz.*, ultraviolet and visible radiations) but impedes the passage of long wave length, *i.e.*, infrared radiations (or heat radiations). *The CO_2 present in the atmosphere thus acts as a barrier against the flow of heat from the earth to the atmosphere. This results in an increase of temperature of the earth's surface.* This is known as the **green house effect** because like the glass of the green house, CO_2 permits the passage of radiations of short wave lengths and impedes the passage of radiations of long wave lengths, *i.e.*, heat radiations. It has been calculated that with a doubling of CO_2 concentration, the temperature of earth's surface increases by about 1·9°C. Such an increase would have considerable adverse effect on world's climate. It can cause melting of glaciers, flooding of coastal planes, changing of the biological activity of oceans and altering the patterns of cropping, etc.

Chlorine. In the absence of rigid precautions, chlorine is liable to escape into the atmosphere from the sites of industrial units manufacturing paper, plastics, dyes, chlorinated hydrocarbons and other chlorochemicals. There is also a possibility of accidental leakage in storage tanks and pipe lines.

Chlorine has a sharp irritating odour and is poisonous when inhaled in larger quantity, the maximum allowable exposure being 1 ppm for 8 hours.

Oxides of Nitrogen (NO, NO_2). Nitric Acid Rain. Although small amounts of NO_2 produced by microbiological processes in the soil do not constitute a serious pollution factor, yet significant amounts of NO and NO_2 are emitted to the atmosphere by human activity which cause considerable pollution. These oxides are produced by the interaction of atmospheric N_2 and O_2 when combustion of carbonaceous matter occurs at considerably high temperature exceeding 1100°C, followed by fast cooling.

$$N_2 + O_2 \overset{\text{high temp}}{\rightleftharpoons} 2NO$$
$$2NO + O_2 \rightleftharpoons 2NO_2$$

Thus, considerable amounts of nitrogen oxides are produced during combustion of coal, oil and natural gas in industrial units and of gasoline and diesel in automobile engines. These gases are removed

from the atmosphere in the form of nitric acid through the following sets of reactions :

(*a*)
$$2NO + O_2 \longrightarrow 2NO_2$$
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

(*b*)
$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
$$NO_2 + NO_3 \longrightarrow N_2O_5$$
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

(HNO_3, formed as above, comes down from the atmosphere in the form of **nitric acid rain**. The acid gets converted into nitrate salts on coming in contact with bases such as ammonia, lime, etc.)

Acid rain may cause the *p*H of water to fall below 5·4. The water having *p*H below 5·4 may affect vegetation as well as freshwater fish. The acid rain may corrode building materials and metallic structures.

Nitrogen oxides cause fading of textile dyes and deterioration of cotton and nylon. Several sensitive plants get adversely affected by NO_x concentrations as low as 1 ppm for a day or 0·35 ppm for a few months. The affected plants start shedding their leaves and fruit.

Inhaling of the nitrogen oxides by humans results in pulmonary odema and haemorrhage.

Nitric oxide alone does not have any adverse effect on humans at concentrations that occur in the atmosphere, even in highly polluted areas. No doubt Hb has extraordinary affinity for NO (about 1500 times its affinity for CO) but, luckily, atmospheric NO is unable to enter the blood stream to react with Hb. However, high concentrations of NO are otherwise dangerous because of the possibility of its oxidation to produce NO_2 which is highly toxic. A concentration of even 100 ppm for a few minutes can be lethal to humans and animals. An exposure to 5 ppm concentration of NO_2 for a few minutes leads to adverse effects on the respiratory system. Long term exposure to even as low a concentration as 0·06 ppm aggravates respiratory diseases in humans. Exposure of monkeys to 15–50 ppm for 2 hours has been reported to damage their lungs, heart, liver and kidneys.

Sulphur Oxides. Sulphuric Acid Rain. The common oxide of sulphur emitted by pollution sources is sulphur dioxide. This is the most harmful gaseous pollutant released into the atmosphere through volcanic eruptions (natural activity) and through combustion of sulphur-bearing fuels such as coal and oil (human activity). This pollutant is also produced during roasting of sulphide ores such as iron pyrites (FeS_2), copper pyrites ($CuFeS_2$), copper glance (Cu_2S), zinc blende (ZnS), galena (PbS), etc. (human activity). About 66 per cent of total SO_2 is contributed by natural activity and the rest by human activity.

A part of SO_2 undergoes photolytic and catalytic oxidation to give SO_3. Thus, SO_2 present in the atmosphere is generally contaminated with SO_3 although the amount of SO_3 is not more than a few per cent of SO_2. The SO_3 formed as above changes to H_2SO_4 in the presence of moisture. This acid comes down from the atmosphere in the form of **sulphuric acid rain**, just as NO_2 comes down in the form of nitric acid rain. Both SO_2 and H_2SO_4 are dangerous pollutants.

SO_2 irritates the respiratory system of animals and humans. A concentraiton of 0·5 ppm for full day or 0·2 ppm lasting for 3–4 days has been reported to damage the lungs and increase the rate of mortality. Elderly persons and patients with heart or lung diseases are very severely affected by this pollutant.

SO_2 and sulphuric acid are known to affect vegetation adversely even at concentrations below 0·03 ppm. High concentrations even over short periods cause leaf injuries such as *necrotic blotching* of broad-leaved plants and grasses and brownish discolouration in the tips of pine needles. Lower concentrations over longer periods (days or weeks) hampers the production of chlorophyll which results in chronic leaf injury including loss of green colour by plants.

Sulphur oxides are liable to damage materials and property primarily through their conversion into highly corrosive H_2SO_4. Building materials such as lime stone, marble, roof slate and mortar undergo physical deterioration due to the corrosive action of SO_2 and H_2SO_4. The corrosion of most metals, particularly iron, steel, zinc and aluminium, is accelerated by atmosphere polluted by SO_2. Fabrics (such as cotton, nylon and rayon), leather and paper also undergo deterioration and fading. The drying time, gloss and even colours of paints are affected by the presence of SO_2 in the atmosphere.

The sulphuric acid rain is hazardous. Along with nitric acid rain, it adversely affects agricultural crops, forests, metallic and marble structures, humans and human artefacts.

(Sulphuric acid rain, however, reacts with ammonia emitted by biological processes to form $(NH_4)_2SO_4$, an effective chemical fertilizer.)

(Marble structures, lime stone and geological sources of ammonia thus act as *sinks* for atmospheric SO_2.)

Hydrogen Sulphide. The main natural sources of H_2S are volcanic activity and anaerobic biological decay of protein matter in stagnant water and swamps. Anaerobic reactions occurring in sewage, sludge and sanitary landfills also produce H_2S. Industrial units manufacturing pulp and paper, hydrofluoric acid by reacting fluorspar with H_2SO_4, etc., also generate considerable amounts of H_2S. Since H_2S is readily oxidised to SO_2, the two gases are present together in the atmosphere.

H_2S has an objectionable smell like that of rotten eggs. Its presence in the atmosphere affects the white lead pigments and the silverware due to conversion of lead and silver to black PbS and Ag_2S, respectively.

DEPLETION OF OZONE LAYER

Before we discuss the role of ozone in protecting human beings from the harmful effects of ultraviolet radiations of the sun, it is worthwhile to have a rough idea about the temperature distribution in the atmosphere. The temperature of the atmosphere depends upon the rate at which energy is received from the sun and distributed to the atmosphere, the oceans and the earth's land surface by various energy transport mechanisms such as electromagnetic radiation, convection, evaporation, etc. As a result, the temperature of the atmosphere is not constant but varies with season, time of day, cloud cover, wind velocity and many other factors. The approximate distribution of temperature with height is shown in Fig. 1. The various regions which can be easily identified are named as *troposphere, stratosphere, mesosphere* and *thermosphere*.

As can be seen from Fig. 1, the temperature steadily decreases from the ground temperature to about −60°C as we go up to a height of about 12 km. The fall of temperature is due to fall of pressure and density of air. The minimum temperature occurs at the limit of troposphere which is known as the *tropopause*. The tropopause usually lies between 10 and 15 km above the earth's surface and the temperature here varies between −50°C and −60°C. The troposphere is turbulent due to differences of heating and cooling rates between the equator and the poles.

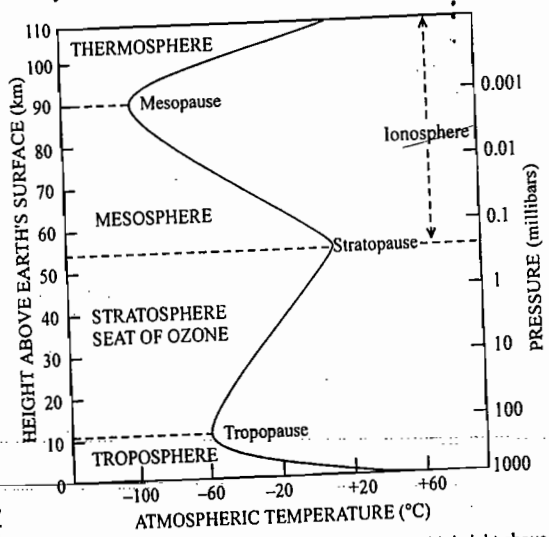


Fig. 1. Distribution of atmospheric temperature with height above th earth's surface.

Above the tropopause lies the stratosphere. The temperature curve shows a warming trend with increasing height. This is due to absorption of solar ultraviolet radiation by ozone present in this region whose concentration ranges between 1 to 5 ppm by volume. The maximum temperature attained in this region due to ultraviolet absorption is at the limiting position of stratosphere which is known as the *stratopause*. This lies at a height of about 50 km from earths's surface and the temperature here is close to the ground temperature.

The stratosphere is comaratively calm and is much less dense than the troposphere. If the pollutants somehow reach the stratosphere, they will stay there for quite a long time and hence will become long term health hazard.

The *stratosphere* plays an important role since it is the seat of a stable layer of ozone which absorbs ultraviolet radiations coming from the sun and prevents most of them from reaching the earth's surface. The ultraviolet radiations are known to produce skin cancer particularly in white males. A decrease in the concentration of ozone would increase the flux of ultraviolet radiations which, in turn, would increase the risk of skin cancer.

Above the stratopause is the *mesosphere* in which the temperature again decreases with height to an exceedingly low value of about −100°C. The region of the minimum temperature is the limit of mesosphere and is known as the *mesopause*.

Above the mesopause, temperatures rise very rapidly to very high values. This high temperature region constitutes the *thermosphere*.

The region above the stratosphere (*i.e.*, mesosphere and thermosphere) is also called **ionosphere** because of the presence of ions like O_2^+, O^+, NO^+ and free electrons. These ions are generated in daytime by ultraviolet radiations and have long life times due to rarified conditions prevailing in this region. Some pollutants, on reaching this region, get converted to free radicals which also have long life time.

$$RH + O_2 + O \xrightarrow{h\nu} R\dot{O}O + \dot{O}H$$

$$CH_3CHO \xrightarrow{h\nu} \cdot CH_3 + H\dot{C}O$$

Effect of Oxides of Nitrogen on Ozone Layer. The oxides of nitrogen play a key role in destroying ozone by a simple chemical effect. The oxides of nitrogen catalyse the decomposition of ozone and are themselves regenerated to repeat the cycle which thus involves the following reactions :

$$NO_2 + \text{ultraviolet light} \longrightarrow NO + O$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow NO + O_2$$

The cycle may destroy about 70 per cent of ozone formed in the stratosphere. The greater the concentration of nitrogen oxides in the atmosphere, the greater is the extent of destruction of ozone. Flights of supersonic aircrafts involve high temperature combustion of the fuel. Explosion tests of nuclear weapons generate exceedingly high temperatures. Since the oxidation of atmospheric nitrogen by oxygen is favoured by high temperature, both the above operations increase the concentration of NO in the stratosphere which causes greater destruction of ozone. Thus, continuation of nuclear tests would be a major health hazard apart from the adverse effects of radioactive fallout.

Fluorocarbons and Their Effect on Ozone Layer. A very serious threat to the existence of ozone in the stratosphere comes from the use of fluorocarbons (*viz.*, chlorofluoromethanes) such as Freon-1 ($CFCl_3$) and Freon-12 (CF_2Cl_2) as propellants in aerosol spray cans, refrigerants, fire fighting reagents and solvents for cleaning electronic components. Flurocarbons are stable compounds and are chemically inert. They do not react with any substance with which they come in contact and thus upfloat through the atmosphere unchanged and eventually enter the stratosphere. There they absorb solar ultraviolet radiations and break down liberating free atomic chlorine which causes decomposition of ozone. This results in the depletion of the ozone layer.

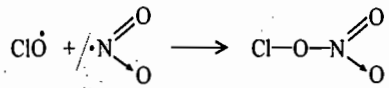
$$\dot{C}l + O_3 \longrightarrow Cl\dot{O} + O_2$$

$$Cl\dot{O} + O_3 \longrightarrow \dot{C}l + 2O_2$$

The space from which the ozone layer gets depleted is known as **ozone hole**.

The problem of ozone depletion is more serious at the poles due to the production of Cl atoms from the photochemical dissociation of flourocarbons and other chlorine-containing reagents in the stratosphere. The Cl atoms react with ozone to produce $Cl\dot{O}$ radicals which further decompose ozone, as discussed

above. Normally, the decomposition of ozone retards due to 'eating up' of $\dot{ClO}$ radicals by NO_2 present in the atmosphere in the following manner:



But at the low temperatures prevailing at the poles, NO_2 (or N_2O_4) solidifies and is not available for eating up $\dot{ClO}$ radicals. Besides this, the ice crystals in the clouds over the poles provide a convenient surface and thus act as calalysts for the photochemical reactions involving the decomposition of ozone by $\dot{Cl}$ and $\dot{ClO}$ radicals.

It has recently been reported that even very small amounts (of the order of 2 ppb) of fluorocarbons produce *green house effects* (as is done by CO_2) and thus increase the temperature of earth's surface by several tenths of a degree.

The use of fluorocarbons, therefore, shall have to be banned one day to save the ozone layer.

The hydroxy radicals produced from the photochemical reactions of organic pollutants with oxygen in the stratosphere also deplete ozone layer.

$$O_3 + \dot{O}H \longrightarrow O_2 + \dot{O}OH$$

It may be pointed out that our knowledge about the source or the mechanism of the production of ozone in the stratosphere is totally inadequate uptil now.

PARTICULATES

Solid and liquid aerosols suspended in the atmosphere are called **particulate matter**. The size of particulates varies from about 0·0002 μ to about 500 μ (1μ = 10^{-4} cm). In polluted air, the number of particulate particles may be as high as 10^{11} per m^3. In urban areas, the mass level of particulates varies from about 60 μg to 2000 μg per m^3. The particulates which are directly introduced into the atmosphere due to volcanic eruptions, erosions, grinding, spraying, etc., are named as *primary particulates* whereas those which result from chemical reactions such as combustion are named as *secondary particulates*. The particulates tend to settle down under the force of gravity. Their rates of settling are governed by the Stokes' law.

The particulates usually present in atmosphere are *soot, metals, metal oxides and metal salts, fly ash, asbestos powder, dust, solid hydrocarbons,* etc. Liquid aerosols include *sulphuric acid* and *nitric acid mists.*

Sources of Particulates. The most common particulate injected into the atmosphere through human activity is **soot** which is produced by incomplete combustion of carbonaceous fossil fuels such as coal, fuel oil, natural gas, wood, etc., in insufficient supply of oxygen.

Metal particles are released by various metal-finishing operations. The microparticles of toxic metals and SO_2 gas present in the polluted atmosphere get adsorbed on the metal particles rendering them highly toxic.

Metal oxides are generated by combustion of fuels containing metallic compounds. For example, the particulate Fe_3O_4 is produced by the combustion of coal containing iron pyrites.

$$3FeS_2 + 8O_2 \longrightarrow Fe_3O_4 + 6SO_2$$

Lead tetraethyl is the source of lead salts in the atmosphere. Lead tetraethyl, $Pb(C_2H_5)_4$, is added to gasoline at the rate of 0·5 to 0·8 g per litre to increase its octane number, *i.e.*, to improve its antiknock property. The tetraethyl lead is oxidised to PbO which tends to deposit on spark plugs and valves. This is, evidently, undesirable. In order to avoid deposition of PbO, suitable amounts of $C_2H_4Cl_2$ and $C_2H_4Br_2$ are added to gasoline alongwith $Pb(C_2H_5)_4$. These halides convert PbO into $PbCl_2$ and $PbBr_2$ both of which are volatile and get eliminated through the exhaust. The complete reaction may be represented as

follows:

$$2Pb(C_2H_5)_4 + 32O_2 + C_2H_4Br_2 + C_2H_4Cl_2 \longrightarrow 20CO_2 + 24H_2O + PbCl_2 + PbBr_2$$

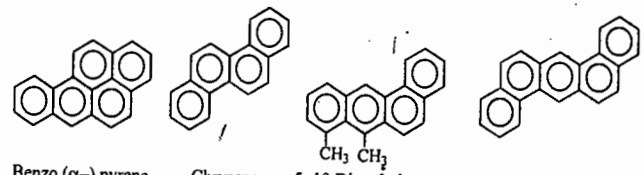
Thus, while the engine of the automobile is saved, the atmosphere gets polluted with highly toxic $PbCl_2$ and $PbBr_2$. Upto 1975, about 200000 tonnes of lead salts were dumped into the atmosphere every year from USA alone.

Fly ash results from the combustion of high-ash fossil fuels. This pollutant is released into the atmosphere from power plants, smelters and from mining operations.

Asbestos dust originates from industrial units manufacturing asbestos sheets, gaskets, ropes, etc. Asbestos flooring and asbestos insulations also contribute towards asbestos dust in the atmosphere. The pollutant is also released into the atmosphere during the mining and processing operations.

Dust particulates are thrown into the atmosphere by volcanic eruptions, blowing of dust by wind, mining operations and by spraying of salts and other solid particles by the oceans.

Solid hydrocarbons are obtained from petroleum refineries and comprise of alkanes, alkenes and aromatics. The polynuclear aromatic hydrocarbons such as benzo(α-) pyrene, chrysene and dibenzanthracenes are carcinogens. These substances are mostly solids. Their structures are given below.



Benzo (α–) pyrene Chrysene 5, 10 Dimethyl 1, 2 dibenzanthracene 1, 2, 5, 6 Dibenzanthracene

These compounds are readily adsorbed on the surface of soot particles present in the atmosphere and thus become serious health hazards.

Sulphuric acid mist is produced when SO_3 present in the atmosphere comes in contact with moisture. Similarly, **nitric acid mist** is produced when oxides of nitrogen, *viz.*, NO and NO_2, undergo the following sets of reactions:

(*a*) $$2NO + O_2 \longrightarrow 2NO_2$$
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

(*b*) $$2NO_2 + O_3 + H_2O \longrightarrow 2HNO_3 + O_2$$

as already discussed.

Toxic Effects of Particulates. Effect on Humans. The toxic effects of particulate matter on humans are numerous. These pollutants seriously affect the human respiratory system and cause several respiratory illnesses. The particles with small size are more harmful since the larger particles are easily checked by the hairlike cilia in the nose. The smaller particles remain unchecked and reach the lungs more readily and get accummulated there. The smaller particles because of larger surface areas also provide effective sites for the sorption of carcinogenic substances such as polynuclear aromatic hydrocarbons, asbestos, etc.

The particulates thus become the carriers of various toxic substances from the atmosphere to the humans and cause big health hazards. They cause bronchitis, bronchial asthma and lung cancer.

Effect on Visibility. Particulates in the atmosphere reduce visibility by scattering and absorption of sunlight. Particulates also reduce visibility by attenuating the light from objects and illuminating the air thereby reducing the contrast between the objects and their background. Reduced visibility is not only undesirable aesthetically but is also dangerous practically for aircraft and motor vehicles.

Effects on Materials. The adverse effects of particulates on materials include corrosion of metals (when the atmosphere is humid), erosion and soiling of buildings, sculptures and painted surfaces and soiling of clothes and draperies.

Particulate matter also damages the electronic equipment through chemical or mechanical action on electrical contacts.

SMOG

Classical Smog. The word 'smog' was coined to describe the 'smoke fog' prevalent in London. The odd combination of particulates with gaseous oxides of sulphur present in the atmosphere constitutes what is now known as **classical smog**. The principal source of classical smog is the combustion of industrial and household fuels (coal and petroleum). Because of the presence of SO_2 and carbon (soot) particles, classical smog has a reducing character. It occurs in winter months particularly in early morning hours. It causes severe lung and throat irritation.

Photochemical Smog. There is another type of smog, *viz.*, the *Los Angeles type of smog*, which is distinctly different from the *London type of smog*. The principal constituents of the Los Angeles type of smog are ozone and oxides of nitrogen (see below). Because of the presence of O_3, NO_2 and some photochemical oxidants, this type of smog is oxidising in character. It causes irritation in eyes due to the presence of ozone. It is now known that *this type of smog is formed through photochemical reactions involving solar radiations.* Hence, this smog is named as **photochemical smog**. It is formed around mid day of summer months when the intensity of solar radiation is very high.

Mechanism of the formation of photochemical smog. Photochemical smog is formed only if, apart from soot particles, the atmosphere contains hydrocarbons and oxides of nitrogen (NO_2) and if such an atmosphere is exposed to sunlight. The combustion of petroleum in automobile engines produces hydrocarbons as well as oxides of nitrogen. NO_2 is an effective absorber of ultraviolet portion of the solar spectrum. Thus when exposed to sunlight, NO_2 undergoes photolysis giving NO and O (atomic oxygen). Atomic oxygen reacts with molecular oxygen to give O_3. The ozone thus produced reacts with NO to regenerate NO_2 and O_2. This completes the photolytic cycle of NO_2 in the atmosphere. The reactions involved may be represented as follows :

$$NO_2 + \text{ultraviolet light} \longrightarrow NO + O$$

$$O + O_2 \longrightarrow O_3$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

The situation, however, becomes different if hydrocarbons are also present in the atmosphere. In that case, the atomic oxygen resulting from photolysis of NO_2 reacts with hydrocarbons to yield free radicals which bring about a variety of reactions, as shown below :

$$NO_2 + \text{ultraviolet light} \longrightarrow NO + O$$

$$\underset{\text{(Hydrocarbon)}}{O + HC^*} \longrightarrow \underset{\text{(Free radical)}}{HC\dot{O}}$$

$$HC\dot{O} + O_2 \longrightarrow \underset{\text{(Free radical)}}{HC\dot{O}_3}$$

$$\cancel{HC\dot{O}_3 + HC^* \longrightarrow \text{Aldehydes, Ketones, etc.}}$$

$$HC\dot{O}_3 + O_2 \longrightarrow HC\dot{O}_2 + \underset{\text{(Ozone)}}{O_3}$$

The most crucial role played by these free radicals is that they react with NO also to give back NO_2.

$$HC\dot{O}_3 + NO \longrightarrow HC\dot{O}_2 + NO_2$$

* HC is used here as a general symbol for hydrocarbons and does not represent a species with one C and one H atom.

Since NO gets eliminated by interaction with free radicals, the consumption of O_3 by NO gets reduced. As a result, the levels of O_3 and NO_2 in the atmosphere increase. The presence of excessive O_3, together with aldehydes, ketones, etc. , induces eye irritation.

It is clear from the above discussion that formation of photochemical smog is possible only in day time. If a mixture of hydrocarbons and NO_2 is not exposed to sunlight, there is no formation of ozone. *Thus, there is no formation of photochemical smog at night time or even in early morning hours due to* poor availability of sunlight at that time. During the day, because of increased vehicular traffic, there is greater availability of NO_2 and hydrocarbons, greater extent of photolysis of NO_2, greater production of hydrocarbon free radicals, hence there is greater production of ozone. Thus, photochemical smog formation occurs around mid-day of summer months.

The excessive amount of ozone present in photochemical smog adversely affects vegetation. It also attacks and cracks stretched rubber.

Ozone also converts hydrocarbons present in the atmosphere directly into aldehydes (such as formaldehyde, acrolein) and ketones. In conjunction with NO_2, it converts hydrocarbons into peroxyacyl nitrates ($RCOOONO_2$). All these compounds are strong eye-irritants.

Although CO is the major pollutant resulting from combustion of fuel in automobile engines, it does not play any important role in the formation of photochemical smog.

Monitoring of Air Pollutants

The air pollutants are generally monitored through infra-red spectroscopy, gas chromatography, spectrophotometry, etc. Some other techniques are also employed in many cases. The monitoring of some common air pollutants is discussed below.

Carbon Monoxide. The standard technique for monitoring carbon monoxide is non-dispersive infra-red spectrometry. This is based on the principle that CO strongly absorbs infrared radiations at certain specific wave lengths. The extent of absorption is directly related to the concentration of the gas. This technique permits estimation of CO upto a level of 150 ppm.

Estimation of CO in the concentration range around 10 ppm, is carried out through gas chromatography employing a flame ionization detector. If the concentration range is very low, *i.e.*, less than 10 ppm, the gaseous sample is subjected to catalytic reduction by hydrogen gas over a nickel catalyst at 360°C and the hydrocarbon thus formed ($CO + 3H_2 \longrightarrow CH_4 + H_2O$) is estimated by gas chromatography using the flame ionization detector. The response of the detector is better in the case of CH_4 than in the case of CO.

Oxides of Nitrogen. Oxides of nitrogen are estimated conveniently through chemiluminescence. In this technique, oxides of nitrogen are made to react with ozone to yield electronically excited species. For instance, NO on interaction with ozone yields electronically excited species NO_2^*. These electronically excited species quickly return to the ground state with the emisssion of light in the range of 600–3000 nm.

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$

The intensity of the light emitted is measured with the help of photomultipliers. Since intensity is directly related to the concentration of the excited species and hence of NO molecules, the concentration of NO can be easily determined.

Sulphur Dioxide. The standard method for monitoring SO_2 gas in polluted air in the range of 0·005–5 ppm is the one devised by West and Gacke. In this method, the polluted air is pumped through a solution of $[HgCl_4]^{2-}$ ($HgCl_2 + KCl$) when about 95% of SO_2 present in air is scrubbed to form the complex $[HgCl_2(SO_3)]^{2-}$:

$$[HgCl_4]^{2-} + SO_2 + H_2O \longrightarrow [HgCl_2(SO_3)]^{2-} + 2H^+ + 2Cl^-$$

The scrubbing solution is made to react with formaldehyde and then with para rosaniline hydrochloride to yield a red-violet dye.

The absorbance of the red-violet dye is recorded with the help of a spectrophotometer at 548 nm. The extent of absorbance is a measure of the concentration of the dye and hence of the sulphur dioxide.

NO_2, if present at a level of 3 ppm or more, interferes with the above technique. However, NO_2 can be easily eliminated by treatment with sulphamic acid, H_2NSO_3H which reduces NO_2 to non-interfering N_2.

Hydrogen Sulphide. The sample of air containing H_2S gas is pumped into a solution containing N,N diethyl p-phenylenediamine in 50% H_2SO_4 and small amounts of $NaClO_4$ and ferric ammonium sulphate. H_2S reacts with the diamine to form a blue dye known as ethylene blue.

The absorbance of the ethylene blue is recorded with the help of a spectrophotometer at 670 nm. The extent of absorbance is, evidently, related directly to the concentration of ethylene blue and hence of H_2S.

Hydrocarbons. Estimation of hydrocarbons is generally carried out through gas chromatography employing a flame ionization detector, as in the estimation of carbon monoxide. Gas chromatography, in conjunction with mass spectrometry, is now being used with immense success for identification and estimation of low levels of hydrocarbons present in polluted air.

Particulate Matter. The amount of particulate matter present in the atmosphere is estimated conveniently by the so-called *high volume method*. In this method, a large volume of air, measured by means of a rotameter, is passed through a special filter. Before sampling, the filter is maintained at 15°–35°C at about 50% humidity for about 24 hours and weighed. The air is passed through the filter at the rate of about two m^3 per minute for about 24 hours. The filter is again weighed and from the increase in mass and the total volume of air passed, amount of the particulate matter per unit volume of air is easily calculated. The constituents of the particulate matter can be characterised with the help of chemical microscopy (visible or electron microscopy).

Control of Air Pollutants

The presence of various air pollutants in the atmosphere is not of much concern if their concentrations remain below the permissible limits. For instance, 5 ppm of SO_2, 5 ppm of NO_x, 50 ppm of CO, 500 ppm of $C_2F_2Cl_4$ and even 5000 ppm of CO_2 can be tolerated for an exposure of about 8 hours without any serious consequences. However, it becomes hazardous if the concentrations of the air pollutants exceed the permissible limits. This necessitates strict control of the air pollutants. The procedures adopted in this context are discussed below in brief.

Control of Carbon Monoxide Pollution. About 75% of CO discharged into the atmosphere originates from gasoline-fed internal combustion engines. Hence, major efforts for controlling CO pollution are directed at the functioning of automobiles. As mentioned before, the emissions from internal combustion engines consist of a mixture of CO, NO_x, hydrocarbons and particulate matter. These emissions are subjected to the action of antipollution catalysts to convert them into more acceptable materials before discharging them into the atmosphere. The catalytic converters operate in two stages. In the first converter, oxides of nitrogen are reduced to nitrogen and ammonia under the catalytic action of finely divided platinum. The production of ammonia is kept at a minimum by suitably controlling the conditions. In the second converter, air is introduced to provide an oxidising atmosphere in order to affect complete oxidation of CO and hydrocarbons in the catalytic presence of finely divided platinum to yield CO_2 and H_2O.

Lead tetraethyl, which is added to gasoline to improve its antiknock property, gets oxidised to PbO which tends to poison the platinum catalyst.

As described earlier, large amounts of $PbCl_2$ and $PbBr_2$ get introduced into the atmosphere during the combustion of leaded gasoline. These compounds not only pollute the atmosphere but also poison the platinum catalyst used for the conversion of CO into CO_2. Both these factors can be done away with by using unleaded gasoline. However, for this purpose, the internal combustion engines need some modification. The needful is now being done in almost all countries.

Honda Corporation of Japan is experimenting on a new type of internal combustion engine in which the exhaust would contain a very low concentration of NO_x and practically no carbon monoxide. This engine contains an extra chamber in which a fuel-rich mixture of air and gasoline is ignited by a spark.

Since combustion now occurs at a relatively low temperature, the formation of oxides of nitrogen is reduced to a minimum. The burning mixture is then transferred to a larger chamber in which it gets mixed with a lean fuel mixture (containing excess of air). In the presence of excess air, combustion of fuel proceeds to completion resulting in the formation of CO_2 and H_2O.

Control of CO_2 Pollution. Carbon dioxide is produced by the combustion of fossil fuels, decomposition of carbonates and biological decay. In nature, sizeble amount of the gas is converted into carbohydrates through photosynthesis. In order to reduce the extent of carbon dioxide in the atmosphere, the most effective operation would be to increase the forest cover. The larger the number of trees, the greater would be the extent of photosynthesis and hence the greater would be the elimination of carbon dioxide from the atmosphere.

Control of NO_x Pollution. The oxides of nitrogen present in vehicular exhausts are converted into N_2 and minor amounts of ammonia by catalytic reduction in the first stage of the convertors used for controlling the CO pollutions, as discussed above.

The large amounts of nitrogen oxides emitted from power plants and industrial units can be removed by scrubbing the flue gases with sulphuric acid. SO_2 and NO_2 present in the flue gases first react to give NO and H_2SO_4.

$$NO_2 + SO_2 + H_2O \longrightarrow H_2SO_4 + NO$$

NO and NO_2 then react to form N_2O_3 which is scrubbed by sulphuric acid to form $H(NO)SO_4$:

$$NO + NO_2 \longrightarrow N_2O_3$$

$$N_2O_3 + 2H_2SO_4 \longrightarrow 2H(NO)SO_4 + H_2O$$

The flue gases are thus freed of NO_2 as well as SO_2. The cleaned flue gases are then released into the atmosphere.

The compound $H(NO)SO_4$ is decomposed in a separate chamber by heating where the following reaction takes place :

$$2H(NO)SO_4 + 1/2\,O_2 + H_2O \longrightarrow 2H_2SO_4 + NO_2$$

The liberated H_2SO_4 is recycled into the scrubbing chamber.

In order to reduce the formation of the oxides of nitrogen in the power plants, the fuel is burnt in two steps :

In the first step, the fuel is burnt at high temperature in a limited supply of air. Under these conditions only a limited quantity of NO is formed.

In the second step, the unburnt fuel is burnt at lower temperature in excees of air. Since the formation of NO requires higher temperature, only a small quantity of NO is formed at the lower temperature in the second step.

Both NO_x and SO_2, being acidic in nature, can also be scrubbed by alkaline solutions containing $Ca(OH)_2$ and $Mg(OH)_2$.

Control of SO_2 Pollution. SO_2 from flue gases is commonly removed by using chemical scrubbers consisting of a slurry of $CaCO_3$ (lime stone) when SO_2 is absorbed forming $CaSO_3$.

$$CaCO_3 + SO_2 \longrightarrow CaSO_3 + CO_2$$

If the flue gases happen to contain SO_3, $CaSO_4$ is formed :

$$CaCO_3 + SO_3 \longrightarrow CaSO_4 + CO_2$$

The above method is quite economical. However, it involves the problem of disposal of huge amounts of $CaSO_3$ and $CaSO_4$ formed during scrubbing.

In an alternative method, the flue gases are cooled to about 50°C and passed through a solution containing citrate ions when SO_2 is absorbed forming a citrate complex :

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$$

$$HSO_3^- + H_2Cit^- \rightleftharpoons [HSO_3.H_2Cit]^{2-}$$

The above solution is transferred to a closed vessel into which H_2S is passed when we get a precipitate of sulphur alongwith regeneration of H_2Cit^- ions. The sulphur obtained is 99·99% pure. It is a valuable by-product.

Control of Pollution Caused by Particulates. Various methods have been used for the elimination of particulates from the gases. The most effective and efficient method comprises of **electrostatic precipitation.** It is based on the principle that particles of all sizes acquire electrical charge when exposed to a high potential electric field. The flue gases are passed through a tall chamber fitted with two electrodes as shown in Fig. 2.

The central electrode is subjected to a potential of 30000–100000 volts while the peripheral electrode is earth-connected. Because of the high potential difference, the air inside the chamber gets ionised into positively charged ions and free electrons. The free electrons get attached to the particles present in flue gases which thus get negatively charged. The negatively charged particles are attracted towards the positive (grounded) peripheral electrode and settle down there. These are dislodged by vibrating the electrode and collected in a reservoir. In this way, about 99 per cent of the particulate matter gets removed from the flue gases.

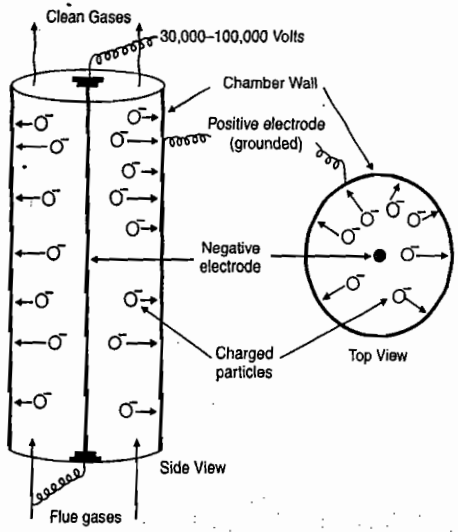


Fig. 2. An electrostatic precipitator.

PESTICIDES and THEIR ADVERSE EFFECTS

Pesticides. Depending upon their target, pesticides are classified as *insecticides, fungicides, herbicides, rodenticides, algaecides, etc.*

Insecticides

Insectides are further classified as (*a*) *Stomach poisons* (*b*) *Contact poisons* and (*c*) *Fumigants.* These are discussed below in some details.

a. Stomach Poisons. Stomach poisons are those insecticides which are introduced into the body of the insect through mouth and is absorbed into the body through the digestive system. Evidently, stomach poison insecticides would be effective against insects which have biting mouth parts, as, for example, caterpillars.

The most important stomach poison insecticides are the compounds of arsenic and fluorine although some other types are also in use.

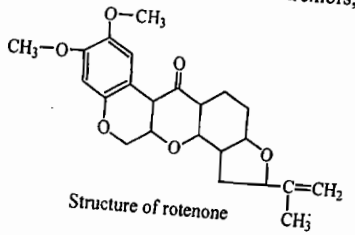
Arsenic compounds or arsenicals are generally arsenites and arsenates. Arsenites are highly toxic to animals and plants. Arsenates are comparatively less toxic and their poisonous effects occur generally when they are chemically reduced to arsenites. The common arsenicals in use are acid lead arsenate, basic lead arsenate, calcium arsenate, copper acetate metaarsenate, etc. In insects, the primary effect of arsenicals is to inhibit the function of respiratory SH enzymes (arsenic combines with the SH groups of enzymes and causes their coagulation).

Inorganic fluorine compounds which are used as stomach poison insecticides are cryolite (Na_3AlF_3), sodium fluoride (NaF) and sodium & barium fluosilicates (Na_2SiF_6 and $BaSiF_6$). The fluorides exercise their toxic effect on pests by complexing with enzymes containing metals such as iron, calcium and magnesium and thereby grossly inhibiting their function.

Other stomach poison insecticides are mercury compounds (such as $HgCl_2$), boron compounds (such as boric acid), thallium compounds (such as Tl_2SO_4 and CH_3COOTl), yellow phosphorus and formaldehyde (HCHO).

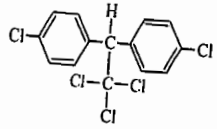
b. Contact Poisons. Contact poisons are those which affect the insect on contact. The contact poison insecticides enter the body of the insect through their body walls or respiratory system and affect their nerves or blood streams. Most of the organic insecticides developed recently fall into the category of contact poison insecticides. These include chlorinated hydrocarbons, organophosphates, carbamates, etc. Certain botanical compounds have also insecticidal properties. These are extracted from plants and used as contact poisons. For instance, *pyrethrum* insecticides are extracted from dried flowers of certain chrysanthemums and used as contact poisons. They cause rapid paralysis in insects by affecting their nerves or muscles. Nicotine sulphate is another contact poison insecticide. It produces tremors, convulsions and eventually paralysis in insects.

Rotenone, having the structure as shown, is an effective contact poison insecticide (this can also act as a stomach poison insecticide) which is extracted from the roots of derris and other leguminous plants. It interferes with the intake of oxygen by insects and is highly toxic.

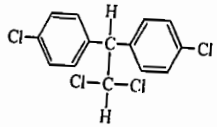


Structure of rotenone

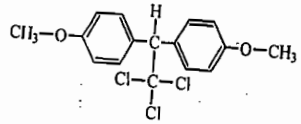
An importat family of contact poison insecticides is constituted by chlorinated hydrocarbons including DDT, its metabolites DDD and DDE, BHC, dieldrin, aldrin, methoxychlor, mirex, toxaphene, chlordane, and many others. Structures of some of these insecticides are given below :



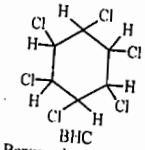
DDT
(Dichloro diphenyl trichloroethane)



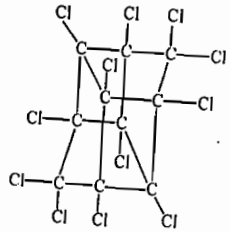
DDD
(Dichlorodiphenyl dichloroethane)



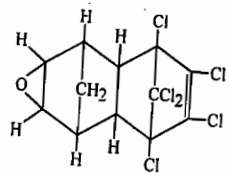
Methoxychlor
(Dimethoxy diphenyl trichloroethane)



BHC
Benzene hexachloride or hexachloro hexane



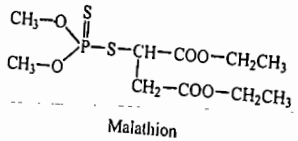
Mirex



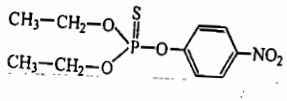
Dieldrin

DDT and other chlorinated hydrocarbons are believed to have their primary effect on the central nervous systems of insecticides. In the environment, DDT gets metabolized into DDD, DDE, DDA $(ClC_6H_4)_2CHCOOH)$, kelthane $(ClC_6H_4)_2C(OH)CCl_3)$ etc. The chlorinated hydrocarbons affect a large number of different species of insecticides. Their residues persist in the environment for long periods, *viz.*, months and years. These qualities, no doubt, make these compounds very useful and desirable insectides but at the same time they produce serious undesirable side effects which would be discussed a little later in this section.

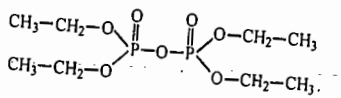
Organophosphorus compounds are the most toxic insecticides. Structures of some common organophosphorus insecticides are given below .



Malathion



Parathion

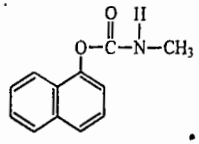


TEPP

Other organophosphorus insecticides are thimet, tetram, phosdrin, paraoxon, HETP, pyrazoxon, di-syston, etc.

The function of organophosphates as insectides involves inhibition of the enzyme *cholinesterase* which results in disruption of nervous activity of the insecticides. Organophosphates undergo biodegradation more easily than chlorinated hydrocarbons. These insecticides, therefore, do not persist in the environment for long.

Another group of contact poisons are the carbamates which are derived from carbamic acid (NH_2COOH). Sevin is a common insecticide belonging to this group. Its structure is as shown :



Sevin

These insecticides are less toxic than organophosphates. They, like organophosphates, inhibit the function of the enzyme *cholinesterase* and produce similar effects on the nervous systems of insects.

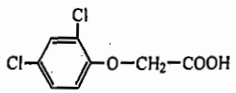
c. Fumigants. Fumigants are gaseous chemicals that kill insects and other pests by entering directly into their respiratory systems. These insecticides are generally applied in closed space to kill pests which damage stored products or nursery stock. Sometimes they are also used in the open keeping the products under tents. Common fumigants are HCN gas (released from calcium cyanide by atmospheric moisture), methyl bromide, carbon tetrachloride, carbon disulphide, naphthalene, nicotine and a host of other compounds.

Fungicides

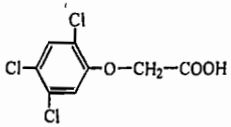
Fungicides are chemicals which are used for preventing or eradicating fungal diseases of plants. **Preventive fungicides** which can check the fungal growth are compounds of sulphur and copper. **Eradicant fungicides** are lime, sulphur, formaldehyde (formaline) and a number of dinitro compounds.

Herbicides

Herbicides are compounds which can kill plants. **Non-selective herbicides** such as sodium chlorate, sodium arsenite and some oils kill all types of plants. **Selective herbicides**, on the other hand, kill only certain specific types of plants. Two commonly used selective herbicides for killing weeds are 2,4-D (2,4 dichlorophenoxy acetic acid) and 2,4,5-T (2,4,5 trichlorophenoxy acetic acid) and their esters. These compounds kill a number of broad-leaved plants but do not injure narrow-leaved plants. These herbicides are commonly employed for killing weeds which tend to grow alongwith wheat and rice plants. The structures of these herbicides are given below :



2, 4-D



2, 4, 5-T

Other important herbicides are trichloroacetic acid, atrazine, picloram, propazine and 2,3,6-trichlorobenzoic acid.

Rodenticides

Rodenticides are chemical compounds which are used against rodents such as rats and mice. Some rodenticides such as strychnine, sodium fluoro acetate, thallium phosphones and ANTU (alpha naphthyl urea), are very fast in their action while others such as wanfarin are comparatively slow in their action.

Adverse Effects of Pesticides

The use of pesticides is a must if we want to save our crops from pests. In parts of the world in which pesticides are not used, there is sizeable reduction in agricultural production. For example, the fraction of total production lost to insects in Asia is reported to be about 41% for rice, 18% for cotton, 14% for maize,

13% for vegetables and 6·5% for wheat. The use of pesticides naturally reduces the loss of agricultural production.

However, the use of pesticides has multifarious ***adverse envirnmental effects*** also. The pesticides not only kill the inimical insects but kill the friendly insects also. For example, the use of pesticides causes immense harm to trees which are otherwise highly beneficial to humanity. The use of DDT reduces the number of ladybugs, a class of friendly insects, whose presence is so helpful in controlling the scale disease in citrus plants.

The pesticides cause considerable occupational illness among farm workers. Almost all the pesticides are toxic towards humans. They can prove lethal if their intake exceeds a certain maximum limit. Organophosphates are the most toxic. They would be lethal even at an oral doze of 10 to 20 mg. Deaths have occurred in several cases in which humans ate food contaminated accidentally with pesticides. There is apprehension that long term effects of pesticides may get related to carcinogenic, mutagenic and teratogenic properties. It has been reported that sufficiently large quantities of DDT, aldrin, dieldrin, heptachlor and mirex induce tumors including malignant ones in mice. As a corollary, these pesticides are likely to produce similar effects in humans also. Likewise 2,4,5-T and some organophosphorus pesticides are known to be teratogenic to certain animals with the implication that they may also be so to humans as well.

Pesticides have been reported to have minor effects on reproductive activity as well. Agricultural workers exposed to a variety of pesticides such as malathion, dieldrin, 2, 4-D, etc., were found to suffer from impotency.

The effects of pesticides on wild life are highly alarming. Health and reproductive ability of birds and mammals are reported to be seriously affected when they derive their food from sources treated with pesticides. The population of birds, belonging to a variety of breeds such as peregrine falcons, grebes, woodcocks, bald eagles, fish hawks, sparrow hawks, etc., is reported to have decreased considerably as a result of intake of food treated with chlorinated hydrocarbons. This was due io an adverse effect of pesticides on their reproductive ability. Reproductive failure is reported to be the greatest in areas in which pesticides, especially the chlorinated hydrocarbons, are used persistenly. Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs) are reported to be awfully toxic. These are both teratogenic as well as carcinogenic. In 1973, PBB (which is also a fire retardent) accidentally got mixted in Michigan's Farm Bureau animal feed which resulted in the death of over 30,000 cattle and countless other farm animals. A flock of 6300 hens stopped laying eggs. The milk, meat and eggs supplied to about 60 countries also got contaminated with severe adverse effects.

Pesticides are reported to have adverse effects on fish as well. Endrin, even in traces, is reported to be toxic for catfish and other varieties of fish. DDT is reported to affect the central nervous system of fish and toxaphene is reported to cause bone degeneration in fish.

Herbicides used for killing undesirable plants can have both desirable and undesirable effects. The excessively volatile herbicides often kill or injure vegetation in neighbouring areas. The use of 2, 4-D by corn growers is reported to decrease the production of grapes in adjoining areas to the extent of about 96%. The valued plants of home-owners are harmed by the use of herbicides by their next door neighbours.

Herbicides used by the U.S. army in South Vietnam as a part of the defoliation programme, destroyed one-fifth to one-half of South Vietnam's mangrove forests. There has been no useful plant life in areas where spraying was done, even after a lapse of several years. Only worthless shrubs and undesirable ferns have grown there. It might take several decades to restore the forests. The spraying on hard wood forests killed countless timber plants which could serve the needs of that country for at least 30 years. The forest lands damaged by the spraying of herbicides have been invaded by tenacious bamboos and grasses which are likely to hold on for years together.

It is evident from the above discussion that the use of chemical pesticides is fraught with the danger

of causing immense environmental pollution. There is another problem which is encountered in the use of chemical pesticides. This is related to the development of resistant strains of pests against these pesticides. An insectide which today is effective in killing a large fraction of the population of a particular inimical insect, may become ineffective when used against some subsequent generation of the same insect. Exposure to one pesticide sometimes leads to resistance to other pesticides. Resistance is reported to occur for every pesticide in every part of the world. Pests that have demonstrated resistance to chlorinated hydrocarbons include the housefly, some mosquitoes, the cabbage maggot, the cotton ball weevil, the sheep blowfly and many others. Resistance has been a problem with rodenticides as well. For instance, some years ago in U.K., the rats completely resisted the attack of warfarin. These rats earned the title of 'super rats'. A day may come when all the chemical pesticides used may only add to environmental pollution without killing a single pest.

Alternative Methods of Pest Control

In view of the above, a number of alrernative pest control methods have been either developed or are being developed which would be more effective and at the same time would lead to much less environmental pollution. Some of the methods which have been developed so far are briefly described below.

Autocide Technique. This technique aims at eliminating the pests by inhibiting their reproduction. For instance, experiments were conducted to eliminate screw worm fly which is so troublesome to livestock. The experiments comprised of raising a large number of screw worm flies in the laboratory, sterilising them by exposure to X-rays and releasing them to mate with the natural population without producing offspring. In one of the experiments, as many as 2·75 billion sterilized flies were released by an airplane. The result was a tremendous decrease in the population of the flies. Sterilized flies are released from time to time whenever potent flies reappear. Autocide technique has been employed successfully against some other pests also. This technique is particularly useful when the pest population is very low.

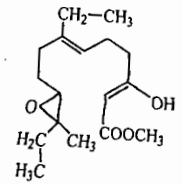
Chemosterilization. This method is similar to the autocide technique with the difference that the sterilization of the natural pest population is carried out by application of suitable chemosterilants. This method, however, suffers from the drawback that the pests refuse to take chemosterilants. Also the effect on reproduction may be only temporary.

Use of Sex Attractants. Certain chemicals known as *pheromones* are secreted into the environment by animals. These chemicals act as sex attractants for other members of the same species. A large number of sex attractants have now been identified for different species of pests. Several compounds having similar effects have been synthesised in the laboratory as well. These sex attractants can help a great deal in pest control. The modus operandi is to mix sex attractants with suitable insecticides which are pasted on fibre board pieces. These pieces are dropped by airplanes over the required areas. The insects, lured by the sex-attractants, easily come closer to the insecticides and get killed. There is no adverse effect on the environment. Field tests are now being carried out in several locations to develop sex-attractants for large-scale use against specific pests.

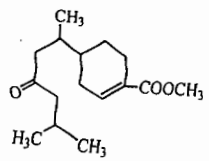
Use of Juvenile Hormones. Juvenile hormones are internal secretions of insects which regulate their growth from larva to pupa to adult. If, however, the insects are exposed to these very hormones beyond the above stage in their life cycle, adverse effects are produced. The eggs fail to hatch or immauture insects die without reproducing. These facts are made use of in controlling pests. The pests are exposed to juvenile hormones or synthetic compounds having similar effects, at appropriate time in their life cycle. This exposure produces adverse effects as mentioned above and helps in controlling the pests. These compounds, having no effects on other types of life, may not have adverse effects on humans, fish and wild life. Since these hormones are essential to the insect's life cycle at some stage, the insects would not develop resistance to them. This is an important advantage.

The juvenile hormone of each insect is believed to be a specific chemical compound and attempts have been made for isolation and identification of these compounds in certain cases. The structures of

juvenile hormones secreted by *cecropia moth* and the insect family *pyrrohocoridae* are as shown :



Juvenile hormones of the cecropia moth



Juvenile hormones of the insect family pyrrhocoridae.

Knowing the structure, it has been possible to synthesise compounds with identical activity which have proved to be as useful as the natural juvenile hormones. These synthetic hormones are known to affect only the insects.

Some other techniques involving the use of natural predators, parasites, specific types of bacteria and viruses have also been developed or are being developed for controlling the pests. The discussion of these techniques is, however, beyond the scope of the present volume.

WATER POLLUTION

Water, in abundant amounts, is required for used in agriculture, industry and household. After use, however, it gets highly polluted. The various water pollutants can be classified into as many as ten categories. These are discussed below in some details.

VARIOUS WATER POLLUTANTS

1. Sewage and other Oxygen-demanding Wastes. Sewage from municipalities and other oxygen-demanding wastes from industry and agriculture comprise of organic matter which undergoes oxidation readily under the action of microorganisms. These wastes are generally disposed off by dumping them into nearby rivers. If the amount of sewage or other wastes discharged is relatively small, the dissolved oxygen is sufficient to convert carbon into carbon dioxide, sulphur into sulphates, phosphorus into phosphates and nitrogen into ammonia and nitrates and the river water is not so badly polluted. If, however, the amount of discharge is heavy and the dissolved oxygen becomes insufficient, carbon is converted to methane and nitrogen compounds are converted to amines which give offensive odour of rotten fish decaying in a cesspool. The sulphur compounds change into hydrogen sulphide which gives smell like that of rotten eggs and phosphorus compounds produced give a wormy odour. Thus, sewage and other oxygen-demanding wastes become water pollutants on two accounts : 1. They give rise to compounds which have an extremely annoying odour. 2. They deplete the dissolved oxygen from water which is rendered harmful because water deviod of dissolved oxygen cannot sustain aquatic life. It affects or even kills fish and other aquatic living beings.

2. Infectious Agents. Sewage from municipalities is almost invariably associated with disease microorganisms. This is due to the fact that in a fair-sized community, a few inhabitants at any given time must be suffering from diseases such as dysentery, typhoid, cholera, etc. The faeces and urine of such patients would contain disease microorganisms which are transmitted through water supplies. Thus, waste water from municipalities would almost invariably carry agents (becteria or other microorganisms) which produce disease in other living beings, men and animals including live stock.

3. Plant Nutrients. The presence of plant nutrients in lakes and slow-moving waters (introduced through runoffs from farmlands, sewage treatment discharges and from fertilizer factories) supports high population of aquatic plants which on decay produce disagreeable odour. Not only this ; these plants also deplete dissolve oxygen making the survival of aquatic life (fish, etc.) problematic.

The enrichment of water by nutrients is known as *eutrophication*. Lakes and slow-moving waters age through eutrophication and over periods of several millennia, they get converted into swamps and marshes.

Eutrophication has an adverse effect on fish as well. The aquatic plants which bloom in lakes sink in autumn and winter and decay the next summer depleting oxygen from the *lower colder parts* of the lake. The cold-water fish which according to Darvin's theory get habituated to require more oxygen (cold water dissolves more oxygen) for their growth have to face shortage of dissolved oxygen. As a result, the cold water fish lose out to warm-water fish which need less oxygen. Humans, who prefer cold-water fish, are thus deprived of getting their choice fish.

4. Exotic Organic Chemicals. The exotic organic chemicals include pesticides, surfactants amongst detergents, many industrial products and several decomposition products of other organic compounds. Analyses of polluted water reveal the presence of a wide cross-section of these compounds as also many others. These organic chemicals are generally toxic to fish. Some of these are toxic even at extremely low concentrations around 1 ppm.

With the fast development of chemical industry, several new organic chemical compounds are introduced every year which may find their way into rivers and lakes. Since the effects of these new compounds on natural ecosystems may not be known, there is every possibility that an irreparable damage is done before scientists realise it.

5. Inorganic Minerals and Chemical Compounds. A large variety of inorganic chemicals find their way into normal water from municipal and industrial waste waters and urban run offs. These pollutants (comprising of compounds of Hg, Pb, As, Cd, Na, Ca, F, etc.) injure or kill fish and other aquatic life and also render the water unfit for drinking or for industrial use.

A prominent example is the presence of mercury in water. At one time it was believed that metallic mercury sinks into the sediments and remains there in chemically inert metallic form. But now it is known that anaerobic bacteria in bottom muds convert inorganic mercury into methyl mercury, CH_3Hg^+, which can lead to mercury poisoning in living being.

In petroleum drilling, brine is discharged alongwith crude oil when the latter is pumped to the surface. Sometimes the volume of brine may be more than three times the volume of crude oil recovered. This brine is a potential pollutant for water.

Minerals containing sulphur (*e.g.*, iron pyrites, copper pyrites) on coming in contact with air and water yield sulphuric acid which is carried into lakes and rivers by water draining from the mines. The presence of the acid affects aquatic life.

In cold countries, NaCl and $CaCl_2$ are added in large amounts to melt snow from the roads in winter. These salts eventually run off the roads and contaminate well water and also find their way into lakes and rivers and seriously affect the aquatic life.

Some other metals whose compounds frequently act as water pollutants are lead, arsenic and cadmium.

Lead. Compounds of lead which enter into water are $PbCl_2$, $PbBr_2$, PbBrCl, PbO, PbS, which originate from lead minerals. Lead in the form of $Pb(OH)_2$ gets its entry into water from lead pipes.

Excessive intake of lead by humans causes disruption of synthesis of haemoglobin. It also results in loss of appetite, anaemia, kidney malfunctioning, nervous disorder and brain damage.

Arsenic. The main sources of arsenic compounds in water are pesticides, fungicides and herbicides. Arsenic contamination may also occur due to discharge of some industrial wastes. Dissolution of arsenic minerals is another source of arsenic compounds.

As(III) compounds are highly toxic. The toxicity arises from the complexation of As(III) with the SH groups of enzymes which leads to inhibition of enzymatic action in human body. Since arsenic is structurally similar to phosphorus, its presence interferes with the process of phosphoxylation in human body. Higher doses of arsenic result in coagulation of proteins which causes cramps, paralysis and even death.

Cadmium. Cadmium finds its way into water from industrial discharge and from Ni–Cd batteries. It is highly toxic. Excessive dose causes kidney malfunctioning, anaemia, disorder of bone marrow, etc.

It may be mentioned that according to the 'International Register of Potentially Toxic Chemicals' of United Nations Environment Programme, there are nearly five million known chemicals in the world today and about 40,000 new chemicals are added to this list every year. Of these, about 75,000 chemicals are in eommon use amongst which a large number are positively known to be toxic. A brief

list of toxic elements whose toxic ions are most commonly present in municipal and industrial waters is given in Table 2 alongwith their sources and adverse effects.

TABLE 2

Toxic Elements Commonly Present in Municipal and Industrial Waste Waters

Element	Sources	Adverse Effects
Arsenic	Pesticides, chemical wastes, mining bi-product.	Enzyme-inhibitor, carcinogenic
Beryllium	Nuclear power and space industries, coal.	Toxic, carcinogenic.
Boron	Industrial wastes, detergent formulations, coal.	Toxic to some plants.
Cadmium	Industrial discharge, metal plating, Ni–Cd batteries, mining waste.	Causes high blood pressure, kidney malfunctioning, anaemia, disorder of bone marrow.
Chromium	Metal plating industries.	Cr(VI) is carcinogenic
Copper	Metal plating industries, mining, mineral leaching.	Not very toxic to animals, toxic to plants and algae.
Fluorine (F^-ion)	Natural geological sources, industrial waste.	Causes bone damage, mottled teeth.
Lead	Plumbing, mining, coal, gasoline	Causes anaemia, kidney malfuctioning, nervous disorder.
Manganese	Mining industrial waste, microbial action on Mn minerals at low *p*H.	Non-toxic to animals, toxic to plants, stains materials.
Mercury	Pesticides, coal, industrial waste, mining.	Highly toxic in the form of CH_3Hg^+, Hg^{2+}.
Molybdenum	Natural sources, industrial waste.	Toxic to animals
Selenium	Natural sources, sulphur, coal.	Toxic
Zinc	Metal plating industries, industrial waste.	Toxic to plants.

As is well known, the normal growth and development of animals and human beings are brought about by specific enzymes present in their bodies. The toxic ions, in general, attack the active sites of these enzymes, react with the SH groups of the enzymes and thus cause their complete inactivation, as for example,

The functioning of metallo-enzymes is inhibited by the replacement of the harmless metal ions of the enzyme by the toxic metal ions.

It is to be noted pertinently that it is not the presence of a particular chemical but its concentration which actually matters in chemical toxicology. Thus, elements such as As, Al, Sb, Ba, Be, Cd, Co, Cu, Ce, Pb, Mo, Hg, Zn, etc., which are listed as environmental hazards, act as nutrients in trace concentrations and are essential for normal growth and development of animals and human beings. Arsenic trioxide, a deadly poison, is known to act as a tonic at trace concentrations. This means that for pollution control we have only to control the concentrations of the toxic elements. Any number of toxic elements may be present in drinking water but as long as their concentrations are below the prescribed limits, they are harmless. The permissible limits for some common elements as laid down by the United States Public

Health Drinking Water Standards are given in Table 3. The BIS (Bureau of Indian Standards) values, wherever available, are also included in the Table.

The drinking water should be colourless and odourless. *Its pH* should lie between 6 and 9. *It* should be free from harmful microorganisms and its dissolved oxygen content should lie between 4 and 6 ppm. It should not contain the above mentioned chemicals beyond their permissible limits of concentrations.

TABLE 3

Permissible Amounts (ppm) of Various Elements in Drinking Water

Element	According to USPH Standard	According to BIS Standard
Arsenic	0·05	0·2
Barium	1·0	—
Beryllium	1·0	1·5
Boron	1·0	—
Cadmium	0·01	—
Chloride	250	600
Chromium (VI)	0·05	0·05
Copper	1·0	—
Cyanide	0·05	0·01
Fluoride	1·5	3·0
Phosphate	0·1	—
Lead	< 0·05	0·1
Manganese	< 0·05	—
Mercury	< 0·05	—
Molybdenum	0·05	0·10
Selenium	0·05	0·05
Zinc	5·5	—

6. Sediments. Sediments are particles of soil and minerals which are washed from crop lands, undeveloped lands, unprotected forest soils, overgrazed pastures, strip mines, roads, bulldozed urban areas, etc., by storms and flood waters. Sediments fill reservoirs and stream channels, plug water filters, erode power turbines and pumping equipment and reduce the amount of sunlight available to green aquatic plants. The sediments also cover the fish nests, the eggs laid by them in water and their food supplies. This reduces the population of fish and shell fish.

7. Radioactive Substances. Radioactive substances from nuclear power plants, wastes of uranium and thorium mining and refining and from industries and institutions (medical and scientific) which utilise radioactive materials, if carried by water, become sources of harmful radiations.

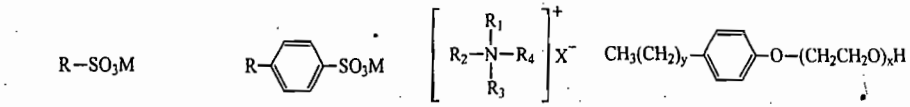
8. Heat. Large amounts of water are used for cooling purposes in thermal and nuclear power plants. Water is also used as a coolant in some industries. Cooling water is thus discharged at a raised temperature. The increased temperatures have several adverse effects on certain properties of water. The rates at which chemical reactions occur increase considerably. This results in faster assimilation of water wastes and hence faster depletion of dissolved oxygen which affects aquatic life. The rate of evaporation also increases appreciably with increase in temperature. This results in greater wastage of water in the form of its vapour and so on.

9. Oil. Oil pollution results from the discharge of oil from oil tankers and offshore drilling rigs accidentally or intentionally. An example of accidental oil discharge was the release of about 100000 metric tons of Kuwaiti oil on March 18, 1967 when the ship ran aground off Cornwall near England and broke into three pieces. The Royal Air Force spent several days trying to set the oil afire with high explosives. Even now, several large tanker accidents are occurring every year. The most serious enviornmental hazard in living history was caused by the spilling and burning of tremendous quantities of oil emanating from the Kuwaiti oil wells which were blasted off in the Gulf War by the Iraqi troops when they were forced to retreat. The awfully hazardous pollution which was caused to the surrounding atmosphere and adjoining oceans was unprecedented. Enormous damage was done to aquatic life.

Oil is also discharged from oil tankers intentionally. A tanker carrying a cargo of crude oil after discharging the oil at the sea port, fills up its tanks with sea water to act as ballast on the return trip. Before the tanker docks, the sea water ballast contaminated with the small residues of oil left in the tank, is returned to the ocean. Some vessels which use oil fuel also tend to produce oil slicks when waste oil or sea water ballast is dumped into the ocean from their fuel tanks.

The most adverse effect of oil pollution is on the sea birds. The oil penetrates their feathers displacing the air which is normally trapped in the feathers and provides buoyancy and insulation against cold. The elimination of entrapped air makes the birds colder and more susceptible to disease. In the absence of entrapped air, the birds experience difficulty in flying. For instance, about 100000 birds lost their lives when the Kuwati oil tanker met with an accident on March 18, 1967. Oil pollution adversely affects the other ocean life as well. Some of the constituents of oil, such as 3,4 benzpyrene are carcinogenic.

10. Detergents. *Detergents comprise of surfactants, i.e.,* surface active agents which are organic compounds having polar or hydrophilic groups such as COOH, OH, SO_3H, NH_4^+, or non-polar groups soluble in water. Some common detergents are given below :



Linear alkyl sulphonates (LAS) | Alkyl benzene sulphonates (ABS) | Quaternary ammonium salt | Poly oxyethylene nonylphenol

where R, R_1, R_2, R_3 are straight hydrocarbon chains, R_4 is an aromatic chain, X is a halogen or an acid group, M is a cation such as Na^+.

The surfactants in detergents cause a variety of pollution problems, some of which are as follows :

1. The surfactants are highly resistant to the action of biological agents and thus do not undergo biodegradation. Since the surfactants tend to retain their identity, their elimination from municipal waste waters by the usual treatments becomes problematic.

2. Surfactants tend to inhibit oxidation of organic substances present in waste waters by forming a sort of envelope around them with the result that these substances do not undergo oxidative degradation during the treatment of waste water. These substances, generally being toxic, cause severe water pollution for which there is no remedy.

3. Being surface active, the surfactants cover the surfaces of small particles in colloidal suspensions thereby stabilising them considerably. These colloidal particles thus do not aggregate and hence cannot be easily filtered off during subsequent treatment. The stabilised colloidal particles also reduce the activity of biological filter beds and activated sludge.

4. The most undesirable effect of sufactants is their tendency to produce stable foam in rivers, sometimes several metres high especially at lock gates. These foams extend over several hundred metres of the river water.

The builders, used in the preparation of detergents, mostly consist of sodium phosphates which form stable soluble complexes with hardness of water liberating ions such as Ca^{2+} and Mg^{2+}. These complexes act as plant nutrients and support rich growth of aquatic plants which deplete dissolved oxygen when alive and produce disagreeable smell on decay.

In view of the above problems, research is now going on to discover surfactants which are biodegradable and builders which are nonphosphatic.

TREATMENT OF DOMESTIC WASTE WATER

The composition of municipal sewage depends largely on the wealth and habits of the municipal population and the amount and nature of industrial waste waters added to the domestic sewage. Sewage treatment processes are designed to remove oxygen-demanding organic wastes, suspended and dissolved solids and bacteria. The treatment processes are generally divided into three categories, *viz.*, 1. *Primary Treatment Processes* 2. *Secondary Treeatment Processes* and 3. *Tertiary Treatment Processes.* These are described below in some details.

1. Primary Treatment Processes. Primary treatment processes involve removal of grit, screening, grinding, flocculation, sedimentation and skimming. Systems for grit removal and screening are designed to remove the larger suspended or floating materials such as rags, paper, twigs, wires, roots, glass and

other matter. The materials removed by screening are incinerated or buried. Flocculation is carried out by agitating waste water by mechanical stirrers or air injection. This causes small suspended solids to collide and form bigger aggregates which settle down more rapidly, Sedimentation, *i.e.*, removal of suspended solids by gravitational settling, is carried out in large basins having a continuous flow with detention time of 4–6 hours. Specific wastes from industrial sources are subjected to removal of oil or grease in a skimming tank, neutralisation of excessive alkalinity or acidity and precipitation or ion-exchange treatment for heavy metals.

2. Secondary Treatment Processes. Secondary treatment processes include the use of biological methods employing trickling filters and activated sludge plants. The use of both the techniques is described below.

Use of Trickiing Filters. Trickling filters comprise of beds of crushed stone imbedded with biological slimes. Waste water is allowed to percolate through these beds when the organic matter present in waste water gets adsorbed on slimes and undergoes decomposition by bacteria and fungi present in the slimes. When the slime layers become very thick they slough off and can be easily removed.

Activated Sludge Process. This process involves continuous circulation of biologically active growths through waste water in the presence of oxygen supplied as fine bubbles of compressed air. The suspended and dissolved organic wastes, well aerated and mixed, undergo adsorption, flocculation, oxidation and biological degradation. After a few hours, the sludge is transferred to sedimentation tanks and allowed to settle out. A part of the sludge which is not rich in organisms, is used to seed the next batch of waste from the primary settling tanks. The activated sludge performs two functions : 1. It clarifies the water by adsorbing most of the colloidal and suspended solids on the surface of sludge particles. 2. It causes oxidative degradation of the organic matter present in waste water. The sludge from secondary treatment plants is disposed off in several ways. A common method consists in digesting the sludge in circular digesters 6–10 metre deep which are maintained at a temperature of about 35°C. During digestion the organic matter is eventually reduced to gases consisting of about 70% methane and 30% CO_2 with small amounts of NH_3, H_2S, H_2 and N_2. Methane is recovered and used as fuel for heating the digester. After digestion for a few weeks, the sludge gets converted into a stable humus material which is used as a soil conditioner.

Other sludge-handling methods are : (*i*) *Dewatering on sand beds* (*ii*) *Vacuum filtration* and (*iii*) *Centrifuging*. ***Dewatering on sand beds*** is carried out by filtering water through sand beds and evaporating water from the sludge surface. ***In vaccum filtration***, a horizontal drum covered with suitable filter media is partially submerged in wet sludge. Vacuum is applied on the inside to extract water out of the wet sludge into the drum which is constantly rotated. The sludge which forms a layer on the drum is scrapped off. ***Centrifuging*** is generally applied for dewatering paper-mill wastes, packing-house wastes, foundry sludges, water-softening and refinery sludges. The dewatered sludge is then disposed off in two different ways : A common procedure is to *incinerate* the dried sludge. The sludge itself furnishes suffcient heat to maintain combustion. This process, however, can lead to air pollution. An altenative to incineration is *composting* which permits recovery of some of the organic matter and plant nutrients of the sludge.

3. Tertiary Treatment Processes. Advanced Waste Water Treatment Processes. These processes aim at improving the waste water quality to the point at which it can be reused. The increasing costs of water supplies and the increasing emphasis on waste water quality are leading engineers to devise methods for total recycling of decontaminated water. Some common advanced waste water treatment processes are discussed below.

Chemical Coagulation and Filtration. *In this* process, the waste water is treated with chemical coagulants such as alum, ferric sulphate, ferric chloride, etc., as a result of which the suspended matter gets coagulated to form flocs. In recent years, a number of synthetic, high-molar mass water-soluble polymers have been developed as highly effective coagulants. One such coagulant is 'calgon', *viz.*, polydiallyldimethyl ammonium chloride. The flocs are filtered with the help of sand, diatomaceous earth or several other multimedia filters. Microscreens can also be used for this purpose.

Adsorption. The waste water is treated with activated carbon which is a porous and highly adsorbent form of carbon with a large surface area. This treatment because of adsorption eliminates materials responsible for undesirable tastes and odours.

Chemical Oxidation. Waste water treatment can also be carried out by using strong oxidants such as ozone, hydrogen peroxide, chlorine and chlorine dioxide. However, oxidants do not eliminate the dissolved inorganic compounds which are present in waste water even after secondary treatment. These compounds are removed by ion-exchange, electrodialysis and reverse osmosis. These techniques are described below briefly.

Ion Exchange. Ion exchange can be carried out by using ion exchange resins. Cation-exchange resins exchange their H^+ ions for metallic cations present in waste water whereas anion-exchange resins exchange their OH^- ions for chloride and other anions present in water. The resins are conveniently regenerated by treatment with sulphuric acid for cationic resins and sodium hydroxide for anionic resins. Ion exchange process is highly effective and produces high quality water.

Electrodialysis. In this process, the waste water is exposed to an electrical potential difference in big tanks which are fitted with membranes consisting of sheets of ion-exchange resins. These sheets are permeable to only cations or only anions (Fig. 3). The anions and cations present in waste water thus migrate through the membranes towards the anode and the cathode, respectively, as shown in the figure.

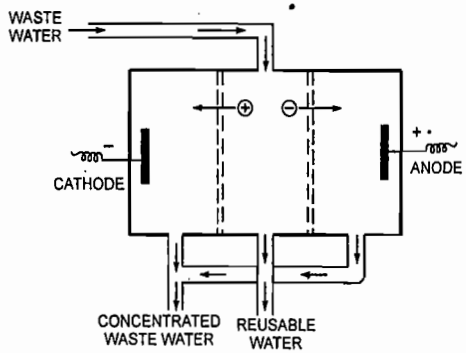


Fig. 3. Apparatus for electraodialysis.

Electrodialysis does not eliminate the organic matter from the waste water.

Reverse Osmosis. In this process, waste water is separated from fresh water by a semipermeable membrane (SPM) which is permeable to water but not to the dissolved materials. Pressure considerably higher than the osmotic pressure of waste water is applied on the waste water as a result of which pure water is forced to the other side of the membrane (Fig. 4). This process is known as reverse osmosis (RO). It eliminates organic as well as inorganic matter from the waste water.

The rate of flow of water Q_w through the SPM is given by

$$Q_w = (\Delta P - \Delta\Pi)\, \chi_w) A/\delta$$

where

ΔP = Hydraulic pressure differential across the membrane
$\Delta\Pi$ = Osmotic pressure differential across the membrane
χ_w = Membrane permeability coefficient for water
A = Membrane area
δ = Membrane thickness

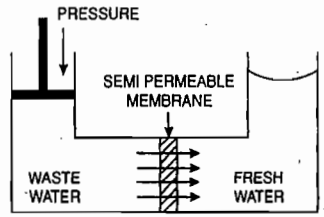


Fig. 4. Apparatus for reverse osmosis.

Depending upon the salt concentrations, the osmotic pressures of domestic waste waters are considerably high. This implies that for effective treatment of the waste waters, the pressures to be applied for reverse osmosis are considerably high. For quite some time, it was a problem to have commerical semipermeable membranes which could withstand such high pressures. These days, however, the problem of the availability of such SPMs has been completely solved. SPMs for RO were first obtained in late 1950s from cellulose acetate. But their use in RO was impractical since, being dense, they permitted very low flow rates. A few years later, techniques were developed for the fabrication of cellulose acetate membranes with *asymmetric density*. By using proper casting-solution composition and proper casting and quenching conditions, it has been now possible to prepare cellulose acetate membranes withthin 0·1–1·0 μm dense surfaces (termed as 'skin' of the membranes) supported by porous cellulose

structures, as shown in Fig. 5.

These membranes permit high water flow rates since the rate-determining factor for water transport is only the thickness of the skin of the membrane which is now evidently very small. Still better semipermeable membranes have recently been obtained from aromatic polyamides.

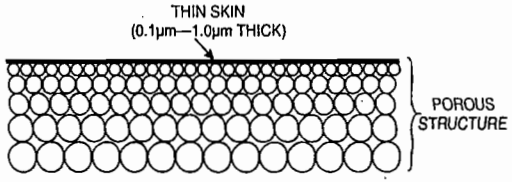


Fig. 5. A cellulose acetate membrane with asymmetric density.

It is to be clearly understood, however, that none of the membranes prepared so far is perfectly semipermeable. Some quantities of salts almost invariably pass through the membranes. Since, however, these quantities are very small, their presence does not pose any pollution problem.

INDUSTRIAL WASTE WATER : ITS CONTAMINATION AND TREATMENT

Industrial waste water is invaribaly contaminated, the nature of contaminants depending upon industries from which the waste water is obtained. These aspects are discussed below briefly.

Waste Water from Food Processing Industry. Food processing units such as beat sugar refining, brewing, distilling and canning, etc., dealing with meat and dairy products, yield waste water which contains high content of decomposable organic matter which leads to heavy oxygen depletion. The dairy industry produces organic wastes high in proteins, fat and lactose. The beet sugar refining industry produces wastes which have a high biochemical oxygen demand (BOD). Breweries and distilleries produce organic solids including fermented starches. The processing of food to produce canned or frozen products leads to large amounts of wet solids. The wastes from meat processing industry are associated with blood, fats, proteins, feathers and other organic wastes, and so on.

Waste Water from Textile Industries. The waste water from textile mills is generally alkaline and has a high biochemical oxygen demand. The textile wastes arise from impurities in the fibres and from the chemicals used in processing, *viz.*, cooking the fibres, desizing the fabrics, etc.

Waste Water from Paper and Pulp Industries. The effluents from paper and pulp industry contain chemicals used in the craft process, bits of barks, wood chips, cellulose fibres and dissolved lignin. About 50 per cent of the wood used as input is eventually discharged as waste material. The effluents contain compounds which are toxic to fish and shell fish.

Waste Water from Chemical Industries. The waste water from chemical industries is very heavily contaminated. Chemical plants manufacturing acids, bases, pesticides, synthetic fibres, detergents and many other organic and inorganic compounds produce wastes which are associated with a wide variety of contaminants numbering into thousands, many of which are highly toxic.

Waste Water from Petroleum Industry. Waste water from oil drilling includes drilling muds, brine pumped out of the well along with crude oil and some oil as well. Oil refineries and petrochemical plants yield a large number of contaminants such as hydrocarbons, acids, alkalies, cyanides, numerous sodium salts, phenolic compounds, inorganic and organic sulphur compounds and halogenated hydrocarbons. Many of these compounds generate undesirable odours and tastes and many of them cause fish flesh to acquire adverse taste.

Waste Water from Metal Industries. Steel mills produce waste water from coking of coal, washing of blast furnace flue gases and pickling of the steel. These wastes contain phenol, cyanogen, coke, lime stone, mill scale and fine suspended solids. The waste water may also contain metals such as Cr, Pb, Ni, Cd, Zn, Cu and Ag as well as acids, alkaline cleaners, grease and oil.

Waste water from **metal-plating industry** is highly toxic on account of the presence of metal cyanides.

Waste Water from Other Industries. Waste water from other industries is associated with a wide variety of contaminants. For instance, leather tannery wastes contain high content of solids, salts causing hardness, sulphides, chromium salts and lime. These wastes have high biochemical oxygen demand (BOD). Radioactive wastes originate from nuclear power plants and research laboratories using radio isotopes. Soft drinks bottling plants produce highly alkaline wastes with high BOD from the washing of

bottles which involves removal of cigarrete butts, paper and other debris left in the bottles by previous users. Laundries have turbid wastes that are alkaline and contain organic solids, and so on.

Treatment of Industrial Waste Water

It is evident from the above discussion that if industrial waste water is discharged into lakes, rivers or oceans as such, it would cause severe pollution. The waste water thus has to be treated properly before it can be disposed off. Most of the water treatment methods used by industries are in general the same as used for the treatment of municipal waste water. However, some specific treatments have been used with advantage in specific cases. For example, while biological treatments are more suited for wastes from dairy and food industries, chemical treatments have worked well for wastes from metal-plating industries.

Since large amounts of water are required by many large industries, there is great emphasis on subjecting industrial waste waster to advanced treatments, *viz.*, tertiary treatments, to render the water suitable for reuse. These treatments are essentially the same as carried out in the case of municipal waste water.

SOIL POLLUTION

Soil mainly comprises of inorganic minerals such as silica, quartz, silicates, aluminosilicates, oxides of iron and the compounds of many other elements. The cations such as Ca^{2+}, Mg^{2+}, K^{+}, NH_4^{+} which are so essential for the growth of the plants, are also present in the soil. The soil also contains decayed organic matter to the extent of about 45% which is called humus. The humus contanis a number of complexing agents which are capable of binding a number of nutrients and micro nutrients present in the soil.

Any factor which deteriorates the quality, texture and mineral content of the soil and/or which disturbs the biological balance of the organisms in the soil and as a result has a lethal effect on plant growth is called **soil pollutant.** There are several factors such as the indiscriminate use of fertilizers and pesticides, accumulation of excreta of grazing animals, dumping of urban, industrial and radioactive wastes, etc., which cause pollution of the soil. Some of these factors not only pollute the soil but also affect the quality of drinking water due to the seepage of harmful soluble salts down below the soil. The fertilizers added to soil may also get washed by rain into low land lakes. Due to excessive nutrition received from the fertilizers, there is undesirable overgrowth of water weeds (a phenomenon called eutrophication, as already mentioned) which results in choking of the entire ecosystem of the lakes.

Causes of Soil Pollution

The various factors which cause pollution of the soil are discussed below in some details

1. Indiscriminate Use of Fertilizers. Fertilizers contaminate the soil with impurities which come from the raw materials used for the manfacture of the fertililzers. For instance, As, Pb and Cd present in trace amounts in rock phosphate mineral get transferred to superphosphate fertilizers. Since the metals are not degradable, their accumulation in the soil (due to exessive use of phosphate fertilizers) above their toxic levels becomes an indestructible poison for crops. Some metal ions such as Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+} etc., are added to the soil in trace amounts as micronutrients. However, the excessive use of these micronutrients may lead to their accumulation above their toxic levels in the soil. This may decrease the fertility of the soil instead of increasing it. Although Mg, Fe, Zn and V are involved in photosynthesis yet their excess in soil has lethal effects on crops. The quality of vegetables and crops grown on soil which is constantly treated with fertilizers over the years, goes down. For instance, the indiscriminate use of NPK fertilizers reduces the protein content of wheat, maize, grams, etc., grown on that soil. The carbohydrate quality of such crops also gets degraded. Excess potassium content in soil decreases vitamin C and carotene content in vegetables and fruits. The vegetables and fruits grown on over-fertilised soil are more prone to attacks by insects and disease.

2. Indiscriminate Use of Pesticides. Studies have shown that a single pesticide cannot eliminate all species of a target pest. As a result, the number of commerical pesticides has tremendously increased during the last about 20 years and their number has now exceeded one thousand. Depending upon their target, pesticides, as already mentioned, are classified as insecticides, fungicides, herbicides, rodenticides, etc. The most important pesticides are the chlorinated hydrocarbons, organophosphates, DDT, BHC, TEPP, aldrin, endrin, malathion, parathion, metasystox, mirex, dieldrin, etc. The structures of some of these

pesticides have already been given in this chapter. The remnants of the pesticides used on pests may get adsorbed by the soil particles which may contaminate root crops grown in that soil. Through the consumption of these crops, the remnants may enter the human biological systems affecting them adversely. Some of the pesticides are quite stable and their biodegradation may take weeks and even months.

Apart from the normal pesticides, a number of soil conditioners are now-a-days used for killing the insects and thus to protect the fertility of the soil. The soil conditioners are compounds of toxic metals such as As, Pb, Cd, Hg, Co, etc. After the decomposition of these compounds, the resulting metals accumulate in the soil from where they enter the growing crops and from crops to animals. It is thus evident that indiscriminate use of pesticides not only harms the human beings and animals but also affects the fertility of the soil by causing changes in the natural food cycle within the soil. Alternatives to pesticides have already been discussed in this chapter.

3. Accumulation of Animal Excreta on Soil. The excreta of grazing animals get accumulated as wet slurry on land when the sheds in which animals are kept are washed. The slurry may seep into ground water and pollute it. When the raw cattle dung is dumped on the soil, it becomes a breeding place for several types of insects, pathogenic bacteria and viruses which pollute the soil. From the soil, they enter plant metabolism and animal metabolism. Burning of dried animal waste also produces benzopyrene in smoke which is carcinogenic.

To avoid pollution of soil from animal waste, the latter should be collected in cemented pits and covered by soil. It should be allowed to biodegrade in a scientific manner to yield manure. The gobar gas produced from cattle dung is a much cleaner fuel than the cattle dung itself. Not only that; the residue left behind in the gobar gas plant is a much better manure than the cattle dung itself.

4. Dumping of Urban Solid Waste. The urban solid waste contains domestic waste, garbage, plastics, glasses, metallic cans, rubble, burnt up fuels, discarded articles of domestic use, etc. In cities like Delhi, Mumbai, Calcutta, Kanpur, etc., 3000 to 4000 tonnes of solid refuse is collected from houses, streets and roads and dumped into the landfills every day which causes serious pollution of land. The problem is even more acute in big cities of developed countries. New York alone throws around 30,000 tonnes of solid urban waste into its already choked landfills. Urban domestic wastes are not biodegraded easily. Also, the slimmy water oozing out of the dumping sites of urban waste is extremely toxic as it emits poisonous gases due to anaerobic decomposition of organic matter. Apart from this, the water harbours many disease-causing bacteria.

The excreta of dairy animals harbour extremely harmful bacteria and viruses which ultimately enter the soil from where they infect animals and human beings.

In view of the above hazardous effects, several measures are taken to dispose off the urban solid waste and thus avoid its dumping into the landfills. Some of these measures are discussed below.

a. Recycling of Reusable Waste. Waste paper, rags and cotton waste are separated from urban waste and converted into card board and low grade paper. In recent years, new techniques have been developed to convert the above wastes into document paper, album paper and even high grade stationery. Japan recycles about 40% of its waste paper to obtain new high grade paper. It has been estimated that recycling of one tonne of waste paper saves 16–17 trees from the axe.

Waste plastic articles are extremely stable and do not biodegrade. Polyethene, polyethene tetraphthalate (PET) and PVC, etc., are recycled to yield low quality plastics which are used in making plastic toys, hard low grade slippers, buckets, cans, etc.

Tin cans, scrap iron, etc., picked up from the urban waste are recycled to get iron.

Similarly, glass and glass articles picked up from urban waste are recycled to manufacture low grade glass for making bottles.

Urban authorities in developed countries have started putting separate garbage bins for collecting different types of wastes. There are, thus, separate bins for papers, plastics, metals, glass, etc.

b. Bioremediation of waste. The solid municipal waste which is rich in organic matter is subjected to biodegradation with the help of genetically engineered bacterial strains resulting in useful manure. Efforts are being made to synthesise plastics which can be easily degraded by common microbes. The farm

waste consisting of cattle dung is converted into biogas with the help of a variety of bioorganisms. The main constituents of biogas are methane, carbon monoxide and carbon dioxide. The residual slurry from biogas plants is a very good manure.

In small towns and villages, the human waste is disposed off in pour flush toilets which are linked to biogas plants. About a lakh of such toilets are linked with biogas units in several states in the country such as Maharashtra, West Bengal and Gujarat. The biogas produced is utilised for cooking purposes and the residue is used as manure.

c. Incineration. The technique involves burning of solid waste at high temperature (>2000°C) in incinerators. The bulk of the solid waste is reduced to a small volume of ash and the heat generated is utilised for raising steam for turbines. For incineration to be successful it is essential that the waste contains enough burnable material so that the smoke produced is minimum. Incineration is, of course, a costly process and requires high technical know-how to burn almost the entire waste without causing air pollution. If the solid waste contains materials such as plastics, papers, synthetic polymers, etc., their combustion produces toxic vapours. Therefore, as for as possible such materials should be sorted out of the solid waste.

5. Dumping of Urban Waste in Landfills. The low lying, untilled and uninhabited land can be used for dumping urban waste. However, the most commonly anticipated danger in unscientific dumping of urban waste in landfills is the contamination of the soil of the landfills with toxic constituents of the waste. Also the dumping sites become the breeding grounds for several disease-spreading microbes.

Now-a-days, the urban waste is dumped in landfills by controlled tipping process. In this process, the waste is spread on the ground and is compactly pressed by bulldozers into a layer about 10 cm thick over which a layer of soil is laid. Piling of many such compressed layers of waste and soil can slowly convert a low lying patch of land or a dried unusable lake into a park, play ground or an area for raising buildings. The compact clay layer spread over the compressed urban waste checks the escape of gases which result from the decomposition of the waste. The unwanted gases are removed from the landfills with the help of special techniques.

6. Dumping of Industrial Waste. A large number of industries generate huge quantities of industrial wastes whch pollute the soil. In some industries, as much as half of the raw material becomes a waste. Many industrial effluents are dumped into the surroundings which in the long run pollute the soil because the chemicals present in the waste are absorbed by the soil. This alters the chemical and biological properties of the soil. The toxic chemicals absorbed by the soil enter the animal food chain through plants grown on the polluted soil which may cause serious biological disorder in animals and human beings.

It is to be noted that both biodegradable and non-biodegradable parts of industrial wastes pollute the soil. For instance, the biogradable wastes from food processing units contain nitrogen, phosphorus and other micronutrients. The dumping of such wastes may increase the nitrate concentration in the soil which, as already mentioned, has an adverse effect on the fertility of soil. The high nitrogen and phosphorus content causes excessive growth of weeds growing under water which leads to choking of aquatic life.

A number of industries such as textile, pesticides, paints, dyes, soaps, detergents, tanneries, drugs, rubber, petroleum, paper, sugar, steel, glass, electroplating and chemical industries pour their hazardous effluents containing a variety of harmful chemicals into the soil, creating disastrous effects on biological systems. Some industries discharge their effluents containing inorganic salts such as $CaSO_4$, $CaCO_3$, $Ca(HCO_3)_2$, etc., on the soil. This makes the soil unproductive. The metallic contaminants in industrial wastes (such as Hg^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Cd^{2+}, Cr^{3+}, Na^{+}, Cu^{2+} etc.) destroy useful bacteria present in the soil. The wastes from chemical industries also change the *p*H of the soil which affects the productivity of the soil.

Industrial sludges cause much greater soil pollution than the solid industrial waste because the hazardous chemicals in the sludges seep into the soil more easily. The composition of an industrial sludge varies with the type of industry which produces the sludge. For example, in the coal fired power plants, a stirred slurry of lime stone is used for trapping SO_2 from the escaping flue gases. Apart from SO_2, the slurry also absorbs harmful and toxic volatile elements thrown out by the burning coal. Thus, when

flue gases are passed through the lime slurry, As, Se, Hg, Cd, etc., also get trapped in the slurry. Such a slurry which is known as FGDS (Flue Gas Desulphurisation Sludge) pollutes the soil immensely. The toxic metals of the waste sludge get absorbed by the soil and from the soil they enter plants and from plants they enter animals and human beings. It is thus very essential that the industrial waste be treated to make it free from the hazardous chemicals. Since each industry produces it own typical industrial waste, each type of industrial waste has to be treated separately.

7. Dumping of Radioactive Waste. The radioactive fall out from nuclear explosions consists of radioactive particles which fly into the atmosphere during explosion and the dust of the crater. All these particles eventually settle down on earth's surface. They comprise of both the longer-lived radio elements such as ^{137}Cs, ^{141}Ce, ^{90}Sr, ^{147}Pm, ^{151}Sm, etc., and the shorter-lived radio elements such as ^{131}I, ^{132}I, etc. The shorter-lived radio elements deposited on the soil are comparatively less harmful since they decay to normal isotopes of the elements within a short duration. The longer-lived radio elements, on the other hand, are very harmful since they retain their identity for a long time and emit alpha paticles as well as gamma radiations. The gamma radiations are highly penetrating and cause mutation of biological cells by disrupting the molecules which come in their path. Thus, water molecules of the cells get dissociated into ions (H^+ and OH^-) and free radicals (such as $\dot{H}$, $\dot{O}H$, etc.) The ionic spacies deactivate the enzymes as a result of which the cell growth and cell multiplication may stop. Similarly, the free radicals being highly reactive, react with protein molecules in the living cell setting a chain of events which destroys the living cells or makes them function abnormally. The alpha pasticles emitted from the radioactive fallout may damage or break DNA molecules. The broken parts of the DNA molecules recombine producing modified DNA molecules which have scrambled genetic code. The modifid DNA molecules generate cancerous cells.

The radioactive ^{90}Sr and ^{137}Cs enter plants through soil. From plants they enter grazing animals and from there to man through animal milk or meat. ^{90}Sr replaces Ca from bones once it enters the body through food. Similarly, ^{137}Cs replaces K from the living cells. These replacements produce highly damaging effects.

It would be awfully hazardous if the radioactive waste recovered from nuclear power plants and nuclear reactors is dumped as such into the soil. The waste is, therefore, subjected to specialised chemical and electrochemical treatments to eliminate the unreacted ^{235}U and the nuclear by-product ^{239}Pu so as to bring down the radioactivity to as low a level as possible and the residual waste is then stored in underground thick steel containers which are further protected by a thick covering of concrete. The method, however, is not completely safe because even the strongest steel tanks may get corroded with the passage of time.

An alternative technique for disposing off the nuclear waste obtained from nuclear power plants and nuclear reactors with high and intermediate levels of activity, is in the offing. In this technique, the radioactive waste is "imprisoned" in crystalline structures of some special types of synthesised materials which are practically insoluble in water. These crystalline materials are capable of imprisoning the radioactive waste for millions of years. The crystalline materials with imprisoned radioactive waste are enclosed in nickel-iron alloy containers which are inserted into holes made in granite rocks. These rocks are then dumped deep into the earth.

It was previously thought that low activity (·01 μCi per litre) radioactive aqueous solutions resulting from radio therapeutic treatments being given in hospitals were reasonably safe and thus could be discharged into surface water. However, recent studies have shown that the radio isotopes eventually get concentrated and contaminate sea weeds, oysters and fish.

8. Deforestation and Overgrazing. Deforestation and overgrazing causes soil erosion, that is, detachment and removal of loosened soil material by rains, floods, etc. The denuded soil does not have enough soaking capacity. Hence, during rains the soil does not soak enough water with the result that the underground aquifers do not receive sufficient water. The aquifers constitute a vital source for maintaining river flows in dry weather for providing water for irrigation. Erosion of soil resulting from deforestation and over grazing, causes "pollution" of the soil. Soil erosion can be checked by afforestation and growing erosion-resisting plants.

QUESTIONS

1. Define the term pollutant. Discuss briefly how does environmental pollution affect humans, animals, plants and other materials. Comment on long distance movement of pollutants.
2. Name the gases which cause pollution of air. What are the major sources of each of these pollutants ?
3. *What are the natural and human sources of CO whose emission causes air pollution ? What is is meant by the term 'sink' ? What are the toxic effects of CO ?*
4. In what way, CO_2 causes air pollution ? Explain how extensive forestation would reduce the level of CO_2 in the atmosphere. What is meant by green house effect ?
5. How does chlorine enter into the atmosphere ?
6. What are the natural and human sources of oxides of nitrogen which tend to cause severe pollution of air ? How do these gases get removed from the atmosphere ? What are the adverse effects of these gases. What is meant by nitric acid rain ?
7. What are the natural and human sources of sulphur dioxide which is emitted into the atmosphere. What are adverse effects of this gas. What is meant by sulphuric acid rain ?
8. What are the natural and human sources of H_2S. What are the adverse effects of this gas ?
9. Discuss the distribution of temperature with height in the atmosphere. With the help of a diagram, identify the regions named as troposphere, stratosphere, mesosphere and thermosphere.
10. What is the function of ozone present in the troposphere. Explain clearly how oxides of nitrogen and fluorocarbons tend to deplete the ozone layer. What is the effect of this depletion ?
11. What are particulates ? Name the particulate pollutants which are commonly present in the atmosphere. What are the sources of these particulates ? Discuss the toxic effects of particulates.
12. What is smog ? What is the difference between classical smog and photochemical smog ? Discuss carefully the mechanism of the formation of photochemical smog. What are the adverse effects of photochemical smog ?
13. Name the common air pollutants. How are they monitored ? What procedures are adopted to control pullution of air by these pollutants.
14. What are pesticides ? How are they classified ?
15. What are insecticides ? Discuss in details their classification into stomach poisons, contact poisons and fumigants, giving suitable examples.
16. What are fungicides, herbicides and rodenticides ? Give examples
17. What are pesticides ? Discuss in details the enviromental effects of pesticides.
18. Discuss in details the latest methods of pest control which do not cause environmental pollution.
19. Discuss the autocide technique, chemosterilization, use of sex attractants and use of juvenile hormones for pest control. What are the specific advantages of these techniques compared to the use of pesticides.
20. What are pesticides ? Discuss the effects of pesticides on wild life.
21. Outline the various materials which are likely to cause pollution of water.
22. Discuss briefly how the following agents can cause pollution of water :

    1. Sewage and other oxygen-demanding wastes. 2. Infectious agents 3. Plant nutrients 4. Exotic organic chemicals. 5. Inorganic minerals and chemical compounds 6. Sediments. 7. Radioactive substances. 8. Heat 9. Oil 10. Detergents.
23. What are detergents ? How do they cause water pollution ? What remedies have been suggested to avoid pollution by detergents.
24. What are the main domestic water pollutants ? Discuss in details the primary, secondary and tertiary treatment processes for depollution of the domestic waste water.
25. Describe in details the advanced waste water treatment processes to improve the quality of waste water to a point at which it can be reused.
26. "Industiral waste water is polluted differently depending upon the industry from which it is obtained". Comment on this statement.
27. (*a*) What type of pollutants are present in waste water obtained from the following industry ;

    1. Food processing industry. 2. Textile industry. 3. Paper and pulp industry. 4. Chemical industry 5. Petroleum industry and 6. Metal industries.

    (*b*) How is the industrial waste water treated to get fresh water for reuse in industries ?
28. What is meant by soil pollution ? Discuss briefly the various factors which cause pollution of soil. What remedial measures can be taken to avoid pollution of soil.

39 NUCLEAR CHEMISTRY

Nuclear chemistry deals with the study of nuclear particles, nuclear forces and nuclear reactions. This field began with the discovery of *radioactivity*. A good deal of knowledge was accumulated during the next few decades and this led to the discovery of *artificial radioactivity*. The release of a tremendous amount of energy through nuclear reactions became possible with the development of artificial radioactivity. Nuclear chemistry, therefore, constitutes an important branch of science. The release of nuclear energy holds out great hope for the future as the present natural resources of energy are fast approaching exhaustion.

Nuclear Particles. Before we discuss the various types of nuclear reactions, it would be of interest to make an acquaintance with the various particles that are now known to be present in the nucleus of an atom. The most commonly known nuclear particles are protons and neutrons.

It is now known that neutron is not a stable particle. Inside the nucleus it may be stable for billions of years but when it comes outside the nucleus it has a very short life (half-life =12·8 minutes) after which it decomposes into a proton and an electron.

Shortly after the experimental verification of de Broglie's theory of wave nature of electron, P.A.M. Dirac, a British scientist, suggested that *the entire universe is a single quantum system* in which there is a vast number of energy levels just as there is a simpler set of energy levels in an atom and a more complicated set in a metallic crystal. Based on these ideas Dirac presented in 1930 an elegant quantum mechanical treatment of electron which included relations stemming from Einstein's theory of relativity. Based on this treatment, he put forth his bold **antiparticle theory** according to which there must be present in the universe not only the familiar particles such as electrons, protons and neutrons but also **antiparticles** which in their properties are opposite to the familiar particles. Thus, corresponding to electron, proton and neutron, there must exist antielectron, antiproton and antineutron.

At that time, the antiparticle concept was severely criticised by other theoretical physicists. However, their doubts were set at rest by Anderson's discovery of antielectron (later named **positron**) in 1932. Bombardment of light elements such as boron and aluminium with alpha particles resulted in the emission of positrons.

$$^{10}_{5}B + ^{4}_{2}He \longrightarrow ^{13}_{7}N + ^{1}_{0}n$$

$$^{13}_{7}N \longrightarrow ^{13}_{6}C + \underset{\text{(Positron)}}{^{0}_{+1}e}$$

A positron has the same negligible mass and the same amount of charge as the electron. However, the charge in this case is positive and hence the name *positron*. Positrons have very brief existence (about 10^{-8} sec). *They quickly unite with electrons producing* γ-ray photons :

$$^{0}_{+1}e + ^{0}_{-1}e \longrightarrow h\nu + h\nu'$$

The discovery of positron was followed by the discovery of antiprotons and antineutrons. In 1955, Segre' and his associates at the University of California obtained **antiprotons** by bombarding a

copper target with accelerated protons. The mass and spin of antiprotons were found to be identical with those of protons but the charge was opposite, *i.e.*, –1. Through similar experiments in 1956, Cork and his associates obtained **antineutrons**. These antiparticles are identical with neutrons except that their spin is opposite. It has been shown that when a proton strikes an antiproton, a neutron and an antineutron are emitted.

$$\underset{\text{proton}}{^{1}_{+1}p} + \underset{\text{antiproton}}{^{1}_{-1}p} \longrightarrow \underset{\text{neutron}}{^{1}_{0}n\,(\uparrow)} + \underset{\text{antineutron}}{^{1}_{0}n\,(\downarrow)}$$

The arrows in opposite directions indicate opposite spins of neutrons.

As mentioned above, a free neutron is unstable. It decays rapidly into a proton and an electron. It has been observed that during this decay, there is loss of mass equivalent to 1·5 electron mass. This loss of mass should have been manifested in the form of increase in the energy of the protons and electrons emitted. But the decay products are not found to be associated with so much of energy. Pauli in 1927 postulated that an undetectable particle with zero mass is formed simultaneously in neutron decay. This particle, later named **neutrino** by Fermi, accounts for the discrepancies of kinetic energy. The charge on neutrino is zero and mass, though variable, is always less than that of an electron. Allen and Rodeback demonstrated, in 1952, the free existence of this particle.

Fermi, in 1934, indicated the existence of **antineutrino** as well. Antineutrino is a particle identical to the neutrino but has opposite spin. According to Fermi, a neutron decays as follows :

$$\underset{\text{neutron}}{^{1}_{0}n} \longrightarrow \underset{\text{proton}}{^{1}_{+1}p} + \underset{\text{electron}}{^{0}_{-1}e} + \text{antineutrino}$$

Reins and Cowan obtained, in 1953, direct proof of the existence of antineutrino. In fact, they deduced from the existence of antineutrino, the properties of neutrino which are in close agreement with theoretical requirements.

In 1935, H.Yukawa, a Japanese theoretical physicist, predicted the existence of another nuclear particle called **meson** (*meso* means middle, in Greek), with a mass in between that of electron and proton. Since then three kinds of mesons have been found both in cosmic rays and in laboratory. One variety, called **μ meson**, has been shown to have a mass 206 times that of electron and a charge which may be negative or positive. The second variety, called **pi meson**, has a mass about 270 times that of electron and a charge which may be positive, negative or zero. The third variety, called ***K* meson**, has mass about 970 times that of electron and a charge that may be positive, negative or zero. Mesons have now been actually detected in certain radiation experiments.

Nuclear particles with mass larger than that of proton have also been obtained. These particles are called **hyperons**. The masses of hyperons have been found to be about 2180, 2330 and 2580 times that of the electron at rest. Some of these particles are electrically neutral while others are positively or negatively charged.

Mesons and hyperons are very short-lived. Mesons, depending upon their category (whether μ, pi or *K*), decompose into other mesons (there are as many as fifteen additional types of mesons), electrons, positrons, neutrinos, antineutrinos and γ-ray photons. Hyperons break down to other hyperons, mesons, neutrons and protons.

At the time of Rutherford, a nucleus was considered to be a simple species containing only neutrons and protons. But, the position at present is totally different. The nucleus now is known to contain as many as nearly one hundred subatomic particles associated with different energies, different masses, different spins, different charges and having different life times. To call these particles fundamental particles is also a misnomer because, by definition, a **fundamental particle** is one that does not change into anything else and is not derived from anything else, *i.e., it exhibits an invariant behaviour throughout the course of time.* According to the above definition, while some nuclear particles can be called fundamental particles others cannot. The various nuclear particles can be divided in two categories, *viz.*, **leptons** which are

infinitely small particles (such as an electron, positron, neutrino and antineutrino) and, by definition, are fundamental particles and **hadrons** (such as a neutron, proton and meson) which are bigger particles having size of the order of 1 fm (1×10^{-15} m) and which undergo reactions and interactions (as mentioned above for proton and neutron) and as such cannot be called fundamental particles. Hadrons, in fact, are composed of smaller particles called **quarks** and **antiquarks**. Thus, a proton and a neutron is composed of three quarks each while a meson is composed of a quark and an antiquark. No free quark has ever been seen. Quarks only exist within the matter that is made of them. The structure of the nucleus, is evidently highly complex. No theory has yet been developed which can account for the origin of nearly one hundred nuclear particles, their mutual interactions and how these particles are held together in the exceedingly small nucleus. The subject constitutes one of the hottest fields of research in theoretical physics.

Nuclear Forces. As is well known, the common particles, protons and neutrons, are packed together in a very small nuclear space. Since protons are positively charged particles, the strong repulsive forces between them should render the nucleus highly unstable and liable to disintegrate. But, this does not happen except in heavier elements which are radioactive. A simple explanation for stability of the nucleus appears to be that the neutrons whose number is either equal or largely much greater than the number of protons, some how act as shields between the protons thus making their repulsive forces ineffective.

Further, it was avgurd that just as atoms in a molecule are held together due to an exchange of electrons between them, a similar situation involving the exchange of 'some thing' between the protons and neutrons ought to work in the nucleus as well. This 'something' has now been shown to be the **mesons**, as discussed below :

Hideki Yukawa, suggested, in 1939, that pi mesons *oscillate between neighbouring nucleons (protons and neutrons) with a velocity close to that of light.* They interact with protons and neutrons as a result of which a proton may change into a neutron and a neutron may change into a proton, for a part of the time. This may be represented as below :

$$\text{Proton} + \text{negative pi meson} \rightleftharpoons \text{Neutron}$$

$$\text{Neutron} + \text{positive pi meson} \rightleftharpoons \text{Proton}$$

There is thus an exchange of pi mesons back and forth between neighbouring nucleons. *This results in an attraction between neutron and proton.*

Nuclear Size. Some indication about the size of the nucleus was obtained from Rutherford's experiments on scattering of alpha particles. More accurate information has now been obtained from experiments on *scattering of neutrons.* The results can be summarised by the equation

$$r = R_0 A^{1/3} \qquad \ldots(1)$$

where r is the radius of a nucleus of mass number A and R_0 is a constant whose value is equal to $1\cdot5\times10^{-15}$ m. The nuclear radius is very small being of the order of 10^{-14} m. It is generally measured in *fermi units*, f ($f = 10^{-13}$ cm $= 10^{-15}$ m). Evidently, protons and neutrons, collectively called nucleons, as mentioned above, are packed together in a very small space in the nucleus.

Example 1. (a) Estimate the radius of $^{27}_{13}$Al nucleus. (b) Why is the atomic radius of Al comparatively so much large ?

Solution : (*a*) According to Eq. 1, the radius of a nucleus is given by $r = R_0 A^{1/3}$ where $R_0 = 1\cdot5\times10^{-15}$ m and A is the mass number.

For $^{27}_{13}$Al nucleus, $A = 27$, Hence $r = (1\cdot5\times10^{-15}\text{ m})\,(27)^{1/3} = \mathbf{4\cdot5\times10^{-15}\ m = 4\cdot5}\,f$

(*b*) Atomic radius of Al, by definition, is taken as the distance between the centre of its nucleus and the outermost shell of electrons. This distance is tremendously large as compared to the radius of the nucleus. To quote an analogy, if the neucleus is of the size of a cricket ball, the outermost shell of electrons would be nearly 2 kilometres from the nucleus. This explains why the atomic radius is so very large compared to the nuclear radius.

Atomic mass unit (a.m.u.). According to the latest convention, the mass of the standard carbon atom, $^{12}_{6}$C, is taken to be 12 a.m.u. (atomic mass unit). Thus, one a.m.u. is exactly 1/12th of the mass of $^{12}_{6}$C atom.

A neutron, on this scale, has a mass of 1·008665 a.m.u., a proton of 1·007277 a.m.u. and an electron of 0·0005486 a.m.u. The mass of hydrogen atom (1 proton + 1 electron), therefore, is 1·0078256 a.m.u.

As metioned above, 1 a.m.u. = 1/12th of mass of a $^{12}_{6}$C atom

$$= \frac{1}{12}\times\frac{12\text{ g mol}^{-1}}{N_A} \quad \text{where } N_A \text{ is the Avogadro's number}$$

$$= \frac{1\text{ g mol}^{-1}}{N_A} = \frac{1\text{ g mol}^{-1}}{6\cdot022\times10^{23}\text{ mol}^{-1}} = 1\cdot66\times10^{-24}\text{ g}$$

Thus, $\mathbf{1\ a.m.u. = 1\cdot66\times10^{-24}\ g = 1\cdot66\times10^{-27}\ kg}$

Nuclear Density. As mentioned above, the radius (r) of a nucleus is extremely small being of the order of 10^{-14} m. Since the nucleus is believed to be spherical, its volume ($= 4/3\pi r^3$) would be far too smaller, being of the order of 10^{-42} m^3. As a result, *the density (mass/volume) of the nucleus would be tremendously high.* This has been illustrated in the following solved examples.

Example 2. Calculate the density of a nucleus of mass number A.

Solution : The nucleus of mass number A would contain A nucleons. Since the mass of a nucleon is approximately 1 a.m.u., hence the mass (m) of the nucleus of mass number $A = A\times1\cdot66\times10^{-27}$ kg since 1 a.m.u. = $1\cdot66\times10^{-27}$ kg (Eq. 3).

According to Eq. 1, the radius (r) of the nucleus is given by

$$r = R_0 A^{1/3} \quad \text{where } R_0 = 1\cdot5\times10^{-15}\text{ m}$$

$\therefore$ The volume V of the nucleus $= (4/3)\pi r^3 = (4/3)\pi(R_0A^{1/3})^3 = (4/3)\pi(1\cdot5\times10^{-15})^3 A$ m^3

Hence, the density of the nucleus, $\rho = \dfrac{m}{V} = \dfrac{A\times1\cdot66\times10^{-27}\text{ kg}}{(4/3)\pi(1\cdot5\times10^{-15})^3 A\text{ m}^3} = \mathbf{1\cdot77\times10^{17}\ kg\ m^{-3}}$

As can be seen, *the density of the nucleus is tremendously high and is independent of the mass number of the nucleus.* Thus, ***all nuclei** have approximately the same nuclear density.*

Example 3. Calculate the average density of the nuclear material in the $^{12}_{6}$C nuclide, given that the nuclear radius is equal to 3 f. Compare this density with that of water (1 a.m.u. = $1\cdot66\times10^{-27}$ kg).

Solution. We know that the density ρ is given by $\rho = m/V$ where m is the mass and V is the volume. Assuming that the nucleus is spherical, $V = 4/3\pi r^3$ where r is the nuclear radius. In the present case,

$$r = 3f = 3\times10^{-15}\text{ m}$$

$$m = (12\text{ a.m.u.})\,(1\cdot66\times10^{-27}\text{ kg/a.m.u.}) = 12\times1\cdot66\times10^{-27}\text{ kg}$$

$$\therefore \quad \rho = \frac{12\times1\cdot66\times10^{-27}\text{kg}}{(4/3)\pi(3\times10^{-15}\text{ m})^3} = \mathbf{1\cdot76\times10^{17}\ kg\,m^{-3}}$$

$$\frac{\rho}{\rho_{water}} = \frac{1\cdot76\times10^{17}\text{ kg m}^{-3}}{1{,}000\text{ kg m}^{-3}} = \mathbf{17\cdot6\times10^{14}}$$

Notice the fantastically high nuclear density compared with the density of water.

Example 4. "We need a very powerful crane to lift a nuclear mass of even microscopic size". Why is it so?

Solution. Suppose we are to lift a nuclear mass of *microscopic size*, say, a mass occupying an extremely small volume of 10^{-5} cm^3.

As illustrated in Example 2, the density of the nucleus = $1\cdot77\times10^{17}$ kg m^{-3}

Volume of the nuclear material, $V = 10^{-5}$ cm^3 = 10^{-11} m^3

$\therefore$ Mass of the nuclear material = volume × density = 10^{-11} m$^3\times1\cdot77\times10^{17}$ kg m^{-3} = $\mathbf{1\cdot77\times10^{6}}$ **kg**

This is indeed a **huge mass** which can be lifted only by a very **powerful crane.**

Equivalence of a.m.u. and energy. According to Einstein's mass-energy relationship, $E = mc^2$ where m is mass in kg, c is velocity of light in m s^{-1} and E is energy in joules. Therefore, ***energy equivalent to one***

a.m.u. is given by

$$E = 1{\cdot}66\times10^{-27}\ \text{kg}\times(2{\cdot}998\times10^{8}\ \text{m s}^{-1})^2 = 1{\cdot}4925\times10^{-10}\ \text{J} \qquad (\text{J} = \text{kg m}^2\ \text{s}^{-2})$$

$$= \frac{1{\cdot}4925\times10^{-10}\ \text{J}}{1{\cdot}602\times10^{-19}\ \text{J/eV}} = \frac{1{\cdot}4925\times10^{-10}\ \text{J}}{1{\cdot}602\times10^{-13}\ \text{J/MeV}} = 931{\cdot}65\ \text{MeV} \qquad (\because\ 1\ \text{eV} = 1{\cdot}602\times10^{-19}\ \text{J})$$

Using more accurate values of m, e and c, 1 a.m.u. comes out to be equivalent to 931·478 MeV. In this book, 931·5 has been used as the conversion factor. Thus,

1 a.m.u. ≡ 931·5 MeV

Packing Fraction. It has been observed that isotopic masses of elements are close to but not exactly equal to whole numbers. The mass numbers, however, are invariably whole numbers. Aston expressed the *variation of isotopic mass from mass number* of the isotope in terms of a quantity called **packing fraction** which is defined as

$$\textbf{Packing fraction} = \frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

Packing fraction may have a *negative* or a *positive sign*. The *negative sign* of the packing fraction means that the isotopic mass is *less* than the mass number of the isotope. In such cases, some mass gets transformed into energy in the formation of that nucleus, in accordance with Einstein's equation, $E=mc^2$. Such nuclei, therefore, are more stable. A *positive packing fraction*, on the other hand, would imply a tendency towards instability. But this is not quite correct especially for elements of low atomic masses.

A plot of packing fraction against the corresponding mass numbers of the various elements is shown in Fig. 1.

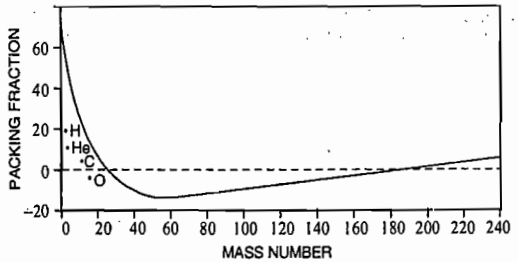


Fig. 1. The Packing Fraction

It has been observed that hydrogen, helium, carbon and oxygen atoms of mass number 1, 4, 12 and 16, respectively, do not fall on this curve. The packing fractions of H, He and C, although positive, have small values. These elements are, therefore, stable. The packing fraction of oxygen with mass number 16 and isotopic mass 15·999 is *negative*. The oxygen atom is, therefore, stable. The transition elements with mass numbers in the neighbourhood of 45, such as Mo, Tc, Ru, Rh, Pd, Ag, have lowest packing fractions with a negative sign which indicates their high stability. The packing fraction beyond mass number 200 becomes *positive* and increases with increase in mass number. This indicates increasing instability of these elements. Elements with mass numbers beyond 230 are radioactive and undergo disintegration spontaneously.

A quantitative measure of stability of a nucleus, however, became possible with the development of the concept of **mass defect**.

Mass Defect. Binding Energy of the Nucleus

It has been found that the actual isotopic mass of an element is almost invariably less than the sum of the masses of protons, neutrons and electrons present in it. The ***difference*** between the two is known as **mass defect**.

Suppose A is the mass number and Z is the atomic number (nuclear charge) of an element. Evidently, its atom contains Z protons, $(A-Z)$ neutrons and Z electrons. Let m_p be the mass of a proton, m_n that of a neutron and m_e that of an electron. The atomic mass M' of the isotope, therefore, should be given by

$$M' = Z m_p + Z m_e + (A-Z)\, m_n$$
$$= Z(m_H) + (A-Z)\, m_n \qquad (\because\ m_p + m_e = m_H)$$

where m_H is the mass of a hydrogen atom.

The actual atomic mass of the element, however, is found to be *less* than M'. Suppose it is M. Then,

$$\textbf{Mass defect} = M' - M = \Delta M = Z(m_H) + (A-Z)\, m_n - M$$

The quantity ΔM represents the loss of mass in the formation of the nucleus of the atom. The loss of mass is equivalent of the energy released in the formation of the given nucleus from individual protons and neutrons. The release of energy results in the stability of the nucleus. *The energy released in the formation of a nucleus from its constituent nucleons is called the* **binding energy of the nucleus**. This much energy will naturally be required to break up the nucleus into its component nucleons.

If ΔM a.m.u. is the mass defect, then the binding energy of the nucleus will be given by $\Delta M\times931{\cdot}5$ MeV because 1 a.m.u. is equivalent to 931·5 MeV of energy. The greater the mass defect, the greater is the binding energy of the nucleus, evidently,

This binding energy of a nucleus when divided by the number of nucleons gives the **mean binding energy per nucleon**. The binding energy per nucleon is a measure of the **stability of the nucleus**. The greater the binding energy per nucleon, the more stable is the nucleus.

A few examples are given below to illustrate various steps involved in calculating binding energies of different nuclei.

Example 5. Calculate the binding energy per nucleon of oxygen atom $^{16}_{8}O$ which has a mass of 15·994910 a.m.u. Mass of neutron = 1·008665 a.m.u., mass of proton = 1·007277 a.m.u. and mass of electron = 0·0005486 a.m.u.

Solution : Oxygen atom contains 8 protons, 8 neutrons and 8 electrons

Mass of 8 neutrons = 8×1·008665 = 8·069320 a.m.u.

Mass of 8 protons = 8×1·007277 = 8·058216 a.m.u.

Mass of 8 electrons = 8×0·005486 = 0·0043888 a.m.u.

Total mass of 16 nucleons and 8 electrons, M' = 16·1319248 a.m.u.

Actual mass of oxygen atom, M = 15·994910 a.m.u.

Hence, mass defect, $\Delta M = M' - M$ = 0·1370148 a.m.u.

But, 1 a.m.u. ≡ 931·5 MeV of energy

∴ Binding energy of the nucleus = 931·5 MeV/a.m.u.×0·1370148 a.m.u. = 127·62 MeV

∴ **Binding energy per nucleon** $= \dfrac{127{\cdot}62\ \text{MeV}}{16} = 7{\cdot}976\ \textbf{MeV}$

Example 6. Calculate the binding energy per nucleon in helium atom $^{4}_{2}He$ which has a mass of 4·00260 a.m.u. Mass of 1 neutron = 1·008665 a.m.u. and mass of 1 hydrogen atom = 1·007825 a.m.u. Express the result in joules also.

Solution. Helium atom contains 2 protons, 2 electrons and 2 neutrons.

Mass of 1 proton + 1 electron = Mass of 1 hydrogen atom = 1·007825 a.m.u.

Mass of 2 protons + 2 electrons = 2×1·007825 = 2·015650 a.m.u.

Mass of 2 neutrons = 2×1·008665 = 2·017330 a.m.u.

Total mass of 2 neutrons, 2 protons and 2 electrons, M' = 4·0398 a.m.u.

Actual mass of helium atom, M = 4·00260 a.m.u.

Mass defect, $\Delta M = M' - M$ = 4·03298 − 4·00260 = 0·03038 a.m.u.

∴ Binding energy of helium atom = 931·5 MeV/a.m.u.×0·03038 a.m.u. = 28·298 MeV

Binding energy per nucleon = 28·298/4 = **7·0747 MeV**

= 7·0747 MeV×1·602×10^{-13} J/MeV = **11·33×10^{-13} J** (1 MeV = 1·602×10^{-13} J)

Example 7. Calculate packing fraction, mass defect and energy released in the formation of argon atom $^{40}_{18}Ar$. Isotopic mass of Ar = 39·96238 a.m.u.

Solution : Argon atom, evidently, contains 18 protons, 18 electrons (*viz.*, 18 hydrogen atoms) and 22 neutrons.

$$\textbf{Packing Fraction} = \frac{39{\cdot}96238 - 40}{40}\times10^4 = \textbf{−9·4025}$$

$$M' = 18\times1{\cdot}007825 + 22\times1{\cdot}008665 = 40{\cdot}33148 \text{ a.m.u.}$$
$$M = 39{\cdot}96238 \text{ a.m.u.}$$
$$\textbf{Mass defect, } \Delta M = M' - M = \mathbf{0{\cdot}36910 \text{ a.m.u.}}$$
$$\textbf{Energy released} = 0{\cdot}36910 \text{ a.m.u.} \times 931{\cdot}5 \text{ MeV/a.m.u.} = \mathbf{343{\cdot}816 \text{ MeV}}$$

Binding Energies and Stability of Nuclei. Binding energies per nucleon of a number of isotopes are plotted in Fig. 2, against the corresponding mass numbers. It is seen that the *maximum* occurs at about mass number 56 (iron). Thus, nucleus of iron is thermodynamically *most stable*. It is also seen that the points for helium (mass number = 4), carbon (mass number = 12) and oxygen (mass number = 16) lie quite high in the graph. This shows that the nuclei of these elements are *exceptionally* stable. The maximum binding energy per nucleon is seen to be about 8·7 MeV. *This is the energy required to remove a proton or a neutron from a most stable nucleus.*

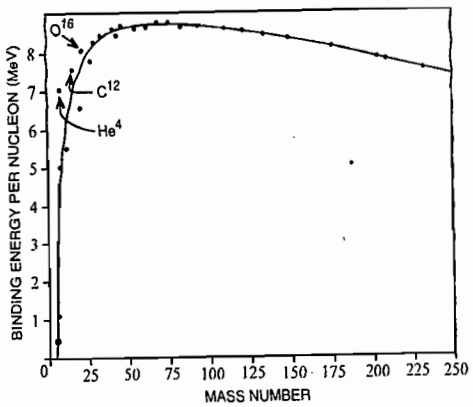


Fig. 2. Mean binding energies of various nuclei.

The graph near the maximum is almost flat from $A = 50$ to about $A = 100$. This shows that the addition of a single nucleon to any nucleus in this region increases the binding energy by roughly the same amount.

The Nuclear Models

Our knowledge about the *nuclear structure* made progress only after the discovery of neutron by James Chadwick in 1932. Two models have been suggested regarding the nuclear structure. These are briefly discussed below.

1. The Nuclear Shell Model

Scientists have been trying to find out if the nucleons also exist in certain energy shells like the electrons. They have also been curious to know if the electronic shell rule of 2, 8, 18, 18, 32 (magic numbers) is applicable for the closing of nuclear shells as well. These ideas have not made much advance. However, there is some evidence to show that nuclei containing certain specific number of protons or neutrons are particularly stable in comparison to their immediate neighbours. Some of the evidence is given below.

1. Helium with mass number 4 (Z=2, N=2, where Z stands for the number of protons and N for the number of neutrons) and oxygen with mass number 16 (Z=8, N=8) are highly stable as is evident from the mean binding energy curve plotted in Fig. 2. We may thus conclude that *the numbers 2 and 8 of neutrons and protons indicate high nuclear stability.*

2. There is a group of *isotones* (*i.e.*, elements having the same number of neutrons) with N=82 (*e.g.*, $^{140}_{58}Ce$ and $^{138}_{56}Ba$) which are highly stable. Another group of isotones with N=20 (*e.g.*, $^{38}_{18}Ar$ and $^{40}_{20}Ca$) and N=50 (*e.g.*, $^{90}_{40}Zr$ and $^{92}_{42}Mo$) are also highly stable. Thus, *neutron numbers 20, 50 and 82 indicate high nuclear stability.*

3. Sn with atomic number 50, *i.e.*, the element with 50 protons (Z = 50), has ten *stable* isotopes. Similarly, Ca with 20 protons (Z = 20) is *highly stable*. This means that the *numbers 20 and 50 whether associated with neutrons or with protons indicate high nuclear stability.*

4. There is a good deal of experimental evidence to show that the numbers, 2, 8, 20, 50, 82 and 126 for either Z or N are associated with higher nuclear stability in comparison to their immediate neighbours. For example, the isotopes with N = 9 (*e.g.*, $^{17}_{8}O$) or 51 (*e.g.*, $^{87}_{36}Kr$) or 83 (*e.g.*, $^{137}_{54}Xe$) emit a neutron each spontaneously to acquire stable configuration with N = 8, 50 and 82, respectively.

5. It has also been found that if some of the important nuclear properties are plotted against Z or N, the graphs show distinct peaks or troughs at numbers 2, 8, 20, 82 and 126. This is similar to what we observe by plotting properties of elements against the corresponding atomic numbers. The above numbers are thus called **magic numbers** *for nuclear shells* and *correspond to closed nuclear shells.*

An attempt has been made to correlate these numbers with the subshell numbers which have been developed in the distribution of electrons in atoms. The magic number 2, for example, can be associated with the occupancy of 2*s* orbital. The magic number 8 may be associated with the occupancy of 2*s* and the three 2*p* orbitals. The magic number 20 corresponds to pairs of nucleons occupying 1*s* orbital, 2*s* orbital, *three* 2*p* orbitals and *five* 3*d* orbitals. The larger magic numbers can also be explained in a similar manner although not so exactly.

2. The Nuclear Liquid Drop Model

The nuclear liquid drop model is statistical in nature and was developed by N. Bohr and J. Wheeler. It treats the nucleus as a homogeneous entity containing a certain number of nucleons, each nucleon being assumed to interact strongly with all its neighbours.

Bohr tried to compare properties of a nucleus with a drop of liquid and found many similarities. Some of these are given below.

1. A liquid drop has a large number of molecules just as a nucleus has a large number of nucleons.

2. Both the liquid drop and the nucleus are *homogeneous* and *incompressible*. The density, charge and other properties are the same throughout the liquid drop and the nucleus except at the surface boundaries. It can be easily visualised that the nuclear volume $\propto$ nuclear mass $\propto A$, where A is the mass number. Thus, it has been found that the nuclear radius $r \propto A^{1/3}$ or $r = R_0 A^{1/3}$ where $R_0 = 1{\cdot}5\times10^{-15}$ m.

3. Comparison of a nucleus with a liquid drop implies that the force between all the nucleons is the same, that is, $f_{n-n} \approx f_{n-p} \approx f_{p-p}$. The nuclear force is thus independent of charge and spin.

4. Heat of vaporisation of a liquid corresponds to binding energy of nucleons in a nucleus.

5. Evaporation of a liquid drop corresponds to radioactive emission from a radioactive isotope.

6. Surface tension in a liquid arises from the fact that surface molecules in a drop are not so tightly bound as are the molecules in the interior. There is evidence to show that this is so in the case of nucleons present in a nucleus as well.

7. In a liquid drop, molecules are influenced only by those which lie in immediate neighbourhood. This means that intermolecular forces are short-range forces only. The same is the case in a nucleus. The nucleon–nucleon forces operate within short ranges only, as has been discussed before.

8. A nucleus may form a *compound nucleus* by capturing a high energy particle from outside, as does a liquid drop, to *get excited*. The excess energy of the captured particle is shared by all the particles of the nucleus or the liquid drop.

9. The compound nucleus or the liquid drop may get *de-excited* by undergoing any of the following changes :

Compound Nucleus	*Liquid Drop*
(*a*) By emission of radiation	(*a*) By cooling
(*b*) By emission of a nucleon	(*b*) By evaporation
(*c*) By nuclear fission	(*c*) By breaking up into droplets

10. Just as *two* liquid drops may undergo *fusion* to give a bigger drop, similarly, two light nuclei may undergo *fusion* to give a bigger nucleus.

Based on these and some other similar ideas, it has been possible to develop an equation for calculating binding energies of different nuclei. *The values obtained are in good agreement with experimental data.* This provides a good evidence in favour of the liquid drop model.

Another evidence in favour of the liquid drop model follows from the ability of the model to *explain nuclear fission*, as will be discussed shortly.

With the help of this model, it is possible to explain why $^{235}_{92}U$ isotope of uranium can undergo fission when bombarded by slow moving neutrons of low energies of about 0·025 eV while $^{238}_{92}U$ isotope requires fast neutrons having high energies of about 1·2 MeV. The absorption of low energy neutron by ^{238}U results in the formation of an excited nucleus which instead of undergoing fission, undergoes β-ray decay to ultimately give plutonium (see the section describing the Plutonium Bomb).

NUCLEAR FISSION

O. Hahn and F. Strassmann observed during 1934–38 that when ^{235}U is bombarded with slow moving thermal neutrons (energy = 0·025 eV), it undergoes fission giving barium as one of the products of fission. In order to explain this observation, L. Meitner and O.R. Frisch suggested that after the capture of a neutron, the uranium nucleus gets excited and then splits into two fragments of approximately equal mass. *The splitting of a heavy nucleus into two smaller fragments of approximately equal mass is known as* **nuclear fission**. There is invariably mass defect during fission, *i.e., the total mass of products of fission is less than the total mass of the neutron and the* ^{235}U *atom. The loss of mass appears in the form of energy* according to Einstein's mass-energy relation, $E = mc^2$. The fission of U^{235} giving barium as one of the products is represented as follows :

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow \underset{\text{(Excited atom)}}{(^{236}_{92}U)} \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n$$

The fission products are, in fact, radioactive themselves. They are rich in neutrons and decay by emitting β particles, or neutrons + γ radiations and ultimately change into stable elements.

An impression may be formed from above that nuclear fission yields only *specific fission fragments* which decay by β-ray or neutron emissions to give stable end products. This is not actually so. There are *no unique products* of a nuclear fission. Nearly 50 modes of fission reactions of ^{235}U are known. What particular fission reaction actually occurs is often a matter of chance. The fission produces fragments with mass numbers ranging from approximately 75 to 150 (roughly from bromine to barium). One fission process yielding barium and krypton has already been referred to above. Another fission process, actually observed, takes place as under :

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{90}_{38}Sr + ^{143}_{54}Xe + 3\,^{1}_{0}n$$

The energy released in one fission reaction is different from the energy released in another fission reaction. The number of neutrons released also varies from one fission reaction to another. But, on an average, approximately 200 MeV energy and 2·5 neutrons are released in the fission of an atom of $^{235}_{92}U$.

Since the intermediate fission products are highly radioactive, their identification has been very difficult. The total number of identified nuclides resulting from uranium fission is about 300. Out of these nearly 200 are β-emitters.

Calculation of Energy Released in Nuclear Fission. The energy released in a fission process can be calculated from the *binding energies* of the nuclei as well as from the *mass defect*. This is illustrated below.

Calculation of energy release from binding energies. As can be seen from the mean binding energy curve plotted in Fig. 2, the binding energy in the case of uranium of mass number 235 lies around 7·6 MeV per nucleon while that in the case of products of fission (*e.g.*, barium and krypton (of mass numbers 141 and 92, respectively) lies close to 8·5 MeV per nucleon. This means that while the formation of uranium nucleus from its nucleons can release 235×7·6 MeV of energy, the formation of nuclei of products of fission can release about 235×8·5 MeV of energy. Hence, *the energy released during the fission of uranium of mass number 235 will be* = 235(8·5 – 7·6) MeV = 211·5 MeV.

Thus, the fission of an atom of ^{235}U releases around 211·5 MeV of energy. Evidently, fission of 1 *mole* of atoms (*i.e.*, Avogadro's number of atoms) of ^{235}U would release around $211{\cdot}5 \times 6{\cdot}022 \times 10^{23}$ MeV of energy. This is equal to $211{\cdot}5 \times 6{\cdot}022 \times 10^{23} \times 1{\cdot}602 \times 10^{-16}$ kJ = $20{\cdot}41 \times 10^{9}$ kJ of energy. In other words, the fission of 235 gram of uranium would release $20{\cdot}41 \times 10^{9}$ kJ of energy. Evidently, the fission of 1 gram of

^{235}U would release $8{\cdot}68 \times 10^{7}$ kJ of energy. *This is a tremendous amount of energy indeed.* It may be recalled that the combustion of 1 gram of carbon releases only 393·48/12 = 32·79 kJ of energy. The energies involved in nuclear reactions are thus several million times greater than those involved in most of the highly thermochemical reactions.

Calculation of energy release from mass defect. The energy released in a fission process can be calculated more accurately from the *mass defect*. This is illustrated by considering once again the fission of $^{235}_{92}U$ (atomic mass 235·044 a.m.u.) by the capture of a neutron.

During this fission, in one of the experiments, the stable fission products obtained ultimately were found to be barium (atomic mass 140·908 a.m.u.) and krypton (atomic mass 91·905 a.m.u.). The nuclear fission reaction is represented as follows :

$$^{235}_{92}U + \underset{\text{neutron}}{^{1}_{0}n} \longrightarrow \underset{\text{stable}}{^{141}_{56}Ba} + \underset{\text{stable}}{^{92}_{36}Kr} + 3\,^{1}_{0}n$$

Taking the mass of neutron as 1·009 a.m.u.,

Total mass of the reactants = 235·044 + 1·009 = 236·053 a.m.u.

Total mass of the products = 91·905 + 140·908 + 3·207 = 235·840 a.m.u.

Mass defect, ΔM = 236·053 a.m.u. – 235·840 a.m.u. = 0·213 a.m.u.

The fission reaction is thus accompanied by a *loss* of mass of 0·213 a.m.u., which is converted into energy.

∴ Energy released = 0·213 a.m.u. × 938·5 MeV/a.m.u. = 191·41 MeV

This value is fairly close to 211·5 MeV calculated from the binding energy curve assuming that the products of fission are barium and krypton.

Otto Hahn won the 1944 Chemistry Nobel prize for the discovery of fission of heavy nuclei accompanied by the release of tremendous amount of energy.

Liquid Drop Model and Threshold Neutron Energy. It has been found that ^{235}U isotope is more readily fissionable than ^{238}U. Thus, while even slow moving neutrons of low energies of the order of 0·025 eV can cause fission of ^{235}U, fast moving neutrons of high energies of the order of 1·2 MeV are needed to cause fission of ^{238}U. One of the reasons for this is that ^{235}U nucleus contains odd number (143) of neutrons while U^{238} nucleus contains even number (146) of neutrons. The higher stability of nuclei containing even number of neutrons or protons or both neutrons and protons, has already been referred to in earlier pages. Bohr and Wheeler used the **liquid drop model** of the nucleus to work out a semi-quantitative equation for calculating *threshold neutron energy* required to cause fission of a given nucleus. The energies thus obtained in the case of ^{235}U and ^{238}U are in fair agreement with the experimental values. This provides an evidence in favour of the liquid drop model of the nucleus.

Liquid Drop Model and Nuclear Fission. The liquid drop model is also capable of explaining the phenomenon of nuclear fission. A liquid drop has a spherical form due to internal molecular forces responsible for surface tension. However, on applying a large external force, the sphere may change into an ellipsoid. If the external force is sufficiently large, the ellipsoid may change into a dumb-bell shape and may even break at the narrow end into two portions.

The analogy may be extended to a nucleus which, according to Bohr-Wheeler theory, behaves like a liquid drop. When a nucleus (behaving as a liquid drop) absorbs a neutron falling on it, it forms a *compound nucleus* which, as already mentioned, is highly energetic. The extra energy possessed by it comes mostly from the binding energy of the neutron absorbed by it. It also comes partly from the kinetic energy of the neutron absorbed but this may not be much if slow moving neutrons are used in the fission process. The extra energy may set up a series of rapid oscillations in the spherical compound nucleus labelled as *A* in Fig. 3. As a result of these oscillations, the shape of the nucleus may change at times from spherical to ellipsoidal, labelled as *B* in the same figure. If the extra energy is large, oscillations may be so violent that stage *C* and ultimately stage *D* may be approached. The nucleus is now dumb-bell

shaped and both parts of the dumb-bell which are not necessarily of equal size carry positive charge. The energy absorbed by the nucleus to change from stage *A* to *D* is the *threshold energy* required for the fission process. The nucleus is now in critical state because once the stage *D* is approached, the final fission into stage *E* is inevitable on account of repulsion between the parts, as shown.

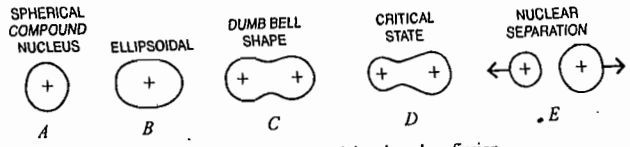


Fig. 3. The liquid drop model and nuclear fission

The Fission Chain Reaction. The Concept of Critical Mass. Nuclear fission is important not only because it is accompanied by the release of enormous amount of energy but also because the nuclear reaction resulting from the capture of a neutron is accompanied by the emission of two or more neutrons (see fission reaction of ^{235}U given above). *The neutrons thus released may cause fission of other nuclei of ^{235}U thereby setting up a* **chain reaction**. Hence, once started, the fission process would be self-sustaining accompanied by a continuous release of energy. But actually this does not happen. The reason is that *all the neutrons produced in a fission process do not remain available for maintaining the fission chain*. A large proportion of the neutrons is lost in *non-fission reactions* involving their capture by ^{238}U as well as by other nuclei that may be present. A sizeable proportion of neutrons *escapes* from the system as such. *As a result, less than one neutron per fission remains and hence the chain reaction cannot be sustained.* This explains why considerable amounts of ^{235}U exist in nature in uranium minerals without undergoing fission in spite of the availability of neutrons.

In order to secure a self-sustaining chain reaction in a fission process, it is essential that the number of neutrons produced in a fission process must be at least equal to the number of neutrons absorbed in both fission and non-fission reactions plus the number of neutrons which escape from the system. This objective is achieved by *increasing the size* of the material undergoing fission. By doing so the ratio of area to volume *decreases* (with increase in size, the increase in surface area is *less* than the increase in volume). Since neutrons are produced throughout the whole volume but their escape occurs only at the surface, hence with the decrease in surface area, the number of neutrons which escape from the system also *decreases*. *The size of the material whose surface permits the escape of neutrons to such an extent that at least one neutron is positively left behind per fission* is known as **critical size** and the corresponding mass of the material is known as **critical mass**. It is evident that if the mass of the fissionable material is less than its critical mass, nuclear fission would not be sustained. The system is then said to be **subcritical**. Fission would be sustained only if the mass is more than the critical mass. The system is then said to be **supercritical**. *For any specific system, the critical mass has always a definite value.*

It is to be noted that fast neutrons are *not captured* by ^{235}U nuclei and hence no fission of ^{235}U would occur no matter how large is the size of the mass of the fissionable material. The neutrons have to be slowed down to render them catchable by the nuclei of ^{235}U. This is done by the use of **moderators**, *i.e.*, the materials which slow down the neutrons. The common moderators are graphite and heavy water.

Modes of Release of Fission Energy. The fission energy can be released:

1. In an Uncontrolled Manner 2. In a Controlled Manner.

1. Uncontrolled Release of Fission Energy. Production of Atom Bomb. In this process, a *subcritical quantity of fissionable material is suddenly made highly supercritical so that approximately two neutrons are available per fission*. This results in a self-sustained chain reaction which accelerates at a tremendous rate so that the entire fissionable material gets exploded within a fraction of a second releasing in the process a huge amount of energy. *Such uncontrolled chain reaction resulting in sudden explosion of the fissionable material forms the basis of the production of the so called* **atom bomb**.

Two procedures are followed for quickly converting a subcritical system of fissionable material to a supercritical system. In the first procedure, *two or more masses of subcritical size are brought together rapidly so as to form a supercritical mass.* The second procedure involves the conversion of the subcritical mass into supercritical one by *compressing the material*. This results in a decrease of surface area without changing the mass. Consequently, the proportion of neutrons which can escape from the system decreases appreciably. A sufficient number of neutrons thus become available to maintain the fission chain.

2. Controlled Release of Fission Energy. In this method, the chain reaction, which is carried out in a device called a **nuclear reactor**, is controlled in such a way that *on an average one neutron is left from each fission to excite further fission*. The chain thus remains steady and within control. Cadmium rods are used to *absorb the excess of neutrons*. The neutrons permitted to cause fission are *slowed down* by passing through a moderator such as graphite or heavy water. *Most of the fission energy is released in the form of heat which can be put to useful purposes.* The fissionable radioactive materials thus serve as an **excellent fuel**. The heat produced is used for driving turbo-generators for *production of electricity*. Nuclear fuels are also used in *marine-propulsion* as, for example, *in warships* and *submarines*.

Nuclear Reactors. Two types of nuclear reactors are in common use. These are : Thermal reactors and Fast breeder reactors.

1. Thermal Reactors. In these reactors the neutrons released during the fission of ^{235}U are made to collide with light nuclei so as to lower their speed. Such a nucleus is called a moderator. Commonly used moderators, as mentioned above, are heavy water and graphite. Most thermal reactors use oxide of ^{235}U as fuel taken in the form of aluminium-plated rods. There is a provision to insert cadmium rods into the reactor to absorb the excess of neutrons in case the rate of the fission reaction becomes very high.

The heat generated in the reactor is removed by circulating a liquid called coolant around the reactor. The coolant is generally an alloy of sodium and potassium metals.The collant pipes are led to a heat exchanger where they are immersed in water which gets converted into steam by the heat of the coolant. The steam is used to run the turbines for the generation of electricity.

A sufficiently thick special concrete structure is built around the reactor to protect the workers from the damaging effects of gamma radiations.

A diagrammatic sketch of the plant is shown in Fig. 4.

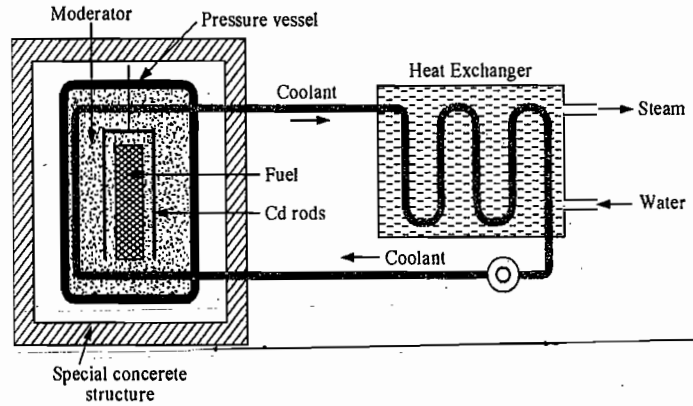


Fig. 4. Diagrammatic sketch of a thermal nuclear reactor.

2. Fast Breeder Reactors. In these reactors, the moderators are not used. The non-fissionable $^{238}_{92}U$ is used as a fuel. The fast neutrons produced in the fission of ^{235}U are used to convert the non-fissionable ^{238}U into fissionable ^{239}Pu, as shown in the next section. The plutonium produced undergoes fission even by slow neutrons. More plutonium is produced than is used in fission, hence the name fast breeder reactor.

The non-fissionable $^{232}_{90}Th$ can also be used as a fuel. Irradiation of this fuel in fast breeder reactors with fast neutrons produces fissionable $^{233}_{92}U$, as shown below:

$$^{232}_{90}Th + ^{1}_{0}n \longrightarrow ^{233}_{91}Pa + ^{0}_{-1}e$$

$$^{233}_{91}Pa \longrightarrow ^{233}_{92}U + ^{0}_{-1}e$$

$^{233}_{92}U$ produced as above can be fissioned as usual by slow neutrons.

In this type of reactor, the coolant is the same as used in thermal reactors. A pressurised water reactor has also been designed in which water under high pressure is used as a coolant.

Disposal of Radioactive Waste from Nuclear Reactors. Radioactive waste is any waste material whose radioactivity exceeds certain limits established by the regulations of the International Commission on Radiation Protection (ICRP). The intention of regulations controlling the release of radioactive waste from nuclear installations is to keep the level of radioactivity in the environment well below the levels recommended by the ICRP.

The radioactive wastes are classified into two types : those of **low activity** and those of **high activity**. For low activity wastes, **shallow burial** is considered adequate. In this technique, the low activity solid waste is buried into the sea beds in coastal areas. For high activity wastes, **deep sea burial** is essential. In this technique holes are drilled into the bottom of the deep sea which are then filled with the solid waste and sealed properly. The water covering the disposal site acts as an additional barrier between waste and human beings. Alternatively, the high activity solid waste which generally consists of waste oxides is fused with additives such as SiO_2, B_2O_3, Al_2O_3, Na_2O and CaO. On solidification, the melt forms a glass with good stability. The glassy material thus obtained is filled in steel containers which are embedded in rocks, rock salt, granite or shale.

Liquid nuclear wastes which consist of aqueous solutions or sludges are disposed off as follows: The volume of the waste is first reduced by evaporation, ion–exchange or flocculation. The residual material is filled in stainless steel containers which are then burried deep under ground.

Some exotic alternatives to get rid of radioactive waste that are occasionally mentioned are the disposal of the waste into the earth's ice caps or into the outer space. It is, however, doubtful if these disposal techniques would be as safe as anticipated.

Plutonium as Fissionable Material. Plutonium Bomb. The liberation of such a tremendous amount of energy as $8{\cdot}68\times10^{7}$ kJ per gram of uranium, places at our disposal a vast source of energy. However, ordinary uranium contains only of about 0·7 per cent of ^{235}U which is fissionable. At the same time, it is extremely difficult to isolate ^{235}U from the other isotopes present in ordinary uranium. It was found that plutonium which does not occur in nature but which can be prepared from the more abundant (99·3%) isotope ^{238}U, undergoes fission readily like ^{235}U.

The preparation of plutonium from uranium involves the following three steps :

$$^{238}_{92}U + ^{1}_{0}n \xrightarrow[\text{by neutron}]{\text{Bombardent}} \underset{\text{(Excited nucleus)}}{^{239}_{92}U}$$

$$^{239}_{92}U \xrightarrow[\text{a } \beta \text{ particle}]{\text{Emission of}} ^{239}_{93}Np + ^{0}_{-1}e$$

$$^{239}_{93}Np \xrightarrow[\text{another } \beta\text{-particle}]{\text{Emission of}} ^{239}_{94}Pu + ^{0}_{-1}e$$

Plutonium, being chemically different from uranium, can be separated relatively easily. It has an additional advantage that its half-life period is quite high close to 24,000 years. The discovery of plutonium solved the problem of release of nuclear energy through nuclear fission. It is estimated that energy released by a gram of plutonium is equal to that released by about 30 tons of T.N.T. This forms the basis of the manufacture of **plutonium bomb**.

Example 8. Why is $^{238}_{92}U$ not suitable for nuclear fission reaction ?

Answer : ^{238}U nuclei do not break up unless the energy of the bombarding neutrons is above 1·2 MeV. Such neutrons are called *fast neutrons*. On the other hand, ^{235}U nuclei of the commonly used fissionable material can be fissioned by slow neutrons, *i.e., thermal neutrons*, possessing as low an energy as 0·025 eV. When bombarded by slow neutrons, ^{238}U does not disintegrate but instead forms an excited isotope, $^{239}_{92}U$, which decays further to give plutonium, as shown above.

Example 9. Estimate the energy released (in MeV) if the fragments of nuclear fission of $^{235}_{92}U$, *viz.*, $^{94}_{38}Sr$ and $^{140}_{54}Xe$, further emit β particles to give $^{94}_{40}Zr$ and $^{140}_{58}Ce$, respectively. Atomic masses of various constituents are given in the text.

Solution : The neutron-induced nuclear fission reaction is

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{94}_{38}Sr + ^{140}_{54}Xe + 2\,^{1}_{0}n$$

Further disintegration reactions are as follows :

$$^{94}_{38}Sr \longrightarrow ^{94}_{40}Zr + 2\,^{0}_{-1}\beta$$

$$^{140}_{54}Xe \longrightarrow ^{140}_{58}Ce + 4\,^{0}_{-1}\beta$$

The overall fission reaction is

$$^{235}_{92}U \longrightarrow ^{94}_{40}Zr + ^{140}_{58}Ce + 6\,^{0}_{-1}\beta + 2\,^{1}_{0}n$$

Mass defect $= \Delta M =$ Masses of reactants – Masses of products

$= 235{\cdot}7437 - [93{\cdot}6061 + 139{\cdot}9053 + 6(0{\cdot}00055) + 2(1{\cdot}00867)] = 0{\cdot}2137$ a.m.u.

$\therefore$ **Energy released** $= 0{\cdot}2137$ a.m.u. $\times$ 931·5 MeV/a.m.u. = **199·06 MeV**

Example 10. A typical neutron-initiated fission of $^{235}_{92}U$ yields $^{97}_{42}Mo$, two neutrons and an isotope of what element ?

Solution : Let the element be $^{A}_{Z}X$.

The fission reaction in this case would be

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{97}_{42}Mo + 2\,^{1}_{0}n + ^{A}_{Z}X$$

$235 + 1 = 97 + 2 + A$, whence $A = 137$

and $92 + 0 = 42 + Z$: whence $Z = 50$

Hence, the element $^{A}_{Z}X$ is $^{137}_{50}Sn$.

Example 11. Calculate the mass of $^{235}_{92}U$ which must undergo nuclear fission to produce the same amount of energy as done by 100 tons of coal. Given that heat of combustion of coal is 8,000 cal g^{-1}, 1 cal = 4 J and fission process of $^{235}_{92}U$ releases 200 MeV of energy per fission (1 ton = 10^6 g).

Solution : Mass of coal = 100 tons = 100 tons$\times10^6$ g/ton = 10^8 g

$\therefore$ Total heat produced in the combustion of coal $= (8{\cdot}000 \text{ cal g}^{-1})(10^8 \text{ g})(4 \text{ J cal}^{-1}) = 3{\cdot}2\times10^{12}$ J

Energy released per fission of $^{235}_{92}U$ = 200 MeV $= (200\times10^6 \text{ eV})(1{\cdot}6\times10^{-19} \text{ J/eV}) = 3{\cdot}2\times10^{-11}$ J

Hence, the number of $^{235}_{92}U$ atoms required to produce the same energy as is done by 100 tons of coal $= 3{\cdot}2\times10^{12} \text{ J}/3{\cdot}2\times10^{-11} \text{ J} = 10^{23}$.

Mass of $6{\cdot}022\times10^{23}$ atoms of uranium = 235 g

$\therefore$ Mass of 10^{23} atoms of uranium $= 235 \text{ g}\times10^{23}/6{\cdot}022\times10^{23} = 39{\cdot}0$ g

Thus, **39 g of ^{235}U** on fission would produce the same amount of energy as is produced by the combustion of **100 tons of coal**.

NUCLEAR FUSION

A reaction in which two lighter nuclei combine to form a heavier nucleus accompanied by release of energy is called **nuclear fusion**. Since the nuclei are charged and repel each other, the fusion can occur only by making one nucleus collide with another highly energetically, that is, the kinetic energy of each nucleus should be kept very high so that it can overcome the repulsive coulombic potential energy barrier between them. Since the

kinetic energy needed to overcome the coulombic repulsion increases rapidly with the atomic number, the lighter the nuclei, the greater the chance for them to approach closely. Thus, hydrogen isotopes are the best candidates for bringing about nuclear fusion.

Let us consider, once again, *the formation of helium* nucleus. The most abundant isotope of helium, ${}^{4}_{2}He$, contains 2 protons and 2 neutrons in the nucleus and 2 electrons outside the nucleus. In other words, it is formed by the combination of two hydrogen atoms (*i.e.*, 2 protons and 2 electrons) and two neutrons. Its atomic mass (M') should be given by

$$M' = 2m_H + 2m_n = 2\times1{\cdot}007825 + 2\times1{\cdot}008665 = 4{\cdot}03298 \text{ a.m.u.}$$

Actual mass of helium atom (M) on the same scale is 4·00260 a.m.u.

$\therefore$ Mass defect, $\Delta M = M' - M = 4{\cdot}03298 - 4{\cdot}00260 = 0{\cdot}03038$ a.m.u.

$\therefore$ Energy released in the formation of helium nucleus $= 0{\cdot}03038 \text{a.m.u} \times 931{\cdot}5$ MeV/a.m.u.

Hence, energy released in the formation of 1 mole of helium nuclei

$$= 0{\cdot}03038\times931{\cdot}5\times6{\cdot}022\times10^{23} \text{ MeV} = 27{\cdot}30\times10^{8} \text{ kJ} \qquad (\because 1 \text{ MeV} = 1{\cdot}602\times10^{-16} \text{ kJ})$$

Thus, as enormous amount of energy is released during the formation of a heavier nucleus from lighter nuclie on account of the mass defect.

Nuclear fusion can also take place by allowing highly accelerated protons and deuterons, etc., to fall on nuclei of lighter elements. Such processes, however, occur at reasonable rates only *at very high temperatures, of the order of a million degree centigrade.* These processes are, therefore, called **thermonuclear reactions**. Once a fusion reaction is initiated, the energy released is sufficient to maintain the temperature and to keep the process going.

Controlled Nuclear Fusion. The major problem in a nuclear fusion reaction is the attainment of a high temperature ($\sim 10^7$ K) required for the purpose. So far attempts to maintain such a high temperature have been successful for only a very small fraction of a second, the reason being that all known containers would vaporize at such a high temperature. At this temperature the atoms become fully ionized and the ions (*i.e.*, nuclei and electrons) form the **plasma state** in which the particles move about independently but in the form of interpenetrating gases. The plasma is electrically neutral.

Nevertheless, the high temperature needed for fusion has, indeed, been produced by passing a very intense electric current (of the order of a million amperes) through deuterium gas contained in a tube at low pressure. The high temperature generated creates the plasma, concentrating it in a narrow beam, known as the *pinch effect.* This effect can be compared to that between two parallel wires carrying a current in the same direction where the parallel current streams forming the discharge attract each other, thereby pinching the discharge into a narrow beam. A magnetic field is used to keep the discharge in the centre of the tube. This is called the *magnetic bottle* which has a doughnut shape. So far attempts to maintain the pinched discharge for more than a fraction of a second have failed. The extremely high magnetic fields required are obtained with electromagnets using a superconducting niobium/tantalum alloy cooled in liquid helium to about 4 K. Inertial confinement involves the rapid collapse of the container to make the fuel so dense that the fusion reactions occur.

Nuclear Fusion in the Sun's Atmosphere

The **energy of the sun** is supposed to arise from the fusion of nuclei of hydrogen present in the atmosphere of the sun to give helium nuclei by the following thermonuclear fusion reactions :

$$(i)\ {}^{1}_{1}H + {}^{1}_{1}H \longrightarrow \underset{\text{Deuteron}}{{}^{2}_{1}H} + \underset{\text{Positron}}{{}^{0}_{+1}e} + \text{Energy}$$

$$(ii)\ {}^{2}_{1}H + {}^{1}_{1}H \longrightarrow \underset{\text{Isotope of helium}}{{}^{3}_{2}He} + \text{Energy}$$

$$(iii)\ {}^{3}_{2}He + {}^{3}_{2}He \longrightarrow \underset{\text{Helium}}{{}^{4}_{2}He} + 2\,{}^{1}_{1}H + \text{Energy}$$

In order to obtain *two* nuclei of the isotope ${}^{3}_{2}He$ of helium required for stage (*iii*), the first two processes must occur twice. Thus, 6 hydrogen nuclei are used in all, four in stage (*i*) and two in stage (*ii*), to get one nucleus of ${}^{4}_{2}He$ in stage (*iii*), But, since two hydrogen nuclei (${}^{1}_{1}H$) are regenerated in stage (*iii*), the net result is the combination of four hydrogen nuclei to give one nucleus of ${}^{4}_{2}He$ alongwith two positrons. The overall reaction, therefore, may be written as

$$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,\underset{\text{Positron}}{{}^{0}_{+1}e}$$

Knowing the masses of hydrogen and helium nuclei and that of the positron (which is the same as that of the electron), the energy released in the process can be calculated. It has been found that in the formation of one mole of ${}^{4}_{2}He$ nuclei from four moles of ${}^{1}_{1}H$ nuclei, as represented above, $27{\cdot}3\times10^{8}$ kJ of energy is released. In other words, the energy released per gram of hydrogen consumed will be $27{\cdot}3\times10^{8}/(4\times1{\cdot}0078) \approx 6{\cdot}77\times10^{8}$ kJ which is, again, a tremendous quantity

It may be noted that the conversion of hydrogen into helium, which is the source of solar energy, is so slow even at such a high temperature as that of the sun that it takes several million years for the conversion of 1 gram of hydrogen into helium. The reason why the sun is capable of producing energy at a high rate lies in its enormous size.

Hydrogen Bomb. The thermonuclear reactions among nuclei of hydrogen isotopes, deuterium and tritium, can serve as possible sources of energy, provided the temperature is very high. These reactions may be represented as

$$\underbrace{{}^{2}_{1}D + {}^{2}_{1}D}_{\text{(Deuterium)}} \longrightarrow {}^{3}_{2}He + {}^{1}_{0}n + \text{Energy} = 3{\cdot}2 \text{ MeV}$$

$${}^{2}_{1}D + {}^{2}_{1}D \longrightarrow \underset{\text{(Tritium)}}{{}^{3}_{1}T} + {}^{1}_{1}H + \text{Energy} = 4{\cdot}0 \text{ MeV}$$

$${}^{2}_{1}D + {}^{3}_{1}T \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + \text{Energy} = 17{\cdot}6 \text{ MeV}$$

These fusion processes are responsible for the release of a tremendous amount of energy in the form popularly known as a **hydrogen bomb**. However, the above nuclear reactions can take place only at very high temperatures. It is necessary, therefore, to have an external source of energy to provide an atmosphere surcharged with the required high temperatures. In the preparation of a ***hydrogen bomb***, therefore, a suitable quantity of deuterium or tritium or a mixture of both, is combined with an atom bomb, *i.e.*, a bomb of nuclear fission type. The function of the atom bomb here is to provide an atmosphere of the required high temperature.

A hydrogen bomb is far more powerful than an atom bomb due to rapid release of tremendous amounts of energy in the nuclear reactions amongst the isotopes of hydrogen. If it were possible to have sufficiently high temperatures, the deuterium present in sea (as D_2O) should be sufficient to provide all energy requirements of the world for millions of years.

Nuclear Reactions

Nuclear reactions differ from chemical reactions in several ways. Chemical reactions involve rearrangements of outermost electrons of atoms but the nuclei remain unaffected. Thus, there is no change in the atomic species taking part in the reactions. Nuclear reactions involve changes in the number of nucleons present in the nucleus. There is, therefore, formation of new atomic species. Thus, nuclear reactions *lead to atomic transformations* or *transmutations*.

Another notable difference lies in the amounts of energy released in the two types of reactions. As has been discussed before and will also be shown shortly, nuclear reactions involve energies a million times greater than those involved in chemical reactions. The reason is that a nuclear reaction, unlike a chemical reaction, involves a small but measurable *loss in mass*. This mass is transformed into energy in accordance with Einstien's equation.

Nuclear reactions may be divided into two broad categories :

A. Those in which *the nucleus undergoes a spontaneous change, i.e.,* a change by itself. These reactions are covered under the general title of **radioactivity.**

B. Those in which *the reaction is brought about artificially through the interaction of two nuclei.* This is done by bombarding a relatively heavier nucleus with a lighter nucleus. The lighter nucleus is commonly a nucleus of protium, deuterium or helium (alpha particle). Such reactions are covered under the general title of **artificial radioactivity.**

The products in a nuclear reaction are generally a heavy nucleus and one of the particles which may be an electron, a proton, a deuteron, a neutron or an alpha particle or merely a γ-ray photon. The heavy nucleus may or may not be stable. If it is stable, no more radioactivity is observed. But if it is unstable, it may itself start disintegrating like the natural radioactive elements. This type of artificial radioactivity is called **induced radioactivity.**

Another important type of nuclear reaction is that in which a heavy nucleus is rendered unstable by the addition of a neutron and which breaks down into two parts of comparable size. At the same time several neutrons are also emitted. This phenomenon is known as **nuclear fission**, which has already been discussed in details in earlier pages.

Radioactivity and *Artificial Radioactivity* have been discussed below in some details.

RADIOACTVITY

The French physicist, Henry Becquerel, in 1895, a year after the discovery of X-rays, observed that a photographic plate, wrapped in a thick black paper, which had been placed, by chance, in the same drawer which contained certain uranium salts, had become affected or fogged. Becquerel concluded that uranium salts emitted certain rays which had penetrating properties similar to X-rays. He found soon after that these rays also cause ionization of air. He called these rays as radioactive rays and the property of giving out these rays as **radioactivity.**

A year later, Marie Curie and her husband, Pierre Curie, discovered the element **polonium** which was many times more radioactive than uranium. Two years later, they discovered another element **radium.** This element was found to be three million times more radioactive than uranium. Shortly afterwards, G.C. Schmidt and M. Curie independently discovered that **thorium compounds** were also radioactive. Since then, a large number of radioactive substances have been discovered. In fact, it is now known that elements having atomic number greater than 83 are all radioactive. The nuclei of these elements are unstable and decompose or disintegrate spontaneously with the emission of radioactive radiations.

Rate of Radioactive Disintegration. If N_0 is the number of atoms of a radioactive substance at any given time and N is the number of atoms of the substance after time t, then the rate of disintegration of the radioactive substance would be given by

$$dN/dt = \lambda N \qquad \ldots (2)$$

where λ is a constant called the **disintegration constant** of the element.

Simple integration of Eq. 2 yields the expression

$$N = N_0 e^{-\lambda t} \qquad \ldots (3)$$

The rate of radioactive disintegration is independent of temperature and pressure, in fact, of any external conditions. A simple law giving the rate of radioactive disintegration was discovered by Rutherford. It states : *A certain constant fraction of any sample of a radioactive element undergoes disintegration in a unit time.* This means that the number of atoms which disintegrate in a unit time is a constant fraction of the total number of atoms present. As the total amount of the radioactive element goes on decreasing with time, the amount which disintegrates in a unit time also goes on decreasing. For instance, suppose half the actual amount of a radioactive element disintegrates per day. If we start with 1 *g* of this substance, only 0·5 *g* will be left at the end of the first day. At the end of the second day, half of 0·5 *g*, *i.e.*, 0·25 *g* will be left, and so on. This goes on infinitely. The radioactive substance never disintegrates *completely* although its actual amount may become too small to be measured.

Suppose, after time $t_{1/2}$, half of the atoms of the radioactive substance have disintegrated, that is, $N = N_0/2$. Substituting in Eq. 3, we have

$$1/2 = e^{-\lambda t_{1/2}} \qquad \ldots (4)$$

or

$$\ln 0{\cdot}5 = -\lambda t_{1/2}$$

$$\therefore \quad t_{1/2} = 0{\cdot}6931/\lambda = \text{constant} \qquad \ldots (5)$$

The time ($t_{1/2}$) required for the disintegration of one half of the original amount of the radioactive substance, is called its **half-life period.** Evidently, half-life period of a given radioactive substance is independent of the amount of the substance present initially. It depends only on the disintegration constant (λ) of the element. The value is *constant* for each radioactive element and it is thus possible to *characterise each element* by this value. The half-life period of radium, for example, is 1580 years. The half-life periods of some of the radioactive elements are, however, a few seconds only.

Unit of radioactivity. The unit of radioactivity, called **curie (ci)**, is defined as that amount of a radioactive substance which has a decay rate of $3{\cdot}7\times10^{10}$ disintegrations per second. This large number is based on the observation that 1 gram of radium disintegrates at the rate of $3{\cdot}7\times10^{10}$ disintegrations per second. Now, smaller units, *viz.*, **millicurie (mci)** and **microcurie (μci)** are often used.

$$1\ mci = \text{Mass which gives } 3{\cdot}7\times10^{7} \text{ disintegrations s}^{-1}$$

$$1\ \mu ci = \text{Mass which gives } 3{\cdot}7\times10^{4} \text{ disintegrations s}^{-1}$$

Example 12. Half-life of radium (molar mass 226 g mol^{-1}) is 1580 years. Show that 1 gram of radium gives $3{\cdot}70\times10^{10}$ disintegrations per second.

Solution : According to Eq. 5, $t_{1/2} = 0{\cdot}6931/\lambda$

$$\therefore \quad \lambda = \frac{0{\cdot}6931}{1580\times365\times24\times60\times60\ \text{s}} = 1{\cdot}391\times10^{-11}\ \text{s}^{-1}$$

According to Eq. 2,

$$-\frac{dN}{dt} = \lambda N = \frac{1{\cdot}391\times10^{-11}\ \text{s}^{-1}\times6{\cdot}022\times10^{23}\ \text{mol}^{-1}}{226\ \text{g mol}^{-1}}$$

$$= \mathbf{3{\cdot}70\times10^{10}\ disintegrations\ s^{-1}\ g^{-1}}$$

Example 13. The half-life of the nuclide ^{220}Rn is 54·5 s. What mass of this nucleus is equivalent to 1 millicurie (mci) ?

Solution : From Eq. 5, $\lambda = 0{\cdot}6931/t_{1/2} = 0{\cdot}6931/(54{\cdot}5\ \text{s}) = 1{\cdot}27\times10^{-2}\ \text{s}^{-1}$

$$1\ \text{mci} = \text{Mass which gives } 3{\cdot}7\times10^{7} \text{ disintegrations s}^{-1} = -dN/dt$$

Since $-dN/dt = \lambda N$ (Eq. 2)

$$\therefore \quad N = \frac{-dN/dt}{\lambda} = \frac{3{\cdot}7\times10^{7}\ \text{s}^{-1}}{1{\cdot}27\times10^{-2}\ \text{s}^{-1}} = 2{\cdot}91\times10^{9}$$

This value for ^{220}Rn can be converted into mass as follows :

$$\text{Mass of nucleus} = \frac{2{\cdot}91\times10^{9}\times220\ \text{g mol}^{-1}}{(6{\cdot}022\times10^{23}\ \text{mol}^{-1})} = \mathbf{1{\cdot}06\times10^{-12}\ g = 1{\cdot}06\times10^{-15}\ kg}$$

Nature of Radiations From Radioactive Elements. The nature of radiations emitted by radioactive elements was investigated by Rutherford in 1904. He established that these elements emit *three types* of radiations designated as *alpha*, *beta* and *gamma rays.*

Alpha rays are not rays but consist of material particles called **alpha particles** which carry *two units of positive charge and are four times as heavy as hydrogen atom*, that is, they are mere nuclei of helium atoms. These particles move with a very high velocity of over *15000* km s^{-1} and ionise the gas through which they pass. They cause luminescence on striking a zinc sulphide plate.

Beta rays are also not rays but consist of negatively charged material particles called **beta particles.** These particles move much faster than the alpha particles, their velocity being *160,000* to *240,000* km s^{-1}. They cause ionization of air but, being lighter than alpha particles, their effect is much less. Due to the same reason, they have very little effect on zinc sulphide plate. Beta particles, being lighter and faster, are nearly 100 times more penetrating than the alpha particles.

Gamma rays are *secondary effects of atomic disintegration*. Their origin is explained as follows : After the emission of an α or a β particle, the nucleus left behind is in an *excited state, i.e.,* in a state of higher energy. *The excess energy is released in the form of a photon of γ radiation.* Thus, *γ-rays arise from energy-rearrangements within the nucleus after the emission of an α or a β particle.* They are similar to X-rays and light rays but have extremely small wave lengths of the order of 10^{-10} to 10^{-13} m. Gamma rays have the shortest wave lengths except for cosmic rays. They have an extremely high penetrating power, even greater than that of X-rays. They can pass through 0·15 m of steel. They cause ionization of air but in an indirect manner. What happens is that as a result of the impact of a γ-photon, an extra nuclear electron is ejected from an atom of the radioactive substance. This electron, being associated with very high energy, behaves like a β particle which causes ionization of the air through which it passes. Gamma rays are harmful to living tissues.

Detection and Measurement of Radioactivity. The radioactivity of a substance can be detected and even measured by the ionization of gases caused by alpha and beta particles and also indirectly by gamma rays. The following instruments are used for the purpose.

The Geiger-Muller Counter. This instrument consists of a copper cylinder closed with a thin mica window at one end. In the middle of the cylinder, but insulated from it, is a tungsten wire which acts as the anode and is kept at a potential of about 1500 volts. The cylinder is filled with an inert gas (such as argon) and alcohol vapour at a pressure of about 10 mm of mercury. The radioactive substance is placed outside the tube close to the window. As a single alpha or beta particle (or gamma ray photon) enters the tube, it causes ionization of the gaseous molecules. A momentary flow of current occurs which is amplified. The current causes a flash of light in a neon tube and a unit movement over a mechanical register.

The Wilson Cloud Chamber. This instrument consists of a chamber with a glass window and is closed by a piston which can be moved up or down. It is filled with dust-free air and water vapour at saturation pressure. When the piston is moved up so as to reduce the pressure within, the air expands. This causes cooling and condensation of water vapour in the form of extremely minute droplets. If the alpha or beta particles from a radioactive source enter the chamber at this stage through the window, the water droplets condense on them and the path can be photographed. This leads to the detection of these particles.

Radioactive Tracers

A number of radioactive isotopes prepared by specialised techniques involving induced radioactivity are used in tracing various processes in surgery, medicine, biology, agriculture, industry and chemistry. In this technique, which is known as **tracer technique**, a radioactive isotope or one of its compounds is introduced at one part of a system and its movement is then traced by measuring radioactivity in different parts of the system. Such isotopes or their compounds are known as **radioactive tracers**. In **surgery**, for example, in order to find out if blood is circulating to a wound or not, a radioactive isotope is injected into the body and after a suitable time the blood from the wound is examined for its radioactivity by means of a Geiger-Muller counter. Similarly, phosphate containing radioactive isotope of phosphorus (^{34}P) is administered to patients suffering from bone fracture to check if phosphorus is being absorbed by the bone or not.

In **agriculture**, calcium phosphate containing radioactive phosphorus is generally used to trace the uptake of phosphorus by plants.

In **industry**, metal castings are tested for cracks by putting them in radioactive salt baths. The castings are inspected afterwards for radioactivity to find out if penetration of the salt into the cracks has taken place or not. Absence of salt-penetration obviously indicates absence of cracks.

The **solubility of a sparingly soluble salt** like lead sulphate may be determined by mixing a *known amount* of radioactive lead with ordinary lead in a *known proportion*, converting it into lead nitrate by dissolving in nitric acid and then precipitating it as lead sulphate by the addition of dilute sulphuric acid. After filtration, the amount of lead sulphate present in solution is obtained by measuring radioactivity of the solution. This, of course, gives only the amount of radioactive lead sulphate in the given solution.

Knowing the proportion in which the two varieties of lead were taken originally, the amount of *ordinary* lead sulphate in the solution can be easily calculated. The sum of the two gives the total lead sulphate present in the solution.

Rock Dating. The Age of the Earth

We know that the ultimate product of disintegration of uranium is stable lead of mass number 206. By the use of a mass spectrograph, it is possible to determine the ratio of the amount of uranium to that of lead in a given rock. Knowing the *overall rate of disintegration of uranium to lead*, it is possible to calculate the age of the mineral, that is, the time for which its disintegration has been going on. This gives an approximate idea of the age of the earth. The assumption implied is that the mineral under examination is as old as the earth. However, as there are reason to believe that the mineral might have originated a little later than the earth, the age obtained by this method is somewhat on the lower side. The age of the earth calculated by this method is, therefore, regarded as the minimum age of the earth. It comes out to be 2–3 billion years. This figure is close to that obtained by geologists from the age of rocks, meteorites and the amount of salt in the sea.

Carbon Dating

Willard F. Libby won the Nobel prize for developing a highly ingenious technique of **radio carbon dating**. Carbon has three important isotopes of mass numbers 12, 13 and 14, *i.e.,* $^{12}_{6}C$, $^{13}_{6}C$ and $^{14}_{6}C$. The first one (^{12}C) is the most common having terrestrial abundance of 98·99 per cent. The last one (^{14}C) is formed only in traces in the atmosphere by cosmic neutron bombardment of nitrogen as

(*i*) $$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

$^{14}_{6}C$ is radioactive. Its half-life period is 5568 years. It undergoes β-ray decay according to the reaction

(*ii*) $$^{14}_{6}C \longrightarrow ^{14}_{7}N + \beta\text{ particle}$$

As a result of the above two nuclear reactions, the quantity of ^{14}C as well as that of $^{14}CO_2$ present in the atmosphere has been constant over a long period of years. This carbon dioxide (alongwith the most common $^{12}CO_2$) is consumed by plants and, in turn, by animals. The concentration of ^{14}C in all living organisms, therefore, remains almost constant during their life-time. But when they die they are no longer in a position to take up carbon dioxide from the atmosphere. The ^{14}C content which the plant or the animal body had assimilated during its life time, now begins to decay by emitting β particles, as shown in equation (*ii*) above, with half-life period of 5568 years. The decay rate, *i.e.,* the number of β-ray disintegrations (N_0) just at the time of the death of the plant, etc. is 16·1±0·3 counts per minute per gram of carbon. By carefully measuring the decay rate of a sample of the dead matter (wood, peat, fossil, etc.) at any period later on, it is possible to tell when the living body had died.

Suppose the decay rate of a sample of wood is found to be N disintegrations per minute per gram of the sample, say, after t years. Then,

$$N = N_0 e^{-\lambda t} \qquad \text{(Eq. 3)}$$

where λ is the disintegration constant and N_0, as already mentioned, is the number of disintegrations per minute per gram when the plant had just died. Taking logarithms,

$$\ln N = \ln N_0 - \lambda t \qquad \ldots(6)$$

But $$\lambda = 0{\cdot}6931/t_{1/2} \qquad \text{(Eq. 5)}$$

Knowing that half-life period of ^{14}C is 5568 years, the value of λ and hence of t, *i.e.,* the life of the specimen, can easily be calculated.

Example 14. A freshly cut piece of wood gives 16100 counts of β-ray emission per minute per kg and an old wooden bowl gives 13200 counts per minute per kg. Calculate the age of the wooden bowl. The half-life period of ^{14}C is 5568 years.

Solution : The decay rate is given by the equation $N = N_0 e^{-\lambda t}$.

In the present case : $N = 13200$, $N_0 = 16100$

$$\lambda = 0{\cdot}6931/t_{1/2} = 0{\cdot}06931/5568 \qquad \text{(Eq. 5)}$$

$$\ln N = \ln N_0 - (0{\cdot}6931/5568)\, t$$

or $$\ln N/N_0 = -(0{\cdot}6931/5568)\, t$$

$\therefore$ Age of the bowl, t = **1576·3 years**

ARTIFICIAL RADIOACTIVITY

A. Artificial Transmutation of Elements

The transmutation or transformation of one element into another as a result of natural disintegration of some of the elements described above, led some workers including Rutherford, Irene Curie and F. Joliot to explore the possibility of **artificial transmutation of elements,** that is, *the conversion of one element into another by artificial means*. The ambition of alchemists in all their pursuits had been to transform a base metal like lead into a noble metal like gold. The physicists and chemists have succeeded in recent years to change one element into another, although not necessarily in any appreciable quantities.

It all started in 1919, twenty years after the discovery of radioactivity, when Rutherford (who had already made such remarkable discoveries in the field of natural radioactivity) thought of bombarding the nucleus of nitrogen with alpha particles and obtained traces of oxygen. It was thus for the first time in history that one element had been obtained from another, that is, artificial transmutation had been achieved. The change may be represented as

$$\underset{}{^{14}_{7}N} + \underset{\text{Alpha particle}}{^{4}_{2}He} \longrightarrow \underset{\text{Oxygen isotope}}{^{17}_{8}O} + \underset{\text{Proton}}{^{1}_{1}H}$$

The $^{17}_{8}O$ nucleus formed as above is stable.

Thus, nitrogen was changed into an isotope of oxygen by alpha particle bombardment.

Since then, numerous other transmutations have been studied and several new radioactive isotopes have been produced by bombardment of different elements by alpha particles.

But it may be noted that this reaction takes place only when an alpha particle makes a head-on collision with a nitrogen nucleus. This may occur only by one particle out of a million. Transmutation, therefore, takes place only in traces.

As stated earlier, Chadwick discovered the sub-atomic particle *neutron* by the bombardment of beryllium with alpha particles.

$$\underset{\text{Beryllium}}{^{9}_{4}Be} + \underset{\text{Alpha particle}}{^{4}_{2}He} \longrightarrow \underset{\text{Carbon}}{^{12}_{6}C} + \underset{\text{Neutron}}{^{1}_{0}n}$$

The neutrons have proved far more useful than alpha particles in the study of artificial transmutations because while the alpha particles, being positively charged, are repelled by the positive nucleus, the neutrons, being neutral, remain unaffected. Thus, certain transmutations which were impossible previously, have been achieved since the discovery of neutrons.

Since alpha particles carry double positive charge, they are not good projectiles or 'bullets' for the purpose of bombardment because they are repelled by the positively charged nucleus. Hardly one alpha particle in a million may hit the nucleus. Protons and deuterons which carry single positive charge are much better projectiles than alpha particles. However, these are not as good as neutrons which carry no charge at all.

Some examples of transmutations by deuterons and neutrons are given below :

Transmutation by Deuterons

$$\underset{\substack{\text{Isotope of lithium}\\ \text{(Mass No. 6)}}}{^{6}_{3}Li} + {^{2}_{1}H} \longrightarrow \underset{\substack{\text{Isotope of lithium}\\ \text{(Mass No. 7)}}}{^{7}_{3}Li} + \underset{\text{Proton}}{^{1}_{1}H}$$

Transmutation by Neutrons

$$^{14}_{7}N + {^{1}_{0}n} \longrightarrow {^{11}_{5}B} + {^{4}_{2}He}$$

$$^{27}_{13}Al + {^{1}_{0}n} \longrightarrow {^{27}_{12}Mg} + {^{1}_{1}H}$$

$$^{23}_{11}Na + {^{1}_{0}n} \longrightarrow {^{24}_{11}Na} + \gamma \text{ rays.}$$

Cyclotron. Alpha particles, protons and deuterons can be made much more effective if they are imparted with high velocity. Several instruments have been developed for accelerating these particles. The most effective apparatus developed by E.O. Lawrence is known as **cyclotron.** In its common form it consists of two flat semicircular boxes, called **dees** (because of their D-like shape), marked D_1 and D_2 in Fig. 5(*a*). These are surrounded by a vessel containing hydrogen, helium or deuterium gas at low pressure. This vessel is placed between the poles of an electromagnet as shown in Fig. 5(*b*). A high frequency alternating potential of several million cycles per second is applied across D_1 and D_2. Positive ions are produced at *A* by the bombardment of hydrogen, helium or deuterium by electrons. Suppose, at a particular instant, the direction of the applied potential is such that D_1 *is positive* and D_2 *is negative.* A positive ion starting from *A* would move into D_2 following a semicircular path due to its deflection caused by the magnetic field. When the ion reaches the gap between D_1 and D_2, it gets exposed to the influence of the applied potential. If the oscillation frequency is such that during the time the positive ion passes through the dee D_2, the sign of the potential is reversed, *i.e.,* D_1 *becomes negative* and D_2 *becomes positive,* the ion would get accelerated towards D_1. The ion now moves faster than before and, therefore, the radius of its path increases. However, the time taken by the ion to traverse the dee remains the same because the increased path is exactly compensated by the increased speed of the ion. This means that *if the oscillation frequency is properly adjusted, the ion would always remain in phase with the changing potential between the dees.* Consequently, each time the ion crosses the gap from D_1 to D_2 it would be accelerated towards D_2 and when it crosses from D_2 to D_1, it would be accelerated towards D_1. As a result of these repeated impulses, the radius of the spiral path of the ion steadily increases and so does its energy. Finally, the ion possessing an energy as high as several hundred million electron volts and velocity as high as 40,000 km s^{-1}, emerges out of the exit *E* of the instrument.

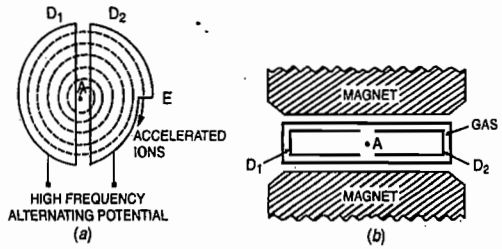


Fig. 5. Diagrammatic sketch of cyclotron with two dees.

B. Induced Radioactivity

In 1934, Frederic Juliot and Irene Curie (son-in-law and daughter of Marie Curie) found that certain light elements such as aluminium, boron and magnesium, when bombarded with alpha particles, change into radioactive isotopes of other elements. These isotopes disintegrate in the same way as the naturally occurring radioactive elements like uranium, radium, etc.

Thus, **induced** or **artificial radioactivity** is a *process by which a new radioactive isotope of a known element can be prepared.*

In the case of magnesium, for instance, the change may be represented as under :

$$^{27}_{12}Mg + {^{4}_{2}He} \longrightarrow \underset{\text{Radioactive}}{^{27}_{14}Si} + {^{1}_{0}n}$$

The silicon produced is radioactive and disintegrates as

$$^{27}_{14}Si \longrightarrow {^{27}_{13}Al} + \underset{\text{Positron}}{^{0}_{+1}e}$$

This was how positron, a counterpart of electron, having a unit positive charge but negligible mass, was first discovered. The artificially prepared radioactive isotopes emit usually either electrons or positrons during their disintegrations.

The bombardment of boron with alpha particles yields a radioactive isotope of nitrogen with mass number 13. It has a short half-life period and disintegrates, as represented below :

$$^{10}_{5}B + ^{4}_{2}He \longrightarrow \underset{\text{(Radioactive)}}{^{13}_{7}N} + ^{1}_{0}n$$

$$^{13}_{7}N \longrightarrow \underset{\text{Stable isotope of carbon}}{^{13}_{6}C} + \underset{\text{Positron}}{^{0}_{+1}e}$$

Preparation of Transuranic Elements. It was found by Seaborg at the University of California that when uranium is bombarded with neutrons of a *certain critical velocity*, one neutron is captured per atom of uranium giving rise to an element of a higher mass number.

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + \gamma \text{ rays}$$

This new isotope of uranium is much more radioactive than the natural uranium. It emits a beta particle and gives a new element of atomic number 93 which does not occur in nature. This element was named neptunium (Np).

$$^{239}_{92}U \longrightarrow ^{239}_{93}Np + ^{0}_{-1}e$$

Neptunium is also radioactive and emits a beta particle giving another new element of atomic number 94, known as plutonium (Pu).

$$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + ^{0}_{-1}e$$

Plutonium (half-life period about 24000 years) is much more stable than ^{239}U (half-life period 23 minutes) and ^{239}Np (half-life period 2·6 days). However, it undergoes a further beta-ray change. In this way, by appropriate nuclear reactions, elements of atomic numbers 95 (americium), 96 (curium), 97 (berkelium), 98 (californium), 99 (einsteinium), 100 (fermium), 101 (mendelevium), 102 (nobelium), 103 (lawrencium), 104 (kurchatovium) and 105 (hahnium) have been prepared artificially. Three more elements of atomic numbers 106, 107 and 108 are also reported to have been discovered. The transuranic elements with atomic numbers beyond 100 are now named according to the IUPAC convention, as already described in Chapter 2.

Q* Values of Nuclear Reactions.** The complete equation for a nuclear reaction should include *the energy change of the reaction* as well. This is usually denoted by ***Q. Thus, the complete equation for Rutherford's transmutation reaction described earlier should be

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H + Q$$

Q is called the *nuclear reaction energy*.

The value of Q may be *positive* when the reaction is said to be **exoergic** or *negative* when the reaction is said to be **endoergic**.

The value of Q for the above reaction can be calculated from the masses of the reactants and products. Thus,

Sum of masses of reactants = 14·0031 + 4·0026 = 18·0057 a.m.u.

Sum of masses of products = 16·9991 + 1·0078 = 18·0069 a.m.u.

$\therefore$ ΔM = Masses of products – Masses of reactants

= 18·0069 – 18·0057 = + 0·0012 a.m.u.

The reaction, evidently, involves *increase of mass* by 0·0012 a.m.u. An equivalent amount of energy is, therefore, *absorbed* in this case. Hence, the Q value, by convention, is *negative*.

Since 1 a.m.u. ≡ 931·5 MeV of energy

$\therefore$ Q = – 0·0012 a.m.u. × 931·5 MeV/a.m.u. = – 1·118 MeV

The reaction is, evidently, *endoergic*.

Example 15. Calculate Q value of the following nuclear reaction :

$$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{14}Si + ^{1}_{1}H + Q$$

The exact mass of $^{27}_{13}Al$ isotope may be taken as 26·9815 a.m.u. and that of $^{30}_{14}Si$ as 29·9738 a.m.u.

Solution :

Sum of the masses of reactants = 26·9815 + 4·0026 = 30·9841 a.m.u.

Sum of the masses of products = 29·9738 + 1·0078 = 30·9816 a.m.u.

ΔM = Masses of the products – Masses of the reactants

= 30·9816 – 30·9841 = – 0·0025 a.m.u.

The reaction evidently involves *decrease* of mass and hence *release of energy*. The Q value is, therefore, *positive*.

Q = + 0·0025 a.m.u. × 931·5 MeV/a.m.u. = **2·329 MeV**

The Q values for most of the nuclear reactions are within 10 MeV. But in the reaction

$$^{6}_{3}Li + ^{2}_{1}H \longrightarrow 2\,^{4}_{2}He$$

the value is quite high, as shown below :

Sum of the masses of reactants = 7·01601 + 1·00783 = 8·02384 a.m.u.

Mass of the product = 2×4·00260 = 8·00520 a.m.u.

$\therefore$ ΔM = Mass of the product – Masses of the reactants = 8·00520 – 8·02384 = – 0·01864 a.m.u.

There is a decrease of mass and hence the energy is *released*. The Q value is, therefore, *positive*. Thus,

Q = 0·01864 a.m.u. × 931·5 MeV/a.m.u. = **17·36 MeV**

Nuclear Coulombic Barrier. When a positively charged particle such as an alpha particle approaches a nucleus, it is repelled by the nucleus. The repulsive force between the nucleus and the approaching positively charged particle is called the **nuclear coulombic barrier**. The energy of repulsion V is given by

$$V = (Ze)_1(Ze)_2/d = Z_1Z_2e^2/d \qquad \ldots (7)$$

where Z is atomic number, e is the unit of protonic charge = $4{\cdot}8\times10^{-10}$ e.s.u. and d is the distance between the nucleus and the positively charged particle.

Example 16. Consider an alpha particle just in contact with a $^{238}_{92}U$ nucleus. Calculate the coulombic repulsion energy (*i.e.*, the height of the coulombic barrier between ^{238}U and alpha particle) assuming that the distance between them is equal to the sum of their radii.

Solution : According to Eq. 1, radius r of a nucleus is given by $r = R_0 A^{1/3}$ where A is mass number and R_0 is a constant = $1{\cdot}4\times10^{-13}$ cm

In this case, d = Radius of $^{238}_{92}U$ + Radius of $^{4}_{2}He$ = $1{\cdot}4\times10^{-23}\,(238)^{1/3}$ cm + $1{\cdot}4\times10^{-13}\,(4)^{1/3}$ cm

$\therefore$ According to Eq. 7,

$$\text{Coulombic barrier, } V = \frac{92\times2\times(4{\cdot}8\times10^{-10})^2 \text{ e.s.u.}}{1{\cdot}4\times10^{-13}[(238)^{1/3}+(4)^{1/3}]\text{ cm}} = \mathbf{3{\cdot}88\times10^{-5}\ erg}$$

We may convert the result from erg to MeV recalling that $1{\cdot}602\times10^{-12}$ erg = 1 eV and 10^6 eV = 1 MeV. Thus,

$$\text{Coulombic barrier, } V = \frac{3{\cdot}88\times10^{-5}\text{ erg}}{1{\cdot}602\times10^{-12}\times10^{6}\text{ erg/Mev}} = \mathbf{24{\cdot}2\ MeV}$$

The above result shows that an alpha particle would require a kinetic energy of at least 24·2 MeV to approach close enough to make a contact with the ^{238}U nucleus. If its kinetic energy is less than this value, it would not be able to overcome the coulombic barrier and would be repulsed before coming in contact with ^{238}U nucleus.

QUESTIONS

1. Name at least ten particles which are now known to be present in the nucleus of an atom. What do you know about the antiparticle theory put forth by Dirac.
2. Discuss the nature of forces which hold nucleons together in a small nucleus. Explain the role of mesons in this connection.
3. Describe the empirical relation which enables us to calculate nuclear radii. Calculate the radii of the following nuclei : ^{4}He, ^{16}O, ^{112}Cd and ^{257}Fm. **(Ans. Radius of $^{112}Cd = 6{\cdot}75\times10^{-15}$m, etc.)**
4. What is meant by a.m.u. ? Show that 1 a.m.u. = $1{\cdot}66\times10^{-27}$ kg = 931·5 MeV of energy.
5. How would you determine the density of nucleus of mass number A ? Calculate the density of ^{27}Al nucleus and compare the result with the density of Al^{3+} ion which is 2·7 g cm^{-3} in the metallic latice ($R_0 = 1{\cdot}5\times10^{-15}$ m and 1 a.m.u. = $1{\cdot}66\times10^{-27}$ kg). **(Ans. $1{\cdot}18\times10^{17}$ kg m^{-3})**
6. Assuming that the mass of neutron is 1·0087 a.m.u., calculate the density of neutron **(Ans. $1{\cdot}02\times10^{17}$ kg m^{-3})**
7. What is meant by packing fraction ? How does it predict the stability or otherwise of a nucleus ?
8. Explain the term Mass defect and Binding energy of a nucleus. How are the two inter-related ? Calculate the packing fraction, mass defect and energy released in the formation of oxygen nucleus. The masses of the various species are given in the text. **(Ans. –3·187 ; 0·137015 a.m.u. ; 127·62 MeV)**
9. What are nuclear fission reactions ? Discuss the release of energy in these reactions. Bring out the significance of critical mass in nuclear fission. What is meant by sub-critical and super-critical states of a system.
10. Distinguish between nuclear fission and nuclear fusion reactions. What is the source of energy in these reactions ? Distinguish between an atom bomb and a hydrogen bomb.
11. Discuss in details the Nuclear Shell Model and the Liquid Drop Model for nuclear structure. Bring out clearly the significance of the Liquid Drop Model.
12. What are nuclear reactions ? How do they differ from chemical reactions ? Distinguish between natural radioactivity, artificial radioactivity and induced radioactivity.
13. Calculate the binding energy in MeV of $^{40}_{20}Ca$ and $^{238}_{92}U$ from the following data : Mass of $^{1}_{1}H$ = 1·0078 a.m.u. ; Mass of neutron = 1·0084 a.m.u. ; Mass of $^{238}_{92}U$ = 238·125 a.m.u. **(Ans. 8·55 MeV, 1694·4 MeV)**
14. Calculate the energy released in kcal as well as in KWH, by the fission of 1 gm of $^{235}_{92}U$. Energy per fission may be taken as 200 MeV. **(Ans. 196×10^{7} kcal, $2{\cdot}27\times10^{4}$ KWH)**
15. Calculate the number of fissions in uranium per second required to produce one kilowatt of power if the energy released per fission is 200 MeV. **(Ans. $3{\cdot}125\times10^{3}$ fissions)**
16. Calculate the energy released in the following nuclear reaction involving the decay of ^{235}U by alpha particle emission :

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He + Q$$

The various mass values in a.m.u. are : ^{238}U = 238·1249, ^{234}Th = 234·1165, ^{4}He = 4·0039 **(Ans. 4·2 MeV)**

17. What is radioactivity ? In what units is radioactivity measured ?
18. Write down the expression for the disintegration of a radioactive substance. What is meant by disintegration constant ?
19. Discuss briefly the nature of radiations emitted by radioactive substances. How is radioactivity detected and measured.
20. What are radioactive tracers ? Explain what is meant by carbon dating and rock dating.
21. (*a*) Explain half-life period of a radioactive substance.
    (*b*) Calculate the amount of time, expressed in units of $t_{1/2}$ in which $N/N_0 = 0{\cdot}125$. **(Ans. 3)**
    (*c*) Calculate the mass of the nucleus ^{14}C (with $t_{1/2}$ = 5730 yrs) that is equal to 1 curie. **(Ans. $1{\cdot}92\times10^{-4}$ kg)**
22. A living plant acquires a definite fraction of $^{14}_{6}C$ nuclei in its carbon contact. If a freshly cut piece of wood gives 16·1 counts per minute per gram and an old wooden bowl gives 9·6 counts per minute per gram of carbon, calculate the age of the wooden bowl. The half-life of $^{14}_{6}C$ is 5770 years. **(Ans. 4304·18 years)**
23. (*a*) What is artificial radioactivity ? Explain the working of a cyclotron.
    (*b*) Describe briefly the preparation of transuranic elements.
24. What is nuclear coulombic barrier ? What is its significance ?
25. Calculate the coulombic barrier in a ^{238}U nucleus to a proton assuming that they are just in contact so that the distance between them is equal to the sum of their radii. **(Ans. 13·1 MeV)**

40 EVALUATION OF ANALYTICAL DATA

Analytical chemistry is one of the most important branches of chemistry which deals with the resolution, separation, identification and determination of the constituents of a given sample of matter. The subject falls under two categories : 1. Qualitative Analysis and 2. Quantitative Analysis. While the former deals with chemical identification of the constituents of a sample, the latter is concerned with the determination of the relative amounts of the constituents. Qualitative information is almost invariably required before carrying out quantitative analysis of a given sample of matter.

In this chapter we shall discuss the evaluation of analytical data obtained in **quantitative analysis.** But, before we discuss the subject, it is essential for the student to understand clearly the terms which are frequently used in this context.

Terms Used in Evaluation of Analytical Data. The various terms commonly used in evaluation of analytical data are as follows.

SIGNIFICANT FIGURES

The significant figures in a numerical expression are defined as *all those digits whose values are known with certainty with one additional digit whose value is uncertain.* For example, if the mass of a substance, determined by using a balance which is capable of measuring accurately to the nearest milligram, is reported as 2·03765 gram, then only the first four figures are meaningful. In actual measurement, the last digit known with certainty is 7. The digit 6 is uncertain and indicates only that the mass is more than 2·037 gram but less than 2·038 gram. The last digit 5 is meaningless and superfluous. Thus, by definition, the expression 2·03765 has only five significant figures, of which four figures are certain and one figure is uncertain.

The position of decimal is of no relevance in determining the number of significant figures. Thus, the numerical expressions 0·2341, 2·341, 23·41, 234·1 and 2341 all have four significant figures. A 'zero' is not a significant figure when used for locating a decimal but becomes significant when used at the end of the expression. Thus, the expression 0·0304 has three significant figures whereas the expression 0·03040 has four significant figures. The number of significant figures can be expressed most clearly if we write the numbers using exponential notation. Thus, a number written as $3{\cdot}04\times10^{3}$ has three significant figures whereas a number written as $3{\cdot}040\times10^{3}$ has four significant figures. Similarly, the number 0·00304 written as $3{\cdot}04\times10^{-3}$ has three significant figures whereas the number 0·003040 written as $3{\cdot}040\times10^{-3}$ has four significant figures and so on.

Rounding off the Numerical Expression. The numerical expressions for various measurements are generally rounded off to express the result to a required number of significant figures. This is done in accordance with the following **rules** :

1. The digits to be rounded off are all removed *together, not one at a time.*

2. If the figure following the last figure to be retained is less than five, the last digit retained is not altered.

3. If the figure following the last figure to be retained is greater than five, the last digit retained is increased by one.

4. If the figure following the last figure to be retained is five and at least one of the other digits to be removed is non-zero, the last digit retained is increased by one.

5. If the figure following the last figure to be retained is five and all other digits to be removed are zero, the last digit retained is not altered if it is even but is increased by one if it is odd.

The above rules are illustrated below by suitable examples.

Example 1. Round off the following numbers to three significant figures (*a*) 75·8437 (*b*) 59·873 (*c*) 68·752 (*d*) 67·250 (*e*) 63·35.

Solution :

(*a*) Applying rules 1 and 2, 75·8437 ⟶ **75·8**

(*b*) Applying rules 1 and 3, 59·873 ⟶ **59·9**

(*c*) Applying rules 1 and 4, 68·752 ⟶ **68·8**

(*d*) Applying rules 1 and 5, 67·250 ⟶ **67·2**

(*e*) Applying rules 1 and 5, 63·35 ⟶ **63·4**

The following two **additional rules** are applied when the computation involves addition, subtraction, multiplication and division :

1. For **multiplication** and **divsion,** the number of significant figures in the result is the same as in the least precise measurement.

2. The result of **addition** or **subtraction** cannot contain more digits to the right of the decimal than the least number of such digits that are present in any of the number being added or subtracted.

These additional rules are illustrated in the following example.

Example 2. Evaluate the following expressions rounding off the answer to the appropriate number of significant figures :

(*a*) 42·71 g + 9·643 g + 8·0 g **(*b*) 0·165 m³ × 10·487 kg m⁻³**

Solution : (*a*) 42·71 g + 9·643 g + 8·0 g = 60·353 g = **60·4 g** (8·0 has only **one** figure to the right of the decimal point)

(*b*) 0·165 m^3 × 10·487 $kg\ m^{-3}$ = 1·730355 kg = **1·73 kg** (0·165 has only **three** significant figures)

ERRORS

Error is defined as *the numerical difference between a measured value and the absolute or true value of an analytical determination.* The absolute or true value of a quantity is, however, never known. All that we can use is only an ***accepted value.*** The value for any quantity is 'accepted' when the uncertainty in this value is less than the uncertainty in some other quantity with which the given quantity is to be compared. The values which we may like to 'accept' can be obtained by a variety of methods which, however, have their own limitations. It is very rare that two different methods may yield identical accepted values.

The error in a measured quantity may be represented either as *absolute error* or as *relative error.*

Absolute Error. The absolute error E in a measurement is expressed as

$$E = x_i - x_t \qquad \ldots (1)$$

where x_i is the measured value and x_t is the true (accepted) value for the given measurement.

Relative Error. The relative error E_r in a measurement is expressed as

$$E_r = \frac{x_i - x_t}{x_t} \qquad \ldots (2)$$

where x_i and x_t have the same significance as mentioned above. Relative error is generally expressed as per cent or as parts per thousand (ppt). Thus,

$$E_r = \frac{x_i - x_t}{x_t} \times 100\ \% \qquad \ldots (3)$$

or

$$E_r = \frac{x_i - x_t}{x_t} \times 1000 \text{ ppt} \qquad \ldots (4)$$

Example 3. In two separate determinations, the concentration of iron in a given sample was found to be (*a*) 20·17 ppm and (*b*) 19·80 ppm. Taking the accepted value as 20·00 ppm, calculate the absolute error as well as the relative error as per cent and as parts per thousand in the two determinations.

Solution : (*a*) Measured value, x_i = 20·17 ppm True or accepted value, x_t = 20·00 ppm

∴ Absolute error, $E = x_i - x_t$ = 20·17 ppm − 20·00 ppm = **0·17 ppm**

Relative error, $$E_r = \frac{x_i - x_t}{x_t} \times 100 = \frac{0{\cdot}17 \text{ ppm} \times 100}{20{\cdot}00 \text{ ppm}} = \mathbf{0{\cdot}85\%}$$

$$= \frac{x_i - x_t}{x_t} \times 1000 = \frac{0{\cdot}17 \text{ ppm} \times 1000}{20{\cdot}00 \text{ ppm}} = \mathbf{8{\cdot}5\ ppt}$$

(*b*) x_i = 19·80 ppm x_t = 20·00 ppm

Absolute error, $E = x_i - x_t$ = 19·80 ppm − 20·00 ppm = **− 0·20 ppm**

Relative error, $$E_r = \frac{x_i - x_t}{x_t} \times 100 = \frac{-\ 0{\cdot}20 \text{ ppm} \times 100}{20{\cdot}00 \text{ ppm}} = \mathbf{-1{\cdot}00\%}$$

$$= \frac{x_i - x_t}{x_t} \times 1000 = \frac{-\ 0{\cdot}20 \text{ ppm}}{20{\cdot}0 \text{ ppm}} \times 1000 = \mathbf{-10{\cdot}00\ ppt}$$

Example 4. The following values for electronic charge were reported in a series of determinations : $4{\cdot}79 \times 10^{-10}$ e.s.u., $4{\cdot}81 \times 10^{-10}$ e.s.u., $4{\cdot}79 \times 10^{-10}$ e.s.u., $4{\cdot}82 \times 10^{-10}$ e.s.u., $4{\cdot}80 \times 10^{-10}$ e.s.u., $4{\cdot}78 \times 10^{-10}$ e.s.u. Calculate the absolute error and the relative error (per cent) if the accepted value for electronic charge is $4{\cdot}8 \times 10^{-10}$ e.s.u.

Solution : The average value of electronic charge is obtained by adding all the above *six* values and dividing by *six.* The value comes out to be = $4{\cdot}798 \times 10^{-10}$ e.s.u.

Accepted value of electronic charge = $4{\cdot}80 \times 10^{-10}$ e.s.u.

Absolute error, $E = x_i - x_t = 4{\cdot}798 \times 10^{-10}$ e.s.u. − $4{\cdot}80 \times 10^{-10}$ e.s.u. = **$-0{\cdot}002 \times 10^{-10}$ e.s.u.**

Relative error, $$E_r = \frac{x_i - x_t}{x_t} \times 100 \text{ per cent} = \frac{-0{\cdot}002 \times 10^{-10} \text{ e.s.u.}}{4{\cdot}80 \times 10^{-10} \text{ e.s.u.}} \times 100 = \mathbf{-0{\cdot}042\%}$$

Types of Errors

The various errors which usually occur in analytical measurements can be classified into two broad categories, *viz., Determinate* or *Systematic Errors* and *Indeterminate* or *Random Errors.*

A. Determinate Errors. Determinate errors have a definte source which can be identified. A given determinate error is generally unidirectional with respect to the true (accepted) value and thus makes the measured value either lower or higher than the true value. These errors would, evidently, render the results of all the replicate measurements either low or high. Determinate errors are often reproducible. They can be readily predicted by an expert analyst. As such, these errors can be either avoided or corrected.

Determinate errors are of three types, namely, *instrument errors, method errors* and *personal errors.*

1. Instrument errors. These errors arise from imperfections in measuring devices. For instance, measuring devices such as pipettes, burettes, measuring cylinders, measuring flasks, etc., deliver or contain volumes that are slightly different from those indicated by their graduations. There can be several reasons for these differences, the most potential among these are : 1. The use of the glassware at a temperature which is significantly different from the temperature at which the glassware was calibrated. 2. Distortions in the walls of the container due to heating while drying the glassware. 3. Errors in the original calibration. 4. Contamination of the inner surfaces of the containers.

Instruments powered by electricity are very much prone to determinate errors because of the following reasons : 1. Fall in voltage of battery-operated instruments. 2. Increased resistance in circuits due to unclean electrical contacts. 3. Effect of temperature on resistors and standard cells. 4. Currents induced from 220V power lines. Nevertheless, these errors can be easily detected and corrected.

2. Method errors. These errors generally arise from the non-ideal behaviour of reagents and reactions involved in a given analysis. The non-ideality originates from : 1. The slowness of reactions. 2. Incompleteness of reactions. 3. Instability of reactants. 4. Non-specificity of reagents and 5. Occurrence of side reactions which interfere with the main process of measurement. Since these errors are inherent in the method, they cannot be easily detected and corrected.

3. Personal errors. These errors arise from *erratic personal judgement,* as also from *prejudice* or *bias*. Many experimental measurements, such as the estimation of the position of a pointer between two scale divisions, judgement of the colour of solution at the end point in a titration, judgement of the level of a liquid with respect to a graduation on a burrette or a pipette, are sources of personal errors. Such errors would vary from person to person and can be reduced to a minimum by experience and careful physical manipulation.

A common source of personal error is *prejudice* or *bias*. Most of us have a natural tendency to record the readings in such a way as to improve the precision of results or to make the results fall closer to a preconceived notion of the true value of the measurement. In order to secure accurate results, therefore, *we must get rid of bias at all cost.*

Determinate errors are further classified into *constant errors* and *proportional errors.*

Constant errors. The magnitude of a constant error is *independent of the size of the sample* or *the size of the quantity that is being measured.* It is also *independent of the concentration* of the substance being analysed. For example, in volumetric analysis, the excess of the titrant (say, 1 drop) that has to be added to bring about a change in colour at the end point remains the same whether we titrate 10 ml or 20 ml or 25 ml of the solution. Similarly, during washing of a precipitate, the amount of the precipitate washed off by a known volume of the wash liquid remains the same whether we take 1 gram or 2 gram of the precipitate for washing. Evidently, the constant errors would become more serious as we *decrease* the size of the quantity being measured. For illustration, let us suppose that 0·25 mg of a precipitate is lost when we wash it with 250 ml of a wash liquid. If we take 500 mg of the precipitate for washing, the relative error due to solubility loss would be $(0{\cdot}25/500)\times 100 = 0{\cdot}05\%$. If, however, we take 50 mg of the precipitate, the relative error due to solubility loss would be $(0{\cdot}25/50)\times 100 = 0{\cdot}5\%$, *i.e.,* the relative error in the latter case increases ten times.

Similarly, in a volumetric titration, the relative error would increase five times if we use a 5 ml pipette in place of a 25 ml pipette, *i.e.,* if we take 5 ml of the solution for titration in place of 25 ml of the solution.

It readily follows from the above that the effect of a constant error can be reduced to a minimum by increasing the size of the sameple to a maximum within the permissible limits. A constant determinate error is represented graphically by the plot E_c, as shown in Fig. 1.

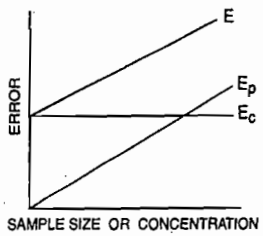


Fig. 1. Graphical representation of constant and proprtional errors.

Proportional errors. Proportional errors are most commonly due to the presence of interfering impurities in the sample. The magnitude of such an error depends upon the *fraction* of the impurity and is independent of the size of the sample. For example, copper in a sample is estimated iodometrically through the reaction of Cu(II) ion with potassium iodide to liberate iodine. If the sample contains Fe(III) as impurity, it would also liberate iodine from potassium iodide. Hence, the analysis of the sample would yield an erroneously high result for the percentage of copper. If we double the size of the sample, the amount of iodine liberated would also become double and thus the estimated percentage of copper would remain the same. This means that the error due to the presence of Fe(III) would remain the same irrespective of the size of the sample. A proportional determinate error is represented graphically by the plot E_p, as shown in Fig. 1. The cumulative effect of constant and proportional errors is given by the plot E.

Correction of Determinate Errors. The determinate *instrument errors* are detected and corrected by periodic calibration of the instruments. It is a common experience that response of most of the instruments changes with time because of wear, corrosion or mistreatment. A periodic calibration, therefore, is a must.

The determinate *personal errors* can be reduced to a minimum by care and self-discipline. It would be certainly desirable to develop a habit of checking the instrument readings, noting the book entries and verifying calculations systematically. The most essential requisite of avoiding personal errors is, however, *to fight actively against bias.*

The determinate *method errors* are rather difficult to detect. The following procedures have nevertheless been suggested for the identification and compensation of method errors.

1. Analysis of standard samples. Method errors can be detected by carrying out the analysis of a standard sample prepared in such a way that its composition is exactly the same as that of the material under test. For this purpose, standard materials containing carefully analysed constituents are available from the National Bureau of Standards.

2. Independent analysis. A dependable procedure for detecting method errors consists in carrying out parallel analysis of the sample by another independent method of established reliability. As far as possible, the independent method should be completely different from the one under study so that there is no possibility that some common factors may have the same effect in both the methods.

3. Blank determination. Blank determination in which all the steps involved in the analysis are carried out in the absence of the sample in exactly the same fashion, is quite useful for exposing method errors which are due to contaminations of the reagents and the glass vessels employed for analysis. Blank experiment also helps us to make correction for the excess reagent (titrant) added in a volumetric titration to bring about a change in the colour of the indicator at the end point.

B. Indeterminate Errors. Indeterminate or random errors arise from uncertainties which are inevitably associated with every physical or chemical measurement. These are random or accidental errors whose sources, though many, cannot be positively identified. As a result of these errors, the data from replicate measurements fluctuate randomly around the mean of the set, as shown in Figs. 2 (*a*), (*b*) and (*c*) for the relative frequency of the combinations of four indeterminate uncertainties, eight indeterminate uncertainties and a very large number of indeterminate uncertainties. It is evident from the these curves that most frequently the deviation from the mean is very small. It is also clear from these curves that there is *almost equal probability of the occurrence of positive and negative errors* with the result that overall magnitude of the indeterminate errors becomes *almost insignificant.* For example, a highly experienced and competent worker made 50 measurements for the calibration of a 10 ml pipette and making all efforts to eliminate determinate errors, he obtained data according to which the minimum, maximum and mean volumes were reported to be 9·969, 9·994 and 9·982 ml, respectively. The standard deviation for the 50 measurements was reported to be 0·0056 ml. The spread volume = 9·994 – 9·969 = 0·025 ml. The deviation (0·0056 ml) which is due to indeterminate errors is, evidently, quite small.

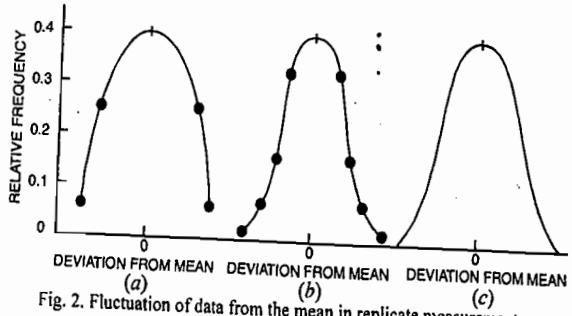


Fig. 2. Fluctuation of data from the mean in replicate measurements.

PRECISION

In the process of analysis, generally three to five portions of the sample under test are subjected to the entire analytical procedure under identical conditions. The results of measurements are, however, seldom identical. They may differ among themselves as well as from the true (accepted) value for the measurement.

The degree of agreement between two or more replicate measurements made on a sample in an identical manner, i.e., exactly in the same fashion, is known as the **precision** *of the measurement.* In other words, precision reflects the closeness among replicate measurements of the same quantity. For illustration, let us suppose that the percentages of lead in a sample of brass determined by one analyst are 2·63, 2·60 and 2·62 while those determined by another analyst are 2·70, 2·75 and 2·81. Evidently, the precision of the first set of results is better than that of the second.

If we make a large number of observations of a single quantity and then plot the number of times a given value occurs against the value of the quantity itself, we usually obtain a curve of the type shown in Fig. 3. This is known as **error distribution curve.**

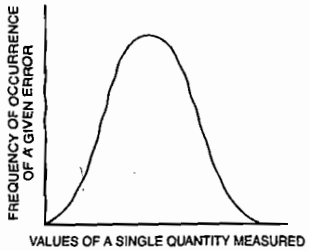


Fig. 3. The error distribution curve.

These curves have two useful qualitative features, *viz., the height of the peak of the distribution curve* and *the spread of the distribution curve* (also called **dispersion**). The precision of a set of measurements is judged from the dispersion, *i.e.,* the spread of the error distribution curve. *The lesser the spread, the greater is the precision of the measurements.* The precision of two sets of measurements of the same quantity can thus be easily compared with the help of their error distribution curves. Thus, in Fig. 4, the curve I with lesser spread and higher peak is characteristic of more precise measurements as compared to the curve II (shown dotted) which represents less precise measurements.

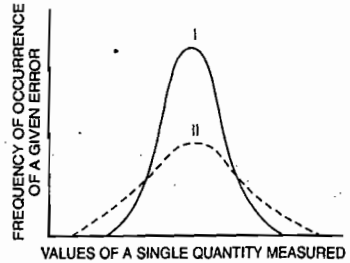


Fig. 4. Characteristics of less precise and more precise result.

Precision of a set of measurements is expressed in a number of ways. Most commonly, precision is expressed in terms of 1. *Average deviation from the mean* 2. *Standard derviation* and 3. *Relative standard deviation.*

1. Average Deviation from the Mean. The precision of experimental data can be expressed conveniently in terms of *average deviation from the mean.* This quantity for a set of results is obtained by the summation of the individual deviations from the mean regardless of sign (because if the signs are retained, the mathematical summation would be equal to zero) and dividing the summation by the number of measurements made in the set. Thus, the average deviation from the mean, $<d>$, may be expressed mathematically as

$$<d> = \sum_{i=1}^{i=N} (x_i - \bar{x}) \Big/ N \qquad \text{... (5)}$$

where x_i is the individual measurement, $\bar{x}$ is the mean of measurements and N is the total number of measurements.

Quite often, the average deviation is expressed relative to the magnitude of the measured quantity. It is then termed as *relative average deviation from the mean.* It may be expressed in terms of percentage (parts per hunderd) or parts per thousand (ppt). Thus,

$$\text{Relative average deviation (\%)} = \frac{<d>}{\bar{x}} \times 100 = \frac{\sum_{i=1}^{i=N}(x_i - \bar{x})}{\bar{x}\,N} \times 100 \qquad \text{... (6)}$$

$$\text{Relative average deviation (ppt)} = \frac{<d>}{\bar{x}} \times 1000 = \frac{\sum_{i=1}^{i=N}(x_i - \bar{x})}{\bar{x}\,N} \times 1000 \qquad \text{... (7)}$$

where $\bar{x}$ is the average magnitude of the measured quantity.

2. Standard Deviation. The term standard deviation is commonly used in statistics as a *measure of precision.* This quantity is obtained by the summation of the squares of the individual deviations from the mean, dividing the sum by $N-1$ where N is the number of measurements and then taking the square root. The standard deviation S is thus expressed mathematically as

$$S = \sqrt{\frac{\sum_{i=1}^{i=N}(x_i - \bar{x})^2}{N-1}} \qquad \text{... (8)}$$

The divisor $(N-1)$, in fact, represents the degrees of freedom for the set of N measurements. It indicates that there can be $(N-1)$ independent deviations from the mean.

By definition, the mean $\bar{x}$ of the set of N measurements is given by

$$\bar{x} = \sum_{i=1}^{i=N} x_i \Big/ N \qquad \text{... (9)}$$

Mathematically, the numerator under the square root in Eq. 8 may be expressed as follows :

$$\sum_{i=1}^{i=N}(x_i - \bar{x})^2 = \sum_{i=1}^{i=N} x_i^2 - \left(\sum_{i=1}^{i=N} x_i\right)^2 \Big/ N \qquad \text{... (10)**}$$

Substituting this value in Eq. 8, we get

$$S = \sqrt{\frac{\sum_{i=1}^{i=N} x_i^2 - \left(\sum_{i=1}^{i=N} x_i\right)^2 \Big/ N}{N-1}} \qquad \text{... (11)}$$

This equation is, evidently, more convenient to use than Eq. 8.

**** Mathematical Derivation of Eq. 10.** The numberator under the square root of Eq. 8 may be expressed as

$\sum_{i=1}^{i=N}(x_1 - \bar{x})^2 = \sum_{i=1}^{i=N}(x_i^2 + (\bar{x})^2 - 2x_i\bar{x})$ where $\bar{x}$ is given by Eq. 9.

The quantity $\bar{x}$, being the mean of N values, has a definite value. It is, therefore, constant for the set of N values.

$$\therefore \sum_{i=1}^{i=N}(x_i - \bar{x})^2 = \sum_{i=1}^{i=N} x_i^2 + \sum_{i=1}^{i=N}(\bar{x})^2 - 2(\bar{x})\sum_{i=1}^{i=N} x_i \qquad \left[\begin{array}{l}(\bar{x}) \text{ is taken out of summation} \\ \text{since it is constant}\end{array}\right.$$

$$= \text{-do-} + N(\bar{x})^2 - 2(\bar{x})\sum_{i=1}^{i=N} x_i \qquad \left[(\bar{x})^2 \text{ taken } N \text{ times is } N(\bar{x})^2\right.$$

$$= \text{-do-} + N\left(\sum_{i=1}^{i=N} x_i\right)^2 \Big/ N^2 - \left(2\sum_{i=1}^{i=N} x_i \Big/ N\right)\left(\sum_{i=1}^{i=N} x_i\right)$$

$$= \text{-do-} + \left(\sum_{i=1}^{i=N} x_i\right)^2 \Big/ N - 2\left(\sum_{i=1}^{i=N} x_i\right)^2 \Big/ N$$

$$\text{Thus, } \sum_{i=1}^{i=N}(x_i - \bar{x})^2 = \sum_{i=1}^{i=N} x_i^2 - \left(\sum_{i=1}^{i=N} x_i\right)^2 \Big/ N$$

Example 5. For titrating 10 ml of a solution with the help of a microburette, the volumes of the titrant used are 9·98, 9·99, 9·98, 9·95, 10·00 and 10·02 ml. Calculate the standard deviation with the help of Eq. 11 as well as Eq. 8.

Solution with the help of Eq. 11 :

Trial	x_i	x_i^2
1	9·98	99·6004
2	9·99	99·8001
3	9·98	99·6004
4	9·95	99·0025
5	10·00	100·0000
6	10·02	100·4004
	$\sum x_i = 59{\cdot}92$	$\sum x_i^2 = 598{\cdot}4038$

$$\frac{(\sum x_i)^2}{N} = \frac{(59{\cdot}92)^2}{6} = 598{\cdot}4011$$

$$\therefore \quad S = \sqrt{\frac{598{\cdot}4038 - 598{\cdot}4011}{6-1}} = \sqrt{\frac{0{\cdot}0027}{5}} = \mathbf{0{\cdot}02324}$$

Solution with the help of Eq. 8 : Mean of six measurements is given by

$$\bar{x} = \sum_{i=1}^{i=N} x_i \Big/ N = \frac{9{\cdot}98 + 9{\cdot}99 + 9{\cdot}98 + 9{\cdot}95 + 10{\cdot}10 + 10{\cdot}02}{6} = 59{\cdot}92/6 = 9{\cdot}99$$

Trial	x_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$
1	9·98	0·01	0·0001
2	9·99	0·00	0·0000
3	9·98	0·01	0·0001
4	9·95	0·04	0·0016
5	10·00	0·01	0·0001
6	10·02	0·03	0·0009

Hence, $\sum_{i=1}^{i=6} (x_i - \bar{x})^2 = 0{\cdot}0028$

$$S = \sqrt{\frac{\sum_{i=1}^{i=N} (x_i - \bar{x})^2}{N-1}} = \sqrt{\frac{0{\cdot}0028}{5}} = \sqrt{0{\cdot}00056} = \mathbf{0{\cdot}02367}$$

3. Relative Standard Deviation (RSD). The relative standard deviation is obtained by dividing the standard deviation by the mean of the set of measurements. It is generally expressed in terms of 'parts per thousand' (ppt). The value of RSD is calculated by multiplying the quotient $S/\bar{x}$ by 1000. Thus,

$$\text{RSD} = (S/\bar{x}) \times 1000 \text{ ppt} \qquad \text{...(12)}$$

RSD is often expressed in terms of per cent by multiplying $S/\bar{x}$ by 100. The RSD thus obtained is named as **coefficient of variation (*CV*)**. Accordingly,

$$CV = (S/\bar{x}) \times 100 \text{ per cent} \qquad \text{...(13)}$$

Example 6. In a set of measurements, the following concentrations of Fe (ppm) were reported : 20·2, 20·4, 20·3, 20·1, 19·9, 20·0, 19·8. Calculate : 1. Average deviation from mean 2. Standard deviation 3. Relative standard deviation and 4. Coefficient of variation.

Solution : The data may be tabulated as follows :

	Conc. of Fe, ppm x_i	Deviation from mean, $x_i - \bar{x}$	$(x_i - \bar{x})^2$
x_1	20·2	0·03	0·0009
x_2	20·4	0·23	0·0529
x_3	20·3	0·13	0·0169
x_4	20·1	0·07	0·0049
x_5	19·9	0·27	0·0729
x_6	20·5	0·33	0·1089
x_7	19·8	0·37	0·1369
	$\sum x_i = 141{\cdot}2$	$\sum (x_i - \bar{x}) = 1{\cdot}43$	$\sum (x_i - \bar{x})^2 = 0{\cdot}3943$

$$\bar{x} = \frac{\sum x_i}{N} = \frac{141{\cdot}12}{7} = 20{\cdot}17 \text{ ppm}$$

1. **Average deviation from mean** $= \sum_{i=1}^{i=N} (x_i - \bar{x}) \Big/ N = 1{\cdot}43/7 = \mathbf{0{\cdot}204}$ **ppm Fe**

2. **Standard deviation,** $S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}} = \sqrt{\frac{0{\cdot}3943}{6}} = \mathbf{0{\cdot}256}$ **ppm Fe**

3. **Relative standard deviation, RSD** $= (S/\bar{x}) \times 1000 \text{ ppt} = \frac{0{\cdot}256 \text{ ppm}}{20{\cdot}17 \text{ ppm}} \times 1000 = \mathbf{12{\cdot}69}$

4. **Coefficient of variation,** $CV = (S/\bar{x}) \times 100 \text{ per cent} = \frac{0{\cdot}256 \text{ ppm}}{20{\cdot}17 \text{ ppm}} \times 100 = \mathbf{1{\cdot}269}$ **per cent**

ACCURACY

The term **accuracy** is defined as *the closeness of a measurement or a set of measurements to the true or accepted value.* Accuracy is generally expressed in terms of *absolute error* and *relative error.*

As already discussed, the **absolute error, *E*,** in the measurement of a quantity is expressed by the equation $E = x_i - x_t$ and the **relative error** is expressed by the equation $E_r = (x_i - x_t)/x_t$ where x_i is the measured value and x_t is the true or accepted value. If, for example, the experimentally determined concentration of Fe comes out to be 20·17 ppm and the true value is 20 ppm, then the absolute error is 0·17 ppm. If, however, the determined value is 19·80 ppm, then the absolute error is – 0·20 ppm. The negative sign, thus, indicates that the experimental value is smaller than the true value. It may be noted that the *sign* has to be retained while reporting absolute error. This is in contrast to the measurement of precision which is regardless of sign.

Difference between Precision and Accuracy. Precision and accuracy are *distinctly different* from each other. The main points of difference are as follows.

1. Accuracy is a measure of the agreement between an experimental result and the true value of a given quantity. Precision, on the other hand, measures the agreement between several experimental results obtained for the same quantity under identical conditions.

2. Precision can be determined almost exactly by replicate measurements of the same quantity. Accuracy, in contrast, can never be determined exactly because it involves the use of absolute or true value of the quantity being measured which is never known. All that we use for measuring accuracy is the 'accepted' value of the quantity.

3. Accuracy is expressed in terms of absolute error or relative error whereas precision is expressed in terms of various types of deviations from the mean.

4. The error distribution curve for a less precise set of measurements differs from that of a more precise set *with respect to its scatter or spread or dispersion* ; the spread being more for a less precise set of measurements, as already shown in Fig. 4. The error distribution curve for a less accurate set of measurements, however, differs from that of a more accurate set only *with respect to the position of the mean value*. The mean value for a more accurate set is in close proximity to the true value (curve I, Fig. 5.) whereas the mean value for a less accurate set of measurements is at a greater distance on either side (curves II and III, Fig. 5),

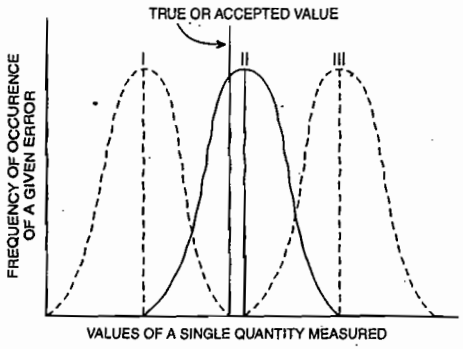


Fig. 5. Error distribution curves for less accurate and more accurate sets of results.

Propagation of Determinate Errors

The final data required to be presented in an analysis is obtained from the results of several measurements by calculations which involve addition, subtraction, multiplication and division. The errors made in individual measurements get transmitted into the final results through calculations, as illustrated below. Suppose the final result R of an analysis is based on the individually measured quantitites A, B and C. Let a, b and c represent the absolute determinate errors in A, B and C, respectively and r represent the maximum resulting error in R. The errors get transmitted to the final result as follows.

1. Transmission through Addition and Substraction. Suppose

$$R = A + B - C \qquad \text{... (14)}$$

Changing each quantity by the amount of its error, we get

$$R + r = (A + a) + (B + b) - (C - c) \qquad \text{... (15)}$$

$$= (A + B - C) + (a + b + c) \qquad \text{... (16)}$$

Subtracting Eq. 14 from Eq. 16, we have

$$r = a + b + c \qquad \text{... (17)}$$

It is obvious that where addition or subtraction is involved, the absolute determinate errors made in individual measurements are transmitted directly as such into the final result.

2. Transmission Through Multiplication and Division. Suppose

$$R = AB/C \qquad \text{... (18)}$$

Changing each quantity by the amount of its error, we get

$$R + r = \frac{(A + a)(B + b)}{C - c} = \frac{AB + aB + bA + ab}{C - c} \qquad \text{... (19)}$$

Assuming that the absolute errors involved in measured quantities are very small, the term ab can be negleted, giving

$$R + r = \frac{AB + aB + bA}{C - c} \qquad \text{... (20)}$$

Substracting Eq. 18 from Eq. 20, we have

$$r = \frac{AB + aB + bA}{C - c} - \frac{AB}{C} \qquad \text{... (21)}$$

$$= \frac{aBC + bAC + cAB}{C(C - c)} \qquad \text{... (22)}$$

Dividing Eq. 22 by Eq. 18, we get

$$\frac{r}{R} = \frac{aBC + bAC + cAB}{AB(C - c)} \qquad \text{... (23)}$$

Neglecting c as compared to C, we have

$$\frac{r}{R} = \frac{a}{A} + \frac{b}{B} + \frac{c}{C} \qquad \text{... (24)}$$

The above fractions, obviously, represent the *relative errors*. Thus, where multiplication and division operations are involved, the relative determinate errors are transmitted directly into the result.

Example 7. In the measurement of the mass of a sample with an analytical balance which has an uncertainty of 0·1 mg, the following data are recorded :

Mass of weighing bottle + sample = 21·8733 g **Mass of weighing bottle = 21·4221 g**

Calculate the mass of the sample indicating the uncertainty in the final result.

Solution : Since the balance has an uncertainty of 0·1 mg, *i.e.*, 0·0001 g,

∴ Mass of weighing bottle + sample = 21·8733 ± 0·0001 g

Mass of weighing bottle = 21·4221 ± 0·0001 g

Since the calculation of the mass of the sample from two actual measurements involves the mathematical operation of substraction, therefore, the total uncertainty in the final result will be given by the sum of the absolute uncertainities in individual measurements.

∴ Mass of sample = (21·8733 ± 0·0001) – (21·4221 ± 0·0001) = **0·412 ± 0·0002**

Example 8. Calculate the absolute error in the following :

(*i*) (15·02 ± 0·02) ml × (0·2000 ± 0·0001) mmol ml^{-1}

(*ii*) (8·000 ± 0·001) mmol ÷ (35·00 ± 0·05) mmol

(*iii*) $\dfrac{(21 \cdot 00 \pm 0 \cdot 02)\ \text{ml} \times (0 \cdot 1010 \pm 0 \cdot 0001)\ \text{mmol ml}^{-1}}{(25 \cdot 00 \pm 0 \cdot 02)\ \text{ml}}$

Solution : We know that when calculations involve operations of multiplication and division, the relative determinate errors are transmitted directly into the final result.

(*i*) Relative error in first term (%) $= \pm \dfrac{0 \cdot 02}{15 \cdot 02} \times 100 = \pm 0 \cdot 13$

Relative error in second term (%) $= \pm \dfrac{0 \cdot 0001}{0 \cdot 2000} \times 100 = \pm 0 \cdot 05$

∴ Total relative error (%) $= \pm\ (0 \cdot 13 + 0 \cdot 05) \pm 0 \cdot 18$

Magnitude of calculated quantity = 15·02 × 0·2000 = 3·004

∴ **Absolute error** $= \dfrac{\pm 0 \cdot 18 \times 3 \cdot 004}{100} = \pm\ 0 \cdot 005$

(*ii*) Relative error in first term (%) $= \pm \dfrac{0 \cdot 001}{8 \cdot 000} \times 100 = \pm 0 \cdot 012$

Relative error in second term (%) $= \pm \dfrac{0 \cdot 05 \times 100}{35 \cdot 00} = \pm 0 \cdot 143$

∴ Total relative error (%) = ± (0·012 + 0·143) = ± 0·155

Magnitude of calculated quantity = 8·000/35·00 = 0·228

Absolute error $= \dfrac{\pm 0 \cdot 155 \times 0 \cdot 228}{100} = \pm \mathbf{0 \cdot 0003}$

(*iii*) Relative error in numerator (%) $= \pm \left(\dfrac{0 \cdot 02}{21 \cdot 00} \times 100 + \dfrac{0 \cdot 0001}{0 \cdot 1010} \times 100 \right)$

$= \pm\ (0 \cdot 095 + 0 \cdot 099) = \pm\ 0 \cdot 194$

Relative error in denominator (%) $= \pm \dfrac{0 \cdot 02 \times 100}{25 \cdot 00} = \pm\ 0 \cdot 08$

$\therefore$ Total relative error (%) $= \pm (0 \cdot 194 \pm 0 \cdot 08) = \pm\ 0 \cdot 274$

Magnitude of calculated quantity $= \dfrac{21 \cdot 00 \times 0 \cdot 1010}{25 \cdot 00} = 0 \cdot 084$

Absolute error $= \pm \dfrac{0 \cdot 274 \times 0 \cdot 084}{100} = \mathbf{\pm 0 \cdot 00023}$

Standard Deviations of Computed Results. Quite frequently we have to determine the standard deviation of a result that has been obtained by the addition, subtraction, multiplication or division of data, each quantity having a standard deviation of its own. The procedures adopted for the above are discussed below in brief.

1. Suppose we want to determine the standard deviation in the result obtained by the summation of the data given below :

$+0 \cdot 75 (\pm 0 \cdot 03) + 3 \cdot 20 (\pm 0 \cdot 02) + 0 \cdot 45 (\pm 0 \cdot 01) - 2 \cdot 30 (\pm 0 \cdot 04)$

The figures in parentheses represent the individual absolute standard deviations.

From statistical considerations, it can be shown that the **standard deviation of a sum or difference** *is given by the square root of the sum of the squares of the individual absolute standard deviations.* Hence, the standard deviation for the summation of the data listed above would be given by

$$S_r = \sqrt{(\pm 0 \cdot 03)^2 + (\pm 0 \cdot 02)^2 + (\pm 0 \cdot 01)^2 + (\pm 0 \cdot 04)^2} = \pm 0 \cdot 055$$

The sum of the above data can thus be reported as $(0 \cdot 75 + 3 \cdot 20 + 0 \cdot 45 - 2 \cdot 30) \pm 0 \cdot 055 = \mathbf{2 \cdot 10 \pm 0 \cdot 055}$

2. Now, suppose we want to determine the standard deviation for the following computation :

$$\frac{3 \cdot 95 (\pm 0 \cdot 03) \times 0 \cdot 035 (\pm 0 \cdot 006) \times 2 \cdot 75 (\pm 0 \cdot 05)}{1 \cdot 68 (\pm 0 \cdot 04) \times 2 \cdot 33 (\pm 0 \cdot 02)}$$

where the figures in parentheses represent the individual absolute standard deviations. The problem is tackled as follows :

Step 1. Write the above computation as

$$\frac{3 \cdot 95 \times 0 \cdot 035 \times 2 \cdot 75}{1 \cdot 68 \times 2 \cdot 33} (\pm ?) = y\ (\pm ?)$$

so that $y = 0 \cdot 097$

Step 2. Determine the relative standard deviation of the result by the summation of relative standard deviations of the various numbers forming the computed result and taking the square root of the sum. The relative standard deviations of the various numbers are $\pm\ 0 \cdot 03/3 \cdot 95$, $\pm\ 0 \cdot 006/0 \cdot 035$, $\pm\ 0 \cdot 05/2 \cdot 75$, $\pm\ 0 \cdot 04/1 \cdot 68$ and $\pm\ 0 \cdot 02/2 \cdot 33$. Hence, the relative standard deviation of the result, *viz.*, S_y / y is given by

$$\frac{S_y}{y} = \sqrt{\left(\frac{\pm 0 \cdot 03}{3 \cdot 95}\right)^2 + \left(\frac{\pm 0 \cdot 006}{0 \cdot 035}\right)^2 + \left(\frac{\pm 0 \cdot 05}{2 \cdot 75}\right)^2 + \left(\frac{\pm 0 \cdot 04}{1 \cdot 68}\right)^2 + \left(\frac{\pm\ 0 \cdot 02}{2 \cdot 33}\right)^2}$$

$$= \sqrt{(0 \cdot 0076)^2 + (0 \cdot 171)^2 + (0 \cdot 018)^2 + (0 \cdot 024)^2 + (0 \cdot 008)^2}$$

$$= \pm\ 0 \cdot 174$$

Step 3. Calculate the absolute standard deviation of the result, *viz.*, S_y, as follows :

$$S_y = y (\pm 0 \cdot 174) = 0 \cdot 097 (\pm 0 \cdot 174) = \pm 0 \cdot 01688$$

Thus, the result of the above computation would be written as $\mathbf{0 \cdot 097 \pm 0 \cdot 0169}$

Example. 9. Compute the result of the following data :

(*a*) $+ 0 \cdot 55 (\pm 0 \cdot 04) + 3 \cdot 77 (\pm 0 \cdot 03) - 1 \cdot 30 (\pm 0 \cdot 02)$ (*b*) $\dfrac{4 \cdot 75 (\pm 0 \cdot 05) \times 0 \cdot 068 (\pm 0 \cdot 02)}{1 \cdot 12 (\pm 0 \cdot 03)}$

Solution. (*a*) Standard deviation in this summation is given by

$$S_r = \sqrt{(\pm\ 0 \cdot 04)^2 + (\pm\ 0 \cdot 03)^2 + (\pm\ 0 \cdot 02)^2} = \sqrt{0 \cdot 0029} = \pm 0 \cdot 0538$$

Hence, the sum of the data may be reported as. $(0 \cdot 55 + 3 \cdot 77 - 1 \cdot 30) \pm 0 \cdot 0538 = \mathbf{3 \cdot 02 \pm 0 \cdot 0538}$

(*b*) The above computation is written as $\dfrac{4 \cdot 75 \times 0 \cdot 068}{1 \cdot 12} (\pm ?) = y (\pm ?)$ so that $y = 0 \cdot 288$

Relative standard deviations of various numbers are : $\pm\ 0 \cdot 05/4 \cdot 75$, $\pm\ 0 \cdot 02/0 \cdot 068$ and $\pm\ 0 \cdot 03/1 \cdot 12$

The relative standard deviation of the result, *viz.*, S_y / y, is given by

$$\frac{S_y}{y} = \sqrt{\left(\frac{\pm\ 0 \cdot 05}{4 \cdot 75}\right)^2 + \left(\frac{\pm\ 0 \cdot 02}{0 \cdot 068}\right)^2 + \left(\frac{\pm\ 0 \cdot 03}{1 \cdot 12}\right)^2} = \sqrt{(0 \cdot 0105)^2 + (0 \cdot 294)^2 + (0 \cdot 0268)^2} = \sqrt{0 \cdot 0873} = \pm 0 \cdot 295$$

$\therefore\ S_y = y \times (\pm 0 \cdot 295) = 0 \cdot 288 (\pm 0 \cdot 295) = \pm 0 \cdot 085$

Thus, the result of (*b*) would be expressed as $\mathbf{0 \cdot 288 \pm 0 \cdot 085}$

Reporting of Analytical Data

While reporting analytical data, it is absolutely essential to indicate the extent of its accuracy or reliability. Without this, a numerical result is of little value. One of the best ways to indicate reliability is to give the absolute standard deviation or the coefficient of variation of the data. The number of data used in obtaining the standard deviation should also be indicated.

The probable uncertainty associated with a given experimental measurement can be represented informatively by indicating the limits of accuracy as the observed number ± uncertainty. For instance, if the temperature of a body is represented as $25 \cdot 0 \pm 0 \cdot 1^\circ C$, it means that the actual temperature lies somewhere between $24 \cdot 9$ and $25 \cdot 1^\circ C$.

Uncertainty in results involving addition and subtraction. The maximum uncertainty in a result involving addition and subtraction is obtained by adding the absolute values of uncertainties in various measurements. For instance, if the absolute uncertainities in the given two data are $\pm 0 \cdot 2$ and $\pm 0 \cdot 3$, then the uncertainty in the summation of the data would be $\pm (0 \cdot 2 + 0 \cdot 3) = \pm 0 \cdot 5$.

Example 10. Calculate the maximum uncertainty in each of the following expressions :

(*a*) $(17 \cdot 3 \pm 0 \cdot 2)$ ml $- (9 \cdot 7 \pm 0 \cdot 3)$ ml $+ (11 \cdot 6 \pm 0 \cdot 1)$ ml

(*b*) $(16 \cdot 6 \pm 0 \cdot 1)$ g $- 2\ (16 \cdot 7 \pm 0 \cdot 2)$ g $+ 3\ (7 \cdot 3 \pm 0 \cdot 1)$ g

Solution :

(*a*)	(*b*)
$17 \cdot 3 \pm 0 \cdot 2$	$16 \cdot 6 \pm 0 \cdot 1$
$-\ 9 \cdot 7 \pm 0 \cdot 3$	$-33 \cdot 4 \pm 0 \cdot 4$
$11 \cdot 6 \pm 0 \cdot 1$	$21 \cdot 9 \pm 0 \cdot 3$
$19 \cdot 2 \pm 0 \cdot 6$ ml	**$5 \cdot 1 \pm 0 \cdot 8$ g**

(Uncertainties are always added)

Uncertainty in results involving multiplication and division. The maximum uncertainty in a result involving multiplication and division is obtained by following the procedure given below :

(*i*) From the given data, calculate the percentage uncertainties.

(*ii*) Add up these percentage uncertainties.

(*iii*) Convert the percertage uncertainty to uncertainty.

The procedure given above is illustrated in the following examples.

Example 11. Calculate the result of the following expression : (23·4 ± 0·1) (17·7 ± 0·05).

Solution :

Step 1. (23·4 ± 0·1) (17·7 ± 0·05) = 414·18 ± ?

Step 2. Percentage uncertainties of the two multipliers are : $\pm \frac{0{\cdot}1}{23{\cdot}4} \times 100$ and $\pm \frac{0{\cdot}05}{17{\cdot}7} \times 100$

Step 3. Summation of percentage uncertainties = ± 0·71

The result may, therefore, be written as 414·18 ± 0·71 %

Step 4. Uncertainty of the result $= \pm \frac{0{\cdot}71}{100} \times 414{\cdot}18 = \pm 2{\cdot}94$

∴ The final result is **414·18 ± 2·94**

Example 12. Calculate the result of the following expression :

$$\frac{(137{\cdot}6 \pm 0{\cdot}3) + (203{\cdot}3 \pm 0{\cdot}1) - (117{\cdot}7 \pm 0{\cdot}1)}{(97{\cdot}8 \pm 0{\cdot}05) + (37{\cdot}3 \pm 0{\cdot}1)}$$

Solution :

$$\frac{(137{\cdot}6 \pm 0{\cdot}3) + (203{\cdot}3 \pm 0{\cdot}1) - (117{\cdot}7 \pm 0{\cdot}1)}{(97{\cdot}8 \pm 0{\cdot}05) + (37{\cdot}3 \pm 0{\cdot}1)} = \frac{223{\cdot}2 \pm 0{\cdot}5}{135{\cdot}1 \pm 0{\cdot}15}$$

$$= \frac{223{\cdot}2 \pm 0{\cdot}22\%}{135{\cdot}1 \pm 0{\cdot}11\%} \qquad \left[\frac{0{\cdot}5}{223{\cdot}2} \times 100 = 0{\cdot}22 \quad \frac{0{\cdot}15}{135{\cdot}1} \times 100 = 0{\cdot}11\right]$$

$$= \left(\frac{223{\cdot}2}{135{\cdot}1}\right) \pm (0{\cdot}22 + 0{\cdot}11)\% = 1{\cdot}65 \pm 0{\cdot}33\% = 1{\cdot}65 \pm 0{\cdot}005 \qquad \left[0{\cdot}33 \times \frac{1{\cdot}65}{100} = 0{\cdot}005\right]$$

Thus, the result of the given expression is **1·65 ± 0·005**

Statistical Treatment of Analytical Data

The statistical treatment of analytical data is based on the assumption that a set of finite number of replicate measurements actually made experimentally is a very small fraction of the set of an infinite number of measurements that could be made if infinite time was available for such measurements. The limited set of data of finite number of values is called '*the sample*' which is regarded as a sub-set of a universe of data that exist only in imagination and is called *the population*.

The Sample Mean and The Population Mean. The *sample mean* is the mean of the 'sample' of measurements, *i.e.*, a finite number of measurements drawn from a 'population' of data, *i.e.*, from an infinite number of measurements. It is denoted by the symbol $\bar{x}$ and is mathematically represented as

$$\bar{x} = \sum_{i=1}^{i=N} x_i \Big/ N \qquad \text{(Eq. 9)} \qquad \ldots (25)$$

where N is usually a relatively small number. The *population mean* is the mean of the entire population of data. It is denoted by the symbol μ and is methematically represented as

$$\mu = \sum_{i=1}^{i=N} x_i \Big/ N \qquad \ldots (26)$$

where N approaches infinity.

Frequently, the value of $\bar{x}$ differs from μ. This is because a 'sample' of data for small values of N cannot be truly representative of a 'population' of data for infinite values of N.

Standard Deviation for Sample and Population of Data. The standard deviation for a sample of measurements, *i.e.*, for a finite number of measurements, is called the **sample standard deviation.** It is denoted by S. The standard deviation for a population of data, *i.e.*, for an infinite set of data, is referred to as the **population standard deviation.** It is denoted by σ.

Confidence Limits. For an infinite number of replicate measurements made on the same material, the mean value, which could be calculated in principle, would be the *population mean*, μ. As already mentioned, the value of μ can never be known in practice. In contrast, the value of sample mean $\bar{x}$ can be known almost exactly from a finite number of measurements.

With the help of statistical theory, it is possible to set limits around experimentally derived mean within which the sample mean $\bar{x}$ is likely to be in agreement with the population mean μ with a given degree of probability. These limits are referred to as the **confidence limits** and the range defined by these limits is known as the **confidence interval.**

Mathematically, the confidence limit is given by the expression.

$$\text{Confidence limit} = \bar{x} \pm \frac{tS}{\sqrt{N}} \qquad \ldots (27)$$

where $\bar{x}$ is the sample or experimental mean, N is the number of measurements ($N < 25$), S is the sample standard deviation and t is a factor whose magnitude depends upon the number of measurements as well as the **confidence level** desired. The confidence level signifies the degree of probability (99%, 95%, 90%, 50%, etc.) acceptable in the results. The factor t is often called the **Student's t.** The values of t corresponding to various levels of probability and varying degrees of freedom are available in Statistical Tables. A portion of one such table is reproduced here for convenience of reference (Table 1).

TABLE 1

Student's t values for Various Levels of Probability and Varying Degrees of Freedom

Number of observations N	Number of degrees of freedom $N-1$	Probability Levels : 50%	90%	95%	99%
2	1	1·000	6·314	12·706	27·320
3	2	0·816	2·920	4·303	9·925
4	3	0·765	2·353	3·182	5·841
5	4	0·741	2·132	2·776	4·604
6	5	0·727	2·015	2·571	4·032
7	6	0·718	1·943	2·447	3·707
8	7	0·711	1·895	2·365	3·500
9	8	0·706	1·860	2·306	3·355
10	9	0·703	1·833	2·262	3·250
11	10	0·700	1·812	2·228	3·169
21	20	0·687	1·725	2·086	2·845
∞	∞	0·674	1·645	1·960	2·576

Example 13. The following volumes of titrant were used in replication of a titration : 30·26, 30·24, 30·30, 30·18, 30·20 ml. Calculate the confidence limit for the following probability levels : 50%, 90%, 95% and 99%.

Solution :

Serial Number	Results of measurement, x_i	Devlaiton $x_i - \bar{x}$	(Deviation)^2 $(x_i - \bar{x})^2$
1	30·26	0·02	0·0004
2	30·24	0·00	0·0000
3	30·30	0·06	0·0036
4	30·18	0·06	0·0036
5	30·20	0·04	0·0016

Mean, $\bar{x}$ = 151·18/5 = 30·24 $\qquad \Sigma(x_i - \bar{x})^2 = 0{\cdot}0092$

Standard deviation, $S = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{N-1}} = \sqrt{\frac{0.0092}{4}} = 0.0479$

Degrees of freedom $= N - 1 = 5 - 1 = 4$

The Student's t values corresponding to various levels of probability reproduced from Table 1 for degrees of freedom = 4, are as follows :

Level of Probability	Student's t value
50 %	0·765
90 %	2·353
95 %	3·182
99 %	5·841

Confidence limit $= \bar{x} + t\,S/\sqrt{N}$ (Eq. 27)

Confidence limit for 50% probability level $= 30.24 \pm \frac{0.0765 \times 0.0479}{\sqrt{5}} = \mathbf{30.24 \pm 0.016}$

The above result implies that the population mean μ would lie with 50% probability within 30·24 + 0·016 and 30·24 – 0·016.

Similarly, the confidence limits for other probability levels come out to be as follows :

Probability level	Confidence limit
90 %	$30.24 \pm \frac{2.353 \times 0.0479}{\sqrt{5}} = \mathbf{30.24 \pm 0.050}$
95 %	$30.24 \pm \frac{3.182 \times 0.0479}{\sqrt{5}} = \mathbf{30.24 \pm 0.068}$
99 %	$30.24 \pm \frac{5.841 \times 0.0479}{\sqrt{5}} = \mathbf{30.24 \pm 0.125}$

Rejection of a Result. It is a common experience that when we perform a large number of replicate analyses, one of the results may differ excessively from the average value, *i.e.*, the particular result may be too high or too low. So we have to take a decision whether we should retain or reject that suspect result. Several statistical tests have been proposed for this purpose but these have to be applied with utmost care.

The simplest test which has been widely used by analysts is called the ***Q* test (Quotient test).** In this test

1. The results of various observations in a given set are arranged in the decreasing order of their numerical values.

2. The difference between the suspected result x_s and its nearest neighbour x_n (ignoring the sign + or –) is divided by the spread w of the entire set (*i.e.*, the difference between the minimum and maximum values in the entire set) to give a quantity Q_{exp}. Thus,

$$Q_{exp} = (x_s - x_n) / w \qquad \text{... (28)}$$

3. The ratio Q_{exp} is then compared with critical values of the rejection ratios obtained statistically at appropriate confidence levels and tabulated as a function of the number of observations. These ratios are termed as $Q_{critical}$.

The critical values for rejection quotient at 90% confidence level are given in Table 2.

TABLE 2

Critical Values for Rejection Quotient at 90% Confidence Level

Number of Observations, N	$Q_{critical}$	Number of Observations, N	$Q_{critical}$
3	0·94	7	0·51
4	0·76	8	0·47
5	0·64	9	0·44
6	0·56	10	0·41

If Q_{exp} is greater than $Q_{critical}$, the suspect result is rejected.

The application of the Q test is illustrated below.

Example 14. In the analysis of an iron ore, the percentages of Fe_2O_3 were found to be 66·00, 65·55, 65·90, 67·85, 66·85, 69·90 and 65·00. The value 69·90 appears to be suspect. Ascertain whether this should be retained or rejected. The $Q_{critical}$ for 7 observations at 90% confidence level is 0·49.

Solution : (*i*) Arranging the various experimental values in the decreasing order of magnitude, we have : 69·90, 67·85, 66·85, 66·00, 65·90, 65·55, 65·00

(*ii*) The difference between the suspect result (x_s) and the nearest neighbour x_n,

viz., $(x_s - x_n) = 69.90\% - 67.85\% = 2.05\%$

(*iii*) Spread of the entire set, $w = 69.90\% - 65.00\% = 4.90\%$

(*iv*) $Q_{exp} = 2.05/4.90 = 0.418$

(*v*) $Q_{critical} = 0.49$ (given)

Since Q_{exp} is less than $Q_{critical}$, hence the suspect result **cannot be rejected.**

Example 15. The amount of mohr salt present in a given solution was determined volumetrically by titration against a standard solution of potassium permanganate. The results obtained in seven observations are as follows : 19·8, 20·2, 19·4, 19·0, 19·6, 21·0 and 23·4 gram per litre. Determine if the suspect result 23·4 can be rejected or not. $Q_{critical}$ for 7 observations at 90% confidence level is reported to be 0·52.

Solution : 1. Arranging the results in the decreasing order of their magnitude, we have :

23·4, 21·0, 20·2, 19·8, 19·6, 19·4, 19·0

2. The difference between the suspect result and the nearest neighbour = 23·4 – 21·0 = 2·4

3. Spread of the entire set = 23·4 – 19·0 = 4·4

4. ∴ $Q_{exp} = 2.4/4.4 = 0.545$

5. $Q_{critical} = 0.52$ (given)

Since Q_{exp} is greater than $Q_{critical}$, hence the suspect result **can be rejected.**

Tests of Significance. As and when a new method is developed for analytical measurements, it is subjected to certain tests in order to ascertain whether there is any *significant difference* between the new method and the standard methods already accepted for these measurements. Two tests are commonly employed for this purpose. These are : 1. *The F-test* and 2. *The t-Test.*

1. The *F*-Test. This test is *based on measurements of standard deviation, S.* The various steps involved in this test are as follows :

1. Determination of standard deviation by employing the standard method. The standard deviation is determined with the help of Eq. 8, *viz.*,

$$S = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{N-1}} \qquad \text{...(29)}$$

where $N-1$ gives the *number of degrees of freedom* which is one less than the number N of the results. The value of N is sufficiently large. The deviation obtained by the standard method is denoted as S_{std}.

2. Determination of standard deviation by employing the newly developed method. The degrees of freedom (or the number of results) used in this determination is small, generally less than 20. Let the standard deviation obtained by the new method be denoted by S_n.

3. Determination of the F-value with the help of the expression

$$F = S_{std}^2 / S_n^2 \qquad \text{...(30)}$$

4. Tabulation of *critical values of F* determined statistically at appropriate levels of confidence by extending the degrees of freedom (N values) to infinity both for the determination of S_{std} and S_n.

5. Comparison of the value of F as obtained from Eq. 30 with the *critical value* of F corresponding to N as infinity. *If the value of F is less than the critical value, there is no significant difference in the precision of the new method and the standard method.*

Example 16. Two sets of results, in mg/litre, one set obtained by a standard method and the other set by a new method are given below :

Standard method	31	27	26	35	23	31	33	
New method	26	22	23	30	24	28	30	25

Determine whether the precision of the new method differs significantly from that of the standard method. The critical value of *F* for 7 degrees of freedom is 2·13.

Solution :

New Method			Standard Method		
x_i	$(x_i-\bar{x})$	$(x_i-\bar{x})^2$	x_i	$x_i-\bar{x}$	$(x_i-\bar{x})^2$
26	0	0	31	1·6	2·56
22	4	16	27	2·4	5·76
23	3	9	26	3·4	11·56
30	4	16	35	5·6	31·36
24	2	4	23	6·4	40·96
28	2	4	31	1·6	2·56
30	4	16	33	3·6	12·96
25	1	1			
$\Sigma x = 208$		$\Sigma(x_i-\bar{x})^2 = 66$	$\Sigma x_i = 206$		$\Sigma(x_i-\bar{x})^2 = 107{\cdot}72$

$\bar{x} = 208/8 = 26$ $\qquad$ $\bar{x} = 206/7 = 29{\cdot}4$

$$S_n = \sqrt{\frac{\Sigma(x_i-\bar{x})^2}{N-1}} = \sqrt{\frac{66}{7}} = 3{\cdot}07 \qquad S_{std} = \sqrt{\frac{107{\cdot}72}{6}} = 4{\cdot}23$$

$$F = S_{std}^2 / S_n^2 = 1{\cdot}90\ ;\ \text{Critical value of } F = 2{\cdot}13 \text{ (given)}$$

Since the value of F is less than the critical value, there is **no significant differenec** in the precision of the new method and the standard method.

Example 17. A standard method for the determination of carbon monoxide in a gaseous mixture shows a standard deviation of 14 ppm CO. A new method based on 10 degrees of freedom shows a standard deviation of 14 ppm CO. The critical value of *F* for 10 degrees of freedom is 0·60. Determine whether the new method is more precise than the standard method.

Solution : According to Eq. 30

$$F = S_{std}^2 / S_n^2 = (11)^2 / (14)^2 = 0{\cdot}617$$

The critical value of F for 10 degrees of freedom = 0·60 (given)

Since the value of F is more than the critical value, **the new method is more precise than the standard method.**

2. The *t* Test. In this test, different samples of the material under test, having different concentrations, are analysed by the new and the standard methods. From the results, the t value is obtained with the help of the relation

$$t = \frac{\bar{d}}{S_d}\sqrt{N} \qquad \text{... (31)}$$

where S_d is the standard deviation defined by the equation

$$S_d = \sqrt{\frac{\Sigma(d_i-\bar{d})^2}{N-1}} \qquad \text{... (32)}$$

In Eq. 32, N is the number of measurements, d_i is the individual difference in results yielded by the two methods and $\bar{d}$ is the mean of the individual differences.

The critical values of t are also obtained statistically at appropriate levels of confidence and tabulated as a function of the number (N) of the measurements made. From the table, the critical value of t corresponding to any degrees of freedom (*viz.*, $N-1$) can be readily picked up.

The experimental value of t as obtained from Eq. 31 is then compared with the critical value of t for the same degrees of freedom. *If the experimental value is less than the critical value of t, there is no significant difference between the two methods.*

Example 18. The amount of oxalic acid present in a given solution was determined by two methods, one standard and the other new, when the following results were obtained :

Sample Number	Amount of Oxalic Acid (g/litre) determined by : Standard Method	New Method
1	8·65	9·35
2	11·70	11·06
3	7·38	8·90
4	13·95	12·58
5	17·26	18·99
6	12·80	11·72

Show that there is no significant difference between the two methods.

Solution : According to the data given above, the values of various expressions are as follows :

Sample No.	$d_i = \left(\text{Result by new method}\right) - \left(\text{Result by standard method}\right)$	$d_i - \bar{d}$	$(d_i-\bar{d})^2$
1	+ 0·70	+ 0·56	0·314
2	− 0·64	− 0·78	0·608
3	+ 1·52	+ 1·38	1·904
4	− 1·37	− 1·51	2·280
5	+ 1·73	+ 1·59	2·528
6	− 1·08	− 1·22	1·488
	Sum = 0·86		$\Sigma(d_i-\bar{d})^2 = 9{\cdot}122$

$$\bar{d} = 0{\cdot}86/6 = 0{\cdot}14$$

$$S_d = \sqrt{\frac{\Sigma(d_i-\bar{d})^2}{N-1}} = \sqrt{\frac{9{\cdot}122}{5}} = 1{\cdot}35$$

$$\therefore \quad t = \frac{\bar{d}}{S_d}\sqrt{N} = \frac{0{\cdot}14}{1{\cdot}35}\sqrt{6} = 0{\cdot}254$$

The critical value of t for 5 degrees of freedom at appropriate confidence level is reported to be 0·48. Since the experimental value is less then the critical value of t, it shows that **there *is no significant difference between* the two methods.**

QUESTIONS

1. Explain the terms : Precision, Average deviation, Standard deviation, Variance, Relative standard deviation, Accuracy, Absolute error, Relative error. Give examples.
2. What types of errors are generally involved in analytical work ? Give examples. Distinguish carefully between determinate and indeterminate errors.
3. Name the three types of determinate errors. How are these errors detected and corrected ?
4. Explain the difference between
   (*i*) Accuracy and precision (*ii*) Determinate and indeterminate errors (*iii*) Constant and proportional errors (*iv*) Variance and standard deviation.
5. What is meant by the term standard deviation ? How would you determine standard deviation in results obtained by (*i*) summation of data (*ii*) devision or multiplication of data
6. Discuss the use of significant figures to describe the uncertainty associated with a given experimental measurement.
7. What are determinate and indeterminate errors ? How do these errors get propagated in additions, subtractions, divisions and multiplications ?
8. Describe carefully the Q test which is applied for rejection or retention of an anomalous result.
9. What is F-test and t-test ? For what purpose are these tests applied ?
10. Assuming that you have developed a new method for analytical measurements, how would you ascertain that the new method is more precise than the standard methods already known.
11. What is meant by the terms , sample, sample population mean and population mean. How are the sample mean and population mean determined.
12. What is meant by the term confidence limit ? How is it determined. What is its significance ?

41 VOLUMETRIC TITRIMETRY

Volumetric titrimetry is one of the most powerful methods of quantitative analysis. In this technique, a known volume of the solution of an *analyte* is reacted completely with a measurable volume of the solution of an appropriate reagent of a known concentration, called the *titrant*.

Some other terms commonly used in volumetric titrimetry are described below.

Standard Solution. The solution of a reagent with a known concentration which is made to react with the solution of an analyte is known as the standard solution or the standard titrant.

Titration. This is a process in which a standard solution is added gradually from a burette to a known volume of the solution of the analyte until the reaction between the analyte and the titrant is judged to be complete. The difference between the initial and the final readings of the burette gives the volume of the titrant required for completing the titration.

Equivalence Point. This is the point in a titration at which the amount of the titrant is *chemically equivalent* to the amount of the analyte in the given sample. For example, in the titration of NaCl with $AgNO_3$, the equivalence point is reached when exactly 1 mole of Ag^+ ions are added to each mole of Cl^- ions present in the solution of the analyte.

End Point. The equivalence point of a titration is only a theoretical point which cannot be determined experimentally. It can only be estimated by observing some visible physical change that happens to be associated with the attainment of equivalence. This change signals the completion of the reaction and the approach of the *end point* for the titration. Evidently, the volume of the titrant required for securing the end point would be a drop or two more than the volume required for the attainment of equivalence point. For accurate work, the additional volume should be as small as possible.

Indicator. An indicator is a chemical substance that is added to the solution of an analyte to produce an observable physical change, as, for example, a change in colour, at or near the end point.

Basic Requirements of a Titration Reaction

The basic reaction involved in a titration must satisfy a number of requirements, the most important of which are as follows.

1. The reaction between the analyte and the titrant must proceed to completion at a fast rate.
2. The reaction should proceed stoichiometrically. The nature of the products should not only be known precisely but should also remain unchanged with alterations in experimental conditions.
3. The equivalence point of the titration reaction should be detectable precisely with the help of an indicator.
4. The exact concentration of the titrant must be known.
5. The equivalence point and the end point should almost coincide with each other.
6. Only one specific reaction should occur between the titrant and the analyte. There should be no side reaction.
7. The reaction between the titrant and the analyte should be simple permitting definite quantitative relation between them.

Standard Solutions. Primary Standards

As mentioned above, a standard solution is one whose concentration is precisely known. Generally, it

is not possible to prepare standard solutions of titrants by taking a known amount of the substance and dissolving it in a solvent to give a known volume of the solution. For example, it is not possible to prepare standard solutions of reagents such as potassium permanganate, ferrous sulphate, sodium hydroxide, iodine, etc., by direct weighing. In most cases, the concentrations of standard solutions are established by titrations with solutions of some other substances, called **primary standards**. These substances should have the following qualities :

1. They must be extra pure and standard methods for confirming their purity should be known.
2. They should be stable towards atmosphere.
3. They should be reasonably soluble in the titration medium.
4. They should be easily available at modest cost.
5. As far as possible, they should have large formula masses so that the error normally associated with weighing is relatively small.

Expressing Concentrations of Standard Solutions

The concentrations of standard solutions are expressed in terms of *normality* or *molarity*.

Normality of a solution is defined *as the number of chemical equivalents of the reagent dissolved per litre of the solution.*

Molarity of a solution is defined *as the number of moles of the reagent dissolved per litre of the solution.*

Previously, the concentrations in volumetric titrimetry used to be expressed in terms of *normality*. But, the use of this term has now been more or less abandoned and concentrations, by far and large, are expressed only in terms of *molarity*. Falling in line with the latest trends, we have also made use of *molarity alone* for expressing concentrations. In order to familiarize the student with the use of the term molarity in volumetric calculations, we have given below some typical solved examples. In these examples, the alphabet M, as usual, stands for *molar*. A 1M $AgNO_3$ solution, thus, contains 1 mol of $AgNO_3$ per litre (l) or 1 mmol per ml of solution. Similarly, a 0·05 M NaCl solution contains 0·05 mol of NaCl per litre or 0·05 mmol per ml of solution. Some useful mathematical correlations frequently involved in volumetric calculations are given below.

If A denotes the chemical species under consideration, then,

$$\text{Number of mols of A} = \left\{\begin{array}{l}\text{Volume of solution in litres} \times \\ \text{concentration of A in mols per litre}\end{array}\right. = V(\text{l}) \times C_A\,(\text{mol l}^{-1}) \quad \ldots (1)$$

$$\text{Number of mmols of A} = \left\{\begin{array}{l}\text{Volume of solution in millilitres} \times \\ \text{concentration of A in millimols per millilitre}\end{array}\right. = V(\text{ml}) \times C_A\,(\text{mmol ml}^{-1}) \quad \ldots (2)$$

$$\text{Number of mols of A} = \left\{\frac{\text{Mass of A (g)}}{\text{Formula mass of A (g/mol)}}\right. \quad \ldots (3)$$

$$\text{Number of mmols of A} = \frac{\text{Mass of A (g)}}{\text{Milli formula mass of A (g/mmol)}} \quad \ldots (4)$$

Example 1. How would you prepare the following solutions :

(1) 2 litres of 0·50 M hypo ($Na_2S_2O_3.5H_2O$; formula mass = 248).

(2) 100 ml of 0·1 M Mohr salt ($FeSO_4.(NH_4)_2SO_4.6H_2O$; formula mass = 392)

Solution. (1) Since the volume is in litres, we make use of Eq. 1 to calculate the amount of hypo required.

Number of mols of hypo = $V(\text{l}) \times C_{hypo}\,(\text{mol l}^{-1}) = 2{\cdot}0 \times 0{\cdot}50\ \text{mol l}^{-1} = 1{\cdot}0$ mol

$$\text{Number of mols of hypo} = \frac{\text{Mass of hypo (g)}}{\text{Formula mass of hypo (g/mol)}}$$

$\therefore$ Mass of hypo = 1·0 mol × 248 g/mol = 248 g

Thus, the solution is prepared by dissolving 248 g of hypo in water and making the volume exactly 2 litres.

(2) Since, in this case, the volume is in millilitres, we make use of Eq. 2 to calculate the amount of Mohr salt required.

$$0{\cdot}1\,M \equiv 0{\cdot}1 \text{ mol } l^{-1} \equiv 0{\cdot}1 \text{ mmol ml}^{-1}$$

Number of mmols of Mohr salt = $V(\text{ml}) \times C_{\text{Mohr salt}}$ (mmol ml^{-1})

$$= 100 \text{ ml} \times 0{\cdot}1 \text{ mmol ml}^{-1} = 10 \text{ mmol}$$

Also,

$$\text{Number of mmols of Mohr salt} = \frac{\text{Mass of Mohr salt (g)}}{\text{Milli formula mass of Mohr salt (g/mmol)}}$$

$\therefore$ Mass of Mohr salt = 10 mmol × 0·392 g/mmol = 3·92 g

Thus, we dissolve 3·92 g of Mohr salt in water and make the volume exactly 100 ml.

Example 2. You are provided with 100 ml of 0·05 M solution of $KMnO_4$. How would you prepare 50 ml of standard solutions of $KMnO_4$ which are (*i*) 0·002 M and (*ii*) 0·001 M ?

Solution. It can be easily visualised that the number of millimoles of $KMnO_4$ in the concentrated solution must be equal to the number of millimoles in the diluted solution,

Making use of Eq. 2, we have

$$V_{\text{concd}} \times C_{\text{concd}} = V_{\text{dil}} \times C_{\text{dil}} \qquad \text{(concd stands for concentrated)}$$

(*i*) For 0·002 M solution,

$$V_{\text{concd}} \times 0{\cdot}05 \text{ mmol ml}^{-1} = 50 \text{ ml} \times 0{\cdot}002 \text{ mmol ml}^{-1}$$

$$V_{\text{concd}} = 2 \text{ ml}$$

The required solution is thus prepared by taking 2 ml of the given solution and diluting it to exactly 50 ml.

(*ii*) Repeating the calculations for the other solution, we come to the conclusion that we get the required solution by taking 1 ml of the given solution and diluting it to 50 ml.

Example 3. 25 ml of HCl solution required 11·95 ml of 0·02 M $Ba(OH)_2$ for exact titration. Calculate the molarity of HCl.

Solution : The titration reaction is

$$\underset{2\text{ mol}}{2HCl} + \underset{1\text{ mol}}{Ba(OH)_2} \longrightarrow BaCl_2 + 2H_2O$$

Step I. In this titration, 1 mol of $Ba(OH)_2$ reacts with 2 mol of HCl. Therefore, the stoichiometric ratio is given by the expression

$$\text{Stoichiometric ratio} = \frac{2 \text{ mol HCl}}{1 \text{ mol } Ba(OH)_2} = 2$$

Step II. Since the volumes of the reactants are in millilitres, we shall have to take their amounts in millimols for expressing their concentrations in mmols per ml.

The number of millimoles of $Ba(OH)_2$ are obtained with the help of Eq. 2. Thus,

Number of mmol of $Ba(OH)_2$ = Volume of $Ba(OH)_2$ × Concentration of $Ba(OH)_2$

$$= 11{\cdot}95 \text{ ml } Ba(OH)_2 \times 0{\cdot}02 \text{ mmol ml}^{-1}\ Ba(OH)_2$$

Step III. The number of millimoles of HCl are obtained by multiplying the result from step II by the stoichiometric ratio obtained in step I. Thus,

Number of mmols of HCl = 11·95 × 0·02 × 2

Step IV. According to Eq. 2,

Number of mmol of HCl = Volume of HCl (*viz.*, 25 ml) × C_{HCl}

Equating this result with the result obtained from step III, we have

$$25 \text{ ml HCl} \times C_{HCl} = (11{\cdot}95 \times 0{\cdot}02 \times 2) \text{ mmol HCl}$$

$$C_{HCl} = \frac{(11{\cdot}95 \times 0{\cdot}02 \times 2) \text{ mmol HCl}}{25 \text{ ml HCl}}$$

$$= 0{\cdot}019 \text{ mmol ml}^{-1} = 0{\cdot}019 \text{ mol l}^{-1} = \mathbf{0{\cdot}019\ M}$$

A Simple Correlation for Quick and Convenient Volumetric Calculations. The above calculations can be summed up in a simple correlation for quick and convenient volumetric calculations. This

correlation may be expressed as follows :

Volume of HCl × C_{HCl} = Volume of $Ba(OH)_2$ × $C_{Ba(OH)_2}$ × (stoichiometric ratio) where

$$\text{stoichiometric ratio} = \frac{\text{Number of mols of HCl}}{\text{Number of mols of } Ba(OH)_2}$$

In general, **for acid-base titrations**, the correlation would be written as follow :

Volume of acid × C_{acid} = (Volume of base × C_{base}) × (Stoichiometric ratio) where

$$\text{stoichiometric ratio} = \frac{\text{Number of mols of acid}}{\text{Number of mols of base}} \qquad \ldots (5)$$

For **oxidation-reduction titrations**, the correlation can be expressed as follows :

Volume of oxidising agent × Concentration of oxidising agent

= (Volume of reducing agent × Concentration of reducing agent) × (Stoichiometric ratio) ... (6)

$$\text{where stoichiometric ratio} = \frac{\text{Number of mols of oxidising agent}}{\text{Number of mols of reducing agent}}$$

The correlations 5 and 6 would be arbitrarily referred to as **volumetric titration correlations.**

The application of these correlations is illustrated in the following examples.

Example 4. 20 ml of HCl solution required 19·85 ml of 0·01 M NaOH for complete titration. Calculate the molarity of HCl solution.

Solution : The titration reaction is $HCl + NaOH \longrightarrow NaCl + H_2O$

Stoichiometric ratio = 1 mol HCl/1 mol NaOH = 1

According to the volumetric titration correlation,

Volume of HCl × C_{HC} = (Volume of NaOH × C_{NaOH}) × Stoichiometric ratio

$$20 \text{ ml} \times C_{HCl} = (19{\cdot}85 \text{ ml} \times 0{\cdot}01 \text{ mmol ml}^{-1}) \times 1$$

$$\therefore \quad C_{HCl} = \frac{19{\cdot}85 \text{ ml} \times 0{\cdot}01 \text{ mmol ml}^{-1}}{20 \text{ ml}}$$

$$= 0{\cdot}0099 \text{ mmol ml}^{-1} = 0{\cdot}0099 \text{ mol l}^{-1} = \mathbf{0{\cdot}0099\ M}$$

Example 5. 25 ml of H_2SO_4 solution required 48·75 ml of 0·02 M NaOH for complete titration. Calculate the molarity of H_2SO_4.

Solution : The titration reaction is

$$\underset{1\text{ mol}}{H_2SO_4} + \underset{2\text{ mol}}{2NaOH} \longrightarrow Na_2SO_4 + H_2O$$

$$\text{Stoichiometric ratio} = \frac{1 \text{ mol of } H_2SO_4}{2 \text{ mol of NaOH}} = \frac{1}{2}$$

According to the volumetric titration correlation,

Volume of H_2SO_4 × $C_{H_2SO_4}$ = (Volume of NaOH × C_{NaOH}) × Stoichiometric ratio

$$25 \text{ ml} \times C_{H_2SO_4} = (48{\cdot}75 \text{ ml} \times 0{\cdot}02 \text{ mmol ml}^{-1}) \times \frac{1}{2}$$

$$\therefore \quad C_{H_2SO_4} = \frac{48{\cdot}75 \times 0{\cdot}02 \text{ mmol ml}^{-1}}{25 \text{ ml}} \times \frac{1}{2}$$

$$= 0{\cdot}0195 \text{ mmol ml}^{-1} = 0{\cdot}0195 \text{ mol l}^{-1} = \mathbf{0{\cdot}0195\ M}$$

Example 6. A solution of $KMnO_4$ was standardised by titration against a standard solution of oxalic acid obtained by dissolving 1·562 g of oxalic acid (formula mass = 126) in 100 ml of solution. 20 ml of this solution required 9·55 ml of $KMnO_4$ for complete titration. What is the molarity of $KMnO_4$?

Solution : The chemical reaction in this case is

$$\underset{2\text{ mol}}{2\,MnO_4^-} + \underset{5\text{ mol}}{5C_2O_4^{2-}} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Stoichiometric ratio = 2 mol $KMnO_4$/5 mol $H_2C_2O_4$ = 2/5

Concentration of oxalic acid = 1·562 g/100 ml = $\frac{1.562}{126}$ mol/100 ml = 0·124 mol l^{-1} = 0·124 mmol ml^{-1}

According to the volumetric titration correlation,

Volume of $KMnO_4 \times C_{KMnO_4}$ = Volume of oxalic acid × $C_{oxalic\ acid}$ × Stoichiometric ratio

9·55 ml × C_{KMnO_4} = (20 ml × 0·124 mmol ml^{-1}) (Stoichiometric ratio)

$$\therefore \quad C_{KMnO_4} = \left(\frac{20\ ml\ H_2C_2O_4 \times 0{\cdot}124\ ml^{-1}\ H_2C_2O_4}{9{\cdot}55\ ml\ KMnO_4}\right) \times \frac{2}{5}$$

= 0·104 mmol ml^{-1} = 0·104 mol l^{-1} = **0·104 M**

Example 7. 25 ml of iodine solution required 24·85 ml of 0·2 M solution of hypo, $Na_2S_2O_3.5H_2O$, for complete titration. Calculate the molarity of iodine solution.

Solution : The titration reaction in this case is

$$\underset{1\ mol}{I_2} + \underset{2\ mol}{2Na_2S_2O_3} \longrightarrow 2NaI + Na_2S_2O_4$$

Stoichiometric ratio = 1 mol I_2/2 mol $Na_2S_2O_3$ = 1/2

According to the volumetric titration correlation,

Volume of $I_2 \times C_{I_2}$ = Volume of $Na_2S_2O_3 \times C_{Na_2S_2O_3}$ × Stoichiometric ratio

25 ml × C_{I_2} = (24·85 ml × 0·2 mmol ml^{-1}) (Stoichiometric ratio)

$$\therefore \quad C_{I_2} = \left(\frac{24{\cdot}85\ ml\ Na_2S_2O_3 \times 0{\cdot}2\ mmol\ ml^{-1}\ Na_2S_2O_3}{25\ ml\ I_2}\right) \times \frac{1}{2}$$

= 0·099 mmol ml^{-1} = 0·099 mol l^{-1} = **0·099 M**

Example 8. 0·6 g of an impure sample of iron was dissolved in sulphuric acid solution, Fe^{3+} present was reduced to Fe^{2+} and volume made upto 100 ml. 25 ml of this solution required 19·55 ml of 0·025 M $KMnO_4$ for complete titration. Calculate the percentage purity of the sample of iron.

Solution : The reaction of the analyte with $KMnO_4$ is given by the equation

$$\underset{1\ mol}{MnO_4^-} + \underset{5\ mol}{5Fe^{2+}} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Stoichiometric ratio = 1 mol $KMnO_4$/5 mol Fe^{2+} = 1/5

According to the volumetric titration correlation,

(Volume of $KMnO_4 \times C_{KMnO_4}$) = (Volume of Fe^{2+} soln. × $C_{Fe^{2+}}$) × (Stoichiometric ratio)

(19·55 ml × 0·025 mmol ml^{-1}) = (25 ml × $C_{Fe^{2+}}$) × 1/5

$$\therefore \quad C_{Fe^{2+}} = \left(\frac{19{\cdot}55\ ml\ KMnO_4 \times 0{\cdot}025\ mmol\ KMnO_4\ ml^{-1}}{25\ ml\ Fe^{2+}}\right) = 0{\cdot}098\ mmol\ ml^{-1} = 0{\cdot}098\ mol\ l^{-1}$$

Mass of Fe^{2+} = 0·098 mol l^{-1} × 56 g mol^{-1} = 5·488 g l^{-1}

Mass of impure sample = 0·6 g/100 ml = 6·0 g l^{-1}

$$\text{Purity of sample of iron} = \frac{5{\cdot}488 \times 100}{6{\cdot}00} = 91{\cdot}47\%$$

It may be emphasized again that while using the so called volumetric titration correlations, the student should keep in mind that in *acid-base titrations*, the stoichiometric ratio (= number of mols of acid/number of mols of base) is a multiplier with the volume and concentration of the base and not the acid and in *oxidation-reduction titrations*, the stoichiometric ratio (= number of mols of oxidising agent/number of mols of reducing agent) is a multiplier with the volume and concetnration of the *reducing agent* and not the oxidising agent.

p-Functions

The concentration of a species in a dilute solution is expressed, more frequently, in terms of its ***p*-function** or ***p*-value** which is defined *as the negative logarithm (to the base 10) of the molar concentration of that species*. Thus, for the concentration C mol per litre of a species X,

$$pC = -\log C \qquad \ldots (6)$$

The advantage of expressing concentrations in terms of *p-function* is that low concentrations which vary over a wide range can be expressed in small positive numbers. For instance, if the molar concentration of a species varies from 0·00004 M to 0·0000003 M, its *p-function* would vary from 4·4 to 6·5.

Example 9. Calculate the *p*-value for each ion in a solution which is 5·00 × 10^{-4} M in KCl and 7·5 × 10^{-5} M in HCl.

Solution : In this case, the concentrations of various ions are as follows :

$[H^+]$ = 7·5×10^{-5} M

$[K^+]$ = 5·0×10^{-4} M

$[Cl^-]$ = 5·0×10^{-4}M + 7·5×10^{-5}M = 5·75×10^{-4} M

Hence,

pH^+ = − log $[H^+]$ = − log (7·5×10^{-5}) = **4·30**

pK^+ = − log $[K^+]$ = − log (5·0×10^{-4}) = **3·30**

pCl^- = − log $[Cl^-]$ = − log (5·75×10^{-4}) = **3·24**

Example 10. Calculate the molar concentration of Ca^{2+} ions in a solution that has a pCa^{2+} of 5·67.

Solution :

pCa^{2+} = − log $[Ca^{2+}]$ = 5·672

log $[Ca^{2+}]$ = − 5·672 = $\bar{6}$·328

$[Ca^{2+}]$ = antilog of $\bar{6}$·328 = **2·128 × 10^{-6} mol l^{-1}**

VOLUMETRIC TITRATIONS

Volumetric titrations commonly comprise of *1. Acid-Base Titrations. 2. Oxidation-Reduction* or *Redox Titrations* and *3. Complexometric Titrations.*

ACID-BASE TITRATIONS

In acid–base titrations, solutions of acids are titrated against standard alkali solutions or vice versa. For instance, a solution of H_2SO_4, HCl, CH_3COOH or oxalic acid may be titrated against standard NaOH solution. Conversely, a solution of NaOH or Na_2CO_3 may be titrated against a standard solution of H_2SO_4 or HCl.

Acid-Base Titrations and Use of Indicators. The process of acid-base titrations is accompanied by a change in *p*H. A plot between *p*H of the solution during titration and the amount of acid (or alkali) added from a burette is called a **titration curve.**

Indicators are frequently employed in detecting end points in acid-base titrations. Since, on account of hydrolysis, the *p*H value at the end point depends upon the relative strengths of the acid and the base being titrated and since different indicators have different *p*H ranges within which they can be used, the selection of a proper indicator for a given titration is very important. The *p*H changes occurring in some acid-base titrations may be first considered.

Some common indicators together with their useful ranges and extreme colours in acidic and alkaline solutions are given in Table 1.

TABLE 1

Some Useful Indicators

Indicator	pH range	Colour in acidic solution	Colour in alkaline solution	Indicator	pH range	Colour in acidic solution	Colour in alkaline solution
Cresol red (acid)	1·2–1·8	Red	Yellow	Phenol red	6·4–8·2	Yellow	Red
m-Cresol purple	1·2–1·8	Red	Yellow	Cresol red (base)	7·0–8·1	Yellow	Red
Thymol blue (acid)	1·2–2·8	Red	Yellow	Thymol blue (base)	8·1–9·6	Yellow	Blue
Bromophenol blue	3·1–4·6	Yellow	Purple	Phenolphthalein	8·0–9·8	Colourless	Pink
Methyl orange	3·1–4·5	Red	Yellow	Thymolphthalein	9·3–10·5	Colourless	Blue
Methyl red	4·2–6·3	Red	Yellow	Alizarine yellow	10·1–12·1	Yellow	Lilac
Bromothymol blue	6·0–7·6	Yellow	Blue				

Titration of a strong acid against a strong base. The titration of a strong acid with a strong base may be illustrated by the reaction of hydrochloric acid and sodium hydroxide. Suppose, 25 ml of 0·1 M HCl is to be titrated against 0·1 M NaOH. The equivalence or end point will, evidently, occur on the addition of 25 ml of the alkali solution. The *p*H values of the solution at different stages of neutralization are plotted graphically as in Fig. 1 against increasing amounts of the alkali added. It is seen that the *p*H changes very slowly at first and rises from 1 to only about 4 when such a large amount as about 24·99 ml of the alkali solution has been added, *i.e.*, when over 99·9 per cent of the acid has been neutralised. Further addition of such a small amount as 0·01 ml of the alkali raises the *p*H by about 3 units to *p*H 7. The acid is now completely neutralised. Further addition of such a small amount as 0·01 ml of the sodium hydroxide solution (0·1 M) will amount to adding free hydroxyl ions and the *p*H will jump to a value above 9. Thus, near the end point, the titration curve is almost vertical and there is a rapid change of *p*H from about 4 to about 10.

Now an indicator is suitable only if it undergoes a change of colour at the *p*H prevailing near the end point. A reference to Table 1 shows that there are a number of indicators including methyl orange, methyl red, bromothymol blue and phenolphthalein which can undergo colour change within the *p*H range 4 to 10. Thus, while titrating a strong acid with a strong base, any of the above indicators may be used to detect the end point. The *p*H ranges of these indicators are also shown in Fig. 1 for convenience of reference.

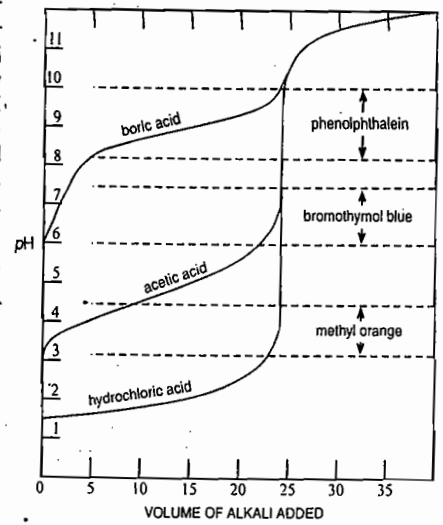


Fig. 1. The *p*H titration curves of different acids with sodium hydroxide. The *p*H ranges of the indicators involved are also shown in the figure.

Titration of a weak acid with a strong base. The titration of a weak acid, like acetic acid, against a strong base like sodium hydroxide, is included in Fig. 1. It will be seen that the vertical portion now does not begin until beyond *p*H 7 and the end point lies somewhere between *p*H 8 and 10. This is due to hydrolysis of sodium acetate. This, being a salt of a weak acid and a strong base, gives excess of free OH^- ions in aqueous solution due to hydrolysis. Hence, phenolphthalein will be a satisfactory indicator but not methyl orange, methyl red or even bromothymol blue. Thymol-phthalein (*cf.* Table 1), though not so common, is another suitable indicator for such titrations.

Fig. 1 also includes a titration curve for boric acid against sodium hydroxide. This titration curve does not show any sharp rise in *p*H. This is because boric acid is so weak (its dissociation constant being $6{\cdot}0\times10^{-10}$) that its salt sodium borate formed during the reaction gets very largely hydrolysed giving alkaline solution. The *p*H, therefore, goes on rising *continuously* and there is *no sharp rise* at the equivalence point. Hence, there is no abrupt change in the colour of the indicator for the addition of a small amount of sodium hydroxide at the equivalence point. Thus, the acids with dissociation constants less than 10^{-7} cannot be successfully titrated.

Titration of a weak base with a strong acid. The titration curve of a weak base like ammonium hydroxide, against a strong acid like hydrochloric acid, is shown in Fig. 2 (dotted line). The *p*H of NH_4Cl (a salt of a weak base and a strong acid) lies in the acid range due to hydrolysis. The *p*H change at the equivalence point, therefore, lies in the range 6 to 4. Thus, methyl orange and methyl red are useful indicators while phenolphthalein cannot be of any use.

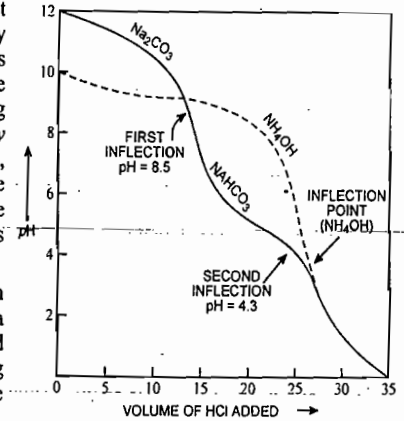


Fig. 2. The *p*H titration curves of weak bases with a strong acid.

Titration of sodium carbonate with hydrochloric acid. The titration curve obtained on reacting sodium carbonate with hydrochloric acid is also included in Fig. 2. It shows two inflection points. The first point of inflection indicates the conversion of sodium carbonate into bicarbonate :

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

This is completed at about *p*H 8·5 and phenolphthalein can be used to detect the end point. The second point of inflection indicates the neutralisation of sodium bicarbonate :

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

This reaction gets completed at *p*H 4·3. Therefore, methyl orange is a highly suitable indicator in this case while phenolphthalein is not of any use.

The Theory of Acid-Base Indicators

Ostwald developed a theory of acid–base indicators which, though incomplete, offers a simple explanation for the colour change with change in *p*H. According to this theory, a hydrogen ion indicator is either a weak organic acid or a base. The undissociated molecule has one colour and the ion furnished by it, on dissociation, has another colour.

Let the indicator be an acid of formula HIn. Then, its ionisation in solution may be represented as

$$\underset{\text{Colour A}}{HIn} \rightleftharpoons H^+ + \underset{\text{Colour B}}{In^-} \qquad \ldots(7)$$

The unionised molecule HIn has one colour, say, colour *A*, while the ion In^- has another colour, say, colour *B*.

The equation for the above equilibrium may be written as

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \qquad \ldots(8)$$

K_{In} is known as **indicator constant.**

Since the species In^- and HIn have different colours, the actual colour shown by the indicator will depend upon the hydrogen ion concentration of the solution. Thus, if the solution is acidic, *i.e.*, it contains excess of H^+ ions, the ratio $[In^-]:[HIn]$ will become low (since K_{In} is constant). In other words, the equilibrium in Eq. 7 will shift towards the left. The indicator will, therefore, show predominantly colour *A* (acidic colour). On the other hand, if the solution is alkaline, *i.e.*, it contains excess of OH^- ions, the H^+ ions furnished by the indicator will be taken up to form unionised water. Therefore, the equilibrium in Eq. 7 will shift towards the right and there will be a larger concentration of the ion In^-. The indicator will, therefore, show predominantly colour *B* (basic colour). Eq. 7, thus, successfully explains the change of colour of an indicator when the solution changes from acidic to alkaline.

Action of Phenolphthalein. Phenolphthalein is a colourless weak acid which ay be represented as HPh. It dissolves in water and dissociates to some extent to give colourless hydrogen ions and pink coloured anions. The equilibrium may be represented as

$$\underset{\text{(Colourless)}}{HPh} \rightleftharpoons \underset{\text{(Colourless)}}{H^+} + \underset{\text{(Pink)}}{Ph^-} \qquad \ldots(9)$$

The actual state of affairs is not so simple. Phenolphthalein, or any other indicator, first undergoes a reversible tautomeric change into a substance of a different colour which then dissociates almost completely to give the coloured anion. The process in the case of phenolphthalein may be represented as

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons \underset{\text{Coloured tautomeric form}}{HPh^*} \rightleftharpoons \underset{\text{Colourless}}{H^+} + \underset{\text{Pink}}{Ph^-} \qquad \ldots(10)$$

But, since the concentration of the undissociated molecules of the tautomeric form is usually very small, the simple dissociation Eq. 9 given above is sufficient for most purposes.

If the solution is acidic, the hydrogen ions furnished by the acid suppress the dissociation of phenolphthalein, shifting the equilibrium towards the left (common ion effect). The solution, therefore,

remains colourless. In the presence of an alkali, however, the hydroxyl ions combine with the H^+ ions furnished by the indicator to form unionised water. The equilibrium, therefore, shifts towards the right, giving more of the coloured anions. The solution, therefore, turns pink. Thus, the indicator appears colourless in acid and pink in alkali solution.

The reason why phenolphthalein is not a suitable indicator for titrating a weak base, like NH_4OH, against a strong acid is that the hydroxyl ions furnished by the weak base at the end point of the titration are too few to shift the equilibrium sufficiently towards the right to raise the *p*H to 8·3, at least and, therefore, pink colour does not appear just at the end point. A sufficient excess of the weak base has to be added to get the pink colour.

Action of Methyl orange. Methyl orange is a weak base which, for simplicity, may be represented as MeOH. It dissolves in water and undergoes dissociation to a small extent. The undissociated molecules are yellow while the cations Me^+ are red in colour. The dissociation may be written as

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + \underset{\text{Colourless}}{OH^-}$$

If the solution is acidic, the hydrogen ions furnished by the acid combine with OH^- ions furnished by the indicator to form unionised water. This shifts the equilibrium towards the right giving more of the red coloured Me^+ ions. Therefore, in acid solution, this indicator gives red colour. In the presence of an alkali, the OH^- ions suppress the dissociation of methyl orange. Hence, the solution in alkaline medium remains yellow in colour.

Methyl orange cannot be used as indicator for titrating a weak acid, like acetic acid, against a strong base because the hydrogen ions furnished by the weak acid at the end point are too few to combine with a sufficient number of hydroxyl ions of methyl orange to shift the equilibrium in favour of the pink coloured Me^+ ions. A sufficient excess of the weak acid has to be added to get the end point.

Mathematical Treatment

The *p*H values obtained experimentally at different stages of an acid-base titration can also be *calculated mathematically*, as illustrated below.

Suppose we are titrating 25 ml of a solution of HCl (0·1 M) against a standard (0·1 M) solution of NaOH and we want to calculate the *p*H of the titration solution after the addition of 20, 24·9, 24·95, 25·00, 25·05, 25·10 and 30 ml of NaOH solution. This is done as follows.

Initial *p*H of the titration solution, *viz.*, 0·1M HCl $= -\log [H^+] = -\log (0{\cdot}1) = 1{\cdot}0$

Since the product of volume in ml and the concentration in mol l^{-1} or mmol ml^{-1} of a solute gives the amount of the solute in millimoles, hence

Amount of HCl initially present in the titration solution = 25 ml×0·1 mmol ml^{-1} = 2·5 mmol

The amount of NaOH in 20 ml of 0·1M solution added during titration = 20 ml×0·1 mmol ml^{-1}

= 2·0 mmol

Amount of HCl left in the titration solution on adding 20 ml of NaOH $= 2{\cdot}5 - 2{\cdot}0 = 0{\cdot}5$ mmol

Total volume of titration solution $= 25 + 20 = 45$ ml

$$\therefore \quad \text{Concn. of HCl or of } H^+ \text{ ions in the solution} = \frac{0{\cdot}5}{1000} \times \frac{1000}{45} \text{ mol } l^{-1}$$

$$\therefore \quad p\text{H of the titration solution} = -\log[H^+] = -\log\left(\frac{0{\cdot}5}{45}\right) = \mathbf{1{\cdot}95}$$

Proceeding as above, the *p*H values of titration solution on the addition of 24·9 and 24·95 ml of NaOH solution come out to be **3·70** and **4·00**, respectively.

On the addition of 25 ml of NaOH, the acid is completely neutralised giving NaCl. The *p*H of the resulting solution is, therefore, 7,

On adding 25·05 ml of NaOH, the additional volume of NaOH = 0·05 ml

Amount of NaOH in 0·05 ml = 0·05 ml×0·1 mmol ml^{-1} = 0·005 mmol

$$\therefore \quad \text{Concn. of NaOH or } OH^- \text{ ions} = \frac{0{\cdot}005}{1000} \times \frac{1000}{50{\cdot}05} \text{ mol } l^{-1}$$

Since, $[H^+][OH^-] = 10^{-14}$ at 25°C

$$\therefore \quad [H^+] = \frac{10^{-14} \times 50{\cdot}05}{0{\cdot}005} = 1{\cdot}001 \times 10^{-10} \simeq 10^{-10} \text{ mol } l^{-1}$$

Hence, $p\text{H} = -\log [H^+] = \mathbf{10{\cdot}00}$

Proceeding as above, the *p*H values of the titration solution after the addition of 25·10 and 30 ml of NaOH solution come out to be **10·30** and **10·96**, respectively.

It is evident from the *p*H values calculated as above that the *p*H increases from 1 to 4 on the addition of 24·95 ml of NaOH. Around the point of equivalence, the *p*H increases from 4 to 7 by the addition of a single drop of NaOH and then from 7 to 10 by the addition of another drop of NaOH. In other words, *around the end point, there is a sharp change in pH from 4 to 10, just by the addition of 2 drops of NaOH solution.*

Now suppose that we are titrating 25 ml solution of **acetic acid** (0·1M) against 0·1M solution of NaOH and we want to calculate the *p*H values of titration solution after the addition of 20, 24·90, 24·95, 25·00, 25·05, 25·10 and 30 ml of NaOH solution. This is now done as follows.

Amount of CH_3COOH present in solution = 25 ml × 0·1 mmol ml^{-1} = 2·5 mmol

Since acetic acid is a weak acid, its H^+ ion concentration is given by the relation

$$[H^+] = \sqrt{cK_a}$$

where *c* is the molar concentration of the acid and K_a is its dissociation constant = $1{\cdot}75 \times 10^{-5}$.

$$\therefore \quad \left.\begin{array}{l}\text{The initial concentration of} \\ H^+ \text{ ions in 0·1 M } CH_3COOH \text{ solution}\end{array}\right\} = \sqrt{0{\cdot}10 \times 1{\cdot}75 \times 10^{-5}}$$

$$= 1{\cdot}32 \times 10^{-3} \text{ mol } l^{-1}$$

$$\therefore \quad p\text{H} = -\log [H^+] = -\log (1{\cdot}32 \times 10^{-3}) = \mathbf{2{\cdot}88}$$

During titration, CH_3COOH gets converted into CH_3COONa. The *p*H of the titration solution would thus depend upon the concentration of CH_3COOH left and of CH_3COONa formed during titration. In a mixture of a weak acid and its salt, the *p*H is given by the relation

$$p\text{H} = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

With the addition of 20 ml of NaOH solution, the amount of NaOH added to the titration solution = 20 ml × 0·1 mmol ml^{-1} = 2·0 mmol

Amount of CH_3COONa formed = 2·0 mmol

Amount of CH_3COOH left $= 2{\cdot}5 - 2{\cdot}0 = 0{\cdot}5$ mmol

*p*H of the titration solution $= 4{\cdot}76 + \log\frac{2{\cdot}0}{0{\cdot}5} = \mathbf{5{\cdot}36}$

(K_a of $CH_3COOH = 1{\cdot}75 \times 10^{-5}$ $\therefore$ $pK_a = -\log K_a = 4{\cdot}76$)

Since volume of the solution is the same for both CH_3COOH and CH_3COONa, the ratio of their amounts in millimoles can be taken as the ratio of their molar concentrations.

Proceedings as above, the *p*H of the titration solution on the addition of 24·90 and 24·95 ml of NaOH solution comes out to be **7·16** and **7·46**, respectively.

On the addition of 25 ml of NaOH solution, the acetic acid is completely neutralised, the resulting product being CH_3COONa. The amount of CH_3COONa formed would be $25 \times 0{\cdot}1 = 2{\cdot}5$ mmol. Since the total volume of the titration solution is 25 + 25 = 50 ml, hence the concentration of $CH_3COONa = \frac{2{\cdot}5 \times 1000}{1000 \times 50} = 0{\cdot}05$ mol l^{-1}. Since CH_3COONa is a salt of a strong base and a weak acid, it would get hydrolysed to give an alkaline solution whose *p*H is given by the relation

$$pH = 14 - \tfrac{1}{2}pK_w + \tfrac{1}{2}\log c + \tfrac{1}{2}pK_a = 14 - \tfrac{1}{2}(14) + \tfrac{1}{2}\log 0{\cdot}05 + \tfrac{1}{2}(4{\cdot}76) = \mathbf{8{\cdot}73}$$

With the addition of 25·05 ml of NaOH, the amount of free NaOH added to the titration solution = $0{\cdot}1 \times 0{\cdot}05 = 0{\cdot}005$ mmol

$\therefore$ Concn. of OH^- ions due to this addition $= \frac{0{\cdot}005}{1000} \times \frac{1000}{50{\cdot}05} = 0{\cdot}0001$ mol l^{-1}

Concentration of OH^- ions due to the hydrolysis of CH_3COONa is given by the expression

$$[OH^-] = \left(\frac{K_w\, c}{K_a}\right)^{\frac{1}{2}} = \left(\frac{10^{-14} \times 0{\cdot}05}{1{\cdot}75 \times 10^{-5}}\right)^{1/2} \text{ mol } l^{-1}$$

$= 0{\cdot}534 \times 10^{-5}$ mol l^{-1} which is negligible as compared to 0·0001 mol l^{-1}

$\therefore$ Total concentration of $[OH^-] = 0{\cdot}0001$ mol l^{-1}

$[H^+][OH^-] = 10^{-14}$ at 25°C

$\therefore$ $[H^+] = 10^{-14}/0{\cdot}0001$

$\therefore$ $pH = \mathbf{10}$

The *p*H of the titration solution on the addition of 25·10 and 30 ml of NaOH solution would be **10·30** and **10·96**, respectively.

The data obtained for the titration of 0·1M HCl and 0·1M CH_3COOH solutions against 0·1M NaOH solution have been summed up in Table 2.

As can be seen, the *p*H in the case of CH_3COOH is higher at each stage upto the end point. This is evidently due to the hydrolysis of CH_3COONa formed during the titration.

TABLE 2

Titrations of 0·1 M HCl and 0·1 M CH_3COOH Solutions against 0·1 M NaOH solution

Volume of NaOH added (ml)	pH values in the titration of :	
	HCl solution	CH_3COOH solutions
0·00	1·00	2·88
20·00	1·95	5·36
24·90	3·70	7·16
24·95	4·00	7·46
25·00	7·00	8·73
25·05	10·00	10·00
25·10	10·30	10·30
30·00	10·96	10·96

If we plot the above data graphically, the *p*H titration curves obtained would be exactly similar to those shown in Fig. 2 for these titrations.

REDOX TITRATIONS

As is well known, an oxidising agent is a substance which can accept one or more electrons and reducing agent is a substance which can furnish one or more electrons. It is, therefore, possible to titrate an oxidising agent against a reducing agent. Such titrations are known as **redox titrations**.

Some of the common oxidising agents used in redox trations are potassium permanganate, potassium dichromate, ceric sulphate, iodine and potassium iodate. Some of the common reducing agents are ferrous sulphate, ferrous ammonium sulphate or Mohr's salt, oxalic acid and alkali oxalates, potassium iodide, arsenious oxide and tartaremetic.

As already stated, the **volumetric titration correlation for redox titrations** may be expressed as

Volume of oxidising agent × Concentration of oxidising agent

= (Volume of reducing agent × Concentration of reducing agent) × (Stoichiometric ratio)

where stoichiometric ratio $= \frac{\text{Number of moles of oxidising agent}}{\text{Number of moles of reducing agent}}$

For instance, for the redox titration involving $KMnO_4$ and $FeSO_4$, for which the chemical reaction is

$$\underset{(1\text{ mol})}{MnO_4} + \underset{(5\text{ mol})}{5Fe^{2+}} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{2+} + 4H_2O,$$

the stoichiometric ratio $= \frac{\text{Number of moles of } KMnO_4}{\text{Number of moles of } FeSO_4} = \frac{1}{5}$

Some Typical Redox Titrations. Some typical redox titrations have been described below.

Titration of Mohr Salt against $KMnO_4$. Mohr salt is titrated against $KMnO_4$ in the presence of dilute sulphuric acid when $FeSO_4$ of the Mohr salt is oxidised to $Fe_2(SO_4)_3$. $KMnO_4$ solution is added to a known volume of Mohr salt solution containing dilute H_2SO_4, *gradually in small amounts.* Rapid addition of $KMnO_4$ results in the formation of hydrated manganese dioxide, $MnO_2.H_2O$, which is brown in colour.

$$2KMnO_4 + 3MnSO_4 + 7H_2O \longrightarrow K_2SO_4 + \underset{\text{Brown colour or ppt}}{5MnO_2.H_2O} + 2H_2SO_4$$

The above reaction also occurs if there is insufficient quantity of H_2SO_4 in the titration solution.

In these titrations, $KMnO_4$ itself acts as the indicator.

Suppose 25 ml of Mohr salt solution requires 15·5 ml of 0·1 M $KMnO_4$ solution for titration. Applying the volumetric titration correlation, we have

$$15{\cdot}5 \times 0{\cdot}1 = (25 \times \text{conc. of Mohr salt}) \times \text{Stoichiometric ratio}$$

The redox reaction in this titration is

$$\underset{5\text{ mol}}{5Fe^{2+}} + \underset{1\text{ mol}}{MnO_4^-} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$\therefore$ Stoichiometric ratio $= \frac{\textit{Number} \text{ of mols of } KMnO_4}{\textit{Number} \text{ of mols of Mohr salt}} = \frac{1}{5}$

$\therefore$ Concentration of Mohr salt solution $= \frac{15{\cdot}5 \times 0{\cdot}1}{25} \times \frac{5}{1} = 0{\cdot}31$ M

Molar mass of Mohr salt is 392 g mol^{-1}

$\therefore$ Amount of Mohr salt = 0·31 mol l^{-1} × 392 g mol^{-1} = 121·52 g l^{-1}

If the concentration of Mohr salt solution is known, we can find out the concentration of $KMnO_4$ solution.

Titration of Oxalic Acid against $KMnO_4$. Oxalic acid, $(COOH)_2.2H_2O$, (or an alkali oxalate) is titrated against $KMnO_4$ in the presence of dilute H_2SO_4, keeping the temperature of oxalic acid solution between 60–70°C. Oxalic acid on oxidation with acidified $KMnO_4$ produces CO_2 according to the reaction

$$\underset{(2\text{ mol})}{2MnO_4^-} + \underset{(5\text{ mol})}{5C_2O_4^{2-}} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The solution is kept hot to expel the CO_2 produced so as *to avoid the back reaction.*

The stoichiometric ratio in this titration is, evidently, 2/5.

Suppose 20 ml of oxalic acid solution require 25 ml of 0·05 M $KMnO_4$ solution for titration. Then, the concentration of oxalic acid solution $= \frac{25 \times 0{\cdot}05}{20} \times \frac{5}{2} = 0{\cdot}156$ M. Accordingly, the amount of oxalic acid (molar mass 126 g mol^{-1}) would be 0·156 mol l^{-1} × 126 g mol^{-1} = 19·656 g l^{-1}.

Titration of $FeSO_4$ against $K_2Cr_2O_7$. Ferrous sulphate can also be titrated against $K_2Cr_2O_7$ in the presence of dilute sulphuric acid using an internal or an external indicator. The redox reaction involved in this titration is

$$\underset{6\text{ mol}}{6Fe^{2+}} + \underset{1\text{ mol}}{Cr_2O_7^{2-}} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

so that the stoichiometric ratio $= \dfrac{\textit{Number of mols of } K_2Cr_2O_7}{\textit{Number of mols of } FeSO_4} = \dfrac{1}{6}$

The **internal indicator** is diphenyl amine (1% solution is conc. H_2SO_4) which is blue in colour.

For this titration, $K_2Cr_2O_7$ solution is gradually added to a known volume of the solution of $FeSO_4$ to which 3–4 drops of the indicator along with suitable amounts of H_2SO_4 and phosphoric acid have been added. The solution which is initially green in colour, develops, at the end point, a permanent intense bluish-violet colour.

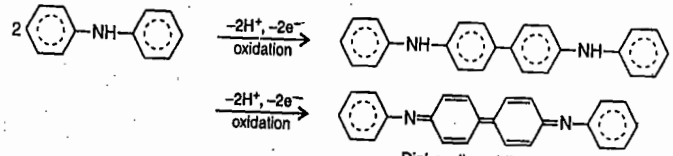
Suppose 20 ml of $FeSO_4$ solution require 12·5 ml of 0·05 M $K_2Cr_2O_7$ for titration. Since the stoichiometric ratio, as mentioned above, is $\frac{1}{6}$, the concentration of $FeSO_4$ solution $= \dfrac{12{\cdot}5\times0{\cdot}05\times6}{20} = 0{\cdot}187\text{ M} = \dfrac{12{\cdot}5\times0{\cdot}05\times6}{20} = 0{\cdot}187\text{ M}$

Therefore, the amount of $FeSO_4.7H_2O$ (molar mass 278 g mol^{-1}) in the solution

$$= 0{\cdot}187\text{ mol l}^{-1}\times278\text{ g mol}^{-1} = 51{\cdot}98\text{ g l}^{-1}.$$

If we know the concentration of $FeSO_4$ solution, we can find out the concentration of $K_2Cr_2O_7$ solution.

As mentioned above, diphenyl amine is used as an internal indicator in dichromate titrations. In the present case, when all the Fe^{2+} ions have been oxidised to Fe^{3+} ions, $K_2Cr_2O_7$ oxidises diphenyl amine to diphenyl benzidine which is *violet* in colour.



Diphenylbenzidine (violet)

The **external indicator** used in the above titration is freshly prepared potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$, which gives a blue colour with Fe^{2+} ion due to the formation of the complex $KFe[Fe(CN)_6]$.

During the titration, drops of the reaction mixture are taken out with the help of a glass rod at intervals and tested with drops of $K_3[Fe(CN)_6]$ placed on a tile. Absence of a colour change indicates absence of Fe^{2+} ions and hence completion of titration. This is, of course, a rough titration. An almost exact end point is obtained in a subsequent titration in which the number of drops taken out from the titration solution is minimum.

Titration of Iodine Solution against Sodium thiosulphate. Iodine solution can be titrated against sodium thiosulphate (as also against sodium sulphite, sodium arsenite, etc.) using starch as the indicator. Iodine gives an intense blue colour with starch due to the formation of a surface complex. The redox reaction involved in the titration is

$$\underset{2\text{ mols}}{2S_2O_3^{2-}} + \underset{1\text{ mol}}{I_2} \longrightarrow S_4O_6^{2-} + 2I^-$$

Stoichiometric ratio in this titration is, evidently, $\frac{1}{2}$.

Suppose 25 ml of an iodine solution requires 20·5 ml of 0·1 M $Na_2S_2O_3$ solution for titration. The concentration of iodine solution would thus be $\dfrac{20{\cdot}5\times0{\cdot}1}{25}\times\dfrac{1}{2} = 0{\cdot}041$ M. The amount of iodine (molar mass 254 g mol^{-1}) would, therefore, be $0{\cdot}041\text{ mol l}^{-1}\times254\text{ g mol}^{-1} = 10{\cdot}414\text{ g l}^{-1}$.

If we know the concentration of iodine solution, we can find the concentration of sodium thiosulphate solution. Suppose 25 ml of thiosulphate solution requires 30·5 ml of 0·05 M solution of iodine for titration. The concentration of $Na_2S_2O_3.5H_2O$ is, then,

$$= \frac{30{\cdot}5\times0{\cdot}05}{25}\times\frac{2}{1} = 0{\cdot}122\text{ M}$$

Thus, the amount of thiosulphate (molar mass 248 g mol^{-1}) in the solution

$$= 0{\cdot}122\text{ mol l}^{-1}\times248\text{ g mol}^{-1} = 30{\cdot}256\text{ g l}^{-1}$$

Iodometric Estimation of $CuSO_4$. The amount of $CuSO_4$ present in a given solution can be easily estimated iodometrically. For this purpose, KI solution is added to a known volume of $CuSO_4$ solution when iodine gets liberated which can be titrated against a standard solution of sodium thiosulphate. The reactions involved are as follows :

$$CuSO_4 + 2KI \longrightarrow K_2SO_4 + CuI_2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$\underset{1\text{ mol}}{I_2} + \underset{2\text{ mol}}{2Na_2S_2O_3} \longrightarrow 2NaI + Na_2S_4O_6$$

Stoichiometric ratio in the redox reaction = 1/2

Suppose, the iodine liberated from 25 ml of copper sulphate solution requires 20·5 ml of 0·1 M solution of thiosulphate for titration. Accordingly, the concentration of iodine solution $= \dfrac{20{\cdot}5\times0{\cdot}1}{25}\times\dfrac{1}{2} = 0{\cdot}041$ M

According to the above equations,

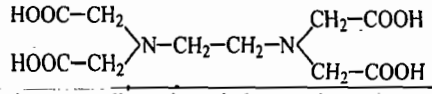
$$1\text{ mol of } I_2 \equiv 1\text{ mol of } CuSO_4$$

Hence, concentration of $CuSO_4$ solution = 0·041 M

∴ Amount of $CuSO_4.5H_2O$ (molar mass 249 g mol^{-1}) present in the solution = $0{\cdot}041\text{ mol l}^{-1}\times249\text{ g mol}^{-1}$ = **10·21 g l^{-1}**.

COMPLEXOMETRIC TITRATIONS

Most of the metal ions react with electron pair donors to form complex ions. The donor species are called **ligands**. A ligand which has only a single donor group, as, for example, NH_3 and H_2O, is called *unidentate* whereas ligands having two or more than two donor groups, are called *polydentate*. Ethylene diamine $H_2N{-}CH_2{-}CH_2{-}NH_2$ and glycine $H_2N{-}CH_2{-}COOH$ are *bidentate* ligands since while the former can coordinate through the two nitrogen atoms, the latter can coordinate through the oxygen of the COOH group and the nitrogen of the NH_2 group. Ethylene diaminetetraacetic acid (**EDTA**),



is a *hexadentate* ligand since it can coordinate through the *two* nitrogen atoms and the *four* oxygen atoms of the four COOH groups.

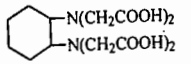
As discussed earlier in Chapter 26, most of the inorganic ligands are unidentate and a few are bidentate. The complexation reactions with these ligands mostly *remain incomplete*. This is because in the formation of a complex with such ligands, more than one ligand molecule or ion has to be added to satisfy the coordination number of the central ion. The process of addition occurs in steps resulting in the formation of intermediate complex ions. For example, in the formation of $[Ag(NH_3)_2]^+$ complex, the intermediate complex ion $[Ag(NH_3)]^+$ also persists in moderate concentrations of ammonia. Similarly, in the formation of $[Cu(CN)_4]^{2-}$ complex, the intermediate complex ion species such as $[Cu(CN)]^+$, $[Cu(CN)_2]$ and $[Cu(CN)_3]^-$ also persist in the solution. The complexation reactions with unidentate ligands remain incomplete in terms of the required amount of ligand for complete complexation.

The polydentate ligands which are generally organic compounds form only 1 : 1 complexes with most of the metal ions. The complexation reaction thus takes place *in one step without the formation of any intermediate species*. The one-step complexation reaction with polydentate ligands proceeds essentially to completion at reasonably fast rates resulting in the formation of stable complexes.

The quick, complete and one-step interaction of polydentate, ligands with metal ions to yield stable complexes, is the basis of the present day **complexometric titrations** *in which metal ion solutions are titrated against solutions of polydentate ligands.* A fairly large number of polydentate titrants are now available for complexometric titrations. Some of these are listed in Table 4.

TABLE 4

Some Common Polydentate Titrants for Complexometric Titrations

Titrant	Abbreviation of the name	Structural Formula
1. Ethylene diamine tetraacetic acid	EDTA	$(CH_2)_2\langle N(CH_2COOH)_2,\ N(CH_2COOH)_2$
2. N-Hydroxymethyl ethylene diamine triacetic acid.	HEDTA	$(CH_2)_2\langle N\langle CH_2OH,\ CH_2COOH,\ N(CH_2COOH)_2$
3. Ethylene glycol-bis-(β-amino ethyl ether) N, N–tetra-acetic acid	EGTA	$(CH_2)_2\langle O(CH_2)_2N(CH_2COOH)_2,\ O(CH_2)_2N(CH_2COOH)_2$
4. Diethylenetri-aminepentaacetic acid	DPTA	$HOOCCH_2{-}N[(CH_2)_2N(CH_2COOH)_2]_2$
5. Ethyl ether diaminetetraacetic acid	EEDTA	$O\langle (CH_2)_2N(CH_2COOH)_2,\ (CH_2)_2N(CH_2COOH)_2$
6. Nitrilotriacetic acid	NTA	$N(CH_2COOH)_3$
7. Cyclohexane diaminetetraacetic acid	CDTA or DCTA	
8. Triethylene tetraminehexaacetic acid	TTHA	$(CH_2)_2\langle N\langle CH_2COOH,\ (CH_2)_2N(CH_2COOH)_2,\ N\langle (CH_2)_2N(CH_2COOH)_2,\ CH_2COOH$
9. Triethylene tetramine	TRIEN	$(CH_2)_2\langle NH{-}(CH_2)_2{-}NH_2,\ NH{-}(CH_2)_2{-}NH_2$
10. Tetraethylene pentamine	TETREN	$HN\langle (CH_2)_2NH(CH_2)_2NH_2,\ (CH_2)_2NH(CH_2)_2NH_2$
11. Pentaethylene hexamine	PENTEN	$H_2N(CH_2)_2\rangle N(CH_2)_2N\langle (CH_2)_2NH_2,\ H_2N(CH_2)_2\rangle N(CH_2)_2N\langle (CH_2)_2NH_2$

Of the various titrants listed in Table 2, EDTA is by far the most commonly used. It is commercially available under a variety of names such as *versone*, *Trilon B*, *sequestrene*, *complexone*, etc. The titrants EGTA, TTHA and DCTA are recommended for use under special conditions. For instance, EGTA is specifically used for estimating Ca^{2+}, Ba^{2+} and Sr^{2+} in which Mg^{2+} does not interfere. The titrants TRIEN, TETREN and PENTEN form stable complexes only with some of the transition elements such as Ag^+, Cd^{2+}, Ni^{2+}, Zn^{2+} and can be used as selective titrants for these elements only. *In this chapter, we would describe only the EDTA titrations in some details.*

EDTA TITRATIONS

The abbreviation EDTA is use for both the original compound, *viz.*, ethylenediaminetetraacetic acid, as well as its disodium salt. The disodium salt is preferred for use because of its adequate solubility in aqueous solutions. The free acid or its disodium salt can be obtained in a primary standard purity. The reagent has a favourably high molar mass and its aqueous solution remains stable over a long period of time.

EDTA forms stable, water-soluble, 1 : 1 complexes with most of the polyvalent metal ions. The structure of the complex ion formed by the interaction of a divalent ion M^{2+} with EDTA is shown in Fig. 3.

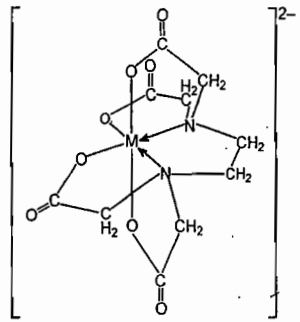


Fig. 3. Structure of EDTA complex with M^{2+} metal ion.

As can be seen, all the six donor groups of the ligand, *viz.*, two nitrogen atoms and four oxygen atoms of the four carboxylic groups are involved in bonding with the metal ion. Also, the complex ion has a cage-like structure in which the metal ion is so well surrounded by the donor groups that it remains almost completely isolated from the solvent molecules. As a result, the complex ion is highly stable.

Since EDTA is a tetraprotic acid, it is usually written as H_4Y, for the sake of brevity and convenience. The dissociation constants for the four COOH groups are : $K_1 = 1{\cdot}0\times10^{-2}$; $K_2 = 2{\cdot}15\times10^{-3}$; $K_3 = 6{\cdot}92\times10^{-7}$ and $K_4 = 5{\cdot}5\times10^{-11}$. From these dissociation constants, it can be easily shown that at $pH > 12$, most of the EDTA exists as the tetra anion, Y^{4-} ; around pH 8, the predominant species is HY^{3-} whereas around pH 5, the main species is H_2Y^{2-}. Most of the EDTA titrations are carried out in neutral or alkaline solutions in which the predominant species are H_2Y^{2-} and HY^{3-}.

Irrespective of the valencies of the metal ions, EDTA reacts with them in a 1:1 ratio. Thus, the reactions with monovalent Ag^+ ion, divalent Ca^{2+} ion and trivalent Al^{3+} ion are represented as follows :

$$Ag^+ + Y^{4-} \rightleftharpoons AgY^{3-}$$

$$Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-}$$

$$Al^{3+} + Y^{4-} \rightleftharpoons AlY^{-}$$

The titration reaction between the metal ion, M^{n+} and EDTA, carried out in neutral or alkaline solution in which the predominant EDTA species would be H_2Y^{2-} and HY^{3-}, may be represented as

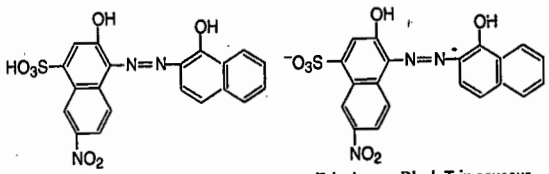
$$M^{n+} + H_2Y^{2-} \rightleftharpoons MY^{(n-4)+} + 2H^+$$

$$M^{n+} + HY^{3-} \rightleftharpoons MY^{(n-4)+} + H^+$$

depending upon the exact pH of the solution.

The protons liberated in these reactions would considerably alter the pH of the solution and would thus cause the back reaction, *i.e.*, the dissociation of the metal-EDTA complex. This is prevented by adding an excess of an innocuous buffer to the titration system.

Indicators for EDTA Titrations. Several organic dyes have been suggested to act as indicators in EDTA titrations. These dyes form complexes with metal ions which are *intensely coloured*. The formation of a metal-indicator complex occurs in a specific range of the concentration of the metal ion. This range is characteristic of the metal ion and the indicator used. The most widely used indicator in these titrations is **Eriochrome Black T.** Its structures in unionised and ionised states are shown in Fig. 4.



Eriochrome Black T unionised form colour : *Black* (*a*)

Eriochrome Black T in aqueous medium ionised form colour : *Red* (*b*)

Fig. 4. Structures and colours of Eriochrome Black T in unionised and ionised states.

The SO_3H group of the indicator gets ionised in aqueous medium giving an anion (Fig. 4*b*) which has a red colour. The phenolic groups of the dye also get ionised, though partially, at higher *p*H values. Representing the indicator as H_3In, for the sake of convenience and brevity, its dissociations may be expressed as follows :

Dissociation of the indicator in solutions of *p*H less than 6 :

$$\underset{\text{Black}}{H_3In} + H_2O \longrightarrow H_3O^+ + \underset{\text{Red}}{H_2In^-}$$

Dissociation of H_2In^- (in solutions of *p*H more than 7) :

$$(i)\quad \underset{\text{Red}}{H_2In^-} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{Blue}}{HIn^{2-}} \;;\quad K_1 = 5\times10^{-7}$$

$$(ii)\quad \underset{\text{Blue}}{HIn^{2-}} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{Orange}}{In^{3-}} \;;\quad K_2 = 2{\cdot}8\times10^{-12}$$

It readily follows from the above that the indicator would exhibit different colours, *viz.*, red, blue or orange, depending upon the manner in which it dissociates which, in turn, depends upon the *p*H of the solution. Thus, in a solution of *p*H less than 6, the indicator, being in the form H_2In^-, is red whereas in a solution of *p*H 7 or above, the indicator, existing predominantly in the form HIn^{2-}, is blue in colour. In more alkaline solutions, in which the indicator exists as In^{3-} species, its colour would be orange.

Thus, Eriochrome Black T behaves not only as a metal ion indicator but also as an acid-base indicator since the acids and their conjugate bases have different colours.

EDTA Titrations. EDTA titrations are carried out by taking the standard solution of the sodium salt of EDTA in the burette and the solution of the metal ions in the titration flask. A suitable amount of the indicator, *viz.*, sodium salt of Eriochrome Black T is added to the metal ions solution. The two species react together to form a metal ion-indicator complex. If the metal ion is bivalent represented as M^{2+}, the complex formed in aqueous solution would be MIn^-. In more than two dozen cases, the metal ion-indicator complexes are red in colour. Assuming that the metal ion M^{2+} is one of these two dozen cases, the complex MIn^- would be red in colour. A buffer solution of appropriate *p*H is added to the titration flask. Let us suppose that this *p*H is around 10. In this solution, EDTA or its sodium salt would exist predominantly as HY^{3-}, as already discussed. The EDTA specie reacts instantaneously with the metal ion-indicator complex to form metal-EDTA complex. This is because the metal ion-indicator complex is much less stable than the metal-EDTA complex. The end point reaction may thus be represented as

$$\underset{\substack{\text{Metal ion-indicator}\\ \text{complex}\\ \text{(Less stable)}}}{MIn^-} + \underset{\substack{\text{EDTA}\\ \text{species}\\ \text{(Red)}}}{HY^{3-}} \rightleftharpoons \underset{\substack{\text{Free}\\ \text{indicator}\\ \text{(Blue)}}}{HIn^{2-}} + \underset{\substack{\text{Metal ion-EDTA}\\ \text{complex}\\ \text{(more stable)}}}{MY^{2-}}$$

As mentioned above, the metal ion-indicator complex MIn^- is *red* in colour. The free indicator HIn^{2-} liberated in the end point reaction would be *blue* in colour since the *p*H of the buffer is around 10. Thus, *a change in colour from red to blue marks the approach of the end point.*

Complexometric Titration Curves. A plot of negative logarithm of the molar concentration of the *uncomplexed metal ion, viz.*, *p*M, as a function of the volume of titrant solution added to the titration solution, gives a complexometric titration curve.

The titration curve obtained for the titration of 50 ml of an approximately 0·005 M Ca^{2+} solution against 0·01 M EDTA solution at *p*H 10 is shown in Fig. 5.

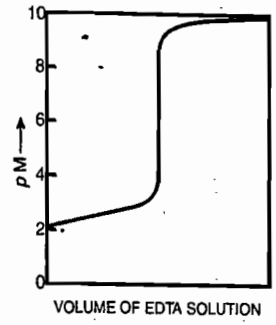


Fig. 5. Titration curve of 0·005 M Ca^{2+} solution against 0·01 M EDTA solution at *p*H 10.

In EDTA titrations, the sharpness of end point depends considerably on the *p*H of the titration solution. The influence of *p*H on the titration of 0·005 M Ca^{2+} solution with 0·005 M EDTA is depicted in Fig. 6. As can be seen, a sharp end point is obtained only when the *p*H of the medium is 8 or above.

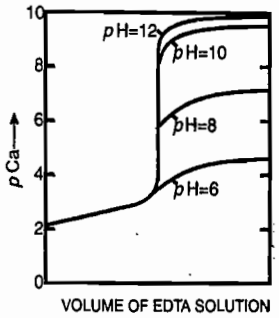


Fig. 6. Titration curves of 0·005 M Ca^{2+} solution against 0·005 M EDTA solution at different *p*H values.

The *p*H of the medium required for getting a sharp end point varies from ion to ion. For example, while cations such as Ca^{2+}, Sr^{2+}, Mg^{2+} give sharp end points in the range of *p*H 8 – 10, cations such as Mn^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+} give sharp end points in the range of *p*H 4 – 6. Cations such as Cu^{2+}, Hg^{2+}, Ga^{3+} exhibit sharp end points in the range of *p*H 2 – 4 whereas Fe^{3+} and In^{3+} show sharp end points in the range of *p*H 1 – 2. In general, cations for which metal ion – EDTA complexes are comparatively less stable give good end points in higher *p*H media whereas cations for which metal ion–EDTA complexes are comparatively more stable exhibit good end points in lower *p*H media.

Thus, moderately acidic media are suitable for titration of many divalent heavy metal cations whereas strongly acidic media are acceptable in the titration of such ions as Fe^{3+} and In^{3+}.

A general idea about the relative stabilities of EDTA complexes formed with various cations can be had from the values of their formation constants (stability constants) given in Table 5.

It should be noted that the above values are very much *p*H dependent and each value applies at a single *p*H value at which it has been determined.

TABLE 5

Formation Constants of EDTA Complexes formed with Various Cations at 20°C

Cation	Formation constant	Cation	Formation constant	Cation	Formation constant
Ag^+	$2{\cdot}0\times10^{7}$	Mn^{2+}	$6{\cdot}3\times10^{13}$	Hg^{2+}	$6{\cdot}3\times10^{21}$
Mg^{2+}	$4{\cdot}9\times10^{8}$	Ni^{2+}	$4{\cdot}3\times10^{18}$	Pb^{2+}	$1{\cdot}0\times10^{18}$
Ca^{2+}	$5{\cdot}0\times10^{10}$	Co^{2+}	$2{\cdot}1\times10^{16}$	Al^{3+}	$1{\cdot}3\times10^{16}$
Sr^{2+}	$4{\cdot}4\times10^{8}$	Cu^{2+}	$6{\cdot}3\times10^{18}$	Fe^{3+}	$1{\cdot}2\times10^{25}$
Br^{2+}	$5{\cdot}9\times10^{7}$	Zn^{2+}	$3{\cdot}2\times10^{16}$	V^{3+}	$7{\cdot}8\times10^{25}$
Fe^{2+}	$2{\cdot}1\times10^{14}$	Cd^{2+}	$2{\cdot}9\times10^{16}$	Th^{2+}	$1{\cdot}6\times10^{23}$

EDTA Titration Methods. The following methods are generally used for carrying out EDTA titrations.

Direct and Back Titration Methods. There are about four dozen elements which can be estimated **by direct titration** with EDTA using metal ion indicators. In the case of many other elements, direct titration method is not applicable either due to non-availability of suitable indicators or due to the reactions between the metal ions and EDTA being too slow making the titration impractical. In such cases, cations are estimated by back titration method.

In **back titration method**, a measured excess of a standard solution of EDTA is added to the analyte solution and the excess of EDTA is back titrated against a standard solution of Mg^{2+} or Zn^{2+} ions using Eriochrome Black T as indicator. It is tacitly assumed that the EDTA complex formed by Mg^{2+} or Zn^{2+} ion is less stable than the corresponding Analyte–EDTA complex. If it is not so, the Mg^{2+} or Zn^{2+} ions would react with the Analyte–EDTA complex also, making the back titration completely erratic.

Displacement Method. This method is useful for the estimation of those cations for which suitable indicators are not available.

In displacement titrations, an unmeasured excess of a solution containing the magnesium or zinc complex of EDTA is added to the solution of the analyte. Assuming that the analyte forms a more stable complex with EDTA than that formed by magnesium or zinc, the following displacement reaction would take place :

$$ZnY^{2-} + M^{2+} \longrightarrow MY^{2-} + Zn^{2+}$$

where M^{2+} stands for the analyte cation. The Zn^{2+} or Mg^{2+} ion, thus liberated, is then titrated against a standard solution of EDTA using Eriochrome Black T as the indicator.

Selectivity in EDTA Titrations. As already mentioned, EDTA combines with metal ions in the ratio of 1:1 irrespective of their valencies to form *almost exactly the same type of complexes*. So, on first sight, the EDTA reagent appears to be totally lacking in selectivity. But, actually, it is not so. The fact that the stability of EDTA complexes depends considerably on *p*H, makes the EDTA titrations adequately selective. For instance, in solutions of *p*H around 1, none of the divalent ions forms complex with EDTA whereas the trivalent ions are quantitatively complexed. Thus, metal ions such as Fe^{3+} and In^{3+} can be estimated without any interference from divalent ions such as Ca^{2+}, Mg^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, etc., if titration is carried out in strongly acidic solution (*p*H around 1).

Ions such as Cd^{2+} and Zn^{2+} form more stable complexes with EDTA than does Mg^{2+} (Table 5). In solutions of *p*H 7, Eriochrome Black T does not form complex with Mg^{2+} ion. Thus, by buffering the reaction mixture to *p*H 7, Cd^{2+} and Zn^{2+} ions can be estimated in the presence of Mg^{2+} ions without any interference from the latter.

Masking of Ions. Selectivity is also provided by what is known as the **masking of interfering cations**. For instance, Mg^{2+} and Ca^{2+} can be titrated in the presence of interfering ions such as Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Pd^{2+} by adding cyanide ions to the reaction mixture as the *masking agent*. The cyanide ion forms stable cyanide complexes such as $[M(CN)_4]^{2-}$ with the latter cations which, therefore, do not react with EDTA.

EDTA titrations permit determination of more than one ion present in a mixture employing the so called **masking and demasking of cations**. For instance, we can estimate Mg^{2+}, Zn^{2+} and Cu^{2+} ions when present in a mixture by following the procedure described below.

1. A measured excess of standard EDTA solution is added to a known volume of the mixture solution. The excess of EDTA is back titrated against standard Mg^{2+} ions solution using Eriochrome Black T as the indicator. This permits determination of the sum of the concentrations of all the ions present in the mixture.

2. A known volume of fresh mixture solution is then titrated against standard EDTA solution after adding to the mixture an excess of KCN solution. This would give the concentration of only the Mg^{2+} ions since Zn^{2+} and Cu^{2+} ions get masked by the cyanide ions.

3. A solution of chloral hydrate ($CCl_3CHO.H_2O$) is then added to the same titration mixture as obtained above in (2), in the ratio of 3:1 by volume. This results in the demasking of Zn^{2+} ions which are titrated by further addition of EDTA till the indicator gives a blue colour. This would give the concentration of Zn^{2+} ions.

4. From 1, 2 and 3, the concentration of Cu^{2+} ions is easily obtained.

CAUTIONS IN VOLUMETRIC TITRIMETRY

Precautions to Avoid Errors in Titrimetric Analysis. The following precautions are required to be taken to get accurate results in titrimetric analysis by warding off errors which are otherwise likely to creep in.

1. The entire apparatus should be thoroughly cleansed with chromic acid mixture and then washed with distilled water.
2. The burette and pipette should be rinsed properly with appropriate solutions.
3. The pipette selected should have small orifice so that the liquid is not discharged too rapidly. The time for the discharge of liquid in the case of 10 ml pipette should be about 20 second and in the case of a 25 ml pipette it should be about 30 seconds.
4. After the continuous discharge of the liquid, the jet of the pipette should be held in contact with the side of the titration flask for about 15 seconds to drain out the liquid held in the jet.
5. The orifice of the burette should be small so that the extra drop required for the appearance of the end point should have the minimum possible volume introducing thereby the minimum possible error.
6. For very accurate work, microburette having 1 ml divided into 20 divisions (instead of 10) should be used. This would enable accurate recording of the volume used for titration upto second place of decimal.
7. The pipette, burette and measuring flask, etc., should be calibrated against standard equipment.
8. The substance to be weighed must be at room temperature. If hot, it must be cooled in a desiccator. If the substance is weighed while hot, the convection currents of air produced in the balance case, would introduce error in weighing.
9. If the substance is volatile, hygroscopic or efflorescent, it must be weighed in a closed vessel.
10. It is understood that the analyst does not suffer from any physical handicap, particularly colour blindness. He should also have a proper height for reading the burette correctly.

Corrections for Unavoidable Errors. Most of the errors which are likely to get involved in volumetric titrimetry can be avoided by observing the precautions mentioned above. There are, however, a couple of errors which cannot be avoided and for these suitable corrections have to be applied. These errors are due to

1. Unequal effect of buoyancy of air on the weights and the substance being weighed.
2. Difference in the temperature at which the standard measuring equipment is calibrated and that at which experiments are performed.

The errors introduced by the above factors and the corrections which are to be applied are discussed below.

1. Buoyancy Factor. According to Archimedes principle, when a body is immersed in a fluid, it experiences an upthrust which is equal to the weight of the fluid displaced. This upthrust is also known as buoyancy. When a solute is being weighed, the buoyancy of air acting on the solute is more than that acting on the weights. This is because the volume of air displaced by the former would be more because of its lower density and hence larger volume. As a result, the weight of the solute recorded by the balance would be less than its actual weight.

If the density of steel (of which the weights are generally made) is taken as 8 gram per c.c. and the mean density of air is taken as 0·00125 gram per c.c., then the true weight of the substance, *i.e.*, the weight in vacuum, would be given by the empirical relation

$$W_v = W_a + W_a \left\{0{\cdot}00125\left(\frac{1}{\rho}-\frac{1}{8}\right)\right\} \qquad ...(11)$$

where ρ is the density of the substance, W_v is the weight of the substance in vacuum and W_a is the weight of the substance in air.

2. Temperature Factor. The standard measuring equipment, *viz.*, the pipette, burette and the measuring flask (against which the equipment under use has to be calibrated) would deliver the same volumes of the liquid as indicated on them only at the temperature marked on them. If the temperature at which

experiments are carried out is different, the volumes of the liquid delivered by them would be different since the coefficient of expansion of water is different from that of glass. Taking into consideration, the coefficients of expansion of soda glass, borosil glass and of water, correction factors have been calculated. The corrections for volumes of water measured by one-litre flask are given in Table 6. The correction factor is to be added if it carries a positive sign and substracted if it carries a negative sign.

TABLE 6
Temperature Corrections for Volumes of Water Measured in 1000 ml Glass Flask Graduated at 60°C

Temperature	Volume Corrections (ml) for :	
	Soda Glass Flask	Borosil Glass Flask
5	+ 1·368	+ 1·605
10	+ 1·245	+ 1·395
15	+ 0·765	+ 0·842
20	+ 0·000	0·000
25	– 1·035	– 1·110
30	– 2·309	– 2·455

QUESTIONS

1. Explain the terms : standard solution, titration, equivalent point, end point, indicator, as used in volumetric titrimetry. What are the basic requirements of a titration reaction ?
2. What are primary standards ? What are the qualities which a primary standard must have ? How are the concentrations of standard solutions expressed ? What is implied by *pX*, *pH*, *pK*, *pCa*, *pCl* ?
3. What is an acid-base titration ? Discuss the use of indicators in acid-base titrations.
4. Give a clear and precise definition of a hydrogen ion indicator. Discuss in details the Ostwarld's theory of acid basc-indicators.
5. What are hydrogen ion indicators ? Discuss in details the use of indicators to acid-base titrations.
6. Why do we use phenolphthalein for the titration of a strong alkali with a weak acid and methyl orange for the titration of a weak alkali with a strong acid ?
7. Wht is a titration curve ? Discuss the titration curves for the neutralisation of
   (*i*) at a strong acid with a strong base (*ii*) at a strong acid with a weak base (*iii*) at a weak acid with a weak basc
8. Write all you know about the theory of indicators, with methyl orange and phenophthalein as examples.
   To a solution of sodium carbonate, two drops of methyl orange and two drops of phenolphthalein are added. It is then completely neutralised by adding sulphuric acid drop by drop. What colour changes take place during neutralisation and why ?
9. Define acid-base indicator. What is the mechanism of its action ? What is meant by the useful range of an indictor ? Show with a rough graphical sketch how to choose an indicator for the titration of a weak acid with a strong base.
10. Explain clearly how the *p*H values obtained experimently at different stages of an acid-basc titration can be calculated mathematically ?
11. What are redox titrations ? Give examples. Discuss briefly the theory of redox indicators.
12. What is a complexometric titration ? Name some important polydentate titrants for complexometric titrations.
13. What is EDTA ? What are EDTA titrations ? What type of indicators are used in EDTA titrations ? Explain clearly the working of these indicators.
14. How are the EDTA titrations carried out ? Why are they so much dependent on *p*H of the titration solution.
15. Distinguish carefully between stability constant and conditional stability constant of a metal-EDTA complex.
16. (*a*) Explain clearly how the *p*M values obtained experimentally at different stages in a complexometric titration can be calculated mathematically.
    (*b*) 25 ml of a solution of Ca^{2+} ions (0·1 M) is being titrated against standard (0·1 M) solution of EDTA. Calculate the *p*M values of the titration solution on the addition of 10, 20, 24·9, 25·0, 25·5, 30, 40 and 50 ml of EDTA solution. Conditional stability constant of Ca-EDTA complex is 5×10^{11}.
17. Describe in details the various methods which are employed for carrying out EDTA titrations.
18. Although EDTA combines with metal ions in the ratio of 1:1 irrespective of their valency to form almost exactly the same type of complexes, yet the EDTA titrations are adequately selective. Comment on this statemeht.
19. What is the cause of selectivity in EDTA titrations ?
    Explain clearly how selectivity is provided by the masking of interfering cations.
20. What is meant by masking and demasking of cations. How is it carried out ? What is the aim of doing so ?
21. Mention briefly the precautions which are required be taken to avoid errors in titrimetric analysis.
22. What sort of errors get introduced due to buoyancy and temperature factors. How are these errors corrected ?

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