

Relationship between molar conductivity and equivalent conductivity

$$\frac{\Lambda_m}{\Lambda_{eq}} = n - \text{factor}$$

Note:

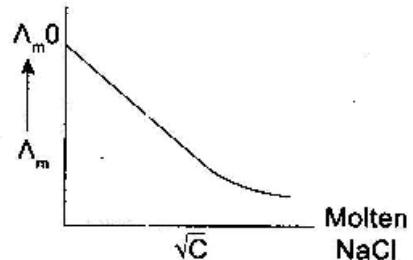
Specific conductance depends upon the number density of ions whose value decreases with increase in dilution; therefore, value of specific conductance also decreases with increase in dilution.

10.5 VARIATION OF MOLAR CONDUCTANCE WITH CONCENTRATION

- (i) **Strong Electrolytes:** For strong electrolytes, Λ_m increases slowly with dilution and can be represented by Debye-Hückel-Onsager equation which gives the variation in molar conductance with concentration as under:

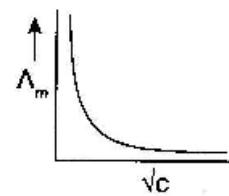
$$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{c}$$

where A and B are called Debye-Hückel-Onsager constant, which depends on temperature coefficient of viscosity and dielectric constant of medium. The limiting molar conductance or the molar conductance at infinite dilution Λ_m^0 of a strong electrolyte can be determined by extrapolating the graph of Debye-Hückel-Onsager equation.



- (ii) **Weak Electrolyte:** The change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte.

■ The limiting molar conductance or the molar conductance at infinite dilution Λ_m^0 of a weak electrolyte cannot be determined by extrapolating the graph between molar conductance (Λ_m) and square root of concentration (\sqrt{c}) because the curve becomes parallel to the molar conductance axis on extrapolation.



10.6 KOHLRAUSCH'S LAW

According to this law each ion makes a definite contribution to the total molar conductivity of an electrolyte at infinite dilution, irrespective of the nature of the other ion of the electrolyte. This individual contribution of an ion towards the total molar conductivity of the electrolyte is called molar ionic conductivity.

The limiting molar conductivity of an electrolyte at infinite dilution is the sum of the limiting ionic conductivities of the cations and the anions each multiplied with the number of ions present in one formula unit of the electrolyte.

$$\Lambda_m^0 \text{ Al}_2(\text{SO}_4)_3 = 2\lambda_{\text{Al}^{3+}}^0 + 3\lambda_{\text{SO}_4^{2-}}^0 ;$$

$$\Lambda_{eq \text{ Al}_2(\text{SO}_4)_3}^0 = \frac{1}{3} \times \lambda_{\text{Al}^{3+}}^0 + \frac{1}{2} \times \lambda_{\text{SO}_4^{2-}}^0 ; \text{ where } \lambda_{\text{Al}^{3+}}^0 \text{ and } \lambda_{\text{SO}_4^{2-}}^0 \text{ are molar ionic conductance of Al}^{3+} \text{ and SO}_4^{2-}, \text{ respectively.}$$

Applications of Kohlrausch's Law: This law is used to calculate the molar conductance at infinite dilution for weak electrolytes which can be further used for calculation of other quantities. Thus, there are many applications of Kohlrausch's law, For example,

1. Calculation of degree of dissociation, (α): $\alpha = \frac{\Lambda^c}{\Lambda_m^0}$, where Λ_m^0 is the limiting molar conductance and Λ_m^c is the molar conductance at any concentration (c).

2. Calculation of dissociation constant (K_a): $K_a = \frac{c\alpha^2}{(1-\alpha)}$, $K_a = \frac{c \left(\frac{\Lambda^c}{\Lambda_m^0} \right)^2}{\left(1 - \frac{\Lambda^c}{\Lambda_m^0} \right)}$

3. Calculation of solubility (S): $S = \frac{\kappa \times 1000}{\Lambda_m^0}$, where S is solubility and κ is specific conductance.

4. Calculation of ionic product of water, (K_w): $[H^-] = \frac{\kappa \times 1000}{\Lambda_m^0}$, where $[H^+]$ is molarity of H^+ ions $[H^+] = [OH^-]$

$$\therefore K_w = [H^+] \times [OH^-]$$

Ionic mobility: Distance travelled by an ion per second under a potential gradient of 1 V/cm is called ionic mobility.

$$\text{Ionic mobility} = \frac{\text{Ionic velocity}}{\text{Potential gradient}}$$

Transport number: The fraction of total current carried by each ion is called transport number.

Transport number of cation, $t_+ = \frac{u_+}{u_+ + u_-}$, where u_+ and u_- are ionic mobility of cation and anion, respectively.

10.7 ELECTROCHEMICAL OR GALVANIC CELL

Electrochemical or galvanic cell is a device for converting chemical energy into electrical energy. The electromotive force (EMF) of such a cell is directly proportional to the intensity of chemical reaction taking place in it.

The chemical reaction responsible for production of electricity takes place in two separate compartments; these compartments are called half-cells.

The galvanic cells usually consist of two electrolytic solutions into which two electrodes of different material are dipped. The Daniel cell is a well-known example in this regard.

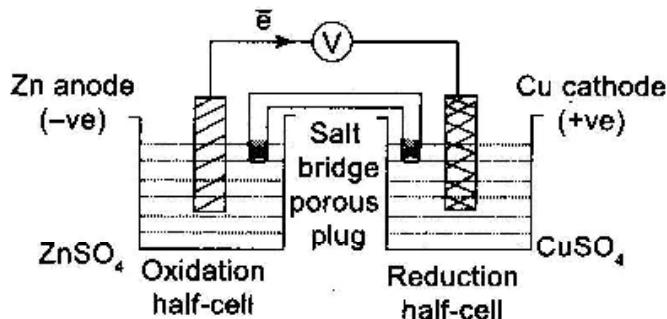
When the two compartments are connected by a 'Salt bridge' and electrodes are joined by a wire through a galvanometer, electricity begins to flow.

Types of Electrochemical Cells: Two main types of electrochemical cells are listed hereunder.

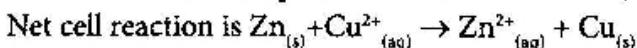
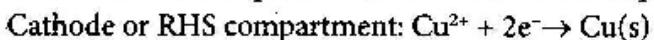
- Chemical cell:** In these cells, electrical energy is produced from the energy change accompanying a chemical reaction or a physical process.
- Concentration cell:** In these cells, electrical energy is produced from the energy change accompanying the transfer of solute or material from one concentration to another.

Daniel Cell: When zinc electrode dipped in $ZnSO_4$ solution and copper electrode dipped in $CuSO_4$ solution are joined by a wire, the following observations are made:

- (a) There is a flow of current through the external circuit.
- (b) The Zn rod loses its mass, while the Cu rod gains its mass.
- (c) The concentration of ZnSO_4 solution increases, while the concentration of CuSO_4 solution decreases.
- (d) The solution in both the compartments remains electrically neutral.



The indirect redox reaction that takes place in the cell will be



Salt Bridge: Salt bridge is usually an inverted U-tube filled with a concentrated solution of inert electrolyte (viz. KCl , KNO_3 , NH_4NO_3 etc.)

Gelatin or agar-agar (plant gel) is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. The ends of the U-tube are plugged with cottonwool as to minimize diffusion.

Significance of Salt Bridge:

- (a) It connects the solutions of two half-cells and completes the cell circuit.
- (b) It prevents transference or diffusion of the solutions from one half-cell to the other.
- (c) It keeps the solutions in two half-cells electrically neutral.

Note:

Inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells.

Representation of a Galvanic Cell: We require two half-cells to produce an electrochemical cell, which can be represented by the following few rules

- (a) The separation of two phases (state of matter) is shown by a vertical line.
- (b) Various materials present in the same phase are shown together with the help of commas.
- (c) Two half-cells are joined with the help of double vertical lines.
- (d) The significant features of the substances, viz. fugacity (pressure) of gas, activity (concentration) of ion, etc., are indicated in brackets immediately after writing the substance.
 - Daniel cell can be represented as $\text{Zn} | \text{ZnSO}_4(1\text{M}) || \text{CuSO}_4(0.1\text{ M}) | \text{Cu}$
 - Gas electrode cell will be represented as $\text{Pt} | \text{H}_2(\text{g}) | \text{NaOH(aq.)} || \text{Ni}^{2+}(\text{aq.}) | \text{Ni}$

Electromotive Force or EMF: We will represent EMF of the cell by the symbol E_{cell} .

$$\text{or } E_{\text{cell}} = E_{\text{red, cathode}}^{\circ} - E_{\text{red, anode}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = E_{\text{oxi, anode}}^{\circ} - E_{\text{oxi, cathode}}^{\circ} \text{ or } E_{\text{cell}}^{\circ} = E_{\text{oxi, anode}}^{\circ} + E_{\text{red, cathode}}^{\circ}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

Free energy change in galvanic cells

- (i) When a cell operates, work is done on the surroundings as electrical energy flows through an external circuit. By convention, such work done by the cell is negative.
- (ii) The quantity of electrical work done is measured in terms of free energy change, ΔG . This value is equal to the product of number of moles of electrons and emf of the cell to $\Delta G = -nFE_{\text{cell}}$. If reactants and products are in the standard states, then $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$.

10.8 ELECTRODE

It is a metallic conductor dipped inside the solution of its own ions. Electrodes are of two types.

- (i) Electrode of 1st kind and
- (ii) Electrode of 2nd kind.

10.8.1 Electrode Potential

When a metal rod is placed inside the solution of its own ions, then the metal acquires either a +ve or -ve charge with respect to the solution; under such conditions a potential difference is developed. This potential difference is termed as electrode potential. It is of two types.

- (i) Oxidation potential and
- (ii) Reduction potential.

Dependency of Electrode Potential: It depends upon the following factors.

1. Nature of the conductor.
2. Concentration of the metallic ions in solution.
3. Temperature.

10.8.2 Types of Electrodes

10.8.2.1 Gas-ion electrode

- (a) In such an half-cell, an inert collector of electrons (Pt or graphite) is in contact with gas and a solution containing a specified ion, e.g., standard hydrogen electrode (SHE).
- (b) Half-cell reaction is $E_{\text{H}^{\circ}/\text{H}_2/\text{Pt}}^{\circ} \quad 1/2\text{H}_2 \rightleftharpoons \text{H}^{\circ} + \text{e}^{-}$

$$E_{\text{H}^{\circ}/\text{H}_2/\text{Pt}}^{\circ} = 0.00 \text{ (assumed)}$$

- 2. **Metal-Metal ion Electrode:** This cell consists of a bar (electrode) of metal 'M' in contact with a solution containing M^{n+} ions. E.g., ZnZn^{2+} ion, CuCu^{2+} ion, AgAg^{+} ion, etc., Half-cell reaction is $M^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow M(s)$

3. Metal Amalgam-Metal ion Electrode: In this half-cell, metal amalgam is placed in contact with a solution containing metal ion. Electrical contact is made by a Pt wire dipping into the amalgam pool.

The schematic diagram of normal calomel electrode is given below, represented as $\text{Cl}/\text{Hg}_2\text{Cl}_2/\text{Hg}(\text{Pt})$. Half cell reaction is $\frac{1}{2}\text{Hg}_2\text{Cl}_2 + \text{e}^- \rightleftharpoons \text{Hg} + \text{Cl}^-$

4. Metal-metal insoluble Salt Electrode: In this half-cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt, e.g., $\text{AgCl} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-$...

5. Redox Electrode: An oxidation reduction half-cell has an inert metal collector (Pt) immersed in a solution which contains two ions of the same element in different states of oxidation, e.g.,

$\text{Fe}^{3+}, \text{Fe}^{2+}$ half-cell; represented as $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$ and the equilibrium reaction is, $\text{Fe}^{3+}_{(\text{aq})} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}_{(\text{aq})}$

10.9 NERNST EQUATION

- (i) For a general reaction such as; $fL + mM \rightleftharpoons pP + qQ$; occurring in a cell, the Gibbs free energy change is given by, $\Delta G = \Delta G^\circ + 2.303RT\log_{10} Q$

Since $\Delta G = -nFE_{\text{cell}}$ and $\Delta G^\circ = nFE^\circ_{\text{cell}}$:

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log_{10} Q \text{ at } T = 25^{\circ}\text{C}$$

$$E_{cell} = E'_{cell} - \frac{0.0591}{n} \log_{10} Q$$

10.9.1 Applications of Nernst Equation

1. Determination of Equilibrium constant: According to Nernst equation

$$E = E^\circ - \frac{0.0591}{n} \log_{10} Q \text{ at } 25^\circ\text{C}$$

But $E = 0$ and $Q = K_{\mu\nu}$.

$$\text{So, } K_{eq} = \text{antilog} \left[\frac{n E^\circ}{0.0591} \right]$$

2. Work done by a cell: work done by a cell = Decrease in free energy

So, $-\Delta G = nFE$ or $W = +nFE^\circ$ where E° is standard emf of the cell.

3. Heat of Reaction in a Electrochemical cell:

- Let 'n' faraday charge flow out of a cell of emf 'E'; then, $-\Delta G = n \cdot FE$

Gibbs-Helmholtz equation from thermodynamics may be given as

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \dots \text{(ii)}$$

From equation (i) and (ii), we get

$$-nFE = \Delta H + T \left[\frac{\partial (-nFE)}{\partial T} \right] = \Delta H - nFT \left[\frac{\partial (E)}{\partial T} \right]$$

$$\text{or } \Delta H = -nFE + nFT \left(\frac{\partial(E)}{\partial T} \right)_p$$

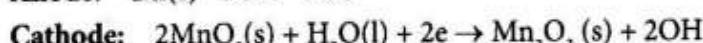
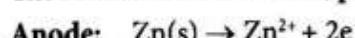
Here, $\left(\frac{\partial(E)}{\partial T} \right)_p$ = Temperature coefficient of the cell.

10.10 COMMERCIAL CELLS

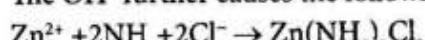
Some of the electrochemical cells which are commonly employed as a source of electrical energy can be classified as listed hereunder.

1. Primary Cells: Such cells can be used only as long as the reactive materials are present. Once they are exhausted, the cell cannot be recharged by passing current through it.

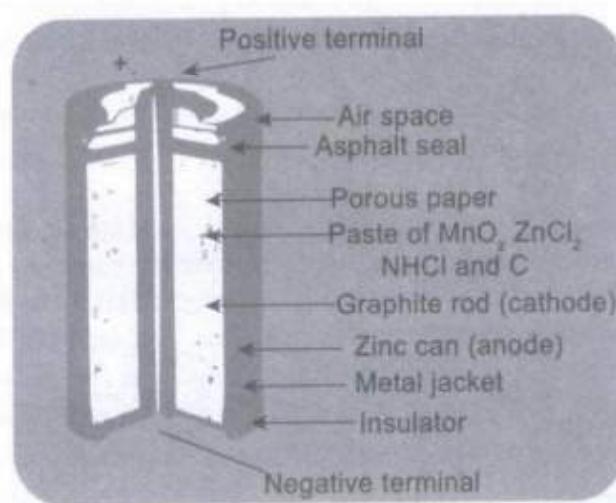
(i) **Leclanche dry cell:** The cell representation is $Zn | NH_4Cl$ (20 per cent), $ZnCl_2 | MnO_2$ | Graphite. The reactions involved are, provided hereunder.



The OH^- further causes the following secondary reactions, $NH_4Cl + OH^- \rightarrow NH_3 + Cl^- + H_2O$

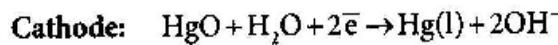


The emf of the cell is 1.25 to 1.5 Volts.



(ii) **Button cell:**

Mercury cell, suitable for low current devices like hearing aids, watches, etc. consists of zinc-mercury amalgam as anode and a paste of HgO and carbon as the cathode reactions for the cell are given hereunder.



The overall reaction is represented by $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

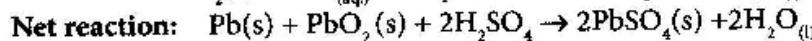
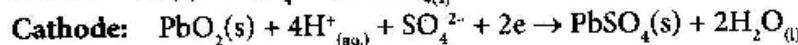
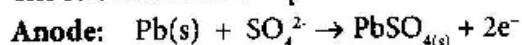
2. Secondary cells (Secondary Batteries): They are also called storage cells or accumulator cells. Energy efficiency of the secondary cell is represented by (η).

$$\eta = \frac{\text{energy produced during discharging}}{\text{energy consumed during charging}} = \frac{\text{amp hour} \times E_{\text{avg}} \text{ during discharging}}{\text{amp hour} \times E_{\text{avg}} \text{ during charging}}$$

As overall reactions do not involve any ion whose concentration may change, therefore this cell gives a constant potential of 1.35 V throughout its life.

(i) **Lead storage battery:**

- (a) Such type of cells can be used again and again by recharging the cell. One of the example in this regard is lead storage battery.
- (b) In lead storage battery, Pb acts as anode and lead impregnated with lead oxide (PbO_2) acts as cathode. The electrolyte is a solution of approximately 38 per cent H_2SO_4 with specific gravity of about 1.30 at 298 K.
- (c) The relevant reactions provided hereunder.



From the above reaction, it is clear that H_2SO_4 is used up during discharging. Therefore, the density of H_2SO_4 falls. When its density falls below 1.20 g/cm³, the battery needs recharging.

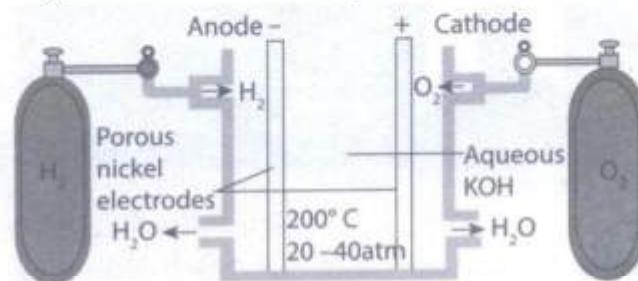
- (d) To recharge the cell, it is connected with a source of potential higher than that of the cell in such a way, that the cell now acts as the electrolytic cell, where Pb is deposited on the cathode. PbO_2 is hence formed at the anode and H_2SO_4 is regenerated. Specific gravity of the solution rises due to the increase in H_2SO_4 concentration.

Note:

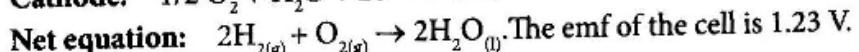
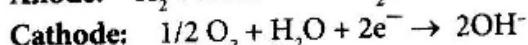
Due to some electrolysis of H_2O , H_2 and O_2 gases are evolved. This makes the periodic supplement of H_2O necessary in lead storage battery.

3. Fuel cell

- (i) Fuel cells are electrochemical devices, which convert the energy of fuel by oxidation reaction into electrical energy. A fundamental example of a fuel cell is the hydrogen–oxygen cell.



- (ii) Fuel cells based on combustion of hydrocarbons are also in operation. e.g., hydrogen–oxygen cell.
- (iii) Another example of fuel cell is hydrocarbon–oxygen fuel cell. In such cells, hydrocarbons and their oxygenated derivatives such as CH_4 , C_2H_6 , C_3H_8 , alcohols, etc., are used.
- (iv) **Schematic diagram of hydrogen:** Oxygen cell is given above. It consists of two electrodes made of porous graphite. Platinum is coated on the surface of the electrodes. The electrodes are placed in an aqueous solution of KOH or NaOH. H_2 and O_2 are bubbled into the cell under high pressure. The operating temperature is 400–525 K.



Thermodynamic efficiency: If ΔH is the heat of combustion and ΔG is the useful work done i.e., electrical energy produced, then thermodynamic efficiency (η) of a fuel cell is $\eta = \frac{\Delta G}{\Delta H} = -\frac{nEF}{\Delta H}$

10.11 ELECTROCHEMICAL SERIES

When the elements are arranged in the order of their standard reduction potentials on the hydrogen scale, we get electromotive series or electrochemical series (ECS) of the elements.

- The elements occupying the higher position in the ECS are able to reduce the lower metal ions in the same series. Thus, Zn can reduce Cu^{2+} ions and Fe can reduce Ag^+ ions.
- The metals with more negative potentials can displace those with positive or less negative potentials from their solutions.
- The metals high up in the series are strong reducing agents and their ions are stable, whereas those near the bottom of the series are inactive stable elements and their ions are easily reduced to the metals.
- Any element above hydrogen will displace hydrogen from a dilute acid solution and will reduce the oxidized form of any metal lying below it in the series.
- The -ve sign of E_{red}° indicates that an electrode when joined with standard hydrogen electrode acts as anode. Similarly, the +ve sign of E_{red}° indicates that the electrode when joined with standard hydrogen electrode acts as cathode.

10.12 APPLICATIONS OF ELECTROCHEMICAL SERIES

10.12.1 Reactivity of Metals

- The activity of a metal depends on its tendency to lose electrons. This tendency depends on the magnitude of SRP (Standard reduction potential). The metal which has high -ve value (or smaller +ve value) of SRP, readily loses the electrons and is converted into cations. Such a metal is said to be chemically active.
- The chemical reactivity of metals decreases from top to bottom in the series. e.g.,
 - Alkali metals and alkaline earth metals having high -ve values of SRP are chemically active. These react with cold water and evolve H_2 gas. These readily dissolve in acids forming their corresponding salts and combine with those substances which accept electrons.
 - Metals like Fe, Pb, Sn, Ni, Co, etc., which lie just below in the series do not react with cold water but react with steam to evolve hydrogen.
 - Metals like Cu, Ag, Au, etc., which lie below hydrogen are less reactive and do not evolve hydrogen from water.

10.12.2 Electropositive Character of Metals

The electropositive character also depends on the tendency to lose electrons, like reactivity, the electropositive character of metals decrease from top to bottom. On the basis of SRP values, metals are divided into three groups.

A strongly electropositive metals have an SRP near about -2.0 Volt or more negative.

Moderately electropositive metals have an SRP between 0.0 and -0.2 V.

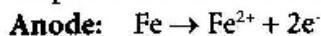
Weakly electropositive metals lie below hydrogen and have +ve SRP.

10.12.3 Displacement Reactions

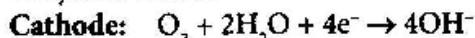
- (i) A metal higher in the series displaces the metal from its salt solution which is lower in the series.
 - (ii) A non-metal having high value of SRP will displace another non-metal with lower SRP (i.e., occupying position above in the series). E.g., Cl_2 can displace Br and I_2 from bromides and iodides.
 - (iii) Fe and the metals above Fe are capable of liberating $\text{H}_2(\text{g})$ from water. The tendency decreases from top to bottom in ECS.
 - (iv) In case two or more types of positive and negative ions are present in solutions during electrolysis certain ion are discharged or liberated at the electrodes in preference to other.
In general, in such competitions the ion which is a stronger oxidizing agent (high value of SRP) is discharged first at cathode i.e., $\xrightarrow{\text{K}^+, \text{Ca}^{2+}, \text{Na}^+, \text{Mg}^{2+}, \text{Al}^{3+}, \text{Zn}^{2+}, \text{Fe}^{2+}, \text{H}^+, \text{Cu}^{2+}, \text{Ag}^+, \text{Au}^{3+}}$ (increasing order of deposition).
- Similarly, the anion which is a stronger reducing agent (low value of SRP) is liberated first at the anode.
i.e., $\xrightarrow{\text{SO}_4^{2-}, \text{NO}_3^-, \text{OH}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-}$ (increasing order of deposition).

10.13 CORROSION

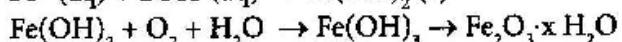
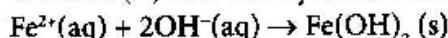
- (i) Corrosion is an electrochemical process. When iron is in contact with air, even with a microscopic drop of water the iron tends to oxidize and give up electrons.



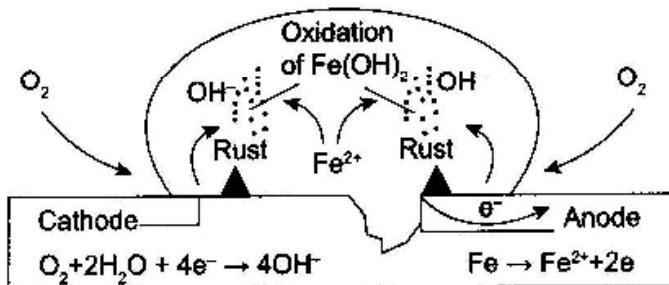
The electrons pass through the iron to the edge of the drop, where they reduce oxygen from the air to hydroxide ion.



The iron (II) ions and hydroxide ions diffuse together and form insoluble iron (II) hydroxide.

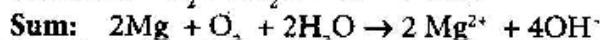
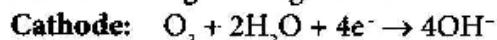
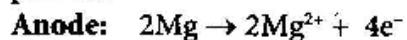


This precipitate is rapidly oxidized by oxygen to rust, an iron (III) compound with the approximate composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

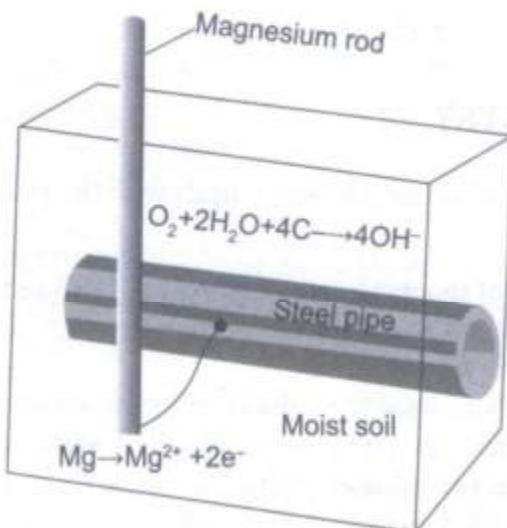


- (ii) Many methods and devices have been employed to prevent corrosion. We protect iron by coating it with paint, lacquer, grease or asphalt; with another metal such as zinc, copper, nickel chromium or tin; with a ceramic enamel or with an adherent tough coating of Fe_3O_4 .

- (iii) Another means of preventing the corrosion of iron or steel is called cathodic protection. Cathodic protection is used such as in underground pipeline that is in contact with soil. The iron is connected by a wire to a more active metal, such as Zn, Al or Mg and the iron becomes cathode at which oxygen is reduced rather than an anode where iron is oxidized. The difference in activity of the two metals causes a current to flow between them producing corrosion of the more active metal and protecting the iron with magnesium as the more active metal. The following reactions occur in this process.



In this series of reactions, no iron is oxidized. The active metal is slowly consumed and must be replaced periodically, but this is less expensive than replacing a pipeline.



- (iv) Some of the more active metals such as aluminium and magnesium, which might be expected to corrode rapidly, are protected by a tightly adhering oxide coat of the metal oxide that forms when the metal is exposed to air. The metal is made passive by this coating.

TOTAL SELECTIONS

IN AIPMT IN 2016 = 32



**MAHWISH
FATIMA**

NEET 2016 AIR **562**

NITESH SINHA

AIIMS

AIR 1302

Roll No. 6719530

NEET 2016 AIR **1078**

ABHIJEET KUMAR

NEET 2016 AIR **1478**

ARVIND SINGH

NUCLEAR CHEMISTRY

11.1 NUCLEAR CHEMISTRY

Nuclear chemistry is that branch of chemistry which deals with the phenomena involving the nuclei of the atoms.

Radioactivity is the phenomenon of spontaneous emission of certain kinds of radiations by some elements. The elements emitting such radiations are called radioactive elements. The phenomenon of radioactivity was discovered by Henry Bacquerel (in 1896).

Two most important elements isolated from pitchblende (an ore of uranium, mainly U_3O_8) by Marie Curie and her husband Pierre Curie (in 1898) were **polonium** and **radium**, the latter being the most radioactive element. Polonium was named after Poland the native place of Marie Curie and radium was so called because of its exceptionally high radioactivity (about 2 million times more than uranium).

Radiations emitted from radioactive elements and their characteristics:

S. No.	α -rays	β -rays	γ -rays
(i)	Deflected towards negative plate, but the deflection is small	Deflected towards positive plate, but the deflection is large	Remains undeflected.
(ii)	Each particle has charge $=+2$ units and mass $= 4$ units, i.e., they are helium nuclei	Each particle has charge and mass \approx that of electrons, i.e., they are same as electrons	They have no charge and no mass. They are simply electromagnetic radiations
(iii)	Their velocity is $1/10$ th to $1/20$ th of that of light	Their velocity is 3% to 99% of that of light	Their velocity is same as that of light
(iv)	Their penetrating power is low	Their penetrating power is 100 times greater than α -rays	Their penetrating power is 100 times greater than β -rays
(v)	Ionizing power is very high	It is $1/100$ th of α -rays	Ionizing power is very poor
(vi)	Affect photographic plate and produce fluorescence on ZnS screen	Effect on photographic plate is more but very low on ZnS screen	Little effect on both

Note:

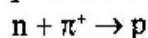
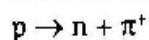
- (i) γ -rays are not produced simultaneously with α and β -rays but are produced subsequently through secondary effect.
- (ii) Radioactivity of solids and liquids is detected and measured with the help of Geiger-muller counter or a device called Proportional counter and that of gases by Ionization chambers.

11.2 NUCLEAR FORCE

The force which holds the neutrons and protons (nucleons) together within is called the nuclear force. The origin of this force has been explained by Yukawa by discovery of a new fundamental particle called **meson**. The nuclear forces (unlike electrostatic forces) operate over very small distance (10^{-15} m, i.e., 1 fermi) and are called short range forces. Further, these forces are nearly 10^{21} times stronger than electrostatic forces.

A meson has mass between that of electron and proton and its charge +1, -1 or 0. (π^+ , π^- , π^0).

This particle was discovered by Yukawa in 1935. The nucleons are held together due to their fast exchange into one another through mesons:

**Some other fundamental particles:**

- (i) Positron or antielectron (charge = +1, mass = that of electron) represented as $+le^0$.
- (ii) Neutrino (ν), has almost no charge but very small mass.

Isotopes, Isobars, Isotones, Isomers, Isosters and Isodiaphers: (Z = Atomic number No., A = Mass Number, N = Neutrons, P = Protons)

S. No.	Term	Characteristics	Examples
(i)	Isotopes	Z = Same, A = Different	${}_1^1H$, ${}_2^3H$, ${}_1^3H$; ${}_{92}^{235}U$, ${}_{92}^{238}U$; ${}_{17}^{35}Cl$, ${}_{17}^{37}Cl$
(ii)	Isobars	Z = Different, A = Same	${}_{88}^{228}Ra$, ${}_{40}^{228}Ar$, ${}_{90}^{228}Th$, ${}_{18}^{40}Ar$, ${}_{19}^{40}K$
(iii)	Isotones	N = Same, A = different, Z = different	${}_{18}^{39}Ar$, ${}_{19}^{40}K$; ${}_{14}^{30}Si$, ${}_{15}^{31}P$
(iv)	Isomers	N = Same, Z = Same	$U-X(t_{1/2} = 1.4\text{ min})$, $U-Z(t_{1/2} = 6.7\text{ hr})$
(v)	Isosters	No. of atoms = Same, number of e = same physical properties = same	CO_2 , N_2O ; N_2 , CO ; HCl , F_2
(vi)	Isodiaphers	Isotope number = Same, isotope number = N-P	${}_{92}^{235}U$, ${}_{90}^{234}Th$; ${}_{19}^{39}K$, ${}_{9}^{19}F$

Notes:

- (i) Nuclear radius is 10^{-15} m, atomic radius is 10^{-10} i.e., nuclear radius is $1/10,000$ th of atomic radius.
- (ii) Nuclear radius (r) of any atom is related to its mass no. A as $r = R_0 A^{1/3}$ where R_0 = constant = 1.4×10^{-15} m
- (iii) Area of cross section of nucleus is expressed in barns (1 barn = 10^{-24} cm 2)
- (iv) Loss of α or β -particle is to change N/P ratio so that it lies within the stability belt, loss of α -particle increases N/P ratio while loss of β -particle decreases N/P ratio.
- (v) Parent and daughter element which are related through α -emission are isodiaphers.

Group Displacement Laws (put forward by Soddy, Fajan and Russell)

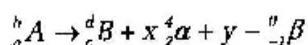
- (i) When an α -particle is emitted, the new element has atomic number less by 2 units and mass number less by 4 units, i.e., new element is two positions on the left in the periodic table
e.g., $^{238}_{92}\text{H} \rightarrow ^{234}_{90}\text{Th} + ^4_2\text{He}$ (α -particle)
- (ii) When a β -particle is emitted, the new element has atomic number greater by 1 units but mass number is same, i.e., new element is one position on the right in the periodic table
e.g., $^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + ^{-1}_0\text{e}$ (β -particle)

Notes:

(i) β -particle (electron) is not present in the nucleus, yet it is emitted from the nucleus because a neutron changes into a proton, increasing atomic number by 1 units.

$$n \rightarrow p + ^{-1}_0\text{e}$$

(ii) To find α and β particles emitted in the reaction $^b_a\text{A} \rightarrow ^d_c\text{B}$, we write



Then, $b = d + 4x + 0y$ and $a = c + 2x - y$, solving for x and y .

11.2.1 Magic Numbers

Nuclides containing 2, 8, 20, 28, 50, 82 and 126 protons or neutrons or both are highly stable due to high binding energy per nucleon.

Number of protons	Number of neutrons	Number of nuclides known
Even	Even	165
Even	Odd	55
Odd	Even	50
Odd	Odd	5

11.3 KINETICS OF RADIOACTIVE DISINTEGRATION

All radioactive disintegration follows first-order kinetics. Starting with N_0 atoms of the radioactive element A, if N is the number of atoms after time t

Rate of disintegration, $-\frac{dN}{dt} = \lambda N$; where λ is called disintegration constant

Rewriting, $-\frac{dN}{N} = \lambda dt$

Expression for the disintegration constant $\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$

$$\text{or } N = N_0 e^{-\lambda t} = N_0 \left(\frac{1}{2}\right)^n$$

where $n = \frac{t}{t_{1/2}}$ is the number of half-lives in time t.

Hence, disintegration constant may be defined as the fraction of the total number of atoms which disintegrate in 1.

Note:

Rate of disintegration (activity of a radioactive element) is directly proportional to the amount of the substance. It does not depend upon temperature, pressure, state of combination, etc.

11.4 HALF-LIFE PERIOD

Half-life period of a radioactive element is the time in which half of the original substance disintegrates:

$$\text{Expression for half-life period is } t_{1/2} = \frac{0.693}{\lambda}$$

11.4.1 Average Life Period

It is the sum of the periods of existence of all the atoms divided by the total number of atoms of the radioactive substance present initially, or time during which 63.21 per cent of the substance undergoes decay is called average life. It is represented by t_{av} or τ .

$$\text{Average life} = \frac{\text{Total life time of all the atoms}}{\text{Total number of atoms}}$$

$$= \frac{\int_0^\infty t dN}{N_0} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$$

$$\tau = t_{av} = \frac{1}{\lambda} = 1.44 t_{1/2}$$

$$\text{per cent remaining amount at } \tau = \frac{N}{N_0} \times 100 = 36.79 \text{ per cent}$$

$$\text{per cent decayed amount at } \tau = 100 - 36.79 = 63.21 \text{ per cent}$$

11.4.2 Units of Radioactivity

Units of disintegration rate is Curie or Becquerel or Rutherford. Curie is the amount of a radioactive substance which undergoes 3.7×10^{10} disintegrations per second.

i.e., 1 Curie (1 Ci) = $3.7 \times 10^{10} \text{ ds}^{-1}$. Similarly, 1 Becquerel (1 Bq) = 1 ds^{-1} and 1 Rutherford (1 Rd) = 10^6 ds^{-1} .

11.5 RADIOACTIVE DISINTEGRATION SERIES

Radioactive disintegration series is the series of spontaneous changes that take place starting from the parent element (with unstable nucleus) upon to formation of stable nucleus.

Four important disintegration series along with their starting elements and stable end products are as under

Series	Name of the series	Starting element	Stable end product
4n	Thorium series	$^{232}_{90}\text{Th}$	$^{208}_{82}\text{Pb}$
4n + 1	Neptunium series	$^{241}_{94}\text{Pu}$	$^{209}_{83}\text{Bi}$
4n + 2	Uranium series	$^{238}_{92}\text{U}$	$^{206}_{82}\text{Pb}$
4n + 3	Actinium series	$^{235}_{92}\text{U} (^{227}_{89}\text{Ac})$	$^{207}_{82}\text{Pb}$

They are so called because mass numbers of atoms belonging to these series when divided by 4 give a remainder of 0, 1, 2 and 3, respectively. Among these four series, (4n + 1) is artificial while the other three are natural.

Radioactive equilibrium: Though radioactive changes are irreversible still equilibrium is established for intermediate daughter element at equilibrium $\text{A} \xrightarrow{\lambda_A} \text{B} \xrightarrow{\lambda_B} \text{C}$

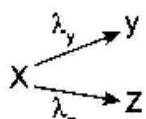
At equilibrium rate of formation of B = rate of disintegration of B, $\lambda_A N_A = \lambda_B N_B$

$$\Rightarrow \frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{\tau_A}{\tau_B} = \frac{(t_{1/2})_A}{(t_{1/2})_B}$$

11.5.1 Parallel Path Decay

Overall decay constant, $\lambda_o = \lambda_y + \lambda_z$

$$\text{Fractional yield of } y = \frac{\lambda_y}{\lambda_o} = \frac{\lambda_y}{\lambda_y + \lambda_z}$$



$$\text{Fractional yield of } z = \frac{\lambda_z}{\lambda_o} = \frac{\lambda_z}{\lambda_y + \lambda_z}$$

Series path decay: $\text{X} \xrightarrow{\lambda_x} \text{Y} \xrightarrow{\lambda_y} \text{Z}$

$$\begin{array}{lll} t=0 & N_0 & 0 \\ t & N_x & N_y & N_z \end{array}$$

Number of nuclei of daughter element y remaining at time t.

$$N_y = \frac{N_0 \lambda_x}{\lambda_y - \lambda_x} \left[e^{-\lambda_x t} - e^{-\lambda_y t} \right].$$

If maximum activity of daughter element is observed at time t_{\max}

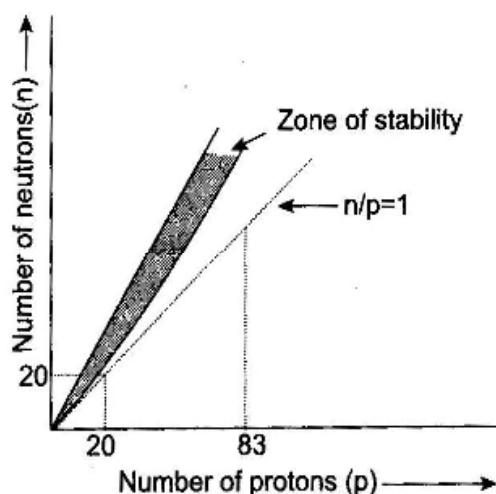
$$t_{\max} = \frac{2.303}{\lambda_y - \lambda_x} \log_{10} \left[\frac{\lambda_y}{\lambda_x} \right]$$

Nuclear stability: Stability of a nucleus can be determined by the following three methods.

1. n/p ratio
2. Packing fraction
3. Binding energy (BE) per nucleus.

11.5.1.1 *n/p ratio*

By plotting the number of neutrons (n) against the number of protons (p) for nuclei of various elements, it has been observed that most of the stable nuclei lie in a well-defined belt called **stability belt** or **zone of stability**.



11.5.1.2 *Analysis of curve*

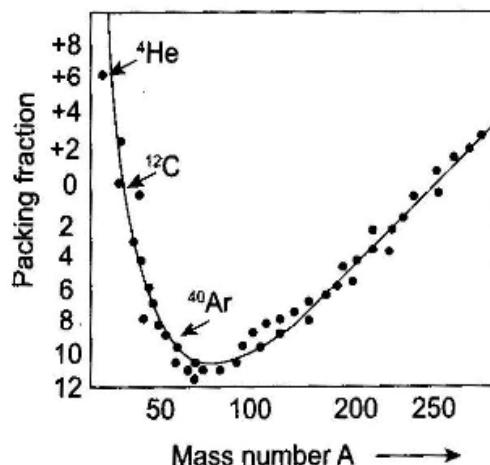
- Nuclei whose n/p ratio lies outside the stability belt are unstable and therefore undergo spontaneous radioactive disintegration.
- Nuclei having $Z \leq 20$ for which number of neutrons is equal to number of protons are stable.
e.g., ${}^4_2\text{He}$, ${}^{12}_6\text{C}$, ${}^{16}_8\text{O}$, ${}^{28}_{14}\text{Si}$, ${}^{40}_{20}\text{Ca}$.
- If $Z > 83$, then nuclei has no stable isotope at all and are radioactive.
- for $Z > 20$, because of increasing repulsive forces between protons large number of neutrons must be present due to which size of nucleus increases and force of repulsion decreases and so nucleus stabilizes and hence n/p ratio increases. E.g., for Bi the n/p ratio is about 1.5 : 1.

11.5.2 *Packing Fraction*

The concept of packing fraction was introduced by Aston. It has been observed that mass of an isotope of an element obtained experimentally using mass spectrograph is invariably less than the calculated mass of the isotope (i.e., the sum of mass of proton, neutrons and electrons. This mass difference is termed as mass defect).

This lost mass is converted into energy that is released during the nuclear reaction and is thus a direct measurement of the binding energy holding the nucleus. Larger the BE, the more stable will be the nucleus.

$$\text{mass defect } (\Delta m) = \text{isotopic mass } (m) - \text{mass number } (A)$$



$$\text{Packing fraction} = \frac{\Delta m}{A} \times 10^4$$

Packing fraction may have a negative or a positive sign. Packing fraction does not have any precise theoretical significance but it gives an indication about the stability of the nucleus.

11.5.2.1 Significances of packing fraction

- (i) The negative value of packing fraction shows that the isotopic mass is less than the mass number. In such cases, some mass gets transformed into energy in the formation of that nucleus. Hence the more negative the packing fraction of an element, the more stable should be the nucleus.
- (ii) A positive fraction indicates that the concerned nuclear is less stable.

11.5.2.2 Analysis of curve

A plot of packing fraction against the corresponding mass number of the various elements gives the following results.

- (a) The packing fractions of the stable nuclides lie more or less on a smooth curve.
- (b) The curve passes through a minima in the mass number range 50–60, implying the maximum stability.
- (c) After the minima, packing fraction steadily increases and ultimately becomes positive for elements of high mass number.

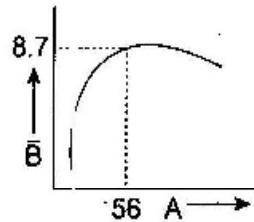
11.5.3 Binding Energy per Nucleon

The energy released in the formation of a nucleus from its constituent nucleons is called the binding energy (BE) of the nucleus.

The binding energy of nucleus when divided by the number of nucleons gives the mean binding energy per nucleon (\bar{B}). The binding energy per nucleon is a measure of the stability of the nucleus.

$$\text{Binding energy (BE)} = \Delta m \times c^2 = \Delta m \text{ (in amu)} \times 931 \text{ MeV}$$

$$\text{Binding energy per nucleon } (\bar{B}) = \frac{B}{A} = \frac{\text{total binding energy}}{\text{Total number of nucleons}}$$

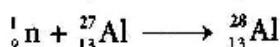


11.5.4 Significance of Binding Energy per Nucleon

- (i) The greater the binding energy per nucleon, the more stable is the nucleus.
- (ii) If we plot a graph between binding energy per nucleon versus mass numbers, following results are observed.
 - (a) The value of \bar{B} is maximum for mass number (56). Thus, nucleus of iron is thermodynamically most stable.
 - (b) It is also seen that the points for He($A = 4$), C($A = 12$), O($A = 16$) lie quite high in the graph. This shows that the nuclei of these elements are exceptionally stable.
 - (c) The maximum value of \bar{B} is equal to 8.7 MeV.

11.6 ARTIFICIAL TRANSMUTATION

Artificial transmutation of elements means the process of converting one element into another by bombardment of ${}_0^1n$, ${}_1^1H$, ${}_1^2H$ respectively,



The first artificial transmutation was carried out by Rutherford in 1919 according to the first reaction given above.

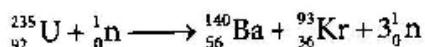
Representation of a nuclear reaction: Reactant nucleus (bombarding particle, particle emitted) Product nucleus e.g., the above reactions may be represented as ${}_{7}^{14}N(a, p) {}_{8}^{17}O$

Some Important Points

- (i) The best bombarding particles are neutrons because they have no charge (and hence not repelled by the nucleus being bombarded) but have considerable mass (one unit).
- (ii) Cyclotron is a machine used for accelerating the particles. The machine used for accelerating protons is called synchrotron. Another machine used for accelerating particles is called bevatron.
- (iii) Reactions of the above type are called nuclear reactions. Total charge and total mass on the two sides must be same. A nuclear reaction is called (n, p) or (n, α) or (p, α) , etc. depending upon the bombarding particle (named first) and the particle emitted (named later).
- (iv) Artificial radioactivity or induced radioactivity (first studied by Irene Curie) is the phenomenon in which the artificial disintegration of a stable nucleus leads to the formation of a radioactive isotope, e.g., ${}_{13}^{27}Al + {}_2^4He \xrightarrow[\text{(stable)}]{} {}_0^1n + {}_{15}^{30}P \xrightarrow[\text{(Radioactive)}]{t_{1/2}=2.55\text{ min}} {}_{14}^{30}Si + {}_{+1}^0e$ (Positron)

11.7 NUCLEAR FISSION

Nuclear fission is the splitting of a heavier atom like that of Uranium-235 into a number of fragments of much smaller mass by bombardment with subatomic particles with liberation of huge energy, e.g.,



Neutrons emitted during first fission bombard more uranium atoms and the reaction goes on. It is called a chain reaction.

- (i) The minimum size which the fissionable material must have so that one of the neutrons released in every fission hits another nucleus and causes fission so that chain reaction continues at a constant rate is called **critical mass**. For U-235, it is 1–100 kg. Critical mass is inversely proportional to square of density.
- (ii) Naturally occurring uranium is 99.3 per cent U-238 which is not fissionable. Only U-235 is fissionable.
- (iii) If chain reaction is not controlled, it can be used for destructive purposes, i.e., in atomic bomb.
- (iv) Transuranic elements are the elements coming after uranium, i.e., with atomic numbers greater than 92. These have been prepared by artificial disintegration. Hence, they are also called synthetic elements.

11.8 NUCLEAR REACTOR

Nuclear reactor is an arrangement in which the energy produced (in the form of heat) in a nuclear fission can be used in a controlled manner to produce steam which can run the turbine and produce electricity.

- (i) In the reactor core, the fuel rods are of U-235, control rods are of Cd or B (because they can absorb the neutrons), moderator (to slow down the speed of neutrons) and coolant (to carry away the heat). Lead apertures are used by workers because they absorb harmful radiations.
- (ii) Breeder reactors are those reactors in which the neutrons produced from fission of U-235 are partly used to carry on the fission of U-235 and partly used to produce some other fissionable material e.g., PU-235 from U-238

11.9 NUCLEAR FUSION

Nuclear fusion is the process in which lighter nuclei fuse together to form heavier nucleus. These take place at extremely high temperature ($\approx 10^6$ K), i.e., in the sun. Hence, these are called thermonuclear reactions ($4^1\text{H} \longrightarrow ^4\text{He} + 2 + ^1\text{e} + \gamma + \text{Energy}$)

- (i) Hydrogen bomb has fissionable material in the centre and deuterium (^2H) and ^6Li isotopes surrounding it. Heat produced in the centre gives the required high temperature and neutrons emitted convert Li-6 isotope into tritium (^3H) for fusion.
- (ii) Hydrogen bomb is much more powerful than atom bomb because for the same mass of deuterium or tritium undergoing fusion and uranium undergoing fission. The number of atoms present in the former is much more than in the latter. Moreover, there is no restriction of critical mass in the fusion reactions.

Applications of Radioactivity

- (i) In medicines-radiotherapy, e.g., Co^{60} for cancer, I^{131} for thyroid disorders and P^{32} for leukaemia.
- (ii) In geological dating, i.e., in predicting the age of the earth and rocks.
- (iii) In radiocarbon dating, i.e., in predicting the age of a fallen tree or dead animal.
- (iv) In tracer technique, i.e., following the path taken up by a particular radio isotope, e.g., circulation of blood by injecting saline solution containing Na^{24} isotope, uptake of a fertilizer containing P^{32} isotope, etc.
- (v) In neutron activation analysis. It is a technique of finding the trace of one element present in another by activating the trace element by bombarding with neutrons. E.g., traces of Ag present in a lead painting.

Radio Carbon Dating: It is used to determine the age of a dead plant or a dead animal. This method is based upon the fact that in a living organism, ratio of C^{14} to C^{12} is always fixed. However, in dead organism, this ratio decreases because C^{14} is radioactive in nature and therefore undergo spontaneous disintegration.

$$\text{If } N_0 = \frac{\text{C}^{14}}{\text{C}^{12}} \text{ ratio in living organisms, then } t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N} = \frac{t_{1/2}}{0.3010}$$

Rock Dating: It is used to determine the age of a planet or a star. This method is based upon natural

$$\text{disintegration series, e.g., uranium series } t = \frac{2.303}{\lambda} \log \frac{N_0}{N} = \frac{2.303}{\lambda} \log_{10} \left[\frac{N_{\text{pb}} + N_U}{N_U} \right]$$

SURFACE CHEMISTRY**12.1 DEFINITION**

The term catalysis was introduced by **Berzilius in 1836**. A catalyst is defined as a substance which increases the rate of reaction without undergoing any change and can be recovered as such at the end of the reaction. The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as catalysis. Catalysis are of two types:

1. **Positive catalysis:** The phenomenon in which presence of a catalyst accelerates the rate of a reaction.
2. **Negative catalysis:** The phenomenon in which presence of a catalyst retards the rate of a reaction. Such substances are also known as inhibitors or **negative catalysts**.

12.1.1 Characteristics of Catalysis

- (i) A catalyst remains unchanged chemically at the end of a reaction, however, its physical state may change. E.g., MnO_2 is used as a catalyst in granular form for the decomposition of $KClO_3$, and is left in powder form at the end of reaction.
- (ii) A catalyst never initiates a chemical reaction. It simply influences the rate of reaction. Exception: combination of H_2 and Cl_2 takes place only when moisture (catalyst) is present.
- (iii) A small quantity of a catalyst is sufficient to influence the rate of a reaction. E.g., 1 g atom of Pt is sufficient to catalyse 10^8 litre of H_2O_2 decomposition.
- (iv) A catalyst does not influence the equilibrium constant of a reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward and backward reactions equally.
- (v) A catalyst does not affect the heat and free energy change of a reaction.
- (vi) Catalyst's activity is more or less specific. A catalyst for one reaction is not necessary to catalyse the another reaction.
- (vii) A catalyst is poisoned by certain substance. It has been found that impurities of any type, even if present in small amount, inhibit or retard the rate of catalysed reactions to a large extent. These impurities are called catalytic poisons. E.g., the rate of combination of SO_2 and O_2 may be slowed down considerably if some arsenic compound are present even in traces.

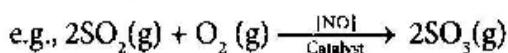
12.1.2 Classification of Catalysis

Catalysis is classified into two broad types:

12.1.2.1 Homogeneous catalysis

The reactions in which catalyst and the reactants are in same phase. Homogeneous catalysis are of two types:

1. **Gaseous phase catalysis:** When reactants and catalyst are in gaseous phase.

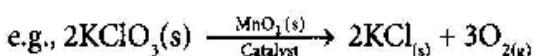


2. **Solution phase catalysis:** The reactions in which catalyst and reactants are in solution phase or liquid phase and are completely miscible, e.g., $\text{RCOOR}'_{(l)} + \text{H}_2\text{O}_{(l)} \xrightarrow{\text{H}^+_{(aq)}} \text{RCOOH} + \text{R'OH}$

12.1.2.2 Heterogeneous catalysis

The reactions in which catalyst and reactants have more than one phase.

1. **Solid-solid catalysis:** Reactions in which reactants and catalyst both are in solid phase.

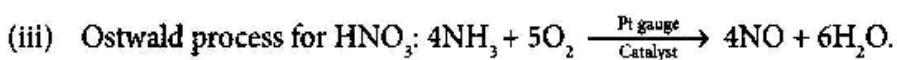
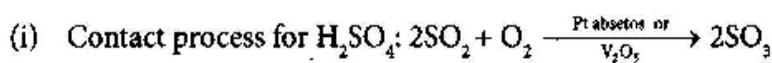


2. **Solid-liquid catalysis:** Reaction in which reactants are in liquid phase and catalyst are in solid phase and both are immiscible, e.g., $2\text{H}_2\text{O}_2(\text{l}) \xrightarrow[\text{Catalyst}]{\text{Pt}(\text{s})} \text{O}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{e})}$

3. **Liquid-liquid catalysis:** Reaction in which both reactants and catalyst are in liquid phase and are miscible to each other, e.g., $2\text{H}_2\text{O}_2(\text{l}) \xrightarrow[\text{Catalyst}]{\text{Pb}(\text{f})} 2\text{H}_2\text{O}_{(\text{e})} + \text{O}_{2(\text{g})}$

4. **Solid-gas catalysis:** Reactions in which reactants are in gaseous phase and catalyst is in solid phase.

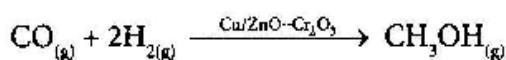
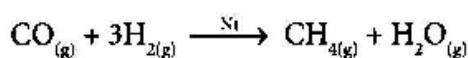
Some example of solid-gas catalysis are



Two properties of a solid catalyst is most important, one is **activity** and the other is **selectivity**.

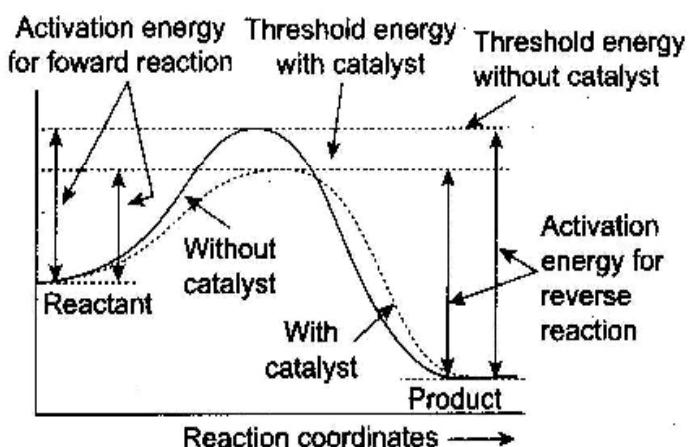
Activity: Activity is the ability of a catalyst to accelerate a chemical reaction; the degree of acceleration is as high as 10^{10} times in certain reactions.

Selectivity: Selectivity is the ability of a catalyst to direct a reaction to yield particular reaction product excluding others.



12.1.3 Effect of a Catalyst

A catalyst is a substance that takes part in a reaction system by providing a new path way with a lower activation energy between the two fixed points of reactants and product. By the addition of a catalyst the activation energy for the reverse reaction is lowered by exactly the same amount as for the forward reaction. Thus, a catalyst speeds up both the forward and the backward reactions by the same amount.



12.1.4 Catalytic Poisoning or Inhibitor for Catalyst

The phenomenon in which presence of a substance in small amounts even decreases or ruins the activity of a catalyst. The poisoners are preferentially adsorbed on the surface of catalyst to make it inert, e.g., CO for Fe catalyst in Haber process.

Classification of Poisoning:

Temporary Poisoning

- (i) The poisoners are held at active centres by weak forces.
- (ii) Catalyst surface is regenerated by scratching the surface.

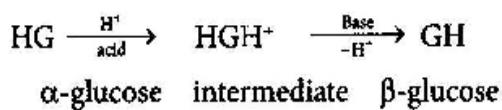
Permanent Poisoning

- (i) The poisoners are held on active centres by free valencies.
- (ii) Catalyst surface is regenerated only by chemical treatment.

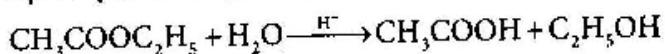
12.2 ACID-BASE CATALYSIS

Acid-base catalysis includes reactions in solutions which are catalysed by acids or bases or both. An acid donates a proton to a reactant to form an intermediate, which then loses the proton to a base to give a product.

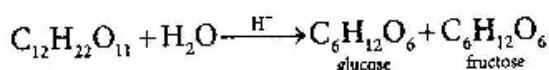
- (a) **Mutarotation of glucose:** The phenomenon in which optical activity of a freshly prepared α -glucose solution in water rapidly decreases with time till equilibrium is reached between α and β form and similarly rotation for β -glucose solution increases with time.



(b) Hydrolysis of ethyl acetate:



(c) Inversion of cane sugar:

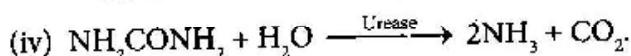
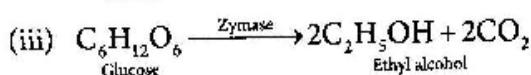
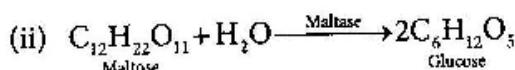
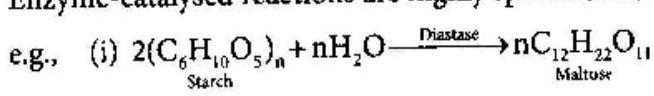


12.3 ENZYME CATALYSIS

The phenomenon in which reactions are catalysed by enzymes is called enzyme catalysis. Enzymes are proteins with high relative molar mass of the order of 10,000 or even more and are derived from living organisms.

12.3.1 Characteristics of an Enzyme Catalyst

(i) Enzyme-catalysed reactions are highly specific, i.e., one enzyme for one reaction.



(ii) Enzyme-catalysed reactions are normally hydrolytic in nature.

(iii) Enzyme-catalysed reactions take place with evolution of gases.

(iv) The rate of reaction depends upon enzyme concentration.

(v) Enzyme-catalysed reactions are highly susceptible to pH of medium. Favorable range of pH is 5 to 7.

(vi) The optimum temperature for an enzyme-catalysed reaction is nearly 30°C.

(vii) Enzymes are colloidal in nature and thus their action is ruined by electrolytes.

(viii) The activity of an enzyme is increased in the presence of certain substances known as coenzymes or activators.

E.g., non-protein (vitamins).

12.3.2 Mechanism of Enzyme-Catalysed Reactions

The mechanism of enzyme-catalysed reactions is due to specific shapes of enzymes. The reactant molecules having a complementary shape to an enzyme fit into these cavities just like a key fits into a lock. This results in the formation of the intermediate which then decomposes to give products.

Step 1: Binding of enzyme to substrate to form an activated complex, $\text{E} + \text{S} \rightarrow \text{ES}$.

Step 2: Product formation in an activated complex $\text{ES} \rightarrow \text{EP}$.

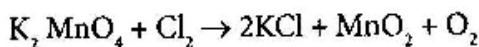
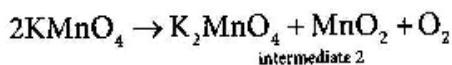
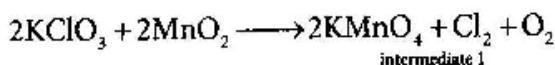
Step 3: Decomposition of an activated complex to products, $\text{EP} \rightarrow \text{P} + \text{E}$.

12.4 THEORY OF CATALYSIS

12.4.1 Intermediate Compound Formation Theory

A catalyst combines with one or more of the reactants to give an intermediate product which either decomposes or reacts with other reactants to give a product along with regeneration of catalyst.

E.g., catalytic decomposition of KClO_3 :



12.4.1.1 Adsorption theory

The term adsorption was first used by **Kayser**. The phenomenon of attracting and retaining the molecules of a substance on the surface of a solid or a liquid resulting in the higher concentration on the surface is called **adsorption**. The substance adsorbed on the surface is called an **adsorbate** and the substance on which it is adsorbed is called an **adsorbent**.

12.4.1.2 Desorption

The reverse process, i.e., removal of an adsorbed substance from the surface is called **desorption**.

12.4.1.3 Occlusion

The adsorption of gases on the surface of metals is called **occlusion**.

12.4.1.4 Sorption

If absorption and adsorption occur simultaneously, then the phenomenon is called **sorption**. Adsorption is a surface phenomenon, whereas absorption is a bulk phenomenon.

12.4.1.5 Positive adsorption

When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, then it is called **positive adsorption**.

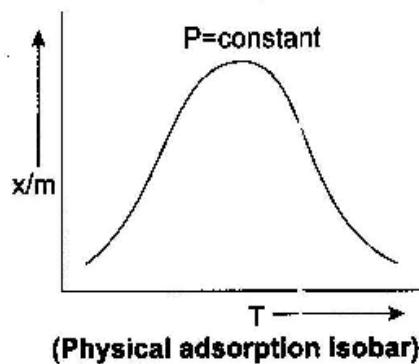
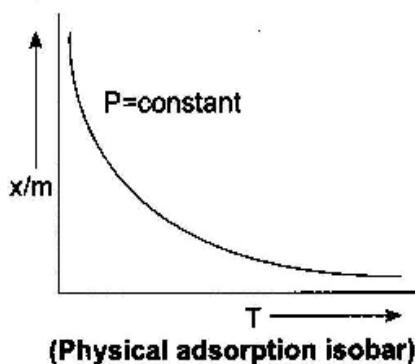
12.4.1.6 Negative adsorption

When the concentration of an adsorbate is less relative to its concentration in the bulk, then it is called **negative adsorption**.

12.4.2 Characteristics of Adsorption

- (i) Adsorption is specific and selective in nature. However, physical adsorption is less specific and chemical adsorption is more specific.

- (ii) Adsorption is accompanied with decrease in free energy (i.e., $\Delta G = -ve$). Therefore, adsorption is a spontaneous process.
- (iii) Factors which influence the extent of adsorption are:
 - (a) **Nature of adsorbent:** Transition metals are good adsorbents for gases because of vacant or half-filled d orbitals and high charge-size ratio.
 - (b) **Nature of adsorbate:** Easily liquefiable gases (e.g., HCl, NH₃, CO₂ etc.) are adsorbed to a greater extent than others (e.g., H₂, N₂, O₂ etc.).
 - (c) **Surface area of adsorbent:** Larger the surface area of an adsorbent, more is the adsorption. The surface area per gram of the adsorbent is called **specific surface area** of the adsorbent.
 - (d) **Pressure:** An increase in pressure at constant temperature increases the rate of adsorption.
 - (e) **Temperature:** An increase in temperature decreases physical adsorption, whereas chemisorption first increases and then decreases. This is because chemisorption requires some activation energy like an ordinary chemical reaction.



Physical Adsorption

- (i) Reactant molecules are adsorbed on surface by weak Van der Waals forces.
- (ii) Reversible with temperature, usually occurs at low temperature.
- (iii) Exothermic, about 20–40 kJ/mol heat energy is given out.
- (iv) Does not require activation energy.
- (v) Weak, multilayer, non-directional and non-specific.

Chemical Adsorption

- (i) Reactant molecules are adsorbed on the surface by free valencies.
- (ii) Irreversible with temperature, usually occurs at high temperature.
- (iii) Exothermic, about 200–400 kJ/mol and heat is liberated.
- (iv) Requires activation energy.
- (v) Strong, unilayer, non-directional and specific.

12.5 FREUNDLICH ADSORPTION ISOTHERM

Freundlich studied the influence of pressure on adsorption and obtained the following results. $x/m = k P^{1/n}$. By taking log of both sides, we get, $\log x/m = \log k + 1/n \log P$; where x is the amount of adsorbate on m gram of adsorbent.

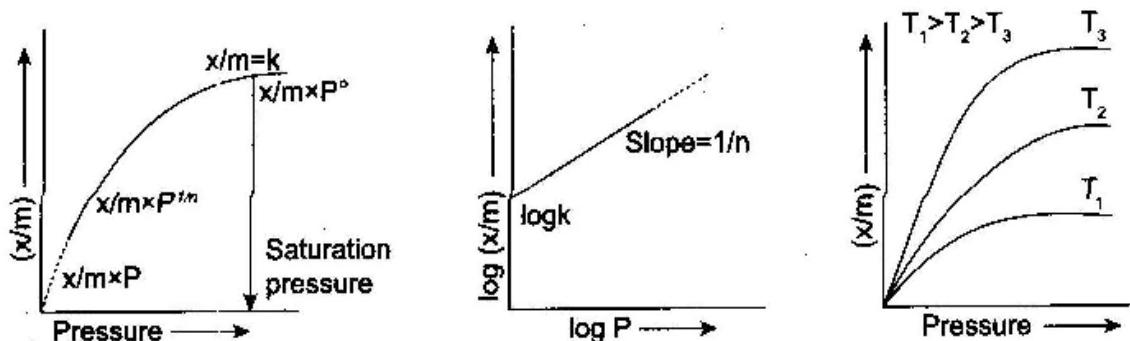
Note:

The plots of extent of adsorption (x/m) vs P at constant temperature are called adsorption isotherm.

12.5.1 Analysis of Adsorption Isotherm

- (i) At lower pressure $\frac{x}{m} = kP$. The graph is nearly straight line with slope k .
- (ii) At higher pressure, $\frac{x}{m} = k$; $\frac{x}{m}$ is found to be independent of pressure.
- (iii) At intermediate range of pressure, $\frac{x}{m} = kP^{1/n}$; $\frac{x}{m}$ is proportional to pressure raised to some fractional value between 1 and 0.

Freundlich isotherm is also used for equilibrium concentration. $\frac{x}{m} = kc^{1/n}$ where c is concentration of solute in the solution.



12.6 COLLOIDAL SOLUTION

Finely divided particles of any substance with diameter lying within 1 to 100 nm range dispersed in any medium constitute to form a colloidal solution. Colloidal solutions are intermediate between true solutions and suspensions.

12.6.1 Comparative Study Between True Sols, Colloidal solutions and Suspension

Prop	True sols	Colloidal sols	Suspension
Size	Less than 1 nm	Between 1 nm and 100 nm	Greater than 100 nm.
Visibility	Invisible under ultramicroscope	Visible only under ultramicroscope	Visible even to naked eye
Diffusion	Diffuse readily through parchment membrane	Diffuse slowly through parchment membrane	No diffusion
Filtration	Impossible through filter paper and parchment membrane or both	Impossible through filter paper but possible through parchment membrane	Possible through filter paper and parchment membrane or both
Scattering	No scattering	Scattering takes place and Tyndall effect is observed	Do not show Tyndall effect

12.6.2 Phases of Colloids

It consists of two phases, namely a dispersed phase and a dispersion medium.

12.6.2.1 Dispersed phase

It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the sulphur is a dispersed phase.

12.6.2.2 Dispersion medium

It is normally the component present in excess and is just like a solvent in a solution. The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

12.6.3 Types of Colloidal system

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various types alongwith their characteristic names are given in the table hereunder.

Dispersed Phase	Dispersion Medium	Colloidal System	Examples
Gas	Liquid	Foam or froth	Soap sols, lemonade froth
Gas	Solid	Solid foam	Pumice stone, styrene, foam
Liquid	Gas	Aerosols of liquid	Fog, clouds, fine insecticide sprays
Liquid	Liquid	Emulsions	Milk
Liquid	Solid	Gels	Cheese, butter, boot polish, table jelly
Solid	Gas	Aerosols of solid	Smoke, dust
Solid	Liquid	Sols	Starch dispersed in water, gold sol
Solid	Solid	Solid sols	Ruby glass, some gem stones

12.7 CLASSIFICATION OF COLLOIDS

Colloids can be classified in a number of ways based upon some of their important characteristics.

12.7.1 Based Upon Appearance

- (i) A colloidal system in which the dispersion medium is a liquid or gas is called a **solution**. They are called **hydrosols** or **aqua sols**, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called **alcosols** or **benzosolution**. They have a fluid-like appearance.
- (ii) Colloidal systems in which the dispersion medium is a gas are called **aerosols**.

- (iii) Colloids in which the dispersion medium is a solid are called gels, e.g., cheese, etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosolution. But at low temperature and high gelatin concentration, the hydrosol can change into a gel. The phenomenon of sol-gel transformation is called **thixotropy**.

12.7.2 Based Upon Charge

The colloids can be classified into positive or negative colloids according to the charge present on the dispersed phase particles. Metal hydroxides are generally positively charged while metal sulphides carry a negative charge.

12.7.2.1 Positive and negative charged sol

Positively Charged Sol	Negatively Charged Sol
Ferric hydroxide, aluminium hydroxide	Metals such as Pt, Au, Ag,
Basic dyes such as methylene blue	Metals sulphides, e.g., As_2S_3 ,
Haemoglobin	Starch, clay, silicic acid, acid dyes, such as eosin.

12.7.3 Based on Interaction or Affinity of Phases

On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types:

12.7.3.1 Lyophilic colloids

The colloidal system in which the particles of dispersed phase have great affinity for the dispersion medium are called **lyophilic (solvent-loving) colloids**. In such colloids, the dispersed phase does not get easily precipitated and the solutions are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence, lyophilic colloids are reversible.

12.7.3.2 Lyophobic colloids

The colloidal system in which the dispersed phase has no affinity for the dispersion medium is called **lyophobic (solvent-hating) colloids**. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte or by heating or by shaking. They are less stable and irreversible.

S. No.	Property	Lyophilic Sol	Lyophobic Sol
1.	Nature	Reversible	Irreversible
2.	Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. They do not require any electrolyte for stabilization.	They are difficult to prepare. Special methods are used. Addition of stabilizer is essential for their stability.

S. No.	Property	Lyophilic Solns	Lyophobic Solns
3.	Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
4.	Charge	Particles carry no or very little charge depending upon the pH of the medium.	Colligative particles have characteristic charge (positive or negative).
5.	Viscosity	Viscosity is much higher than that of the medium.	Viscosity is nearly the same as that of the medium.
6.	Surface Tension	Surface tension is usually higher than that of the medium.	Surface tension is nearly the same as that of the medium.
7.	Solvation	Particles are heavily solvated.	Particles are not solvated.
8.	Visibility	The particles cannot be seen under an ultramicroscope.	The particles though invisible, can be seen under an ultra microscope.
9.	Tyndall effect	Less distinct.	More distinct.
10.	Colligative property	They have relatively higher osmotic pressure, high depression of freezing point and high lowering of vapour pressure.	They have low osmotic pressure, small depression of freezing point, less elevation of boiling point and less lowering of vapour pressure.
11.	Action of electrolyte	Large amount of electrolyte is required to cause coagulation.	Small amount of electrolyte is sufficient to cause coagulation.
12.	Conductivity	They show high conductivity which can be measured.	Due to their sensitivity in electrolyte, conductivity can rarely be measured over a considerable range of concentration.
13.	Examples	Mostly organic substances, e.g., starch, gums, proteins, gelatin, etc.	Generally inorganic substances e.g., metal sols, sulphide and oxides sols.

12.7.4 Based on Molecular Size

Depending upon the molecular size, the colloidal system has been classified into three classes:

12.7.4.1 Multimolecular colloids

The multimolecular colloidal particles consists of an aggregate of atoms of small molecules with diameters less than 10^{-9} m or 1 nm. E.g., a solution of gold contains particles of various sizes having several atoms. A solution of sulphur consists of particles containing a thousand or so S_2 molecules. These particles are held together by Van der Waal's forces. They are usually lyophobic sols.

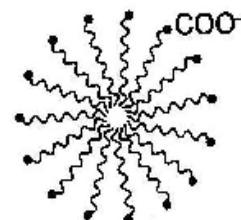
12.7.4.2 Macromolecular colloids

The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousands to millions. These substances are generally polymers. Naturally occurring

macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules is comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respects.

12.7.4.3 The associated colloids or micelles

Colloids which behave as normal electrolytes at low concentration, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called **micelles** are referred to as **associated colloids**. The micelles are formed by the association of dispersed particles above a certain concentration and certain minimum concentration is required for the process of aggregation to take place.



The minimum concentration required for micelle formation is called **critical micellisation concentration (CMC)** and its value depends upon the nature of the dispersed phase. For soaps, CMC is 10^{-3} mole L⁻¹. Micelles may contain 100 molecules or more.

The formation of a micelle takes place above a particular temperature called **kraft temperature (T_k)** and above a particular concentration called critical micellisation concentration (CMC).

12.8 PROPERTIES OF COLLOIDAL SOLUTIONS

12.8.1 Physical Properties

12.8.1.1 Heterogeneity

Colloidal solutions are heterogeneous in nature consisting of two phases, viz. the dispersed phase and the dispersion medium. Experiment like dialysis and ultrafiltration clearly indicate the heterogeneous character of a colloidal system. Recent investigations, however, have shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.

12.8.1.2 Filterability

Colloidal particles readily pass through ordinary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.

12.8.1.3 Non-settling nature

Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus, there is no effect of gravity on the colloidal particles.

12.8.1.4 Colour

The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors:

- (a) Size and shape of colloidal particles
- (b) Wavelength of the source of light
- (c) Method of preparation of the colloidal solution

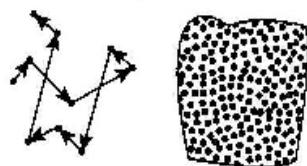
- (d) Nature of the colloidal solution
- (e) The way an observer receives light, i.e., whether by reflection or by transmission.
e.g., (i) Finest gold is red in colour. As the size of particles increases, it becomes purple. Due to this fact, gold sol is also called purple of cassius.
- (ii) Dilute milk gives a bluish tinge in reflected light, whereas reddish tinge in transmitted light.

12.8.2 Mechanical Properties

12.8.2.1 Brownian movement

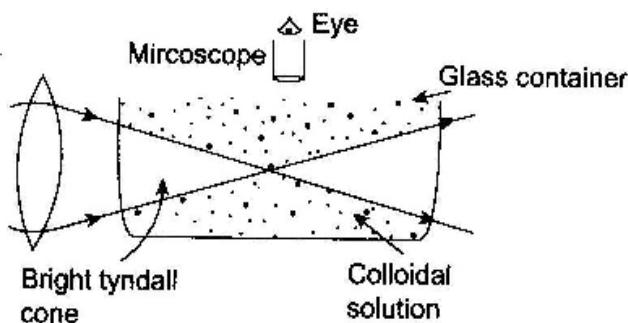
Robert Brown first observed this motion with pollen grains suspended in water. Colloidal particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called **Brownian movement**.

Cause of movement: Brownian movement is due to bombardment of the dispersed phase particles by the molecules of the dispersion medium. Brownian movement depends upon the size of sol particles. With the increase in the size of the particle, the chance of unequal bombardment increases, and Brownian movement disappears. Due to this fact, suspension fails to exhibit this phenomenon. It should be noted that Brownian movement does not change with time but changes with temperatures.



12.8.3 Optical Properties (Tyndall Effect)

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light. This effect is called **Tyndall effect**. The light is observed as a bluish cone which is called **Tyndall cone**.



Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wavelength of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the plane of incident light, it becomes visible when seen from that direction.

12.8.3.1 Condition for tyndall effect

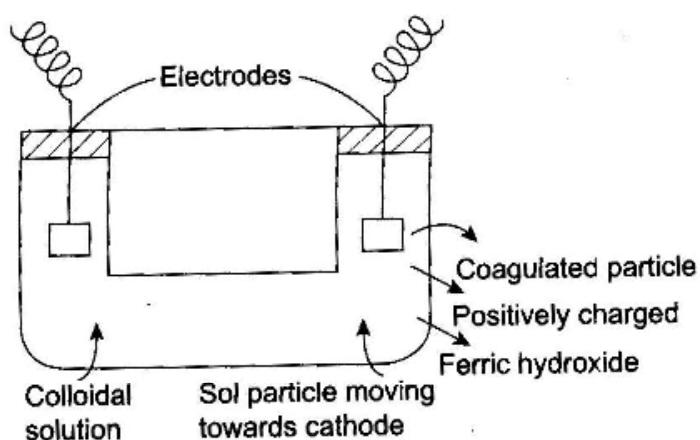
- (i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.

- (ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids. It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultramicroscope and in determining the number of a colloidal solution.

12.8.4 Electrical Properties

Electrophoresis or cataphoresis: In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus, colloidal solution as a whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where they coagulate due to loss of charge.

The phenomenon involving the migration of colloidal particles under the influence of an electric field towards the oppositely charged electrode is called **electrophoresis or cataphoresis**.

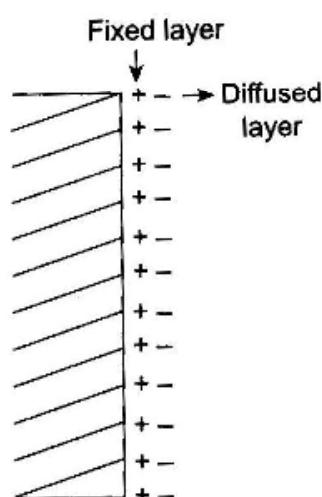


This phenomenon is used to determine the charge on the colloidal particles. For example, when a solution of ferric hydroxide is taken in a U-tube and subjected to an electric field, the ferric hydroxide (solution) particles get accumulated near the cathode. This shows that ferric hydroxide solution particles are positively charged.

The solution particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue, haemoglobin are positively charged while acid dyes like eosin are negatively charged.

12.8.4.1 Electrical double layer

The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve and -ve charges, respectively. The charged layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles, i.e., one due to adsorbed ions and the other due to oppositely charged ions forming a **diffused layer**. This layer consists of ion of both the signs, but its net charge is equal and opposite to those absorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite charge is called **electrokinetic potential or zeta potential (Z)**.



$Z = \frac{4\pi\eta v}{D}$; where η is coefficient of viscosity, D is dielectric constant and v is velocity of colloidal particles when an electric field is applied.

12.9 COAGULATION

The colloidal solutions are stable due to the presence of electric charges on the colloidal particles. Because of the electrical repulsion, the particles do not come close to one another to form precipitates. The removal of charge by any means will lead to the aggregation of particles and hence precipitation will occur immediately.

The coagulation process by means of which the particles instead of settling at the bottom of the container, float on the surface of the dispersion medium is called **flocculation**. Most of the solutions are coagulated by adding an electrolyte of opposite sign.

Note:

The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called coagulation value or flocculation value of the electrolyte for the solution. The reciprocal of coagulation value is regarded as the coagulating power, e.g., the coagulation values of NaCl; BaCl₂ and AlCl₃ for arsenic sulphide solution are 51, 0.69 and 0.093 millimoles/litre, respectively. Thus, their coagulating powers are $\frac{1}{51}$, $\frac{1}{0.69}$ and $\frac{1}{0.093}$, i.e., 0.0196, 1.449 and 10.75, respectively.

12.9.1 Hardy-Schulze Rules

H. Schulze (1882) and W B Hardy (1900) suggested the following rules to discuss the effect of electrolytes on the coagulation of the solution

- Only the ions carrying charge opposite to the one present on the solution particles are effective to cause coagulation, e.g., the negative charged solution is best coagulated by cation and a positive solution is coagulated by anion.
- The charge on coagulating ion influences the coagulation of solution.

"Higher is the valency of the active ion, greater will be its power to precipitate the solution"

Thus, coagulating power of cation is in the order of Al³⁺ > Ba²⁺ or Mg²⁺ > Na⁺ or K⁺.

Similarly, to coagulate the positively charged solution the coagulating power of anion is in the order of [Fe(CN)₆]⁴⁻ > PO₄³⁻ > SO₄²⁻ > Cl⁻.

12.10 PROTECTIVE COLLOIDS

Lyophilic solutions are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic solutions are more easily coagulated by the addition of a suitable electrolyte. To avoid the precipitation of lyophobic solution by the addition of electrolyte, some lyophilic colloid is added to it. Such a lyophilic colloid is called **protective colloid**. The substances commonly used as protective colloids are gelatin, albumin, gum arabic, casein, starch glue, etc. A gold solution containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the solution.

12.10.1 Gold Number

The protective power of the lyophilic colloids is expressed in terms of gold number, a term introduced by Zsigmondy. Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 ml of red gold solution when 1 ml of a 10 per cent solution of sodium chloride is added to it.

Note:

Thus, smaller the gold number of lyophilic colloid, the greater is its protective power.

Congo rubin number: The amount of protective colloid in milligram which prevents colour change in 100 ml of 0.01 per cent congo rubin solution to which 0.15 gram equivalent of KCl is added when observed after 10–16 minutes.

12.11 EMULSION

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquid dispersed in one another in the form of droplets whose diameter, in general, exceeds 0.1 g. The emulsions are classified as:

12.11.1 Classification of Emulsion

12.11.1.1 Oil in water type

In this emulsion, an oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk, vanishing cream, etc. fall under this category.

12.11.1.2 Water in oil type

In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc. The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two compounds liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsion can be interconverted into each other by changing the concentration of one of the liquids.

12.11.2 Distinction Between two Types of Emulsion

The two types of emulsions may be distinguished from each other in a number of ways.

12.11.2.1 Dye test

It involves the addition of an oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion.

12.11.2.2 Conductivity test

It involves the addition of an electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of the electrolyte, it is oil-in-water type emulsion and if conductivity is very small, it is water-in-oil type emulsion.

12.11.2.3 Dilution test

As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is water-in-oil type.

12.11.3 Preparation of Emulsion (Emulsification)

An emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layer upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers.

To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance which stabilizes the emulsion is called **emulsifier or emulsifying agent**. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence, milk is a fairly stable emulsion.

Function of emulsifier: The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus help in the intermixing of two liquids.

12.11.4 Uses of Emulsion

1. Many pharmaceutical preparations such as medicines, ointments, creams and various lotions are emulsions. It is believed that medicines are more effective and easily assimilated by the body tissues when they are in colloidal form, i.e., emulsion.
2. The digestion of fat in the intestines is facilitated by emulsification.
3. Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil-in-water type emulsion.
4. In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore move to the surface due to formation of foams while the other impurities are left at the bottom of the vessel.

12.12 GELS

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium is called a **gel**. The common examples are boot polishes, gum arabic, agar agar, processed cheese and silicic acid .

Gels are divided into two categories, i.e., elastic and non-elastic gels.

Comparative Study Between Elastic and Non-Elastic Gels

Elastic Gels	Non-Elastic Gels
<ol style="list-style-type: none"> 1. They change to solid mass on dehydration which can be changed back to original form with water. 	<ol style="list-style-type: none"> 1. They change to solid mass on dehydration which cannot be changed back to original form with water.
<ol style="list-style-type: none"> 2. They absorb water when placed in with simultaneous swelling. This phenomenon is called imbibition. 	<ol style="list-style-type: none"> 2. They do not exhibit imbibitions.

Note:

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids which accumulate on its surface. This action of gels is known as syneresis or weeping. Some gels such as silica, gelatin and ferric hydroxide liquefy on shaking and reset on following to stand. This phenomenon of sol-gel transformation is called thixotropy.

12.13 APPLICATIONS OF COLLOIDAL SOLUTION

12.13.1 Medicine

The medicines containing gold, silver or calcium, etc. in colloidal form are more effective and easily assimilated by the human systems.

12.13.2 Smoke Screens

Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.

12.13.3 Formation of Delta

The river water carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.

12.13.4 Purification of Water

The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e., Al^{3+} ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus water becomes clear.

12.13.5 Artificial Rain

Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solution or charged particles of water in air.

12.13.6 Sewage Disposal

Sewage water consists of particle of dirt, rubbish, mud, etc. which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When an electric field is created, then the dust particles are coagulated on the oppositely charged electrodes. The deposit may be utilized as a manure.

12.13.7 Blue Colour of the Sky

Colloidal particles scatter only blue light and the rest of it is absorbed. In sky there are number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.

12.14 PREPARATION OF COLLOIDAL SOLUTIONS

12.14.1 Preparation of Lyophilic Sols

The colloidal solutions of lyophilic colloids like starch, glue, gelatin, etc. can be readily prepared by dissolving these substances in water either in cold or on warming.

12.14.2 Preparation of Lyophobic Solutions

To get a solution in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension or increasing the size of molecular particles as to form larger aggregates. A third substance is usually added to increase the stability of the solution. These substances are called stabilizers.

There are two ways by which lyophobic solutions can be prepared.

- Dispersion method:** By splitting coarse aggregates of a substance into colloidal size. Dispersion can be done by any one of the following methods.
 - Mechanical dispersion:** Solid material is first finely ground by usual methods. It is then mixed with dispersion medium, e.g., water (hydrosols); alcohol (alcosols); benzene (benzosols) and air (aerosols) which gives a coarse suspension. The suspension is now introduced into a colloid mill. A machine in which two metal discs are held at a small distance and revolving with very high speed (700 rev/sec) in opposite direction. The particles are ground down to colloidal size and are then dispersed into the liquid. A stabilizer is added to stabilize the colloidal sols. Colloidal graphite (a lubricant) and printing ink are made by this method. Tannin is used as a stabilizer for preparation of colloidal graphite and gum arabic in printer ink.
 - Electrodispersion:** i.e., Bredig's arc method: This method is suitable for the preparation of colloidal solutions of metal like gold, silver, platinum, etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agent such as a trace of KOH. The water is cooled by immersing the container in an ice bath. The intense heat of the arc vapourizes some of the metal which condenses under cold water. This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs. This method involves both dispersion and condensation.
 - Ultrasonic dispersion:** The sound waves of high frequency are usually called ultrasonic waves. These waves can be used for preparation of colloidal solution. e.g., oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily by this method.
 - Peptization:** The dispersion of a freshly precipitated material into colloidal solutions by the action of an electrolyte in solution is termed as **peptization**. Electrolyte used for this purpose is known as **peptizing agent**. Some examples of salts obtained by peptization are

- (i) Freshly prepared $\text{Fe(OH)}_3 + \text{FeCl}_3 \rightarrow$ Reddish brown solutions.
 (Small amount) (Peptizing agent)
- (ii) $\text{SnO}_2 + \text{HCl} \rightarrow$ colloidal solution of SnO_2
- (iii) $\text{AgCl} + \text{HCl} \rightarrow$ Colloidal solution of AgCl
- (b) **Condensation method:** By aggregating very small particles (atoms, ions or molecules) into colloidal size. Condensation can be done by any one of the following methods.
- 1. By exchange of solvent:** Substance whose colloidal solution can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble. e.g., solution of S or P prepared in alcohol and poured in water in which it is less soluble.
 - 2. By change of physical state:** Colloidal solutions of certain elements such as Hg and S are obtained by passing their vapour through cold water containing a stabilizer as an ammonium salt of a citrate.
 - 3. Chemical methods:** The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super saturation is produced but the actual precipitation is avoided.
 - As_2S_3 colloidal solution is obtained on passing H_2S gas into cold As_2O_3 solution.
$$\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \longrightarrow \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$$

(Yellow solution)

 - Sb_2S_3 colloidal solution is obtained on passing H_2S gas into 0.5 per cent solutions of potassium antimonyl tartrate solution.
$$\begin{array}{ccc} \text{HO}-\text{CH}-\text{COOK} & & \text{HO}-\text{CH}-\text{COOK} \\ | & + 3\text{H}_2\text{S} \rightarrow & | \\ \text{HO}-\text{CH}-\text{COO}(\text{SbO}) & & \text{HO}-\text{CH}-\text{COOH} \end{array} + \text{Sb}_2\text{S}_3 + 2\text{H}_2\text{O}$$

(Orange solution)

 - A colloidal solution of S is obtained by passing H_2S into a solution of SO_2 .
$$2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$$
 - Colloidal solutions of metals like gold, silver, platinum, etc. can be obtained when these salts are acted upon by a reducing agent. $2 \text{AuCl}_3 + 3\text{SnCl}_2 \rightarrow 2\text{SnCl}_4 + 2\text{Au}$
 Organic reducing agent such as formaldehyde, phenylhydrazine, tannic acid, etc. can also be used.
 $\text{AgNO}_3 + \text{Tannic acid} \rightarrow$ Silver solution
 $\text{AuCl}_3 + \text{Tannic acid} \rightarrow$ Gold solution
 - Colloidal solution of Fe(OH)_3 can be obtained by boiling a dilute solution of FeCl_3 .
$$\text{FeCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Fe(OH)}_3 + 3\text{HCl}$$

Red sol.

PERIODIC CLASSIFICATION

13.1 LONG FORM OF PERIODIC TABLE

Long form of periodic table is also called Modern periodic table (MPT). In 1913, Moseley showed that the position of an element in the periodic table depends on its atomic number and not on its atomic mass and gave the following periodic law. 'The physical and chemical properties of the elements vary in relation to their atomic numbers.'

13.1.1 Characteristics of Modern Periodic Table

On the basis of electronic configuration of element.

- (i) The MPT is divided into 4 blocks namely s, p, d and f. All elements have their last electron in the s, p, d and f subshell and are placed in s, p, d and f block, respectively.
- (ii) The MPT is divided into 7 horizontal rows called the **periods**. The period number tells us the PQN of the outermost occupied orbit of the element.

e.g., x^{15} [Ne]3s²3p³ y^{35} 4s²4p⁵

Thus, element x and y will be present in the third and fourth periods, respectively.

- (iii) The MPT is also divided into a number of vertical columns called groups. The group number tells us the total number of electrons present in the outermost orbit of an element.
e.g., the elements in above example, x and y will be kept in 5th and 7th group, respectively.
- (iv) Groups I to VII are further divided into subgroups A and B. All elements having their last electron in 's' or 'p' orbital are kept in the subgroup A, whereas the subgroup B contains the elements having their last electron in the 'd' or 'f' orbitals.
- (v) In the modern periodic table, the VIII group is divided into three vertical columns, so that all nine elements are given different positions. Hence, MPT contains '18' vertical columns.

13.1.2 Advantages of MPT over Mendeleef's Periodic Table

- (i) Subgroups A and B are given separate positions.
- (ii) In the eighth group, all elements were given separate position.
- (iii) The lanthanides and actinides are given a definite position in the form of f block below the main body of MPT.
- (iv) All isotopes of an element are given same position as they have same atomic number, e.g., $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$.

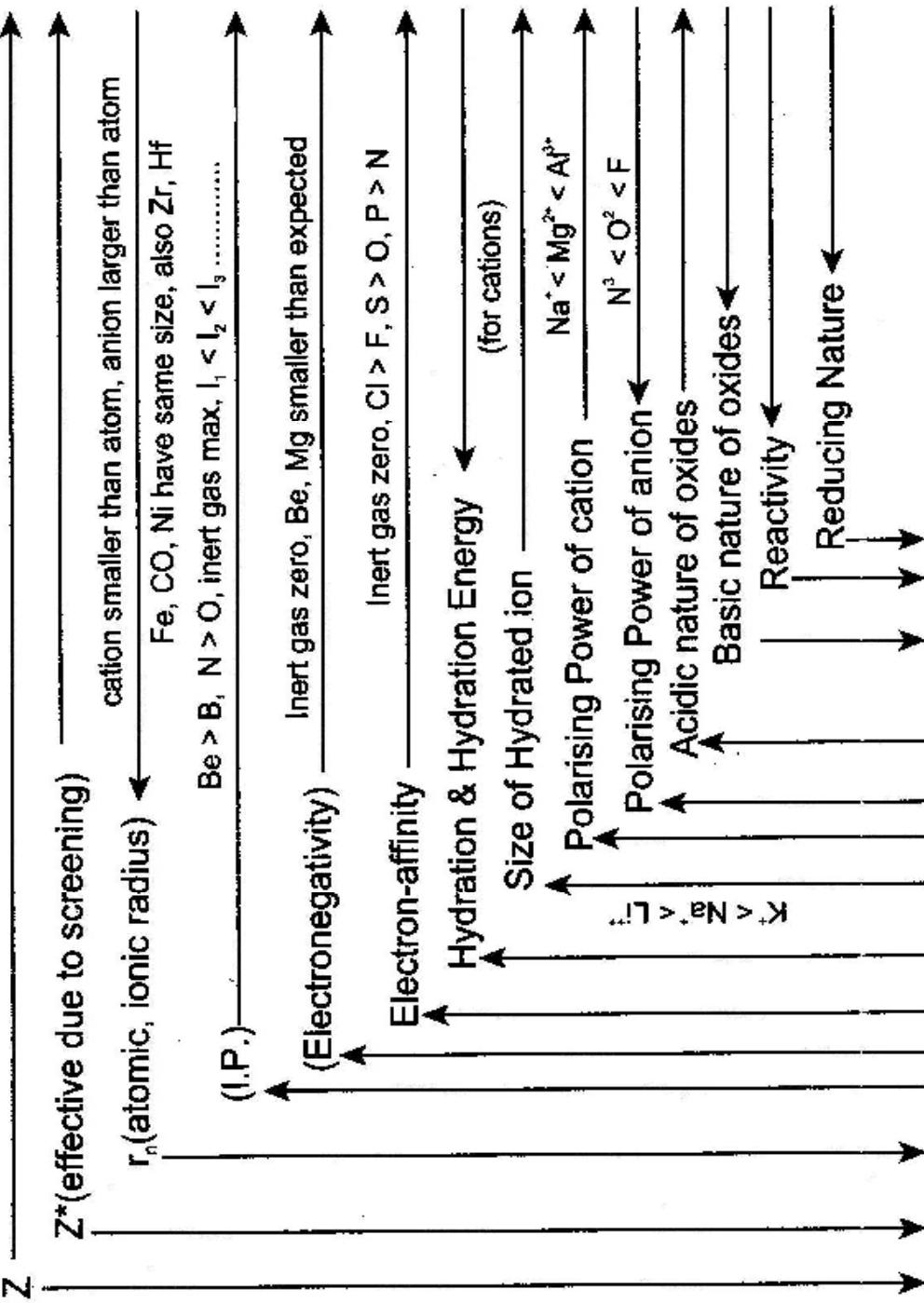
- (v) The highly electropositive and electronegative nature of I A and VII A group may be explained on the basis of electronic configuration EC.
- (vi) The variable valencies of 'd' block elements may also be explained with the help of EC.
- (vii) It also explains the cause of periodicity and magic numbers.

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PERIODICITY

Along a Period(→)
(Along a Group ↓)

Max.
Constant ↑
Max.

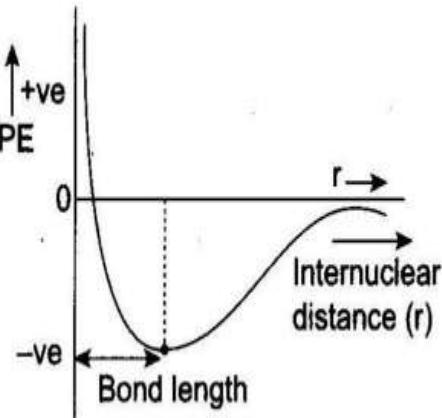


CHEMICAL BONDING

14.1 INTRODUCTION

Whenever two or more than two atoms combine, then a smallest stable species called molecule is produced. The binding forces holding together the atoms inside a molecule is called chemical bond. During the formation of chemical bond PE of the system decreases and therefore energy is released. Formation of chemical bond occurs at that stage where PE of the system is minimum.

The nature of a compound depends upon the type of bond present inside it which in turn is governed by the nature of combining atom.



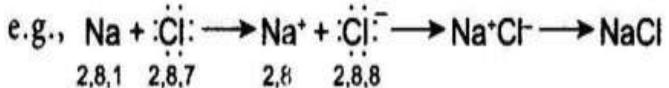
14.2 THEORY OF CHEMICAL BONDING

The bond formation takes place to make the system more stable. Stability is in two forms either lowering of energy of a system or a well defined arrangement of its constituents. For this, two factors are there to explain atomic interaction.

1. Tendency to acquire noble gas configuration.
2. Tendency to acquire minimum energy.

14.3 ELECTROVALENT OR IONIC BOND

Electrovalent bonding requires two atoms of different nature. One atom should have the tendency to lose electron, i.e., electropositive in nature and the other atom should have the tendency to accept electron, i.e., electronegative in nature. Ionic bonds are formed by loss and gain of e^- between two atoms. The electrostatic force of attraction developed between the cation and anion is known as ionic bond. It is also called electrovalent bond due to involvement of electrostatic forces of attraction.



Condition for formation of ionic bond: The following conditions favour the formation of an electrovalent bond.

- (i) In general atoms having 1, 2 or 3 valence electrons in outermost shell changes into cation and atoms having 5, 6 or $7e^-$ in valency shell changes into anion.
- (ii) **Electronegativity difference:** With a great difference in electronegativity of two atoms, it is easier to form an ionic bond.
- (iii) **Overall lowering of energy:** Energy must be released during ionic bond formation.
- (iv) **Lattice energy:** Higher the lattice energy greater, will be the ease of formation of the ionic compound.

Factors influencing magnitude of lattice energy are as follows:

- (a) **Size of ions:** Smaller the size of the ions, lesser is the internuclear distance. Consequently, the interionic attraction will be high and lattice energy will also be large.
- (b) **Charge on ions:** Larger the magnitude of charge on the ions, greater will be the attractive forces between the ions. Consequently, the lattice energy will be high.

Note:

Lower the value of IE and higher the value of EA there is more ease of formation of the cation and anion from it respectively and consequently more chances of electrovalent bond formation.

14.3.1 Characteristic of Ionic Compounds

General properties of ionic compounds are as follows:

- (i) They are not true bond because they are neither rigid nor directional.
- (ii) In the solid state each cation surrounds itself with anions and each anion with cations. These large number of ions are arranged in an orderly manner called ionic crystal.
- (iii) They are hard and brittle.
- (iv) They are good conductors of electricity in fused state and in aqueous solution.
- (v) They are soluble in polar solvents and insoluble in non-polar solvents.
- (vi) They have high mp and bp

14.4 COVALENT BOND

A covalent bond may be defined as the bond formed by mutual sharing of electrons between the combining atoms (which are short of electrons) of comparable electronegativity. The combining atoms thus achieve inert gas configuration. The shared electron contribute towards the stability of both atoms.

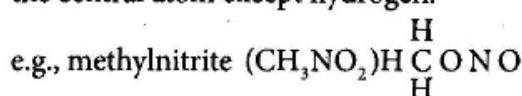
14.4.1 Covalency

It is defined as the number of electrons contributed by an atom of the element for sharing with other.

14.4.2 Lewis Dot Structure

Six steps are involved in writing Lewis dot structure.

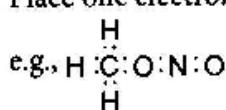
- (i) Arrange the atoms in space as per their actual configuration. Least electronegative atom should be the central atom except hydrogen.



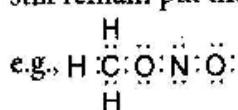
- (ii) Count all the valence electrons including the charge and divide this number by 2 to obtain number of electron pairs.

e.g., in CH_3NO_2 , number of valence electron = $4 + 1 \times 3 + 5 + 6 \times 2 = 24$
 \Rightarrow Number of electron pair = $24 / 2 = 12$.

- (iii) Place one electron pair each between the atoms actually connected by bond.

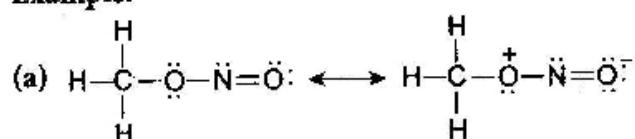


- (iv) Place the remaining electron pairs on terminal atoms till their octet is completed. If electron pairs still remain put them on central atom.

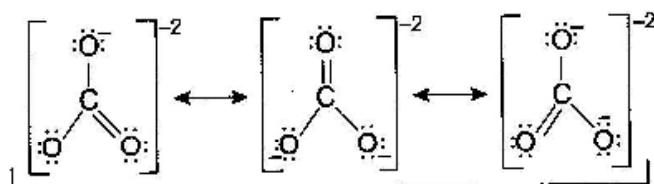


- (v) Check whether the octet of central atom is complete or not. If not, then convert one or more lone pair on terminal atoms in double or triple bonds.

Example:



(b) CO_3^{2-} number of valence electron = $2 + 4 + 6 \times 3 = 24 e^-$
Number of electron pair = $24 / 2 = 12$



3 resonating structures.

- (vi) Formal charge of central atom should be kept as low as possible. Normally it is equal to zero.
Formal charge = number of valence electrons - number of bond pair - $2 \times$ number of lone pair.

14.4.3 Characteristics of Covalent Compounds

- (i) **Physical state:** Under the normal conditions of temperature and pressure, they exist as gases or liquids of low boiling points. Because of weak forces of attraction, Van der Wall's forces exist between discrete molecules.
- (ii) **Melting and boiling points:** With the exception of few which have giant three-dimensional structures such as diamond, carborundum (SiC), Silica (SiO_2), others have relatively low melting and boiling points.
This is due to the presence of weak attractive forces between the molecules.
- (iii) **Electrical conductivity:**
- (a) In general, covalent substances are bad conductors of electricity.
 - (b) Substances which have polar character like HCl in solution, can conduct electricity.
 - (c) Covalent solids having giant molecules, are bad conductors since they do not contain charged particles or free electrons.
 - (d) The graphite can conduct electricity since electrons can pass from one layer to the other.

(v) Solubility:

- (a) Polar compounds are soluble in a polar solvent (i.e., ΔEN from 0.9 to 1.8), polar solvents are H_2O , $CHCl_3$, alcohol, etc.

(b) Non-polar compounds are soluble in a non-polar solvent. Non-polar solvents are CCl_4 , benzene, CS , etc.

14.4.4 Coordinate Covalent Bond

A covalent bond in which both the electrons in the shared pair come from one atom is called a coordinate covalent bond. Such type of bond is formed between atoms (or ions), one of which is deficient in at least two electrons while the other atom has already acquired a stable noble gas configuration. The atom which contributes both the electrons is called the donor while the other which only shares the electron pair is known as acceptor. This bond is usually represented by an arrow (\rightarrow) pointing from donor to the acceptor atom.

14.5 THE VALENCE BOND THEORY

14.5.1 Heitler and London Concept

- (i) For a covalent bond to form, two atoms must come closer to each other so that their orbitals overlaps with each other.
 - (ii) Overlapping orbitals must have half-filled nature, i.e., they must have unpaired electron and anti-spin electrons.
 - (iii) As a result of overlapping, a new localized bond orbital is formed, in which probability of finding an electron pair is maximum.
 - (iv) Covalent bond arises due to electrostatic attraction between nuclei and the accumulated electron cloud.
 - (v) Greater is the overlapping, lesser will be the bond length, more will be attraction and more will be bond energy, and the stability of bond.

14.5.2 Pauling and Slater Extension

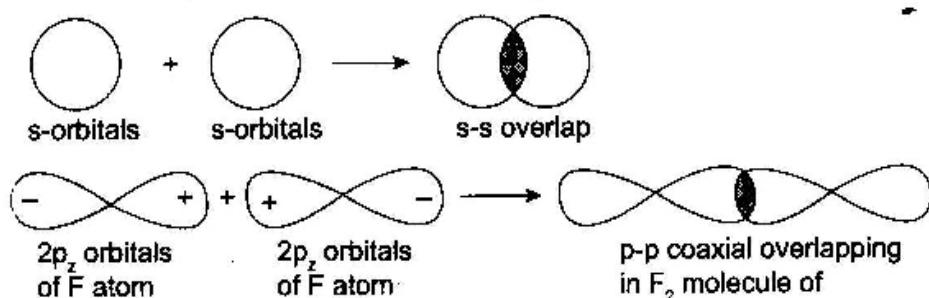
- (i) According to this theory the extent of overlapping of orbitals depends upon nature of orbitals involved in overlapping and nature of overlapping.
 - (ii) More closer the valence shell of orbital to the nucleus, more will be the overlapping, and the bond energy will also be high. Bond energy of $1 - 1 > 1 - 2 > 2 - 2 > 2 - 3 > 3 - 3$.
 - (iii) Between two subshells of same energy level, the subshell which is more directionally concentrated shows more overlapping. Bond energy: $2s - 2s < 2s - 2p < 2p - 2p$.
 - (iv) s-orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand, p-orbitals are directionally concentrated and thus show either head on overlapping or lateral overlapping.

14.5.3 Types of Overlapping and Nature of Covalent Bonds

Depending upon the type of overlapping, the covalent bonds may be divided into two types.

(i) Sigma (σ) bond :

- (a) Sigma bond is formed by the end-to-end overlapping of bonding orbitals along the internuclear axis.

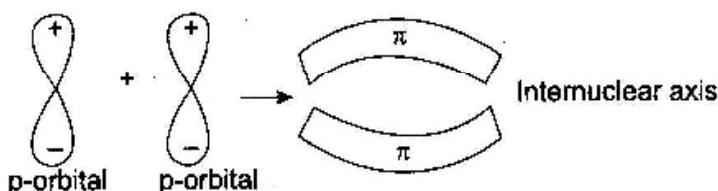


- (b) The overlap is known as head on overlap or axial overlap.

- (c) The sigma bond is formed by any one of the following type of combinations of atomic orbitals
 (d) Free rotation about σ bond is possible.
 (e) Geometry of a covalent molecule entirely depends upon σ bond pair.

(ii) Pi (π) bond:

- (a) This type of covalent bond is formed by sidewise overlapping of half-filled atomic orbitals of bonding atoms.
 (b) The orbitals involved in overlap must be parallel to each other and perpendicular to the internuclear axis.



- (c) It is always accompanied by a σ bond and consists of two charge clouds, i.e., above and below the plane of sigma bond.
 (d) Since overlapping takes place on both sides of the internuclear axis, free rotation of atoms around a π bond is not possible.
 (e) Furthermore, formation of a π bond shortens the bond distance between the two atoms involved, e.g., C – C, C = C, C ≡ C, bond lengths are 1.54 Å, 1.3 Å and 1.20 Å, respectively.

14.6 HYBRIDIZATION

The concept of hybridization was introduced by Pauling. Hybridization is defined as the intermixing of dissimilar orbitals of the same atom but having slightly different energies to form same number of new orbitals of equal energies and identical shapes.

The new orbitals so formed are known as hybrid orbitals whose shape is similar to p-orbital except that the two lobes are unequal in size.

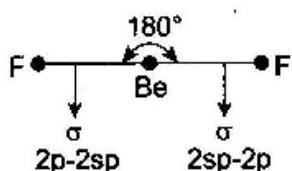
14.6.1 Characteristics of Hybridization

- Only orbitals of almost similar energies and belonging to the same atom or ion undergo hybridization.

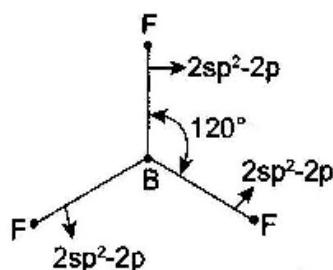
2. The number of hybrid orbitals produced is equal to the number of pure orbitals mixed during hybridization, e.g., four hybrid orbitals are produced by mixing one s and three p(p_x , p_y and p_z) pure orbitals.
3. Half-filled orbitals, fully filled vacant orbitals of equivalent energy can involve in hybridization.
4. Hybrid orbitals are identical in terms shape, size and energy.
5. Orbitals involved in π bond formation do not participate in hybridization.
6. Hybridization never takes place in an isolated atom but it occurs only at the time of bond formation.
7. The hybrid orbitals are distributed in space as far apart as possible resulting in a definite geometry of molecule.
8. Hybridized orbitals provide efficient overlapping than overlapping by pure s, p and d-orbitals.
9. The number of 'p' orbitals that take place in hybridization is called hybridization index (m) and for organic molecules $\cos \alpha = -1/m$, where α is the bond angle between two hybrid orbitals.
e.g., for sp hybridization, $m = 1$, hence, $\cos \alpha = -1$ or $\alpha = 180^\circ$
for sp^2 hybridization $m = 2$, hence, $\cos \alpha = -\frac{1}{2}$ or $\alpha = 120^\circ$

14.6.2 Type of Hybridization

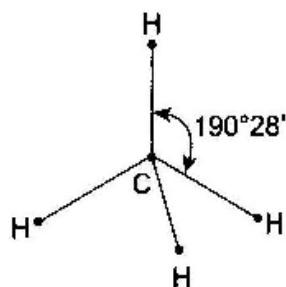
(a) **sp hybridization:** (linear geometry), e.g., BeF_2



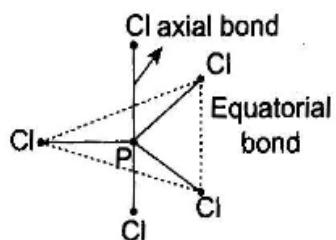
(b) **sp^2 hybridization:** (trigonal planar geometry), e.g., BF_3



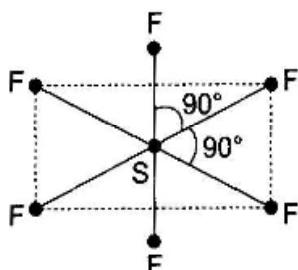
(c) **sp^3 hybridization:** (tetrahedral geometry), e.g., CH_4



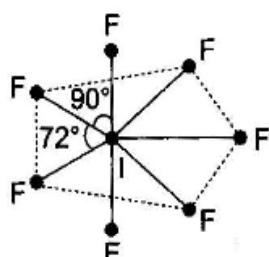
(d) **sp^3d hybridization:** (trigonal bipyramidal geometry), e.g., PCl_5



(e) sp^3d^2 hybridization: (octahedral geometry), e.g., SF_6



(f) sp^3d^3 hybridization: (pentagonal bipyramidal geometry), e.g., IF_7

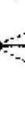
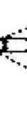


14.7 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

The basic concept of this theory as suggested by Sidgwick and Powell (1940) has provided a highly useful idea for predicting geometries of molecules. According to this model, the arrangement of bonds around the central atom depends upon the repulsions operating between pairs of electrons (bonded or non-bonded) around the central atom.

The main postulates of VSEPR theory are

- (i) For polyatomic molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.
- (ii) The geometry of a molecule depends upon the total number of valence shell electron pair (bonded or non-bonded) present around the central atom and their repulsion due to relative sizes and shapes.
- (iii) The lone pair of electrons in a molecule occupy more space as compared to the bond pair of electrons. This results in greater repulsion between lone pair of electrons as compared to bond pair.
- (iv) If the central atom is linked to similar atoms, the repulsion between them are also similar. It gives the symmetrical shape to the molecule.
- (v) If the central atom is linked to atoms of different sizes or is surrounded by lone pairs as well as bond pairs of e^- then the molecule has a distorted geometry. The relative order of repulsion between electron pairs is as: $Lp - Lp > Lp - Bp > BP - BP$

Types of orbitals involved		Type of Hybridization	Number of Electron Pairs	Arrangement of Pairs	Shapes of Molecules	Bond Angle	Examples		
s	p	d	IP	BP	Total				
1	1	-	sp	2	2	Linear (AX_2)		180°	$BeCl_2$, BeF_2 , Co_2 , CS_2 , $HgCl_2$, C_2H_2 , $MgCl_2$
1	2	-	sp ²	3	3	Trigonal (AX ₃) planar		120°	BCl_3 , BF_3 , CO_3^{2-} , SO_3^{2-} , NO_3^- , C_2H_4 , graphite, BH_3 , $AlCl_3$, SO_2 , NO_2 , O_3 , $SiCl_4$
1	3	-	sp ³	4	4	Tetrahedral (AX ₄)		109.5°	CCl_4 , CH_4 , Diamond, SO_4^{2-} , $S_2O_3^{2-}$, PO_4^{3-} , $SiCl_4^+$, $SnCl_4^+$, CIO_4^- , BF_4^- , BH_4^- , AlH_4^- , NH_4^+ , PCl_4^+ , NH_3 , PH_3 , AsH_3 , SO_3^{2-} , NF_3
1	2	1	2	3	Angular (AX ₂ E)		119°		
Distorted									
1	3	-	sp ³	4	4	Tetrahedral (AX ₄)		190°28'	CCl_4 , CH_4 , Diamond, SO_4^{2-} , $S_2O_3^{2-}$, PO_4^{3-} , $SiCl_4^+$, $SnCl_4^+$, CIO_4^- , BF_4^- , BH_4^- , AlH_4^- , NH_4^+ , PCl_4^+ , NH_3 , PH_3 , AsH_3 , SO_3^{2-} , NF_3
Distorted	1	3	1	3	4	Trigonal (AX ₃ E) Pyramidal		107°48'	
Distorted	1	3	1	3	4	Pyramidal (AX ₂ E) V or bent shape (AX ₂ E ₂)		102°30'	
Distorted	2	2	2	4	4	Pyramidal (AX ₂ E) V or bent shape (AX ₂ E ₂)		104°27'	H_2O , F_2O (102°), H_2S (90°), I_3 , Cl_2O , NH_2
Distorted	1	4	1	4	5	Triangular Bipyramidal (AX ₅)		120° and 90°	PCl_5 , PFS , $SbCl_5$, SF_5 , $TcCl_4$
Distorted	1	4	1	4	5	Seesaw of distorted tetrahedron (AX ₄ E)		101°36', 86°33'	

Type of orbitals involved	Type of Hybridization	Number of Electron Pairs	Arrangement of Pairs	Shapes of Molecules	Bond Angle	Examples
s p d	sp ³ d ²	5	T shape (AX_3E_2)	180°	37°40'	ICl ₃ , ClF ₃ , BrF ₃ , XeF ₄
Distorted	Distorted	3	Linear (AX_2E_2)	180°	90°	SF ₆ , SiCl ₄ , PF ₅ , SeF ₆ , UF ₆ , ReF ₆
		2	sp ³ d ²	180°	34°30'	IF ₇ , XeOF ₄ , BrF ₅
		1	sp ³ d ²	90°	72°, 90°	XeF ₆
		0	sp ³ d ²	90°	90°	[Na(CN)] ₂ , [P(NH ₃) ₃] ₂ , [Cu(NH ₃) ₄] ₂ , [PbCl ₆] ₂

14.8 MOLECULAR ORBITAL THEORY

- (a) There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by Mulliken and Hund, which explains the bonding characteristics in a better way.
- (b) The MOT considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecule.
- (c) This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.

14.8.1 Important Features of MOT

- (a) Like an atomic orbital, which is around the nucleus of an atom there are molecular orbitals which are around the nuclei of a molecule.
- (b) The molecular orbitals are entirely different from the atomic orbitals from which they are formed.
- (c) The valence electrons of the constituent atoms are considered to be moving under the influence of nuclei of participating atoms in the molecular orbital.
- (d) The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.
- (e) The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.
- (f) Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.
- (g) The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.
- (h) Like atomic orbitals, the filling of electrons in molecular orbitals is governed by the three principles such as Aufbau principle, Hund's rule and Pauli's exclusion principle.

14.8.2 Conditions for Atomic Orbitals to Form Molecular Orbitals

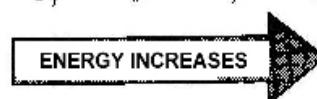
- (a) The combining atomic orbitals should be of a comparable energy.
- (b) The combining atomic orbitals must overlap to a large extent. Greater the overlap, stable is the molecule formed.
- (c) They should be properly oriented.

14.8.3 Relative Energies of Molecular Orbitals and Filling of e^-

- (a) Two general criteria, which determine the energy of the molecular orbitals are
 - (i) Initial energy of the atomic orbitals
 - (ii) The extent of the overlap of the atomic orbitals.
- (b) It is obvious that molecular orbitals formed from lower energy atomic orbitals have lower energy than the molecular orbitals formed from higher energy atomic orbitals.
- (c) The relative energies of the molecular orbitals are obtained experimentally from spectroscopic data.
- (d) For diatomic species having less than or equal to $14e^-$.
 $\sigma 1s, \sigma^*1s, \sigma 2s, \sigma^*2s, \pi 2p_x = \pi 2p_y, \sigma 2p_z, \pi^*2p_x = \pi^*2p_y, \sigma^*2p_z$



- (e) For diatomic species having greater than $14e^-$.
 $\sigma 1s, \sigma^*1s, \sigma 2s, \sigma^*2s, \sigma 2p_x, \pi 2p_x = \pi^*2p_x, \pi^*2p_y = \pi^*2p_z$



14.8.3.1 Stability of molecules in terms of bond order

- (a) The relative stability of a molecule is further evaluated by a parameter known as bond order.
- (b) Bond order = $\frac{1}{2}$ [Number of electrons in bonding orbitals – Number of electrons in anti-bonding orbitals].
- (c) The bond order of 1, 2 and 3 corresponds to single, double and triple bonds, respectively. It may be mentioned that according to the MO theory, even a fractional bond order is possible. Thus
- (d) Stability of molecule μ bond order
- (e) Dissociation energy μ bond order
- (f) Bond length $\propto \frac{1}{\text{Bond order}}$
- (g) If all the electrons in a molecule are paired, the substance is diamagnetic. On the other hand, if there are unpaired electrons in the molecule, the substance is paramagnetic. More the number of unpaired electrons in the molecule, greater is the paramagnetism of the substance.

14.9 COVALENT CHARACTER IN IONIC COMPOUNDS: FAZAN'S RULE

Although in an ionic compound like M^+X^- the bond is considered to be 100 per cent ionic, but it has some covalent character. Likewise, a covalent bond has some ionic character. The partial covalent character of an ionic bond has been explained by Fazan as follows:

- (a) When a cation approaches an anion, the electron cloud of the anion is attracted towards the cation and hence anion gets distorted. This effect is called polarization of the anion.
- (b) The power of the cation to polarize the anion is called its polarizing power.
- (c) The tendency of the anion to get polarized is called its polarizability.
- (d) The greater is the polarization produced, more is the neutralization of the charges (i.e., charge of the cation by the electron cloud of the anion) and hence the ionic character decreases or the covalent character increases.

The formation of covalent bond is favoured by the following factors:

$$\text{Covalent character} \propto \frac{1}{\text{Cationic size}}$$

- (a) μ anionic size (b) μ cationic charge and (c) μ anionic charge.
- (d) Electronic configuration of the cation: For the two ions of the same size and charge, one with a pseudonoble gas configuration (i.e., 18 electrons in the outermost shell) will be more polarizing than a cation with noble gas configuration (i.e., 8 electron in outer most shell).

14.9.1 Applications of Fajan's Rule (Ionic Potential ϕ)

The polarizing power of a cation can be expressed in terms of ionic potential, ϕ .

- (i) Ionic potential, $\phi = \frac{\text{Charge on cation}}{\text{size of cation}}$
- (ii) ϕ μ is polarizing power and μ is covalent character.
- (iii) In a period ϕ increases and in a group ϕ decreases on moving from top to bottom.
- (iv) There is a correlation between nature of oxide and value of ϕ as follows:
 $\sqrt{\phi} < 2.2 \rightarrow \text{Basic}$
 $\sqrt{\phi} = 2.2 \text{ to } 3.3 \rightarrow \text{Amphoteric}$
 $\sqrt{\phi} = 3.3 \rightarrow \text{Acidic in nature}$
- (v) Tendency to form complex compounds increases as the value of ϕ increases.
- (vi) Thermal stability of a compound involving polyatomic anion is inversely proportional to polarizing power of cation and vice versa for monoatomic anion.

14.10 DIPOLE MOMENT

- (a) In a polar molecule, one end of the molecule is negative and the other is positive. In other words, there are two poles present in the molecule and hence the molecule is said to possess an electric dipole.
- (b) The product of magnitude of negative or positive charge (q) and the distance (d) between the centres of positive and negative charges is called dipole moment. It is usually denoted by μ . $\mu = q \times d$
- (c) The most commonly used unit of dipole moment is debye (D). $1\text{D} = 1 \times 10^{-18} \text{ esu cm}$.

14.10.1 Characteristic of Dipole Moment

- (i) Dipole moment is a vector quantity, i.e., it has magnitude as well as direction. It is often represented by an arrow with its tail at the positive centre and head pointing towards the negative end (+ → -).
- (ii) As a polar diatomic molecule possess only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar bond.
- (iii) As a polyatomic molecule has more than one polar bond, the dipole moment is equal to the resultant dipole moment of all the individual bonds.
- (iv) Again in case of symmetrical molecules such as BF_3 , CH_4 and CCl_4 the molecular dipole moment is found to be zero. This is again because of the fact that individual dipole moments cancels out on account of the symmetry of the molecule.

14.10.2 Application of Dipole Moment

14.10.2.1 In determination of polarity of bonds

Greater is the magnitude of dipole moment, higher will be the polarity of the bond. But in the strict sense, this concept is applicable to molecules containing only one polar bond.

14.10.2.2 In determination of per cent ionic character

The percentage of ionic character of a bond can be calculated from the ratio of the observed dipole moment to the calculate dipole moment (considering 100 per cent ionic character).

i.e., per cent ionic character = $\frac{\text{Observed dipole moment}}{\text{dipole moment considering 100 per cent ionic character}} \times 100$

Dipole moment for 100 per cent ionic character can be calculated as follows $\mu(\text{ionic}) = e \times d \text{ esu cm}$

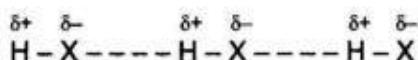
In case of organic compounds $\mu_{\text{cis}} > \mu_{\text{trans}} > \mu_{\text{para}}$

If groups present on benzene ring are of same nature.

$\mu_{\text{ortho}} > \mu_{\text{meta}} > \mu_{\text{para}}$;

14.11 HYDROGEN BONDING

- (i) When a hydrogen atom linked to a highly electronegative atom (like F or N) comes under the influence of another strongly electronegative atom, then a weak bond is developed between them which is called as hydrogen bond or proton bond.
- (ii) Hydrogen bond never involves more than three atoms and atoms must be collinear.
- (iii) It is represented by dotted line as follows:



- (iv) As a result of hydrogen bonding, a H-atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. Hence, it is said to form a hydrogen bridge.
- (v) It is merely a strong electrostatic attractive forces and not a normal chemical bond. It is very weak (strength about 2–10 K cal/mol).

14.11.1 Condition For Hydrogen Bonding

The molecule must contain a highly electronegative atom linked to H-atom. The higher the electronegativity, more is the polarization of the molecule.

14.11.2 Types of Hydrogen Bonding

14.11.2.1 Intermolecular hydrogen bonding

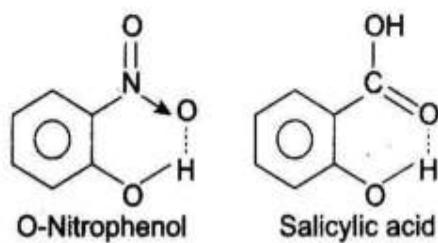
When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding, e.g., HF, H_2O , ROH (same compound) water-alcohol, water-ammonia (different compound, etc.).

14.11.2.2 Intramolecular hydrogen bonding

The hydrogen bonding which takes place within a molecule itself is called intramolecular H-bonding or chelation.

Conditions of intramolecular hydrogen bonding:

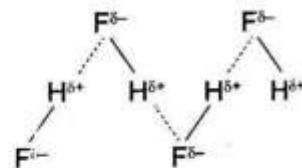
1. The molecules should contain two groups such that one group contains H-atom linked to a highly electronegative atom and the other group should also contain a highly electronegative atom linked to a lesser electronegative atom.



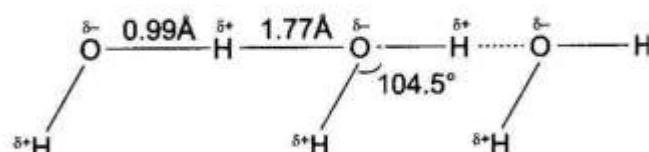
2. The molecule should be planar.
3. The hydrogen bonding should lead to the formation of a figure of six a membered ring including the H-atom.

14.11.3 Examples of Hydrogen Bonding

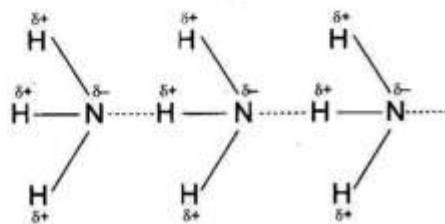
1. **HF-** due to highest value of electronegativity, fluorine forms the strongest hydrogen bonds.



2. **Water (H_2O):** The bond between oxygen and hydrogen is polar due to electronegativity difference between oxygen and hydrogen. Electrostatic attraction between the negative end of one molecule and the positive end of the other molecule results in the formation of hydrogen bond.



4. **Ammonia:** An ammonia molecule has an electronegative nitrogen atom covalently linked to three hydrogen atoms. Due to their electronegativity difference, each hydrogen acquires positive charge and nitrogen becomes negatively charged. Hence, electrostatic attraction between ammonia molecules takes place resulting in the formation of an associated molecule as shown below.

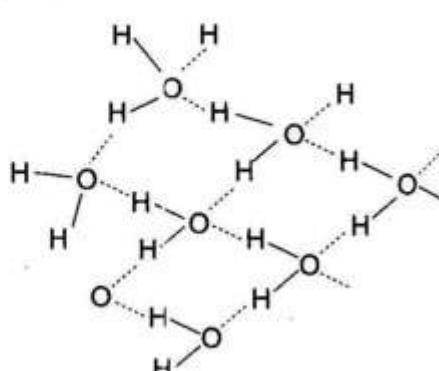


Chlorine has the same electronegativity value (3.0) as that of nitrogen (3.0) but does not form hydrogen bonded due to its large atomic size.

14.11.4 Effect of Hydrogen Bonding

Hydrogen bond helps in explaining the abnormal physical properties in several cases as described below.

1. **Association:** Due to hydrogen bonding carboxylic acid exist as dimers due to intermolecular hydrogen bonding as shown below. The molecular masses of these acids are found to be double than that calculated from their simple formula.
2. **Dissociation:** In aqueous solution, hydrogen fluoride dissociates and gives the difluoride ion (HF_2^-) instead of fluoride ion (F^-). This is due to H-bonding in HF. This explains the existence of KHF_2 .
3. **High melting and boiling points:** The compound having hydrogen bonding shows abnormally high melting and boiling points, e.g., HF has higher BP than HCl and boiling point of alcohols is larger than ethers.
4. **Solubility in water:** Compounds which can form hydrogen bonding with water will dissolve in water. For example, lower alcohols are soluble in water because their molecules can form H-bonds with water. Similarly, ammonia and amines are soluble in water due to H-bonding with water
5. **Viscosity:** The substances which can give more extensive hydrogen bonding will have higher viscosity.
E.g., ethanol < glycol < glycerol.



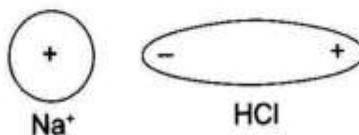
6. Density of Water: In case of solid ice, the hydrogen bonding gives rise to a cage like structure of water molecules due to which volume of the system increases which results in decrease in density.

14.12 VAN DER WAAL'S FORCES

- (a) This type of attractive forces occur in case of non-polar molecules such as H_2 , O_2 , Cl_2 , CH_4 , CO_2 , etc.
- (b) The existence of weak attractive forces among the non-polar molecule was first proposed by the dutch scientist J D Van der Waal.
- (c) Van der Waal force μ molecular weight
 μ Atomic weight
 μ Boiling point

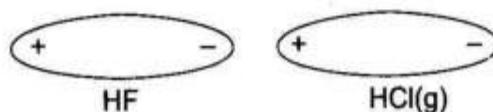
14.12.1 Ion-dipole Attraction

This force is between an ion such as Na^+ and a polar molecule such as HCl .



14.12.2 Dipole-Dipole Attraction

It is again in between two polar molecules such as HF and HCl(g) .



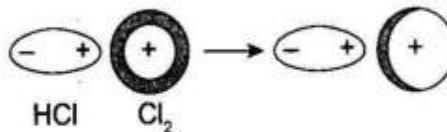
14.12.3 Ion-induced Dipole Attraction

In this case a neutral molecule is induced by an ion as a dipole as shown in the figure.



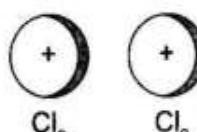
14.12.4 Dipole-Induced Dipole Attraction

In this case a neutral molecule is induced as a dipole by another dipole as shown in the figure.



14.12.5 Induced Dipole-Induced Dipole Attraction

Induced dipole attraction or London dispersion force: It occurs between two non-polar molecules as in Cl_2 , He , etc.



Note:

The relative strength of various bonds is as follows:

Ionic bond > Covalent bond > Metallic bond > H-bond > Van der Waal forces.

S-BLOCK ELEMENTS

15.1 ALKALI METALS

s-block elements are those in which the differentiating electron enters into n-s orbital. Since n-s orbital can accommodate two electrons so s-block consists of two vertical rows numbered as group I and group II. Group I members are called alkali metals and have ns¹ configuration.

These are called alkali metals because their oxides and hydroxides form strong alkali like NaOH, KOH, etc. Members are Li, Na, K, Rb, Cs and Fr (Francium is radioactive).

15.2 TRENDS IN PROPERTIES

Density: It increases down the group because increase in atomic mass compensates more than the increase in atomic size. K is lighter than Na due to the abnormal increase in atomic size.

Melting and boiling point: For alkali metals, there are low and decrease down the group. Francium is a liquid at room temperature. Alkali metals are soft, malleable, ductile and have metallic luster which is due to the oscillation of electrons.

Ionization enthalpy: For alkali metals, it is minimum in their respective period and decreases down the group. Due to the low ionization enthalpy alkali metals are the most electropositive elements and form unipositive cations.

All alkali metals have body centred cubic structure with coordination number.

Flame colouration: Alkali metals impart characteristic colour to the flame because when heated in Bunsen flame the electrons gets excited to the higher energy level due to low ionization enthalpy. Excited electron when drops back to the ground state emit radiations in the visible range and impart characteristic colour.

Li	Na	K	Rb	Cs
Crimson red	Golden yellow	Paleviolet	Purple	Sky blue

Photoelectric effect: Due to the low ionization enthalpy alkali metals (except Li and Na) show photoelectric effect. K and Cs are used in photoelectric cells.

Electrical conductivity: Alkali metals are good conductors due to the presence of loosely held valence electrons. Electrical conductivity increases down the group due to the decrease in ionization enthalpy.

Reducing power: Alkali metals are the strongest reducing agents in their respective period due to their lowest ionization enthalpy.

Reducing power is in the order Li > Cs > Rb > K > Na.

During reducing property following changes occur:

$M(s) \rightarrow M(g)$, sublimation energy

$M(g) \rightarrow M^{+}_{(g)} + e^{-}$, ionization enthalpy

$M^{+}_{(g)} + H_2O \rightarrow M^{+}_{(aq)}$, hydration energy

Hydration energy outweighs ionization enthalpy in lithium. So, lithium is the strongest reducing agent.

Ionic mobility: Smaller the size, greater the extent of hydration and hence lesser the ionic mobility. Lithium ion has the lowest ionic mobility due to its high hydration energy.

Chemical properties: Alkali metals have a tendency to form ionic compounds. Alkali metals do not occur free in nature due to their low ionization enthalpy. When exposed to air these form oxides, hydroxides, carbonates and bicarbonates.

Reaction with water: Alkali metals react with water to give hydrogen: $2M + 2H_2O \rightarrow 2MOH + H_2$

Their reactivity increases down the group.

Alkali metal hydroxides are strong bases.

Thermal stability, solubility and basicity increases down the group.

All alkali metal hydroxides are thermally stable except LiOH.

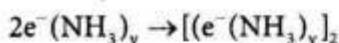


Reaction with oxygen: Lithium forms Li_2O ; Na forms peroxide (Na_2O_2) and K forms superoxide (KO_2). Superoxides are coloured and paramagnetic due to the presence of unpaired electrons. All oxides, peroxides and superoxides are basic in nature.

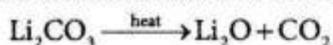
Reaction with hydrogen: Stability of hydrides of alkali metals decreases down the group. Hydrides of alkali metals are strong reducing agents.

Reaction with halogen: Alkali metals react with halogens to form ionic halides which are soluble in water. Melting point of alkali metal halides is in the order: MF > MCl > MBr > MI.

Solubility in liquid ammonia: All alkali metals are soluble in liquid ammonia and give deep blue colour. This blue colour is observed due to ammoniated electron, solution is a good conductor of electricity, paramagnetic and a strong reducing agent. Paramagnetism decreases with increasing concentration of metal due to the association of ammoniated electrons. Colour also changes to copper bronze due to the formation of metal ion clusters.

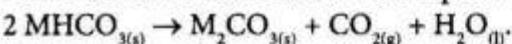


Nature of carbonates and bicarbonate: Except Li_2O , all other alkali metal carbonates are stable.



$LiHCO_3$ does not exist in the solid state, whereas other bicarbonates exist in solid state.

Bicarbonates of alkali metals decompose easily on heating as follows:



Solubility of carbonates and bicarbonates increases down the group.

Nature of Nitrates: Except $LiNO_3$, alkali metal nitrates decompose to give nitrite and oxygen.



Nature of sulphate: Except Li_2SO_4 , all alkali metal sulphates are soluble in water.

Diagnol relationship between Li and Mg: Due to the same charge-to-size ratio and hence same polarizing power lithium resembles magnesium. These both decompose water only on heating. Both react with oxygen to give monoxide. Hydroxides and carbonates of both decompose on heating. Both react with nitrogen to form nitrides.

Carbonates, oxalates, phosphates and fluorides of lithium and magnesium are sparingly soluble in water. Nitrates of both on heating give NO_2 and O_2 .

Anomalous behaviour of lithium: Lithium forms only Li_2O .

Lithium combines with nitrogen to form nitride.

Lithium hydride is stable.

LiOH and Li_2CO_3 are thermally unstable.

LiNO_3 decomposes to give NO_2 and O_2 .

Li cannot be stored in kerosene oil as it floats in oil due to its low density.

Li_2SO_4 does not form alum because it is too small to have coordination number six.

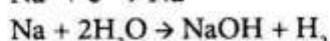
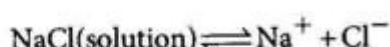
Key Points

- Fire caused due to alkali metals is extinguished by CCl_4 .
- 28 per cent solution of NaCl is known as brine.
- Mixture of Na_2O_2 and dil. HCl is called oxane.
- Sodium sesqui carbonate is $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$.
- Common salt fused with little Na_2CO_3 , 5 to 10 per cent Na_2SO_4 and a little sugar is called kala namak.
- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ – Glauber's salt
- NaNO_3 – Chile salt petre
- KNO_3 – Indian salt petre

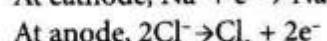
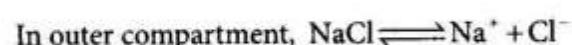
15.3 PREPARATION OF NaOH

It is prepared by the electrolysis of brine by 1. Nelson cell and 2. Castner-Kellner cell

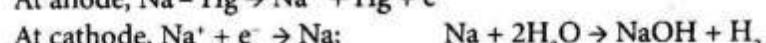
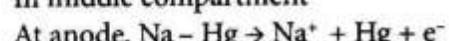
15.3.1 Nelson Process



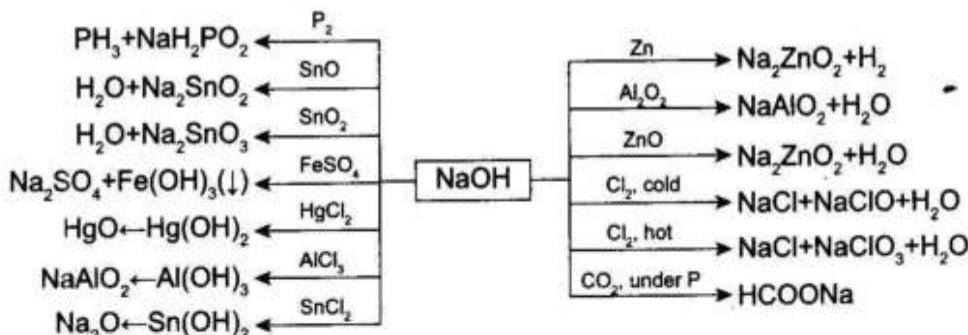
15.3.2 Castener-Kellner Process



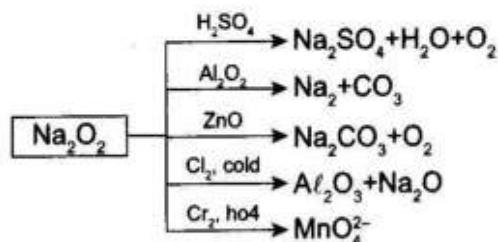
In middle compartment



Properties of NaOH

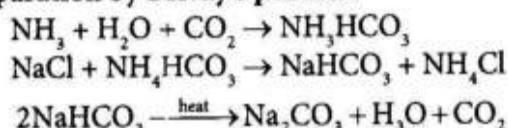


Properties of sodium peroxide



15.3.3 Preparation of Sodium Carbonate

Preparation by Solvay's process:



Properties of Na_2CO_3 ,

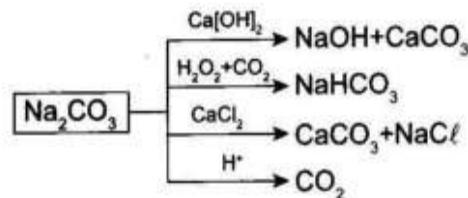
$\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ is a fusion mixture.

NaHCO_3 is used as an antacid (Eno), in baking powder, in fire extinguishers and in effervescent drinks.

Preparation of potassium carbonate, K_2CO_3 , (potash or pearl ash)

It is not prepared by Solvay process as KHCO_3 is more soluble in water than NaHCO_3 , therefore it is prepared by Le Blanc process.

K_2CO_3 is a colourless and deliquescent powder used in making soft soap.



15.3.4 Preparation of Alkali Metals

Since alkali metals are the strongest reducing agents, they cannot be prepared by chemical reduction of their oxides.

These cannot be extracted by the electrolysis of their aqueous solution because the metal extrated at once reacts with water. So, alkali metals are prepared by the electrolysis of the fused halides and impurities are added to lower the melting point. During the manufacture of lithium, electrolyte used is 55 per cent LiCl and 45 per cent KCl . During the manufacture of sodium, electrolyte used is 40 per cent NaCl and 60 per cent CaCl_2 . Potassium is obtained by the electrolysis of fused KOH .

15.4 ALKALINE EARTH METALS

They are Be, Mg, Ca, Sr, Ba and Ra (Ra is radioactive). Their electronic configuration is ns^2 .

Ionization enthalpy: For alkaline earth metals, it is more than group IB and group 1 elements because the electron is being removed from fully filled ns orbital: Second ionization energy of group

II elements is less than group I elements because in alkali metals second electron is being removed from the fully filled inner energy level. They are less electropositive than alkali metals due to higher ionization energy.

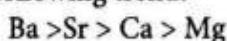
Reducing property: These are weaker reducing agents than alkali metals due to higher ionization enthalpy.

Flame colouration: Be and Mg do not impart colour to flame due to higher ionization enthalpy.

Ca	Sr	Ba	Ra
Brick red	Crimson red	Grassy green	Crimson red

15.4.1 Chemical Properties

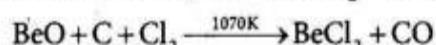
Reaction with water: They react with water to produce hydrogen gas. Their reactivity with water follows the following trend:



Reaction with oxygen: Be, Mg and Ca have a tendency to form Ba and Sr forms peroxide.

Reaction with hydrogen: Hydrides of alkaline earth metal: $\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$, BeH_2 and MgH_2 are covalent and polymeric hydrides are good reducing agents. Stability and solubility of hydrides increase down the group.

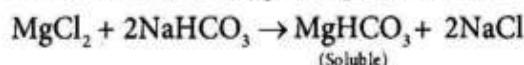
Reaction with halogen: $\text{M} + \text{X}_2 \rightarrow \text{MX}_2$



BeCl_2 exists as a polymer in solid state. BeF_2 is soluble in water, whereas fluorides of other alkaline earth metals are insoluble, Chlorides, bromides and iodides of Mg, Ca, Sr and Ba are ionic, and have lower melting point than the fluorides.

Solubility decreases in the order of $\text{MgX}_2, \text{CaX}_2 > \text{SrX}_2 > \text{BaX}_2$.

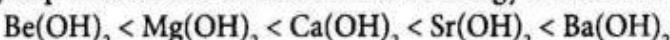
All the halides are hygroscopic in nature.



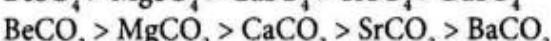
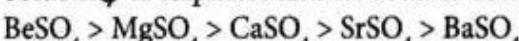
15.4.2 Nature of Hydroxides

$\text{Be}(\text{OH})_2$ is amphoteric. Basic character of hydroxides increases from Be to Ba.

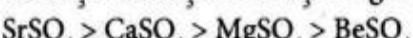
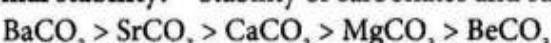
Solubility of alkaline earth metal compounds: For hydroxides of these compounds it increases down the group because the decrease in lattice energy is more than the decrease in hydration energy.



Solubility of sulphates and carbonates decreases down the group.



Thermal stability: Stability of carbonates and sulphates increases down the group.



15.4.3 Diagonal Relationship Between Be and Al

1. Both become passive on treatment with concentrated nitric acid due to the formation of protective oxide film.
2. Both dissolve in conc. NaOH to form beryllate and aluminate.
 $\text{Be} + 2\text{NaOH} \rightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2$; $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_3 + 3\text{H}_2$
3. Oxides of both are amphoteric.
4. Carbides of both react with water to give methane.
 $\text{Be}_2\text{C} + 4\text{H}_2\text{O} \rightarrow 2\text{Be(OH)}_2 + \text{CH}_4$; $\text{Al}_4\text{C}_3 + 2\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4$
5. Anhydrous halide of both are Lewis acids.
6. Both form complexes, e.g., BeF_4^{2-} , AlF_6^{2-} .

15.4.4 Anomalous Behaviour of Be

1. Be is hard but other alkaline earth metals are soft.
2. Be forms covalent compounds; however, others generally form ionic compound.
3. BeO is amphoteric while other oxides are basic in nature.
4. The m.pt., b.pt and ionization energy of Be is maximum amongst alkaline earth metals.
5. Be has bridged polymeric structure.
6. Be does not liberate hydrogen gas from acids while other metals liberate.

Key Points

- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salt) is used as purgative.
- $\text{K}_2\text{SO}_4 \cdot \text{MgSO} \cdot 6\text{H}_2\text{O}$ is sold as potash magnesia, a fertilizer.
- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is called gypsum.
- $\text{CaSO} \cdot 1/2\text{H}_2\text{O}$ is plaster of paris.
- $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, called alabaster, is used to make ornaments
- Anhydrous CaCl_2 is used as a desiccating agent.
- Fire caused due to alkali and alkaline earth metals is extinguished by asbestos.
- $\text{MgCl}_2 \cdot 5\text{MgO}, \text{XH}_2\text{O}$ is called Sorell's cement which is used in dentistry.
- Hardening of plaster of paris is due to the transition of orthorhombic form of gypsum to monoclinic form.
- Mg has the lowest melting point and calcium has the lowest density amongst alkaline earth metals.
- Most of the kidney stones are made up of calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.
- Aqueous solution of Ba(OH)_2 is known as baryata water.

P-BLOCK ELEMENTS

16.1 GROUP 13 (BORON FAMILY)

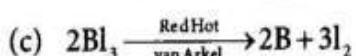
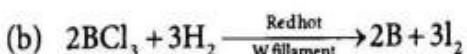
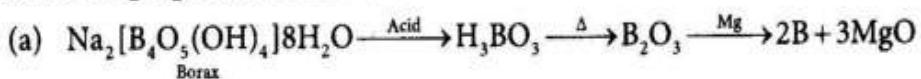
General electronic configuration of this group is $ns^2 np^1$ and except B all are metals; B exist in crystalline and amorphous forms with icosahedral geometry with B at all 12 corners. Properties of Al are different from Ga, In and Tl due to intervening transition metals.

Ionization energy: Decreases down the group but ionization energy of Ga is more than Tl due to intervening $(n - 1)d$ orbitals and that of Tl is more than In, due to poor shielding effect of $(n - 2)f$ orbital. First ionization energy is in the order:

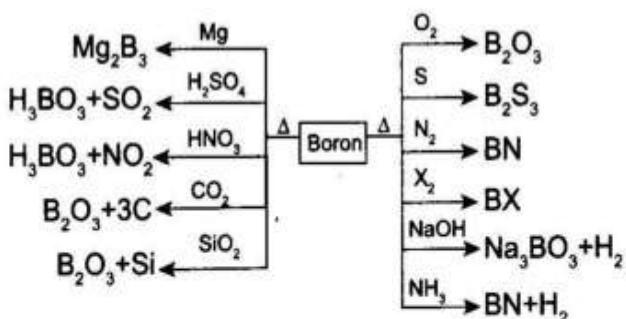


Oxidation state: All the element exhibit +3 oxidation state. On moving down the group, +1 oxidation state becomes dominant due to inert pair effect. Inert pair effect increases after In. Tl (III) is a strong oxidizing agent > 4 and increases with the increasing value of n. Reducing character of the elements increases as we move down the group.

Method of preparation of boron



Chemical properties of boron



Hydroxide: Al and Ga hydroxides are amphoteric, hydroxide of In is more basic than Ga. Tl reacts with steam and form TlOH.

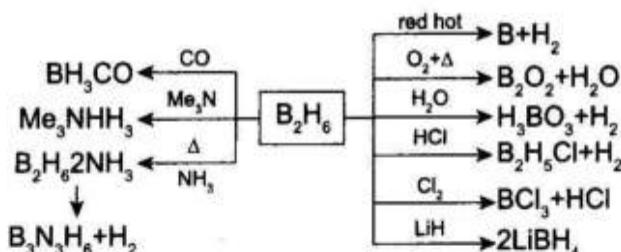
Halides: Boron halides are monomeric and make up the deficiency either by back bonding (in halides) or by dimerization (in hydrides). The shortening of B-X bond, and also their lewis acidic character is because of back bonding. Inability of heavier elements to form multiple bond is due to large size of the central atom, less effective overlapping of more diffused np orbitals and repulsion of inner filled orbitals. Lewis acidic character of boron halides is in the order $\text{Bl}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$.

Hydrides: Hydrides of boron are known as boranes ($\text{B}-\text{sp}^3$ hybridized) which are electron deficient, catch fire in air and get hydrolyzed by water.

Method of preparation of B_2H_6

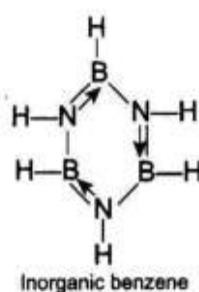
- $4\text{BCl}_3 + 3\text{LiAlH}_4 \rightarrow 2\text{B}_2\text{H}_6 + 3\text{LiCl} + 3\text{AlCl}_3$
- $2\text{BCl}_3 + 6\text{H}_2 \xrightarrow[\text{discharge}]{\text{Slent electric}} \text{B}_2\text{H}_6 + 6\text{HCl}$
- $8\text{BF}_3 + 6\text{LiH} \rightarrow \text{B}_2\text{H}_6 + 3\text{LiBF}_4$

Chemical properties of B_2H_6

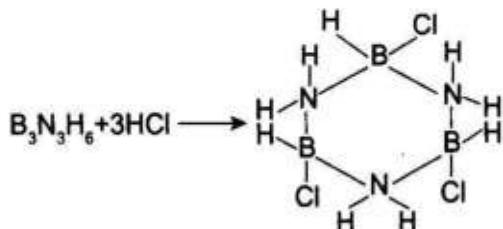


Maximum covalency of boron is four but for other elements is six. Boron shows diagonal relationship with silicon. Boron halides undergo hydrolysis and give orthoboric acid.

Important compounds of boron: Borazole also called inorganic benzene is isosteric with benzene. Borazole on heating at 3000°C and 10,000 atm pressure produces BN also called inorganic graphite and is as hard as diamond. It is chemically inert and do not react with mineral acids.



Borazole reacts with HCl to produce an addition product as follows:

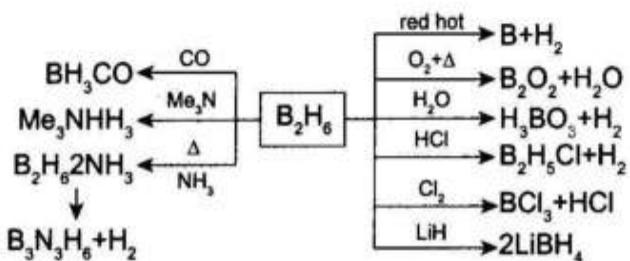


Aluminium: Al, the third most abundant element in earth's crust, occurs as complex aluminosilicates (clay, feldspar).

Ores of aluminium are bauxite and cryolite. If bauxite contains silica as the major impurity it is known as white bauxite and if it contains red oxide as an impurity it is known as red bauxite. Aluminium is soft, light and weak when pure but become hard, strong and resistant to corrosion.

Extraction of aluminium: Bayer's process [Alumina + caustic alkali] and Hall's process [Alumina + Na_2CO_3] are used for the purification of red bauxite and Serpeck's process [Alumina + N_2 + C] is used for the purification of white bauxite. Pure bauxite is mixed with cryolite (to increase conductivity) and fluorspar (to lower the melting point) and subjected to electrolysis by Hall and Heroult process to obtain aluminium. Aluminium is purified by Hoop's process.

Chemical properties of aluminium



Key Points

- Alloy duralumin [Al, Cu, Mg, Mn] is used in the construction of aeroplanes, cable rivets, etc.
- Aluminium bronze [Al, Sn, Cu] is used in making utensile, coins, statues, etc.
- Alnico [Al, Ni, Co, Fe] is used in making permanent magnets.
- Magnalium [Al, Mg] is used for making balances and machine parts.
- **Nickeloy:** Al + Cu + Ni.
- Alcold [duralumin coated with pure Al] is used in making sea planes.
- Y alloy contains Al + Cu + Ni + Mg.
- Due to the corrosion resistant and non-toxic nature aluminium foil is used for wrapping in food industry. Mixed with linseed oil, aluminium powder is used in silver paints and lacquers.
- Due to its low SRP (-1.66 V) it should reduce water but due to the presence of a protective layer of Al_2O_3 on its surface it cannot. Aqueous salts of aluminium are acidic due to cationic hydrolysis.

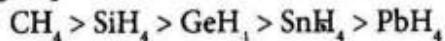
Alums: Double salt of aluminium and monovalent metals like sodium and potassium with $24\text{H}_2\text{O}$ are known as alums $[\text{M}_2^{\text{I}}\text{SO}_4\text{M}^{\text{III}}(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$. Alums acts as coagulants, germicides, antiseptic and mordants.

16.2 GROUP 14 (CARBON FAMILY)

C, Si, Ge, Sn and Pb have electronic configuration as $ns^2 np^3$ and show +2 and +4 oxidation states. Tendency to show +2 oxidation state increases down the group due to inert pair effect. Except lead, all other element of this group show allotropy.

All elements, except carbon, can expand their octet due to the presence of vacant d-orbitals. Silicon, due to its large size, is unable to form $p\pi-p\pi$ bond and therefore does not exhibit graphite like structure.

Hydrides: Stability of hydrides decreases down the group and reducing power of hydrides increase down the group.



16.2.1 Oxides

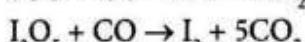
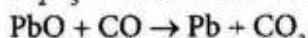
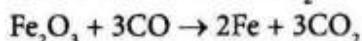
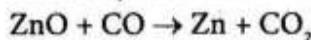
1. Carbon monoxide: Neutral, colourless, odourless and poisonous gas.

Method of preparation:

- $\text{HCOOH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CO} + \text{H}_2\text{O}$
- $\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$
- $\text{ZnO} + \text{C} \xrightarrow{\Delta} \text{Zn} + \text{CO}$

Properties:

CO forms carboxy haemoglobin with blood which is fatal. CO due to the presence of a lone pair of electrons on carbon as well as oxygen form metal carbonyls with transition elements in which carbon is directly attached to the metal. It is a good reducing agent.

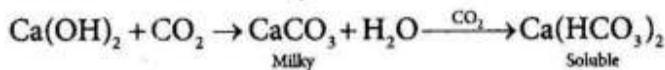


2. Carbon dioxide: It is an acidic oxide, colourless and odourless gas. Acidic nature of dioxides $\text{CO}_2 > \text{SiO}_2 > \text{GeO}_2 > \text{SnO}_2 > \text{PbO}_2$

Method of preparation:

- $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$
- $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$
- $2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$

It turns lime water milky.



3. Silica: It is an acidic oxide. It is widely found as sand and quartz. The main forms of SiO_2 are quartz, tridymite and crystobalite. Coloured quartz are used as gems. Amethyst (violet), rose quartz (pink), etc.

Application of silica:

- Flint, opal, agate, onyx and jasper are amorphous silica.
- Kieselguhr is a siliceous rock composed of remains of minute sea organisms.
- SiO_2 is soluble in $\text{HFSiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 \xrightarrow{2\text{HF}} \text{H}_2\text{SiF}_6$
- Silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate and is used as a drying agent.
- Amongst dioxides, only CO_2 is a gas, and PbO_2 is a strong oxidizing agent due to the greater stability of +2 oxidation state.

4. Carborundum (SiC): Carborundum or artificial diamond $\text{SiO}_2 + 3\text{C} \xrightarrow{\Delta} \text{SiC} + 2\text{CO}$

Very hard (Diamond > $\text{B}_4\text{C} > \text{SiC}$). Chemically inert.

Soluble in alkali in presence of oxygen $\text{SiC} + \text{O}_2 + 4\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$.

It is used as an abrasive.

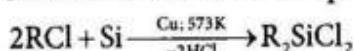
- 5. Halides:** Form tetrahalides, except carbon, others form dihalide also. PbBr_4 and PbI_4 does not exist due to strong oxidizing power of Pb^{4+} and strong reducing power of Br^- and I^- .

Stability of dihalides increases down the group. Thermal stability of halides is in the order $(\text{CX}_4 > \text{SiX}_4 > \text{GeX}_4 > \text{SnX}_4 > \text{PbX}_4)$.

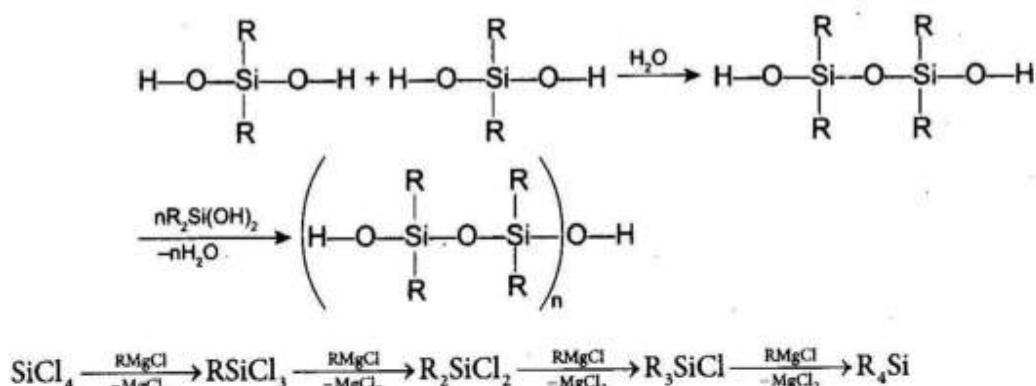
For the common central atom the thermal stability and volatility of tetrahalides is in the order $\text{MF}_4 > \text{MCl}_4 > \text{MBr}_4 > \text{MI}_4$.

Except carbon halides the other tetrahalides act as strong Lewis acids.

Silicones are Si-O-Si compounds, formed by the hydrolysis of alkyl substituted chlorosilanes.



$\text{R}_2\text{SiCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{R}_2\text{Si}(\text{OH})_2$ (dialkylsilanol) which polymerizes to give linear thermoplastic silicon.



- 6. Tin and lead:** Tin occurs as cassiterite (SnO_2) from which tin is obtained by carbon reduction and tin is purified by zone refining.

Lead occurs as galena (PbS), which is concentrated by froath floatation process, roasted and then the oxide is reduced by coke to give lead.

Pewter [$\text{Pb} = 80$ per cent, $\text{Sn} = 20$ per cent] Solder [Pb 50 per cent; Sn 50 per cent]; Type metal [Pb , Sb , Sn] Stannous chloride which is prepared by boiling tin with conc. HCl in a mild reducing agent and reducing $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$; $\text{Hg}(\text{II})$ to $\text{Hg}(\text{I})$ and finally to Hg , $\text{Mn}(\text{VI})$ to $\text{Mn}(\text{VI})$; $\text{Cr}(\text{VI})$ to $\text{Cr}(\text{II})$. Lead oxide (PbO , litharge) is yellow when cold and orange when hot.

Pb_3O_4 , red lead, decomposes to PbO and PbO_2 on heating.

Except nitrate and acetate Pb^{2+} salts are insoluble in water.

Lead is used in making vessels for radioactive materials and for making cathode (PbO_2) in lead storage batteries. Since Pb_3O_4 is a strong oxidizing agent, it is used to give a coating on steel before painting.

Tetraethyllead is used as antiknock in petrol but its use has been restricted due to its toxicity as it inhibits the action of certain enzymes.

- PbSO_4 is soluble in acetic acid due to the formation of stable acetate complexion.

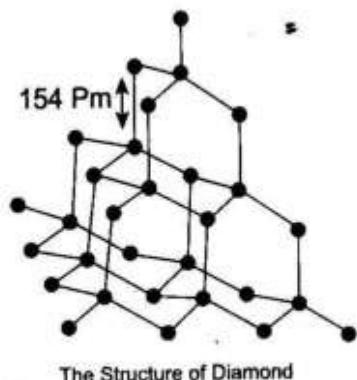
16.3 ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as fullerenes was discovered by H W Kroto, E Smalley and R F Curl.

16.4 DIAMOND

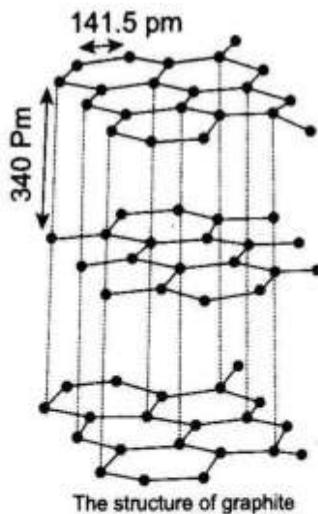
It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridization and linked to four other carbon atoms by using hybridized orbitals in tetrahedral fashion. The C – C bond length is 154 pm. The structure extends in space and produces a rigid 3D network of carbon atoms. In this structure, directional covalent bonds are present throughout the lattice.

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.



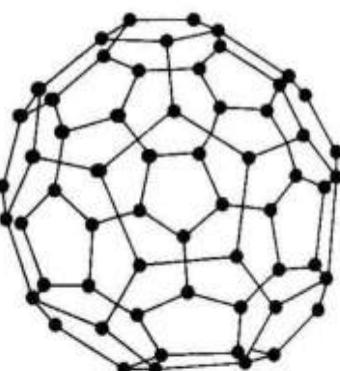
16.5 GRAPHITE

Graphite has a layered structure. Layers are held by van der waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridization and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π -bond. The electrons are delocalized over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.



16.5.1 Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourized C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling bonds. Fullerenes are cage-like molecules. C_{60} molecule has a shape like a soccer ball and is called Buckminsterfullerene.



It contains twenty six-membered rings and twelve five-membered rings. A six-membered ring is fused with six or five-membered rings but a five-membered ring can only fuse with six-membered rings. All the carbon atoms are equal and they undergo sp^2 hybridization. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electrons at each carbon is delocalized in molecular orbitals, which in turn give aromatic character to molecule. This ball-shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short.

The structure of C_{60} . Buckminster fullerene: Note that the molecule has the shape of a soccer ball (football).

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^\circ$ of graphite is taken as zero. $\Delta_f H^\circ$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1} , respectively.

16.6 ZEOLITES

If aluminium atoms replace few silicon atoms in 3D network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+ , K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites. Zeolites, are widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization, e.g., ZSM-5 (a type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of 'hard' water.

16.7 SILICATES

Silicate minerals together with silica and aluminosilicate clay make 95 per cent of the Earth's crust. They contain different modes of combination of $(\text{SiO}_4)^{4-}$ tetrahedral units. The Si–O bond is 50 per cent ionic and 50 per cent covalent.

The radius of Si^{4-} (0.4 \AA) and O^{2-} (1.4 \AA) makes the radius ratio 0.29 with coordination number 4 around Si.

The $(\text{SO}_4)^{4-}$ tetrahedral units may be single or share 1, 2, 3 or 4 O-atoms through corners only giving rise to various types

16.7.1 Type of Silicates

- Orthosilicates:** (Neso-silicates). No O-atoms are shared

Contain discrete SiO_4^{4-} units with the general formula, $M_2\text{SiO}_4$.

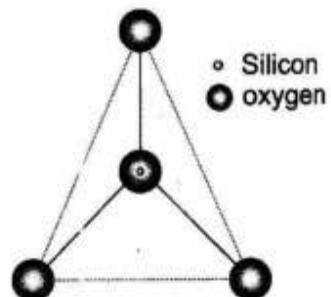
e.g., Zircon = $Z\text{SiO}_4$

Olivine = $(\text{Mg}, \text{Fe})_2 \cdot [\text{SiO}_4]$

Fenacite = Be_2SiO_4

Forsterite = Mg_2SiO_4

Williemite = Zn_2SiO_4



- Pyrosilicates (Soro-silicates)**

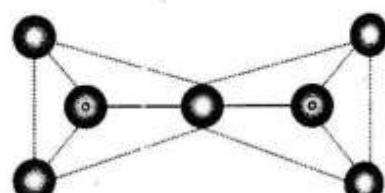
One O-atom is shared at one corner.

Contains discrete $(\text{Si}_2\text{O}_7)^{6-}$ unit.

e.g., Thortveitite: $\text{Sc}_2\text{Si}_2\text{O}_7$

Hemimorphite: $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$

Pyrosilicates are rare.



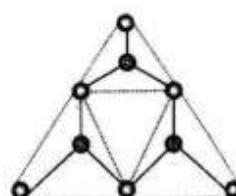
- Ring (cyclic) silicates:**

Two O-atoms are shared per tetrahedron

and contain $(\text{SiO}_3)_n^{2n-}$ units

e.g., Benitoite: $\text{BaTiSi}_3\text{O}_9$

Beryl: $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$



4. Chain silicates:

(a) Single chain (pyroxenes)

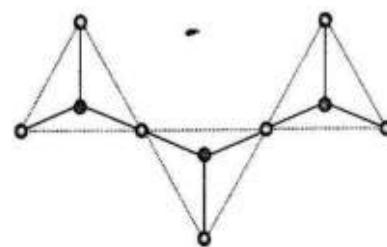
Two O-atoms are shared per tetrahedron and contain $(\text{SiO}_3)_n^{2-}$ units.

E.g., Spodumene: $\text{LiAl}(\text{SiO}_3)_2$

Diopsite: $\text{CaMg}(\text{SiO}_3)_2$

Enstatite: $\text{Mg}_2(\text{SiO}_3)_2$

Wollastonite: $\text{Ca}_3(\text{SiO}_3)_3$



(b) Double chains (amphiboles)

Contain $(\text{Si}_4\text{O}_{11})_n^{6n-}$ units, asbestos minerals. Some tetrahedrons share two and some share three corners $\left(2\frac{1}{2}\text{O-atoms}\right)$.

E.g., Tremolite: $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$

Crocidolite: $\text{Na}_2\text{Fe}^{\text{II}}_3\text{Fe}^{\text{III}}_2(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$

5. Sheet silicates (phyllo-silicates)

Three O-atoms are shared at three corners of the tetrahedron. Contains $(\text{Si}_2\text{O}_5)_n^{2n-}$.

e.g., Muscovite: $\text{KAl}_2(\text{OH})_2\text{AlSi}_3\text{O}_{10}$ Mica

Talc: $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$

Kaolin: $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$ Clay

6. 3D silicates

Four O-atoms are shared from all corners of SiO_4 tetrahedron resulting in 3D lattice of formula SiO_2

e.g., Quartz: $(\text{SiO}_2)_n$

Due to replacement of Si atoms it forms

(a) Orthoclase feldspar: KAlSi_3O_8

(b) Zeolite: $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \times \text{H}_2\text{O}$

(c) Ultramarine: $\text{Na}_8[(\text{AlSiO}_4)_6]\text{S}_2$

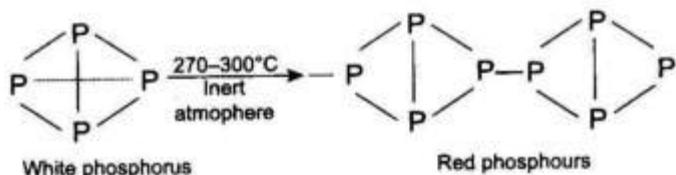
16.8 GROUP 15 ELEMENTS (NITROGEN FAMILY)

- The group 15 elements are collectively called as pnictogens.
- General outer electronic configuration: $\text{ns}^2 \text{np}^3$ (where, n = 2 to 6)

Element	Electronic configuration	Oxidation number
Nitrogen (N)	$[\text{He}]2\text{s}^2 2\text{p}^3$	-3, -2, -1, +1, +2, +3, +4, +5
Phosphorus (P)	$[\text{Ne}]3\text{s}^2 3\text{p}^3$	-3, +3, +4, +5
Arsenic (As)	$[\text{Ar}]3\text{d}^{10} 4\text{s}^2 4\text{p}^3$	-3, +3, +5
Antimony (Sb)	$[\text{Kr}]4\text{d}^{10} 5\text{s}^2 5\text{p}^3$	-3, +3, +5
Bismuth (Bi)	$[\text{Xe}]4\text{f}^1 5\text{d}^{10} 6\text{s}^2 6\text{p}^3$	+3, +5

- Non-metals: N, P Metalloids: As, Sb Metal Bi
- Allotropy: All elements of group 15 (except N and Bi) show allotropy.
- Atomic radii and density order N < P < As < Sb < Bi.

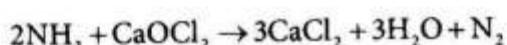
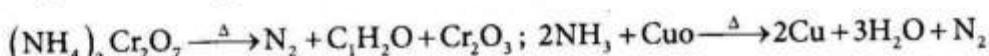
- I E and E N order $N > P > As > Sb > Bi$
- $N_2(N\equiv N)$ is diatomic, white P, As, Sb are tetraatomic (P_4 , As_4 , Sb_4) and tetrahedral with a bond angle of 60° .



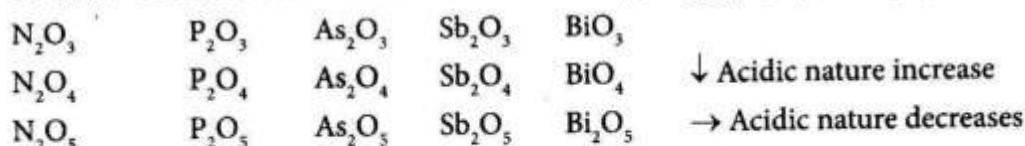
White phosphorus	Red phosphorus	Black phosphorus
Soft, whitish yellow, waxy solid	Red powdery, microcrystalline solid	Black solid
Spontaneously inflames in air above $50^\circ C$ to give P_4O_{10} and P_4O_6 in limited supply of O_2	Only ignites at temperature greater than $260^\circ C$	Does not ignite even above $400^\circ C$
Combines violently with all halogens	Combines slowly with halogens	Kinetically inert/stable
Volatile, highly reactive	Non-volatile, less reactive	Non-volatile, chemically inert
Structure consists of discrete P_4 tetrahedra	Structure consist of chain/sheets	Structure is sheet-like similar to graphite
Poisonous, insoluble in H_2O	Non-poisonous, insoluble in H_2O but soluble in CS_2	Non-poisonous, insoluble in both H_2O and CS_2

- Black phosphorus is of two types: α -block and β -block. α -block phosphorus do not conduct electricity, where, as β -block phosphorus can conduct electricity.

Preparation of N_2 : $NH_4Cl + NaNO_3 \rightarrow N_2 + 2H_2O + NaCl$



- Oxides:** All these elements form oxides of the type X_2O_3 , X_2O_4 and X_2O_5 .



As the electronegativity increases, acidic character of the oxide also increases. Among the oxides of the same element, higher the oxidation state, greater the acidic character.

- Nitrogen—does not form pentahalide due to inability to expand octet and Bi does not form pentahalide due to inert pair effect.
- Holme's signals:** The spontaneous combustion of phosphine is used in Holme's signals. Containers containing CaC_2 and Ca_3P_2 are pierced and thrown into the sea where on reaction with H_2O , PH_3 and C_2H_2 is produced along with traces of P_2H_4 which are highly inflammable. This ignites acetylene which burns with a luminous flame.

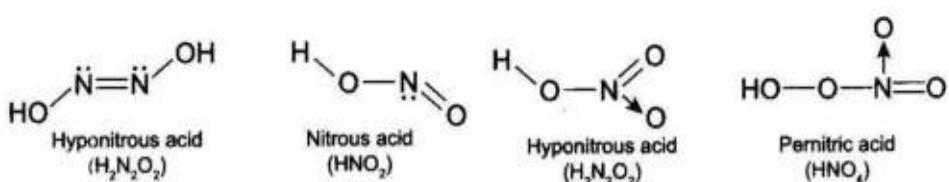
- Oxo acids of phosphorus:

Oxoacid	Structure	Basicity	Preparation
Phosphinic acid (hypo phosphorus acid), H_3PO_2		1	White P_4 + alkali
Phosphonic acid (ortho phosphorus acid or phosphorous acid), H_3PO_3		2	$\text{P}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_3$ $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
Orthophosphoric acid H_3PO_4		3	$\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$
Meta phosphoric acid (glacial phosphoric acid), $(\text{HPO}_3)_n$		1	$3\text{H}_3\text{PO}_3 + 3\text{Br}_2 \xrightarrow[\text{Solid tube}]{\Delta} (\text{HPO}_3)_3 + 6\text{HBr}$
Pyrophosphorous acid (diphosphorus acid), $\text{H}_4\text{P}_2\text{O}_5$		2	$\text{PCl}_3 + 5\text{H}_3\text{PO}_3 \rightarrow 3\text{H}_4\text{P}_2\text{O}_5 + 3\text{HCl}$
Pyrophosphoric acid (diphosphoric acid), $\text{H}_4\text{P}_2\text{O}_7$		4	$2\text{H}_3\text{PO}_4 \xrightarrow{250^\circ\text{C}} \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$
Hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$		4	$2\text{P(red)} + 4\text{NaOCl} + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{P}_2\text{O}_6 + 4\text{NaCl}$

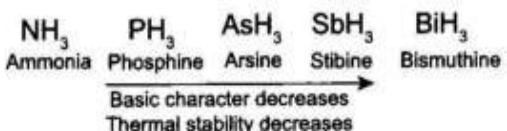
States decrease gradually with decrease in electronegativity of the central atom.



- Oxoacids of nitrogen



- Hydrides:** MH_3 type hydrides



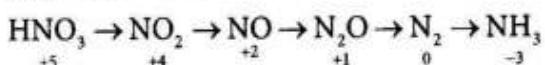
- As the size increases, the electron density gets diffused over a larger region (due to bigger size) and hence the ability to donate the electron pair (basic nature) decreases.

16.8.1 Important compounds of nitrogen family

Structure	Preparation	Properties	Uses
NH_3 	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H_f^\circ = -92.4 \text{ kJ/mol}$ (Haber's process)	$[Ag(NH_3)_2]^+$ $NH_3 + O_2 \rightarrow N_2$ $NH_3 + AgCl \rightarrow [Ag(NH_3)_2]^+$ $NH_3 + K_3[Fe(CN)_6] \rightarrow NO$ $NH_3 + H_2O \rightarrow NH_4^+ + NH_4Cl + N_2$ (If NH_3 is in excess) $NH_3 + Hg^{2+} \rightarrow H_2NHgOHgI$ (Brown ppt.)	Used in refrigerators manufacturing of rayon, HNO_3 , $NaHCO_3$, nitrogenous fertilizers
PH_3 	$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$	$NH_3 \cdot PH_3 \rightleftharpoons PH_3 \rightleftharpoons NH_3 + P_4 + H_2$ (at $440^\circ C$) $PH_3 \rightleftharpoons PH_4^+ + Cl^-$ $PH_3 + O_2 \rightarrow H_3PO_4$ $PH_3 + Cu_3P_2 + H_2SO_4 \rightarrow Cu_3P_2 + H_3PO_4 + Ag + H_3PO_3$	Used as dehydrating agent
HNO_3 	$2KNO_3 + H_2SO_4 \rightarrow 2HNO_3 + K_2SO_4$	$H_2SO_4 + NO_2 \rightarrow HNO_3 + SO_2$ $HNO_3 \xrightarrow[-H_2O]{C_{12}H_{22}O_11} (COOH)_2$ $HNO_3 \xrightarrow{HF} H_2SnO_3$ $HNO_3 \xrightarrow{HCl} H_2O + NOCl + [Cl]$	Used as fertilizers, explosives, perfumes and dyes
PCl_5 	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ (White or red)	$PCl_5 \xrightarrow{P_4O_{10}} POCl_3$ $PCl_5 \xrightarrow{H_2O \text{ (in excess)}} H_3PO_4 + HCl$ $PCl_5 \xrightarrow{S} PSCl_3$ $PCl_5 \xrightarrow{Br_2} SOCl_2 + POCl_3$	Used as chlorinating and dehydrating agent

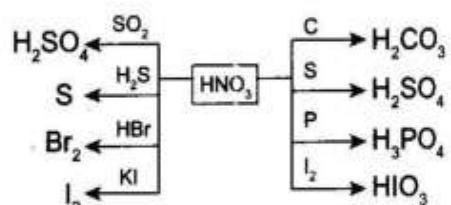
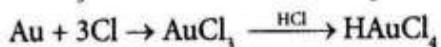
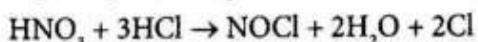
Properties of HNO_3 : HNO_3 is a powerful oxidizing agent; it oxidizes almost all metals, non-metals and many compounds.

It gets reduced as



Greater the change in oxidation state, weaker the oxidizing action of HNO_3 . Non-metals are oxidized to their higher oxyacids and HNO_3 is reduced to NO_2 :

Aqua regia ($HN_3 + 3HCl$):



16.8.1.1 Action of HNO_3 with metal

HNO_3	Metal	Main Product
Very dilute	Mg, Mn →	$H_2 + MNO_3$,
	Fe, Zn, Sn →	$NH_4NO_3 + MNO_3$,
Dilute	Pb, Cu, Ag, Hg →	$NO + MNO_3$,
	Fe, Zn →	$N_2O + MNO_3$,
Concentrated	Sn →	$NH_4NO_3 + Sn(NO_3)_2$
	Zn, Pb, Cu, Ag →	$NO_2 + MNO_3$,
	Sn →	$NO_2 + H_2SnO_3$,
Fe, Ni, Co, Cr, Al →		Passive (inert)

Key Points

- Stability:** $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
- Boiling point:** $PH_3 > AsH_3 > NH_3 > SbH_3 > BiH_3$.
- Bond angle:** $NH_3(107.8^\circ) > PH_3(93.6^\circ) > AsH_3(91.8^\circ) \approx SbH_3(91.3^\circ) > BiH_3(90^\circ)$.
- Basicity:** $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
- Reducing power:** $N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5$.
- Reducing power:** $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$.
- Stability:** $N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$.
- $$\underbrace{N_2O}_{\text{Neutral}} < \underbrace{NO}_{\text{Neutral}} < \underbrace{N_2O_3}_{\text{Acidic}} < \underbrace{N_2O_4}_{\text{Acidic}} < \underbrace{N_2O_5}_{\text{Acidic}} \text{ (acidity)}$$
- Nitrous oxide (N_2O):** Diamagnetic, produces hysteria (laughing gas), used as an anaesthetic.
- Conc. HNO_3 appears yellow due to the presence of dissolved NO_2 formed by the photochemical decomposition of HNO_3 .

16.9 GROUP 16 ELEMENTS (OXYGEN FAMILY)

- They are collectively called chalcogens.
- General outer electronic configuration is ns^2np^4 (where n = 2 to 6).

Element	Electronic configuration	Oxidation number
Oxygen (O)	[He]2s ² 2p ⁴	-2, -1, +1, +2
Sulphur (S)	[Ne]3s ² 3p ⁴	-2, +2, +4, +6
Selenium (Se)	[Ar]3d ¹⁰ 4s ² 4p ⁴	-2, +2, +4, +6
Tellurium (Te)	[Kr]5d ¹⁰ 5s ² 5p ⁴	-2, +2, +4, +6
Polonium (Po)	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	+2, +4, +6

All element of this group except oxygen are diamagnetic. At room temperature, O_2 gas is paramagnetic.

- **Atomicity:**

O	Multiple bonds ($p\pi - p\pi$)	Diatomeric
S, Se, Te	single bonds	Octaatomic
	Multiple bonds ($p\pi - d\pi$)	

Atomic radii and density order: O < S < Se < Te

Ionization energy and electronegativity order: O > S > Se > Te

O_2 (O=O) is diatomic but others are octaatomic (S_8)

- **Catenation:** Sulphur has highest bond strength of S-S bond. Therefore, S > Se > O > Te.

- **Allotropy:** This property is shown by all. Sulphur occurs in a number of allotropic forms such as rhombic (α), monoclinic (β), plastic (γ), colloidal (δ), λ and μ -sulphur. These are all non-metallic in nature.

Sulphur (R) $\xrightleftharpoons{95.6}$ Sulphur (M)

- **Hydrides:** H_2M type (where, M is sp^3 hybridized)

Melting and boiling points: $H_2O > H_2Te > H_2Se > H_2S$

Acidic nature of hydrides: $H_2Te > H_2Se > H_2S > H_2O$

Stability order: $H_2O > H_2S > H_2Se > H_2Te$

Thermal stability: $H_2O < H_2S < H_2Se < H_2Te$

Volatility: $H_2O < H_2Te < H_2Se < H_2S$

Reducing character: $H_2S < H_2Se < H_2Te$

Bond angle and dipole moment: $H_2Te < H_2Se < H_2S < H_2O$

16.9.1.1 Halides

Element	Fluorine	Chlorine	Bromine	Iodine
Oxygen	F_2O	Cl_2O, ClO_2, Cl_2O_7	Br_2O	I_2O_5
Sulphur	$SF_6, S_2F_{10}, SF_4, S_2F_2$	SCl_4, SCl_2, S_2Cl_2	S_2Br_2	-----
Selenium	SeF_6, SeF_4, Se_2Fe_2	$SeCl_4, SeCl_2, Se_2Cl_2$	$SeBr_4, SeBr_2, Se_2Br_2$	-----
Tellurium	TeF_6, Te_2F_{10}, TeF_4	$TeCl_4, TeCl_2$	$TeBr_4, TeBr_2$	TeI_4
Polonium	PoF_6	$PoCl_4, PoCl_2$	$PoBr_4, PoBr_2$	PoI_4

- **Oxides:** The most important oxides are of the MO_2 and MO_3 type.

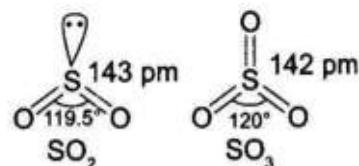
SO_2 and $SeO_2 \rightarrow$ Acidic

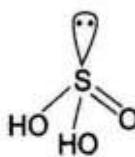
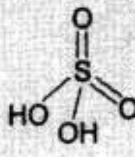
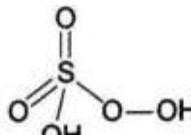
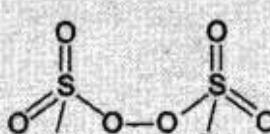
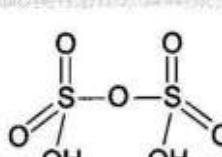
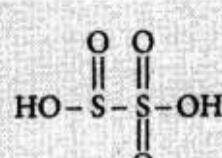
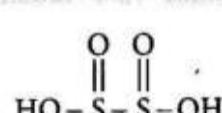
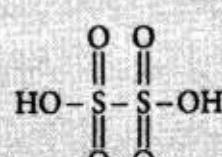
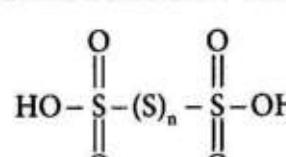
TeO_2 and $PoO_2 \rightarrow$ Amphoteric

- **Acidity:** $SO < SO_2 < SO_3$ (acidity increases with increase in oxidation number).

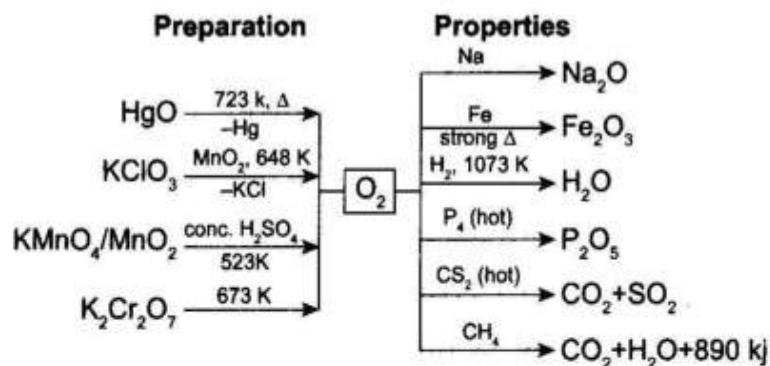
- **Thermal stability:** $SO_2 > TeO_2 > SeO_2 > PoO_2$

- Oxoacids of sulphur

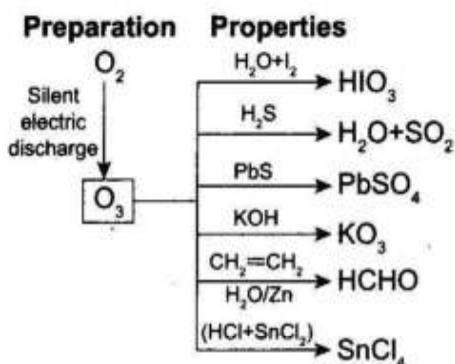


Oxoacid	Oxidation state, basicity and salt type	Structure	Properties
Sulphurous acid (H ₂ SO ₃)	S = +4, dibasic, and forms two series of salts, sulphites (SO ₃ ²⁻) and bisulphites (HSO ₃ ⁻)		Does not exist in free form Acts as reducing as well as oxidizing agents
Sulphuric acid (H ₂ SO ₄) or oil vitriol	S = +6 monobasic and forms two series of salts, sulphates (SO ₄ ²⁻) and bisulphates (HSO ₄ ⁻)		Stable, acts as oxidizing and dehydrating agents
Peroxomonosulphuric acid (H ₂ SO ₅) or Caro's acid	S = +6 monobasic and forms single type of salt, peroxy disulphates (S ₂ O ₈ ²⁻)		Stable crystalline and hygroscopic solid. Powerful oxidizing agent
Peroxodisulphuric acid (H ₂ S ₂ O ₈) or Marshall's acid	S = +6 and forms single type of salt, peroxydisulphates (S ₂ O ₈ ²⁻)		Stable crystalline and hygroscopic solid. Strong oxidizing agent
Pyrosulphuric acid, disulphuric acid (H ₂ S ₂ O ₇) or Oleum	S = +6, dibasic		Acts as a strong dehydrating agent
H ₂ S ₂ O ₅ , Di or pyrosulphurous acid	S(+5), S(+3) dibasic		Corrosive oily, hygroscopic
H ₂ S ₂ O ₄ , Dithionous acid	S(+3), 5(+3) dibasic		Unstable in pure form
H ₂ S ₂ O ₄ , Dithionic acid	S(+5) dibasic		Water soluble mild oxidizing and reducing agents
H ₂ S _n O ₆ , Polythionic acid	S(+5), S(0) dibasic n < 80		Stable in aqueous solutions, interact with strong reducing agents

16.9.1.2 Dioxygen (O_2)



16.9.1.3 Ozone



Oxygen is soluble in alkaline pyrogallol, whereas ozone is soluble in turpentine oil also called oil of cinnamon.

Compound	Oxidation state of O	Compound	Oxidation state of O
In oxides	-2	In dioxygen	0
In peroxides	-1	In oxygen difluoride	+2
In superoxides	-1/2	In oxygen monofluoride	+1

16.10 GROUP 17 ELEMENTS (HALOGEN FAMILY)

- General outer electronic configuration is ns^2np^5 (where n = 2 to 6)

Element	Electronic configuration	Oxidation number
Fluorine (F)	[He]2s ² 2p ⁵	-1
Chlorine (Cl)	[Ne]3s ² 3p ⁵	-1, +1, +3, +5, +7
Bromine (Br)	[Ar]3d ¹⁰ 4s ² 4p ⁵	-1, +1, +3, +5, +7
Iodine (I)	[Kr]4d ¹⁰ 5s ² 5p ⁵	-1, +1, +3, +5, +7
Astatine (At)	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	-----

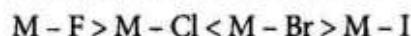
- Atomic radii, ionic radii and density increase from F to I.
- Electro negativity: F > Cl > Br > I
F is the most electronegative element in the periodic table.
- Electron gain enthalpy: Cl > F > Br > I
- Bond energy: Cl₂ > Br₂ > F₂ > I₂.
- Solubility and oxidizing power: F₂ > Cl₂ > Br₂ > I₂.
- Oxidizing nature order is F > Cl > Br > I.
- Reducing nature order is Cl⁻ > Br⁻ > I⁻.
- The solution of iodine (I₂) in water increases with addition of KI or NaI due to the formation of polyamide (triiodide, I₃⁻) ion. $KI_{(aq)} + I_{2(s)} \rightleftharpoons KI_{3(aq)} = K^+_{(aq)} + I_3^{-}_{(aq)}$
- Bond length, melting and boiling point: F₂ > Cl₂ > Br₂ > I₂.
- Heat of hydration: F⁻ > Cl⁻ > Br⁻ > I⁻.

16.10.1 Comparison of Halogens

Property	Fluorine	Chlorine	Bromine	Iodine
Physical state	Gas	Gas	Liquid	Solid
Colour	Pale yellow	Greenish yellow	Reddish brown	Violet
Oxidizing nature	Very strong oxidizing agent	Strong oxidizing agent	Good oxidizing agent	Mild oxidizing agent
Bleaching action	Destroys the reducible coloured substance	Bleaches vegetable colours easily	Mild bleaching agent	-----
Chemical reactivity	Highly reactive	Quite reactive	Less reactive than chlorine	Least reactive
Reaction with (i) Hydrogen	Combines explosively even in the dark	Explosive in light, slow in dark	Only on heating	On heating and in presence of a catalyst
(ii) Water	Decomposes forming HF, O ₂ and O ₃	Forms chlorine hydrate with ice cold water. Decomposes slowly forming HCl and HClO or HCl and O ₂ .	Decomposes slowly in presence of light, forming HBr and HBrO or HBr and O ₂	No action
(iii) Metals	Reacts with all metals to form fluorides	Reacts with almost all metals forming chlorides.	Many metals are acted upon and bromides are formed	Reacts only with few metals to form iodides
(iv) Starch	No reaction on starch	No action on starch	Yellow colour with starch	Blue colour with starch

- Halides:** Halogens combine with all elements except He, Ne and Ar forming a large number of binary halides.

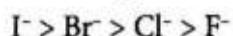
Ionic character of M-X bond and melting point and boiling point



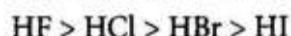
Melting and boiling point of metal halides



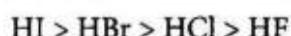
Reducing character



Hydrogen halide: Percentage of ionic character, thermal stability and dipole moments



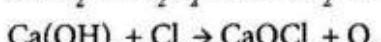
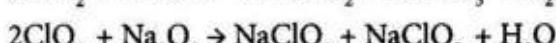
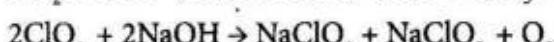
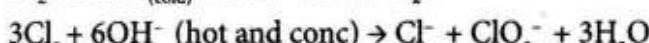
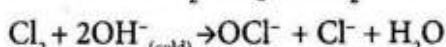
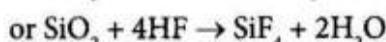
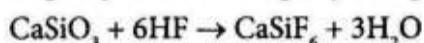
Acidity and bond length



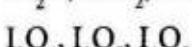
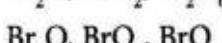
Stability order HF > HCl > HBr > HI

Boiling point order HCl > HBr > HI > HF

- Here, HF is not stored in glass vessels since it reacts with SiO_2 of glasses. It is stored in copper, wax polythene or gutta-percha.
- Here, HF reacts with glass to form sodium and calcium fluorosilicates Na_2SiF_6 and CaSiF_6 . So, it is used for etching of glass (mixture of sodium and calcium silicates).



- Oxides:** OF_2 , O_2F_2



All are covalent and powerful oxidizing agents

- Oxidizing power:** $\text{Cl}_2\text{O} > \text{ClO}_2 > \text{Cl}_2\text{O}_6 > \text{Cl}_2\text{O}_7$

- Stability:** $\text{Cl}_2\text{O} < \text{ClO}_2 < \text{Cl}_2\text{O}_6 < \text{Cl}_2\text{O}_7$.

- Solid Cl_2O_6 is ionic and exists as ClO_2^+ and ClO_4^- ions.

- Oxoacids:** Hypohalous acid: HXO , Halous acid: HXO_2 , Halic acid: HXO_3 , Perhalic acid: HXO_4 .
- Acidity of hypohalous acids:** $\text{HOCl} > \text{HOBr} > \text{HOI}$
Oxygen is more electronegative than halogens. As the electronegativity decreases from Cl to I, electrons density on the oxygen atom increases from Cl to I, therefore tendency to attract electrons of O-H bond decreases from Cl to I, hence acidity decreases.
- Oxidizing power of hypohalous acids:** $\text{HOCl} \approx \text{HOBr} > \text{HOI}$
Oxidising power decreases as the thermal stability of O-H bond increases with increase in the size of X from Cl to I.
- Acidity of perhalic acids:** $\text{HOClO}_4 > \text{HOBrO}_4 > \text{HOIO}_4$
As the electronegativity decreases from Cl to I, tendency to withdraw electrons of O-H bond by XO_3 group decreases and hence the acidity decreases from Cl to I.
- Oxidizing power of perhalates:** $\text{BrO}_4^- > \text{IO}_4^- > \text{ClO}_4^-$
- Acidity of oxoacids with same halogen in different oxidation states:** Acidic strength increases with increase in oxidation state of the halogen atom. $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
This is based on the stability of their conjugate bases. Greater the number of oxygen atoms, greater will be the dispersal of the negative charge through $p\pi-d\pi$ back bonding.
 $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$
- Oxidizing power of oxoacids with same halogen in different oxidation states:**
 $\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$
Oxidizing power decreases, as the stability of their conjugate bases increases.

16.11 INTERHALOGEN COMPOUNDS

Molecules	Hybridization	Shape	Examples
XY	Sp^3	Linear	$\text{ClF}, \text{BrF}, \text{BrCl}, \text{ICl}, \text{IBr}, \text{IF}$ (very unstable)
XY_3	Sp^3d	T-shaped	$\text{ClF}_3, \text{BrF}_3, \text{ICl}_3, \text{IF}_3$
XY_5	Sp^3d^2	Square pyramidal	$\text{ClF}_5, \text{BrF}_5, \text{IF}_5$
XY_7	Sp^3d^3	Pentagonal bipyramidal	IF_7

- Pseudohalogens and pseudohalides:
- Molecules like cyanogens (CN_2), thiocyanogen (SCN_2) and selecyanogen (SeCN_2) have properties similar to those of the halogens. Therefore, these are called pseudohalogens.
- They form anions such as CN^- , OCN^- , etc. which are called as pseudohalides. CN^- resembles Cl^- , Br^- and I^- .
- Polyhalides:** Halide ions often react with molecules of halogens or interhalogen and form polyhalide ions. Iodine is only slightly soluble in water. Its solubility is greatly increased if some iodide ions are present in the solution due to formation of polyhalide ion, I_3^- . $\text{I}^- + \text{I}_2 \rightarrow \text{I}_3^-$
Polyhalides are formed from interhalogens and metal halides: $\text{K}[\text{ICl}_2]$, $\text{K}[\text{ICl}_4]$, $\text{Cs}[\text{IBrF}]$ and $\text{K}[\text{IBrCl}]$.

Key Points

- Because of the tendency to form hydrogen bond, metal fluorides are solvated by HF giving species of the type HF_2^- , etc. KHF_2 ($\text{KF} \cdot \text{HF}$), KH_2F_3 ($\text{KF} \cdot 2\text{HF}$) and KH_3F_4 ($\text{KF} \cdot 3\text{HF}$) are known examples.
- Concentrated H_2SO_4 (a strong oxidizing agent) cannot be used since it would oxidize HBr to Br_2 and HI to I_2 , etc.
- Magnesium perchlorate, $\text{Mg}(\text{ClO}_4)_2$ is used in dry batteries and is also an effective desiccant called anhydronite. KClO_4 is used in fireworks and flares.

16.12 GROUP 18 ELEMENTS (NOBLE GASES)

- General outer electronic configuration is ns^2np^6 (where $n = 2$ to 6)

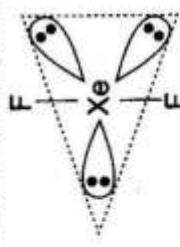
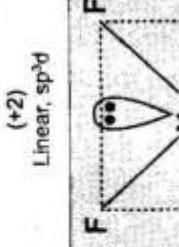
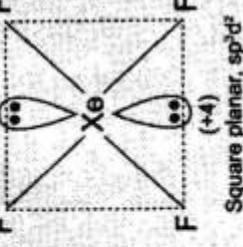
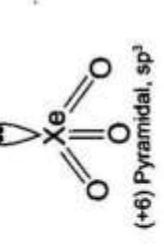
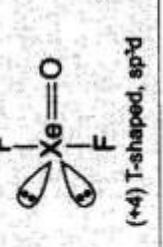
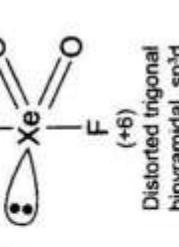
Known as	Reason
Rare gases	Occur in very minute quantities
Noble gases	Obtained under specific conditions
Intert gases	Do not react at ordinary temperature
Zero valent element	Show zero valency

Element	Electronic configuration
Helium (He)	$1s^2$
Neon (Ne)	$1s^2 2s^2 2p^6$
Argon (Ar)	$1s^2 2s^2 2p^6 3s^2 3p^6$
Krypton (Kr)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
Xenon (Xe)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
Radon (Rn)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

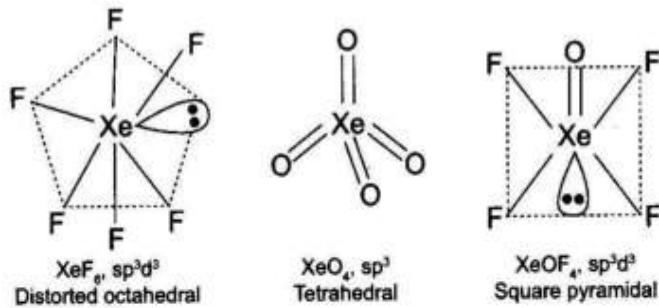
Properties:

- Because of fully filled electronic configuration, they have very high ionization energies.
- They can be liquefied with great difficulty. It is because of the existence of weak Van der Waal's forces in these gases.
- Most abundant noble gas:** Argon
- Melting point, boiling point, polarizability, ease of liquefaction and solubility in water:**
 $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$
- Ionization enthalpy:** $\text{He} > \text{Ne} > \text{Ar} < \text{Kr} > \text{Xe} > \text{Rn}$
- Electron gain enthalpy:** $\text{Ne} > \text{Ar} = \text{Kr} > \text{Xe} > \text{Rn} > \text{He}$
- Noble gases form clathrate compounds except He and Ne. Noble gases compressed with water or quinol gets entrapped between water molecules; such compounds are called clathrates or enclosures.

16.13 COMPOUNDS OF XENON

Compound	Structure	Preparation	Properties
XeF ₂ (Xenon difluoride)	 (2:1)	$\text{Xe} + \text{F}_2 \xrightarrow[400^\circ\text{C}]{\text{Ni tube}} \text{XeF}_2$ $\text{Xe} + \text{F}_2 \xrightarrow[\text{discharge}]{\text{Electric}} \text{XeF}_2$	Acts as fluorinating agent $\text{XeF}_2 + \text{H}_2\text{O} \rightarrow \text{XeOF}_2 + 2\text{HF}$
	 (2:1)	$\text{Xe} + \text{F}_2 \xrightarrow[(\text{Hg vapour})]{\text{h}\nu} \text{XeF}_2$	
XeF ₄ (Xenon tetrafluoride)	 (+2) Linear, sp ³ d	$\text{Xe} + \text{F}_2 \xrightarrow[600^\circ\text{C}]{(0:5)} \text{XeF}_4$ $\text{Xe} + \text{F}_2 \xrightarrow[\text{discharge} -78^\circ\text{C}]{(\text{2:1})} \text{XeF}_4$	Colourless crystalline solid with melting point = 117.1°C $\text{XeF}_4 + 2\text{H}_2 \rightarrow 4\text{Xe} + 4\text{HF}$ Undergoes disproportionation in water $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$ Gives adduct $\text{XeF}_4 + \text{SbF}_5 \rightarrow [\text{XeF}_3] + [\text{SbF}_6]^-$ Acts as oxidizing and fluorinating agent Dissolves in anhydrous HF
XeO ₃ (Xenon trioxide)	 (+6) Pyramidal, sp ³	$\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 2\text{XeO}_3 + 4\text{Xe} + 3\text{O}_2 + 24\text{HF}$ $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$	Complete hydrolysis of XeF ₄ and XeF ₆ With water forms xenic acid $\text{XeO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{XeO}_4$ Undergoes disproportionation when dissolved in alkali $2\text{XeO}_3 + 4\text{OH}^- \rightarrow \text{Xe} + \text{O}_2 + \text{XeO}_6^{4-} + 2\text{H}_2\text{O}$
XeOF ₂ (Xenon oxy- difluoride)	 (+4) T-shaped, sp ³ d	$\text{XeF}_4 + \text{H}_2\text{O} \xrightarrow{-80^\circ\text{C}} \text{XeOF}_2 + 2\text{HF}$	Partial hydrolysis of XeF ₄ Unstable
XeO ₂ F ₂ (Xenon dioxy difluoride)	 (+6) Distorted trigonal bipyramidal, sp ³ d	$\text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_{2\text{F}_2} + 2\text{HF}$ $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_{2\text{F}_2} + 4\text{HF}$ Action of SiO ₂ on XeOF ₄ $2\text{XeOF}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_{2\text{F}_2} + \text{SiF}_4$	Partial hydrolysis of XeOF ₄ or XeF ₆ Colourless solid Undergoes hydrolysis readily $\text{XeO}_{2\text{F}_2} + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}$

Structure of some other important compounds



16.13.1 Uses of Noble Gases

	Uses	Reasons
He	Filling of observation balloons He-O ₂ mixture for deep-sea breathing instead of N ₂ -O ₂ mixture Diluent for gaseous anaesthetics He-O ₂ mixture for respiratory patients Heat transfer medium for nuclear reactions Liquid He to maintain very low temperature in research (cryogenics)	Non flammable; 93 per cent lifting power as compared to flammable H ₂ Low solubility in blood; prevents nitrogen narcosis and 'bends' Non flammable, non-reactive Low density flows easily through restricted passages Transfers heat readily, does not become radioactive, chemically inert Extremely low boiling point
Ne	Neon is used for filling discharge tubes for optical decorations and advertisements. It is used for filling sodium vapour lamps. It is also used in beacon light as safety signal for air navigators	Even at low pressure, moderate electric current causes bright orange-red glow, can be modified by coloured glass or mixing with Ar or Hg vapour
Ar	Argon is used for filling incandescent metal filament of electric bulbs. It is used in advertising signs, for filling radio-values, rectifiers and fluorescent tubes	Inert; prevents vapourization of tungsten and blackening of bulbs
Kr	Airport runway and approach lights	Gives longer life to incandescent lights than Ar but more expensive
Xe	Xe and Kr mixture in high-intensity, short exposure photographic flash tubes	Both have fast response to electric current
Rn	Rn is used in radiotherapy	Its ability to control cell growth

D-AND F-BLOCK ELEMENTS

17.1 D-BLOCK (TRANSITION ELEMENTS)

- Their general outer electronic configuration is $(n - 1) d^{1-10} ns^{0-2}$ (where n is the outermost shell).

Known as	Reason
First transition series (3d-series)	Sc (At. No. 21) to Zn (At. No. 30)
Second transition series (4d-series)	Y (At. No. 39) to Cd (At. No. 48)
Third transition series (5d-series)	La (At. No. 57) to Hf (At. No. 72) to Hg (At. No. 80)
Fourth transition series (6d-series)	Ac (At. No. 89) to Rf (At. No. 104) to Cn (At. No. 112)

17.1.1 Electronic Configuration

The d-orbitals of the transition elements project to the periphery of an atom more than the other orbitals (i.e., s and p), hence they are more influenced by the surroundings as well as affecting the atoms or molecules surrounding them.

These elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands.

In case of transition elements there is greater horizontal similarities in the properties. It is due to the fact that in a transition series there is no change in the number of electrons of outermost shell and only change occurs in the $(n - 1)d$ electrons from member to member in a period.

17.1.2 Physical Properties

Presence of unpaired d-electrons favours covalent bond formation, hence greater the number of unpaired d-electrons, more is the number of covalent bonds resulting in hard metals.

The high melting points of these metals are attributed to the involvement of greater number of electrons from $(n - 1)d$ in addition to the ns electrons in the interatomic metallic bonding. In any row, the melting points of these metals rise to a maximum at d^5 . The maxima at about the middle of each series indicate that one unpaired electron per d-orbital is particularly favourable for strong interatomic interaction.

Cr, Mo and W are very hard metals as they have maximum number of unpaired orbitals while Zn, Cd and Hg are softer in nature as they do not have any unpaired d-orbitals.

All transition elements have higher melting points as compared to s-block elements due to strong metallic bonding as well as unpaired d-electron leading to covalence nature.

17.1.3 Variation in Atomic and Ionic Sizes

In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is due to the fact that effective nuclear charge increases gradually with ineffective shielding created by d-electrons.

When atomic sizes of one series are compared with those of the corresponding elements in the other series, the curves show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called

lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number.

The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii (e.g., Zr 160 pm and Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship. The shielding of one 4f electron by another is less than that of one d-electron by another, and as nuclear charge increases along the series, there is fairly regular decrease in the size of the entire 4fⁿ orbitals.

17.1.4 Density

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in density. In a period on moving from left to right density increases significantly and then, decreases for the last element. However, while moving from top to bottom in a group of d-block density increases. Highest density is observed in case of osmium which is equal to 22.57 g/cm³.

17.1.5 Ionization Energy

Due to an increase in nuclear charge there is an increase in ionization enthalpy along each series of the transition elements from left to right. These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. The magnitude of the increase in the second and third ionization enthalpies for the successive elements, in general is much higher, and removal of one electron alters the relative energies of 4s and 3d orbitals. So, the unipositive ions have dⁿ configurations with no 4s electrons. Due to transfer of electron from 4S to 3d orbital, exchange energy increases which compensate the ionization energy. Smaller the ionization enthalpy of a metal greater will be the thermodynamic stability of its compound.

	$IE_1 + IE_2$ (MJ/mol)	$IE_3 + IE_4$ (MJ/mol)
Ni	2.49	8.8
Pt	2.66	6.7

From these values it is clear that Ni²⁺ compounds are more stable than Pt²⁺ compound but the Pt⁴⁺ compounds are more stable than Ni⁴⁺ compounds.

17.1.6 Standard Electrode Potentials

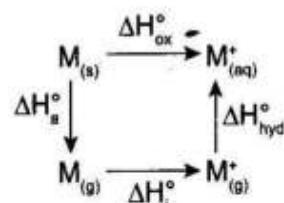
More the negative standard reduction potential of an ion greater will be its stability inside the solution.

Standard reduction potential value depends upon following factors:

- (i) Heat of atomization
- (ii) Ionization energy
- (iii) Heat of hydration

$$\Delta H_{ox}^{\circ} = \Delta H_a^{\circ} + \Delta H_i^{\circ} + \Delta H_{hyd}^{\circ}$$

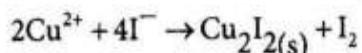
Metals having negative E° values have high enthalpy of atomization, high enthalpy of ionization and low enthalpy of hydration.



17.1.7 Oxidation State

The stability of a particular oxidation state depends upon the nature of the element with which the transition metal forms the compound. The highest oxidation states are found in fluorides and oxides. Since fluorine and oxygen are the most EN elements, their compounds possess highest lattice enthalpy as well as bond strength. Ruthenium in second transition series and osmium in third transition series has +8 oxidation states.

In case of transition elements their oxidation state differ by unity contrary to main group elements where oxidation state differ by two units. In case of p-block element while moving from top to bottom in the group stability of lower oxidation state increases, whereas in case of d-block element on moving from top to bottom in the group stability of higher oxidation state increases. M_n acquired +7 oxidation state in the form oxyfluoride MnO_3F rather than simple halide and beyond manganese no metal has trihalide except FeX_3 and CoF_3 . However, fluorides are unstable in the lower oxidation state and similar result is observed. In case of CuX ($X = Cl, Br, and I$), on the other hand, all cupric halides are unknown except the iodide because Cu^{2+} oxidizes I^- to I_2 .



In aqueous solution, Cu^{2+} is more stable when compared to Cu^+ because of high hydration enthalpy of Cu^{2+} .

17.1.8 Complexes

Tendency to form complexes by transition metals is due to

- their smaller size
- higher nuclear charge
- presence of low energy vacant d-orbitals to accept lone pair of electrons donated by ligands
- Complexes where the metal is in +3 oxidation state are generally more stable than those where the metal is in +2 oxidation state.

17.1.9 Chemical Reactivity and E° values

They differ widely in terms of their chemical reactivity. The metals of first series with the exception of copper are relatively more reactive and oxidized by $1M - H^+$. However, the rate of liberation of H_2 is very

poor because some of these metals get protected due to the formation of an inert oxide film on their surface e.g., Cr inspite of having highly -ve standard red potential values is SQ unreactive that it does not liberate H_2 on account of the formation of coating of Cr_2O_3 on its surface.

This general trend towards less negative E° values is related to the increase in the sum of the first and second ionization enthalpies. It is interesting to note that the E° values for Mn, Ni and Zn are more negative than expected from the general trend. However, the stabilities of half-filled d-subshell (d^0) in Mn^{2+} and completely filled d-subshell (d^{10}) in zinc are related to their E° values; for nickel, E° value is related to the highest negative enthalpy of hydration. Mn^{3+} and Co^{3+} ions are the strongest oxidizing agents in aqueous solutions. The ions Ti^{2+} , V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from a dilute acid.

17.1.10 . Oxides/Hydroxides

Covalent character and acidity of oxides and hydroxides directly depend on oxidation state of transition metal atom present. As the oxidation state increases, their acidity and covalent character also increases.

Element	Basic	Amphoteric	Acidic
V	VO , V_2O_3	VO_2	V_2O_5
Cr	CrO , $Cr(OH)_2$	Cr_2O_3 , $Cr(OH)_3$	CrO_3 , $CrO_2(OH)_2$, $H_2Cr_2O_7$
Mn	MnO	Mn_3O_4 , Mn_2O_3 , MnO	MnO_3 , Mn_2O_7
Fe	FeO , Fe_2O_3 , Fe_3O_4	-----	-----
Co, Ni,	CoO , NiO	-----	-----
Cu, Zn	CuO , ZnO	-----	-----

17.1.11 Colour

They form coloured compounds. 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. The energy required for d-d electron excitations is 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 colour. The colour of light absorbed directly depends upon the nature of ligand present.

17.1.12 Magnetic Properties

Different substances possess mainly two types of magnetic behaviour. Those which are repelled by applied magnetic field are diamagnetic, whereas those which are attracted by applied field are paramagnetic substances. Another kind of substances which are attracted very strongly are called ferromagnetic. Ferromagnetism is the extreme form of paramagnetism. Total magnetism of electrons due to its orbital and spin motion is given by $\mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)}$

S is total spin, i.e., sum of spin quantum number L is the sum of orbital angular momentum quantum number. In many compounds including those of the first row transition elements the orbital contribution is compensated by the electric field of the surrounding atoms and as an approximation the observed magnetic moment may be considered to arise only from unpaired spins. Putting L = 0

$$\mu_s = \sqrt{4S(S+1)} = \sqrt{4 \times \frac{N}{2} \times \left(\frac{N}{2} + 1\right)} = \sqrt{N(N+2)}$$

$$\therefore S = N \times 1/2$$

17.1.13 Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the metallic crystal lattice.

C and N always occupy octahedral holes. Hydrogen is smaller and therefore, always occupy tetrahedral holes. As only transition metals form such compounds, the d-electrons are presumably involved in such bonding. The structure of a metal generally changes during the formation of such compounds.

17.1.14 Catalytic Properties

Compounds of transition metals are able to act as catalysts due to:

- utilisation of $(n - 1)d$ and ns -orbitals
- their ability to adopt different oxidation states
- their ability to form complexes

17.1.15 Alloy formation

Alloy is homogeneous mixture of metals. In alloys, the atoms of one metal are distributed randomly among the atoms of the other. Alloys are formed readily by transition metals because of their similar atomic size. E.g.

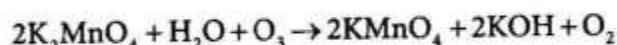
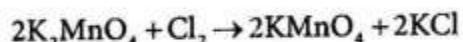
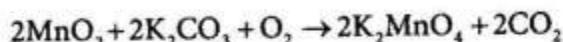
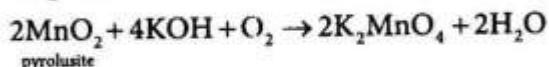
Ferrous alloys: Contains Cr, V, W, Mo and Mn along with Fe

Brass: Cu + Zn

Bronze: Cu + Sn

Potassium permanganate ($KMnO_4$)

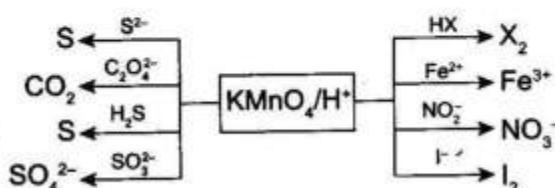
Preparation:



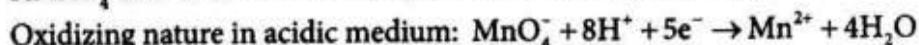
Properties:

It is a purple coloured crystalline substance. It is well soluble in water.

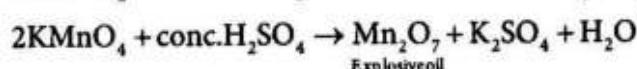
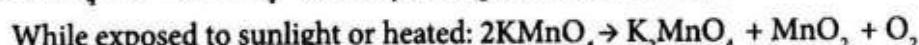
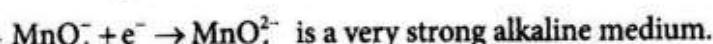
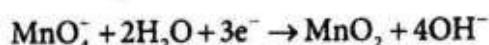
Colour of MnO_4^- is due to charge transfer by oxygen to Mn, because of which Mn changes from +7 to +6 with one unpaired e⁻ in 3d.



KMnO_4 acts as an OA in acidic, neutral and alkaline media.



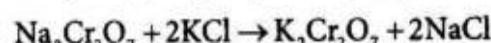
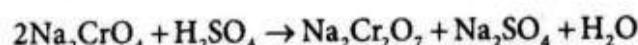
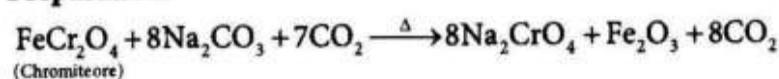
Oxidizing nature in neutral medium:



(KMnO_4 is excess)

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)

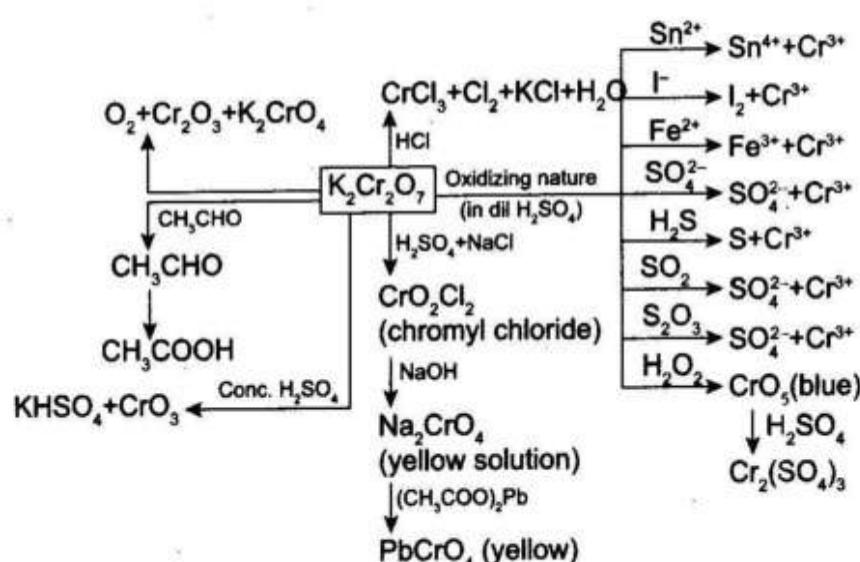
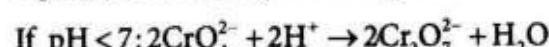
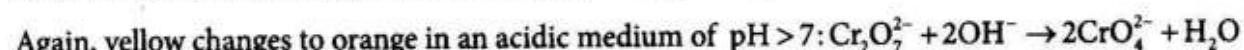
Preparation:



Properties:

Orange red coloured crystalline substance. Moderately soluble in cold water but freely soluble in hot water.

In alkaline solutions, orange colour of $\text{Cr}_2\text{O}_7^{2-}$ change into yellow colour due to formation of CrO_4^{2-} .



17.2 F-BLOCK (INNER-TRANSITION ELEMENTS)

- The F-block consists of two series of elements known as lanthanides and actinides.
- The general outer electronic configuration of the f-block elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.

- Lanthanide ions with less than one electron have similar colour to those with $(14 - x)f$ electrons. E.g., La^{3+} and Lu^{3+} are colourless, Sm^{3+} and Dy^{3+} are yellow coloured and Eu^{3+} and Tb^{3+} are pink coloured.
- Lanthanides differ from transition metals in the fact that their magnetic moments do not obey spin only formula. This is because in case of transition elements the orbital contribution is quenched by the electric field of the environment but in case of lanthanides 4f orbitals lie too deep to be quenched.
- Silvery white soft metals tarnish rapidly in air, samarium being steel hard, in this regard.
- General outer electronic configuration is $4f^{1-14} 5d^{0-1} 6s^2$.

Element	Atomic Number	Electronic Configuration	Oxidation Number
La	57	$[\text{Xe}] 5d^1 6s^2$	+3
Ce	58	$[\text{Xe}] 4f^1 5d^1 6s^2$	+3, +4
Pr	59	$[\text{Xe}] 4f^2 6s^2$	+3, (+4)
Nd	60	$[\text{Xe}] 4f^3 6s^2$	(+2), +3, +4
Pm	61	$[\text{Xe}] 4f^4 6s^2$	+3
Sm	62	$[\text{Xe}] 4f^5 6s^2$	(+2), +3
Eu	63	$[\text{Xe}] 4f^6 6s^2$	+2, +3
Gd	64	$[\text{Xe}] 4f^7 5d^1 6s^2$	+3
Tb	65	$[\text{Xe}] 4f^8 6s^2$	+3, (+4)
Dy	66	$[\text{Xe}] 4f^9 6s^2$	+3, (+4)
Ho	67	$[\text{Xe}] 4f^{10} 6s^2$	+3
Er	68	$[\text{Xe}] 4f^{11} 6s^2$	+3
Tm	69	$[\text{Xe}] 4f^{12} 6s^2$	(+2), +3
Yb	70	$[\text{Xe}] 4f^{13} 6s^2$	+2, +3
Lu	71	$[\text{Xe}] 4f^{14} 5d^1 6s^2$	+3

- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f-electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f-level. The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.
- Their oxides are used in glass industry for polishing glass and for making coloured glasses for goggles as they gives protection against UV light and as phosphor for television screen and similar fluorescing surfaces.
- The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A (~95 per cent) and iron (~5 per cent) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets. Shell and lighter flint, mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screen and similar fluorescing surfaces.

Lanthanide contraction: It is the decrease in size of atoms and ions with increase in atomic number in lanthanide series.

- Consequences of lanthanide contraction
Similar chemical properties
Decrease in basicity with decrease in the size
Similarly of II and III transition series
- Low ionization energies
- Lanthanides have low values of first and second ionization energies (IE_1 and IE_2) which are closer to alkaline earth metals specially to calcium. On account of fairly low ionization energy and large atomic size, lanthanoids are strong electropositive elements

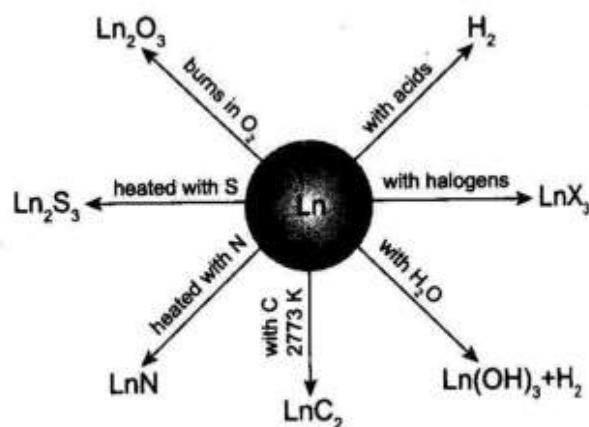
17.2.1 Oxidation States

Lanthanoids show limited number of oxidation states because the energy gap between 4f and sd subshell is range

The E° value of Ce^{4+}/Ce^{3+} is +1.74 V, which suggest that it can oxidize water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.

- Coloured ions: Due to partially filled f-orbitals which allow f-f transitions.

- La^{3+} ($4f^0$), Gd^{3+} ($4f^7$), Lu^{3+} ($4f^{14}$) → Colourless
- Ce^{3+} ($4f^1$) and Yb^{3+} ($4f^{13}$) → Colourless despite of having unpaired electrons (exceptions)
- Chemical reactivity: The oxides are ionic and basic.
- With air: forms M_2O_3 type oxides, (except Ce which forms CeO_2)
- With hydrogen: forms MH_3 type hydrides
- With halogen: forms MH_3 type halides
Fluorides → insoluble
Chlorides → deliquescent and soluble



17.2.2 Actinides

- General outer electronic configuration is $5f^{1-4} 6d^{0-1} 7s^2$.

Element	Atomic Number	Electronic Configuration	Oxidation Number
Ac	89	[Rn] $6d^1, 7s^2$	+3
Th	90	[Rn] $6d^2, 7s^2$	+3, +4
Pa	91	[Rn] $5f^1, 6d^1, 7s^2$	+3, +4, +5
U	92	[Rn] $5f^2, 6d^1, 7s^2$	+3, +4, +5, +6
Np	93	[Rn] $5f^3, 6d^1, 7s^2$	+3, +4, +5, +6, +7
Pu	94	[Rn] $5f^4, 7s^2$	+3, +4, +5, +6, +7
Am	95	[Rn] $5f^7, 7s^2$	+3, +4, +5, +6
Cm	96	[Rn] $5f^7, 5d^1, 6s^2$	+3, +4

Element	Atomic Number	Electronic Configuration	Oxidation Number
Bk	97	[Rn]5f ⁰ 7s ²	+3, +4
Cf	98	[Rn]5f ⁰ , 7s ²	+3
Es	99	[Rn]5f ¹ , 7s ²	+3
Fm	100	[Rn]5f ² , 7s ²	+3
Md	101	[Rn]5f ³ , 7s ²	+3
No	102	[Rn]5f ⁴ , 7s ²	+3
Lr	103	[Rn]5f ⁴ , 6d ¹ , 7s ²	+3

- Actinide contraction is similar to lanthanide contraction.
- The ions having 2 to 6 electrons in 5d orbitals are coloured, both in crystalline and in aqueous solution, due to f-f transition.
- Ions with 5f⁰, 5f¹ and 5f⁴ configurations are colourless.

Unlike lanthanoids, actinoids show a large number oxidation states. This is because of very small energy gap between 4f, 6d and 7s subshells; hence, all these electrons can take part in bonding.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most nonmetals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers, whereas, alkalies have no action in this regard.



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 PUJA KUMARI AIR 163	 SATYAM SAGAR AIR 518	 PRVEEN AIR 712	 KUMARI JYOTI AIR 978
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METALLURGLCAL EXTRACTION**18.1 INTRODUCTION**

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called ores. An ore is usually contaminated with earthy or undesired materials known as gangue. Hence, all minerals are not ores but all ores are minerals.

Oxides and hydroxides: Fe, Cu, Zn, Ni, Bi, Cd and Sn; Carbonates: Fe, Cu, Zn, Pb, Ca, Mn and Mg.

Silicates: Cu, Zn Ni, Al, Li, Na, K and Be;

Sulphates: Mg, Ba, Ca and Pb

Phosphates: Li, Na, K, Ca, Fe and Mn;

Nitrates: Na and K

Nitrate ores are rare because all nitrates are water soluble and at higher temperature they decomposes into oxides of their metal.

18.1.1 Important Ores of Some Metals

1. Iron: In the combined state iron occurs in the following minerals.

- (i) Haematite (Fe_2O_3): main ore
- (ii) Magnetite (Fe_3O_4)
- (iii) Limonite ($3\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)
- (iv) Siderite (FeCO_3).

2. Tin: Cassiterite or tin stone (SnO_2): main ore

3. Copper: Occurs in the native state as well as in the compound form. The natural ores of copper are

- (i) Copper pyrites (CuFeS_2): main ore
- (ii) Malachite ($\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$) (green colour)
- (iii) Cuprite or ruby copper (Cu_2O)
- (iv) Azurite ($\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$)
- (v) Copper glance (Cu_2S)

4. Lead

- (i) Galena (PbS): main ore
- (ii) Cerrusite (PbCO_3)
- (iii) Anglesite (PbSO_4)
- (iv) Wulfenite (PbMnO_4)
- (v) Stozite (PbWO_4)

5. Magnesium:

- (i) Dolomite ($MgCO_3 \cdot CaCO_3$): main ore (ii) Carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$)
 (iii) Asbestor: ($CaSiO_3 \cdot 3MgSiO_3$) (iii) Magnesite ($MgCO_3$).
 (vi) Schonite ($MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$) (vii) Epsom salt ($MgSO_4 \cdot 7H_2O$)

6. Aluminium: Aluminium is the third most abundant element of earth's crust.

7. Silver: In the native form it is associated with copper and gold. The main ores of silver are

- (i) Argentite or silver glance (Ag_2S): **main ore**
 - (ii) Horn silver (AgCl)
 - (iii) Proustite or ruby silver ($3\text{Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$)
 - (iv) Pyrargyrite ($3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$) i.e., $\text{Ag}_2\text{Sb}_2\text{S}_3$.

8. Manganese: (i) Pyrolusite, (MnO_2) (ii) Braunite, (Mn_2O_3)

8 Zinc: (i) Zinc blende (ZnS) (ii) Calamine ($ZnCO_3$) (iii) Zincite (ZnO)

Oxygen is the most abundant element in the earth's crust by weight.

Aluminium is the most abundant metal in the earth's crust.

Most abundant element in the atmosphere is nitrogen.

18.1.3 Other Important Ores

- | | |
|--|---|
| <input type="checkbox"/> Fluorspar (CaF_2) | <input type="checkbox"/> Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) |
| <input type="checkbox"/> Pitch blende (U_3O_8) | <input type="checkbox"/> Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) |
| <input type="checkbox"/> Cinnabar (HgS) | <input type="checkbox"/> Chile salt peter (NaNO_3) |
| <input type="checkbox"/> Indian salt peter (KNO_3) | <input type="checkbox"/> Rutile (TiO_2) |

18.2 METALLURGICAL OPERATIONS

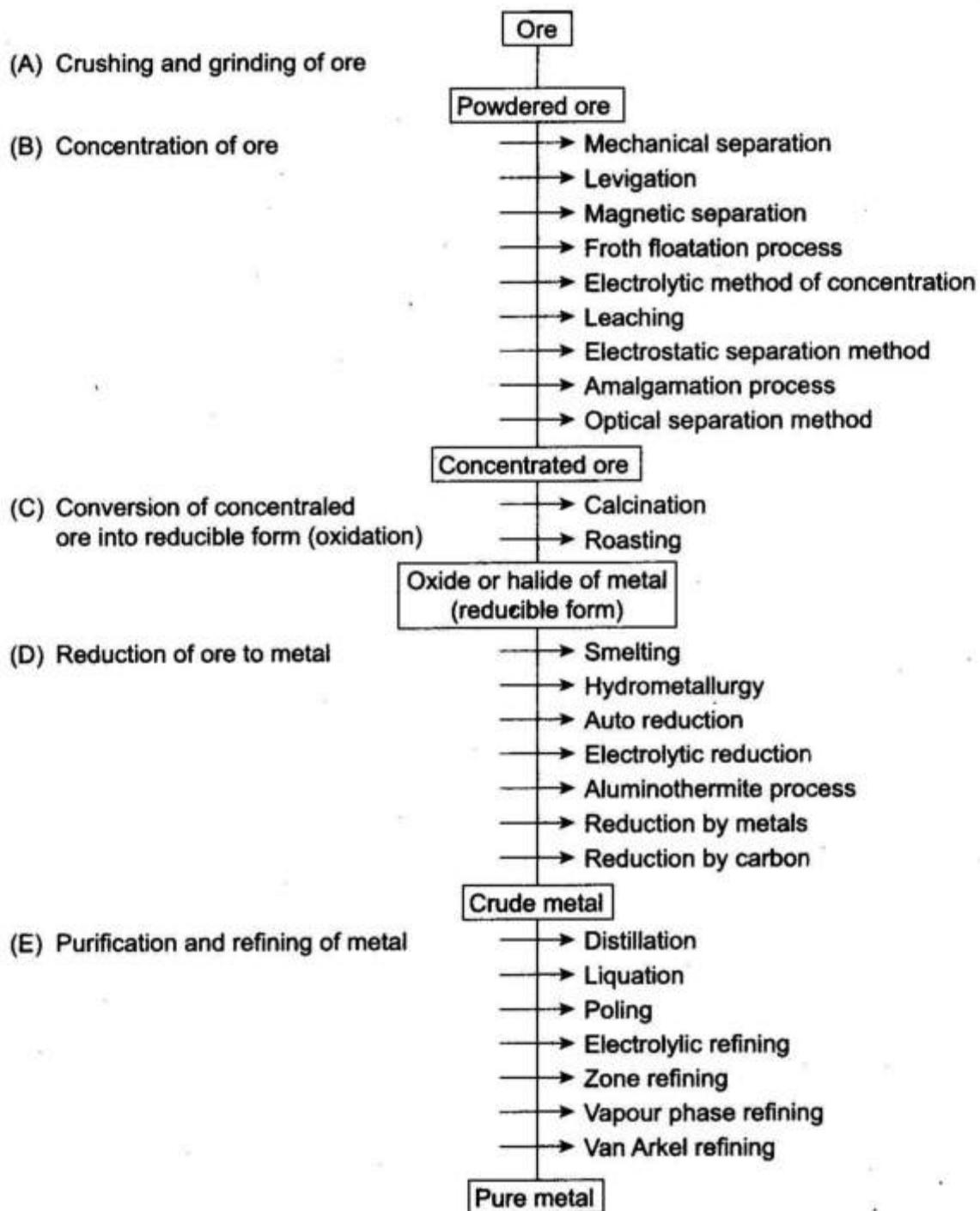
Flow sheet for the general metallurgical operation is given below. In the flow sheet, the functions of process are given on the right side, whereas the methods employed are denoted on the left.

(A) **Crushing and grinding:** The ore is first crushed by jaw crushers and ground in various size reduction equipments like ball mill, jaw crusher, etc.

(B) Concentration or dressing of the ore: The process of removal of the unwanted material (gangue) from the ore is called concentration or dressing or benefaction of the ore. The important methods for concentration are listed hereunder.

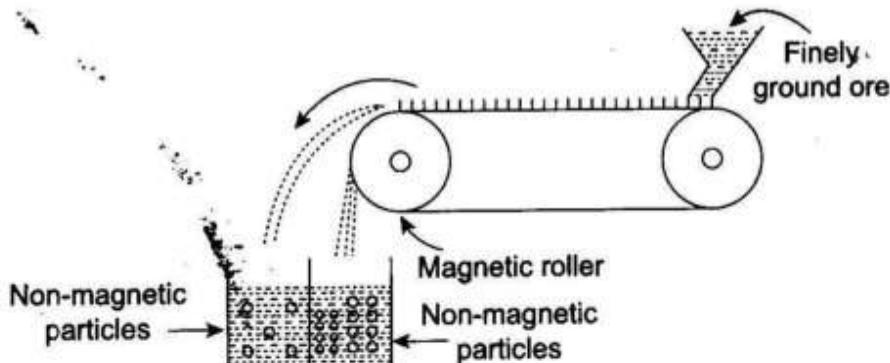
(i) **Hydraulic washing or gravity separation or levigation method:** The method is based on the difference in specific gravities of the ore and gangue particles. It is also known as gravity separation method. The powdered ore is washed with an upward stream of running water, where the lighter gangue particles are washed away while the heavier ore particles are left behind, e.g., ores [like tinstone (SnO_2), haematite (Fe_2O_3), chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$), etc.] are concentrated by this method.

Gangue or matrix: The non-metallic impurities such as mica, earth particles, etc. associated with crude ore are known as gangue or matrix.



- (ii) **Magnetic separation:** The method is based on magnetic and non-magnetic properties of the two components of the ore. This method has limited application. The ground ore is carried on a travelling band which passes over a magnetic roller. The ore leaves the band and falls from it. The particles attracted by the magnetic field form a separate pile. This method is useful for separating tin ore particles from cassiterite (SnO_2). The process may also be employed for separating other transition metal ores such as magnetite (Fe_3O_4), chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) and pyrolusite (MnO_2) from unwanted gangue.

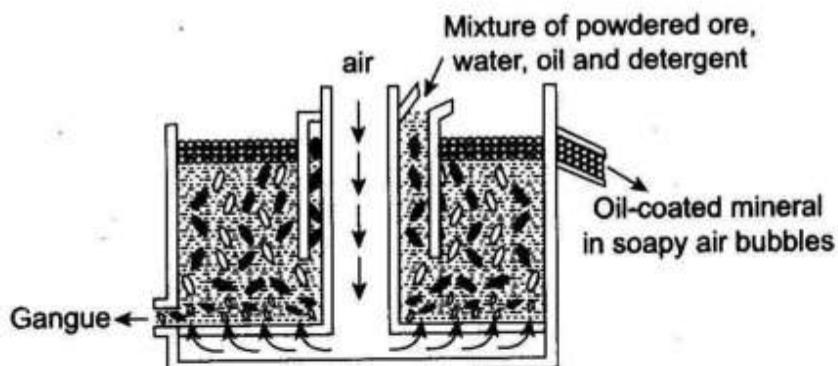
The method is used for strongly ferromagnetic ores of Fe, Sn, etc. Wolframite (FeWO_4) is a magnetic ore that can be separated from the non-magnetic ore cassiterite (SnO_2).



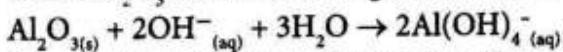
- (iii) **Froth floatation method:** This is a very useful technique especially for separating sulphide ores of zinc, copper and lead from the gangue. A suspension of the finally powdered ore is made with water. Suspension is mixed with 3.5 per cent by weight of eucalyptus oil (or some other cheap oil) and the mixture is stirred by compressed air. Froth is generated at surface. Sulphide particles in ores are preferentially wetted by this froth and rise to the surface. They are skimmed off by a skimmer. Gangue is preferentially wetted by water and sinks to bottom.

Reagents used in froth floatation process

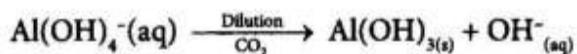
- Frothers:** Which create froth, e.g., palm oil.
- Collectors:** The surface of collectors adsorb small ore particles and these collector particles come with froth air bubbles. E.g., ethyl xanthate or potassium ethyl xanthate.
- Activators:** Simple inorganic compounds which enhance the effect of collectors, e.g., Na_2S , CuSO_4 , etc.



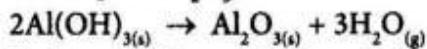
- Depressants:** Depressants are used to prevent certain type of particles from forming the froth with the bubbles. E.g., sodium cyanide can be used as a depressant in the separation of zinc sulphide ore (ZnS) and lead sulphide ore (PbS). NaCN acts as a depressant for ZnS but does not prevent PbS from the formation of froth, e.g., NaCN , Na_2CO_3 , KCN , etc. NaCN forms a layer of zinc complex, $\text{Na}_2\text{Zn}(\text{CN})_4$, on the surface of ZnS and thereby prevents it from the formation of froth.
- Leaching:** This method is useful in cases where ore is soluble in a suitable solvent, but impurities are insoluble. E.g., in Baeyer's process pure aluminium oxide is obtained from the bauxite ore by treating the powdered ore with a concentrated solution of sodium hydroxide where Al_2O_3 dissolves leaving behind the impurities.



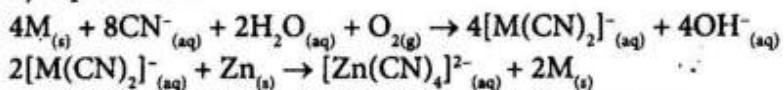
The solution of sodium aluminate is filtered and cooled and its pH is adjusted downward by dilution and/or neutralization with CO_2 where aluminium hydroxide is precipitated; seeding with a little freshly precipitated aluminium hydroxide quickens the process.



The precipitate of Al(OH)_3 is filtered, dried and finally heated to about 1473 K to obtain pure Al_2O_3 .



In the metallurgy of silver and that of gold, the respective metal/ore leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement.



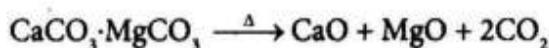
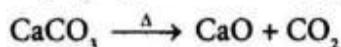
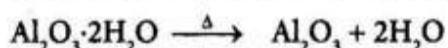
(C) Extraction of the crude metal from the concentrated ore

The concentrated ore must be converted into a form which is suitable for reduction to the metal. If the ore is a hydroxide (hydrated oxide), carbonate or sulphide it is subjected to calcination or roasting/melting and thereby converted to the oxide form, for thermodynamic reasons it is easier to reduce an oxide than the sulphide.

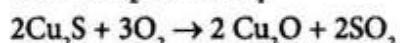
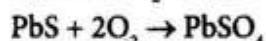
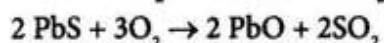
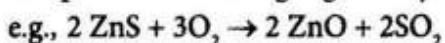
- (i) **Calcination:** When the ore is heated below its melting point in limited supply of air, mainly decomposition reactions occur. This process is known as calcination. Calcination is highly endothermic. A reverberatory furnace is usually employed for carrying out calcination.

During calcination:

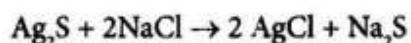
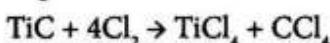
- (a) All the volatile impurities are lost.
- (b) Water of crystallization is lost. E.g., $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}_{(\text{g})}$



- (ii) **Roasting:** Roasting is done at a temperature slightly higher than that of calcination in excess of air. The ore does not melt during roasting. All the combustible organic matter burns away and the ore becomes more porous. Exothermic reactions supply much of the heat and much lesser energy is required in this case. In the roasting process, ore is converted into its oxide or sulphate. The process of roasting is generally carried out in a reverberatory furnace or blast furnace.



In chloridizing roasting, the ore is changed into metal chloride by heating with common salts in presence of air.



Note:

The free energies of formation (ΔG°_f) of most sulphide ore are greater than those for CS_2 and H_2S . CS_2 is, in fact, an endothermic compound. So neither carbon nor hydrogen is a suitable reducing agent for metal sulphides. Moreover, the roasting of a sulphide to the oxide is quite advantageous thermodynamically. Hence, the common practice is to roast sulphide ore to the oxide prior to reduction.

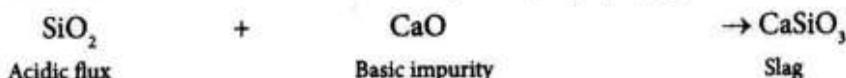
- (iii) **Smelting:** The process of extraction of metal in fused (molten) state is called smelting. This process is carried out in blast furnace. During melting, the ore is heated with suitable reducing agent in order to obtain the metal.

During this process, some infusible impurities are also removed from molten metal by adding suitable substance known as flux. Even after concentration, ore may contain some infusible impurities, which may be acidic, i.e., non-metallic oxides like SiO_2 , P_2O_5 , etc. or basic, i.e., metallic oxides like CaO , FeO , etc.

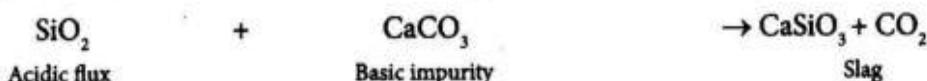
$\text{Impurity} + \text{Flux} \rightarrow \text{Slag}$ (fusible mass, which floats over molten metal)

Slag is a fusible mass and has low m.pt. It is lighter than metal and is immiscible with molten metal; hence, it floats over the metal. The layer of slag over molten metal prevents the metal from oxidation.

- (a) **Acidic flux:** They are used to remove basic impurities like CaO , MgO , FeO , etc. They are acidic in nature, i.e., oxides of non-metals, e.g., SiO_2 , P_2O_5 , B_2O_3 , etc.



- (b) **Basic flux:** Basic flux removes acidic impurities like SiO_2 , P_2O_5 , etc. and is basic in nature. e.g., CaO , (obtained from limestone), MgO (obtained from magnesite MgCO_3), etc.



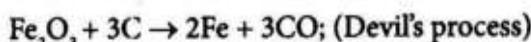
Some important reduction process are described below:

18.3 REDUCTION CONVERSION OF ORE TO METAL

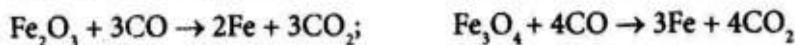
The ore, obtained after calcination or roasting, is reduced to metal and choice of reducing agent depends upon the nature of the ore. Some common reducing agents are listed hereunder:

(a) Reduction by Carbon and Carbon Monoxide

- (i) Due to cheapness and high availability, carbon is widely used as a reducing agent. The process is known as carbon reduction process.
- (ii) The metals which are less electropositive and do not form carbides with carbon are reduced by this method, e.g., oxides of Pb , Fe , Zn , Sn , etc.
- (iii) For reduction, the ore is strongly heated with coke or coal in blast furnace, where metal is obtained in the form of vapours, which are condensed (Zn) or in molten state (Sn , Fe , etc.) e.g.,



- (iv) Some disadvantages of carbon reduction process are that sometimes metallic oxide may form carbide instead of the metal, e.g., $\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}$. In some cases, reversible reaction may take place and so during the cooling, formation of oxide may take place, e.g., $\text{MgO} + \text{C} \rightleftharpoons \text{Mg} + \text{CO}$, thus carbon is not fit for reducing CaO and MgO .
- (v) Carbon monoxide also acts as a reducing agent. e.g.,

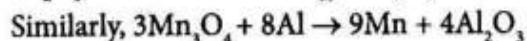
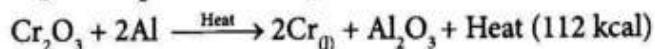
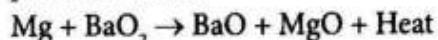


Note:

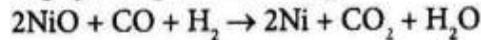
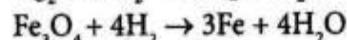
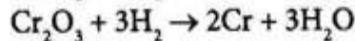
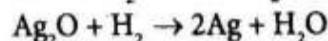
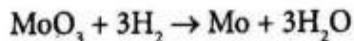
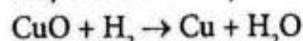
- (i) Below 710°C , CO is a better reducing agent than carbon and the reverse is true at temperature higher than 710°C . It can explained on the basis of Ellingham diagrams given in the thermodynamics of metallurgy.
- (ii) Carbon is a good reducing agent for oxides but not for sulphides.

(b) Reduction by Metals:

- (i) Highly electropositive metals like Na, K, Li, Al, etc. are used to reduce the less electropositive metals like Cr, Cu, Mn, etc.
- (ii) Reduction by powdered aluminium is known as Gold-Schmidt aluminothermite process. This process is employed in cases where metals have very high m.pt. and are to be extracted from their oxides. In this process thermite (mixture of ore and powdered aluminium) is taken in a steel crucible. The reaction is started by using ignition mixture (Mg powder and barium peroxide). It is called thermite process because large amount of heat is released during the reduction, which fuses both ore and metal. E.g., reduction of Cr_2O_3 by Al powder takes place as follows:

**(c) Reduction by H_2 or water gas ($\text{CO} + \text{H}_2$)**

- (i) The oxides of metals, which are less electropositive than hydrogen (e.g., CuO, FeO, Ag_2O , etc.) may be reduced by this method. E.g.,



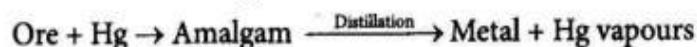
- (ii) Water formed during the reaction escapes out in the form of vapours.

(d) Self-reduced or auto reduction: Oxides of unreactive metals (like those of Hg, Pb, Cu, etc.) are reduced by air/anion of ore. Here, no external reducing agent is added. E.g.,

- (i) Extraction of Hg from cinnabar: $2\text{HgS} + 3\text{O}_2 \rightarrow 2\text{HgO} + 2\text{SO}_2$; $2\text{HgO} + \text{HgS} \rightarrow 3\text{Hg} + \text{SO}_2$
- (ii) Extraction of Cu from copper glance: $2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 3\text{Cu}_2\text{O} + 2\text{SO}_2$; $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$
- (iii) Extraction of Pb from galena: $2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2$; $2\text{PbO} + \text{PbS} \rightarrow 3\text{Pb} + \text{SO}_2$

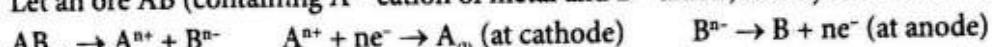
(e) Hydrometallurgy or displacement method

- (i) This method is based on the fact that a more reactive metal displaces less reactive metal from its salt solution.
- (ii) In this method, ore is converted into soluble form where more reactive metal is added in it. E.g.,
 - (a) Extraction of copper from malachite: $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \rightarrow 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2$
 $\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}; \text{CuSO}_4 + \text{Zn} \rightarrow \text{ZnSO}_4 + \text{Cu} \downarrow$
 - (b) Cyanidation process for Ag and Au: $\text{Ag}_2\text{S} + 4\text{NaCN} \rightleftharpoons 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$
 $\text{Na}_2\text{S} + 2\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4; 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag} \downarrow$

(f) Amalgamation process: The process is used for extraction of noble metals like Pt, Au, Ag, etc. Finely powdered ore is treated with Hg to form amalgam. Amalgam, on distillation, is decomposed to the metal and Hg.

(g) **Electrolytic reduction:** It is the most commonly used method of reduction. The ores of highly electropositive metals like alkali metals and alkaline earth metals cannot be reduced by common reducing agents like H₂, C, etc., because of formation of carbides. For electrolytic reduction, oxide, hydroxide or halide (as suitable) ore is fused. If melting point is quite high, some substances are added to lower the fusion temperature. The quantitative aspects of electrolytic reduction are based on Faraday's laws of electrolysis. The cell used for electrolysis is known as electrolytic cell and its functioning may be explained as given below.

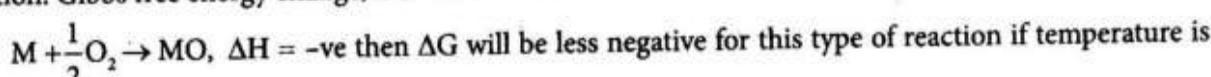
Let an ore AB (containing Aⁿ⁺ cation of metal and Bⁿ⁻ anion) is subjected to electrolytic reduction.



The nature of electrode, EMF applied, etc. depends upon the nature of the metal.

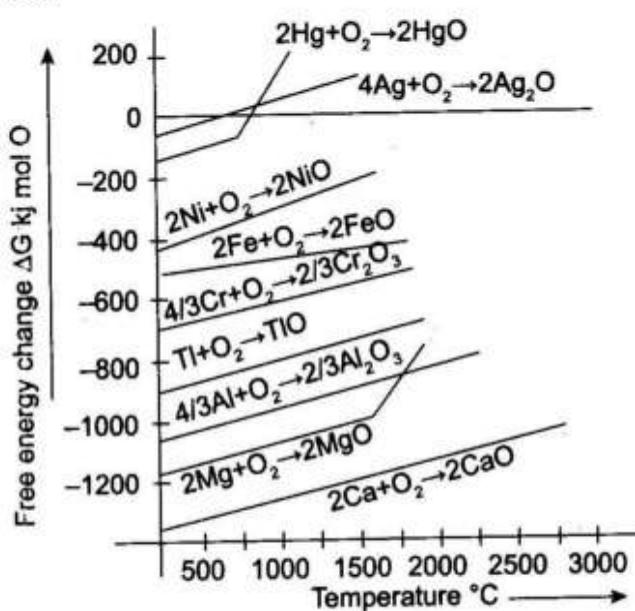
18.4 ELLINGHAM DIAGRAM

During combination reactions, the entropy of system decreases. Therefore ΔS is negative for combination reaction. Gibbs free energy change, $\Delta G = \Delta H - T\Delta S$



increased as $T\Delta S$ becomes more negative. After a certain temperature, reaction will become non-spontaneous as the value of ΔG will become positive.

When activity of all reacting substances is unity, then $\Delta G = \Delta G^\circ$. For one mole common reactant (like oxygen, halogen, sulphur, etc.) value of ΔG° may be plotted against temperature. These ΔG° vs T curves are known as Ellingham diagrams.



18.4.1 Important Features of Ellingham Diagrams

- (i) A typical Ellingham diagram follows a straight line unless there is large entropy change due to melting or vapourization.
- (ii) All the plots slope upwards because ΔG° becomes more positive when temperature increases.
- (iii) At a certain temperature $\Delta G^\circ = 0$ and above this temperature, it is positive. The metal oxide (or other products like sulphide or halide) formation is spontaneous below this temperature. Theoretically, all oxide are thermally unstable provided that this temperature can be attained.