

Black body: An ideal body, which emits and absorbs all frequencies of electro magnetic radiation.

Quantum: The smallest quantity of energy that can be emitted or absorbed in the form of electro magnetic radiation. Quantum is just an energy packet and it has no mass.

Planck's Quantum Theory:

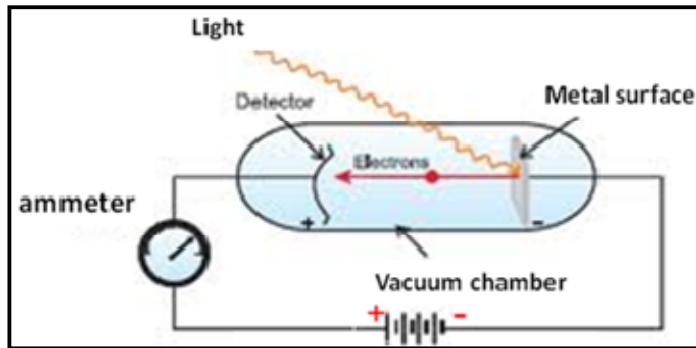
Planck's quantum theory explains the black body radiation. It supports particle nature of electro magnetic radiation.

Features of Planck's Quantum Theory:

- 1) The emissions of radiation are due to vibrations of charged particles (electrons) in the body.
- 2) The emission of radiant energy is not continuous. It happens in the form of small discrete packets of energy called 'Quanta'.
- 3) The energy of quantum is given by $E = h\nu$
Where, $h = \text{Planck's constant} = 6.625 \times 10^{-27}$ erg sec.
 ν = frequency of radiation
- 4) Moreover, $E = n(h\nu)$, $n = 1, 2, 3, \dots$ thus, energy is quantized.
i.e. the energy emitted or absorbed by a black body, is an integral multiple of 'quanta'.
- 5) 'Quants' will propagate in the form of waves.
- 6) The frequency distribution of the emitted radiations from a black body depends only on its temperature.

Photoelectric effect:

It is phenomenon in which electrons are ejected from the clean surface of certain metals (alkali metals, Ex: K, Rb, Cs), when the metals are exposed to a light.



The results observed in this experiment were:

- 1) The electrons are ejected from the clean metal surface as soon as the beam of light strikes the surface.
- 2) The number of electrons ejected is proportional to the intensity or brightness of light.
- 3) For each metal, there is a characteristic minimum frequency, v_0 (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency $v > v_0$ the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with frequency of the light used.

BOHR'S ATOMIC MODEL:

To overcome the objections of Rutherford's model and to explain the hydrogen spectrum, Bohr proposed a quantum mechanical model of the atom.

Postulates:

- i) The atom has a nucleus where all the protons and neutrons are present. The size of the nucleus is very small. It is present at the centre of the atom.
- ii) Negatively charged electrons are revolving around the nucleus in the same way as the planets are revolving around the sun.
- iii) The path of electron is circular. The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.
- iv) Out of infinite number of possible circular orbits around the nucleus, the electron can revolve only on those orbits whose angular momentum is an integral multiple of $h/2\pi$, i.e., $mvr = nh/2\pi$.

Where m = mass of electron, v = velocity of electron, r = radius of the orbit

$n = 1, 2, 3, \dots$ number of the orbit

therefore angular momentum can have values such as $1h/2\pi$, $2h/2\pi$, $3h/2\pi$, ...etc. but cannot have a fractional value. Thus, angular momentum is quantized. The specified or circular orbits are called **stationary orbits**.

- v) By the time, the electron remains in any of the stationary orbits, it does not lose energy. Such a state is called ground or normal state.
- vi) Each stationary orbit is associated with a definite amount of energy. These orbits are also called energy levels and are numbered as 1, 2, 3, 4, ..., or K, L, M, N, from nucleus outwards. i.e., $E_1 < E_2 < E_3 < E_4 \dots$
 $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) \dots$
- vii) The emission or absorption of energy in the form of radiation can only occur when an electron jumps from one stationary orbit to another.

$$\Delta E = E_{\text{high}} - E_{\text{low}} = h\nu$$

Energy is absorbed when the electron jumps from inner to outer orbit (excited state) and is emitted when it moves from outer to an inner orbit.

Limitations of Bohr's theory:

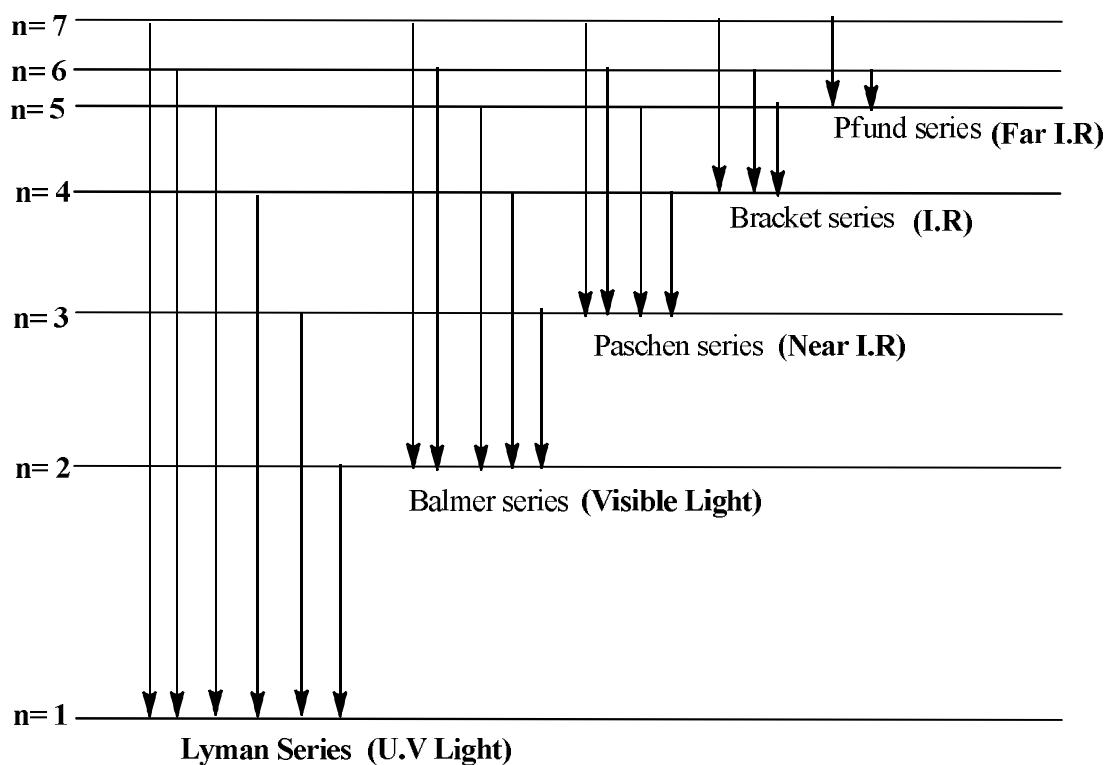
- i) It does not explain the spectra of multi-electron atoms.
- ii) Bohr's theory does not explain the fine spectra of even hydrogen atom.
- iii) It does not explain the splitting of spectral lines in presence of magnetic field (Zeeman effect) and electric field (stark effect).
- iv) Bohr's theory is not in agreement with Heisenberg's uncertainty principle.

Hydrogen spectrum – Bohr's Explanation:

- 1) When electric discharge is passed through gaseous hydrogen, the electrons in various hydrogen atoms absorb various amounts of energies.
- 2) Then they enter into higher energy orbits.
- 3) In higher orbits, the energy is more but stability is less.
- 4) So, the excited electrons fall back to lower orbits.
- 5) This happens in one step or in multiple steps.
- 6) Energy released during this process appears in the form of spectral lines of hydrogen spectrum.
- 7) The transmission of energy of electrons from any higher orbit to
 - i) $n = 1$ produces spectral lines in the UV region. This is named as **Lyman Series**.
 - ii) $n = 2$ produces spectral lines in the visible region. This is named as **Balmer Series**.
 - iii) $n = 3, 4, 5$ produces spectral lines in the IR region. These are named as **Paschen, Brackett and Pfund Series** respectively.

Formula to find wavenumber (\bar{v}) and wavelength (λ) of spectral lines:

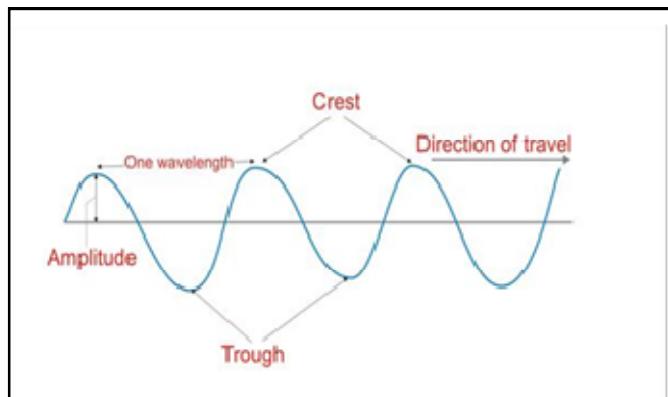
$$\bar{v} = 1/\lambda = R_H [1/n_1^2 - 1/n_2^2]$$



Energy level diagram of Hydrogen spectrum

Electromagnetic radiation:

An electromagnetic radiation is generated by oscillations of a charged body in a magnetic field or a magnet in an electrical field. These radiations or waves have electrical and magnetic fields associated with them and travel at right angle to these fields.



- 1) **Wavelength:** The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ .

Units: cm, nm, , μm .

$$1' = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

$$1 \mu\text{m} = 10^{-4} \text{ cm} = 10^{-6} \text{ m}$$

$$1 \text{ nm} = 10^{-7} \text{ cm} = 10^{-9} \text{ m}$$

$$1 \text{ cm} = 10^8' = 10^4 \mu\text{m} = 10^7 \text{ nm}$$

- 2) **Frequency:** It is defined as the number of waves which pass through a point in one second. It is denoted by the ϑ . It is expressed in Hz.

$$\vartheta = c/\lambda$$

- 3) **Velocity:** It is defined as the distance covered in one second by the wave. It is denoted by c . It is expressed in cm/sec.

$$c = \vartheta\lambda$$

- 4) **Wave number:** This is the reciprocal of wavelength, i.e. the number of wave length per cm. It is denoted by \bar{v} . It is expressed in cm^{-1} or m^{-1} .

$$\bar{v} = 1/\lambda$$

- 5) **Amplitude:** It is defined as the height of the crest or depth of the trough of a wave. It is denoted by a . it determines the intensity of radiation.

- 6) **Time Period:** time taken by the wave for one complete cycle or vibration is called time period. It is denoted by T . Units: sec/cycle

$$T = 1/v$$

Dual nature of matter:

de Broglie proposed that micro particles like electrons exhibit both particle and wave like properties. Thus, electron should also have momentum as well as wave length.

- i) According to Planck's quantum theory of radiation, the energy of photon is given by
$$E = h\nu \longrightarrow E = h c/\lambda \dots\dots\dots\dots\dots(1)$$
- ii) According to Einstein's mass-energy equivalence equation, $E = mc^2 \dots\dots\dots\dots\dots(2)$
From (1) & (2), $h c/\lambda = mc^2$
 $\longrightarrow h/\lambda = mc$
 $\longrightarrow \lambda = h/mc = h/p \dots\dots\dots\dots\dots(3)$ [since $mc = p$ = momentum]

de Broglie hypothesized that, equation (3) applicable to photons, can be extended to all micro particles like electrons, moving with high speeds.

Hence (3), the velocity of photon (c) can be replaced by the velocity of microparticle (v).

Therefore equation (3) be re-written as $\lambda = h/p = h/v \dots\dots\dots\dots\dots(4)$

This equation (4) is called de Broglie equation.

Here λ = particle wave length

Thus, the micro particle electron posses wave length λ , given by the above expression. Hence, electron is associated with wave nature.

Significance or importance: Equation (4) should hold true for all the moving material bodies.

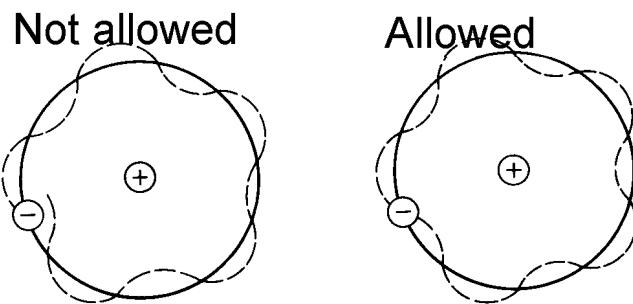
In (4) 'm' is in the denominator. For macroscopic bodies like planets, the value of m is very large. Hence λ becomes very small, so that it is neglected.

But, microscopic particles like electrons posses very low masses. Hence, the value of λ is very significant.

Further, for an electron moving around the nucleus in circular path, two different types of waves of different wave lengths are possible.

One is due to constructive interference (when $n\lambda = 2\pi r$) and the other is due to destructive interference ($n\lambda \neq 2\pi r$).

If the circumference of the electron orbit is an integral multiple of λ , the electron waves are said to be 'in-phase'. Otherwise, they are 'out of phase'.



If the electron wave is in ‘in – phase’, then $n\lambda = 2\pi r \longrightarrow \lambda = 2\pi r/n \dots\dots\dots(5)$

From eq (4) & (5) we get, $h/mv = 2\pi r/n \longrightarrow mvr = nh/2\pi \dots\dots\dots(6)$

Eq (6) is nothing but the relation of Bohr’s quantization of angular momentum.

Thus, de Broglie’s theory and Bohr’s theory are in well agreement with each other, in the quantization of angular momentum.

Heisenberg uncertainty principle:

It is impossible to measure simultaneously the exact position and the momentum of a body as small as an electron. Mathematically represented as

$$\Delta x \cdot \Delta p \geq h/4\pi$$

Where Δx = uncertainty of measurement of position

Δp = uncertainty of measurement of momentum

h = Planck's constant = 6.625×10^{-27} erg-sec

We know that momentum $p = mv$,

Therefore $\Delta p = \Delta mv$ and Heisenberg uncertainty principle mathematically can be written as

$$\Delta x \cdot \Delta mv \geq h/4\pi$$

or

$$\Delta x \cdot \Delta v \geq h/4\pi m$$

For an electron of mass $m = 9.10 \times 10^{-28}$ g, the product of uncertainty is

$$\begin{aligned}\Delta x \cdot \Delta v &\geq h/4\pi m \\ &\geq 6.625 \times 10^{-27} / 4\pi m \\ &\geq 6.625 \times 10^{-27} / 4 (3.14) 9.10 \times 10^{-28} \\ &\geq 0.56 \text{ erg sec/g}\end{aligned}$$

$\Delta x \cdot \Delta v$ = uncertainty in product

When $\Delta x = 0$, $\Delta v = \infty$ and $\Delta x = \infty$, $\Delta v = 0$.

In case of bigger particles, the value of uncertainty product is negligible. If the position is known accurately *i.e.*, Δx is very small, Δv becomes large and vice-versa. Thus, uncertainty principle is important only in the case of smaller moving particles like electrons.

Quantum Numbers:

In order to locate a particular electron in an atom, quantum numbers are required. These are

1) Principl Quantum Number (n) : it is given by Bohr.

It represents the **name, size and energy of the shell** to which the electron belongs. The value of n is 1 to ∞ . i.e., $n = 1, 2, 3, 4, \dots, \infty$

$n =$	1	2	3	4	5	6
Shell =	K	L	M	N	O	P

i) Higher the value of 'n', greater is the distance of the shell from nucleus.

$$r_1 < r_2 < r_3 < r_4 < r_5 < \dots$$

ii) Higher the value of 'n', greater is the magnitude of energy.

$$E_1 < E_2 < E_3 < E_4 < E_5 < \dots$$

Energy separations between two shells decreases on moving away from nucleus.

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > (E_5 - E_4) \dots$$

iii) Maximum number of electrons in a shell = $2n^2$.

iv) Angular momentum can be calculated by using principal quantum number

$$mv = nh/2\pi$$

2) Azimuthal Quantum Number (l): it is given by Sommerfeld. It is also called as angular quantum number, subsidiary quantum number or secondary quantum number.

value of l is $l = 0, 1, 2, 3, 4, \dots, (n-1)$

it describes the spatial distribution of electron cloud and angular momentum. It gives the name of the subshell associated with the main shell.

$l = 0$	s-subshell
$l = 1$	p-subshell
$l = 2$	d-subshell
$l = 3$	f-subshell

Orbital angular momentum of an electron is calculated by using $\mu_l = \sqrt{l(l+1)} h/2\pi$

The magnitude of magnetic moment $\mu_L = \sqrt{l(l+1)} B.M.$

$$1 B.M. = eh/4\pi mc = 9.273 \times 10^{-14} J$$

Maximum electrons present in a subshell = $2(2l+1)$

s-subshell	2 electrons
p-subshell	6 electrons
g-subshell	10 electrons

3. Magnetic Quantum Number (m): it is given by Linde. It explains about **Zeeman effect**. It describes the orientation of electron cloud.

value of m is, $m = -l, 0, +l$ i.e., total $(2l+1)$ values.

$l = 0, m = 0$	s-subshell	$l = 1, m = -1, 0, +1$	p-subshell
$l = 2, m = -2, -1, 0, 1, +2$	d-subshell;	$l = 3, m = -3, -2, -1, 0, +1, +2, +3$	f-subshell

4. Spin Quantum Number (s): it is given by Gold Schmidt. It represents the direction of electron around its own axis.

For clockwise spin, $s = +1/2$ (\uparrow)

For anticlockwise spin, $s = -1/2$ (\downarrow)

Spin electron produces angular momentum is $\mu_s = \sqrt{s(s+1)} h/2\pi$

Spin magnetic moment $\mu_s = \sqrt{s(s+1)} eh/2\pi mc$

Each orbital accommodate two electrons with opposite spin or paired.

Pauli's exclusion principle:

"No two electrons in an atom can have same values of all the four quantum numbers"

Ex: nitrogen (N) and its atomic number is 7.

Electronic configuration	1s ²	2s ²	2p ³		
			2p _x ¹	2p _y ¹	2p _z ¹
n	1	2	2	2	2
l	0	0	1	1	1
m	0	0	-1	0	+1
s	+1/2 -1/2	+1/2 -1/2	+1/2 -1/2	+1/2 -1/2	+1/2 -1/2

Aufbau principle:

The subshell with minimum energy is filled up first and when this obtains maximum quota of electrons, then the next subshell of higher energy starts filling.

The sequence of various subshell is filled as 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s

The subshell with lowest (n+l) value is filled up first. When two or more subshells have same (n+l) values, the subshell with lowest value of n is filled up first.

Ex: [write Potassium (K) electronic configuration here]

Hund's rule of maximum multiplicity:

electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons with parallel spins.

Ex: [write C, N, O, F electronic configuration here]

Atomic number

- Protons present in atom are called Atomic number. It is denoted by ‘Z’. All atoms of an element have the same atomic number Z. In fact, elements are defined by the number of protons they possess.
- For hydrogen, Z = 1, because in hydrogen atom, only one proton is present in the nucleus.
- Similarly, for carbon, Z = 6. Therefore, the atomic number is defined as the total number of protons present in the nucleus of an atom.

Electronic configuration

- Distribution of electrons in to different shells, sub shells and orbitals of an atom is called electronic configuration.
- The electronic configuration of any orbital can be represented as : nl^x
- Where n: represents principle quantum number,
l: Orbital or sub shell,
x: number of electrons present in the orbital..
- For example: $4p^1$ means p sub shell of 4th main shell contains one electron.

Electronic configuration of some elements are given below,

Name	Atomic Number	Electron Configuration
Period 1		
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Period 2		
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Carbon	6	$1s^2 2s^2 2p^2$
Nitrogen	7	$1s^2 2s^2 2p^3$
Oxygen	8	$1s^2 2s^2 2p^4$
Fluorine	9	$1s^2 2s^2 2p^5$
Neon	10	$1s^2 2s^2 2p^6$
Period 3		
Sodium	11	$1s^2 2s^2 2p^6 3s^1$

Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Period 4		
Potassium	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Unit-II

Periodic Classification of elements

Construction of long form of periodic table:

Modern periodic table: ‘the physical and chemical properties of elements are the periodic functions of their atomic numbers’.

Long form of periodic table: In this table all the elements are arranged in the increasing order of atomic numbers. It is a graphical representation of Aufbau’s principle.

Construction: The table is divided into 7 horizontal rows called periods and 18 vertical columns called groups. Also, the table is divided into 4 blocks.

Periods: periods represents principle quantum number of the outer shell. Each period starts with an alkali metal and ends with a noble gas element.

- 1) The 1st period contains only 2 elements H and He. Hence it is called shortest period.
- 2) The 2nd period contains 8 elements from Li to Ne. It is called short period.
- 3) The 3rd period contains 8 elements from Na to Ar. It is also called short period.
- 4) The 4th period contains 18 elements from K to Kr. It is called long period.
- 5) The 5th period contains 18 elements from Rb to Xe. It is also called long period.
- 6) The 6th period contains 32 elements from Cs to Rn. It is called the longest period.
- 7) The 7th period is an incomplete period. It starts from Fr.
- 8) The 14 Lanthanides and 14 actinides are placed at the bottom of the table.
- 9) Each period starts with an alkali metal and ends with an inert gas element.
- 10) Most of the physical and chemical properties of elements change gradually in periods.

Groups:

- 1) All the 18 groups are numbered 1 to 18 according to IUPAC format. The previous format: IA (1), IIA (2), IIIB to VIIIB (3 to 7), VIII (8, 9, 10), IB (11), IIB (12), IIIA to VIIIA (13 to 17) and 0 group (18).
- 2) Zero group elements are placed at the extreme right side of the table. They are called noble gas or inert gas elements. They have stable octet configuration.
- 3) All the elements in a group have same valency. Hence, all the elements in a group show similar properties.

Blocks:

Based on the entry of the differentiating electron in to subshell of main shell, all the elements are divided into 4 blocks. They are s-block, p-block, d-block and f-block.

Essay on s, p, d and f block elements: Basing on the entry of differentiating electron into sub-shells of main shells, all the elements are classified into 4 blocks. They are s-block, p-block, d-block and f-block.

1. s-block elements:

- 1) The elements in which differentiating electrons enter into ns-subshell are called s-block elements.
- 2) Their general electronic configuration is ns^{1-2} .
- 3) s-block elements are arranged in 2 groups. They are group 1(1A), group 2 (IIA).
- 4) First group (1A) elements are called Alkali metals. Second group (IIA) elements are called Alkaline earth metals.
- 5) s-block is placed on the left side of the periodic table.

2. p-block elements:

1. The elements in which differentiating electrons enter into np-subshell are called p-block elements.
2. Their general electronic configuration is $ns^2 np^{1 \text{ to } 6}$.
3. p-block elements are arranged in 6 groups. They are from group 13(IIIA) to group 18.
4. p-block elements starts with 13th group and ends with 18th group.
 - i) 13th group or IIIA group is called Boron family.
 - ii) 14th group or IVA group is called Carbon family.
 - iii) 15th group or VA group is called Nitrogen family.
 - iv) 16th group or VIA group is called Chalcogen family.
 - v) 17th group or VIIA group is called Halogen family.
 - vi) 18th group or 0 group is called Noble gas family.
5. p-block is placed on the right side of the periodic table.

3. d-block elements:

- 1) The elements in which differentiating electrons enter into (n-1)d-subshell are called d-block elements.
- 2) Their general electronic configuration is $(n-1)d^{1 \text{ to } 10} ns^1 \text{ or } 2$.
- 3) d-block elements are arranged in 10 groups. They are from group 3(IIIB) to group 12 (IIB).
- 4) d-block elements are further classified into 4 transition series. They are 3d, 4d, 5d and 6d- series.
- 5) d-block is placed at the middle of the periodic table.

4. f-block elements:

- 1) The elements in which differentiating electrons enter into (n-2)f-subshell are called f-block elements.
- 2) Their general electronic configuration is $(n-2)f^{1 \text{ to } 14}(n-1)d^0 \text{ or } 1 ns^2$.
- 3) f-block elements are arranged in 14 columns.
- 4) f-block elements are further classified into 2 series. They are 4f-series known as Lanthanide series. 5f-series known as Actinide series.
- 5) f-block is placed separately at the bottom of the periodic table.

Periodic property: In the period table, some properties of elements change gradually with a change in their electronic configurations. Such properties are called periodic properties.

- 1) **Atomic radius:** The distance between centre of the atomic nucleus and the electronic cloud of the outer most energy level is called atomic radius.
 - a) In a group, from top to bottom the atomic radius increases. This is because of the differentiating electron enters into the next orbit. Hence atomic radius increases.
 - b) In a period, from left to right the atomic radius decreases. This is because of the differentiating electron remains in the same orbit. Hence atomic radius decreases.
- 2) **Electron affinity (EA):** The amount of energy released when an electron is added to neutral isolated gaseous atom is called electron affinity (EA) or electron gain enthalpy.
 - a) In a group, from top to bottom, electron affinity decreases. This is because in a group atomic size increases. Hence the effective nuclear attraction on outer electrons decreases. Therefore, electron affinity decreases from top to bottom in a group.
 - b) In a period, from left to right the electron affinity increases. This is because in a period atomic size decreases. Hence the effective nuclear attraction on outer electrons increases. Therefore, electron affinity increases from left to right in a period.
- 3) **Ionisation potential(IP):** The minimum energy required to remove an electron from the outer most valence shell from an isolated, neutral, gaseous atom is called ionization energy (IE) or ionization potential (IP) or first ionization enthalphy (IE_1).
 - a) In a group, from top to bottom, the ionization potential value decreases. This is because in a group atomic size increases. Hence the effective nuclear attraction on outer electrons decreases. Therefore, ionization potential value decreases from top to bottom in a group.
 - b) In a period, from left to right the ionization potential value increases. This is because in a period atomic size decreases. Hence the effective nuclear attraction on outer electrons increases. Therefore, ionization potential value increases from left to right in a period.

- 4) **Electronegativity(EN):** The tendency of an atom in a molecule to attract the shared pair of electrons towards itself is known as electronegativity(EN).
- In a group, from top to bottom, the electronegativity(EN) value decreases. This is because in a group atomic size increases. Hence the effective nuclear attraction on outer electrons decreases. Therefore, electronegativity(EN) value decreases from top to bottom in a group.
 - In a period, from left to right the electronegativity(EN) value increases. This is because in a period atomic size decreases. Hence the effective nuclear attraction on outer electrons increases. Therefore, electronegativity(EN) value increases from left to right in a period.

Factors effecting on ionization enthalpy (IE):

- Atomic radius:** When atomic radius increases, the nuclear force of attraction on the valence electrons decreases. So, I.E value also decreases.
- Nuclear charge:** When the nuclear charge increases, the nuclear force of attraction on the valence electrons increases. So, I.E value also increases.
- Screening effect:** The electrons present in the ‘inner orbits’ decrease the nuclear attraction between nucleus and the outer electrons. This is known as screening effect. When the number of inner shells increases, the attraction of nucleus on the outer electrons decreases. So, the I.E value also decreases.
- Penetrating effect:** In a given shell, the penetrating power of the valence electrons decreases in the order of s > p > d > f. So, ‘ns’ electrons are more tightly held by the nucleus. So, the I.E value decreases in the same order.
- Completely filled or half-filled sub-shells:** Atoms with completely filled or half-filled sub-shell are more stable than the others. Such elements have slightly higher I.E values than expected.

Metallic-non metallic nature:

The metallic nature of an element depends upon the IE. The elements with low IE are metallic nature. The smaller the IE of an element, the greater will be its tendency to lose electrons and thus greater will be its metallic character.

Variation of metallic and non-metallic character:

IE decreases down the group and increases from left to right in a period.

The most reactive metals are on the left side of the periodic table. Whereas the least reactive metals are on middle of the periodic table.

In a group as we move from top to bottom metallic character increases and non-metallic character decreases.

Ex: VA group: N, P are non-metals; As, Sb are metalloids; Bi-metal.

In a period as we move from left to right non-metallic character increases and metallic character decreases.

Ex: 3rd group: Na, Mg and Al are metals; Si, P, S, Cl are non metals.

Reducing and oxidizing characters and nature of oxides:

Reducing agents	Oxidizing agents
Electropositive elements can lose electrons easily and hence, can act as good reducing agents.	Elements which gain electrons easily acts as good oxidizing agents.
Metals are good reducing agents. Down the group, this reducing character increases.	Non metals are good oxidizing agents. Down the group, decreases oxidizing nature.
From left to right in a period, decreases reducing character.	From left to right in a period, increases oxidising character.
Li is the strongest reducing agent due to high hydration energy of Li ⁺ ion.	F is the strongest oxidizing agent due to its highest E.N.

Variation of acidic and basic character:

Metals are characterized by basic character and non-metals are characterized by acidic character.

Basic character increases and acidic character decreases down the group.

Ex: N-N₂O₃ and P-P₂O₃ are acidic

As-As₂O₃ and Sb-Sb₂O₃ are amphoteric

Bi-Bi₂O₃ is basic

From left to right in a period, the basic character decreases and acidic character increases.

Ex: Na and Mg-Basic

Al-Amphoteric

Si, P, S, Cl-acidic

Valency and oxidation state:

Valence of an element is the number of H-atoms (or) double the number of O-atoms that can combine with one atom of that element.

Ex: CH₄: Valency of carbon = 1 X 4 = 4

SO₂: Valency of sulphur = 2 X 2 = 4

Exhibition of more than one valency by one element is known as variable valency.

Ex: FeCl₂-valency of Fe = 2

FeCl₃-valency of Fe = 3

Oxidation state:

The possible charge with which an atom appears in a compound is called oxidation state.

s-block elements, oxidation state is equal to its group number for alkali metals '+1', for alkaline earth metals '+2'.

p-block elements show multi valency.

III group elements can show '+3' oxidation state. Stable oxidation state of Tl is '+1', it is due to inert pair effect.

IVA group elements can show '+4' oxidation state. Stable oxidation state of Pb is '+2' and '+4', it is due to inert pair effect.

V A group elements can show '+5' oxidation state. +3 is more stable than +5 for Bi due to inert pair effect.

VIA group elements oxidation state is '-2'.

VIIA group elements oxidation state is '-1'.

The common oxidation state of d-block elements is '+2'. All the transition elements show variable valency. Highest oxidation state shown by the elements Ru and Os is '+8'.

The common oxidation state of f-block elements is '+3'. Maximum oxidation state of an element never exceeds its group number.

Diagonal relationship:

The first few elements of period 2 resemble those placed diagonally across them, in period. More generally the element of a group is different from the rest in that group and resembles with an element of the next group in the period.

Group	1	2	13	14	15	16	17
	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Period 2	Li	Be	B	C	N	O	F
Period 3	Na	Mg	Al	Si	P	S	Cl

The relationship is called a diagonal relationship. The pairs of electrons Li, Mg, Be, Al are called diagonal pairs. This relationship however does not exist in the latter half of the period.

Unit-III

Chemical Bonding

Kossel – Lewis approach:

Kossel- Lewis approach gave a logical explanation to the formation two types of chemical bonds.

According to them, atoms combine to acquire nearest inert gas configuration by transferring or sharing of valence electrons.

Kossel's approach: A chemical bond can be formed by the transfer of valence electrons from one atom to another.

Kossel proposed that the highly electronegative elements like halogens, gain electrons and convert into anions. The highly electropositive alkali metals lose electrons and convert into positive ions.

During their conversion into ions, they get the noble gas octet configuration. Now the positive and negative ions unite together by electrostatic attraction between them. Thus, Kossel proposed the ionic bond formation.

Lewis approach: A chemical bond can be formed by the mutual sharing of valence electrons.

Lewis considered the atom as a positively charged ‘Kernel’ (Kernel consists of inner electrons and nucleus). Lewis assumed that the outer shell can accommodate a maximum of 8 electrons which occupy the eight corners of a cube surrounding the Kernel. He assumed that noble gases are stable due to this type of arrangement. The atoms which do not have this type of arrangement achieve the stable octet, by sharing of electrons to form chemical bonds.

Thus, Lewis approaches the covalent bond formation and Kossel proposed ionic bond formation.

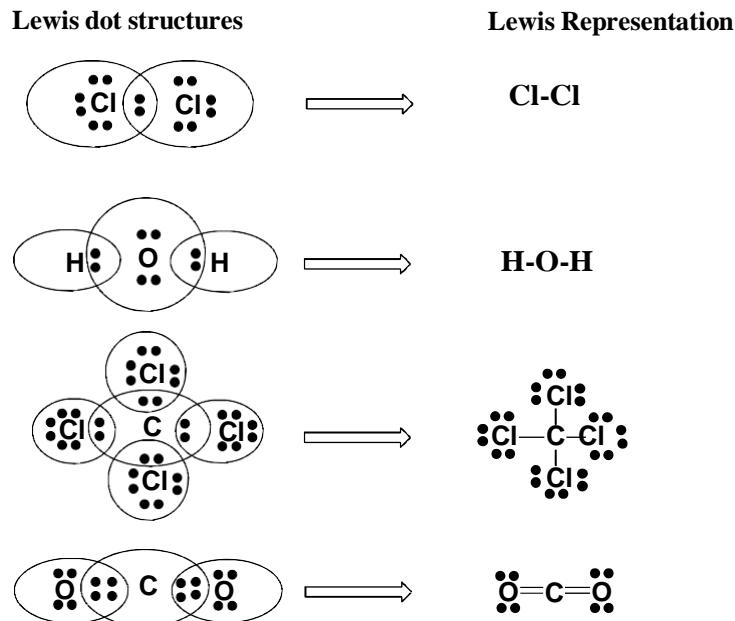
Lewis symbols:

Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols.

Ex:



Lewis dot structures:



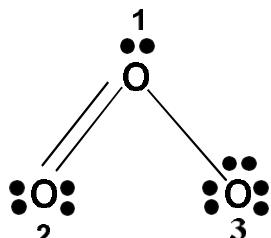
Draw the Lewis dot structures for below given molecules:

- i) Ethylene (C_2H_4)
- ii) Ethyne (C_2H_2)
- iii) N_2
- iv) O_2
- v) H_2
- vi) NH_3
- vii) HNO_3
- viii) CO_3^{2-}
- ix) O_3

Formal Charge:

$$\text{Formal charge on an atom in a Lewis structure} = \left[\begin{array}{l} \text{total number of valence electrons in} \\ \text{the free atom} \end{array} \right] - \left[\begin{array}{l} \text{total number of non-bonding (lone} \\ \text{pair) electrons} \end{array} \right] - \left(\frac{1}{2} \right) \left[\begin{array}{l} \text{total number of bonding (shared)} \\ \text{electrons} \end{array} \right]$$

Ex: Ozone (O_3):



Formal charge on oxygen atom marked as 1 = $6 - 2 - \frac{1}{2}(6) = +1$

Formal charge on oxygen atom marked as 2 = $6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on oxygen atom marked as 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Octet rule:

Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as octet rule.

Significance:

- 1) It is the basis of electronic theory of valency.
- 2) It explains the chemical inactivity of zero group elements.
- 3) It is useful for understanding the structure of most of organic compounds.

Limitations of the octet rule:

1) The incomplete octet of the central atom:

In some compounds, the number of electrons surrounding the central is less than eight. This is especially the case with elements having less than four valence electrons.

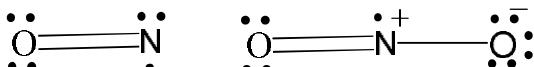
Ex: LiCl, BeH₂, BCl₃, BF₃.

Li : Cl H : Be : H

Li, Be and B have 1, 2 and 3 valence electrons.

2) Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide (NO), nitrogen dioxide (NO₂), the octet rule is not satisfied for all the atoms.

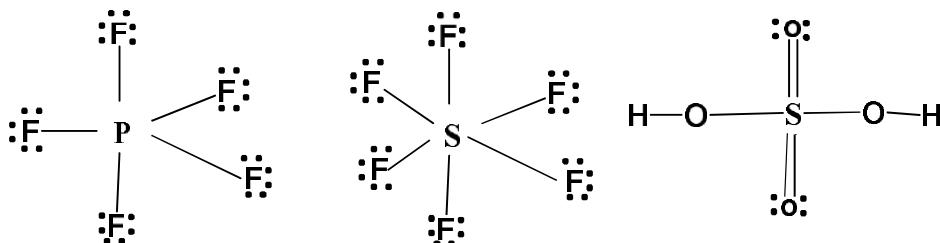


3) Expanded octet:

In some compounds, the number of electrons surrounding the central is more than eight.

This is termed as the expanded octet.

Ex: PF₅; SF₆ and H₂SO₄.



10 electrons around the P atom 12 electrons around the S atom 12 electrons around the S atom

Other drawbacks of octet theory:

- Octet rule is based upon the chemical inertness of noble gases. However, some noble gases (Ex: Xe and Kr) also combine with oxygen fluorine to form a number of compounds like XeF₂, KrF₂, XeOF₂ etc.
- This theory does not account for the shape of molecules.

- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

VSEPR Theory (Valence Shell Electron Pair Repulsion Theory):

This theory was proposed to explain the deviations in the bond angles of some molecules.

Postulates

- 1) The shape of molecule is determined by the repulsion between all the electron pairs present in the valence shell of central atom.
- 2) A lone pair of electrons occupies more space around the central atom than bond pair. Because lone pair is attracted to only one nucleus, but the bond pair is attracted by two nuclei.
Here repulsion between lone pairs is greater than bond pairs.
- 3) If the central atom contains only bond pairs then the shape of the molecule and bond angles will be according to the expected values.
- 4) If the central atom contains lone pairs, along with the bond pairs, then the shape of the molecule gets deviated from the expected values. This is due to repulsive forces between various electron pairs. The order of repulsion between various electron pairs:
(lone pair – lone pair) > (lone pair – bond pair) > (bond pair – bond pair)
- 5) The order of repulsion between various bonds: Triple bond > Double bond > Single bond
Ex: i) In BeCl_2 molecule there are two Be-Cl bonds.

The two bond pairs are arranged in the opposite directions.

The repulsive force between two bond pairs is negligible.

Therefore, the bond angle is 180° .

- i) In H_2O molecule, ‘O’ has two lone pairs. Here the expected bond angle is $109^\circ 28'$.
But it is reduced to $104^\circ 30'$ due to the repulsion between two LP-LP and LP-BP.
- ii) In CH_4 molecule, all the four electron pairs are ‘bond pairs’ only. Hence the shape of the molecule is tetrahedral with bond angle $109^\circ 28'$.

Valence Bond (VB) Theory:

This theory explains the shapes of covalent molecules as well as the directions of the bonds in them.

Postulates of VB Theory:

- 1) A covalent bond is formed by the overlapping of half-filled atomic orbital of one atom with half-filled atomic orbital of another atom.
- 2) The electrons involved in overlapping must have opposite spin.

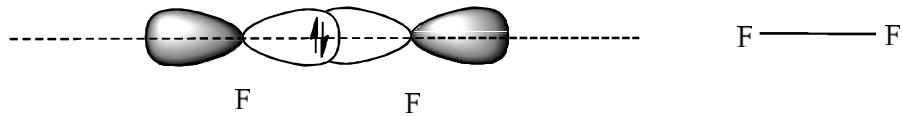
- 3) Except the bond pair of electrons, the remaining electrons do not lose their identity. Such electrons are called non-bonding electrons or lone-pair electrons.
- 4) Greater the extent of overlap, greater is the strength of covalent bond.
- 5) The direction of covalent bond lies in the direction of maximum overlapping side.
- 6) All atomic orbitals, except s-orbital, are directional. So the bonds formed due to their overlap are also directional. This determines the shape of the molecule.
- 7) A covalent bond formed by the axial overlap of atomic orbitals is called a sigma bond. Thus, inter nuclear axial (head-on) overlappings of s-s, s-p, p-p orbitals leads to the formation of σ bonds.
- 8) A covalent bond formed by the lateral or sidewise overlap of atomic orbitals called a π bond.
- 9) A sigma bond is always stronger than a π bond. This is because, during the formation of a sigma bond, the orbitals overlap along the inter nuclear axis hence the standard pair of electrons is concentrated just in between the nuclei. Where as in π bond formation the orbitals overlap laterally. The electron cloud is present, above and below the inter nuclear axis. Hence a sigma bond is always stronger than a π bond.
- 10) Formation of a π bond is possible only after the formation of a σ bond.
- 11) In the case of a double bond, there will be one σ bond and one π bond.
In the case of a triple bond, there will be one σ bond and two π bonds.

Examples:

- 1) **Formation of H₂ molecule:** Each hydrogen atom has one electron in 1s orbital. The 1s orbitals of 2 hydrogen atoms overlap axially to form a sigma bond between two H atoms.



- 2) **Formation of F₂ molecule:** fluorine has one half filled 2P_z orbital. The 2P_z orbitals of two fluorine atoms overlap axially to form a sigma bond between two F atoms.

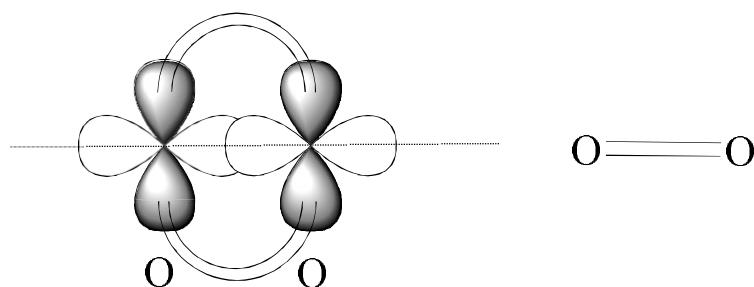


- 3) **Formation of O₂ molecule:**

The electronic configuration of oxygen is 1s² 2s² 2P_x² 2P_y¹ 2 P_z¹.

Oxygen has two half filled p orbitals. The 2P_y orbital of one atom overlap axially with 2P_y orbital of another O atom to form a sigma bond. The 2P_z orbitals of two oxygen

atoms overlap laterally to form a π bond. Thus a double bond with one strong σ bond and one weak π bond, is formed.



Hybridisation: The intermixing of atomic orbitals to form new hybrid orbitals is known as hybridization. The number of hybrid orbitals formed is equal to number of atomic orbitals mixed. There are different types of hybridizations involving s, p and d orbitals. They are sp, sp^2 , sp^3 , sp^3d ; sp^3d^2 hybridisations.

- 1) **sp hybridization:** The inter mixing of one s-orbital and one p-orbital of the outer most shell of an atom is called sp hybridisation.

In this process, we get two sp hybrid orbitals. The bond angle 180° and its shape is linear.

Ex: $BeCl_2$, CO_2 , C_2H_2 .

Formation of $BeCl_2$:

- i) In $BeCl_2$, the central atom is Be.
- ii) The electronic configuration of Be in the ground state is $1s^2 2s^2$.
- iii) The electronic configuration of Be in the excited state is $1s^2 2s^1 2p_x^1 2p_y^0 2p_z^0$.
- iv) In the excited state, the central Be atom undergoes sp hybridisation and forms two sp hybrid orbitals.
- v) The two sp-orbitals of Be overlap with p-orbitals of two Cl atoms and they form two σ bonds.
- vi) The bond angle is 180° and shape of the $BeCl_2$ is Linear.



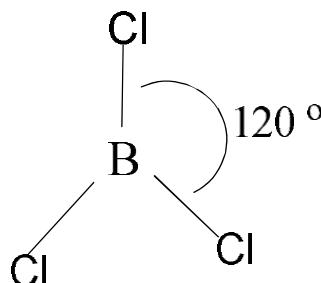
- 2) **Sp^2 hybridisation:** The inter mixing of one s-orbital and two p-orbitals of the outer most shell of an atom is called sp^2 hybridisation.

In this process, we get three sp^2 hybrid orbitals. The bond angle is 120° and shape is Trigonal planar. Ex: BCl_3 , BF_3 , C_2H_4 .

Formation of BCl_3 :

- i) In BCl_3 , the central atom is B.
- ii) The electronic configuration (E.C) of B in the ground state $1s^2 2s^2 2p^1$.
- iii) The E.C of B in the excited state is $1s^2 2s^1 2p^1 2p_y^1 2p_z^0$.

- iv) In the excited state, the central B atom undergoes sp^2 hybridisation and forms three sp^2 hybrid orbitals, each having single electron.
- v) The three sp^2 orbitals of B overlap with half filled p_z orbitals of three Cl atoms in a head-on position and they form three σ bonds.
- vi) The bond angle is 120° and shape of the BCl_3 molecule is trigonal planar.

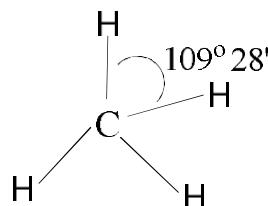


- 3) **Sp^3 hybridisation:** The inter mixing of one s-orbital and three p-orbitals of the outer most shell of an atom is called sp^3 hybridisation.

Here, we get four sp^3 hybrid orbitals. The bond angle is $109^\circ 28'$ and shape is Tetrahedral.
Ex: CH_4 , H_2O .

Formation of CH_4 :

- i) In CH_4 , the central atom is Carbon (C).
- ii) The electronic configuration of C in the ground state is $1s^2 2s^2 2p^2$.
- iii) The electronic configuration of C in the excited state is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$.
- iv) In the excited state, the central C atom undergoes sp^3 hybridisation and forms four sp^3 hybrid orbitals, each having single electron.
- v) The four sp^3 orbitals of C overlap with half filled s-orbitals of four H atoms in a head-on position and they form four σ bonds.
- vi) The bond angle is $109^\circ 28'$ and shape of the CH_4 molecule is Tetrahedral.



- 4) **Sp^3d hybridisation:** The inter mixing of one s-orbital, three p-orbitals and one d-orbital of the outer most shell of an atom is called sp^3d hybridisation.

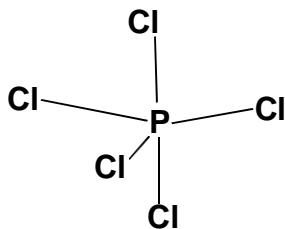
Here, we get five sp^3d hybrid orbitals.

Ex: PCl_5 . shape is Trigonal bipyramidal.

Formation of PCl_5 :

- i) In PCl_5 , the central atom is phosphorous (P).
- ii) The electronic configuration of P in the ground state is $1s^2 2s^2 2p^6 3s^2 3p^3$.

- iii) The electronic configuration of P in the excited state is $1s^2 2s^2 2p^6 3s^1 3p_x^1 3p_y^1 3p_z^1 3d^1$.
- iv) In the excited state, the central P atom undergoes sp^3d hybridisation and forms five sp^3d hybrid orbitals, each having single electron.
- v) The five sp^3d orbitals of P overlap with half filled s-orbitals of five Cl atoms and they form five σ bonds.
- vi) The shape of the PCl_5 molecule is Trigonal bipyramidal.



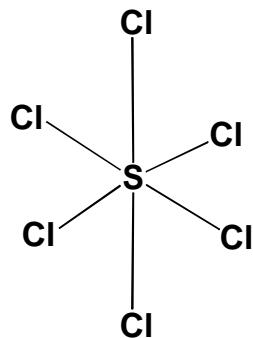
- 5) **Sp^3d^2 hybridisation:** The inter mixing of one s-orbital, three p-orbitals and two d-orbital of the outer most shell of an atom is called sp^3d^2 hybridisation.

Here, we get six sp^3d^2 hybrid orbitals.

Ex: SF_6 . Shape is Octahedral.

Formation of SF_6 :

- i) In SF_6 , the central atom is sulphur (S).
- ii) The electronic configuration of S in the ground state is $1s^2 2s^2 2p^6 3s^2 3p^4$.
- iii) The electronic configuration of S in the excited state is $1s^2 2s^2 2p^6 3s^1 3p_y^1 3p_z^1 3d^2$.
- iv) In the excited state, the central S atom undergoes sp^3d^2 hybridisation and forms six sp^3d^2 hybrid orbitals, each having single electron.
- v) The six sp^3d orbitals of S overlap with half filled s-orbitals of six F atoms and they form six σ bonds.
- vi) The shape of the SF_6 molecule is Octahedral.



Molecular Orbital (MO) Theory:

MO Theory was proposed by Hund and Mulliken. It is explained by LCAO (Liner Combination of Atomic Orbitals) method.

Salient Features of MO Theory:

- 1) The molecular orbitals are formed when the atomic orbitals of nearly equal energies combined linearly.
- 2) Only such atomic orbitals which are of symmetry with respect to the inter nuclear axis combine to form molecular orbitals.
- 3) The total number of molecular orbitals formed is equal to the total number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is called bonding molecular orbital while the other is called anti-bonding molecular orbital.
- 4) Molecular orbital having lesser energy than atomic orbitals are called bonding molecular orbitals and they are represented by σ and π .
- 5) Molecular orbitals having higher energy than atomic orbitals are called anti-bonding molecular orbitals and they are represented by σ^* and π^* .
- 6) The order of energies of bonding, anti-bonding and non-bonding orbitals:
Bonding orbitals < Non-bonding orbitals < Anti-bonding orbitals.
- 7) A molecular orbital is polycentric whereas an atomic orbital is monocentric.
- 8) The shapes of the molecular orbitals depend on the shapes of atomic orbitals.
- 9) Filling up of electrons in the molecular orbitals is done according to Hund's rule, Paulis exclusion principle and Aufbau principle.
- 10) MO Theory successfully explained the magnetic nature of molecules.
- 11) MO Theory is useful to calculate the bond order (number of bonds between atoms) of molecules.

Hydrogen bond:

The week electrostatic force of attraction between hydrogen atom of one molecule and most electronegative atom of another molecule (or) same molecule is called hydrogen bond.

Condition for formation of hydrogen bond:

- 1) The size of electronegative atom should be small.

- 2) The electronegativity of the atom to which hydrogen is attached should be high.

Strength of hydrogen bond:

The strength of hydrogen bond is between 5-10K Cal/mol. It is, thus weaker than a covalent bond and stronger than Vander waals force of attraction.

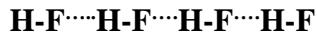
Types of Hydrogen bonds:

- 1) Inter molecular Hydrogen bond
- 2) Intra molecular Hydrogen bond

1) Inter molecular Hydrogen bond :

Hydrogen bond formed between two different molecules is called inter molecular hydrogen bond.

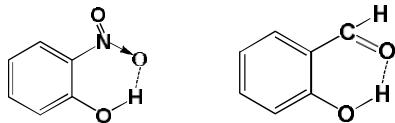
Ex: The bonds presents in NH_3 , H_2O , HF.



2) Intra molecular Hydrogen bond:

A hydrogen bond formed within the same molecule is called intra molecular hydrogen bond.

Ex: the bonds present in Orthoitrophenol, Orthohydroxy benzaldehyde.



Questions

- 1) Define hybridization? Explain the types of hybridisation involving s and p orbitals with one example each.
- 2) Give an account VSEPR theory and its applications.
- 3) Give an account VB theory and its applications.
- 4) Explain the structure and hybridization of a) BeCl_2 ; b) BCl_3 ; c) BF_3 ; d) Methane e) PCl_5 ; f) SF_6 .
- 5) Explain the hybridization of a) Ethane; b) Ethene and c) Ethyne.
- 6) Write the salient features of MO Theory.
- 7) Give the MO Energy diagram of a) H_2 ; b) C_2 ; c) N_2 ; d) O_2 ; e) O_2^+ ; f) O_2^- ; g) O_2^{2-} molecules. Calculate the respective bond order. Write the magnetic nature of N_2 and O_2 molecules.
- 8) What is Hydrogen bond? Explain different types of hydrogen bonds with examples.
- 9) Write the differences between σ and π bonds

Gaseous State

Ideal gas equation:

The ideal gas equation is derived from Boyle's law, Charles law, Avogadro's law.

Let V = volume, P = Pressure, T = Absolute temperature and n = no of moles of an ideal gas.

- 1) **Boyle's law (Pressure – Volume relationship):** "At constant temperature, the volume of a given mass of gas is inversely proportional to its pressure".

Thus, $V \propto 1/p$ (at constant T , n) ----- (1)

$$\Rightarrow V = K(1/p)$$

$$\Rightarrow PV = K = \text{constant}$$

$$\Rightarrow P_1V_1 = P_2V_2 = K = \text{constant}$$

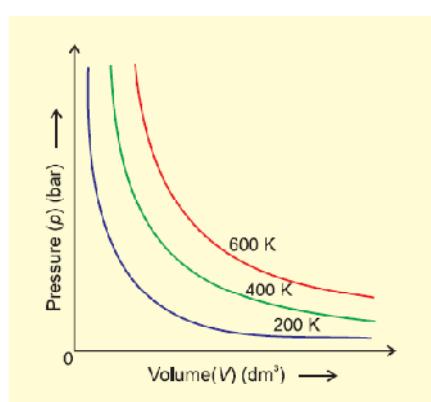


Fig. 5.5(a) Graph of pressure, p vs. Volume, V of a gas at different temperatures.

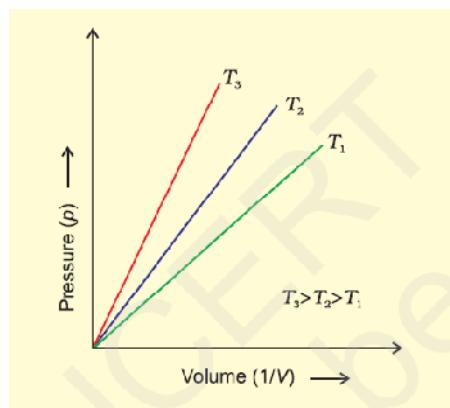


Fig. 5.5 (b) Graph of pressure of a gas, p vs. $\frac{1}{V}$

- 2) **Charles law (Volume - Temperature relationship):** "At constant pressure, the volume of a given mass of gas is directly proportional to its absolute temperature".

Thus, $V \propto T$ (at constant n , p) ----- (2)

$$V = K T$$

$$\Rightarrow V/T = K = \text{constant}$$

$$\Rightarrow V_1/T_1 = V_2/T_2 = K = \text{constant}$$

$$\Rightarrow V_1/V_2 = T_2/T_1 = K = \text{constant}$$

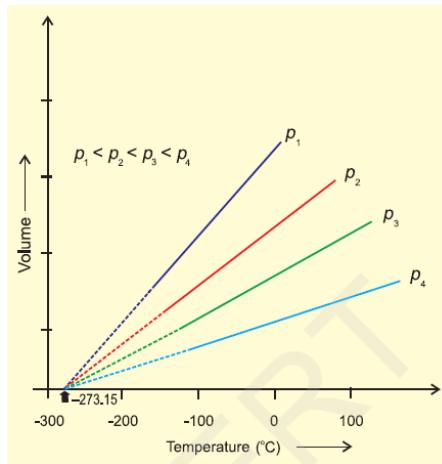


Fig. 5.6 Volume vs Temperature (°C) graph

3) Avogadro's law (Volume – Amount relationship): “At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles”.

Thus, $V \propto n$ (at constant p, T) ----- (3)

$$V = K n$$

We know that, $n = m/M$ (since, m = mass of gass and M = molecular weight of gas)

$$\Rightarrow V = K m/M = \text{constant}$$

$$\Rightarrow M = K m/V = K = \text{constant}$$

$$\Rightarrow M = K d$$

Combining the equations (1), (2) and (3),

$$\Rightarrow \text{We get, } V \propto 1/p \cdot T \cdot n$$

$$\Rightarrow V = R \cdot 1/p \cdot T \cdot n$$

$$\Rightarrow pV = nRT$$

The above equation is called ‘ideal gas equation’ or ‘equation of state’.

In the ideal gas equation, R is called gas constant and it is independent of the amount of gas.

Value of gas constant R: the value of gas constant ‘R’ is same for all gases. So it is called as ‘Universal Gas constant’.

The value of gas constant depends on units of pressure and volume.

Ex: $R = 0.0821 \text{ lit. atm. mole}^{-1} \text{K}^{-1}$.

$$= 8.314 \times 10^7 \text{ ergs. mol}^{-1} \text{ K}^{-1}$$

$$= 8.314 \text{ J. mol}^{-1} \text{ K}^{-1}$$

$$= 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$$

Gay Lussac's law (Pressure – Temperature relationship): “At constant volume, the pressure of a mass of gas is directly proportional to its absolute temperature”.

Thus, $p \propto T$ (at constant V, n) ----- (3)

$$p = K T$$

$$p/T = K = \text{Constant}$$

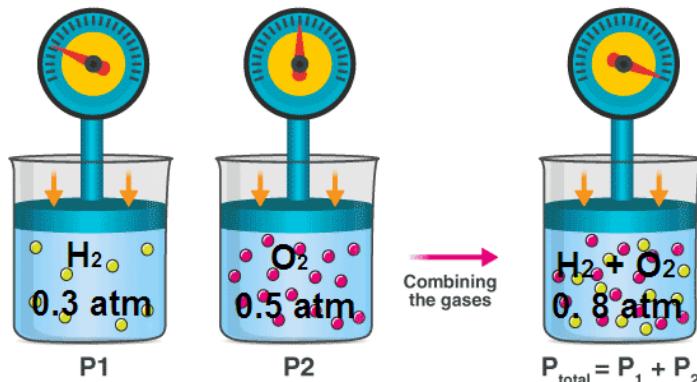
Dalton's law of partial pressure:

"At constant temperature, the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of all the components gases".

Therefore, total pressure, $P_{\text{total}} = p_1 + p_2 + p_3 + \dots + p_n$.

Explanation:

Let 3 vessels of equal volumes are taken and attached with 'manometers'. Let n_1 moles of hydrogen and n_2 moles of oxygen are taken in the first and second vessels respectively. Let the pressure exerted by hydrogen and oxygen be 0.3 atm and 0.5 atm. respectively. These two gases are send into third vessel of same volume. Then the total pressure of the gaseous mixture is found to be 0.8 atm. That means the total pressure exerted by the gaseous mixture is equal to the sum of individual pressures of the gases.



Relation between partial pressure and mole fraction:

The number of moles of the three gases are n_1 , n_2 and n_3 .

From the Ideal gas equation, we have

$$\text{Partial pressure of the first gas } p_1 = n_1 RT/V \quad \dots \dots \dots (1)$$

$$\text{Partial pressure of the second gas } p_2 = n_2 RT/V \quad \dots \dots \dots (2)$$

$$\text{Partial pressure of the third gas } p_3 = n_3 RT/V \quad \dots \dots \dots (3)$$

From the Dalton's law of Partial pressures, total pressure of the mixture is

$$\begin{aligned} P_{\text{total}} &= p_1 + p_2 + p_3 = n_1 RT/V + n_2 RT/V + n_3 RT/V \\ &= (n_1 + n_2 + n_3) RT/V = n RT/V \quad \dots \dots \dots (4) \end{aligned}$$

Here n = total number of moles of mixture

From (1) and (4) we get $p_1/p = n_1 RT/V / n RT/V = n_1/n = X_1$

Here X_1 = mole fraction of first gas.

Therefore, $p_1 = X_1 p$

Similarly we get $p_2 = X_2 p$ and $p_3 = X_3 p$

Conclusion: partial pressure of a gas in the gaseous mixture is equal to the product of its mole fraction and total pressure of mixture.

Postulates of kinetic molecular theory of gases:

- 1) Every gas contains large number of tiny particles called molecules.
 - 2) The gas molecules move randomly in all directions with high velocities.
 - 3) There will be no attractive or repulsive forces among gas molecules.
 - 4) There will be no effect of gravitational force on the movement of gas molecules.
 - 5) The total volume of gas molecules is negligible when compared to the entire volume of the container.
 - 6) Pressure of gas is due to collisions of the gas molecules on the walls of the container.
 - 7) All collisions are perfectly elastic.
- On the basis of above assumptions, the kinetic gas equation is $PV = 1/3 mnC^2$
- 8) The average kinetic energy of a gas is directly proportional to the absolute temperature.
Thus, $KE \propto T$.

From this equation we deduce various gas laws mathematically,

The average kinetic energy of a gas molecule is given by $KE = 1/2 mC^2$

Where m = mass of the molecule and C = velocity

The quantity C^2 is called mean square velocity; it is the average of the squares of the speeds of all the molecules:

$$C^2 = C_1^2 + C_2^2 + C_3^2 + C_4^2 + \dots + C_n^2/n$$

Where, n = number of molecules and C_1, C_2, C_3, \dots are velocities of first, second and third.....gas molecules

From above,

$$\begin{aligned} KE &\propto T \\ \frac{1}{2} mC^2 &\propto T \\ \frac{1}{2} mC^2 &= kT \end{aligned}$$

Where k = proportionality constant and T = Absolute temperature

- 1) Boyle's law:

According kinetic gas equation,

$$PV = 1/3 mnC^2$$

$$PV = 2/2(1/3 mnC^2)$$

The kinetic energy of ' n ' molecules of the gas = $1/2 mnC^2$

We know that, $1/2 mnC^2 = kT$

Therefore, $PV = 2/3 kT$

At constant temperature (T), $PV = \text{Constant}$, this is Boyle's law.

- 2) Charles law:

$$PV = 2/3 kT$$

$$V = 2/3 kT/P$$

At constant pressure, $V = \text{constant} \times T$ or $V \propto T$, (because n, P are constants). This is Charles law.

Deviations from ideal behavior:

It is identified that real gases deviation from gas laws are more at high pressures and low temperatures.

van der Waals suggested that these deviations are due to the following two wrong assumptions in the kinetic theory of gases.

- i) Actual volume of the gas molecules is negligible as compared to the total volume of the container.
- ii) Intermolecular attractions are absent in gases.

van der Waals pointed out that in the case of real gases, molecules do have a volume and also exert intermolecular attractions particularly when the pressure is high and temperature is low.

He made two corrections. a) Volume correction; b) Pressure correction

a) Volume correction:

van der Waals assumed that molecules of a real gases are rigid spherical particles which possess a definite volume. Thus, the volume of a real gas, i.e., volume available for compression or movement is, therefore, actual volume minus the volume occupied by gas molecules. If b is the effective volume of the molecules per mol of the gas, the ideal volume for the gas equation is $(V-b)$ and not V , i.e.,

Corrected volume ' V_i ' = $V - b$ for one mole of the gas

For n mole of the gas, ' V_i ' = $V - nb$.

b is termed the excluded volume which is constant and characteristic for each gas.

b) Pressure correction:

A molecule in the interior of the gas is attracted by other molecules on all sides. These forces, thus, are not effective, as equal and opposite forces cancel each other. However, a gas molecule which is just going to collide the wall of the container experiences an inward pull due to unbalanced attractive forces. Therefore, it collides the wall with less momentum and the observed pressure will be less than the ideal pressure.

$$P_{\text{ideal}} = P_{\text{obs}} + P^1$$

Where, P^1 is the pressure correction.

Pressure correction depends upon two factors.

- i) The attractive force exerted on a single molecule about to collide the wall is proportional to the number of molecules per unit volume in the bulk of the gas.
- ii) The number of molecules striking the wall which is also proportional to the number of molecules per unit volume of the gas.

The above two factors are proportional to the density of the gas. Therefore, the attractive force is proportional to the square of the density of the gas.

$P^1 \propto$ total attractive force

$$\propto d^2$$

$$\propto 1/V^2$$

$$P^1 = a/V^2$$

Where a is the constant depending upon the nature of the gas and V is the volume of the one mole of the gas.

Hence, corrected pressure, $P_{\text{ideal}} = P_{\text{obs}} + a/V^2$

Therefore, the gas equation $PV = RT$ can be written as

$$\left[P + \frac{a}{V^2} \right] (V - b) = RT$$

This equation is known as van der Walls equation for one mole of gas.

Similarly, for van der Walls gas equation for n moles of gas is,

$$\left[P + \frac{n^2 a}{V^2} \right] (V - nb) = nRT$$

The constants ‘ a ’ and ‘ b ’ are called van der Walls constants and they are characteristic of each gas.

Types of Molecular velocities:

R.M.S. velocity (C):

It is the square root of mean of squares of velocities of the molecules present in the gas. It is represented by 'C'. RMS velocity of gas molecules is the square root value of the ratio of the sum of the squares of velocities of all the molecules to the total number of molecules.

$$C = \sqrt{\frac{C_1^2 + C_2^2 + C_3^2 + \dots + C_n^2}{n}}$$
$$C_{RMS} = \sqrt{\frac{3 RT}{M}}$$

In the expression, if the value of R used is $8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$, the units of 'C' will be in cm s^{-1} and if the value of R used is $8.314 \text{ joule mol}^{-1} \text{ K}^{-1}$, the units of 'C' will be in ms^{-1} and M is in kg mol^{-1}

$$\boxed{C_{RMS} = \sqrt{\frac{3 RT}{M}}}$$
$$= \sqrt{\frac{3 PV}{M}} = \sqrt{\frac{3 P}{d}}$$

$$\text{Since, } \frac{V}{M} = \frac{\text{Gram molar volume}}{\text{Gram molecular mass}} = \frac{1}{(\text{density})}$$

$$\therefore C_{RMS} = \sqrt{\frac{3 p}{d}}$$

Average velocity (\bar{C}):

Average velocity of gas molecules is the ratio of the sum of the velocities of gas molecules to the total number of molecules. It is the average of the velocities of the molecules in a gas.

$$\bar{C} = \left[\frac{C_1 + C_2 + C_3 + \dots + C_n}{n} \right]$$

Where $C_1, C_2, C_3, \dots, C_n$ are the individual velocities of molecules. The average velocity (\bar{C}) is calculated as follows.

$$\bar{C} = \sqrt{\frac{8 RT}{\pi M}} = \sqrt{\frac{8 PV}{\pi M}} = \sqrt{\frac{8 P}{\pi d}}$$

Also average velocity $\bar{C} = 0.9213 \times$ RMS velocity.

Most probable velocity (C_p):

It is the velocity possessed by the maximum number of molecules present in the gas. It is represented by ' C_p ' and calculated as follows

$$C_p = \sqrt{\frac{2 RT}{M}} = \sqrt{\frac{2 PV}{M}} = \sqrt{\frac{2 P}{d}}$$

Most probable velocity $C_p = 0.923 \times$ RMS velocity.

Ratio of the molecular velocities:

The ratio of the three types of molecular velocities can be calculated from the relation

$$C_p : \bar{C} : C = \sqrt{\frac{2 RT}{M}} : \sqrt{\frac{8 RT}{\pi M}} : \sqrt{\frac{3 RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$C_p : \bar{C} : C_{RMS}$$

$$= 1 : 1.128 : 1.224$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= \sqrt{2} : \sqrt{\frac{8 \times 7}{22}} : \sqrt{3} = 1.000 : 1.128 : 1.224$$

Stoichiometry

Mole:

The amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the ^{12}C isotope.

One mole of carbon weighs 12 g,
the number of atoms in it is =

$$\frac{12 \text{ g/mol } ^{12}\text{C}}{1.992648 \times 10^{-23} \text{ g}/^{12}\text{C atom}} \\ = 6.0221367 \times 10^{23} \text{ atoms/mol}$$

It is known as 'Avogadro constant', or Avogadro number denoted by NA.

We can, therefore, say that 1 mol of hydrogen atoms = 6.022×10^{23} atoms

1 mol of water molecules = 6.022×10^{23} water molecules

1 mol of sodium chloride = 6.022×10^{23} formula units of sodium chloride

Molecular mass (Molecular weight):

Molecular weight or molecular mass of a molecule of a substance is the sum of the atomic weights or atomic masses of all atoms present in the molecule.

Ex: C_2H_6 molecule

$$2(12.01 \text{ amu}) + 6(1.008 \text{ amu}) = [24.02 + 6.048] \text{ amu} = 30.068 \text{ amu.}$$

Similarly molecular weights or molecular masses of other molecules can be calculated.

Ex:

Sno	Molecule	Molecular Mass
1	HCl	36.5 g/mol
2	H_2SO_4	98 g/mol
3	HNO_3	63 g/mol
4	NaOH	40 g/mol
5	KOH	56 g/mol
6	H_3PO_4	98 g/mol

Atomic mass:

The mass of an atom is known atomic mass. Hydrogen, mass was arbitrarily assigned a mass of 1 (without any units) and other elements were assigned masses relative to it.

Carbon-12 is one of the isotopes of carbon and can be represented as ^{12}C . In this system, ^{12}C is assigned a mass of exactly 12 atomic mass unit (amu) and masses of all other atoms are given relative to this standard.

One atomic mass unit (1 amu) is defined as a mass exactly equal to one-twelfth of the mass of one carbon – 12 atom.

And 1 amu = 1.66056×10^{-24} g

Mass of an atom of hydrogen = 1.6736×10^{-24} g

Thus, in terms of amu, the mass of hydrogen atom = 1.6736×10^{-24} g / 1.66056×10^{-24} g

$$= 1.0078 \text{ amu}$$

$$= 1.0080 \text{ amu}$$

At present, 'amu' has been replaced by 'u', which is known as unified mass.

When we use atomic masses of elements in calculations, we actually use *average atomic masses of elements*.

Concept of equivalent weight:

Equivalent weight: "a number which denotes the number of parts by weight of the element required to combine with or displace 8 parts by weight of oxygen, 1.008 parts by weight of hydrogen or 35.5 parts by weight of chlorine."

There is a simple relationship between the atomic weight of an element and its equivalent weight.

Suppose one atom of an element 'A' combines with 'n' atoms of hydrogen. The hydride formed has the formula AH_n .

We know the atomic weight of hydrogen is 1.008. Let the atomic weight of the element 'A' be x. According to the above formula, an atom of 'A', weighing x, combines with $n \times 1.008$ parts by weight of hydrogen to form the hydride. Then by definition, the equivalent weight of 'A' is (x/n) .

Where x = mass of an atom of A.

$$\frac{\text{Atomic weight of A}}{\text{Equivalent weight of A}} = \frac{x}{(x/n)} = n.$$

This is the valency of the element 'A'. Similarly it can be deduced for any element.

$$\frac{\text{Atomic weight of the element}}{\text{Equivalent of the element}} - \text{Valency of the element.}$$

The valency of an element may vary, though the atomic weight of the element is constant. Hence, the same element may possess more than one equivalent weight.

Ex:

$$\text{Equivalent weight of iron in ferrous compounds} = \frac{\text{At.wt of Fe}}{\text{valency}} = \frac{55.84}{2} = 27.92$$

$$\text{Whereas its equivalent weight in ferric compounds is } \frac{55.84}{3} = 18.613$$

Radicals too possess equivalent weights. A radical behaves like an element. Hence, the equivalent weight of a radical is equal to its molecular weight divided by its valency.

$$\text{Sulphate radical } (\text{SO}_4^{2-}) \text{ has an equivalent weight} = \frac{\text{mass of the radical}}{\text{valency}} = \frac{96}{2} =$$

48

The equivalent weight of an element or radical expressed in grams is called gram equivalent weight.

Thus gram equivalent weight of oxygen is 8 g.

The gram equivalent weight of carbonate radical is $60/2$ g = 30 g.

Calculation of equivalent weights of substances:

The equivalent weights can be calculated not only for elements but for compounds also. The compounds may be considered as acids, bases, salts, oxidants or reductants for the present calculations.

1. Equivalent weights of acids:

"The number of hydrogen (H) atoms, in a molecule of the acid, which can be displaced by metal ions is known as basicity of the acid".

$$\text{Equivalent weight of an acid} = \frac{\text{Mol. Wt. or Formula Wt of acid}}{\text{Basicity of the acid}}$$

S.N o	Name of the acid	Mol. Formul a of acid	No. of displaceab le hydrogens 'n'	Equivalent weight calculated = [Mol.Wt/n]	Equivalent weight
1	Hydrochloric acid	HCl	1	$\left[\frac{\text{Mol. Wt. of HCl}}{1} \right]$	$\left[\frac{35.5 + 1.008}{1} \right] = 36.58$
2	Nitric acid	HNO ₃	1	$\left[\frac{\text{Mol. Wt. of HNO}_3}{1} \right]$	$\left[\frac{1.008 + 14 + 48.0}{1} \right] = 63.008$
3	Sulphuric acid	H ₂ SO ₄	2	$\left[\frac{\text{Mol. Wt. of H}_2\text{SO}_4}{2} \right]$	$\left[\frac{2.016 + 32 + 64}{2} \right] = \left[\frac{98.016}{2} \right] = 49.008$
4	Phosphoric acid	H ₃ PO ₄	3	$\left[\frac{\text{Mol. Wt. of H}_3\text{PO}_4}{3} \right]$	$\left[\frac{3 + 30 + 64}{3} \right] = \left[\frac{97.0}{3} \right] = 32.33$
5	Phosphorous acid	H ₃ PO ₃	2	$\left[\frac{\text{Mol. Wt. of H}_3\text{PO}_3}{2} \right]$	$\left[\frac{3 + 30 + 48}{2} \right] = \left[\frac{81.0}{2} \right] = 40.50$

Fig: Some common acids – their equivalent weights

Even though there are three hydrogen atoms in H₃PO₄. Only two of them can be displaced by metal ions. Hence, the basicity of H₃PO₄ is 2.

2. Equivalent weights of bases:

In chemistry generally one sees Arrhenius acids. And frequently bases of this type contain hydroxyl groups.

Example:

NaOH, KOH, Ba(OH)₂ etc.

"The number of hydroxyl groups present in a molecule of the Arrhenius base" is known as its acidity of the base. Each OH group unites with one equivalent weight of hydrogen (i.e. one hydrogen ion) that means the weight of one OH group is the same as its equivalent weight. From this we know that the number of parts by weight of a base containing the

weight of one OH group is equivalent weight of the base. If there are 'n' OH groups in one molecule of a base, then the equivalent weight of the base can be written as follows;

$$\text{Equivalent weight of a base} = \frac{\text{Mol. Wt. or Formula Wt. of a base}}{\text{'acidity' or 'n'}}$$

S.N o	Name of the base	Mol. Formul	No. of displaceab	Equivalent weight calculated =	Equivalent weight
a of base		le base 'n'		[Mol.Wt of base/n]	
1	Sodium hydroxide	NaOH	1	$\left[\frac{\text{Mol. Wt. of NaOH}}{1} \right]$	$\left[\frac{23 + 16 + 1}{1} \right] - 10.0$
2	Potassium hydroxide	KOH	1	$\left[\frac{\text{Mol. Wt. of KOH}}{1} \right]$	$\left[\frac{39 + 16 + 1}{1} \right] = 56.0$
3	Calcium hydroxide	Ca(OH) ₂	2	$\left[\frac{\text{Mol. Wt. of Ca(OH)2}}{2} \right]$	$\left[\frac{40 + 2(16 + 1)}{2} \right] - \left[\frac{74}{2} \right] = 37$
4	Barium hydroxide	Ba(OH) ₂	2	$\left[\frac{\text{Mol. Wt. of Ba(OH)2}}{2} \right]$	$\left[\frac{137 + 2(16 + 1)}{2} \right] = \left[\frac{171}{2} \right] = 85.5$

iii. Equivalent weight of a salt

Equivalent weight of a salt is given by the formula

$$E = \frac{\text{Molecular weight of the salt}}{[(\text{total no. of the charges on cations}) \text{ or } (-\text{ve charges on anions})]}$$

S.no:	Name of the salt	Formula of the salt	Total No. of +ve charges on cations	Equivalent weight of the salt = $\frac{\text{Mol.wt. of the salt}}{\text{No. of + ve charges on the cations}}$
1	Sodium chloride	NaCl	1	$\text{Mol. wt. /1} = \frac{58.5}{1} = 58.5$
2	Sodium carbonate	Na ₂ CO ₃	2	$\text{Mol. wt. /2} = \frac{106}{2} = 53.0$
3	Calcium phosphate	Ca ₃ (PO ₄) ₂	-6	$\text{Mol. wt. /6} = \frac{310}{6} = 51.6$

Balancing Chemical Equations

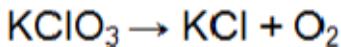
Suppose we want to write an equation to describe a chemical reaction.

- The first step is to identify the reactants and products.
- The next step is to write their chemical formulas.
- We assemble them in the conventional sequence- reactants on the left separated by an arrow from products on the right.
- The equation written at this point is likely to be *unbalanced chemical equation (skeleton equation)*; that is the number of each type of atom on one side of the arrow differs from the number on the other side.

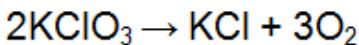
For balancing the equation,

- We look for elements that appear only once on each side of the equation with the same number of atoms on each side: The formula containing these elements must have the same coefficient.
- Next, look for elements that appear only once on each side of the equation but in unequal number of atoms. Balance these elements.
- Finally, balance elements that appear in two or more formulas on the same side of the equation.

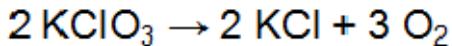
Example 1:



All three components (K, Cl, and O) appear only once on either side of the equation, but only for K and Cl do we have equal numbers of atoms on both sides. Thus, KClO_3 and KCl must have the same coefficient. The next step is to make the number of O atoms the same on both sides of the equation. Then, to balance oxygen atoms, we write;



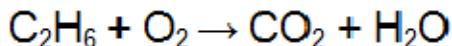
Now K and Cl become unbalanced. Therefore we balance the K and Cl atoms.



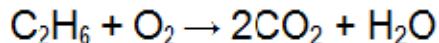
Example 2:

The combustion of the ethane (C_2H_6) in oxygen or air, which yields carbon dioxide (CO_2) and water.

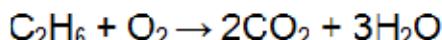
The unbalanced equation is



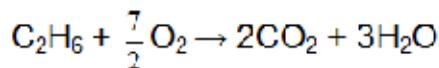
We see that the number of atoms for any of the elements (C, H, and O) is not the same on both sides of the equation. In addition, C and H appear only once on each side of the equation; O appears in two compounds on the right side (CO_2 and H_2O). To balance the C atoms, we place a 2 in front of CO_2 :



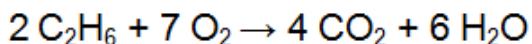
To balance H atoms, we place 3 in front of H_2O :



At this stage, the C and H atoms are balanced, but the O atoms are not balanced because there are seven O atoms on the right-hand side and only two O atoms on the left-hand side of the equation. This inequality of O atoms can be eliminated by writing $\frac{7}{2}$ in front of the O_2 on the left-hand side:

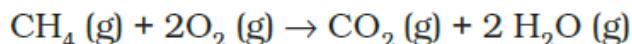


The equation is now balanced. However, we normally prefer to express the coefficients as whole numbers rather than as fractions. Therefore, we multiply the entire equation by 2:



We note that the coefficients used in balancing the last equation are the smallest possible set of whole numbers. And finally we get the balanced equation.

Relation between mass, moles and volumes:



- One mole of $\text{CH}_4(\text{g})$ reacts with two moles of $\text{O}_2(\text{g})$ to give one mole of $\text{CO}_2(\text{g})$ and two moles of $\text{H}_2\text{O}(\text{g})$.
- One molecule of $\text{CH}_4(\text{g})$ reacts with 2 molecules of $\text{O}_2(\text{g})$ to give one molecule of $\text{CO}_2(\text{g})$ and 2 molecules of $\text{H}_2\text{O}(\text{g})$.
- 22.7 L of $\text{CH}_4(\text{g})$ reacts with 45.4 L of $\text{O}_2(\text{g})$ to give 22.7 L of $\text{CO}_2(\text{g})$ and 45.4 L of $\text{H}_2\text{O}(\text{g})$.
- 16 g of $\text{CH}_4(\text{g})$ reacts with 2×32 g of $\text{O}_2(\text{g})$ to give 44 g of $\text{CO}_2(\text{g})$ and 2×18 g of $\text{H}_2\text{O}(\text{g})$.

$$\text{mass} \rightleftharpoons \text{moles} \rightleftharpoons \text{no. of molecules}$$

$$\frac{\text{Mass}}{\text{Volume}} = \text{Density}$$

Definition of Empirical formula:

An empirical formula represents the simplest whole number ratio of various atoms present in a compound.

If the mass per cent of various elements present in a compound is known, its empirical formula can be determined.

Ex: Glucose empirical formula is CH_2O

Acetic acid empirical formula is CH_2O

Definition of molecular formula:

- The molecular formula shows the exact number of different types of atoms present in a molecule of a compound. Molecular formula can further be obtained, if the molar mass is known.

Ex: Glucose molecular formula is $\text{C}_6\text{H}_{12}\text{O}_6$

Acetic acid molecular formula is $\text{C}_2\text{H}_4\text{O}_2$

Stoichiometry

Module 5.3: Concept of Empirical and Molecular formulae of compounds

Empirical Formula:

We can determine the empirical formula of a compound if we know its percent composition. This enables us to identify compounds experimentally. The procedure is as follows.

The empirical formula of a compound gives the simplest ratio of the number of atoms of different elements present in one molecule of the compound. It does not give the actual number of atoms of different elements present in one molecule of the compound.

“Empirical formula of a compound is the simplest formula showing the relative number of atoms of different elements present in one molecule of the compound”.

Example:

1. Empirical formula of ethene (ethylene) is CH_2 . The ratio of atoms of carbon to hydrogen in ethene is 1 : 2, which is the simplest ratio.

Molecular formula of ethene is C_2H_4 . This formula gives the actual number of carbon and hydrogen atoms present in one molecule of the compound.

There are many compounds that can have the empirical formula CH_2 . These include:

- C_2H_4 (ethene or ethylene) molecular mass=28.0 g/mol and n=2
- C_3H_6 (propene or propylene) molecular mass=42.0 g/mol and n=3
- C_3H_6 (cyclopropane) molecular mass=42.0 g/mol and n=3
- C_4H_8 (butene or butylene) molecular mass=56.0 g/mol and n=4
- C_4H_8 (cyclobutane) molecular mass=56.0 g/mol and n=4

2. Empirical formula of acetic acid: CH₂O

Molecular formula of acetic acid: C₂H₄O₂.

The empirical formula of a compound can be calculated by using the following steps:

1. Detect elements present in the compound
2. Find out experimentally, the percentage composition by weight of each element present in the compound
3. Divide the percentage of each element by its atomic weight to get the relative number of atoms of each element.
4. Divide each number obtained for the respective elements in step (3) by the smallest number among those numbers so as to get the simplest ratio.
5. If any number obtained in step (4) is not a whole number then multiply all the numbers by a suitable integer to get whole number ratio. This ratio will be the simplest ratio of the atoms of different elements present in the compound. Empirical formula of the compound can be written with the help of this ratio.

Example:

A carbon compound on analysis gave the following percentage composition, carbon 14.5 %, hydrogen 1.8 %, chlorine 64.46 %, oxygen 19.24 %. Calculate the empirical formula of the compound. (Atomic masses: C = 12; H = 1.0; Cl = 35.5; O=16)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 14.5	$\frac{14.5}{12} = 1.21$	$\frac{1.21}{1.20} = 1$
H = 1.8	$\frac{1.8}{1} = 1.8$	$\frac{1.8}{1.2} = 1.5$
Cl = 64.46	$\frac{64.46}{35.5} = 1.81$	$\frac{1.81}{1.2} = 1.5$
O = 19.24	$\frac{19.24}{16} = 1.2$	$\frac{1.2}{1.2} = 1$

Multiplication by a suitable integer, we get whole number ratio.

C H Cl O

(1×2) (1.5×2) (1.5×2) (1×2)

2 3 3 2

The simplest ratio of the atoms of different elements in the compound is:

$$\text{C : H : Cl : O} = 2 : 3 : 3 : 2$$

Therefore the empirical formula of the compound is C₂H₃Cl₃O₂.

Chemical analysis tells us the number of grams of each element present in a given amount of compound. Next, we can calculate the percentage composition of the given compound. Then, we find the empirical formula of the compound.

The same results can be obtained by following a different approach.

As a specific example, let us consider the compound ethanol. When ethanol is burned in an apparatus with an adequate input of oxygen through an inlet pipe, carbon dioxide (CO_2) and water (H_2O) are given off, and they are absorbed in CO_2 and H_2O absorbers, respectively. Because neither carbon nor hydrogen was in the inlet gas, we can conclude that both carbon (C) and hydrogen (H) were present in ethanol and that oxygen (O) may also be present. (Molecular oxygen was added in the combustion process, but some of the oxygen may also have come from the original ethanol sample.)

The masses of CO_2 and of H_2O produced can be determined by measuring the increase in mass of the CO_2 and H_2O absorbers, respectively.

Suppose that in one experiment the combustion of 11.5 g of ethanol produced 22.0 g CO_2 and 13.5 g of H_2O . We can calculate the mass of carbon and hydrogen in the original 11.5 g sample of ethanol as follows:

$$\text{mass of C} = 22.0 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 6.00 \text{ g C}$$

$$\text{mass of H} = 13.5 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 1.51 \text{ g H}$$

Thus 11.5 g of ethanol contains 6.00 g of carbon and 1.51 g of hydrogen. The remainder must be oxygen, whose mass is

$$\begin{aligned}\text{Mass of O} &= [\text{mass of sample} - (\text{mass of C} + \text{mass of H})] \\ &= [11.5 \text{ g} - (6.00 \text{ g} + 1.51 \text{ g})] = 4.0\end{aligned}$$

The number of moles of each element present in 11.5 g of ethanol is

$$\text{Moles of C} = 6.00 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.500 \text{ mol C}$$

$$\text{Moles of H} = 1.51 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 1.50 \text{ mol H}$$

$$\text{Moles of O} = 4.0 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.25 \text{ mol O}$$

The formula of ethanol can be written, therefore, as $\text{C}_{0.50}\text{H}_{1.5}\text{O}_{0.25}$.

Because the number of atoms must be an integer, we divide the subscripts by 0.25, the smallest of the subscripts, and obtain the empirical formula $\text{C}_2\text{H}_6\text{O}$.

Chemists often want to know the actual mass of an element in a certain mass of a compound. For example, in the mining industry, this information will tell the scientists about the quality of the ore.

The word "empirical" literally means "based only on observation and measurement." The empirical formula of ethanol is determined from analysis of the compound in terms of its constituent elements. No knowledge of how the atoms are linked together in the compound is required.

Molecular Formula:

The formula calculated from percent composition by mass is always the empirical formula because the subscripts in the formula are always reduced to the smallest whole numbers. To calculate the actual, molecular formula we must know the approximate molar mass of the compound in addition to its empirical formula. Knowing that the molar mass of a compound must be an integral multiple of the molar mass of its empirical formula, we can use the molar mass to find the molecular formula.

Calculation of molecular formula:

"Molecular formula represents the actual number of atoms of different elements present in one molecule of the compound".

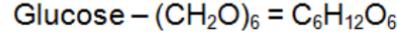
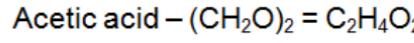
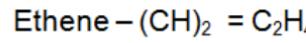
For certain compounds the molecular formula and the empirical formula may be one and the same.

The molecular formula of a compound may be same as empirical formula or a whole number multiple of it. Thus,

$$\text{The molecular formula} = (\text{empirical formula})_n$$

Where n is an integer 1, 2, 3, etc.

Example:



$$\text{Since molecular formula} = (\text{Empirical formula})_n$$

$$\text{Molecular weight} = \text{Empirical formula weight} \times n$$

$$\text{i.e. } n = \frac{\text{molecular weight}}{\text{empirical formula weight}}$$

If the vapour density of the substance is known, its molecular weight can be calculated by using the equation.

$$2 \times \text{vapour density} = \text{molecular weight.}$$

Example:

A sample of a compound contains 1.52 g of nitrogen (N) and 3.47 g of oxygen (O). The molar mass of this compound is 90 g. Determine the molecular formula and the accurate molar mass of the compound.

Solution:

Let 'n' represent the number of moles of each element. We write

$$n_N = 1.52 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.108 \text{ mol N}$$

$$n_O = 3.47 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.217 \text{ mol O}$$

Thus, we arrive at the formula $\text{N}_{0.108}\text{O}_{0.217}$, which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers. By dividing the subscripts by the smaller subscript (0.108), we obtain NO_2 as the empirical formula.

The molecular formula might be the same as the empirical formula or some integral multiple of it. This integral relationship is determined by comparing the molar mass to the molar mass of the empirical formula. The molar mass of the empirical formula NO_2 is (46.01)

$$\text{Empirical molar mass} = 14.01 \text{ g} + 2(16.00 \text{ g}) = 46.01$$

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{90 \text{ g}}{46.01 \text{ g}} \approx 2$$

The molar mass is twice the empirical molar mass. This means that there are two NO_2 units in each molecule of the compound, and the molecular formula is $(\text{NO}_2)_2$ or N_2O_4 .

The actual molar mass of the compound is two times the empirical formula mass, that is, $2(46.01 \text{ g})$ or 92.02 g .

P1.Q) Ascorbic acid (vitamin C) cures scurvy (A disease). It is composed of 40.92 % carbon (C), 4.58 % hydrogen (H), and 54.50 % oxygen (O) by mass. Determine its empirical formula.

(Atomic masses: C = 12; H = 1.0; O = 16)

Solution:

In a chemical formula, the subscripts represent the ratio of the number of moles of each element that combine to form one mole of the compound.

If we have 100 g of ascorbic acid, there will be 40.92 g of C, 4.58 g of H, and 54.50 g of O. Because the subscripts in the formula represent a mole ratio, we need to convert the grams of each element to moles. No. of moles of C = $n_C = 40.92 \text{ g} \times \frac{1 \text{ mol}}{12.01 \text{ g}} = 3.407 \text{ mol}$

$$\text{Simple atomic ratio of C} = \frac{3.407}{3.406} = 1$$

$$\text{No. of moles of H} = n_H = 4.58 \text{ g} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 4.54 \text{ mol}$$

$$\text{Simple atomic ratio of H} = \frac{3.407}{4.54} = 1.33$$

$$\text{No. of moles of O} = n_O = 54.50 \text{ g} \times \frac{1 \text{ mol}}{16.00 \text{ g}} = 3.406 \text{ mol}$$

$$\text{Simple atomic ratio of O} = \frac{3.406}{3.406} = 1$$

Thus we arrive at the formula $C_1H_{1.33}O_1$, which gives the identity and the mole ratios of atoms present. However, chemical formulas are written with whole numbers, so all the subscripts are multiplied by 3, we get the simple atomic ratio is 3:4:3.

Thus, $C_3H_4O_3$ is the empirical formula for ascorbic acid.

P2.Q) 0.200 g of an organic compound gave, on combustion, 0.147 g of carbon dioxide and 0.12 g of water and 46.03 % of N₂. Calculate the empirical formula of the compound.

Solution:

Calculation of percentage composition

a. The amount of C in 0.147 g of CO₂

$$= \frac{(\text{Wt of CO}_2) (\text{At. wt of C})}{(\text{Mol. wt of CO}_2)} = \left(\frac{0.147 \text{ g} \times 12 \text{ g}}{44 \text{ g}} \right)$$

$$\text{The percentage of C} = \left(\frac{0.147 \text{ g} \times 12 \text{ g}}{44 \text{ g}} \right) \times \frac{100 \text{ g}}{0.200 \text{ g}} = 20.014$$

b. The amount of H₂ in 0.12 g of H₂O

$$= \frac{(\text{Wt of H}_2\text{O}) (\text{At. wt of H}_2)}{(\text{Mol. wt of H}_2\text{O})} = \left(\frac{0.12 \text{ g} \times 2 \text{ g}}{18 \text{ g}} \right)$$

$$\text{The percentage of H} = \left(\frac{0.12 \text{ g} \times 2 \text{ g}}{18 \text{ g}} \right) \times \frac{100 \text{ g}}{0.200 \text{ g}} = 6.66$$

c. The percentage of N = 46.03

d. The percentage composition of oxygen = [100 – (20.04 + 6.66 + 46.03)]

$$= 26.67$$

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 20.04	$\frac{20.04}{12} = 1.67$	$\frac{1.67}{1.66} = 1$
H = 6.6	$\frac{6.66}{1} = 6.66$	$\frac{6.66}{1.66} = 4$
N = 46.03	$\frac{46.03}{14} = 3.3$	$\frac{3.3}{1.66} = 2$
O = 26.67	$\frac{26.67}{16} = 1.66$	$\frac{1.66}{1.66} = 1$

Therefore the empirical formula of the compound CH₄N₂O

P3.Q) A carbon compound contains 12.8% carbon, 2.1% hydrogen, 85.1% bromine. The molecular weight of the compound is 187.9. Calculate the molecular formula. (Atomic masses: C = 12; H = 1.0; Br = 80)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 12.8	$\frac{12.8}{12} = 1.067$	$\frac{1.067}{1.067} = 1$
H = 2.1	$\frac{2.1}{1} = 2.1$	$\frac{2.1}{1.067} = 2$
Br = 85.1	$\frac{85.1}{80} = 1.067$	$\frac{1.067}{1.067} = 1$

The empirical formula is CH_2Br

Empirical formula weigh $12 + (2 \times 1) + 80 = 94$.

The molecular weight = 187.9 (given)

$$\therefore n = \frac{187.9}{94} = 2$$

Molecular formula = $(\text{CH}_2\text{Br})_2 = \text{C}_2\text{H}_4\text{Br}_2$

P4.Q) A sample of a compound containing boron (B) and hydrogen (H) contains 6.444 g of B and 1.803 g of H. The molar mass of the compound is about 30 g. What is its molecular formula?

$$(B = 11.0; H = 1.0)$$

Solution:

Given that;

$$B = 6.444 \text{ g}$$

$$H = 1.803 \text{ g}$$

Molar mass of the compound = 30 g.

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
B = 6.444	$\frac{6.444}{11} = 0.58$	$\frac{0.58}{0.58} = 1$
H = 1.803	$\frac{1.803}{1} = 1.803$	$\frac{1.803}{0.58} \approx 3$

Empirical formula = BH₃.

Empirical formula mass = 14

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

$$= \frac{30}{14} \approx 2$$

Therefore molecular formula = (empirical formula)₂

$$= (\text{BH}_3)_2$$

$$= \text{B}_2\text{H}_6.$$

AP1) Peroxy acetyl nitrate (PAN) is one of the components of smog. It is a compound of C, H, N, and O. Determine the percent composition of oxygen and the empirical formula from the following percent composition by mass: 19.8 percent C, 2.50 percent H, 11.6 percent N. What is its molecular formula given that its molar mass is about 131 g mol^{-1} ? ($\text{N} = 14$; $\text{O} = 16$; $\text{C} = 12$; $\text{H} = 1$)

AP2) What are the empirical formulas of the compounds with the following compositions?

(C = 12; H = 1; O = 16; N = 14)

- a. 40.1 percent C, 6.6 percent H, 53.3 percent O

- b. 18.4 percent C, 21.5 percent N, 60.1 percent K

AP3) The empirical formula of a compound is CH. If the molar mass of this compound is about 78 g, what is its molecular formula?

AP4) Mono sodium glutamate (MSG), a food-flavor enhancer, has been blamed for “Chinese restaurant syndrome,” the symptoms of which are headaches and chest pains. MSG has the following composition by mass: 35.51 percent C, 4.77 percent H, 37.85 percent O, 8.29 percent N, and 13.60 percent Na. What is its molecular formula if its molar mass is about 169 g mol^{-1} . ($\text{C} = 12$, $\text{H} = 1$; $\text{O} = 16$; $\text{N}=14$; $\text{Na}=23$)

AP5) Determine the empirical formula of a compound having the following percent composition by mass: K : 24.72 percent; Mn : 34.77 percent; O : 40.51 percent. (K = 39; Mn = 54.94; O = 16)

LAQ1) Chemical analysis of a carbon compound gave the following percentage composition by weight of the elements present, carbon = 10.06%, hydrogen = 0.81%, Chlorine = 89.10%, Calculate the empirical formula of the compound.

(Atomic masses: C = 12; H = 1.0; Cl = 35.5)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 10.06	$\frac{10.06}{12} = 0.84$	$\frac{0.84}{0.84} = 1$
H = 0.84	$\frac{0.84}{1} = 0.84$	$\frac{0.84}{0.84} = 1$
Cl = 89.10	$\frac{89.10}{35.5} = 2.51$	$\frac{2.51}{0.84} = 3$

Ratio of the atoms present in the molecule C : H : Cl

1 : 1 : 3

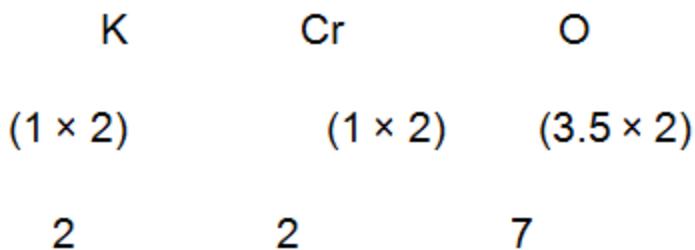
Therefore the empirical formula of the compound $C_1H_1Cl_3$ or $CHCl_3$.

LAQ2) Calculate the empirical formula of a compound having percentage composition: potassium (K) = 26.57, chromium (Cr) = 35.36; oxygen (O) = 38.07. (Given the atomic weights of K, Cr and O as 39; 52 and 16 respectively.)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
K = 26.57	$\frac{26.57}{39} = 0.68$	$\frac{0.68}{0.68} = 1$
Cr = 35.36	$\frac{35.36}{52} = 0.68$	$\frac{0.68}{0.68} = 1$
O = 38.07	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{0.68} = 3.5$

Multiplication by a suitable integer to get whole number ratio.



Therefore the empirical formula of the compound is $K_2Cr_2O_7$.

Stoichiometry

Module 5.6: Oxidation number Concept

In our daily life we come across processes like rusting of iron articles, fading of colour of clothes, burning of combustible substances such as cooking gas, wood, coal etc. All such processes fall in the category of specific type of chemical reactions called reduction- oxidation reactions or *Red-ox reactions*. A large number of industrial processes like electroplating, manufacture of caustic soda, extraction of metals like aluminium and sodium etc., are based on red-ox reactions. Red-ox reactions form the basis of *electrochemical* and *electrolytic cell*.

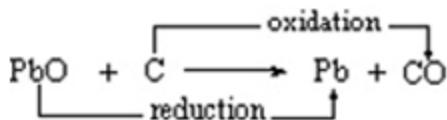
Oxidation and Reduction Reactions

Oxidation is a process of addition of oxygen or removal of hydrogen.

Reduction is the process of removal of oxygen or addition of hydrogen.

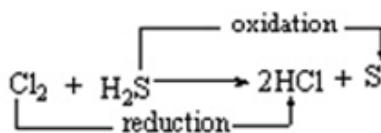
Examples:

Reaction of PbO on carbon.



Here oxygen is being removed from lead oxide (PbO) and is being added to carbon C. Therefore PbO is reduced while C is oxidised.

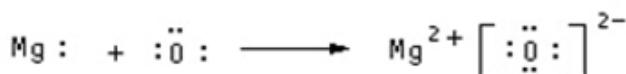
Reaction of H₂S and Cl₂



Here hydrogen being removed from hydrogen sulphide (H₂S) and is being added to chlorine (Cl₂). Thus H₂S is oxidised and Cl₂ is reduced.

Electronic concept of Oxidation and Reduction

Electrochemical reactions occur as a result of transference of electrons from one species to the other. For example, if magnesium is burnt in oxygen it gets oxidised to magnesium oxide (MgO). In the formation of magnesium oxide, two electrons from magnesium atom are transferred to oxygen atom.

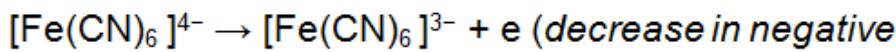
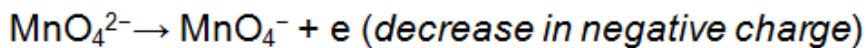
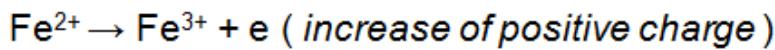
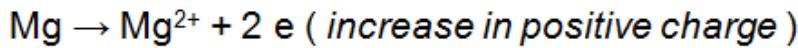
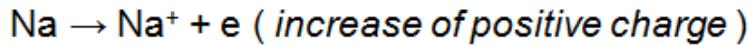


The process of transference of electrons is described as *red-ox process*.

Oxidation

It is a process in which an atom or group of atoms taking part in chemical reaction loses one or more electrons. Loss of electrons results in the increase of positive charge or decrease in negative charge of the species.

For example:



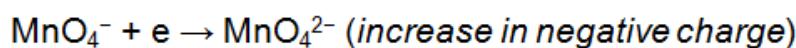
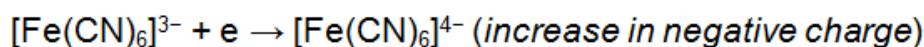
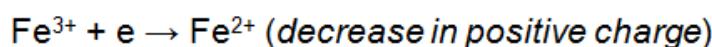
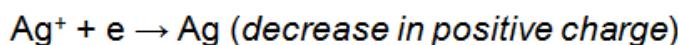
charge)

- The species which undergo the loss of electrons during the reactions are called *reducing agents* or *reductants*.
- MnO₄²⁻, Fe²⁺, and Mg are reducing agents in the above examples.

Reduction

It is a process in which an atom or group of atoms taking part in a chemical reaction *gains* one or more electrons. The gain of electrons results in the decrease of positive charge or increase in negative charge of the species.

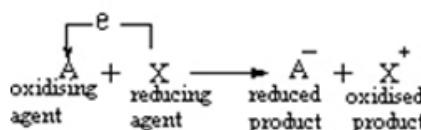
For example:



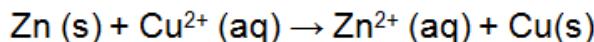
- The species which undergo *gain* of electrons during the reactions are called oxidising agents or *oxidants*.
- In the above example, Ag^+ , Fe^{3+} , $[\text{Fe}(\text{CN})_6]^{3-}$ ions are oxidising agents.

Simultaneous occurrence of Oxidation and Reduction

In any process, oxidation can occur only if reduction is also taking place side by side and *vice versa*. Thus neither oxidation nor reduction can occur alone. That is why chemical reactions involving reduction-oxidation are called *red-ox* reactions. During the *red-ox reaction* there is transference of electrons from *reducing agent* to the *oxidising agent* as shown below :



For example, consider a reaction between zinc and copper ions :



In this reaction, zinc lose electrons and are *oxidised* to zinc ions (Zn^{2+}) whereas cupric ions (Cu^{2+}) gain electrons and are *reduced* to copper atoms. The cupric ions act as oxidising agent and zinc act as reducing agent. In fact, the oxidising agent gets *reduced* while reducing agents *oxidised* during redox reactions.

Oxidation: Loss of electrons.

Reduction: Gain of electrons

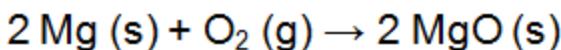
Oxidising agent: Species which gains electrons

Reducing agent: Species which loses electrons

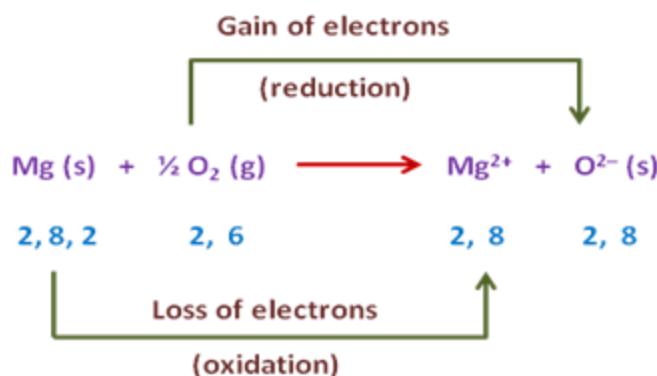
Competitive Electron Transfer Reactions

Example 1:

Magnesium burns in air with a brilliant white light giving white substance, magnesium oxide. The reaction is represented by the equation.

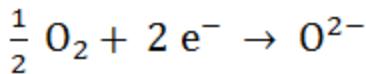
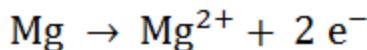


This may be rewritten as an equation, indicating the electronic configuration of various atoms of the elements participating in the reaction.



In the above equation, magnesium gives up two electrons or transfers them to oxygen atom. This process can be considered to take place in two separate steps one involved the loss of two electrons by the magnesium atom and the other the gain of the two electrons by oxygen atom.

Thus,



The reaction that involves loss of electrons is called an oxidation reaction and that involving gain of electrons is called a reduction reaction. The overall reaction is called as "oxidation – reduction". The number of electrons lost in the oxidation reaction is equal to the number of electrons gained in the reduction reaction. In the above reaction this number is equal to two.

Example 2:

When a piece of zinc metal is placed in a blue solution of copper nitrate, red metallic copper is deposited on the zinc, and at the same time the blue colour of the copper nitrate solution disappears.

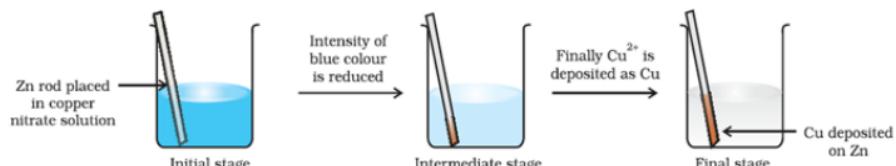
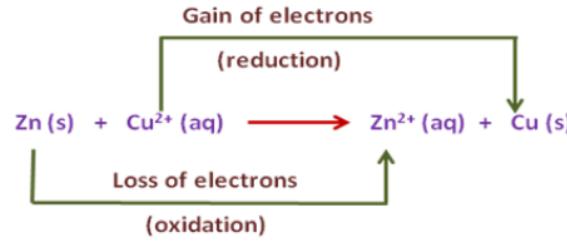
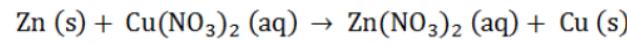


Fig: Red-ox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.

The reaction may be represented as



Hence Zn loses two electrons and forms Zn²⁺, and thus undergoes oxidation while Cu²⁺ gains two electrons to form Cu, and undergoes reduction. Thus zinc is oxidized to Zn²⁺ ions and Cu²⁺ ions are reduced to metallic copper.

Let us extend electron transfer reaction to copper metal and silver nitrate solution in water and arrange a set-up as shown in following Fig.

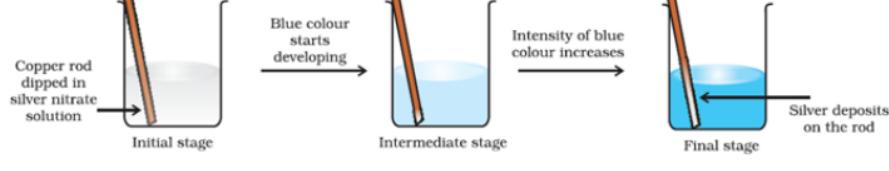
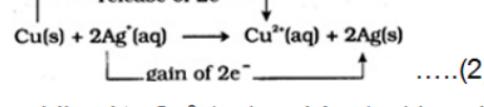


Fig: Red-ox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.

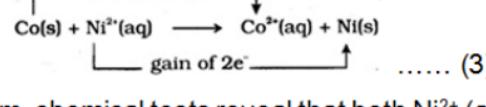
The solution in the beaker develops blue colour due to the formation of Cu²⁺ ions on account of the reaction:



Here Cu(s) is oxidised to Cu²⁺(aq) and Ag⁺(aq) is reduced to Ag(s).

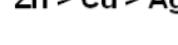
Equilibrium greatly favours the products Cu²⁺(aq) and Ag(s). Let us also compare the reaction of metallic cobalt placed in nickel sulphate solution.

The reaction that occurs is :



At equilibrium, chemical tests reveal that both Ni²⁺ (aq) and Co²⁺(aq) are present at moderate concentrations. In this case, neither the reactants [Co(s) and Ni²⁺ (aq)] nor products [Co²⁺(aq) and Ni(s)] are greatly favoured.

By comparison we know that zinc releases electrons to copper and copper releases electrons to silver. The electron releasing tendency of the metals is in the order:

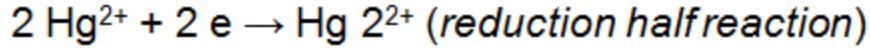
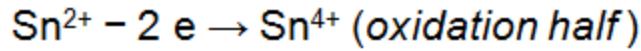
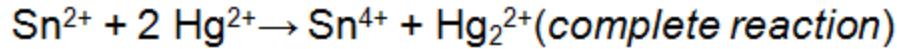
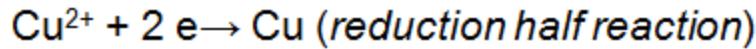
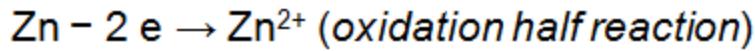
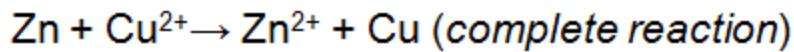


The competition for electrons between various metals helps us to design a class of cells, named as *galvanic cells* in which chemical reactions become the source of *electrical energy*.

Oxidation half and Reduction half reactions

Every reaction can be split up into half reactions, one representing loss of electrons *i.e.*, oxidation half-reaction, while other representing gain of electrons, *i.e.*, reduction half reaction.

Some examples are given below:

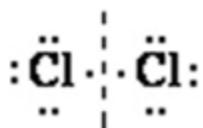


Oxidation number or Oxidation state:

Oxidation number (ON) of an element is defined as the residual charge which its atom appears to have when all other atoms from the molecule are removed as ions. *Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron in a covalent bond belongs entirely to more electronegative element.*

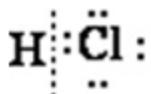
During the removal of atoms, the electrons are counted according to the following rules:

- Electrons shared between two similar atoms are divided equally between the sharing atoms. For example, in chlorine molecule (Cl_2) the electron pair is equally shared between two chlorine atoms. Therefore, one electron is counted with each chlorine atom as shown below:



Now there is no net charge on each atom of chlorine. In other words, oxidation number of chlorine in Cl_2 is zero.

- Electrons shared between two dissimilar atoms are counted with *more electronegative atom*. For example, in hydrogen chloride molecule chlorine is more electronegative than hydrogen. Therefore, the shared pair is counted towards chlorine atom as shown below:



As a result of this, chlorine gets one extra electron and acquires a unit negative charge. Hence oxidation number of chlorine is -1 . On the other hand hydrogen atom without electron has a unit positive charge. Hence, oxidation number of hydrogen in hydrogen chloride is $+1$. Thus, atoms can have positive zero or negative value of oxidation numbers depending up on their state of combination. In fact, oxidation number is the charge assigned to the atom in a species according to some arbitrary rules as described below.

General rules for assigning Oxidation Number to an atom

The following rules are employed for determining oxidation number of the atoms.

1. The oxidation number of the element in the free or elementary state is always zero.

For example

Oxidation number of helium in He = 0

Oxidation number of chlorine in Cl_2 = 0

Oxidation number of sulphur in S_8 = 0

Oxidation number of phosphorus in P_4 = 0

2. The oxidation number of the element in the monoatomic ion is equal to the charge on the ion.

For example, in K^+ Cl^- , the oxidation number of K is +1 , while that of Cl is -1 . In the similar way, oxidation number of all alkali metals (Li, Na, K, Rb, Cs and Fr) is + 1 , while those of alkaline earth metals (Be, Mg, Ca, Sr, Ba and Ra) is +2 in their compounds.

3. The oxidation number of fluorine is -1 in all its compounds.
4. Hydrogen is assigned oxidation number of +1 in its compounds except in metal hydrides like NaH , MgH_2 , CaH_2 , LiH in which its oxidation number is -1.
5. Oxygen is assigned oxidation number of - 2 in most of its compounds, however in peroxides like H_2O_2 , BaO_2 , and Na_2O_2 etc. Its oxidation number is -1. Similarly the exception also occurs in compounds of fluorine like OF_2 and O_2F_2 in which the oxidation number of oxygen is +2 and + 1 respectively. In super oxides like KO_2 it is - 1/2.
6. The algebraic sum of the oxidation numbers of all the atoms in neutral molecule is zero. But in the case of compound ion, the sum of the oxidation numbers of all its atoms is equal to the charge on the ion.

STOCK NOTATIONS

The names of compounds are written by the use of O.N's of the metal atoms. The O.N's are written in the form of Roman numerals in brackets after the name of the metal. For example, O.N of copper in Cu_2O is +1 and that in CuO is +2. Thus their names are copper(I) oxide and copper(II) oxide. This system of naming the compounds by the use of the oxidation numbers of representative metal atoms was proposed by *Albert Stock* and is referred as *System of Stock Notations* after his name. Some more examples are given below.

Cr_2O_3	:	Chromium (III) Oxide.
SnCl_2	:	Tin(II) chloride
V_2O_5	:	Vanadium (V) Oxide.
SnCl_4	:	Tin(IV) Chloride
$\text{Fe}_2(\text{SO}_4)_3$:	Iron(III) sulphate
FeSO_4	:	Iron(II) sulphate

Although the Stock Notations are generally used for metals, yet some compounds of non-metals have been named by this system. Some examples are given below:

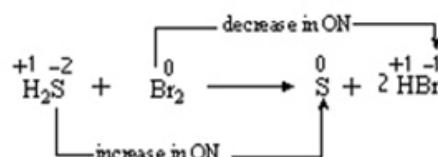
SO_2	:	Sulphur (IV) Oxide
SO_3	:	Sulphur (VI) Oxide

Oxidation and Reduction in terms of Oxidation Number

Oxidation is defined as a chemical process in which oxidation number of the element increases.

Reduction is defined as the chemical process in which oxidation number of the element decreases.

Consider the reaction between hydrogen sulphide and bromine to give hydrogen bromide and sulphur.



In the above example, the oxidation number of bromine decreases from 0 to -1, thus it is reduced. The oxidation number of S increases from -2 to 0. Hence H_2S is oxidised.

Oxidising agent

Oxidising agent is a substance which undergoes the decrease in oxidation number of one or more of its elements.

Reducing agent

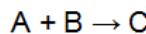
Reducing agent is a substance which undergoes the increase in the oxidation number of one or more of its elements.

In the above example H_2S is the reducing agent while Br_2 is the oxidising agent.

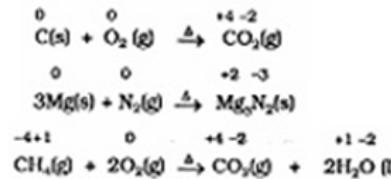
TYPES OF REDOX REACTIONS

1. Combination reactions

A combination reaction can be denoted in the manner:



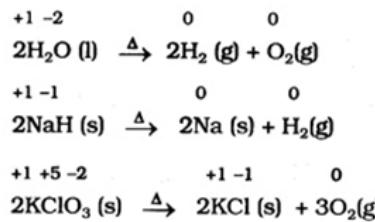
Either A and B or both A and B must be in elemental form for such a reaction to be a red-ox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are red-ox reactions. Some important examples of this category are:



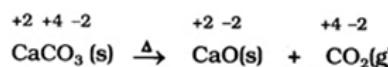
2. Decomposition reactions

Decomposition reactions are the opposite of combination reactions. A decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state.

Examples of this class of reactions are:



It may be noted that there is no change in the oxidation number of hydrogen in methane under *combination reactions* and that of potassium in potassium chlorate (above). This may be noted here that all *decomposition reactions are not red-ox reactions*. For example decomposition of calcium carbonate is not a red-ox reaction.



3. Displacement reactions

In displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be noted as :

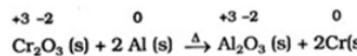
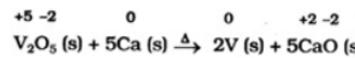
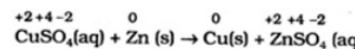


Displacement reactions fit into two categories ; metal displacement and non-metal displacement.

(a) Metal displacement

A metal in a compound can be displaced by another metal in the uncombined state. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores.

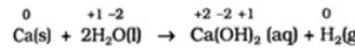
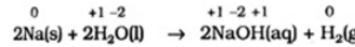
A few such examples are:



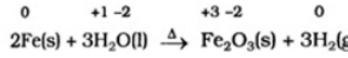
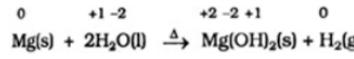
In each case, reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

(b) Non-metal displacement

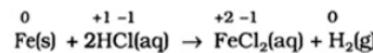
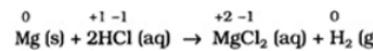
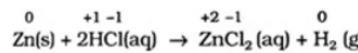
The non-metal displacement red-ox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement. All alkali metals and some alkaline earth metals (Ca, Sr and Ba) which are very good *reductants*, will displace hydrogen from cold water.



Less active metals such as magnesium and iron react with steam to produce dihydrogen gas.

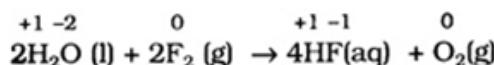


Many metals including those which do not react with cold water are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. A few examples for the displacement of hydrogen from acids are:

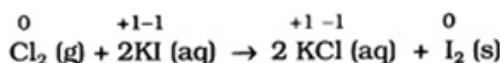
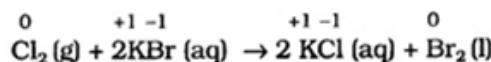


The above reactions are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution , which is the slowest for the least active metal Fe, and the fastest for the most reactive metal Mg. Very less active metals , which may occur in the native state such as silver (Ag) and gold (Au) do not react even with hydrochloric acid.

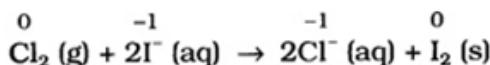
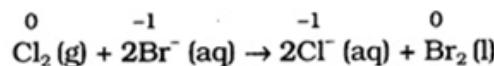
The metals Zn, Cu and Ag through tendency to lose electrons show their reducing activity in the order $Zn > Cu > Ag$. Like metals, activity series also exists for the halogens. The power of these elements as *oxidising agents* decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it displaces the oxygen of water:



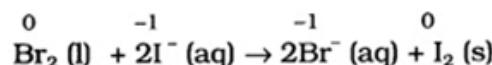
It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:



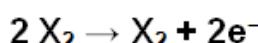
As Br_2 and I_2 are coloured and dissolve in CCl_4 , can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:



The reactions (above) form the basis of identifying Br^- and I^- in the laboratory through the test popularly known as '**Layer test**'. Bromine displace iodide ion in solution.



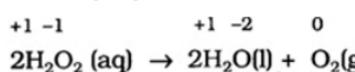
The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:



here X denotes a halogen element. Whereas chemical means are available to oxidise Cl^- , Br^- and I^- , as fluorine is the strongest oxidising agent ; there is no way to convert F^- ions to F_2 by chemical means. The only way to achieve F_2 from F^- is to oxidise electrolytically.

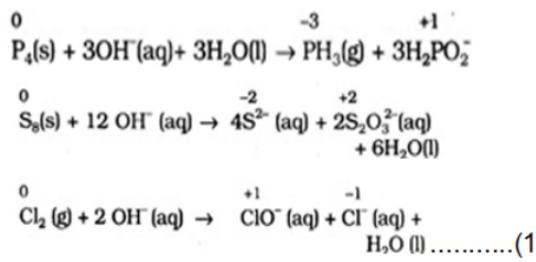
4. Disproportionation reactions

Disproportionation reactions are a special type of red-ox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experience disproportionation.



Here the oxygen of peroxide, which is present in -1 state, is converted to zero oxidation state in O_2 and decreases to -2 oxidation in water.

Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below:



The above reaction describes the formation of household bleaching agents.

The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour bearing stains of the substance to colourless compounds.

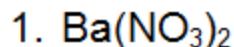
Bromine and iodine follow the same trend as exhibited by chlorine in reaction (1), fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows.



Fluorine in the above reaction will attack water to produce some oxygen also. This departure shown by fluorine is due its most electronegative character. It cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show disproportionation tendency.

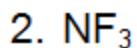
Nitrogen and its compounds	Oxidation number of nitrogen
NH_4^+	-3
NH_3	-3
N_2H_4	-2
NH_2OH	-1
N_2	0
NO	+2
N_2O_3	+3
NO_2	+4
N_2O_5	+5

Calculation of oxidation number:



Steps to solve the problem:

- Barium ion = Ba^{2+}
- Oxidation number for Ba = +2
- Oxygen has a rule....-2 in most compounds
- Oxidation number for O = -2
- By using the above values we will find the oxidation number of N
- Let x = Oxidation number for nitrogen
- Oxidation number of N is calculated by the formula,
$$\text{Sum of oxidation numbers} = 1(+2) + 2(x) + 6(-2) = 0$$
- $x = +5$



Steps to solve the problem:

- Oxidation number of F = -1
- find the oxidation number of N
- Let x = oxidation number of N
- Sum of oxidation numbers = $1(x) + 3(-1) = 0$
- $x = +3$

P1.Q) Calculate the oxidation number of manganese in MnO_4^{2-} ion.

Solution:

Oxidation number of oxygen = -2

Oxidation number manganese = x

Total charge on the ion is -2.

$$\text{i.e., } 1(x) + 4(-2) = -2$$

$$x - 8 = -2$$

$$x = -2 + 8 = +6$$

∴ The oxidation number of manganese in manganate ion MnO_4^{2-} is +6.

P2.Q) Calculate the oxidation number of manganese in permanganate ion



Solution:

Oxidation number of oxygen = - 2

Oxidation number of manganese = x

Total charge on the ion is -1.

$$\text{i.e., } 1(x) + 4(-2) = -1$$

$$x - 8 = -1$$

$$x = -1 + 8 = +7.$$

∴ The oxidation number of manganese in permanganate ion is + 7.

P3.Q) Calculate the oxidation number of chromium in Cr_2O_3 .

Solution:

Oxidation number of oxygen = -2

Oxidation number of chromium = x

Total charge on the molecule is zero.

$$\text{i.e., } 2(x) + 3(-2) = 0$$

$$2x - 6 = 0$$

$$2x - 6 = 0$$

$$2x = +6$$

$$x = +3.$$

∴ The oxidation number of chromium in Cr_2O_3 is +3.

Stoichiometry

Module 5.7: Balancing of Red-ox reactions by ion-electron method

Balancing red-ox reactions:

A chemical reaction is necessarily represented as a balanced equation. To get a balanced equation two different methods can be adopted. Both the methods are based on the calculation of oxidation numbers of the elements constituting the reactants and the products. The methods are

- i. Oxidation number method
- ii. Ion – electron method or half reaction method.

The first method is based on the change in the oxidation number of the reductant and the oxidant and the second method is based on splitting the red-ox reaction into two half reactions one involving oxidation and another involving reduction. Both methods work very well.

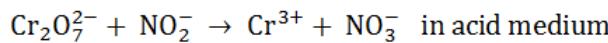
Now let us discuss balancing of a chemical reaction by Ion – electron method.

Balancing of a reaction by this method is done in the following stages.

1. Write an ionic equation with the participating substances. i.e., reactants and products. Locate the oxidation and reduction reactions in it.
2. The oxidation half reaction and the reduction half reaction are written separately.
3. Each of the half reactions is separately balanced according to the following steps.
 - a. Balance all the elements, except hydrogen and oxygen.
 - b. To balance hydrogen atoms, a necessary number of hydrogen ions (H^+ ions) are added on the side deficient in hydrogen atoms, if the reaction takes place in acid medium.
 - c. If the reaction takes place in alkaline medium, the hydrogen atoms are balanced by adding necessary number of water (H_2O) on the side deficient in hydrogen.
 - d. In acid medium, the oxygen atoms are balanced by adding necessary number of H_2O molecules on the side deficient in oxygen.
 - e. If the reaction takes place in alkaline medium, the oxygen atoms are balanced by adding necessary number of OH^- ions on the side deficient in oxygen.
 - f. The operations b), c), d) and e) are repeated until the hydrogen atoms and oxygen atoms are perfectly balanced in both the half reactions.
 - g. Balance the negative charges by adding necessary number of electrons on the side deficient in negative charges.
 - h. The two half reactions are multiplied by suitable integers so as to get identical number of electrons participating in each of the half reactions.
 - i. The balanced half reactions are added in such a manner as to cancel the number of electrons involved.
 - j. Needless to say that the equation thus obtained is completely balanced with respect to atoms as well as charges.

Example – 1:

Balance the following chemical reaction by ion – electron method.

**Solution:**

The oxidation is NO_2^- to NO_3^- since the oxidation state of nitrogen atom increases from + 3 to + 5

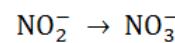
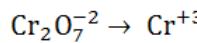
\therefore The oxidation half reaction is $\text{NO}_2^- \rightarrow \text{NO}_3^-$

The reduction is $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} since the oxidation state of Cr decreases from + 6 to + 3. The reduction half reaction is $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$

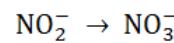
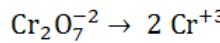
Write the two half reactions as shown below

Reduction half reaction

oxidation half reaction



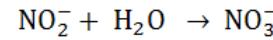
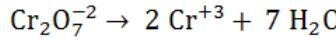
Balance all the other elements. Except H₂ and O₂



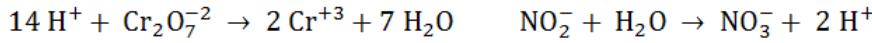
Balance hydrogen's by adding H⁺ ions as the reaction takes place in acid medium.

No hydrogens are present. So need balanced H – atoms.

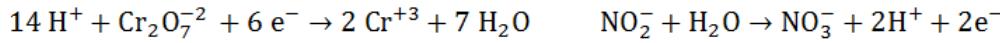
Balance oxygens by adding necessary number of H₂O molecules on the side deficient in oxygen.



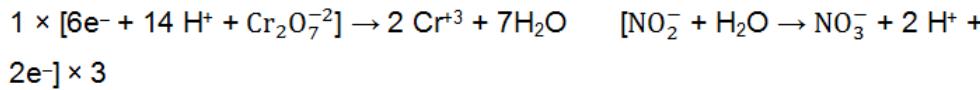
Balance the hydrogens by adding H⁺ ions on the side deficient in hydrogens.



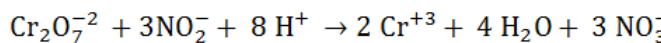
Balance the negative charges by adding electrons on the side deficient in negative charges.



Multiplying the two half reactions with suitable integers to equalize the number of electrons participating in each of the half reactions.



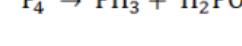
Adding the two half reactions, the overall balanced reaction is obtained.



Example – 2:

Balance the following chemical reaction by ion – electron method

In alkaline medium



Solution:

In the reaction P_4 undergoes both oxidation and reduction

The oxidation half reaction is given by,



Here the oxidation state of Phosphorous increases from '0' to +1.

The reduction half reaction is

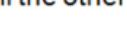


Here the oxidation state of Phosphorous decreases from '0' to -3

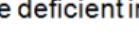
Write the two half reactions as shown below.

Reduction half reaction

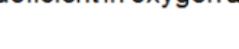
oxidation half reaction



Balance all the other elements except H_2 and O_2



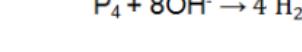
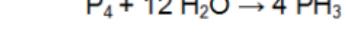
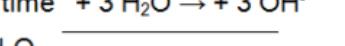
Balance the hydrogen atoms by adding necessary number of H_2O molecules on the side deficient in hydrogen's.



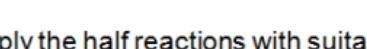
Balance the oxygen atoms by adding necessary number of OH^- ions on the side deficient in oxygen atoms



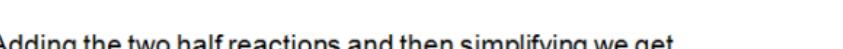
Repeating the balancing of hydrogen and oxygen atoms alternatively



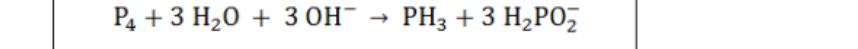
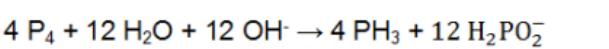
Adding to get balanced half reactions



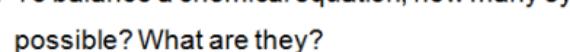
Balance the charges by adding electrons on the side deficient in negative charges.



Multiply the half reactions with suitable integers.



Adding the two half reactions and then simplifying we get,



Assignment questions:

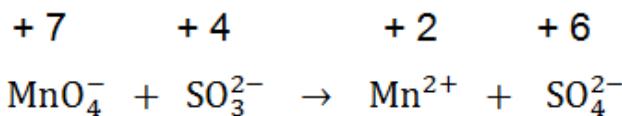
- To balance a chemical equation, how many systematic methods can be possible? What are they?
- Write the postulates followed in the balancing of reactions by ion – electron method.
- Balance oxidation of NO_2^- with $\text{Cr}_2\text{O}_7^{2-}$ in acid medium (ion – electron method)
- Balance the following reaction in basic medium (ion – electron method)



P1.Q) Write the balanced equation for the oxidation of sulphite ions to sulphate ions (in acid medium) by permanganate ions.

Solution:

The ionic skeleton reaction is



The oxidation half reaction $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$ (+4 to +6)

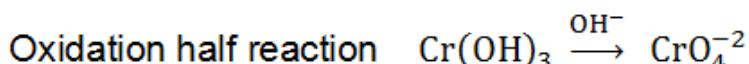
The reduction half reaction $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ (+7 to +2)

Reduction half reaction	Oxidation half reaction
<ul style="list-style-type: none"> • $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ • $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ (Mn is already balanced) • $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$ (O is balanced) • $\text{MnO}_4^- + 8 \text{H}^+ \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$ (H balanced in acid medium) • $\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$ (Charges balanced) • $2(\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O})$ (Electrons balanced) • $2\text{MnO}_4^- + 16 \text{H}^+ + 10 \text{e}^- \rightarrow 2\text{Mn}^{2+} + 8 \text{H}_2\text{O}$ 	<ul style="list-style-type: none"> • $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$ • $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$ (S is already balanced) • $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-}$ (O is balanced) • $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2 \text{H}^+$ (H balanced in acid medium) • $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2 \text{H}^+ + 2 \text{e}^-$ (Charges balanced) • $5(\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2 \text{H}^+ + 2 \text{e}^-)$ (Electrons balanced) • $5\text{SO}_3^{2-} + 5\text{H}_2\text{O} \rightarrow 5\text{SO}_4^{2-} + 10\text{H}^+ + 10\text{e}^-$

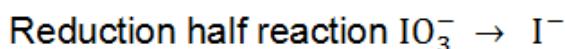
Adding

- $5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 16 \text{H}^+ + 5\text{H}_2\text{O} \rightarrow 5\text{SO}_4^{2-} + 10 \text{H}^+ + 2\text{Mn}^{2+} + 8 \text{H}_2\text{O}$
or
- $2\text{MnO}_4^- + 5\text{SO}_3^{2-} + 6 \text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3 \text{H}_2\text{O}$

P2.Q) Balance the following equation $\text{Cr}(\text{OH})_3 + \text{IO}_3^- \xrightarrow{\text{OH}^-} \text{I}^- + \text{CrO}_4^{2-}$

Solution:

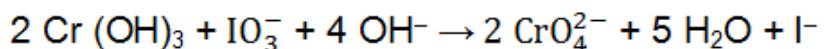
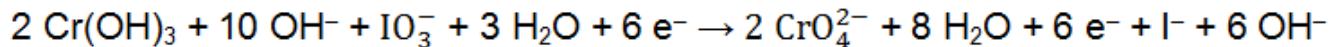
(The oxidation no. of Cr changes from + 3 to + 6)



(The oxidation no. of 'I' changes from +5 to - 1)

Reduction half reaction	Oxidation half reaction
1. $\text{IO}_3^- \rightarrow \text{I}$	1. $\text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{-2}$
2. $\text{IO}_3^- \rightarrow \text{I}$ (I already balanced)	2. $\text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{-2}$ (Cr already balanced)
3. $\text{IO}_3^- \rightarrow \text{I} + 3\text{OH}^-$ (O balanced)	3. $\text{Cr}(\text{OH})_3 + \text{OH}^- \rightarrow \text{CrO}_4^{-2}$ (O balanced)
4. $\text{IO}_3^- + 3\text{H}_2\text{O} \rightarrow \text{I} + 3\text{OH}^- + 3\text{OH}^-$ (H and again O are balanced in basic medium)	4. $\text{Cr}(\text{OH})_3 + \text{OH}^- + 4\text{OH}^- \rightarrow \text{CrO}_4^{-2} + 4\text{H}_2\text{O}$ (H and O balanced in basic medium)
5. $\text{IO}_3^- + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{I} + 6\text{OH}^-$ (Charges balanced)	5. $\text{Cr}(\text{OH})_3 + 5\text{OH}^- \rightarrow \text{CrO}_4^{-2} + 4\text{H}_2\text{O} + 3\text{e}^-$ (Charges balanced)
6. $\text{IO}_3^- + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{I}^- + 6\text{OH}^-$ (Electrons balanced)	6. $2\text{Cr}(\text{OH})_3 + 10\text{OH}^- \rightarrow 2\text{CrO}_4^{-2} + 8\text{H}_2\text{O} + 6\text{e}^-$ (Electrons balanced)

Adding

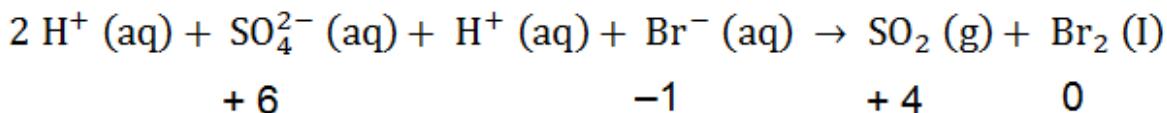


LAQ1) Balance the equation $\text{H}_2\text{SO}_4 \text{ (aq)} + \text{HBr} \text{ (aq)} \rightarrow \text{SO}_2 \text{ (g)} + \text{Br}_2$

Solution:

Write the skeleton equation in the ionic form for the reaction. Both H_2SO_4 and HBr are strong acids. They ionize in solutions. Therefore

The reaction is written as

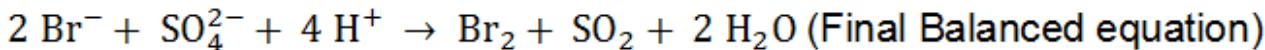


The half reactions are

Oxidation is $\text{Br}^- \rightarrow \text{Br}_2$ and

reduction is $\text{SO}_4^{2-} \rightarrow \text{SO}_2$

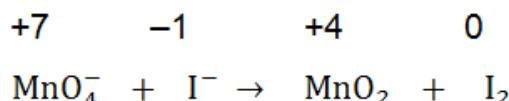
Reduction half reaction	Oxidation half reaction
<ul style="list-style-type: none">• $\text{SO}_4^{2-} \rightarrow \text{SO}_2$• $\text{SO}_4^{2-} \rightarrow \text{SO}_2$• $\text{SO}_4^{2-} \rightarrow \text{SO}_2 + 2 \text{H}_2\text{O}$ (Balancing O)• $\text{SO}_4^{2-} + 4 \text{H}^+ \rightarrow \text{SO}_2 + 2 \text{H}_2\text{O}$ (Balancing H)• $\text{SO}_4^{2-} + 4 \text{H}^+ + 2 \text{e}^- \rightarrow \text{SO}_2 + 2 \text{H}_2\text{O}$ (Balancing and equalizing charges)	<ul style="list-style-type: none">• $\text{Br}^- \rightarrow \text{Br}_2$• $2 \text{Br}^- \rightarrow \text{Br}_2$ (Balancing Br⁻)• $2 \text{Br}^- \rightarrow \text{Br}_2$• $2 \text{Br}^- \rightarrow \text{Br}_2$• $2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^-$ (balancing and equalizing charges)



LAQ2) Write the balanced ionic equation which represents the oxidation of iodide ion (I^-) by permanganate ion in basic medium to give iodine (I_2) and manganese dioxide (MnO_2).

Solution:

The skeleton equation is written as



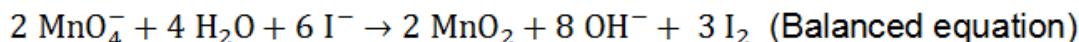
The oxidation half reaction is $I^- \rightarrow I_2$ (oxidation no. changes from –1 to 0)

The reduction half reaction is $MnO_4^- \rightarrow MnO_2$ (oxidation no. changes from +7 to +4)

Hence the two half reactions are as follows:

Reduction half reaction	Oxidation half reaction
<ul style="list-style-type: none"> • $MnO_4^- \rightarrow MnO_2$ • $MnO_4^- \rightarrow MnO_2$ (Mn atoms are already balanced) • $MnO_4^- \rightarrow MnO_2 + 2 OH^-$ (Oxygen atoms balanced) • $MnO_4^- + 2 H_2O \rightarrow MnO_2 + 2 OH^- + 2 OH^-$ (H – atoms and O atoms are balanced in basic medium) • $MnO_4^- + 2 H_2O + 3 e^- \rightarrow MnO_2 + 4 OH^-$ (Charges balanced) • $2(MnO_4^- + 2H_2O + 3 e^- \rightarrow MnO_2 + 4OH^-)$ [Multiplying above equation with 2] • $2 MnO_4^- + 4 H_2O + 6 e^- \rightarrow 2 MnO_2 + 8 OH^-$ 	<ul style="list-style-type: none"> • $I^- \rightarrow I_2$ • $2I^- \rightarrow I_2$ (I atoms are balanced) • $2I^- \rightarrow I_2$ (Oxygen atoms are not present) • $2I^- \rightarrow I_2$ (Hydrogen atoms are not present) • $2I^- \rightarrow I_2 + 2e^-$ (Charges balanced) • $3(2I^- \rightarrow I_2 + 2e^-)$ [Multiplying above equation with 3, then electrons balanced] • $6I^- \rightarrow 3I_2 + 6e^-$

Adding



Stoichiometry

Module 5.8: Balancing of Red-ox reactions by Oxidation number method

Oxidation number method:

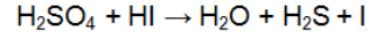
This method is applied to both ionic as well as molecular reactions. The balancing of the equations is done in the following stages.

- Assign the oxidation numbers to all the atoms participating in the reaction. i.e., skeleton equation
- Identify the elements whose oxidation numbers have changed. i.e. Oxidant and reductant. Their atoms are balanced.
- Then increase in oxidation number in the oxidation process is equalized with the decrease in oxidation number in the reduction process (only numerical). This is done by selecting suitable integral coefficients to the changes in oxidation number.
- These coefficients are used for the chemical substances involved in the oxidation and the reduction processes and the equation is written again to get a balanced equation.

The following worked out example will make it clear.

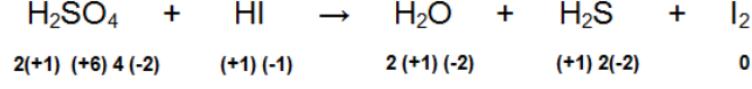
Example – 1:

Balance the following equation by oxidation number method



Solution:

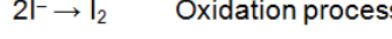
Assign oxidation numbers to the elements in the reaction using the empirical rules.



Identify the elements whose oxidation numbers have changed.



The decrease in oxidation number is $[+6 - (-2)] = 8$



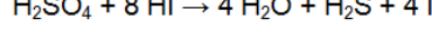
The increase in oxidation number is $[0 - (-2)] = 2$

Equalize the increase in oxidation number in oxidation process with the decrease in the oxidation number in reduction process.

Decrease in oxidation number in reduction = 8

[Increase in oxidation number in oxidation = 2] \times 4

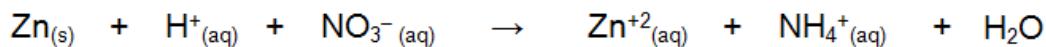
The equation is written again using the coefficients obtained above.



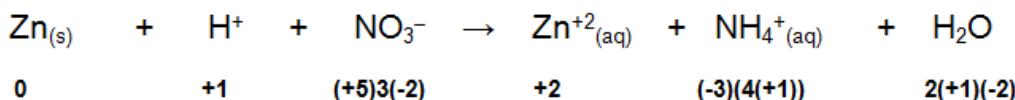
Verify the equation to balance with respect to charges and the atoms.

Example – 2:

Balance the following equation by oxidation number method.

**Solution:**

Assign oxidation numbers to the elements in the reaction using the empirical rules.



Identify the elements whose oxidation



Change in oxidation number is $[+2 - 0] = 2$



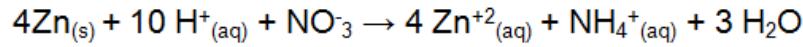
Change in oxidation number is $[+5 - (-3)] = 8$

Equalizing the increase in oxidation number in oxidation process with the decrease in oxidation number in reduction process.

$[\text{Increase in oxidation number in oxidation} = 2] \times 4$

$[\text{Decrease in oxidation number in reduction} = 8] \times 1$

The equation is written again using the coefficients obtained above.



Verify the equation to balance with respect to charges and the atoms.

Assignment questions:

- What are the stages in which the chemical equation is balanced by oxidation number method?
- Balance the following equations by oxidation number method.
 - $\text{H}_2\text{SO}_4 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{H}_2\text{S} + \text{I}_2$
 - $\text{Zn}_{(\text{s})} + \text{H}^{\text{+(aq)}} + \text{NO}_3^{\text{-}(\text{aq})} \rightarrow \text{Zn}^{\text{+}} + \text{NH}_4^{\text{+}} + \text{H}_2\text{O}$

P1.Q)

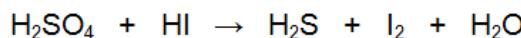
Balance the following equation



Solution:

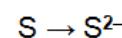
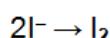
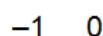
Step – 1:

Indicate the oxidation numbers of the elements in all the molecules.



Step – 2:

Identify the elements whose oxidation state (O.S) have changed and write the equation and balance them with respect to the number of atoms.



Total increase in O.S. is +2.

Decrease in O.S. in – 8

Step – 3:

Equalize the increase in the oxidation number to the decrease in oxidation number.

Increase +2;

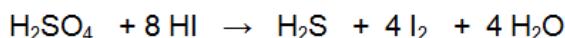
$4(+2) = +8$

decrease –8;

$1(-8) = -8$

Step – 4:

Write down the equation using these coefficients



Step – 5:

Check up whether the equation is balanced or not.

Check the whether the charge is balanced or not. All the reactants and products are in molecular state, the charge on a molecule is zero.

Therefore, the equation is balanced with respect to charge.

Check whether the number of atoms is balanced or not.

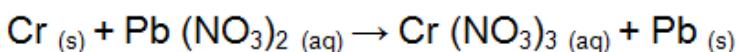
Reactants	Products
10 H	10 H
1 S	1 S
4 [O]	4 [O]
8 [I]	8 [I]

The balanced chemical equation is: $\text{H}_2\text{SO}_4 + 8\text{HI} \rightarrow \text{H}_2\text{S} + 4\text{I}_2 + 4\text{H}_2\text{O}$

AP1) Balance the following equation by the oxidation number method.



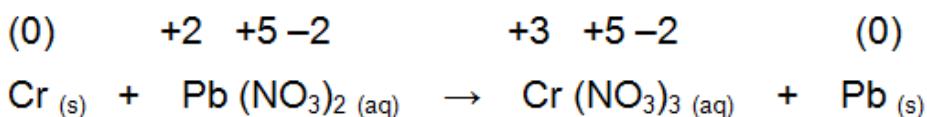
LAQ 1. Balance the following equation by the oxidation number method.



Solution:

Step – 1:

Indicate the oxidation numbers of the elements participating in the reaction.



Step – 2:

Identify the atoms whose oxidation states have changed.

- The oxidation number of chromium is increased from 0 to + 3
- The oxidation number of lead is decreased from + 2 to 0

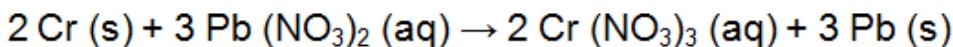
Step – 3:

Equalize the increase in the oxidation number to the decrease in the oxidation number.



Step – 4:

Write the equation using these coefficients.



Step – 5:

Check up whether the equation is balanced or not. Yes the equation is balanced.

Unit-6

Solution

A solution may be regarded as a single phase containing more than one component.

Every solution consists of a solvent and one or more solutes.

Solvent in a solution is its constituent substances which has the same state of aggregation as that of the solution. Generally the component present in greater amount than any or all the other components is called the solvent.

Solutions containing relatively high concentration of solute are called concentrated solutions.

Solutions containing relatively low concentration of solute are called dilute solutions.

Properties of liquids

Vapour pressure:

The Pressure exerted by vapour molecules on the surface area of a liquid, when liquid phase and vapour phase are in equilibrium, at a given temperature, is called vapour pressure of the liquid.

When temperature of a liquid is increased, the rate of vapourisation increases. The temperature at which the vapour pressure of a liquid becomes equal to the external pressure, the liquid boils. The temperature at which the liquid boils is called boiling point.

Thus, the temperature at which the vapour pressure of liquid is equal to the atmospheric pressure is called boiling point.

The boiling temperature of a liquid at 1 atm pressure is called normal boiling point.

The boiling temperature of a liquid at 1 bar pressure is called standard boiling point.

a) Surface Tension:

The force acting along the surface of a liquid at right angles to any line of unit length is called surface tension (γ).

Units: dynes cm^{-1} (C.G.S system)

Nm^{-1} (S.I system)

The phenomenon of surface tension is due to the existence of strong intermolecular forces of attraction in liquids.

Effect of temperature: Increase in the temperature increases the kinetic energy of molecules, then their inter molecular attractions decreases. So surface tension decreases with the increase of temperature.

Examples:

- 1) The liquid drops are spherical, due to surface tension.
- 2) The rise of liquid in a capillary tube is due to surface tension.

b) Viscosity:

The property of resistance flow is called Viscosity. Viscosity of a liquid is a measure of its frictional resistance to the flow of liquid. If viscosity increases then flow of liquid is decreases. Liquid which flow rapidly have low internal resistance. So their viscosity is less. Liquids which flow slowly have high internal resistance. So their viscosity is high.

Examples:

- 1) Glass is not a solid. It is a super-cooled liquid with a very high viscosity.
- 2) H_2SO_4 is viscous, due to H-bonding.

Concentration terms:

Molarity (M):

The number of moles of the solute per litre of the solution, *i.e.*,

Molarity (M) = Number of moles of solute/number of litres of solution

Or Molarity \times number of litres of solution = Number of moles of solute

Let w_A g of the solute of molecular mass m_A be dissolved in V litre of solution.

$$\text{Molarity of the solution (M)} = \left(\frac{w_A}{m_A} \right) \left(\frac{1}{V} \right)$$

Or

If V is taken in mL, then

$$\text{Molarity of the solution (M)} = \left(\frac{w_A}{m_A} \right) \left(\frac{1000}{V} \right)$$

Unit of molarity is mol litre⁻¹

Molality (m):

The number of moles of the solute present in 1 kg of the solvent,

Molality (m) = Number of moles of solute/number of kilo-grams of the solvent

Let w_A grams of the solute of molecular mass m_A be present in w_B grams of the solvent, then

$$\text{Molality (m)} = \left(\frac{w_A}{m_A} \right) \left(\frac{1000}{w_B} \right)$$

Normality (N):

The number of gram equivalents of solute present per litre of solution.

Normality = Number of gram equivalents of solute/Number of litres of the solution

Let w_A g of the solute of equivalent mass E_A be present in V litres of the solution, then,

$$\text{Normality (N)} = \left(\frac{w_A}{E_A} \right) \left(\frac{1}{V} \right)$$

Relation between normality and molarity:

Normality = n X Molarity

Mole fraction:

This method is used when the solution is constituted by mixing two or more components.

It is defined as the ratio of number of moles of one component to the total number of moles of the solution (*i.e.*, all the components).

For example taking three components A, B and C containing solution.

Components	A	B	C
Mass (in grams)	w_1	w_2	w_3
Molecular mass	m_1	m_2	m_3
No. of g moles	w_1/m_1	w_2/m_2	w_3/m_3

$$\text{Total number of gram moles} = \left(\frac{w_1}{m_1} \right) + \left(\frac{w_2}{m_2} \right) + \left(\frac{w_3}{m_3} \right)$$

Thus,

$$\text{Mole fraction of A} = (w_1/m_1) / (w_1/m_1 + w_2/m_2 + w_3/m_3) = f_A$$

$$\text{Mole fraction of B} = (w_2/m_2) / (w_1/m_1 + w_2/m_2 + w_3/m_3) = f_B$$

$$\text{Mole fraction of C} = (w_3/m_3) / (w_1/m_1 + w_2/m_2 + w_3/m_3) = f_C$$

The sum of mole fractions of a solution is equal to 1,

$$i.e., f_A + f_B + f_C = 1.$$

In a binary solution,

$$\text{Mole fraction of solute} + \text{Mole fraction of solvent} = 1$$

Let n moles of solute (A) and N moles of solvent (B) be present in a solution.

$$\text{Mole fraction of solute} = \left(\frac{n}{n + N} \right) = X_A$$

$$\text{Mole fraction of solvent} = \left(\frac{N}{n+N} \right) = X_B$$

Thus, $X_A + X_B = 1$

Mole fraction is independent of temperature of the solution.

Colligative properties of dilute solutions:

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the **number of solute particles** present in the solution irrespective of their nature. These properties are termed as **colligative properties**.

The colligative properties are,

- 1) Lowering in the vapour pressure,
- 2) Elevation in the boiling point,
- 3) Depression in the freezing point, and
- 4) Osmotic pressure.

Colligative properties are the properties of dilute solutions, that is why these are termed as colligative properties of dilute solutions.

The importance of these properties lies in the fact that they provide methods for the determination of **molecular masses** of dissolved solutes. The results are excellent if the following 3 conditions are satisfied.

- 1) The solution should be very dilute.
- 2) The solute should be non-volatile.
- 3) The solute does not dissociate or associate in solution.

1) Lowering in the vapour pressure:

When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons.

- (i) Solvent occupied surface area percentage is decreases. Thus, the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the percentage of surface area occupied by the solvent decreases.

(ii) According to Graham's law of evaporation,

$$\text{Rate of evaporation} \propto \frac{1}{\sqrt{\text{density}}}$$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus both rate of evaporation and vapour pressure are lowered.

If p_0 is the vapour pressure of pure solvent and p_s is the vapour pressure of solution, the difference ($p_0 - p_s$) is known as lowering in vapour pressure and the ratio [$p_0 - p_s / p_0$] is known as relative lowering in vapour pressure

Raoult established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. The relationship is known as **Raoult's law**. It states that "**the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution.**"

If n moles of solute be dissolved in N moles of the solvent, the mole fraction of the solute will be $n/n+N$.

According to Raoult's law,

$$\frac{P_o - P_s}{P_o} = \frac{n}{n+N}$$

This is mathematical expression for Raoult's law.

Modified form of Raoult's law: the above relationship can be written as,

$$\begin{aligned}\frac{P_o}{P_o - P_s} &= \frac{n+N}{n} = 1 + \frac{N}{n} \\ \implies \frac{P_o}{P_o - P_s} - 1 &= \frac{N}{n} \\ \implies \frac{P_s}{P_o - P_s} &= \frac{N}{n} \\ \implies \frac{P_o - P_s}{P_s} &= \frac{n}{N} \\ \implies \frac{P_o - P_s}{P_s} &= \left(\frac{w_A}{m_A} \right) \left(\frac{m_B}{w_B} \right)\end{aligned}$$

2) Elevation of boiling point (ΔT_b) (Ebullioscopy):

The boiling point of the solvent is elevated by the addition of non-volatile solute. **The difference in the boiling point of the solution and the boiling point of the pure solvent is known as elevation of boiling point.**

Elevation of boiling point (ΔT_b) = boiling point of the solution – boiling point of pure solvent

From Raoult's law for dilute solution

$$\frac{P_o - P_s}{P_o} = \left(\frac{w_A}{m_A} \right) \left(\frac{m_B}{w_B} \right)$$

where, p_s = vapour pressure of solution

p_o = vapour pressure of solute

$$P_o - P_s = \left(\frac{w_A}{m_A} \right) \left(\frac{m_B}{w_B} \right) P_o$$

For the pure solvent, p_o (its vapour pressure at the boiling point) and m_B (its molecular mass) are constant.

Therefore,

$$\begin{aligned} P_o - P_s &\propto \left(\frac{w_A}{m_A} \right) \left(\frac{1}{w_B} \right) \\ \Rightarrow \Delta P &\propto \Delta T_b \propto \left(\frac{w_A}{m_A} \right) \left(\frac{1}{w_B} \right) \\ \Rightarrow \Delta T_b &= k_b \left(\frac{w_A}{m_A} \right) \left(\frac{1}{w_B} \right) \end{aligned}$$

Where K_b is called as elevation constant.

3) Depression of Freezing point (ΔT_f) (Cryoscopy):

Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid.

When non volatile solute is added to the solvent, lowers the vapour pressure of the solvent, therefore it will be in equilibrium with solid phase at a lower pressure and hence at lower temperature.

The difference between the freezing points of the pure solvent and its solution is called depression of freezing point.

Depression of freezing point (ΔT_f) = freezing point of the solvent – freezing point of the solution

From Raoult's law for dilute solution

$$\frac{P_o - P_s}{P_o} = \left(\frac{w_A}{m_A} \right) \left(\frac{m_B}{w_B} \right)$$

Where, p_s = vapour pressure of solution

p_o = vapour pressure of solute

$$P_o - P_s = \left(\frac{w_A}{m_A} \right) \left(\frac{m_B}{w_B} \right) P_o$$

For the pure solvent, p_o and m_B are constant.

Therefore,

$$\begin{aligned} P_o - P_s &\propto \left(\frac{w_A}{m_A} \right) \left(\frac{1}{w_B} \right) \\ \implies \Delta P &\propto \Delta T_f \propto \left(\frac{w_A}{m_A} \right) \left(\frac{1}{w_B} \right) \\ \implies \Delta T_f &= k_f \left(\frac{w_A}{m_A} \right) \left(\frac{1}{w_B} \right) \end{aligned}$$

Where K_f is called as depression constant.

4) Osmosis and osmotic pressure:

Osmosis: The spontaneous flow of solvent molecules through semi permeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

Osmotic pressure:

It is defined as the hydrostatic pressure built up on the solution which just stops the osmosis.

Osmotic pressure = hydrostatic pressure

van't Hoff theory of dilute solutions:

van't Hoff realized that an analogy exists between gases and solutions provided osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for dilute solutions of non-electrolytes the following laws hold good.

- 1) **Boyle-van't Hoff law:** the osmotic pressure (P or π) of a solution is directly proportional to its concentration (C) when the temperature is kept constant. The concentration of the solution containing one gram mole in V litres is equal to $1/V$ ($C = 1/V$)

Thus $P \propto C$

$$P \propto \frac{1}{V}$$

or $PV = \text{constant}$ or $\pi V = \text{constant}$

- 2) **Gay-Lussac-van't Hoff law:**

Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), *i.e.*,

$$P \propto T$$

$$\implies \frac{P}{T} = \text{Constant} \text{ or } \frac{\pi}{T} = \text{Constant}$$

Combining above two laws,

$$P \propto CT$$

$$P = SCT$$

$$\implies P = (S) \left(\frac{1}{V} \right) T$$

$$PV = ST \quad \text{or} \quad \pi V = ST$$

Where S is called molar solution constant. $S = 0.082 \text{ lit atm K}^{-1} \text{ mol}^{-1}$

If solution contains n gram moles in V litres, the general equation would become

$$PV = nST \quad \text{or} \quad \pi V = nST$$

- 3) **Third law:**

Equimolecular solutions of different solutes exert equal osmotic pressure under identical conditions of temperature. Such solutions which have the same osmotic pressure are termed as **isotonic solutions**.

Avogadro hypothesis, “equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure, contain equal number of molecules.”

For solution I, $PV = n_1 ST$

For solution II, $PV = n_2 ST$

Thus, n_1 must be equal to n_2 when P , V and T are same.

Determination of molecular masses:

For dilute solutions $PV = nST$,

Instead of one gram mole of the solute present in V litres of solution, let w_A gram of solute (mol. Mass m_A) be present in V_1 litres of solution, then

thus, the equation $PV = nST$ becomes

$$PV_1 = \left(\frac{w_A}{m_A} \right) (ST)$$

$$\implies m_A = \frac{(w_A)(S)(T)}{PV_1}$$

Knowing the value of P experimentally, the value of m_A , i.e., molecular mass of the solute can be determined.

Consider two solutions I and II having n_1 and n_2 moles of the solute in V_1 and V_2 litres of solution respectively. Let P_1 and P_2 be their osmotic pressures at the same temperature (T).

From the equation, $PV = nST$,

For solution I, $P_1 V_1 = n_1 ST$

$$\implies P_1 = \left(\frac{n_1}{V_1} \right) ST$$

For solution II, $P_2 V_2 = n_2 ST$

$$\implies P_2 = \left(\frac{n_2}{V_2} \right) ST$$

If both solutions are isotonic, i.e., $P_1 = P_2$

$$\begin{aligned} \left(\frac{n_1}{V_1} \right) ST &= \left(\frac{n_2}{V_2} \right) ST \\ \implies \frac{n_1}{V_1} &= \frac{n_2}{V_2} \\ \implies \frac{(w_1/m_1)}{V_1} &= \frac{(w_2/m_2)}{V_2} \end{aligned}$$

This is the condition for isotonic solutions.

Raoult's Law:

According to this law, the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

Let a mixture (solution) be prepared by mixing n_A moles of liquid A and n_B moles of liquid B. Let p_A and p_B be the partial pressures of two constituents A and B in solution and p_A^0 and p_B^0 the vapour pressures in pure state respectively.

Thus, according to Raoult's law,

$$p_A = \left(\frac{n_A}{n_A+n_B}\right) p_A^0 = (\text{mole fraction of A}) (p_A^0) = X_A p_A^0$$

$$\text{and } p_B = \left(\frac{n_B}{n_A+n_B}\right) p_B^0 = (\text{mole fraction of B}) (p_B^0) = X_B p_B^0$$

If the total pressure be P , then

$$\begin{aligned} P &= p_A + p_B \\ &= \left(\frac{n_A}{n_A+n_B}\right) p_A^0 + \left(\frac{n_B}{n_A+n_B}\right) p_B^0 \\ &= X_A p_A^0 + X_B p_B^0 \end{aligned}$$

Ideal solutions obey Raoult's law at every range of concentration. Non-ideal solution does not obey Raoult's law. They show either positive or negative deviation from Raoult's law.

Relation between Dalton's law and Raoult's law:

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fractions of vapours A and B be Y_A and Y_B . Let p_A and p_B be the partial pressures of vapours A and B respectively and total pressure P .

$$p_A = Y_A P \quad \text{-----(i)}$$

$$p_B = Y_B P \quad \text{-----(ii)}$$

$$p_A = X_A p_A^0 \quad \text{-----(iii)}$$

$$p_B = X_B p_B^0 \quad \text{-----(iv)}$$

Equating (i) and (iii)

$$Y_A P = X_A p_A^0$$

$$\implies Y_A = \frac{X_A P_A^0}{P} = \frac{P_A}{P}$$

Similarly equating (ii) and (iv)

$$Y_B = \frac{X_B P_B^0}{P} = \frac{P_B}{P}$$