Chapter - 1 : The Solid State

TOPIC-1

Classification of Solids Based on Different Binding Forces, Crystal Lattices, Unit Cells, Packing in Solids

Quick Review

- **Solids :** Solids are chemical substances which are characterised by definite mass, shape and volume, rigidity, high density, low compressibility. The constituent particles (atoms, molecules or ions) are closely packed and held together by strong intermolecular forces.
- **General characteristics of solids are as given below :**
  - **(i)** Solids have definite mass, shape and volume.
  - **(ii)** The intermolecular distance is minimum in solids and have strong intermolecular forces.
  - **(iii)** The constituent particles i.e., atoms, molecules or ions have fixed positions.
  - **(iv)** Solids cannot be compressed except foam, rubber, sponge etc.
  - **(v)** Most of them have high melting and boiling point.
  - **(vi)** Solids are rigid.

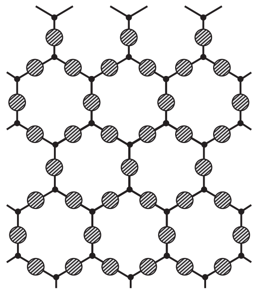


Fig. 1 : Two - dimensional representation of structure of crystalline solid (SiO_2)

- **Types of solids :** There are two types of solids.
  - **(a) Crystalline solids :** The solids in which the constituent particles have an ordered arrangement (long range order) are crystalline solids. For example, Sodium chloride, Diamond, Iodine etc.

    Crystalline solids show following main characteristics :
    - **(i)** Constituent particles are regularly arranged.
    - **(ii)** They possess sharp melting point.
    - **(iii)** Their outer surface also show a regular arrangement during the formation of crystals.
    - **(iv)** These are anisotropic in nature.
    - **(v)** It has a definite geometrical shape with flat faces and sharp edges.
    - **(vi)** It has long range order of arrangement of constituent particles.
  - **Classification of Crystalline solids :** On the basis of binding forces, crystalline solids are classified as follows :
    - **(i)** Molecular solids
    - **(ii)** Ionic solids
    - **(iii)** Metallic solids
    - **(iv)** Covalent solids
  - **(b) Amorphous solids :** The solids in which constituent particles do no have ordered arrangement (short range order) are amorphous solids. These have a range of melting point. For example, Plastic, Glass, etc.

    Amorphous solids show following main characteristics :
    - **(i)** Constituent particles are not arranged regularly and are irregular.
    - **(ii)** These solids do not show sharp melting point.
    - **(iii)** Outer surface does not show regular arrangement during the formation of crystals.
    - **(iv)** These are isotropic in nature.
    - **(v)** It has short range order of arrangement of constituent particles.

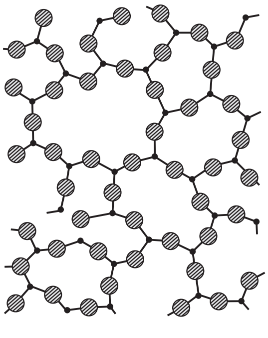


Fig. 2 : Two - dimensional representation of structure of amorphous solid (SiO_2)

Properties of Solids :

- **Isotropy and Anisotropy :** The solids whose some of the physical properties like electrical resistance or refractive index show different values when measured in different directions in the same crystal, this property is called anisotropy. Crystalline solids are anisotropic in nature.

  On the other hand, solids whose value of any physical property would be same along any direction. This property is called isotropy. Amorphous solids are isotropic in nature.

- **Different Types of Solids :**

S. No.	Type of solids	Constituent Particles	Bonding/Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
1.	Molecular solids						
	(i) Non-polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
	(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
	(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
2.	Ionic solids	Ions (positive and negative)	Coulombic or Electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
3.	Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	All metals are alloys	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
4.	Covalent or Network solids	Atoms	Covalent bonding	SiO_2 (Quartz), SiC, C (Diamond), AlN	Hard	Insulators	Very high
				C (Graphite)	Soft	Conductor (exception)	

- **Crystal lattice :** The regular three dimensional arrangement of the constituent particles in a crystal in which each particle is represented by point is called a crystal lattice and points are called lattice points.
- **Unit cell :** It is the smallest, fundamental repeated three dimensional unit of a crystal lattice.
- **Characteristics of unit cell :** A unit cell is characterized by the following parameters :

(i) Axial lengths *a, b* and *c* of the three edges along the three axis *i.e.*, axial distances.

(ii) Axial angles α, β and γ between the pairs of edges (*b, c*), (*c, a*) and (*a, b*) respectively.

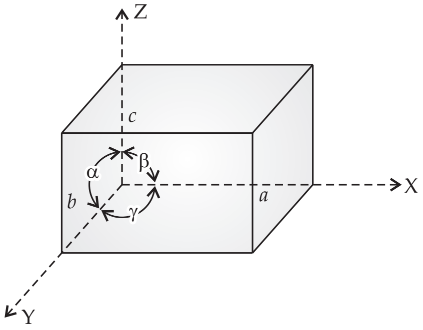


Fig. 3 : Characteristic parameters of a unit cell

Thus, a unit cell is characterized by six parameters edges: *a, b, c* and parameters: α, β and γ.

- **Types of unit cell :** There are two types of unit cells namely, primitive unit cell and centred unit cell.
- **Primitive unit cell :** In the primitive unit cell, constituent particles are present only on the corner positions of a unit cell. There are seven types of primitive unit cells.
- **Centred unit cell or non-primitive unit cell :** In this type of unit cell, particles (or points) are present not only at the corners but also at some other positions.

These are of three types :

(i) Face-centred cubic (*fcc*) : Particles (or points) are located at the corners and also at the centre of each face.

(ii) Body-centred cubic (*bcc*) : Particles (or points) are located at the corners and also at the centre within the body.

(iii) End-centred cubic (*ecc*) : Particles (or points) are located at the corners and also at the centres of the two opposite end faces.

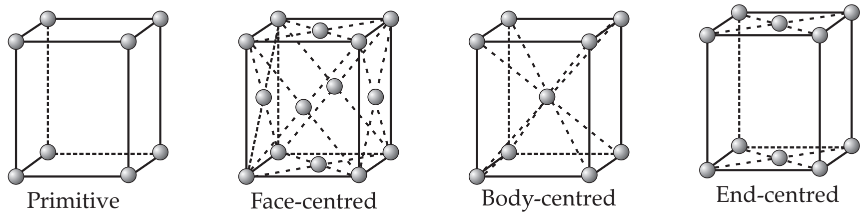

Primitive Face-centred Body-centred End-centred

Fig. 4 : Different types of unit cells

- **Bravais lattices :** These are the arrangement of lattice points in three dimensional space of crystal shown by relative distance and facial angles along the three axis.

There are 14 Bravais lattices, as shown in table below:

S. No.	Unit cell	Crystal system basic	Relative axial distances	Axial angles	Symmetry	Bravais lattice	Examples
1. **2.** **3.**	Primitive Body-centred Face-centred	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	9 planes, 13 axis	3	NaCl, KCl, ZnS, Diamond
4. **5.**	Primitive Body-centred	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	5 planes, 5 axis	2	TiO_2, SnO_2, $PbSO_4$, NH_4Br
6. **7.** **8.** **9.**	Primitive Body-centred Face-centred End-centred	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	3 planes, 3 axis	4	KNO_3, $BaSO_4$, K_2SO_4
10.	Primitive	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	7 planes, 7 axis	1	ZnO, CdS
11.	Primitive	Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	7 planes, 7 axis	1	$NaNO_3$, HgS
12. **13.**	Primitive End-centred	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$	7 planes, 10 axis	2	Monoclinic sulphur, $PbCrO_4$
14.	Primitive	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	No planes, No axis	1	$CuSO_4.5H_2O$, $K_2Cr_2O_7$

- **Number of atoms in a unit cell :** Crystal lattice which includes number of unit cells and constituent particles are represented by lattice points. Number of atoms in a unit cell (Z) : for simple cubic Z = 1, for bcc Z = 2 for fcc Z = 4 and for ecc Z = 2.

Number of atoms per unit cell

Type of cell	Number of atoms at corner	Number of atoms at faces	Number of atoms at centre of cube	Total
Simple cubic Crystal (*scc*)	$8 \times \frac{1}{8} = 1$	0	0	1
Body-centred cubic (*bcc*)	$8 \times \frac{1}{8} = 1$	0	1	2
Face-centred cubic (*fcc*)	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	4

- **Closed-packed structures :** The constituent particles are closely packed in solids and there is minimum space between particles. These structures are called close packed structures.
- **Types of close packing :**

(a) Close packing in one dimension : When the spheres representing particles are touching each other in a row, it is called close packing.

(b) Closed packing in two dimensions : This type of packing is obtained by placing the rows of close-packed spheres. This can be done in two ways :

(i) Square close packing : The particle in the adjacent rows may show a horizontal as well as vertical alignment forming squares. A central sphere is surrounded by four other spheres in two dimensions.

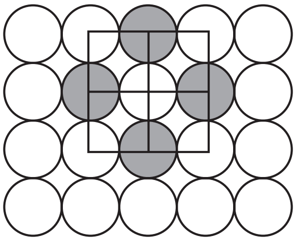


Fig. 5 : Square close packing of spheres in two dimensions

(ii) Hexagonal close packing : The second row (particles) may be placed above the first row. It is repeated in the next row. Each sphere is in contact with six other spheres.

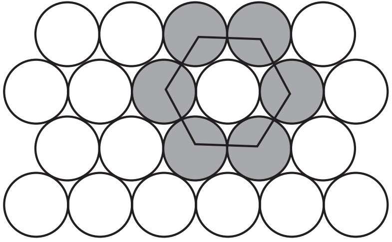


Fig. 6 : Hexagonal close packing of spheres in two dimensions

(c) Close-packing in three dimensions : All the solid exists in three dimensional structures. These structures can be obtained by placing two dimensional layers one above other. They can be of two types :

(i) Square close packed layers : In this arrangement, spheres of both the layers are perfectly aligned horizontally as well vertically. If the arrangement of spheres at the first layer is called 'A' type. All the layers have the same arrangement. Thus, this lattice has AAA type pattern. The co-ordination number is 6 in three dimensions.

(ii) Hexagonal close packed layers : It is more efficient and leaves less space unoccupied by spheres. The central sphere is in contact with six other spheres in two dimensions.

- **Co-ordination number :** The number of closest neighbours of any constituent particle is called its co-ordination number. Co-ordination number of *hcp* and *ccp* is 12 while in *bcc*, it is 8.
- **Atomic radius :** It is defined as half of the distance between neighbouring atom in a crystal. It is expressed in terms of the edge (a) of unit cell of the crystal.

(i) Simple cubic structure (sc) : Radius of atom 'r' $= \frac{a}{2}$, as atoms touch along the edges.

(ii) Body-centred cubic structure (bcc) : Radius of atom 'r' $= \frac{\sqrt{3}}{4}a$.

(iii) Face centred cubic structure (fcc) : Radius of atom 'r' $= \frac{a}{2\sqrt{2}}$.

Know the Terms

- **Order** : It designates the presence or absence of some symmetry or correlation in a many-particle system.
- **Ionic crystal :** A crystal structure that grows from chemical bonds between two oppositely charged atoms which are held together by electrostatic attraction.
- **Fluidity :** The physical property of a substance that enables it to flow.

TOPIC-2

Packing Efficiency, Voids, Calculations Related to Unit Cell Dimensions

Quick Review

- **Voids or holes :** The holes left in the close packing of spheres are called as interstitial sites or voids or holes.

- **Trigonal voids :** The void enclosed by three spheres in contact is called a trigonal void. There are 24 voids around each sphere. There are eight trigonal voids per atom in a crystal. Radius ratio is 0.155.
- **Tetrahedral voids :** The void surrounded by four sphere lying at the vertices of a regular tetrahedron is called tetrahedral void. There are 8 tetrahedral voids around each sphere and two voids per atom of crystal. So, number of tetrahedral voids = 2 × Number of close packed spheres = 2N. The radius of a tetrahedral void in a closest packed arrangement is 22.5% of the sphere involved in this arrangement. Thus,

$$\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.225$$

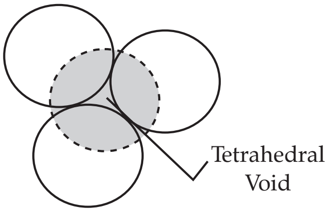


Fig. 7 : Tetrahedral void

- **Octahedral voids :** The void surrounded by six spheres lying at the vertices of a regular octahedron is called octahedral void. There are 6 octahedral voids around such sphere. There is one void per atom in a crystal. So,

$$\begin{aligned}\text{Number of octahedral voids} &= 1 \times \text{Number of close packed spheres}\\ &= \text{N}\end{aligned}$$

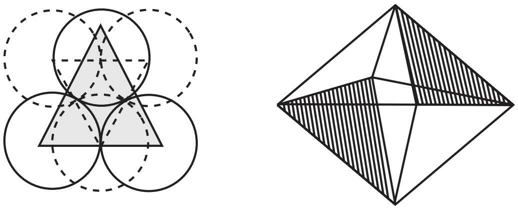


Fig. 8 : Octahedral void

The radius of an octahedral void in a close packed arrangement is 41.4% of the sphere involved in this arrangement. Thus,

$$\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.414$$

- **Packing efficiency :** It is the percentage of entire space which is covered by the particles. Calculation of packing efficiency of various types of structures is as follows :

(i) Packing efficiency of *hcp* and *ccp* structures : Both are equally efficient.

$$\text{Packing efficiency of } hcp \text{ or } ccp = \frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of the unit cell } (a^3)} \times 100$$

$$= \frac{4 \times \frac{4}{3}\pi r^3 \times 100}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 74\% \qquad \left[\text{for } ccp, a = \left(\frac{4r}{\sqrt{2}}\right)\right]$$

(ii) Packing efficiency of *bcc* structure : For *bcc* structure *a* is $\left(\frac{4r}{\sqrt{3}}\right)$.

$$\text{Packing efficiency of } bcc = \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell } (a^3)} \times 100$$

$$= \frac{2 \times \frac{4}{3}\pi r^3 \times 100}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 68\%$$

(iii) Packing efficiency of simple cubic lattice : It has less packing efficiency as compared to *hcc* and *bcc*. For simple cubic lattice *a* = 2*r*.

$$\text{Packing efficiency of simple cubic lattice} = \frac{\text{Volume of one atom or sphere present in the unit cell}}{\text{Total volume of unit cell}}$$

$$= \frac{\frac{4}{3}\pi r^3 \times 100}{(2r)^3}$$

$$= 52.4\%$$

- **Calculations of density involving unit cell dimensions :**

$$\text{Density of unit cell } 'd' = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$\text{Mass of the unit cell} = \text{Number of atoms in the unit cell} \times \text{Mass of each atom}$$

$$= \text{Z} \times m$$

where, 'Z' is the number of atoms in one unit cell and 'm' is mass of each atom.

$$\text{Mass of each atom, } m = \frac{\text{Atomic mass}}{\text{Avogadro's number}}$$

$$m = \frac{\text{M}}{\text{N}_\text{A}}$$

Volume of cube = a^3, where 'a' is the edge length of the cube

$$\text{Density of unit cell } 'd' = \frac{\text{M} \times \text{Z}}{\text{N}_\text{A} \times a^3}$$

It is also the relation between the density 'd' and the edge length 'a' of unit cell.

Know the Formulae

- $$\text{Density of the unit cell } (d) = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{\text{Z} \times \text{M}}{\text{N}_\text{A} \times a^3}$$

- **Various parameters of cubic system :**

Unit cell	No. of atoms per unit cell	Distance between nearest neighbour (d)	Coordination Number	Radius (r)
Simple cubic	1	a	6	$\frac{a}{2}$
Face-centred cubic	4	$\frac{a}{\sqrt{2}}$	12	$\frac{a}{2\sqrt{2}}$
Body-centred cubic	2	$\frac{\sqrt{3}}{2}a$	8	$\frac{\sqrt{3}}{4}a$

$$\text{Packing efficiency} = \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}} \times 100$$

- **Packing efficiency of different crystals :**

Crystal system	Packing efficiency
Simple cubic	52.4%
Body-centred cubic	68%
Face-centred cubic	74%
Hexagonal close-packed	74%

- $$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{r^+}{r^-}$$

- **Structural arrangement of different radius ratio of ionic solids :**

Radius ratio $\left(\frac{r^+}{r-}\right)$	Possible C.N.	Structural arrangement	Examples
0.155 – 0.225	3	Trigonal planar	B_2O_3

0.225 – 0.414	4	Tetrahedral	ZnS, SiO_4^{4-}
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 1	8	Body-centred cubic	CsCl

Know the Terms

- **Void :** Empty space left after packing.
- **Radius ratio :** For ionic solids, the ratio of the radius of cation to that of anion.
- **Packing efficiency :** Percentage of total space filled by the particles in a solid is called packing efficiency.
- **Co-ordination number :** Number of spheres touching one sphere in a close packed structure.

TOPIC-3

Defects in Solids, Electrical and Magnetic Properties, Band Theory of Metals

Quick Review

- **Imperfection (defects) caused by Impurities :**
  (i) Impurity defects in covalent solids.
  (ii) Impurity defects in ionic solids.
- **Defects in solids :** It is also known imperfection in solids. Ideal crystal is that which has definite repeating arrangement of particles of atoms in crystal. Any departure from perfectly ordered arrangement of atom in crystal is called defect or imperfection. Mainly there are two types of defects **(a)** Point defect. **(b)** Line defect.

(I) Point defect : This defect is also known as atomic imperfections. When deviations exist from the regular arrangement around a point or an atom in a crystalline substance, the defect is called point defect.

Types of point defects : Point defects are classified into three types :

(a) Stoichiometric defects
(b) Impurity defects
(c) Non-stoichiometric defects

(a) Stoichiometric defects : Defects which do not change the stoichiometry of solids are called stoichiometric defects. These are also intrinsic or thermodynamic defects. There are four types of this defect :

(i) Vacancy defect : When some lattice sites in a crystalline solid are vacant, then crystal is said to have vacancy defect. This defect arises on heating. As a result, the density of the solid decreases.

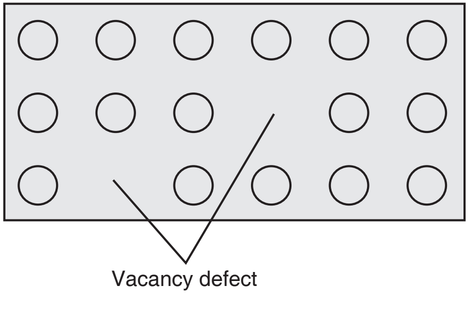


Fig. 9 : Crystalline solid showing vacancy defect

(ii) Interstitial defect : When some extra constituent particles occupy the interstitial site in crystal, defect is known as interstitial defect. It arises by applying high pressure on the crystal. This defect increases the density of the crystal.

Both these defects are shown by non-ionic solids.

(iii) Frenkel defects : This defect arises when an ion leaves its fixed position and occupies an interstitial space. It creates vacancy at lattice point. There is no change in number of ions. This defect is shown by the crystal having lower co-ordination number. The ionic crystals which have large difference in the size of ions, show this defect. This defect does not affect the density of the solid. This defect is found in ZnS, AgCl, AgBr, AgI, etc.

Consequences of Frenkel defect :

- Crystal becomes conductor of electricity.

- Stability of crystal decrease.
- Dielectric constant increases.

(iv) Schottky defect : The Schottky defect is often visually demonstrated using the following layout of anions and cations.

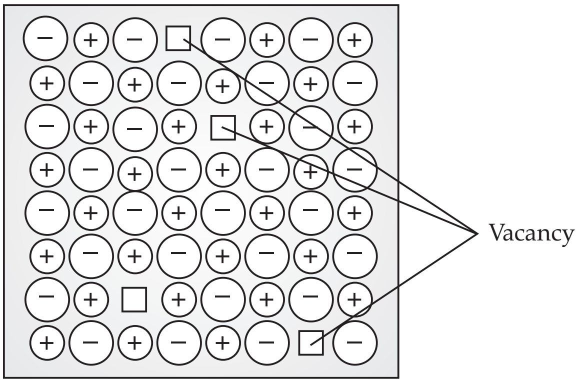


Fig. 10 : Schottky Defect

Positive symbols represents cations (*i.e.*, Na^+) and the negative symbols represents anions (*i.e.*, Cl^-). This defect causes vacancy of equal numbers of cations and anions. In addition, this layout is applicable only for ionic crystal compounds in which cations are of almost similar sizes. For example NaCl, FeO, FeS, etc.

AgBr shows both Frenkel and Schottky defects.

Consequences of Schottky defect :

- Density of crystal decreases
- Lattice energy of crystal decreases
- Stability of crystal decreases
- Crystal becomes conductor of electricity.

(b) Impurity defects : $SrCl_2$ or $CaCl_2$ is added to molten NaCl and it is crystallized. Some of the Na^+ ions are replaced by Sr^{2+} or Ca^{2+} ions. Each Sr^{2+} or Ca^{2+} ions replaces two Na^+ ions. It occupies the site of one of the ions and other site remains vacant. The number of cationic vacancies are equal to the number of bivalent cations added. Similar example of impurity defect is addition of $CdCl_2$ to AgCl.

(c) Non-stoichiometric defects : Those defects which lead to change in composition of solids are called non-stoichiometric defects. These defects are of two types :

(i) Metal excess defect, **(ii)** Metal deficiency defect.

(i) Metal excess defect : This defect arises due to anionic vacancies or due to the presence of extra cation in the interstitial sites. The anionic sites occupied by unpaired electrons. This defect occur in the following ways :

- **Metal excess defect due to anion vacancies :** In this defect, negative ion from the crystal lattice may be missing from its lattice site leaving a hole or vacancy which is occupied by the electron originally associated with anion. In this way crystal remains neutral. Alkali halides like NaCl and KCl show this type of defect.
- **F-Centres :** These are anionic sites occupied by unpaired electrons. F– centres impart colour to crystals. The colour results by the excitation of electrons when they absorb energy from the visible light falling on the crystal. For example NaCl becomes yellow in colour when heated with sodium vapours. LiCl becomes pink, KCl becomes violet.
- **Metal excess defect due to interstitial cation :** In this defect, an extra cation occupies interstitial position in the lattice and the free electron is trapped in the vacancy (vicinity) of this interstitial cation, but crystal remains neutral. For example : Zinc oxide on heating loses oxygen and turn yellow.

$$ZnO \xrightarrow{heat} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The excess of Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial site.

(ii) Metal deficiency defect : In this, a cation is missing from its lattice site. To maintain electrical neutrality, one of the nearest metal ion acquires two positive charges.

This type of defect occurs in compounds where metal can exhibit variable valency. *e.g.*, transition metal compounds like NiO, FeO, FeS etc.

Compounds which act as semiconductors :

➢ **(i) 13-15 compounds :** When the solid state materials are produced by combination of elements of groups 13 and 15, the compounds obtained are called 13-15. For example, GaAs, AlP.

(ii) 12-16 compounds : Combination of elements of groups 12 and 16 yield some solid compounds are called 12-16 compounds. For example, ZnS, CdS.

- **Line Defects :** Deviations or irregularities from the ideal arrangement in entire row of lattice point in a crystalline solid is known as line defects.
- **Types of solids on the basis of electrical conductivity :** Solids are classified into three groups :

  (i) Conductors : The solids which permit maximum flow of electricity are known as conductors. Their conductivity order is 10^4 to 10^7 ohm^{-1} m^{-1}. In metals, conduction takes place due to electrons while in ionic solids due to ions. *e.g.*, all metals, aqueous solution of NaCl etc.

  (ii) Semi-conductors : The solids which permit less flow of electricity as compared to conductors are known as semiconductors. The conductivity order ranges from 10^{-6} to 10^4 ohm^{-1} m^{-1}. As the temperature rises their conductivity value also rises because electrons from the valence band jump to conduction band, *e.g.*, Si, Ge.

  (iii) Insulators : The solids which are unable to conduct the electricity are known as insulators. Their conductivity value ranges from (10^{-20} to 10^{-10}) ohm^{-1} m^{-1}. For example : Sulphur, Phosphorus etc.

- **Band theory :** Band theory explains the conductivities of conductors, insulators and semiconductors. The interaction between the valence band and the conduction band decide the conductivity of a particular material.

  If the energy gap between the two shells is negligible, the electrons can jump easily from valance band to conduction band, they behave as good conductors.

  When the energy gap is small then the electrons can jump from valence band to conduction band on providing little energy then these type of solids behave as semiconductors.

  When this gap is large enough for the electrons to excite themselves from valence band to conduction band then they act as insulators.

  This energy gap between the conduction band and valence band in insulators is known as forbidden zone.

- **Doping :** The mixing of impurity in a solid crystal is known as doping. Due to doping, the conductance of semiconductors can be increased forming extrinsic semiconductors. The number of electrons or cation vacancies can be increased by doping.
- ***n*-type of semiconductors :** Silicon and germanium (Group-14) doped with donor impurity (like P or As of Group-15) are called *n*-type semiconductor. Here *n* means negative, which in fact is nature of charge on electron, doping of phosphorus (P) in silicon (Si). Silicon and phosphorus have 4 and 5 valence electrons respectively. The extra electron of phosphorus increases conductivity of the crystal.
- ***p*-type of semiconductors :** Silicon or germanium (Group-14) doped with acceptor impurity (Like B, Al or Ga of Group-13) is called *p*-type semiconductor. Here '*p*' indicates positive *e.g.*, doping of boron in silicon. Silicon and boron contain 4 and 3 valence electrons respectively. Due to deficiency of one electron in boron (B), positively charged hole increases conductance.
- **Classification of substances on the basis of magnetic properties :**

  (i) Paramagnetic substances : The substances which are attracted in external magnetic field are known as paramagnetic substances. In such type of substances, atoms or molecules have unpaired electrons. In magnetic field, the alignment of magnetic moments develops magnetic property. Thus, substances acquire temporary magnetism in the magnetic field. *e.g.* Cu^{2+}, O_2 etc.

  (ii) Diamagnetic substances : The substances which are repelled in magnetic field are known as diamagnetic substances. The atoms or molecules of these substances have paired electrons only. *e.g.*, Zn, TiO_2, NaCl etc.

  (iii) Ferromagnetic substances : The substances which are attracted most easily in magnetic field are known as ferromagnetic substances. These compounds acquire permanent alignment of magnetic moments in magnetic field. *e.g.*, Fe, Co, Ni, CrO_2 etc.

  (iv) Anti-ferromagnetic substances : Those paramagnetic substances whose resultant magnetic moment due to alignment of magnetic moments in the magnetic field is zero are known as anti-ferromagnetic substances. *e.g.*, MnO. The alignment of magnetic moment is found opposite to each other in equal number.

  (v) Ferrimagnetic substances : Paramagnetic substances in which resultant magnetic moment due to alignment of magnetic moments in magnetic field is less than that of ferromagnetic substances are known as ferrimagnetic substances. In such substances, magnetic moments alignment in parallel way is more than in opposite side. *e.g.* Fe_3O_4, $MgFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$.

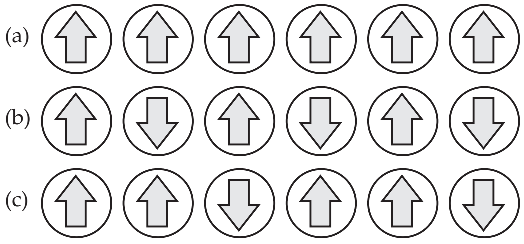
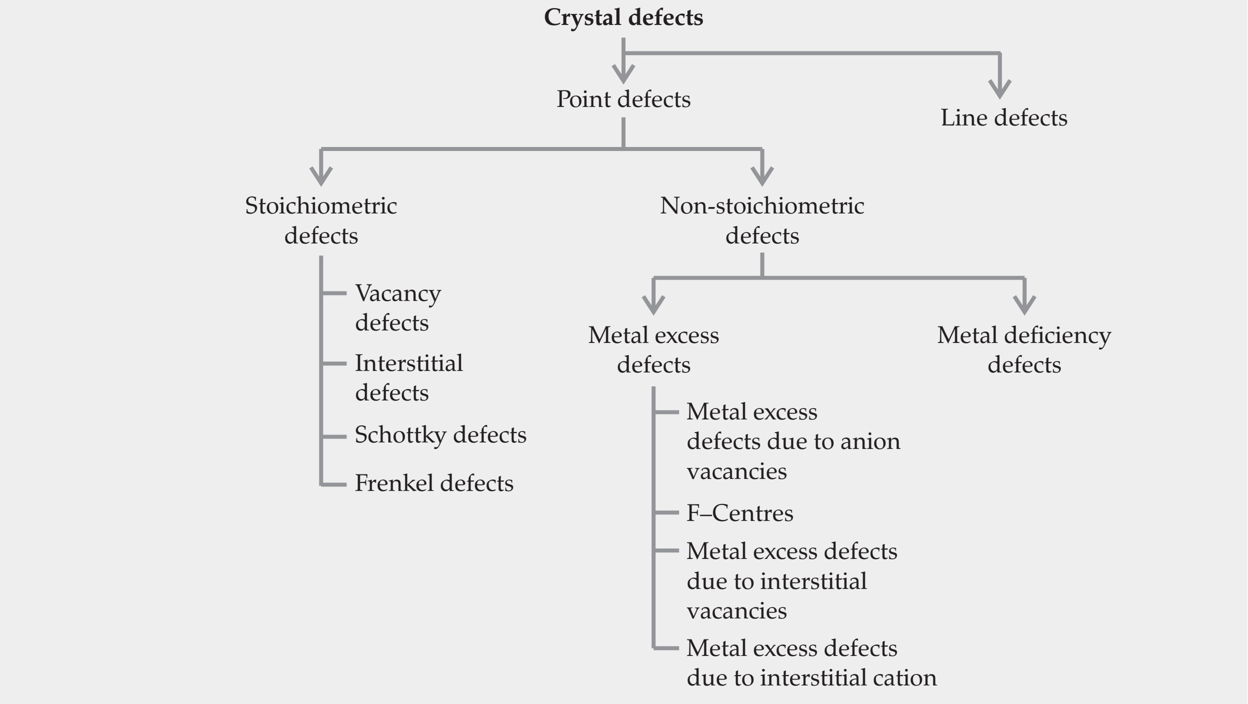


Fig. : 11. Schematic alignment of magnetic moments in (a) ferromagnetic, (b) anti-ferromagnetic and (c) ferrimagnetic substances

Flowchart

- **Imperfection (defects) caused by Impurities :**



Know the Terms

- **Crystal defect :** Irregularity in the packing of atoms in a solid crystal.
- **Interstitials :** Atoms or ions which occupy normal voids in a crystal.
- **Kernel :** Positively charged part of the atoms except electrons.
- **Vacancy :** When one of the constituent particles is missing from the crystal lattice, this unoccupied position is called vacancy.
- **Curie temperature :** Temperature at which a ferromagnetic substance loses its ferromagnetism and attains paramagnetism only is called curie temperature.
- **Domains :** In solid state, metal ions of ferromagnetic substances are grouped together into small regions called domains.
- **Band :** The close arrangement of molecular orbitals made by atomic orbitals according to their energy.
- **Diode :** Combination of *p* and *n*-type semiconductors.
- **Transistor :** *pnp* or *npn* Sandwich semiconductor.
- **Energy gap :** The difference of energy between the bottom of the conduction band and the top of the valence band of the electrons in a crystalline solid.

❑❑

Chapter - 2 : Solutions

TOPIC-1
Types of Solutions, Expression of Concentration and Solutions and Solubility

Quick Review

- **Solution :** A homogeneous mixture of two or more than two pure substances is known as solution.

- If the constituents of the solution are two, it is called binary, if three then ternary, if four then quaternary and so on.
- **Two constituents of the solution are :**
  - **(i) Solute :** A substance that is dissolved in another substance in lesser amount (a solvent), forming a solution. For example : sugar, salt etc.
  - **(ii) Solvent :** A substance in which another substance is dissolved in larger amount forming a solution. For example : water, milk etc.

Note: *Solvent determines the physical state of the solution.*

- **Types of Solutions :** Any state of matter (solid, liquid, or gas) can act both as a solvent and as a solute during the formation of a solution. Therefore, depending upon the physical states of solute and solvent, we can have following nine different types of solutions :

S. No.	Types of Solution	Solute	Solvent	Examples
1.	Solid – Solid	Solid	Solid	Alloys like brass, bronze, etc.
2.	Solid – Liquid	Solid	Liquid	Solution of sugar, salt, urea etc. in water.
3.	Solid – Gas	Solid	Gas	Sublimation of substance like iodine, camphor etc, into air, dust or smoke particles in air.
4.	Liquid – Solid	Liquid	Solid	Hydrated salts, mercury in amalgamated zinc, etc.
5.	Liquid – Liquid	Liquid	Liquid	Alcohol in water, benzene in toluene.
6.	Liquid – Gas	Liquid	Gas	Aerosol, water vapour in air.
7.	Gas – Solid	Gas	Solid	Hydrogen absorbed in palladium.
8.	Gas – Liquid	Gas	Liquid	Aerated drinks.
9.	Gas – Gas	Gas	Gas	Mixture of gases etc.

- **Aqueous solution :** A solution containing water as solvent is known as aqueous solution. *For example,* sugar solution.
- **Non-aqueous solution :** A solution containing solvent other than water is known as non-aqueous solution. *For example,* iodine dissolved in alcohol.
- **Saturated solution :** A solution in which no more solute can be dissolved at the same temperature is known as saturated solution.
- **Unsaturated solution :** A solution in which more amount of solute can be dissolved at the same temperature.
- **Solubility :** Solubility can be defined as the maximum amount of solute that can be dissolved in 100 g solvent to form a saturated solution at a given temperature.
  - **Causes of Solubility :**
    - **(i) Inter-ionic attraction in the solute molecules :** Molecules are stabilised in the lattice due to electrostatic forces and the energy released is known as lattice energy.
    - **(ii)** Inter-molecular attraction between solvent molecules.
    - **(iii) Solvation :** It denotes the force of attraction between solute and solvent molecules.
    - **(iv)** Temperature.
  - **Deciding Factors for Solubility :**
    - **(i) Nature of Solute and Solvent :** "Like dissolve like" *i.e.,* polar solvents like water and ammonia can dissolve polar solute or ionic solute while non-polar solvents can dissolve non-polar organic solutes.
    - **(ii) Temperature :** Solubility increases with increase in temperature. It increases for endothermic reaction while it decreases for exothermic reactions.
    - **(iii) Pressure :** The solubility of solid in liquid is not affected significantly by pressure because solids and liquids can not be compressed.

      Hydration Energy : It is the amount of energy released when ions formed by 1 mole of compound get hydrated. It is an exothermic process.
- **Method of Expressing Concentration of Solution :** The concentration of solution is the amount of solute present in the given quantity of solute or solvent. It can be expressed in any of the following types :
  - **(i) Mass percentage** $\left(\frac{W}{w}\right)$ **:** It is the amount of solute in grams dissolved per 100 gm of solution.

$$\text{Mass\% of a solute} = \frac{\text{Mass of solute in the solution}}{\text{Total mass of the solution}} \times 100$$

(ii) Volume percentage $\left(\frac{V}{v}\right)$ **:** It is defined as volume of a solute dissolved per 100 ml of solution.

$$\text{Volume\% of a solute} = \frac{\text{Volume of solute}}{\text{Total volume of the solution}} \times 100$$

(iii) Mass by volume percentage $\left(\frac{w}{v}\right)$ **:** It is defined as mass of solute dissolved per 100 ml of solution. It is commonly used in medicine and pharmacy.

$$\text{Mass by volume \% of solute} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

(iv) Parts per million (ppm) : It can be defined as the parts of a component per million (10^6) parts of the solution. It is used to express the concentration of a solute present in trace quantities.

$$\text{ppm (A)} = \frac{\text{Number of the parts of the component (A)}}{\text{Total number of parts of all the components of the solution}} \times 10^6$$

Parts per million can be expressed in three ways :

(a) Mass to mass

$$\text{ppm (mass to mass)} = \frac{\text{Mass of a component}}{\text{Total mass of solution}} \times 10^6$$

(b) Volume to volume

$$\text{ppm (volume to volume)} = \frac{\text{Volume of a component}}{\text{Total volume of solution}} \times 10^6$$

(c) Mass to volume

$$\text{ppm (mass to volume)} = \frac{\text{Mass of a component}}{\text{Volume of solution}} \times 10^6$$

(v) Mole Fraction : It is the ratio of number of moles of a particular component to the total number of moles of all the components. *e.g.,* mole fraction of component A.

$$\chi_A = \frac{n_A}{n_A + n_B},$$

where n_A is the number of moles of component 'A' and n_B is the number of moles of component 'B'.

Similarly,

$$\chi_B = \frac{n_B}{n_A + n_B}$$

Sum of mole fractions of all the components is always one.

$$\chi_A + \chi_B = 1$$

(vi) Molarity (M) : It is defined as the number of moles of solute per litre of solution.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in Litre)}} \text{ or } M = \frac{n_B}{V} \text{ or } M = \frac{W_B \times 1000}{M_B \times V}$$

where n_B is number of moles of solute, W_B is weight of solute, V is volume of solution in ml, M_B is molar mass of solute. Unit is mol L^{-1} or M (molar)

(vii) Molality (*m*) : It is defined as the number of moles of solute per 1000 g or 1 kg of solvent.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} \text{ or } m = \frac{n}{W} \text{ or } m = \frac{W_B \times 1000}{W \times W_A}$$

where n is number of moles of solute, W_A is weight of solvent, W_B is quantity of solute, M_B is molar mass of solute. Molality and mole fraction do not change with change in temperature. Unit is mol kg^{-1} or molal (*m*).

(viii) Normality (N) : It is defined as number of gram equivalents of solute dissolved per litre of solution.

$$\text{Normality} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in Litre}} \text{ or } N = \frac{W_B \times 1000}{E_B \times V}$$

where W_B is mass of solute, E_B is equivalent weight of solute, V is volume of solution in Litre.

- **Relationship between Molarity (M) and Molality (m) :**

$$\text{Molality } (m) = \frac{1000\text{M}}{\text{M} \times \text{M}_\text{B} - 1000d}$$

where m is molality, M is molarity, d is density of the solution and M_B is molar mass of solute.

- **Relation between mole fraction of solute (χ_B) and molality (m) :**

$$\boxed{\chi_\text{B} = \frac{m}{m \times \frac{1000}{\text{M}_\text{A}}}}$$

where χ_B is mole fraction of solute, m is molality and M_A is molar mass of solvent.

- **Relationship between molarity and density :**

$$\text{Molarity } (M) = \frac{\%\ \text{Strength} \times \text{Density} \times 10}{\text{M}_\text{B}}$$

where M_B is molar mass of solute.

- **Relationship between normality and density :**

$$\text{Normality } (N) = \frac{\%\ \text{Strength} \times \text{Density} \times 10}{\text{Equivalent mass of solute}}$$

- **Henry's Law :** The relationship between pressure and solubility is guided by Henry's Law. According to this law, ''The mass of a gas dissolved in given volume of the liquid at a constant temperature depends upon the pressure applied.''

It can also be stated as the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution.

$$p = K_H\chi,$$

where K_H = Henry's constant.

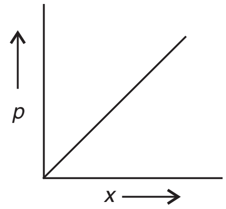


Fig. 1 : The slope of the line is the Henry's constant, K_H

- **Applications of Henry's law :**
  - **(i)** To increase the solubility of CO_2 in soda water and soft drinks, the bottle is sealed under high pressure.
  - **(ii)** To avoid the toxic effects of high concentration of nitrogen in blood, the tanks used by scuba divers are filled with air diluted with, He (11.7%), N_2 (56.2%) and oxygen (32.1%).
  - **(iii)** At high altitudes, low blood oxygen causes climber to become weak and make them unable to think clearly, which are symptoms of a condition known as anoxia.
- **Limitations of Henry's law :** This law is applicable only when :
  - **(i)** The pressure of gas is not too high and temperatures is not too low.
  - **(ii)** The gas should not undergo any chemical change.
  - **(iii)** The gas should not undergo association or dissociation in the solution.

Know the Formulae

- $$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

$$x_1 = \frac{n_1}{n_1 + n_2},\ x_2 = \frac{n_2}{n_1 + n_2}\ (x_1 + x_2 = 1)$$

- $$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume in solution in Litre}}$$
- $$\text{Molality } (m) = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$
- $$\text{Normality (N)} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in Litre}}$$

- $$\text{Mass percentage}\left(\frac{W}{w}\right) = \frac{\text{Mass of solute in the solution}}{\text{Total mass of the solution}}\times 100$$
- $$\text{Volume percentage}\left(\frac{V}{v}\right) = \frac{\text{Volume of solute}}{\text{Total volume of the solution}}\times 100$$
- $$\text{Mass by volume percentage}\left(\frac{W}{v}\right) = \frac{\text{Mass of solute}}{\text{Volume of solution}}\times 100$$
- $$p = K_H.\chi$$
  K_H = Henry's Low constant
  p = partial pressure of the gas in vapour phase
  χ = mole fraction of the gas in the solution
- $$\text{ppm of component A} = \frac{\text{Mass of component A}}{\text{Total mass of solution}}\times 10^6$$
- $$m = \frac{M \times 1000}{1000 \times d - M \times \text{Mol. wt.}}$$

Know the Terms

- **Homogeneous mixture :** A mixture in which composition and properties are uniform throughout.
- **Concentrated solution :** Solutions in which amount of solute is relatively large.
- **Dilute solution :** Solutions in which amount of solute is relatively very small.

TOPIC-2

Vapour Pressure, Raoult's Law, Ideal and Non-ideal Solutions

Quick Review

- Vapour pressure is the pressure exerted by vapours over a liquid at equilibrium state at constant temperature.
- **Vapour pressure depends on the following factors :**
  (i) Nature of the liquid.
  (ii)Temperature : Vapour pressure of a liquid increases with increase in temperature.
- **Raoult's law for a solution of volatile liquids :** It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction in solution.

  Suppose a solution is prepared by mixing two volatile liquids A and B. Let χ_A and χ_B respectively be their mole fractions, and let p_A and p_B be their partial vapour pressures in the solution at a particular temperature.
  If p_A^0 and p_B^0 are respectively their vapour pressures in the pure state, then according to Raoult's law:

  $$p_A = p_A^0\,\chi_A$$
  $$p_B = p_B^0\,\chi_B$$

  Considering Dalton's law of partial pressure

  $$p_{\text{total}} = p_A + p_B$$

  Substituting values of p_A and p_B,

  $$\begin{aligned} p_{\text{total}} &= \chi_A p_A^0 + \chi_B\, p_B^0 \\ &= (1-\chi_B)\, p_A^0 + \chi_B\, p_B^0 \\ &= p_A^0 + (p_B^0 - p_A^0)\chi_B \end{aligned}$$

  The composition of the vapour phase in equilibrium with the solution can be determined from the partial pressure of the two components. If Υ_A and Υ_B are the mole fractions of components A and B respectively in the vapour phase, then

  $$p_A = \gamma_A p_{\text{total}}$$

  and

  $$p_B = \gamma_B p_{\text{total}}$$

  In general $p_i = \gamma_i\, p_{\text{Total}}$
- **Raoult's law as a special case of Henry's law :** According to Raoult's law, the vapour pressure of volatile component (A) in a given solution is given as :

  $$p_A = p_A^0\,\chi_A$$

According to Henry's law, in the solution of a gas in a liquid, the gaseous component is normally so volatile that it exists as a gas and solubility depends upon Henry's law to which :

$$p_A = K_H \chi_A$$

On comparing both expressions $p_A{}^0$ is equal to K_H.

- **Raoult's law for non-volatile solute** : For a solution containing non-volatile solute present in a volatile solvent, Raoult's law may be stated as the relative lowering of vapour pressure for a solution is equal to the mole fraction of solute.

$$\chi_B = \frac{p_A^0 - p_A}{p_A^0},$$

where, χ_B = mole fraction of solute,

$p_A{}^0 - p_A$ = relative lowering of vapour pressure.

- **Ideal Solution :** A solution is called an ideal solution if it obeys Raoult's law over a wide range of concentration at specific temperature.

The enthalpy of mixing of the pure components to form the solution is zero and volume of mixing is also zero.

(i) $p_A = p_A{}^0 \chi_A \;\; p_B = p_B{}^0 \chi_B$

(ii) $\Delta H_{mix} = 0$,

(iii) $\Delta V_{mix} = 0$,

(iv) The force of attraction between A-A and B-B is nearly equal to A-B.

- **Some examples of ideal solutions are :**

(i) *n*-hexane and *n*-heptane,

(ii) ethyl bromide and ethyl chloride,

(iii) benzene and toluene,

(iv) chlorobenzene and bromobenzene.

- **Non-ideal solutions :** A solution which does not obey Raoult's law for all the concentrations is called a non-ideal solution.

For mixing a non-ideal solutions :

(i) Raoult's law is not obeyed.

i.e., $p_A \neq p_A{}^0 \chi_A$ and $p_B \neq p_B{}^0 \chi_B$

(ii) $\Delta H_{mix} \neq 0$,

(iii) $\Delta V_{mix} \neq 0$,

(iv) The force of attraction between A-A and B-B is not equal to A-B.

Some examples are :

(i) Water and ethanol

(ii) Chloroform and acetone

(iii) Ethanol and cyclohexane

A non-ideal solution can show either positive or negative deviation from Raoult's law.

- **Positive deviation from Raoult's law :** In this type of deviation A-B interactions are weaker than the interaction between A-B or B-B and leads to increase in vapour pressure.

Some examples are :

(i) Water and ethanol,

(ii) Chloroform and water,

(iii) Ethanol and CCl_4,

(iv) Methanol and chloroform,

(v) Benzene and methanol,

(vi) Acetic acid and toluene.

- **Negative deviation from Raoult's law :** In this type of deviation in non-ideal solutions, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure.

Some examples are :

(i) Chloroform and acetone,

(ii) Chloroform and methyl acetate,

(iii) H_2O and HCl,

(iv) H_2O and HNO_3,

(v) Acetic acid and pyridine,

(vi) Chloroform and benzene.

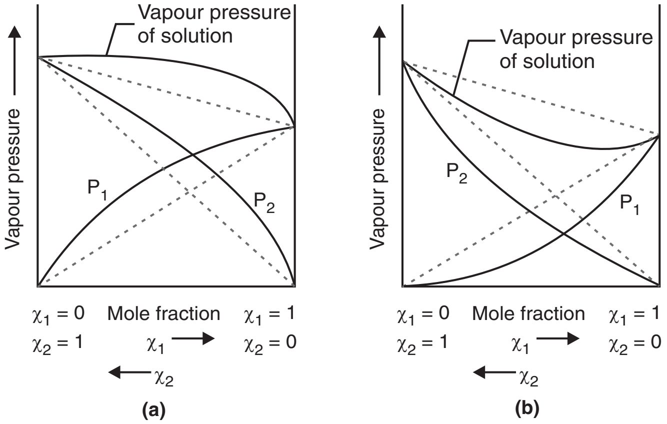


Fig. 2 : The vapour pressures of two component's system as a function of composition :
(a) A solution that shows positive deviation from Raoult's law, and
(b) A solution that shows negative deviation from Raoult's law.

- **Azeotropes :** Liquid mixtures which distil over without change in composition are called constant boiling mixtures or azeotropes or azeotropic mixtures.
- **Minimum boiling azeotropes :** Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes, *e.g,* water and benzene, chloroform and methanol.
- **Maximum boiling azeotropes :** Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which boil at temperature higher than the boiling points of its components. *e.g.* mixture of HNO_3 and H_2O.

Know the Formulae

- Raoult's law for a solution of volatile solute in volatile solvent:

$$p_A = p_A{}^0 \chi_A$$
$$p_B = p_B{}^0 \chi_B$$

- Raoult's law for a solution of non-volatile solute and volatile solvent:

$$\frac{p_A{}^o - p_A}{p_A{}^o} = i\chi_B = i\frac{n_B}{n_A} = i\frac{W_B \times M_A}{W_A \times M_B} \text{ (for dilute solution)}$$

Know the Terms

- **Boiling point :** The temperature at which the vapour pressure of solution becomes equal to the atmospheric pressure.
- **Dalton's Law of Partial Pressure :** When two or more volatile compounds are enclosed in a vessel, the total pressure is equal to the sum of partial pressure of each component.

$$p_{\text{Total}} = p_A + p_B$$

TOPIC-3
Colligative Properties, Determination of Molecular Mass, Abnormal Molecular Mass, Van't Hoff Factor

Quick Review

- **Colligative properties :** Certain properties of solutions depend only on the number of particles of the solute (molecule or ions) and do not depend on the nature of solute, such properties are called colligative properties. These are :
  - **(i)** Relative lowering of vapour pressure,
  - **(ii)** Depression in freezing point,
  - **(iii)** Elevation of boiling point,
  - **(iv)** Osmotic pressure of the solution.

- **Relative lowering of vapour pressure :** The relative lowering of vapour pressure is the ratio of lowering of vapour pressure and vapour pressure of pure solvent which is equal to the mole fraction of solute.

  Vapour pressure of pure solvent → $p_A°$
  Lowering of vapour pressure → $p_A° - p_A$
  Relative lowering of vapour pressure

$$\frac{p_A° - p_A}{p_A°} = \chi_{\text{solute}} = \frac{n}{N+n}$$

  where n and N are the number of moles of solute and solvent respectively.

- **Elevation of the boiling point :** The difference in boiling point of solution and pure solvent is called elevation of the boiling point.

  The boiling point of pure solvent → T_b^0
  The boiling point of solution → T_b
  The increase in boiling point $\Delta T_b = T_b - T_b^0$ is known as elevation of boiling point for dilute solution

$$\Delta T_b \propto \frac{\Delta p}{p°} = x_B$$

$$\Delta T_b = K\chi_B$$

$$\Delta T_b = K \times \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\Delta T_b = K \times M_A \times m$$

$$\Delta T_b = K_b m$$

  K_b → Boiling point elevation constant or molal elevation constant or Ebullioscopic constant.

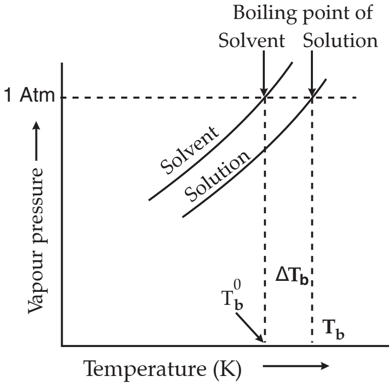


Fig. 3 : The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

- **Depression of freezing point :** According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the difference in the freezing point of pure solvent and that of the solution is known as depression in freezing point.

  The freezing point of pure solvent → T_f^0
  The freezing point when non-volatile solute is dissolved in it → T_f (Freezing point of solution)
  The decrease in freezing point $\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point.
  For dilute solutions,

$$\Delta T_f \propto \frac{\Delta p}{p} = \chi_B$$

$$\Delta T_f = K\chi_B$$

$$\Delta T_f = K\,\frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\Delta T_f = K_f m.$$

We know

(i) $$\frac{W_B \times 1000}{M_B \times W_A} = \text{molality}$$

(ii) $$K \times M_A = K_f$$

K_f = Freezing point depression constant or molal depression constant or cryoscopic constant.

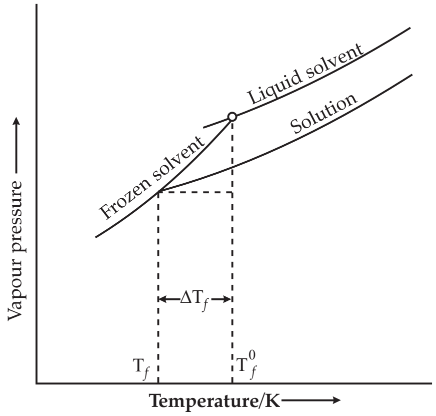


Fig. 4 : Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution.

- **Osmosis :** The process in which, there is net flow of solvent to the solution by a semi-permeable membrane is called osmosis.
- **Osmotic pressure :** The extra pressure that is applied to just stops the flow of solvent to solution across a semi-permeable membrane is called osmotic pressure of the solution.

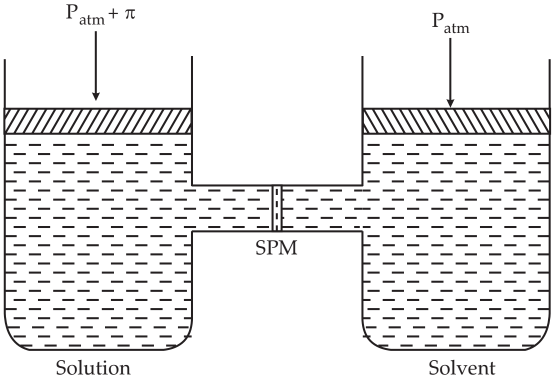


Fig. 5 : The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.

For dilute solutions, osmotic pressure is proportional to the molar concentration (C) of the solution at a given temperature T.

Thus π = CRT as π is the osmotic pressure and R is the gas constant.

$\pi = \frac{n}{VRT}$ (n is the number of moles, V is the volume of solution L)

- **Reverse osmosis :** The direction of osmosis can be reversed, if a pressure larger than the osmotic pressure is applied to the solution side. Now the pure solvent flows out of the solution through the semi-permeable membrane. This phenomenon is called reverse osmosis.

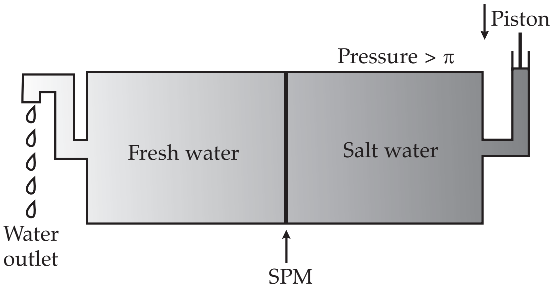


Fig. 6 : Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

- **Abnormal molecular mass :** When the molecular mass calculated with the help of colligative property is different from theoretical molecular mass, it is called abnormal molecular mass.
- **Van't Hoff factor (i) :** The ratio of the observed (experimental) value of a colligative property to the normal (calculated) value of the same property is called as van't Hoff factor.

Mathematically,

$$i = \frac{\text{Observed (experimental) value of a colligative property}}{\text{Normal (calculated) value of the same colligative property}}$$

Or, $$i = \frac{\Delta_{obs}}{\Delta_{cal}},$$

where Δ_{obs} and Δ_{cal} respectively represent the observed and calculated value of a colligative property. Thus,

(i) for lowering of vapour pressure, $i = \frac{(\Delta p)_{obs}}{(\Delta p)_{cal}}$;

(ii) for elevation of boiling point, $i = \frac{(\Delta T_b)_{obs}}{(\Delta T_b)_{cal}}$;

(iii) for depression of freezing point, $i = \frac{(\Delta T_f)_{obs}}{(\Delta T_f)_{cal}}$;

(iv) for osmotic pressure, $i = \frac{\pi_{obs}}{\pi_{cal}}$;

Since a colligative property is proportional to number of particles of solute.

$$i = \frac{\text{Normal molecular mass}}{\text{Obesrved molecular mass}}$$

Normal molecular mass = $i \times$ Calculated molecular mass.

$$i = \frac{\text{Total number of moles of particle after association/dissociation}}{\text{Total number of moles of particle before association/dissociation}}$$

- **Hypertonic solution :** A solution is called hypertonic, if its concentration is higher than that of the solution separating it by a semipermeable membrane.
- **Hypotonic solution :** A solution is called hypotonic, if its concentration is lower than that of the solution separating it by a semipermeable membrane.
- **Isotonic solution :** Two solutions are called isotonic if they exert the same osmotic pressure at a given temperature. Isotonic solutions have same molar concentration. When such solutions are separated by semipermeable membrane no osmosis occurs between them.

Know the Formulae and Equations

- **Modified equations for colligative properties :**

(i) Relative lowering of vapour pressure of solvent

$$\frac{p_A^\circ - p_A}{p_A^\circ} = (i)\left(\frac{n}{N+n}\right)$$

(ii) Elevation of boiling point

$$\Delta T_b = iK_b m$$

(iii) Depression of freezing point

$$\Delta T_f = iK_f m$$

(iv) Osmotic pressure of solution

$$\pi = \frac{inRT}{V}$$

or $$\pi = i\,CRT$$

- **Determination of molecular mass using colligative properties :**

(i) Relative lowering of vapour pressure :

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \chi_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A}$$

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{W_B \times M_A}{W_A \times M_B}$$

$$M_B = \frac{p_A^\circ}{p_A^\circ - p_A} \times \frac{W_B \times M_A}{W_A}$$

(ii) Elevation of boiling point :

$$\Delta T_b = K_b \times m$$

$$\Rightarrow \quad \Delta T_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A \text{ in gms}}.$$

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

(iii) Depression of freezing point :

$$\Delta T_f = K_f \times m$$

$$\Rightarrow \quad \Delta T_f = K_f \times \frac{W_{\text{solute}}}{M_{\text{solute}}} \times \frac{1000}{W_{\text{solvent}}}$$

$$M_B = \frac{1000 \times W_B \times K_f}{\Delta T_f \times W_A}$$

(iv) Osmotic pressure :

$$\pi = CRT,$$

$$\Rightarrow \quad \pi = \frac{\text{no. of moles}}{\text{volume of solution}} \times R \times T$$

$$\pi = \frac{W_B}{M_B} \times \frac{RT}{V}$$

$$M_B = \frac{W_B \times RT}{\pi \times V}$$

- **Degree of dissociation (α) :**

$$\alpha = \frac{i-1}{n-1}$$

$i \rightarrow$ van't Hoff factor

$n \rightarrow$ no. of ions produced per formula of the compound

- **Degree of association (α)**

$$\alpha = \frac{1-i}{1-\frac{1}{n}}$$

- **Strength = Molarity × Mole. wt.**

= Normality × Eq. wt.

$$\text{Molality} = \frac{\text{Solubility} \times 10}{\text{Mol. wt.}}$$

$K_b = 0.512$ K kg/mol for water

$K_f = 1.86$ K kg/mol

Know the Terms

- **Normal boiling point :** Temperature at which the vapour pressure of the liquid equals one atm.
- **Molal boiling point :** Boiling point of a 1 molal solution.
- **Freezing point :** Temperature at which the vapour pressure of liquid solvent is equal to the vapour pressure of solid solvent.
- **Molal depression constant :** It is the depression in freezing point when 1 mole of the solute is dissolved in 1000 g of the solvent.
- **Semipermeable membrane :** Membrane that allows only the selective passage of chemical species. *e.g.* Cellophane.
- **Transition temperature :** This is the temperature at which salt becomes anhydrous and the process becomes exothermic, solubility starts decreasing.
- **Endosmosis :** The inward osmosis of water into the semipermeable membrane is known as endosmosis.
- **Exosmosis :** The outward osmosis of water from the cell membrane is known as exosmosis.
- **Desalination :** Sea water can be converted into potable water fit for drinking purpose by reverse osmosis process known as desalination.
- **Plasmolysis :** When plant cell is placed in hypertonic solution, the fluid from the plant cell comes out and the cell shrinks. This phenomenon is called plasmolysis and is due to osmosis.

❑❑

Chapter - 3 : Electro-Chemistry

TOPIC-1

Conductance in Electrolytic Solutions, Specific and Molar Conductivity, Variations of Conductivity with Concentration, Gibbs Energy, Kohlrausch's Law

Quick Review

- Electrochemistry is the branch of chemistry which deals with the study of the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to result in non-spontaneous chemical transformations.
- **Electrolytic conduction :** The flow of electric current through an electrolytic solution is called electrolytic conduction.
- **Electrolyte :** A substance that dissociates in solution to produce ions and hence conducts electricity in dissolved state or molten state.

  Weak electrolyte – H_2CO_3, CH_3COOH, HCN, $MgCl_2$.
  Strong electrolyte – NaCl, HCl, NaOH.
- **Degree of ionisation :** It is the ratio of number of ions produced to the total number of molecules of electrolyte.
- Resistance is defined as the property of given substance to obstruct the flow of charge. It is directly proportional to the length (l) and inversely proportional to its area of cross-section (A).

  $R \alpha\, l \qquad R \alpha\, \frac{l}{A} \qquad \text{or; } R = \rho\, \frac{l}{A}$

  ρ : Resistivity or specific resistance.
- **Specific resistivity :** If a solution is placed between two parallel electrodes having cross sectional area 'A' and distance 'l' apart, then

  $$R = \rho\, \frac{l}{A}, \qquad \text{where } \rho \text{ is specific resistivity.}$$

  The unit of specific resistivity is Ohm cm or Ohm m.
- **Conductance :** The ease with which current flows through a conductor is called its conductance. It is reciprocal of the resistance. *i.e.,*

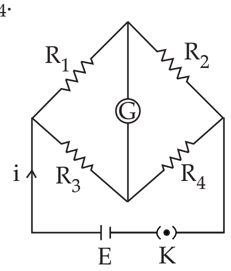
  $$C = \frac{1}{R} = \frac{A}{\rho l} = K\,\frac{A}{l}$$

  The unit of conductance is Siemens, S or ohm^{-1}.
  (*i.e.*, $1\ s = 1\ \text{ohm}^{-1} = 1\ \Omega^{-1}$)
- **Specific conductivity (electrolytic conductivity) :** It is reciprocal of the specific resistivity of an electrolytic solution. It is denoted by κ (Kappa).

  $$\kappa = C \times \frac{l}{A},$$

  where C is conductance of solution, l is the distance and A is the area of cross section.
  Its unit is $\text{ohm}^{-1}\ \text{cm}^{-1}$ or in S. I. unit $S\ m^{-1}$.
  It depends upon the :
  (i) Nature of the material
  (ii) Temperature
  (iii) Pressure
- Metallic conductance is the electrical conductance through metal that occurs due to the movement of electrons. It depends upon the
  (i) Nature and structure of the metal
  (ii) Number of valence electrons per atom
  (iii) Temperature
- Electrolytic or ionic conductance is the conductance of electricity that occurs due to ions present in the solution. It depends upon the
  (i) Nature of electrolyte or interionic attractions
  (ii) Solvation of ions
  (iii) Nature of solvent and its viscosity
  (iv) Temperature

- Wheatstone bridge helps us to measure R_4.



$$R_4 = \frac{R_3R_2}{R_1}$$

- **Cell constant (G) :** It is the ratio of distance between electrodes to the cross-sectional area between electrodes.

$$\text{Cell constant (G)} = \frac{l}{A} \text{ in cm}^{-1} \text{ or m}^{-1}$$

It depends on the
(i) Distance between the electrodes
(ii) Area of cross-section.

- **Molar conductivity :** It is defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a solution. It is denoted by Λ_m.

$$\Lambda_m = \frac{K}{C} \times 100 \text{ S cm}^2 \text{ mol}^{-1},$$

where κ= Conductivity and C = Concentration of solution.

Conductivity decreases with dilution while molar conductivity increases with dilution.

- **Debye Huckel Onsager equation :** It is for strong electrolyte

$$\Lambda = \Lambda^\circ - AC^{1/2},$$

where Λ° = Limiting molar conductivity, Λ = Molar conductivity, A = Constant and C = Concentration of solution.

- **Kohlrausch's law of independent migration of ions :** According to this law, limiting molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of contributions from its individual ions. If the molar conductivity of the cations is denoted by λ_+^∞ and that of the anions by λ^∞ then the law of independent migration of ions is

$$\Lambda_m^\infty = v_+ \lambda_+^\infty + v_- \lambda^\infty \text{ or } \Lambda^0 = v_+ \lambda_+^0 + v_- \lambda_-^0,$$

where, v_+ and v_- are the number of cations and anions per formula of electrolyte.

Application of Kohlrausch's Law :
(i) Calculation of molar conductivities of weak electrolyte at infinite dilution.
(ii) Calculation of degree of dissociation (α) of weak electrolytes.

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\overset{\circ}{\Lambda}_m}$$

(iii) Determination of dissociation constant (K) of weak electrolytes :

$$K = \frac{c\alpha^2}{1-\alpha} = \frac{c\Lambda_m^c}{\overset{\circ}{\Lambda}_m(\overset{\circ}{\Lambda}_m - \Lambda_m)}$$

(iv) Determination of solubility of sparingly soluble salts :

$$\text{Solubility} = \frac{K \times 1000}{\overset{\circ}{\Lambda}_m}$$

Know the Formulae

- $$\text{Current (I)} = \frac{\text{Potential difference (V)}}{\text{Resistance (R)}}$$
- $$\text{Resistance (R)} = \rho\frac{l}{A}$$
- $$\text{Conductance (C)} = K\frac{A}{l}$$

$$\text{Specific conductivity } (k) = \text{C}\times\frac{l}{\text{A}} = \frac{\text{Cell constant}}{\text{R}}$$

- $$\text{Cell constant (G)} = \frac{l}{\text{A}}$$
- $$\text{For strong electrolyte, } \Lambda_m = \Lambda_m^\circ - \text{A}\sqrt{C}$$
  $$\Lambda^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$$
- $$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$
- $$\text{K} = \frac{c\alpha^2}{1-\alpha} = \frac{c\Lambda_m^\circ}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$$
- $$\text{Solubility} = \frac{\text{K}\times 1000}{\Lambda_m^\circ}$$

Know the Terms

- **Superconductors :** Material with a zero resistance.
- **Limiting molar conductivity :** Molar conductivity when concentration approaches zero.
- **Electrolyte :** Substance which splits into ions in dissolved or molten state by passing electricity.
- **Over voltage :** It is the difference between the potential required for the evolution of a gas and its standard reduction potential.

TOPIC-2

Redox Reaction, Electrochemical Cell, Galvanic Cell, EMF of a Cell, Standard Electrode Potential, Nernst Equation

Quick Review

- **Redox reaction :** A chemical reaction in which oxidation and reduction both processes takes place is known as redox reaction. Oxidation is a process in which any substance loses one or more electrons while reduction is the process in which one or more electrons are gained by another substance.
- **Electrochemical cell :** A device in which the redox reaction is carried indirectly and chemical energy is converted to electrical energy. It is also called galvanic cell or voltaic cell.
- **Redox couple :** It is defined as having together the oxidised and reduced form of a substance taking part in and oxidation or reduction half reaction.
- **Galvanic cell or Voltaic cell :** It consists of two metallic electrodes dipped in electrolytic solutions. Electrical energy is produced as a result of chemical reaction which takes place in this cell.
- **Daniell cell :** It is the improved form of galvanic cell. It consists of zinc rod dipped in $ZnSO_4$ solution acts as the oxidation half cell. In the reduction half cell, the copper vessel itself acts as cathode while the saturated solution of $CuSO_4$ acts as the electrolyte. Both solutions are kept apart by taking zinc sulphate in porous pot and putting it in a copper sulphate solution.

  $$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Cu}(s)$$

  Cell is represented as,

  $$\text{Zn(s)}\ |\text{Zn}^{2+}(aq)\ (\text{C}_1)|\ |\ \text{Cu}^{2+}(aq)\ (\text{C}_2)|\ \text{Cu(s)}$$
- **Salt Bridge and its function :** It is an inverted U-shaped glass tube which contains a suitable salt in the form of a thick paste made up in agar-agar. It performs following functions—
  - **(i)** It completes inner cell circuit.
  - **(ii)** It prevents transference of electrolyte from one half cell to the other.
  - **(iii)** It maintains the electrical neutrality of the electrolytes in the two half cells.
- **Electrode Potential :** It is the potential difference set up between the metal and solution of its own ions. It shows the tendency of an electrode to either lose or gain electrons. When the concentration of all the species involved in a half cell is unity, then the electrode potential is called standard electrode potential.

- **Standard Electrode Potential :** Electrode potential at 25°C, 1 bar pressure and 1 M solution is known as standard electrode potential (E^0). The standard electrode potential of any electrode can be measured by connecting it to standard hydrogen electrode (SHE).

  SHE has a standard potential at all temperatures. It consists of a platinum foil coated with platinum black dipped into an aqueous solution in which the $H^+ = 1$ M at 25°C and 1 bar pressure.

  The potential difference between the two electrodes of a galvanic cell is called the cell potential (measured in volts). It is also called the emf of the cell when no current is flowing through the circuit.
- **EMF of the cell :** Electromotive force, also called emf (denoted and measured in volts). It is the voltage developed by any source of electrical energy such as battery or dynamo. It is generally defined as the potential for a source in a circuit.

$$E_{cell} = E_{cathode} - E_{anode}$$

In terms of standard oxidation electrode potential :

$$E^0_{cell} = E^0_{anode} - E^0_{cathode,}$$

where $E^0_{cathode}$ = standard electrode potential of cathode

and E^0_{anode} = standard electrode potential of anode

- **Standard oxidation potential :** It is the potential difference when given electrode is in contact with its ions having 1 molar concentration, undergoes oxidation when coupled with standard hydrogen electrode.
- The higher the value of E^0 for a half cell indicate that reductant in the half cell is stronger reducing agent than hydrogen gas.
- The series in which all the standard electrode potentials have been arranged in order of increasing value is known as electrochemical series. The characteristics of the electrochemical series are :

  (i) The reducing agent with lowest E^0 value, considered as the strongest reducing agent, is placed well above (top) of the electrochemical series. The oxidising agent with highest E^0 value, considered as the strongest oxidising agent, is placed below (bottom) of the electrochemical series.

  (ii) Oxidising power increases with increase in E^0 value.

  (iii) Any metal of lower E^0 value can reduce other metal of higher E^0 value.
  Similarly, any metal of higher E^0 value can oxidise other metal of lower E^0 value.
- **Applications of electrochemical series :** Important applications are as follows—

  (i) In comparing relative reducing or oxidising power of the elements.
  (ii) In predicting the feasibility of spontaneity of a redox reaction.
  (iii) In predicting whether a metal can evolve hydrogen from an acid or not.
  (iv) Comparison of reactivities of metals and non-metals.
  (v) Standard Gibbs energy change.
  (vi) Determination of equilibrium constant.
- **Nernst equation :** If the concentration of species in the electrode reaction is not equal to 1 M, then we use Nernst equation. For a general electrode

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$$

the Nernst equation can be written as

$$E_{\left(M^{n+}/M\right)} = E^0_{\left(M^{n+}/M\right)} - \frac{RT}{nF} ln \frac{[M_s]}{\left[M^{n+}_{(aq)}\right]}$$

where E^0 = Standard electrode potential, R = Gas constant and is 8.31 JK^{-1} mol^{-1}, T = Temperature (K), n = Number of moles of electrons and F = Faraday (96500 C)

At equilibrium,

$$E^0_{cell} = \frac{0.059}{n} \log K_c$$

$$K_c = \text{Equilibrium constant}$$

$$K_c = \frac{[M]}{\left[M^{n+}\right]}$$

For the cell with the net reaction

$$aA + bB \xrightarrow{ne^-} mM + nN$$

the Nernst equation at 298 K can be written as

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[M]^m [N]^n}{[A]^n [B]^b}$$

where $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

- **Gibbs energy :**

$$\Delta G^0 = nFE^0_{cell}$$

for cell reaction to be spontaneous, ΔG must be negative,

Calculations of $\Delta_r G^0$ and $\Delta_r G$:

$$\Delta_r G^0 = -nF\,E^0_{cell}$$

and

$$\Delta_r G = -nF\,E_{cell}$$

We also know that Gibb's energy changes is equal to the useful work done.

For cell reaction to be spontaneous, ΔG must be negative.

$$\Delta G^0 = -2.303\ RT \log K.$$

Know the Formulae

- $E_{cell} = E_{cathode} - E_{anode}$
- $E°_{cell} = E°_{cathode} - E°_{anode}$
- **Nernst equation :**

$$E_{cell} = E°_{cell} - \frac{2.303\ RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ at 298 K}$$

$$E_{cell} = \frac{2.303\ RT}{nF}\log\frac{C_2}{C_1} \text{ where } C_2 > C_1$$

- $\Delta_r G^0 = -nF\,E^0_{cell}$
- $\Delta_r G^0 = -2.303\ RT \log K_C.$

Know the Terms

- **Concentration cell :** A cell in which both electrodes and electrolytic solutions are of same substance but the solution of electrolyte in which they dip have different concentrations.
- **Gibbs energy :** Energy associated with a chemical reaction that can be used to do work.

TOPIC-3

Electrolysis, Laws of Electrolysis, Batteries, Fuel Cells and Corrosion

Quick Review

- Electrolysis is the process of decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten (fused) state. This process takes place in electrolytic cell.
- **Faraday's first law of electrolysis :** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.

$$m = Z \times I \times t, \text{ where } Z = \text{Electrochemical equivalent}$$

- **Faraday's second law of electrolysis :** Amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights.

$$\frac{w}{E_1} = \frac{w}{E_2}$$

- **Products of electrolysis depend on**
  - **(i)** Physical state of material.
  - **(ii)** Types of electrode being used.
- Battery is a combination of galvanic cells in series and used as a source of electrical energy.

  Types of batteries :
  - **(i)** Primary battery are non-chargeable batteries such as Lechlanche cell and Dry cell.
  - **(ii)** Secondary battery are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.
- **Dry cell (Lechlanche cell) :** The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powdered MnO_2 and C. The space is filled with paste of NH_4Cl and $ZnCl_2$.

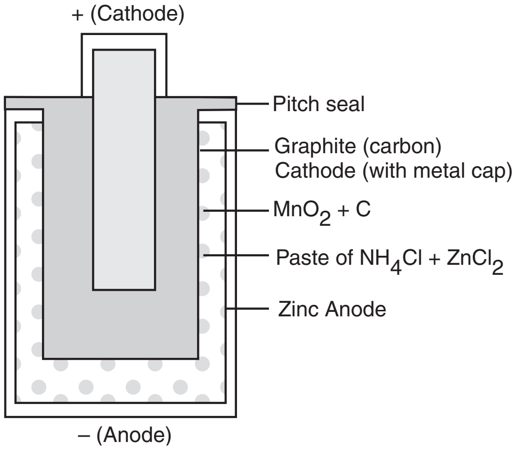


Fig. 1 : A dry cell

At anode : $Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$.

At cathode : $MnO_{2(s)} + NH^+_{4(aq)} + 2e^- \rightarrow MnO(OH) + NH_3$

The net reaction : $Zn + NH^+_{4(aq)} + MnO_2 \rightarrow Zn^{2+} + MnO(OH) + NH_3$

- **Lead storage battery :**

Anode – Spongy lead

Cathode – Lead packed with lead dioxide

Electrolyte – Aqueous solution of H_2SO_4

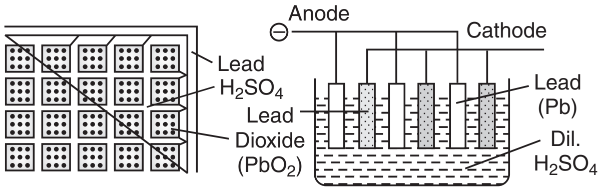


Fig. 2 : Storage battery

Discharge reaction of cell :

At anode : Following reaction takes place at anode :

$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$ (oxidation)

Reaction at cathode : PbO_2 filled in lead grid gets reduced to Pb^{2+} ions which combines with SO_4^{2-} ions to form $PbSO_{4(s)}$.

Complete cathode reaction is as follows :

$PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Complete cell reaction : $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

Recharge reaction of cell : It changes the direction of electrode reaction $PbSO_4$ accumulated at cathode gets reduced to Pb.

$\therefore$ **At cathode :** $PbSO_4 + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$

At anode, $PbSO_4$ gets oxidised to PbO_2

$PbSO_{4(s)} + 2H_2O \rightarrow PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^-$

Complete cell reaction would be as follows :

$2PbSO_{4(s)} + 2H_2O_{(l)} \xrightarrow{\text{charge}} Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

- **Conventions for representing the galvanic cells :**

(i) Double vertical line is used for salt bridge. Left hand side of the double line is anode and the cathode is on the right hand side.

(ii) A single vertical line is used to separate metal and the electrolytic solution.

(iii) If there is no metallic surface involved, we write Pt.

Example :

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

$Zn_{(s)} \mid Zn^{2+}_{(aq)} \mid\mid Cu^{2+}_{(aq)} \mid Cu_{(s)}$

- **Fuel cells :** Electrical cells that are designated to convert the energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called fuel cells.

In the cell :

Anode : $[H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^-] \times 2$

Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Net reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$.

- **Corrosion :** The process of slow conversion of metals into their undesirable compounds (usually oxide) by reaction with moisture and other gases present in the atmosphere.

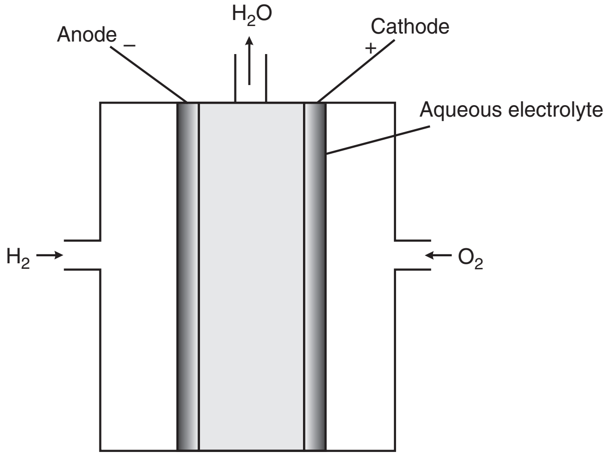


Fig. 3 : Fuel cell using H_2 and O_2 produces electricity

Rusting of iron :

$$Fe_{(s)} + 2H^+_{(aq)} + \frac{1}{2} O_{2\,(g)} \rightarrow Fe^{2+}_{(aq)} + H_2O_{(l)}$$

$$2Fe^{2+}_{(s)} + \frac{1}{2} O_{2\,(g)} + 2H_2O_{(l)} \rightarrow Fe_2O_{3(s)} + 4H^+$$

$$Fe_2O_3 + xH_2O \rightarrow \underset{\text{Rust}}{Fe_2O_3.xH_2O}$$

Prevention of corrosion :

(i) Barrier protection : By covering the surface with paint or a thin film of grease or by electroplating.
(ii) Sacrificial protection : By galvanization.
(iii) Alloying.

Know the Formulae

- $Q = It$
- $m = ZIt$

Know the Terms

- **Electrolytic cell :** A cell in which the electrical energy is used to carry out a non-spontaneous reaction.
- **Faraday constant :** It is the quantity of electricity.
  1 F = 96500 C
- **Electrosynthesis :** It is a method of producing substance through non-spontaneous reaction carried by electrolysis.
- **Tinning :** Coating of iron with tin.

❑❑

Chapter - 4 : Chemical Kinetics

TOPIC-1

Rate of a Chemical Reaction and Factors Affecting Rate of Reactions

Quick Review

- **Chemical Kinetics :** It is the branch of physical chemistry which deals with study of the rate of chemical reaction and the mechanism by which the reaction occurs.
- **Rate of Reaction :** The rate of reaction is the change of concentration of any reactant or product with time for a reaction.

$$A + B \rightarrow C$$

$$\text{Rate of reaction, A} = \frac{\text{Decrease in concentration of A}}{\text{Time taken}} = \frac{-\Delta A}{\Delta t}$$

$$\text{Similarly for reaction, B} = \frac{-\Delta B}{\Delta t} \text{ and for product C} = \frac{\Delta C}{\Delta t}$$

- **Unit of rate reaction :** mol L^{-1} s^{-1} or mol L^{-1} min^{-1} (in liquid), atm s^{-1} or atm m^{-1} (in gaseous form)
- **Instantaneous rate of reaction :** Instantaneous rate is defined as the rate of change in concentration of any one of the reactant or product at a particular time.

  $$\text{Instantaneous rate} = \frac{dx}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt}$$

- **Average rate of reaction :** The rate of reaction measured over a long time interval is called average rate of a reaction. Average rate = $\frac{\Delta x}{\Delta t}$, where, Δx = change in concentration in given time and Δt = Time taken.
- **Factors affecting the rate of a chemical reaction.**

  The following factors affect the rate of a reaction :

  (i) Concentration of reactants : Rate of reaction is directly proportional to the concentration of the reactants. Thus, to increase the rate of a reaction the concentration of the reactants has to be increased.

  (ii) Temperature of the reaction : The temperature of a reaction greatly affects its velocity. The rate of a reaction increases with the increase in temperature. Increase in temperature increases the kinetic energy of the molecules which results in the increase in rate of reaction.

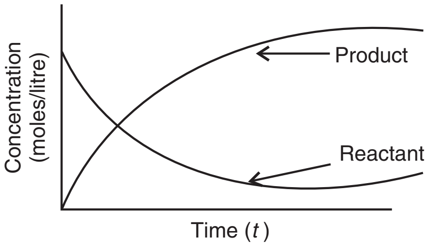
  (iii) Pressure of the reaction : Pressure affects the rate of only gaseous reactions. Increase in pressure decreases volume and increases concentration. Increase in concentration increases the rate of reaction.

  (iv) Presence of catalyst : The rate of many reactions is greatly affected by the presence of a catalyst. In the presence of a catalyst, the activation energy of a reaction decreases due to which the reaction proceeds at a faster rate.

  (v) Nature of the reactants : The nature of the reactants also affects the rate of a reaction. In a chemical reaction, some bonds are broken while some new bonds are formed. Thus, if the molecules are simpler, then less bonds will rupture and the rate of reaction becomes fast while in complex molecules more bonds will rupture and the velocity of reaction decreases.

  (vi) Surface area of the reactants : In some heterogeneous reactions, the reaction takes place at the surface of the reactant. Thus in such reactions, the reaction rate is greatly affected by the surface area. Marble powder reacts faster than marble chips.

  (vii) Effect of radiations : Those reactions which are initiated by the radiations of particular wavelengths are termed as photochemical reactions. These reactions generally proceed at a faster rate than normal thermal reactions.



  (viii) Effect of physical state : Rate of reaction depends upon physical state of the reactant, *e.g.*, $I_{2(g)}$ reacts faster than $I_{2(s)}$. $AgNO_{3(aq)}$ reacts with NaCl but $AgNO_{3(s)}$ does not react with NaCl.

- **Rate Law :** Rate law or rate equation is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality '*k*' is known as rate constant. It states that the rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally.

  $$\text{Rate} = k|A|^m\,|B|^n$$

- **Rate Constant :** Rate constant is also called specific reaction rate. When concentration of both reactants are unity (one), then the rate of reaction is known as rate constant. It is denoted by '*k*'.
- **Molecularity :** Total number of atoms, ions or molecules of the reactants involved in the reaction is termed as molecularity It is always in whole number. It is never more than three. It can not be zero.

  Example :

  $NH_4NO_2 \rightarrow N_2 + 2H_2O$ (Unimolecular reaction)

  $2HI \rightarrow H_2 + I_2$ (Bimolecular reaction)

  $2NO + O_2 \rightarrow 2NO_2$ (Trimolecular reaction)

- **Elementary Reaction :** An elementary reaction is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step and with a single transition state.
- For a complex reaction generally, molecularity of the lowest step is same as the order of the overall reaction.
- **Initial rate of reaction :** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called initial rate of reaction.
- **Rate Determining Step :** The slowest step in the reaction mechanism is called rate determining step.

Know the Terms

- **Catalyst :** A substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.
- **Photochemical reactions :** The chemical reaction whose rate is influenced by radiations, particularly from ultraviolet and visible light is known as photochemical reaction.

TOPIC-2

Order of a Reaction, Integrated Rate Equations and Half life of a Reaction

Quick Review

- **Order of reaction :** Order is defined as the sum of powers of concentration of the reactants in the experimentally derived rate equation or rate law expression. Order of reaction is experimentally determined and is not written from the balanced chemical equation. Order of reaction can be whole number, zero or fractional.
- **Zero order reaction :** The rate of reaction does not change with the concentration of the reactants.

  i.e. $$\text{Rate} = k\,[A]_0,$$

  $$k = \frac{[A]_0 - [A]}{t},$$

  where 'k' is rate constant and unit of the rate constant k is mol L^{-1} s^{-1}.

  This reaction will be zero order reaction.

  Photosynthesis of $HCl_{(g)}$, is an example of zero order reaction.
- **First order reaction :** The rate of reaction is directly proportional to the concentration of reacting substance. Rate constant of the first order reaction is

  $$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

  $$\Rightarrow \qquad k = \frac{2.303}{t}\log\frac{[A_0]}{[A]},$$

  where 'a' is initial concentration $(a - x)$ is the concentration after time 't'.

  The unit of 'k' is s^{-1} or min^{-1}

  Decomposition of NH_4NO_2 is the example.
- **Pseudo first order reaction :** If a reaction is not truly of the first order but under certain conditions become reaction of first order is called pseudo first order reaction, *e.g.*, acidic hydrolysis of ester (ethyl acetate).

  $$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H+} CH_3COOH + C_2H_5OH$$
- **Second order reaction :** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2.

  $$\therefore \qquad \frac{dx}{dt} = k[A]'\,[B]'$$

  Unit of rate constant is mol^{-1} L s^{-1} or M^{-1} s^{-1}, where M is molarity.

Reaction	Order	Unit of rate constant	Example
Zero order	0	mol^{-1} L^{-1} s^{-1}	$H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$
First order	1	s^{-1}	$2N_2O_5 \longrightarrow 4NO_2 + O_2$

Pseudo first order	1	s^{-1}	$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Second order	2	$mol^{-1}\ L\ s^{-1}$	$H_2 + I_2 \rightarrow 2HI$

- **Equation for typical first order gas phase reaction :** $A_{(g)} \rightarrow B_{(g)} + C_{(g)}$

$$k = \frac{2.303}{t}\log\frac{p_i}{p_A}$$

or

$$k = \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

where p_i is the initial pressure of A at time, $t = 0$ and p_t is the total pressure at time t.

- **Half life of a reaction :** The time taken for a reaction when half of the initial value has reacted is called **half life of a reaction.**

For zero order reaction, $$t_{1/2} = \frac{[A]_0}{2k},$$

where $[A]_0$ is initial and last concentration of reaction it means there is no change in concentration and 'k' is rate constant.

For Ist order reaction, $$t_{1/2} = \frac{0.693}{k}$$

- ***n*th order reaction :** In general for n^{th} order reaction of the type

$$A \rightarrow \text{products, where, } \frac{dx}{dt} = k[A]^n$$

$$k_n = \frac{1}{t(n-1)}\left[\frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}\right]$$

where A_0 is initial concentration, A is final concentration after time t and n can have all the values except 1.

- **Half life of a reaction of *n*th order :**

$$t_{1/2}\ \alpha \frac{1}{[A_0]^{n-1}}$$

$t_{1/2} \propto [A]$ for zero order

$t_{1/2}$ is independent of [A] for 1st order

$t_{1/2} \propto \frac{1}{[A]}$ for 2nd order

$t_{1/2} \propto \frac{1}{[A]^2}$ for 3rd order

Amount of substances left after n half-lives $= \frac{A_0}{2^n}$

- **Integrated rate laws for the reactions of zero and first order :**

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half Life	Units of k
0	$A \rightarrow P$	$\frac{d[A]}{dt} = -k$	$kt = [A_0] - [A]$	[A] Vs. t	$\frac{[A]_0}{2k}$	conc. time^{-1}
1	$A \rightarrow P$	$\frac{d[A]}{dt} = -k[A]$	$[A] = [A]_0\, e^{-kt}$ $kt = \frac{ln[A]_0}{[A]}$	ln [A] Vs. t	$ln\frac{2}{k}$	time^{-1}

- **Life time :** The time in which 98% of the reaction is completed is called life time.

Know the Formulae

- **Integrated Rate Equations :**

  (i) For a zero order reaction :

$$t = \frac{[R]_0 - [R]}{k} \text{ and } t_{1/2} = \frac{[R]_0}{2k}$$

  (ii) For a first order reaction :

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \text{ and } t_{1/2} = \frac{0.693}{k}$$

- **Temperature coefficient** $= \dfrac{k\,(T+10)}{k\,(T)}$

Know the Terms

- **Intermediates :** The species which are produced in one step and consumed in another.
- **Simple or elementary reaction :** When a reaction completes in a single step is called as simple or elementary reaction.
- **Complex reaction :** When number of elementary reactions (steps) are combined together and complete the reaction is called complex reaction.
- **Differential rate equation :** The concentration dependance of rate is called differential rate equation.

TOPIC-3

Concept of Collision Theory, Activation Energy and Arrhenius Equation

Quick Review

- The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient.

  Temperature coefficient $= \dfrac{\text{Rate constant at 308 K}}{\text{Rate constant 298 K}}$

  It is observed that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.
- **Activation energy :** It is an extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to the formation of product molecules.
- Activation energy (E_a) for a reaction cannot be zero. It is not possible that every collision between molecules will be effective. E_a cannot have negative value.
- **Threshold energy :** The minimum energy that the reacting species must posses in order to undergo effective collision to form product molecules is called threshold energy.
- **Arrhenius equation :** Activated complex is defined as unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product. Arrhenius equation gives the relation between rate of reaction and temperature.

  $k = Ae^{-E_a/RT}$

  where k = rate constant

  A = frequency factor (Arrhenius factor) E_a = Energy of activation

  R = gas constant   T = Temperature in Kelvin

  $ln\ k = \ln A - E_a/RT$

  $\log k = \log A - \dfrac{E_a}{2.303\ RT}$

  A plot of log k with 1/T gives a straight line with slope $= \dfrac{E_a}{2.303\ R}$

  If k_2 and k_1 are rate constants at temperature T_2 and T_1 respectively, then

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$$

- Those collisions which lead to the formation of product molecules are called effective collisions,

  Rate of reaction $= f \times z$,

  where 'z' is collision frequency and 'f' is fraction of collisions, which are effective.

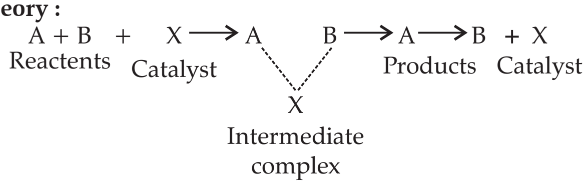
- The number of collisions that take place per second per unit volume of the reaction mixture is called collision frequency. It is represented by 'Z'.
- Activated complex is defined as unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product.
- According to the collision theory, rate of reaction depends on the collision frequency and effective collisions.

  $$\text{Rate} = Z_{AB}e^{-E_a/RT},$$

  where Z_{AB} represents the collision frequency of reactants A and B. $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a.
- According to collision theory, another factor P which is called steric factor refers to the orientation of molecules which collide, is important and contributes to effective collision.

  $$K = PZ_{AB}\,e^{-E_a/RT}$$
- **Catalyst :** A catalyst is a substance that alters the rate of reaction without itself undergoing any chemical change at the end of reaction.

  Intermediate complex theory :



Characteristics of catalyst :

(i) Catalyses only the spontaneous reaction.
(ii) Does not change the equilibrium constant.
(iii) Catalyses both the forward and backward reactions.
(iv) Does not alter the free energy change (ΔG) of a reaction.
(v) A small amount of the catalyst can catalyse large amount of reactions.

Know the Formulae

- Temperature coefficient $= \dfrac{\text{Rate constant at}(T+10)^\circ}{\text{Rate constant at } T^\circ}$
- Rate of reaction $= f \times Z$

  where Z is the collision frequency,
  f is the fraction of collisions.
- **Arrhenius equation :**

  $$k = Ae^{-E_a/RT}$$
- Rate $= pz_{AB}e^{-E_a/RT}$

Know the Terms

- **Effective collisions :** Collisions in which molecules collide with sufficient kinetic energy and proper orientation and result in a reaction.
- **Collision frequency :** Number of collisions per second per unit volume of the reaction mixture.

❑❑

Chapter - 5 : Surface Chemistry

TOPIC-1

Adsorption and its Types, Factors Affecting Adsorption

Quick Review

- **Surface chemistry :** The branch of chemistry which deals with the phenomenon that occur at the surfaces is called surface chemistry. This phenomenon is studied with the help of adsorption and colloidal state.
- **Adsorption :** Adsorption is a surface phenomenon in which the substance gets accumulated on the surface of a solid rather than in the bulk of a solid or liquid. The surface that adsorbs is called **adsorbent** and the one that gets adsorbed is called an **adsorbate. For example :** Pt can adsorb large amount of hydrogen gas.

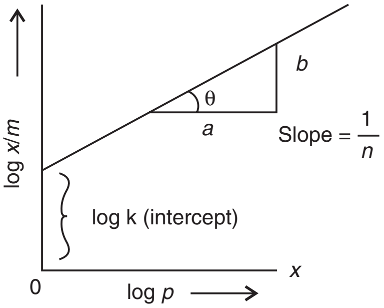
- **Types of adsorption :**
  - **(i) Physisorption :** Physisorption is also called **physical adsorption.** If the adsorbate is held on a surface of adsorbent by weak van der Waals forces, the adsorption is called physical adsorption or physisorption.
  - **(ii) Chemisorption :** Chemisorption is also called chemical adsorption. If the forces holding the adsorbate are as strong as in chemical bonds, the adsorption process is known as **chemical adsorption or chemisorption.**
- **Desorption :** The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption.**
- In **adsorption**, molecules of a substance are uniformly distributed throughout the body of solid or liquid. **For example :** Ammonia absorbed by water, water absorbed by anhydrous $CaCl_2$.
- **Sorption :** When adsorption and absorption take place simultaneously, it is called sorption, *e.g.*, dying of cotton fabrics. The dye is adsorbed on the surface of cotton fibre but after it is dyed, the fibre has dye uniformly throughout.
- **Enthalpy of adsorption :** Adsorption generally occurs with release in energy, *i.e.*, it is exothermic in nature. The enthalpy change for the adsorption of one mole of an adsorbate on the surface of adsorbent is called **enthalpy** or **heat of adsorption.**
- **Differences between Adsorption and Absorption :**

S. No.	Adsorption	Absorption
(i)	It is *surface phenomenon*. Adsorbate molecules are held at the surface of adsorbent.	Absorption occurs in the *bulk* of absorbing substance.
(ii)	The concentration of the adsorbate at the adsorbent is much more than that in the bulk.	Absorbed material is uniformly distributed throughout the bulk. Thus, concentration is same throughout.
(iii)	Initially rate of adsorption is rapid. It decreases slowly till equilibrium is attained.	Absorption occurs with uniform rate.
(iv)	**Example :** Water vapours on silica gel.	**Example :** Water vapours are absorbed by anhydrous $CaCl_2$.

- **Factors affecting adsorption of gases on solids :**
  - **(i)** Nature of gas.
  - **(ii)** Nature of adsorbent.
  - **(iii)** Specific area of the solid.
  - **(iv)** Pressure of the gas.
  - **(v)** Effect of temperature.
  - **(vi)** Activation of adsorbent.
- **Adsorption isobar :** A plot of extent of adsorption (*x/m*) *vs.* temperature at constant pressure is called adsorption isobar.
- **Adsorption isotherm :** The plot of extent of adsorption (*x/m*) *vs.* pressure (P) at constant temperature is called adsorption isotherm, where, '*x*' is the quantity of gas adsorbed by unit mass '*m*' of the solid adsorbed. It is called adsorption isotherm.
- **Freundlich Adsorption Isotherm :** It gives the relationship between magnitude of adsorption (*x/m*) and pressure at a constant temperature. It can be given by mathematical equation.

$$\frac{x}{m} = kp^{1/n} \qquad \text{....(i)}$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \text{...(ii)}$$



A plot of log $\frac{x}{m}$ *Vs*. log *p* gives a straight line with slop $\frac{1}{n}$

and *y* intercept = log *k*.

In case of solution, the isotherm takes the form

$$\frac{x}{m} = k(C)^{1/n} ; \log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

where x is the amount of adsorbate adsorbed on m gram of adsorbent at pressure p or concentration C of the adsorbate, k and n are constants, $n > 1$.

- **Applications of Adsorption :**
  - **(i)** In removing colouring matter from solution.
  - **(ii)** In gas masks
  - **(iii)** In separating noble gases
  - **(iv)** In dyeing of cloth
  - **(v)** In chromatography
  - **(vi)** In froth floatation process
  - **(vii)** In curing diseases
  - **(viii)** In dehumidifiers
  - **(ix)** In adsorption analysis
  - **(x)** In creating high vacuum
  - **(xi)** In ion-exchange resins.

Know the Terms

- **Saturation pressure :** The pressure beyond which adsorption becomes independent of pressure is called as saturation pressure.
- **Competitive adsorption :** A strong adsorbate get adsorbed more efficiently as compared to weak adsorbate. That strong adsorbate can displace already adsorbed one from the surface of the adsorbent. This is known as competitive adsorption or preferential adsorption.

TOPIC-2

Catalysis and Its Types, Enzyme Catalysis

Quick Review

- **Catalysis :** The process in which catalyst is used to increase the rate of reaction without changing itself is called catalysis.

$$2KClO_3 \xrightarrow[473-633K]{MnO_2} 2KCl + 3O_2$$

The catalyst remains unchanged with respect to mass and composition. Catalyst does not affect ΔH, ΔS, ΔG and equilibrium constant k. It is called **catalysis.**

- **Promoters :** Those substances which increase the activity of catalyst are called promoters. *e.g.*, Mo is promoter whereas Fe is catalyst in Haber's process.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[Mo]{Fe} 2NH_3(g)$$

- **Poisons or Inhibitors :** Those substances which decrease the activity of catalyst are called catalytic poisons or inhibitors, *e.g.*, arsenic acts as catalytic poison in the manufacture of sulphuric acid by contact process.
- **Types of catalysis :**

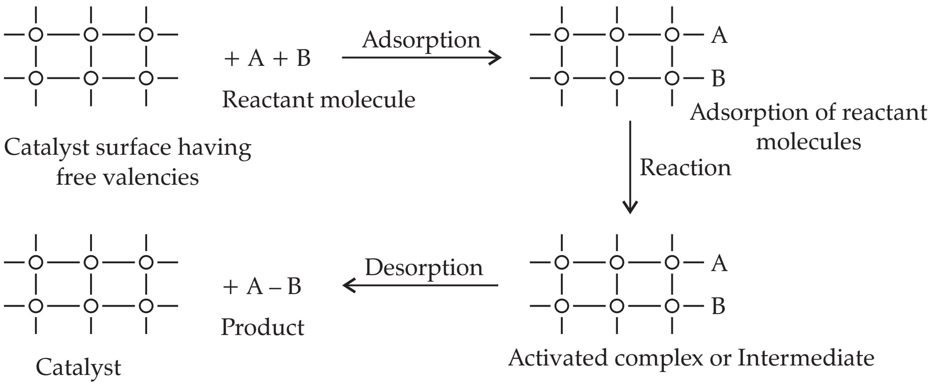
(i) Homogeneous Catalysis : When the catalyst mixes homogeneously with the reactant and forms a single phase, the catalyst is said to be homogeneous and this kind of catalysis is known as homogeneous catalysis. *e.g.*, catalytic oxidation of SO_2 to SO_3 in presence of NO is an example of homogeneous catalysis.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$$

(ii) Heterogeneous Catalysis : When the catalyst forms a separate phase (usually a solid phase) it is said to be heterogeneous catalysis. In a heterogeneous catalysis the reactants are gases and reaction starts from the surface of the solid catalyst. This is the reason why heterogeneous catalysis is also called 'surface catalysis'. *e.g.*

$$CO_{(g)} + 2H_{2(g)} \xrightarrow[ZnO/Cr_2O_3]{Cu(Solid)} CH_3OH_{(l)}$$

- **Adsorption theory of Heterogeneous Catalysis :** According to modern adsorption theory, there are free valencies on the surface of solid catalyst and mechanism involves following five steps :
  - **(i)** Diffusion of reactant molecules on the surface of the catalyst.
  - **(ii)** Adsorption of the reactant molecules on the surface of the catalyst by forming loose bonds with the catalyst due to presence of free valencies.
  - **(iii)** Occurrence of a chemical reaction forming an intermediate on the surface.
  - **(iv)** Desorption of the product molecules from the surface.
  - **(v)** Diffusion of product molecules away from the surface of the catalyst.



- **Important features of solid catalysts :**
  - **(i) Activity :** It is the ability of catalyst to increase the rate of a reaction.
  - **(ii) Selectivity :** It is the ability of a catalyst to direct a reaction to yield a particular product.
- **Shape-selective catalysis by zeolites :** It is the catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules. Zeolites are the shape selective catalyst having honey comb structures. Zeolite catalyst, ZSM-5 is used in petroleum industry to convert alcohols into gasoline by dehydration.
- **Enzyme Catalysis :** In enzyme catalysis, enzymes are biological catalyst which catalyse specific biochemical reactions. They are globular proteins having high molecular mass. *e.g.,*

$$\underset{\text{(Urea)}}{NH_2CONH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

- **Characteristics of enzymes :**
  - **(i)** Enzymes form a colloidal solution in water and hence they are very active catalysts.
  - **(ii)** Like inorganic catalyst they cannot disturb the final state of equilibrium of a reversible reaction.
  - **(iii)** They are highly specific in nature *i.e.,* one catalyst can not catalyse more than one reaction.
  - **(iv)** They are highly specific to temperature. The optimum temperature of their activity is 25°C – 35°C. They are deactivated at 70°C.
  - **(v)** A small quantity of enzyme catalyst is sufficient for a large change.
  - **(vi)** They are destroyed by UV rays.
  - **(vii)** Their efficiency is decreased in the presence of electrolytes.
- **Some examples of enzyme catalyst reaction.**
  - **(i)** $\underset{\text{(Cane sugar)}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Invertase}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$ (Inversion of cane sugar)
  - **(ii)** Maltose $\xrightarrow{\text{Maltase}}$ Glucose + Glucose
  - **(iii)** Lactose $\xrightarrow{\text{Lactase}}$ Glucose + Galactose
  - **(iv)** $\underset{\text{(Glucose)}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{(Ethyl alcohol)}}{2C_2H_5OH} + 2CO_2$
  - **(v)** Proteins $\xrightarrow{\text{Pepsin}}$ Peptides
  - **(vi)** Milk $\xrightarrow[\text{enzyme}]{\text{Lactobacilli}}$ Curd
- **Mechanism of enzyme catalysed reaction :** The enzyme considered to proceed in two steps
  - **(i)** Binding of enzyme to substrate to form an activated complex.

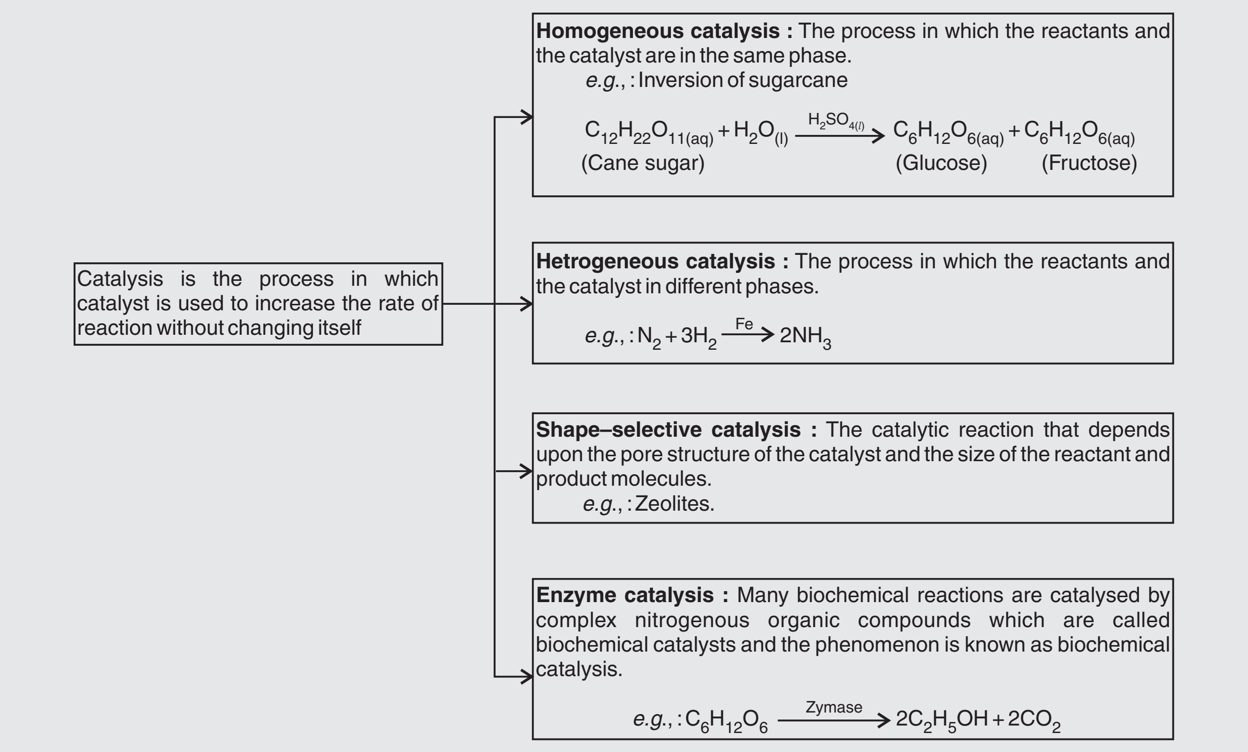
$$E + S \rightarrow ES$$

  - **(ii)** Decomposition of the activated complex to form the product.

$$ES \rightarrow E + P,$$

  where E is enzyme, S is substrate and P is product.
- **Co-enzymes :** Certain substances, which can increase the activity of enzymes are known as Co-enzymes.

Flowchart



Catalysis is the process in which catalyst is used to increase the rate of reaction without changing itself

Homogeneous catalysis : The process in which the reactants and the catalyst are in the same phase.

e.g., : Inversion of sugarcane

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{H_2SO_{4(l)}} C_6H_{12}O_{6(aq)} + C_6H_{12}O_{6(aq)}$$

(Cane sugar) (Glucose) (Fructose)

Hetrogeneous catalysis : The process in which the reactants and the catalyst in different phases.

e.g., : $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$

Shape–selective catalysis : The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules.

e.g., : Zeolites.

Enzyme catalysis : Many biochemical reactions are catalysed by complex nitrogenous organic compounds which are called biochemical catalysts and the phenomenon is known as biochemical catalysis.

e.g., : $C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$

Know the Terms

- **Zeolites :** Aluminosilicate with three dimensional network containing Al—O—Si network which acts as a good shape-selective catalyst.
- **Enzymes :** Complex nitrogenous organic compounds which are produced by living plants and animals.
- **Optimum pH :** Particular pH at which the rate of an enzyme catalysed reaction is maximum.

TOPIC-3

Colloids, Types of Colloids, Characteristics and Preparation of Colloids

Quick Review

- **Colloids :** A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. The size of colloidal particles is in the range 1–1000 nm.
- **Colloidal solution :** A colloidal solution is a heterogeneous system in which a definite substance is distributed in the form of very small particles as dispersed phase in another substance called dispersion medium, *e.g.*, glue, ink, smoke, etc.
- **Dispersed phase :** Dispersed phase is the component present in small proportion like solute in the solution.
- **Dispersion medium :** The medium in which the colloidal particles are dispersed is called dispersion medium.
- **Crystalloids :** The substances whose aqueous solution can pass through the semi-permeable membrane are called crystalloids.
- **Types of Colloidal solutions :**

S. No.	Dispersed phase	Dispersion medium	Name	Examples
1.	Solid	Gas	Aerosol	Smoke, dust particles.
2.	Solid	Liquid	Sol	As_2S_3, Gold sol, starch, gum, muddy water.

3.	Solid	Solid	Solid sol	Coloured gem stones, some alloys, pearls, ruby glass.
4.	Liquid	Solid	Gel	Jellies, cheese, butter.
5.	Liquid	Liquid	Emulsion	Milk, hair cream, cod-liver oil.
6.	Liquid	Gas	Aerosol	Fog, mist, cloud.
7.	Gas	Solid	Solid foam	Pumice stone, foam rubber, cork.
8.	Gas	Liquid	Foam	Whipped cream, froth, soap lather.

➢ **Classification based on nature of interaction between dispersed phase and dispersion medium :**

(i) Lyophilic colloids : Lyophilic means ''solvent loving''. Those substances which when mixed with a suitable solvent as the dispersion medium directly form the colloidal solution are called lyophilic substances and the solution thus formed is called lyophilic solutions. They are also known as intrinsic colloids. **For example :** gum, gelatin, starch, rubber, etc.

(ii) Lyophobic colloids : Lyophobic means ''solvent hating''. These are the substances, when mixed with dispersion medium do not form colloidal solution. Their solution can be prepared only by special method, such substances are called lyophobic and the solutions formed by them are called lyophobic solutions. They are also known as extrinsic colloids. **For example :** metals and their sulphides.

➢ **Classification based on the type of particles of the dispersal phase :** Multimolecular, Macromolecular and Associated colloids :

(i) Multimolecular Colloids : Multimolecular colloids contains dispersed particles less than 1 nm made of aggregates of many molecules. These are lyophobic colloids. In multimolecular colloids, particles are held by weak van der Waals forces. For examples. sulphur sol, gold sol etc.

(ii) Macromolecular Colloids : Macromolecular colloids are molecularly dissolved solutions of a polymer with particle size of colloidal range and are lyophilic colloids. In macromolecular colloids, particles are held by chemical bonds.

For example :

(a) Naturally occurring macromolecular colloids (starch, cellulose, proteins and enzymes).

(b) Man made macromolecular colloids (Polythene, nylon).

(iii) Associated Colloids (Micelles)

Micelles : Those colloids which behave as normal strong electrolytes at low concentrations, show colloidal properties at higher concentrations due to the formation of aggregated particles of colloidal dimensions. Such compounds are also referred to as associated colloids. Surface active agents like soaps and synthetic detergents belong to this class. They also form ions. Micelles may contain 100 molecules or more.

Mechanism of micelle formation : Micelle are generally formed by the specific type of molecules which have lyophilic as well as lyophobic ends. Such molecules are known as surface active molecules or surfactant molecules.

Sodium oleate, $C_{17}H_{33}COO^-Na^+$ (one of the soaps) is a typical example of such type of molecule. The long hydrocarbon part of oleate radical ($C_{17}H_{33}$—) is lyophobic end while COO^- part is lyophilic end. When the concentration of the solution is below its CMC (3×10^{-3} mol L^{-1}) sodium oleate behaves as normal electrolyte and ionises to give Na^+ and $C_{17}H_{33}COO^-$ ions. As the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and are made to approach each other. However, the polar —COO^- parts tend to interact with the solvent. This ultimately leads to the formation of the cluster having the dimensions of the colloidal particles. In each such cluster a large number of (usually 100 or more) oleate groups are clumped together in a spherical manner so that their hydrocarbon parts interact with one another but —COO^- parts remain projected in water. Hence, the mechanism of micelles formation is same as that of soap.

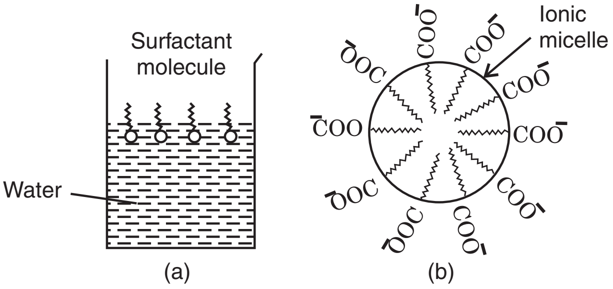


Fig. 1. (a) : Arrangement of oleate ions on the surface of water at low concentrations of soap.

(b) : Arrangement of oleate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap.

➢ **Preparation of colloidal solution :** Colloidal solutions can be prepared by following methods :

(i) Mechanical dispersion : A suspension of coarsely ground particles prepared in dispersion medium is fed into a colloidal mill and speed of rotation is adjusted so as to get the particles of colloidal size.

(ii) Electrodispersion : (Bredig's arc method). In this method, two rods of the metal (Au, Cu, Pt, Ag) to be dispersed are kept immersed in cold and a direct electric arc is struck between them. In this way, vapours of metal are formed which then immediately condense to form particles of colloidal size.

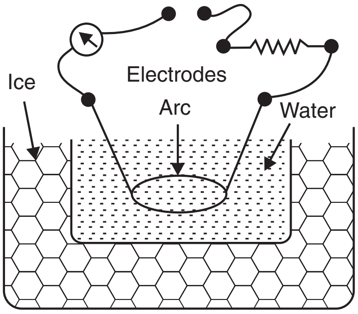


Fig. 2 : Bredig's arc method

(iii) Chemical methods :

- **Oxidation :** Solutions of non-metals are prepared by this method; *e.g.*, colloidal solution of sulphur.

$$2H_2S + 2(O) \xrightarrow{HNO_3\,(conc.)} 2S + 2H_2O$$

- **Reduction :** Metal sols can be prepared by this method; *e.g.*, gold sol

$$2AuCl_3 + 3SnCl_2 \rightarrow 2Au + 3SnCl_4$$

$$2AuCl_3 + 3HCHO + 3H_2O \rightarrow 2Au\ (sol) + 3HCOOH + 6HCl$$

- **Hydrolysis :** Hydroxides sols are prepared by this method; *e.g.*, $Fe(OH)_3$, $Al(OH)_3$

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

- **Double decomposition :** This method is used to prepare colloids from inorganic salts; *e.g.*,

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

- **Exchange of solvent :** Some substances which form true solution in one solvent, forms colloidal solution in another due to lowering of solubility, *e.g.*, sulphur dissolved in alcohol forms colloidal solution in water and phenolphthalein dissolved in alcohol forms colloidal solution in water.
- **Excessive cooling :** The colloidal solution of ice in $CHCl_3$ or ether can be obtained by freezing a solution of water in solvent. The molecules of water combine to form particles of colloidal size.

➢ **Peptization :** The conversion of precipitate into colloidal solution in presence of peptizing agent is called peptization. Peptizing agent is generally an electrolyte.

➢ **Purification methods of colloidal solutions :** Colloidal solution can be purified by following method :

(i) Dialysis : In dialysis, particles of true solutions can pass through parchment paper or cellophane membrane. On the other hand, sol particles cannot pass through these membranes. A bag made up of such a membrane is filled with the colloidal solution and is then suspended in fresh water. The crystalloid particles pass out leaving behind the colloidal sol.

(ii) Electrodialysis : Movement of ions across the membrane can be quickened by applying electric potential through two electrodes. This method is faster than simple dialysis and is known as *electrodialysis*.

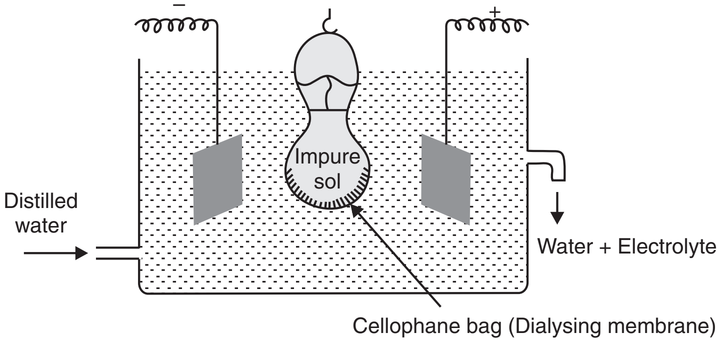


Fig. 3. Electrodialysis

(iii) Ultrafiltration : The process of separating colloidal particles by specially prepared filter papers whose pore size is reduced by dipping it in colloidal solution(e.g., 4% nitrocellulose in mixture of alcohol and ether)

➢ **Properties of colloids :**

(i) Brownian movement : The zig-zag movement of colloidal particles when seen under powerful microscope is called Brownian movement.

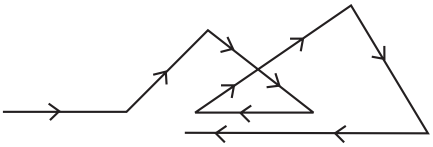


Fig. 4 : Brownian movement

(ii) Tyndall effect : Scattering of light by colloidal particles is called Tyndall effect.

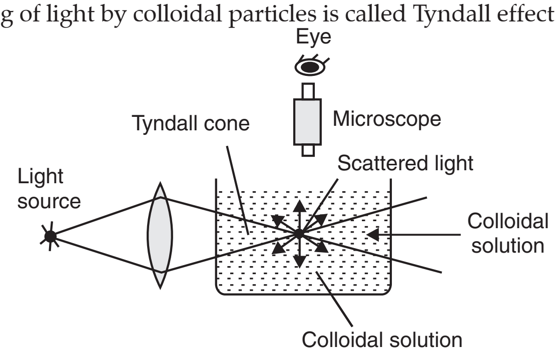


Fig. 5 : Tyndall effect

(iii) Electrophoresis : The movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution is called electrophoresis.

- **Hardy-Schulze rules :**
  (i) Opposite charged ions are effective for coagulation.
  (ii) The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation. *e.g.*, $Al^{3+} > Ba^{2+} > Na^{+}$ for negatively charged colloids.

  $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$ for positively charged colloids.

  The reciprocal of coagulation value is called coagulating power. *i.e.*, lower the coagulation value, higher will be coagulating power.
- **Electrokinetic Potential or Zeta Potential :** The potential difference between the fixed layer and diffused layer of opposite charges is called zeta potential.
- **Coagulation :** Coagulation which can be reversed by shaking is called flocculation.
- **Coagulating value :** The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as coagulation value.

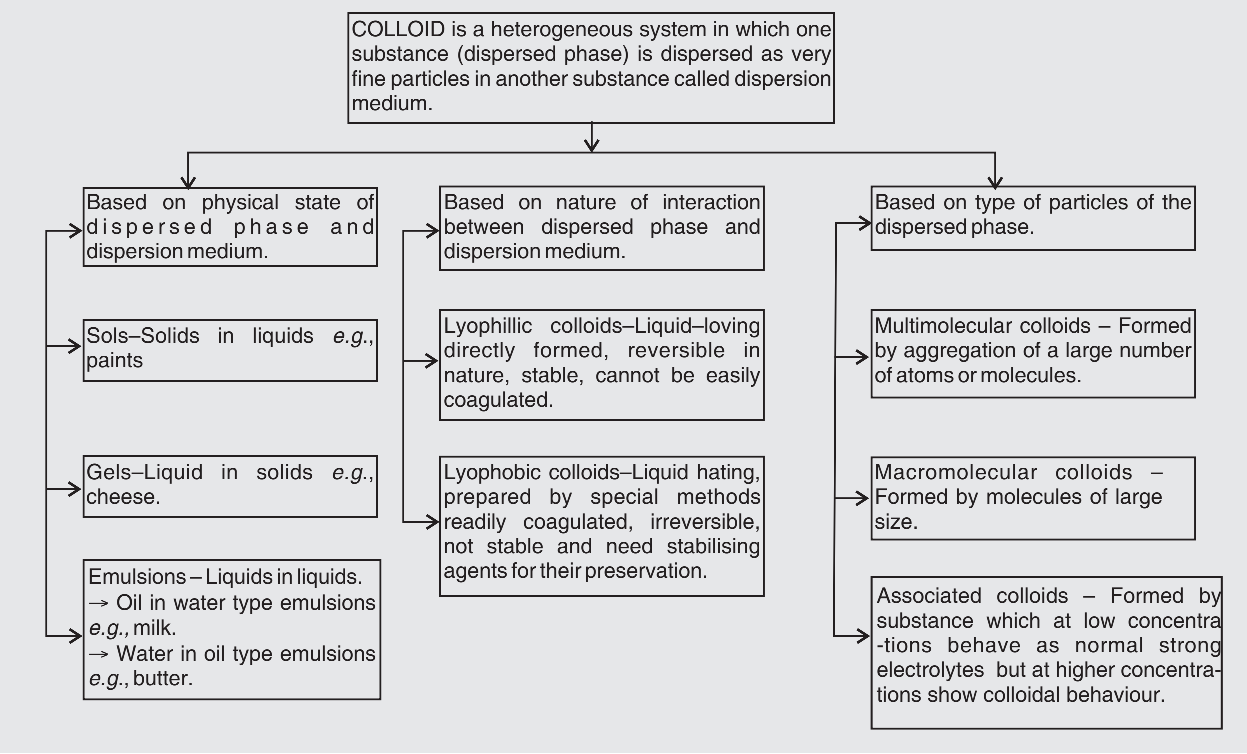
$$\text{Coagulation Value} \propto \frac{1}{\text{Coagulating power}}$$

- **Gold number :** The number of milligram of protective colloids which must be added to 10 ml of given gold sol. so that it is just prevented from coagulation by addition of 1 ml of 10% of NaCl solution.
- **Emulsions :** Emulsions are colloidal system in which both the dispersed phase and dispersion medium are liquids. There are two types of emulsions
  (i) Oil in water : In such emulsion oil is dispersed phase and water is dispersion medium for *e.g.*, milk, vanishing cream.
  (ii) Water in Oil : In such emulsion, water is dispersed phase and oil is dispersion medium for *e.g.*, butter.
- **Emulsification :** The process of making emulsion is called emulsification.
- **Emulsifying agent :** The substances which help in stabilising emulsion are called emulsifying agent or emulsifier. Soap and detergent are most frequently used as emulsifiers.
- **Demulsification :** The process of decomposing an emulsion into its constituent liquids is called demulsification. It is carried out by centrifugation, freezing, boiling or chemical methods which destroy the emulsifying agent.
- **Applications of colloids :**
  (i) Sewage disposal
  (ii) Purification of drinking water
  (iii) Smoke precipitation
  (iv) Medicines
  (v) Tanning
  (vi) Rubber industry.
- **Distinction between true solution, colloids and suspension :**

S. No.	True Solution	Colloids	Suspension
1.	It is homogeneous.	It appears to be homogeneous but actually it is heterogeneous.	It is heterogeneous.

2.	Its particle size is less than 1 nm.	Its particle size is 1 nm to 1000 nm.	Its particles are larger than 1000 nm.
3.	It passes through filter paper.	It passes through ordinary filter paper but not through ultrafilters.	It does not pass through filter paper.
4.	It does not show Tyndall effect.	It shows Tyndall effect.	It does not show Tyndall effect appreciably.
5.	It has higher value of colligative property.	It has low value of colligative property.	It has very low value of colligative property.
6.	Its particles cannot be seen even with powerful microscope.	Its particles can be seen by powerful microscope due to scattering of light.	Its particles can be seen even with naked eye.

Flowchart



Know the Terms

- **Crystalloids :** The substances whose aqueous solution can pass the semipermeable membrane.
- **CMC :** Critical Micellization Concentration is the lowest concentration of surfactant at which micelle formation takes place.
- **Congorobin number :** The protective power of lyophilic colloids can also be compared with another term called congorobin number.
- **Streaming potential :** When a liquid is forced through a porous material or a capillary tube, a potential difference is set up between the two sides. This is known as streaming potential.
- **Dorn potential :** When a particle is forced to move through a resting liquid, a potential difference is set up. It is known as Dorn potential.
- **U-number :** The number of milligrams of a hydrophilic sol which is sufficient to produce the colour change from red to blue in 1 cc of gold sol.

Chapter - 6 : General Principles and Processes of Isolation of Elements

TOPIC-1

Principles and Methods of Extraction

Quick Review

- **Minerals :** The naturally occurring chemical substances in the earth's crust which are obtained by mining.
- **Ore :** The mineral from which the metal is extracted conveniently and economically.
- **Gangue :** The earthy materials associated with the ores.
- **Occurrence of metals :**

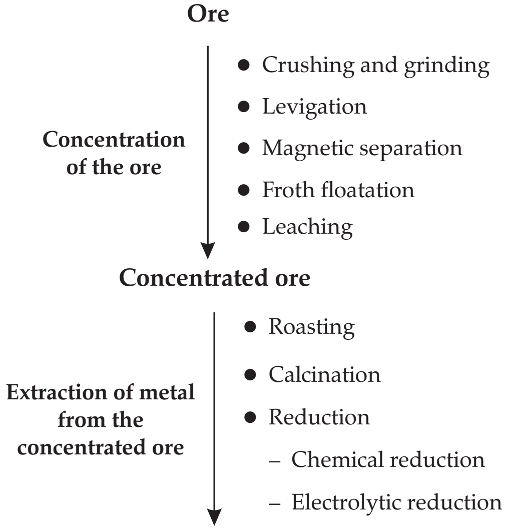
  In free state : Very few metals exist in the free or native state. Only metals like gold, platinum and mercury are occasionally found in the free state, *i.e.*, in the pure form.

  Note : Sometimes, copper and silver may also be found in the free state. Such metals are not acted upon by air or water.

  In the combined state : The rest of the metals occur in the combined form of compounds such as oxides, carbonates, sulphides, sulphates, silicates, chlorides, nitrates, phosphates etc.

  Copper and silver are two metals which occur in free as well as combined state as sulphides, oxides or halides ores.
- **Metallurgy :** Metallurgy is the entire scientific and technological process used to obtain the pure metal from its ore.
- **Flux :** The substance which is added in the ore to convert non-fusible gangue to fusible compound is called flux. There are three types of flux : acidic flux (Silica borax) and basic flux (Limestone) and neutral flux (graphite).
- **Slag :** The fusible compound formed by combination of flux and gangue is called slag.
- **The processes involved in the metallurgy :**
  - **(i)** Concentration of the ore
  - **(ii)** Isolation of metal from its concentrated ore
  - **(iii)** Refining or purification of metals
- **Metallurgy :** The process of extraction of a metal in the free state from its ore is referred as metallurgy.

  A general scheme of various metallurgical operations employed for the extraction of metals from ores is given below :



Crude metal

Purification of crude metal

- Liquation
- Poling
- Chromatographic method
- Electrolytic refining
- Zone refining
- Van Arkel method

Pure metal

- **Concentration of ore :** It is a process used for removing the gangue from the ore and increasing ore's grade on the basis of difference between the physical or chemical properties of the gangue and the ore.

  The concentration of the ore is carried out by the following methods :

  (i) Crushing and Grinding : The huge lumps are first broken into small pieces in the jaw crushers and the powdered with the help of a ball mill or stamp mill. This process is termed as pulverisation.

  (ii) Levigation or Gravity separation : It is based on difference in densities (gravities) of ore and the gangue In this process, ore is washed with stream of water under pressure, light impurities are washed away whereas heavy ore left behind.

  (iii) Magnetic separation method : Magnetic separation method is used to remove tungsten ore particles fro cassiterite (SnO_2). It is also used to concentrate magnetite (Fe_3O_4), chromite ($FeCr_2O_4$) and pyrolusite (MnO_2 from unwanted gangue.

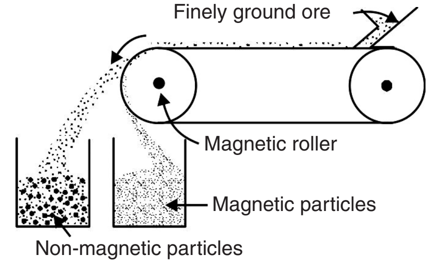


Fig. 1 : Magnetic separation method

  (iv) Froth floatation process : This process makes use of the principle of preferential wetting of solid surfaces by various liquids. This process is used for the concentration of sulphide ores *e.g.*, ores of lead, zinc and copper, because of the fact that metallic sulphides are more wetted by certain oils (pine oil) and less by water. The mixture is then agitated by passing a blast of air through it. The froth is formed which carries the ore particles along with it to the surface leaving the impurities behind. The froth is scummed off and in this wa the ore is concentrated by froth floatation process.

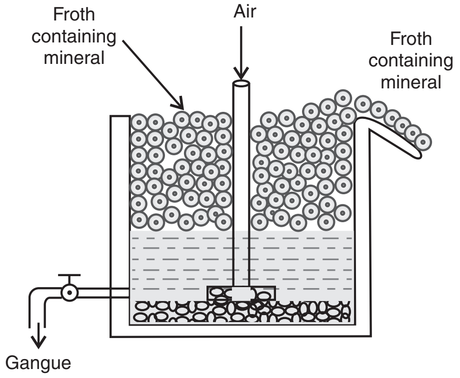


Fig. 2 : Froth floatation process

  (v) Hydraulic washing : It is based on the difference in the gravities of the ore and the gangue particles. An upward stream running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.

  (vi) Leaching : It is used if the ore is soluble in a suitable reagent which can selectively dissolve the ore but not the impurities.

- **Conversion of ore into oxide :** Following two methods are used to convert the ore into oxide. The given ore should be converted into oxide by suitable methods.

(i) Calcination : It is a process in which ore is heated in the absence of air so as to convert carbonate ores into oxides. In this process, the moisture and volatile impurities are removed. *e.g.*,

$$\underset{\text{Siderite}}{FeCO_3} \xrightarrow{\text{Heat}} FeO + CO_2$$

$$Fe_2O_3.xH_2O_{(s)} \xrightarrow{\text{Heat}} Fe_2O_{3\,(s)} + xH_2O_{(g)}$$

(ii) Roasting : It is a process in which ore is heated in regular supply of air at a temperature below the melti point of the metal so as to convert the given ore into oxide ore. It is also used to remove impurities as volatile oxides. Sulphide ores are converted into oxide by roasting. *e.g.*,

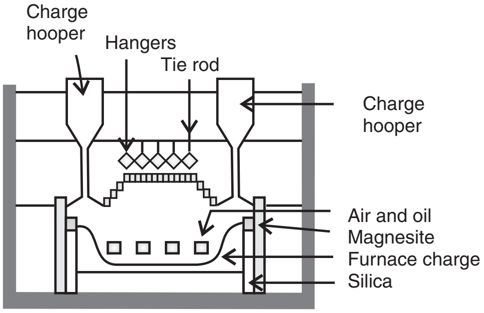


Fig. 3 : A section of a modern reverberatory furnace

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

This process is done in reverberatory furnace.

- **Slag :** The compound formed on reaction of gangue with flux is called **slag**. It is fusible mass which floats over metal.

$$\underset{\text{Iron (II) oxide}}{FeO} + \underset{\text{Silica}}{SiO_2} \rightarrow \underset{\text{Iron (II) silicate}}{FeSiO_3\text{ (slag)}}$$

- **Reduction of oxide to metal :** Reduction of the metal oxide involves heating it with some other substance acting as a reducing agent. The common reducing agent used are carbon, carbon monoxide or any other metal like Al, Mg etc. Some common methods used for the reduction are given below :

(i) Auto reduction : In this method inactive metals can be reduced simply by heating the ore in air. Extraction of copper, lead, antimony, mercury etc. have been carried out by this process. *e.g.*,

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \uparrow$$
$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2 \uparrow$$

(ii) Smelting : In this process metal oxide is reduced to metal with C or CO. *e.g.*,

$$Fe_2O_3 + 3C \xrightarrow{> 1123\text{ K}} 2Fe + 3CO \uparrow$$
$$Fe_2O_3 + 3CO \xrightarrow{1123\text{ K}} 2Fe + 3CO_2 \uparrow$$
$$ZnO + C \rightarrow Zn + CO \uparrow$$

(iii) Aluminothermic reduction : The process of reduction of metal oxide by aluminium is known as alumin thermic reduction. Metals like manganese and chromium are extracted by thermite process.

$$3MnO_4 + 8Al \rightarrow 4Al_2O_3 + 3Mn$$
$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$

(iv) Reduction with hydrogen : It is an efficient reducing agent for metal oxides. For this purpose, the roasted ore is heated in a current of hydrogen and metal oxide is reduced to metal. For example oxides of W, Mo, etc are reduced with hydrogen.

$$WO_3 + 3H_2 \rightarrow W + 3H_2O$$

- **Hydrometallurgy :** The process of extraction of a metal by dissolving the ore in a suitable reagent followed by precipitation or displacement of the metal by a more electropositive metal is known as hydrometallurgy.
- **Refining or Purification of Metals :**

(i) Liquation : It is the process of refining a low melting metal like tin which can be made to flow on a sloping surface.

(ii) Zone refining : This method is particularly used when metals are required in high degree of purity. In this method, a metal rod is placed inside a small high frequency induction furnace. A narrow zone of metal is melted (Fig. 4). This furnace is now slowly moved along the rod. The pure metal recrystallizes out of the melt while impurities remain in the melt which moves along with the melted zone of the rod with the movement of the furnace. The process is repeated several times. The end of the rod where the impurities have collected is cut off. This method is employed for the purification of germanium, silicon, gallium, etc., which are used in semiconductors.

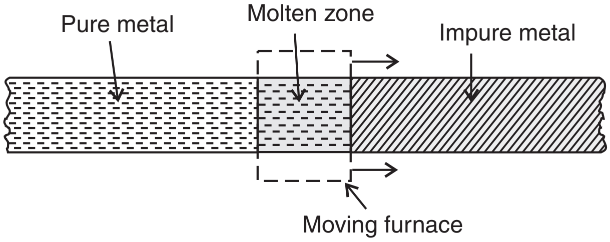


Fig. 4 : Zone refining

(iii) Electrolytic refining : This method is based upon the phenomenon of electrolysis. The crude metal is made anode whereas the thin sheet of pure metal is made cathode. Electrolyte is the solution of same salt of the metal. On passing electricity, the metal from the anode goes into solution as ions due to oxidation, while pure metal gets deposited at the cathode due to reduction of metal ions. The less electropositive impurities settle down below the anode as **anode mud.**

Reaction :

At anode : $M \rightarrow M^{n+} + ne^-$

At cathode : $M^{n+} + ne^- \rightarrow M$

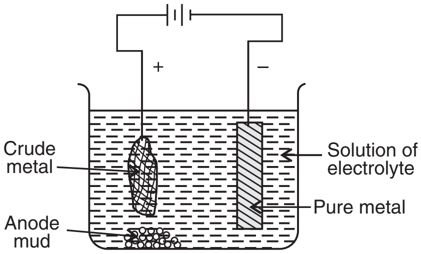


Fig. 5 : Electrolytic refining

(iv) Vapour phase refining : Vapour phase refining is illustrated by the following two methods :

(a) Mond process : This method is applied for purification of nickel. Nickel metal when heated in a stream of carbon monoxide forms volatile nickel carbonyl [$Ni(CO)_4$]. The impurities present in the impure nickel are left behind as solid. The vapour when heated to higher temperature (450-470K) decomposes giving pure nickel and carbon monoxide.

$$\underset{\text{Impure nickel}}{Ni} + 4CO \xrightarrow{330-350K} Ni(CO)_4 \xrightarrow{450-470K} \underset{\text{Pure nickel}}{Ni + 4CO}$$

(b) Van Arkel method : Small amounts of very pure titanium or zirconium metal can be prepared by this method. Impure metal is heated in an evacuated vessel with I_2. TiI_4 is formed which vaporizes leaving behind impurties. The gaseous MI_4 is decomposed on a white hot tungsten filament.

$$\underset{\text{Impure}}{Zr + 2I_2} \xrightarrow{870K} ZrI_4 \xrightarrow[\text{Tungsten filament}]{1800K} \underset{\text{Pure}}{Zr + 2I_2}$$

$$\underset{\text{Impure}}{Ti + 2I_2} \xrightarrow{523K} TiI_4 \xrightarrow[\text{Tungsten filament}]{1700K} \underset{\text{Pure}}{Ti + 2I_2}$$

- **Chromatographic method :** It is based on the principle of separation or purification by chromatography which is based on differential adsorption on an adsorbent. In column chromatography, Al_2O_3 is used as adsorbent. The mixture to be separated is taken in suitable solvent and applied on the column. They are then eluted out with suitable solvent (eluent). The weakly adsorbed component is eluted first, then the more strongly a sorbed and so on.

  This method is suitable for those elements which are available only in minute quantity and the impurities are not very much different in their chemical behaviour from the element to be purified.

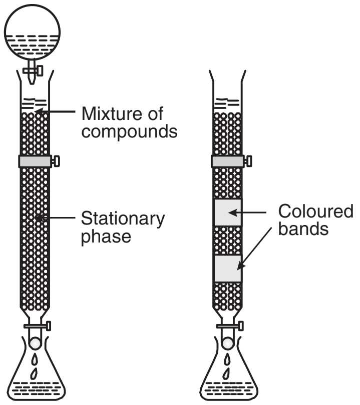


Fig. 6 : Column chromatography (Laboratory Method)

- **Thermodynamic principle of metallurgy :** This principle helps in choosing a suitable reducing agent for the reduction of particular metal oxide to metal. For any process, at any specified temperature, Gibbs free energy change (ΔG) is given by

  $$\Delta G = \Delta H - T\Delta S$$

  where, ΔH is the enthalpy change and ΔS is the entropy change for any process.

  If ΔG is positive for any reaction, then to make such reaction spontaneous, it is coupled with another reactions of large negative ΔG value so that the sum of ΔG becomes negative. This is known as coupling reaction.

- **Ellingham diagram :** This diagram was proposed by Ellingham to select the suitable reductant for the reduction of metal oxide.

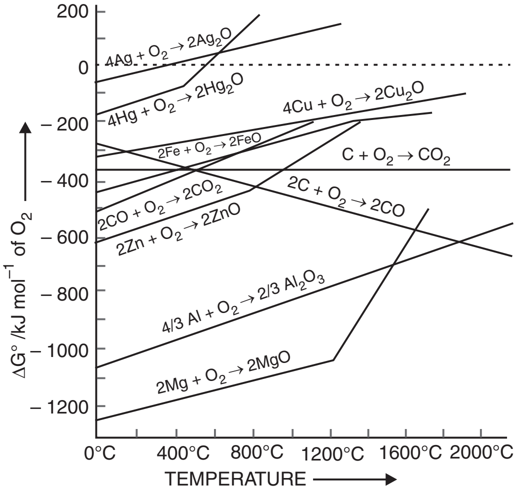


Fig. 7 : Ellingham diagram for some oxides

In this diagram, graph is plotted between change in standard free energy (ΔG°) and absolute temperature (T) for the formation of oxide of elements. This diagram helps in predicting the feasibility of reduction of an ore. The criterion of feasibility of reduction is negative value of change in free energy. This diagram explains the following important facts :

(i) Entropy decreases during formation of metal oxide from metal *i.e.*, ΔS is negative.

$$x\,M(s) + \frac{1}{2}O_2(s) \rightarrow M_xO_y(s)$$

(ii) Change in entropy (ΔS) increases on melting or boiling (change in state) of a substance. Hence, during the change in state, change in free energy takes place suddenly.

(iii) Formation of carbon monoxide is the result of oxidation. It is due to positive change in entropy (ΔS).

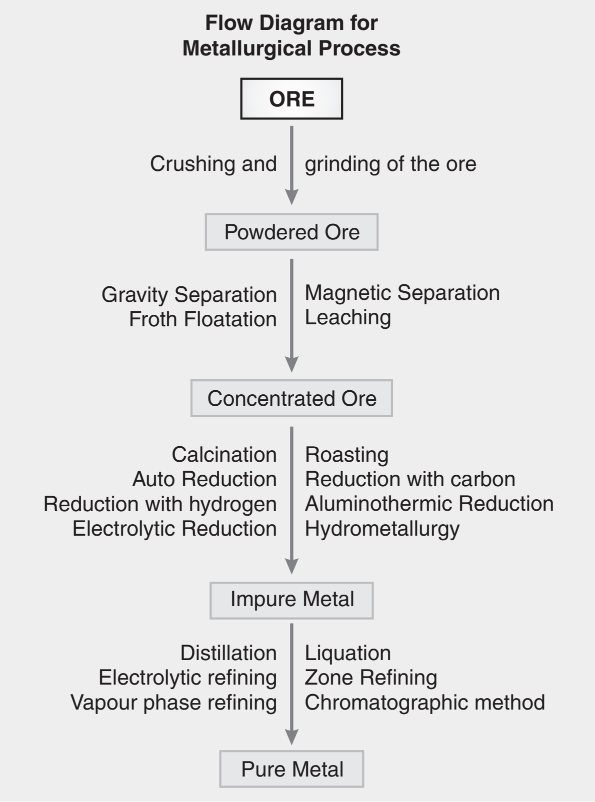
$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

- **Limitations of Ellingham diagram :**

(i) Ellingham diagram simply indicates the feasibility of a reduction process as it is based only on thermod namic principles. It is unable to explain the kinetics of a reduction process. On the basis of Ellingham diagram it can not be predicted that how fast a reduction process will occur.

(ii) Reactions are assumed at equilibrium in this diagram.

Flowchart



Know the Terms

- **Refining :** The process of purifying the impure metals is called refining.
- **Froth stabilisers :** Substances like cresol and aniline which stabilise the froth.
- **Extraction :** The process used to obtain metals in free state from the concentrated ore is called extraction.
- **Ellingham diagram :** The graphical representation of Gibbs energy.

TOPIC-2

Principles of Extraction of Aluminium, Copper, Zinc and Iron

Quick Review

- **Chief Ores and Methods of Extraction of Some Common Metals :**

Metal	Occurrence	Extraction Method	Remark
Copper	Copper pyrites, $CuFeS_2$ Cuprite, Cu_2O Malachite, $CuCO_3.Cu(OH)_2$ Copper glance, Cu_2S Azurite, $2CuCO_3.Cu(OH)_3$	Roasting of sulphide partially and reduction $2Cu_2O+Cu_2S \rightarrow 6Cu+SO_2$	It is self reduction in a specially designed converter. Sulphuric acid leaching is also employed.
Aluminium	Bauxite, $Al_2O_3.xH_2O$ Cryolite, Na_3AlF_6 Kaolinite, $[Al_2(OH)_4Si_2O_5]$ Aluminosilicates	Electrolysis of Al_2O_3 dissolved in molten cryolite or in Na_3AlF_6	A good source of electricity is needed in the extraction of Al.

Zinc	Zinc blende or Sphalerite, ZnS Zincite, ZnO Calamine, $ZnCO_3$	Roasting and then reduction with C.	The metal may be purified by fractional distillation.
Iron	Haematite, Fe_2O_3 Magnetite, Fe_3O_4 Siderite, $FeCO_3$ Iron pyrites, FeS_2 Limonite, $Fe_2O_3.3H_2O$	Reduction with the help of CO and coke in blast furnace. Chemical reduction with CO. Calcination followed by reduction with CO. Roasting followed by reduction. Chemical reduction with CO.	Limestone is added as flux which removes SiO_2 as calcium silicate (slag) floats over molten iron and prevents its oxidation. Temperature approaching 2170 K is required.

- **Flowchart for Extraction of Iron :**

Iron ore :
Haematite (Fe_2O_3) and Magnetite (Fe_3O_4)

↓

Concentration of ore :
Electromagnetic separation

↓

↓

Calcination and roasting :

$$\text{Concentrated Ore} + \text{Air} \xrightarrow{\text{heat}} \text{Moisture, } CO_2, SO_2 \text{ and } As_2O_3 \text{ are removed}$$

FeO is oxidised to Fe_2O_3

↓

Smelting : (Blast furnace)

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

$$FeS + Cu_2S \rightarrow \text{Matte}$$

↓

Bessemerisation in Bessemer's converter lined with lime and magnesia

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \xrightarrow[\text{reduction}]{\text{self}} 6Cu + SO_2$$

- **Flowchart for the Extraction of Zinc :**

Zinc ore :

Zinc blende (ZnS), Calamine ($ZnCO_3$) and Zincite (ZnO)

↓

Concentration by Froth Floatation Process :

Powdered ore + Water + Pine oil + Foam (containing sulphide)

↓

Roasting in Reverberatory Furnace in the presence of air :

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

$$2ZnSO_4 \rightarrow 2ZnO + 2SO_2 + O_2$$

↓

Reduction :

$ZnO + C \rightarrow Zn + CO$

↓

Purification by Electrolytic Method

Anode : Plates of impure Zn

Cathode : Plates of pure Zn

Electrolyte : Solution of $ZnSO_4$

Deposition of pure zinc on cathode

- **Flowchart for Extraction of Aluminium :**

Aluminium ore :

Bauxite $Al_2O_3.xH_2O$

↓

Concentration of ore : Leaching

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)}$$

$$2Na[Al(OH)_4]_{(aq)} + CO_{2(g)} \rightarrow Al_2O_3 . xH_2O_{(s)} + 2NaHCO_{3(aq)}$$

$$Al_2O_3\, xH_2O_{(s)} \xrightarrow{1470K} Al_2O_{3(s)} + xH_2O_{(g)}$$

↓

Electrolytic reduction : (Hall and Heroult process)

At cathode : $Al^{3+}_{(melt)} + 3e^- \rightarrow Al_{(l)}$

At anode : $C_{(s)} + O^{2-}_{(melt)} \rightarrow CO_{(g)} + 2e^-$

$C_{(s)} + 2O^{2-}_{(melt)} \rightarrow CO_{2(g)} + 4e^-$

$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

- **Flowchart for the Extraction of Copper :**

Ores :

Copper pyrite ($CuFeS_2$)

↓

Concentration of ore by Froth floatation method

↓

Roasting :

$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

↓

Smelting :

$FeO + SiO_2 \rightarrow \underset{(Slag)}{FeSiO_3}$

↓

Bessemerisation :

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

↓

Purification : By electrolytic refining by taking impure Cu as anode, pure Cu as cathode and acidified $CuSO_4$ solution as electrolyte :

At anode : $Cu \rightarrow Cu^{2+} + 2e^-$

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

➢ **Varieties of iron and their comparison :**

S. No.	Properties	Cast Iron	Wrought Iron	Steel
1.	Iron content	94 – 96%	98·5 – 98·8%	98·5 – 99·5%
2.	Carbon content	2·5 – 4·5%	0·12 – 0·25%	0·5– 1·5%
3.	Content of Si, P, S and Mn	1·5%	0·95 – 1·4%	—
4.	Hardness	Very hard	Soft	Hard
5.	Melting point	1200°C	1500°C	1300 °C
6.	Malleability	Brittle	Malleable	Malleable
7.	Welding	Not possible	May be done	Can be done but with difficulty
8.	Rust	Does not rust	Rusts	Does not rust

➢ **Properties and uses of some Alloys :**

S. No.	Steel Alloy	Percentage of the component mixed	Properties of the Alloy	Uses of Alloy
1.	Manganese steel	Mn = 7 – 17%	Extremely hard, low effect of abrasives.	In manufacture of railway tracks, machines for road smashing, safe, etc.
2.	Nickel steel	Ni = 2.5 – 5%	Hard, high tensile strength, malleable, does not rust easily.	Electric wires, plates, shafts, aircraft and motor parts.
3.	Invar	Ni = 35%	Coefficient of thermal expansion is equivalent to that of glass.	In pendulum rods, meter and other articles of measurement.
4.	Chromium steel	Cr = 1·5 – 2%	Very hard	In machines for road smashing, cutting tools etc.
5.	Chromium steel or stainless steel	Cr = 12%	No rusting, no action of acids, hard.	In utensils, knives, motor and cycle parts.
6.	Chrome vanadium steel	Cr = 1 – 10% V = 15%	Very hard and strong, high tensile strength.	In ball bearings and gears, spring, car bodies, etc.
7.	Tungsten steel	W = 10 – 20% Cr = 4 – 6%	Extremely hard and tenacious	In cutting tools, magnet, spring, etc.

➢ **Some important types of Ores :**

S. No.	Ore type	Example
1.	Native	Cu, Ag, Au, Hg, As, Bi, Sn, Pd, Pt
2.	Oxides	Al_2O_3, Fe_2O_3, Fe_3O_4, SnO_2, MnO_2, TiO_2, $FeCr_2O_4$, WO_3, Cu_2O, ZnO
3.	Carbonates	$CaCO_3$, $MgCO_3$, $FeCO_3$, $PbCO_3$, $BaCO_3$, $SrCO_3$, $ZnCO_3$, $MnCO_3$, $CuCO_3$
4.	Sulphides	Ag_2S, Cu_2S, PbS, ZnS, HgS, FeS, Bi_2S_3, NiS,CaS, MoS_2
5.	Halides	NaCl, KCl, AgCl, $MgCl_2.6H_2O$, NaCl and $MgCl_2$ (in sea water)
6.	Sulphates	$BaSO_4$, $SrSO_4$, $PbSO_4$, $CuSO_4$, $CaSO_4. H_2O$
7.	Silicates	$Be_3Al_2Si_6O_{18}$, $ZnSiO_4$, $Sc_2Si_2O_7$, $NiSiO_3$, $MgSiO_3$
8.	Phosphates	$CrPO_4$, $LaPO_4$, $Th_3(PO_4)_4$, LiF.$AlPO_4$

Know the Terms

- **Complex ores :** These are the mixtures of several minerals. For example : Lepidolite [K (Li, Al, Rb)$_3$. (Al, Si)$_4$O$_{10}$ (F, OH)$_2$], Triphylite [LiFePO$_4$].
- **Native ores :** These ores contain metals in their elemental form associated with alluvial impurities like clay, sand, etc.

❑❑

Chapter - 7 : The p-Block Elements

TOPIC-1

Group-15 Elements, Properties and Some Important Compounds

Quick Review

- **Elements of *p*-Block :**

Group 13	Boron family	B, Al, Ga, In, Tl
Group 14	Carbon family	C, Si, Ge, Sn, Pb
Group 15	Nitrogen family	N, P, As, Sb, Bi
Group 16	Oxygen family	O, S, Se, Te, Po
Group 17	Halogen family	F, Cl, Br, I, At
Group 18	Noble gases	He, Ne, Ar, Kr, Xe, Rn

- General electronic configuration of *p*-Block elements : $ns^2\ np^{1-6}$
- **Group 15 elements :**
  - **(i) Nitrogen family :** $_{7}$N, $_{15}$P, $_{33}$As, $_{51}$Sb, $_{83}$Bi
  - **(ii) Atomic radii :** Smaller than the corresponding elements of group 14. Down the group, they increase due to addition of new shell.
  - **(iii) Ionisation enthalpy :** Higher than the corresponding elements of group 14. Down the group, it decreases due to increase in atomic size.
  - **(iv) Electronegativity :** Decreases down the group with increasing atomic size.
- **Physical properties of group 15 elements :**
  - **(i)** Except dinitrogen, all are solid.
  - **(ii)** Metallic character increases down the group due to decrease in ionisation enthalpy and increase in the atomic size.
  - **(iii)** Boiling point increases from top the bottom.
  - **(iv)** Melting point increases upto arsenic and decreases upto bismuth.
  - **(v) Oxidation states :** –3 to +5.
- **Chemical properties of group 15 elements :**
  - **(i) Towards hydrogen :** All the elements form hydrides of the type EH$_3$ where E = N, P, As, Sb, Bi. The stability decreases from NH$_3$ to BiH. Reducing character increases down the group. Basic character decreases down the group. Boiling point of NH$_3$ is greater than PH$_3$ because of intermolecular hydrogen bonding. Boiling points increases from PH$_3$ onwards.
  - **(ii) Towards oxygen :** Forms two types of oxides E$_2$O$_3$ and E$_2$O$_5$. The acidic character decreases down the group.
  - **(iii) Towards halogens :** Directly combine with halogens to form trihalides (EX$_3$) and pentahalides (EX$_5$).
  - **(iv) Towards metals :** All the elements react with metals to form their binary compounds exhibiting –3 oxidation state.
- **Anomalous properties of nitrogen :** N does not form pentahalides because of non-availability of *d*-orbitals in its valence shell. It has ability to form pπ-pπ multiple bonds with itself and other elements having high electronegativity. N differs from the rest of the members of group due to small size, high electronegativity, high ionisation enthalpy and non-availability of *d*-orbitals.

- **Oxides of Nitrogen, preparation, properties of oxides of nitrogen.**

S. No.	Formula	Name	Preparation	Properties	O.N.
1.	N_2O	Dinitrogen monoxide	$NH_4NO_3 \xrightarrow{heat} N_2O + 2H_2O$	Colourless gas, rather unreactive.	+1
2.	NO	Nitrogen monoxide	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	Colourless gas, paramagnetic.	+2
3.	NO_2	Nitrogen dioxide	$2Pb(NO_3)_2 \xrightarrow{673K} 2PbO + 4NO_2 + O_2$	Brown gas, reactive, paramagnetic.	+4
4.	N_2O_3	Dinitrogen trioxide	$2NO + N_2O_4 \rightarrow 2N_2O_3$	Dark blue in liquid or solid state, unstable in the gas phase.	+3
5.	N_2O_4	Dinitrogen tetroxide	$2NO_2 \underset{373\text{ K}}{\overset{273\text{ K}}{\rightleftharpoons}} N_2O_4$	Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state.	+4
6.	N_2O_5	Dinitrogen pentoxide	$2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$ Metaphosphoric acid	Unstable as gas; in the solid state exists as $[NO_2]^+ [NO_3]^-$.	+5

- **Structures of Oxides of Nitrogen :**

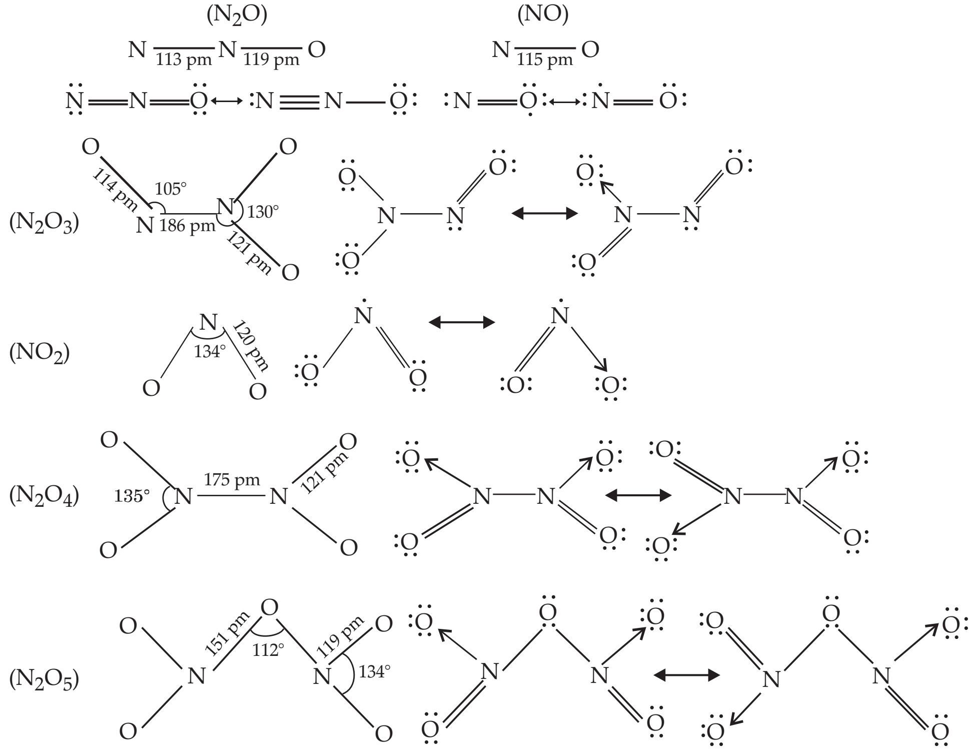


Fig. 1 : The molecule and Lewis dot resonance structure of oxides of nitrogen

- **Dinitrogen (N_2) :**
  Preparation :

  (i) In laboratory : $NH_4Cl_{(aq)} + NaNO_{2(aq)} \xrightarrow{heat} N_{2(g)} + 2H_2O_{(l)} + NaCl_{(aq)}$

  (ii) By thermal decomposition :

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

  Properties :
  (i) N_2 has very little reactivity at ordinary temperature.
  (ii) Forms nitrides with highly electropositive metals like

$$3Mg + N_2 \rightarrow Mg_3N_2$$
$$6Li + N_2 \rightarrow 2Li_3N$$

- **Ammonia (NH_3) :**
  Preparation :

(i) In laboratory : $2NH_4Cl + Ca(OH)_2 \xrightarrow{\text{heat}} CaCl_2 + 2NH_3 + 2H_2O$

(ii) By Haber's process :

$$N_{2(g)} + 3H_{2(g)} \underset{773\text{ K}}{\overset{\text{Fe/Mo}}{\rightleftharpoons}} 2NH_{3(g)}, H = -46.1 \text{ kJ mol}^{-1}$$

Properties :

(i) Extremely soluble in water.

(ii) Acts as Lewis base

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$Cu^{2+} + 4NH_3 \rightleftharpoons \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}}$$

$$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$$

(iii) Forms salts with acids

$$ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$$

$$2FeCl_3(aq) + 3NH_4OH(aq) \rightarrow Fe_2O_3.xH_2O(s) + 3NH_4Cl(aq)$$

(iv) Reaction with Nessler's reagent :

$$2K_2[HgI_4] + NH_3 + 3KOH \rightarrow [OHg_2.NH_2]I + 7KI + 2H_2O$$

- **Nitric Acid (HNO_3) :**

Preparation :

In laboratory : $NaNO_3 + \underset{\text{(conc.)}}{H_2SO_4} \rightarrow \underset{\text{(Brown ppt.)}}{NaH_2SO_4} + HNO_3$

(i) By Ostwald's process :

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Properties :

(i) Colourless liquid.

(ii) Concentrated nitric acid is a strong oxidising agent.

(iii) Reactions :

$$HNO_{3(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$$

$$3Cu + \underset{\text{(dil)}}{8HNO_3} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$4Zn + \underset{\text{(dilute)}}{10HNO_3} \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Zn(NO_3)_2 + 5H_2O + 2NO_2$$

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Uses :

(i) In the manufacturing of explosives, fertilisers etc.

(ii) As a reagent in laboratory.

(iii) In nitration of organic compounds.

(iv) In preparing aqua-regia.

- **Allotropes of phosphorus :**

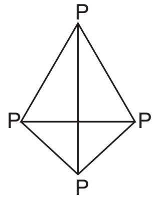
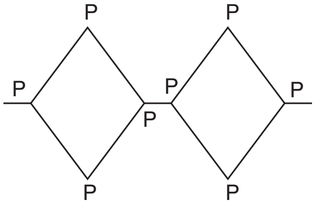
(i) White or yellow phosphorus

(ii) Black phosphorus

(iii) Red phosphorus

- **Differences between white and red phosphorus :**

Property	White Phosphorus	Red Phosphorus
State	Translucent white waxy solid	Iron grey lustrous powder
Odour	Garlic	Odourless
Physiological action	Poisonous	Non-poisonous
Stability	Less stable	More stable than white P

Solubility	Insoluble in water but soluble in CS_2.	Insoluble in water as well as CS_2.
Action of air	Readily catches fire with greenish glow.	Does not glow in dark.
Effect of heat	Changes to α-black P when heated at 473 K under high pressure and changes to red P when heated at 573 K.	Changes to α-black P when heated at 803 K in a solid form.
Structure	P_4 (tetrahedral)  	Tetrahedral units of P_4 joined together through covalent bond. 

- **Phosphine (PH_3)**

Preparation :

(i) In laboratory :

$$\underset{\text{(white)}}{P_4} + \underset{\text{(conc.)}}{3NaOH} + 3H_2O \xrightleftharpoons[\text{inert atmosphere of } CO_2]{\Delta} PH_3 + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

Properties :

(i) Colourless gas with rotten fish smell.

(ii) Highly poisonous.

(iii) Pure sample is not spontaneously inflammable.

(iv) Burns in air or oxygen when heated at 150°C.

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$$
$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$
$$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$$
$$PH_3 + HBr \rightarrow PH_4Br$$

- **Phosphorus Trichloride (PCl_3)**

Preparation :

(i) By passing dry chlorine over heated white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

(ii) By action of thionyl chloride with white phosphorus.

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties :

(i) Colourless oily liquid.

(ii) Hydrolyses in the presence of moisture.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

(iii) $3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$

Shape : Pyramidal in which phosphorus is sp^3 hybridised.

- **Phosphorus Pentachloride (PCl_5)**

Preparation :

(i) Reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

(ii) By the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

Properties :

(i) Yellowish white powder.

(ii) In moist air hydrolyses to $POCl_3$ and finally converts to phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

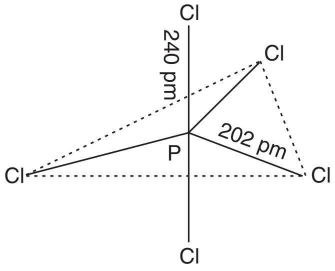
(iii) Decomposes on stronger heating

$$PCl_5 \xrightarrow{\text{heat}} PCl_3 + Cl_2$$

(iv) Gives corresponding halides with transition metals

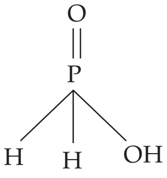
$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$
$$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$$

Shape : Trigonal bipyramidal

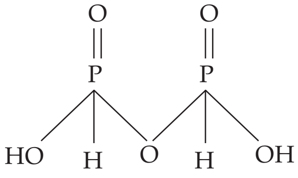


- **Oxoacids of phosphorus with structure :**

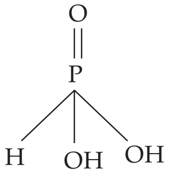
(i) H_3PO_2



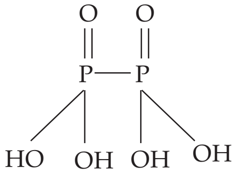
(ii) $H_4P_2O_5$



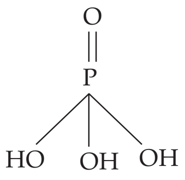
(iii) H_3PO_3



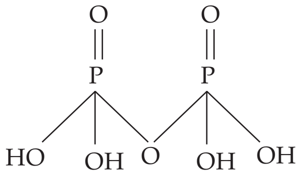
(iv) $H_4P_2O_6$



(v) H_3PO_4



(vi) $H_4P_2O_7$



(vii) $(HPO_3)_3$

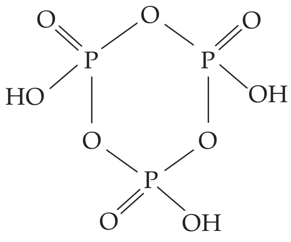


Fig. 2 :Trimer or polymer of HPO_3

- The acids which contain P-H bond have reducing characteristics and act as good reducing agent.

  Example : H_3PO_2 reduces $AgNO_3$ to Ag

  $$4AgNO_3 + 2H_2O + H_3PO_2 \circledR 4Ag + 4HNO_3 + H_3PO_4$$
- The P-H bonds are not responsible for basicity as they do not ionize to give H^+. Only H attached with oxygen are responsible for basicity and are ionisable.

Know the Terms

- **Pnicogens :** The nitrogen group is group-15 of the periodic table and is also collectively named the pnicogens or pnictogens.

  The word pnicogens is derived from the greek word pnigein which means 'to choke or stifle' which is a property of nitrogen.
- **Inert pair effect :** The reluctance of the valance *s*-electrons to be available for bonding as compared to the valence *p*-electrons due to their greater penetration in the nucleus.
- **Fuming nitric acid :** Nitric acid containing dissolved NO_2 is known as fuming nitric acid. It can be obtained by distilling concentrated HNO_3 with a little of starch.
- **Phosphazenes :** These are the cyclic compounds which contain both nitrogen and phosphorus atoms in the alternate position along with two substitutes on each phosphorus atom. These are cyclic trimers, tetramers or polymers in nature.
- **Fuming nitric acid :** Nitric acid containing dissolved nitrogen dioxide.
- **Aqua-regia :** Mixture of nitric acid and hydrochloric acid in ratio of 1 : 3.

TOPIC-2

Group-16 Elements, Properties and Some Important Compounds

Quick Review

- **Oxygen family :** ${}_{8}O$, ${}_{16}S$, ${}_{34}Se$, ${}_{52}Te$, ${}_{84}Po$
- **Physical properties :**
  - **(i) Atomic and ionic radii :** Smaller than the corresponding elements of group 15 due to increase in nuclear charge. Down the group they increase due to addition of a new shell.
  - **(ii) Ionisation enthalpy :** I.E.$_1$ is lower than those of corresponding elements of group 15 due to increase in nuclear charge. I.E.$_2$ is higher than those of group 15 due to smaller size of the ions and greater effective nuclear charge. Down the group I.E. decreases.
  - **(iii) Electron gain enthalpy :** Oxygen has less electron gain enthalpy than sulphur. From sulphur the value again become less negative upto polonium.
  - **(iv) Electronegativity :** More electronegative than group 15 elements. It decreases down the group due to increase in atomic size.
  - **(v)** Oxygen and sulphur are non-metals, selenium and tellurium metalloids and polonium is a metal.
  - **(vi) Melting and boiling points :** Increases regularly from O to Te due to increase in size and hence greater van der Waal's force. Po has lesser melting and boiling point than Te due to maximum inert pair effect.
  - **(vii) Density :** Increases down the group.
  - **(viii) Oxidation state :** Oxygen shows an oxidation state of – 2 only (except OF_2 and H_2O_2). All other elements show +2, +4 and +6 oxidation states.
- **Chemical properties :**

(i) With hydrogen : Form hydroxide of type H_2E (E = O, S, Se, Te and Po).

Properties of hydrides :

(i) Thermal stability : Decreases down the group.

(ii) Acidic character : Increases down the group.

$$H_2E + aq \rightleftharpoons H^+ + HE^-$$
$$HE^- + aq \rightleftharpoons H^+ + E^{2-}$$

(iii) Reducing nature : All are reducing agents except H_2O.

(iv) Boiling point : From H_2O to H_2S there is a sudden drop which increases from H_2S to H_2Te.

(v) With halogens : Form halides of type EX_2, EX_4 and EX_6 where E is an element of group and X is a halogen.

Properties of halides :

(i) Only hexafluorides are the only stable halides.

(ii) All elements except selenium form dichlorides and dibromides. These dihalides are sp^3 hybridised and have tetrahedral structure.

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

(a) Preparation of SF_4 and SF_6 :

$$SCl_2 + 2NaF \xrightarrow{300\ K} SF_4 + S_2Cl_2$$
$$S + 3F_2 \xrightarrow{Burn} SF_6$$

(b) Properties of SF_4 : SF_4 is readily hydrolysed

$$SF_4 + 2H_2O \rightarrow 4HF + SO_2$$

(c) SF_6 is sp^3d^2 hybridised and octahedral whereas SF_4 is sp^3d hybridised and is trigonal bipyramidal with one position occupied by a lone pair of electrons.

(iii) With Oxygen : Form oxides of EO_2 and EO_3.

- **Dioxygen (O_2)**

Preparation :

In laboratory, $$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

Properties :

(i) Slightly soluble in water and appreciable soluble in alkaline pyrogallol solution.

(ii) Paramagnetic.

(iii) Forms oxides with metals and non-metals.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$
$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

➢ **Classification of oxides :** On the basis of chemical nature.

(i) Basic : Na_2O, CaO, etc. metallic oxides.

(ii) Acidic : CO_2, SO_2, etc. non-metallic oxides.

(iii) Amphoteric : SnO_2, Al_2O_3, etc. are amphoteric oxides.

(iv) Neutral : H_2O, CO, etc. are neutral oxides.

(v) Poly-oxide : Oxides having oxygen more than required oxygen such as peroxide (Na_2O_2), super oxide (KO_2), dioxide (PbO_2), higher oxide (Mn_2O_7).

(vi) Sub-oxide : Oxides having oxygen less than required, *e.g.*, C_3O_2.

➢ **Ozone (O_3)**

Preparation : By subjecting pure and dry oxygen to silent electric discharge.

$$3O_{2(g)} \xrightarrow{\text{Discharge}} 2O_{3(g)}, \Delta H = +284 \text{ kJ}$$

Properties :

(i) Poisonous in nature.

(ii) Powerful oxidising agent. It is a stronger oxidising agent than O_2.

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$
$$2I^- + H_2O + O_3 \rightarrow 2OH^- + I_2 + O_2$$

Uses :

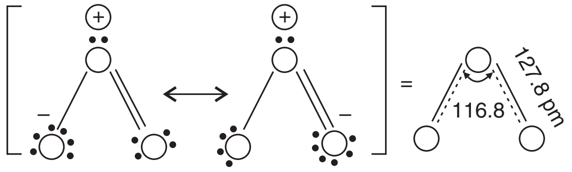
(i) As bleaching agent.

(ii) As disinfectant and germicide.

(iii) For purification of air is hospitals, railway tunnels, cinema house.

(iv) For bleaching oils, ivory flour, starch etc.

Structure :



➢ **Allotropes of Sulphur :**

(a) Rhombic Sulphur (∝-Sulphur) :

(i) Yellow in colour, m. p. 385.8 K and specific gravity 2.06.

(ii) Formed by evaporating the solution of roll sulphur in CS_2.

(iii) Insoluble in water but dissolves to some extent in benzene, alcohol and ether.

(iv) Readily soluble in CS_2.

(b) Monoclinic Sulphur (β-Sulphur)

(i) M. P. is 393 K and specific gravity 1.98.

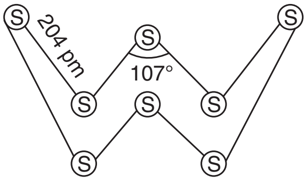
(ii) Soluble in CS_2.

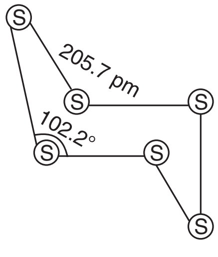
(iii) Prepared by melting rhombic sulphur in a dish and cooling.

(iv) Stable above 369 K and transforms into ∝-sulphur below it.

Both rhombic and monoclinic sulphur have S_8 molecules.

Shape of S_8 and S_6 molecules :





- **Sulphur dioxide (SO_2) :**

Preparation :

$$S + \underset{\text{(conc.)}}{2H_2SO_4} \rightarrow 3SO_2 + 2H_2O$$

$$Cu + \underset{\text{(conc.)}}{2H_2SO_4} \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$Na_2SO_3 + \underset{\text{(dil.)}}{2HCl} \rightarrow 2NaCl + SO_2 + H_2O$$

Properties :

(i) Colourless gas with pungent, suffocating odour.

(ii) Highly soluble in water.

(iii)

$$SO_2 + H_2O \rightleftharpoons \underset{\text{(Sulphurous acid)}}{H_2SO_3}$$

$$2NaOH + SO_2 \rightarrow Na_2CO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

$$Cl_2 + SO_2 \rightarrow SO_2Cl_2$$

$$O_2 + SO_2 \rightarrow 2SO_3$$

(iv) SO_2 act as reducing agent.

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

Uses :

(i) Used in refining petroleum and sugar.

(ii) As bleaching agent for wool and silk.

(iii) As antichlor, disinfectant and preservative.

- **Sulphuric acid (H_2SO_4)**

Preparation : By contact process which involves 3 steps :

(i) Burning of sulphur or sulphide ores in air :

$$S + O_2 \rightarrow SO_2$$

(ii) Conversion of SO_2 to SO_3 with oxygen in the presence of a catalyst V_2O_5.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

(iii) Absorption of SO_3 in H_2SO_4 to give oleum. Oleum is diluted with water to get H_2SO_4 of desired concentration.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

Properties :

(i) Colourless, dense, oily liquid with a specific gravity of 1·84 at 298 K.

(ii) Low volatility.

(iii) Strong acidic character.

(iv) Strong affinity for water.

(v) Acts as an oxidising agent.

$$Cu + \underset{\text{(conc.)}}{H_2SO_4} \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$3S + \underset{\text{(conc.)}}{2H_2SO_4} \rightarrow 3SO_2 + 2H_2O$$

$$C + \underset{\text{(conc.)}}{2H_2SO_4} \rightarrow CO_2 + 2SO_2 + 2H_2O$$

(vi) Acts as a dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

Uses :

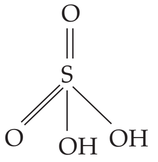
(i) In petroleum refining.

(ii) Manufacture of pigments, paints and dye stuff.

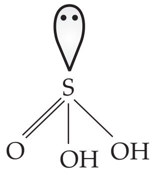
(iii) Detergent industry.

(iv) In storage batteries.

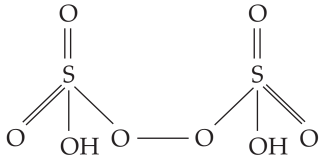
- **Oxoacids of Sulphur :**



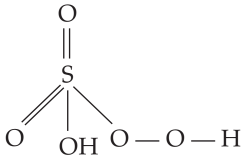
(H_2SO_4)
Sulphuric
acid



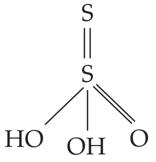
(H_2SO_3)
Sulphuric
acid



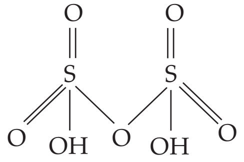
$(H_2S_2O_8)$
Marshall's acid
Peroxodisulphuric
acid



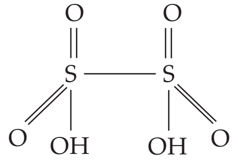
(H_2SO_5)
Caro's acid
Peroxomonosulphuric
acid



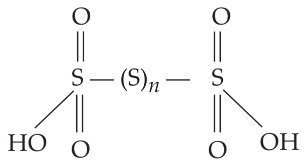
$(H_2S_2O_3)$
Thiosulphuric acid



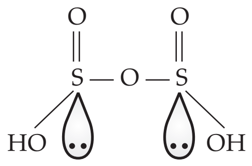
$(H_2S_2O_7)$
Pyrosulphuric acid
(Oleum)



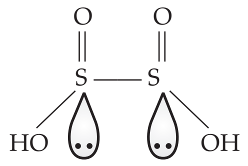
$(H_2S_2O_6)$
Dithionic acid



$(H_2S_xO_6)$



$(H_2S_2O_5)$



$(H_2S_2O_4)$

Know the Terms

- **Chalcogens :** Group-16 elements are also known as chalcogens which means ore forming elements.
- **Oil of vitrol :** Pure sulphuric acid is highly viscous due to the presence of intermolecular hydrogen bonding. It is known as oil of vitrol.
- **Oxide :** A binary compound of oxygen with another element.

TOPIC-3

Group-17 Elements, Properties and Some Important Compounds

Quick Review

- **Halogen family :** $_9F$, $_{17}Cl$, $_{35}Br$, $_{53}I$, $_{85}At$.
- **Physical Properties :**
  - **(i) Atomic and ionic radii :** They are the smallest in their respective periods due to increase in nuclear charge. Down the group, they increase.
  - **(ii) Oxidation state :** Fluorine shows – 1 only. Other elements show oxidation states + 1, + 3, + 5 and + 7.
  - **(iii) Ionisation enthalpy :** Higher than the corresponding members of group 16. Down the group, it decreases.
  - **(iv) Electron gain enthalpy :** Have maximum negative electron gain enthalpy in the corresponding periods.
  - **(v) Metallic characters :** Due to very high ionisation enthalpies are non-metals. The last element I, shows some metallic character as it can form I^+ by loss of electrons.
  - **(vi) Electronegativity :** These are the most electronegative elements in their respective periods. Down the group electronegativity decreases.
  - **(vii)** F_2 and Cl_2 are gases, Br_2 is a liquid while I_2 is solid.
  - **(viii)** All halogens are coloured.
  - **(ix) Melting point and boiling points :** Increases down the group due to increase in size and nuclear charge causing greater van der Waals forces of attraction.
  - **(x) Bond dissociation enthalpy :** Bond dissociation enthalpy decreases from Cl_2 to I_2. $Cl_2 > Br_2 > F_2 > I_2$.
- **Chemical Properties :**
  - **(a) Highly reactive :** The reactivity decreases down the group. Fluorine is the strongest oxidising halogen. A halogen oxidise halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \qquad (X = Cl, Br \text{ or } I)$$

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \qquad (X = Br \text{ or } I)$$
$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hypothalic and hypohalous acids.

$$2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$
$$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq) \qquad (X = Cl \text{ or } Br)$$

(b) Towards hydrogen : All elements form hydrides of the type HX (X = F, Cl, Br, I).

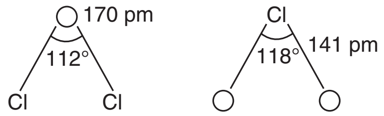
- **(i) Physical state :** Except HF which is a liquid because of H-bonding, all are gases.
- **(ii) Thermal stability :** It decreases down the group due to increase in bond length.
- **(iii) Reducing character :** It increases from HF to HI due to decrease of stability.
- **(iv) Acidic strength :** HF < HCl < HBr < HI.

(c) Towards halogens : They react with all elements except He, Ne and Ar to form binary halides.

(d) Towards metal :

- **(i)** With particular metal, ionic character is M-F > M-Cl > M-Br > M–I.
- **(ii)** With metals having low I.E., halides are ionic.
- **(iii)** With metals having high I.E., halides are covalent.
- **(iv)** With metals showing more than one oxidation states, halides with higher oxidation states are more covalent.
- **(v)** Metals show highest oxidation state in fluorides.

(e) Towards oxygen : Halogens form many binary compounds with oxygen, but most of them are unstable. Cl, Br and I form oxides in their oxidation state + 1 to + 7. Their stability decreases in the order I > Cl > Br.



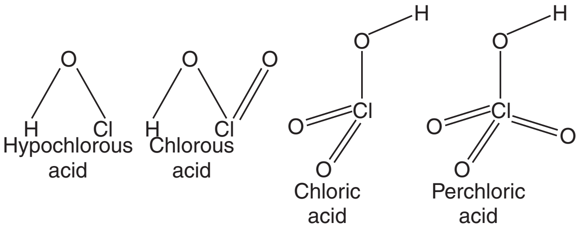
(f) Oxoacids : Because of high electronegativity and small size, fluorine forms only one oxoacid, HOF (hypofluorous acid). The other halogens form acid of the type HOX—hypohalous acid, HOXO–halous acid, $HOXO_2$ – halic acid and $HOXO_3$ – perhalic acid.

Acidic strength : HClO > HBrO > HIO

Acidic strength of oxoacids containing the same halogen :

$HCl > HClO_2 < HClO_3 < HClO_4$

(g) Structure of oxoacids of Chlorine :



➢ **Chlorine (Cl_2)**

Preparation :

$$MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$$
$$2KMnO_4 + 16HCl \xrightarrow{\Delta} 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

In laboratory,

(i) $HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)

(ii) $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

(iii) Electrolytic process : By electrolysis of brine.

At cathode : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$; $Na^+ + OH^- \rightarrow NaOH$

At anode : $Cl^- \rightarrow Cl + e^-$; $Cl + Cl \rightarrow Cl_2$

Properties :

- **(i)** It is a greenish yellow gas with a pungent suffocating smell.
- **(ii)** Soluble in water.
- **(iii)** About 2.5 times heavier than air.
- **(iv)** With metals and non-metals form chlorides.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3;\ 2Na + Cl_2 \rightarrow 2NaCl$$
$$2Fe + 3Cl_2 \rightarrow 2FeCl_3;\ S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$
$$P_4 + 6Cl_2 \rightarrow 4PCl_3;\ H_2 + Cl_2 \rightarrow 2HCl$$

(v) Reacts with compounds containing hydrogen to form HCl

$$H_2S + Cl_2 \rightarrow 2HCl + S;\ C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$$

$$\underset{\text{(excess)}}{NH_3} + 3Cl_2 \rightarrow \underset{\text{(explosive)}}{NCl_3} + 3HCl;\ \underset{\text{(excess)}}{8NH_3} + 3Cl_2 \rightarrow 6NH_4Cl + N_2$$

(vi) With cold and dilute alkalies

$$\underset{\text{(cold and dilute)}}{2NaOH + Cl_2} \rightarrow NaCl + NaOCl + H_2O$$

(vii) With hot and concentrated alkalies

$$\underset{\text{(hot and conc.)}}{6NaOH + 3Cl_2} \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

(viii) With dry slaked lime, it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

(ix) Chlorine water on standing loses its yellow colour. HOCl formed gives nascent oxygen.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$
$$HOCl \rightarrow HCl + O$$

(x) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$
$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$
$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$
$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$

Uses :

(i) For bleaching cotton and textiles.
(ii) In sterilising drinking water.
(iii) In the extraction of gold and platinum.
(iv) Manufacture of dyes, drugs, refrigerant and other organic compounds like $CHCl_3$, DDT, CCl_4, etc.

- **Hydrogen Chloride (HCl) :**

Preparation : In laboratory

$$NaCl + H_2SO_4 \xrightarrow{420\text{ K}} NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \xrightarrow{823\text{ K}} Na_2SO_4 + HCl$$

HCl gas can be dried by passing conc. H_2SO_4 through it.

Properties

(i) Colourless and pungent smelling gas.
(ii) Extremely soluble in water.
(iii) When three parts of conc. HCl and one part of conc. HNO_3 are mixed aqua-regia is formed which is used for dissolving noble metals *e.g.,* gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$
$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

(iv) Reacts with NH_3 giving white fumes of NH_4Cl

$$NH_3 + HCl \rightarrow NH_4Cl$$

(v) Decomposes salts of weaker acids.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$
$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$$

Uses :

(i) In the manufacture of chlorine, glucose and NH_4Cl.
(ii) For extracting glue from bones and purifying bone black.

- **Interhalogen Compounds :** Halogen combines amongst themselves to form a number of compounds known as interhalogen compounds. Their general formula are XX', XX_3', XX_5' and XX_7' where X is halogen of larger size and higher electropositivity and X' of smaller size.

Preparation :

$$\underset{\text{(Equal volume)}}{Cl_2 + F_2} \xrightarrow{437\text{ K}} 2ClF; \qquad \underset{\text{(excess)}}{I_2} + 3Cl_2 \rightarrow 2ICl_3$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\text{ K}} 2ClF_3; \qquad \underset{\text{(Diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

$$\underset{\text{(Equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl; \qquad Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

Properties :
- **(i)** Covalent compounds.
- **(ii)** Diamagnetic in nature.
- **(iii)** More reactive than halogens.
- **(iv)** Undergo hydrolysis.

$$XX' + H_2O \rightarrow HX' + HOX$$

- **Structure :** On the basis of VSEPR theory, XX_3' compounds have bent 'T' shape, XX_5' compounds have square pyramidal and IF_7 has pentagonal bipyramidal shape.

Uses :
- **(i)** As non-aqueous solvents.
- **(ii)** As fluorinating agents.
- **(iii)** ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

Know the Terms

- **Pseudohalide ions :** CN^-, SCN^- and OCN^- ions are called pseudohalide ions while $(CN)_2$, $(SCN)_2$ and $(OCN)_2$ are known as pseudohalogens.
- **Bleaching powder :** $Ca(OCl)_2 + CaCl_2Ca(OH)_2H_2O$

TOPIC-4

Group-18 Elements, Properties and Some Important Compounds

Quick Review

- **Noble gases :** $_4He$, $_{10}Ne$, $_{18}Ar$, $_{36}Kr$, $_{54}Xe$, $_{86}Ra$.
- Also known as rare gases as they are present in very small amounts in the air. Or as inert gases as they were considered chemically unreactive.
- **Electronic configuration :** ns^2np^6 (except He which has $1s^2$)
- **Physical Properties :**
  - **(i)** Gases
  - **(ii)** Atomic radii down the group and highest in their respective periods.
  - **(iii)** Highest ionisation enthalpy in their respective periods. Down the group, it decreases due to increase in atomic size.
  - **(iv)** Large positive values of electron gain enthalpy as noble gases have stable electronic configurations and no tendency to accept electron.
  - **(v)** Low melting points and boiling points due to weak van der Waal's forces. Down the group they increase because of increase in van der Waala' forces.
  - **(vi) Liquefaction :** They are difficult to liquify. Down the group, the ease of liquefaction increases.
- In 1962, Bartlett studied the given reaction :

$$O_2 + PtF_6 \rightarrow \underset{\text{Dioxygenyl hexafluoro platinate}}{O_2^+[PtF_6]^-}$$

As ionisation enthalpy of molecular oxygen was almost similar to xenon, below reaction was also found to occur :

$$Xe + PtF_6 \xrightarrow{289\text{ K}} Xe^+[PtF_6]^-$$

- **Preparation of Xenon fluorides :** Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6.

$$\underset{\text{(excess)}}{Xe(g)} + F_2(g) \xrightarrow{673\text{ K, 1 bar}} XeF_2(s)$$

$$Xe(g) + 2F_2(g) \xrightarrow{873\text{ K, 7 bar}} XeF_4(s)$$

$$\underset{\text{(1 : 20 ratio)}}{Xe(g) + 3F_2} \xrightarrow{573\text{ K, 60-70 bar}} XeF_6(s)$$

$$XeF_4 + O_2F_2 \xrightarrow{143\text{ K}} XeF_6 + O_2$$

- **Preparation of Xenon trioxide (XeO_3) :**

$$6XeF_4 + 12H_2O \rightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$
$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

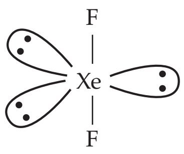
- **Preparation of Xenon oxyfluorides :**

$$XeF_4 + H_2O \rightarrow \underset{\text{Xenon oxydifluoride}}{XeOF_2} + 2HF$$

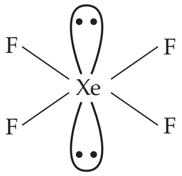
$$XeF_6 + H_2O \xrightarrow[\text{Hydrolysis}]{\text{Partial}} \underset{\text{Xenon oxytetrafluoride}}{XeOF_4} + 2HF$$

$$XeF_6 + OH_2O \xrightarrow[\text{Hydrolysis}]{\text{Complete}} \underset{\text{Xenon dioxydifluoride}}{XeO_2F_2} + 4HF$$

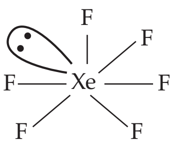
- **Structures of Xenon-fluorine compounds :**



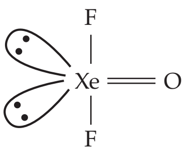
$XeF_2(sp^3d)$
[Linear]



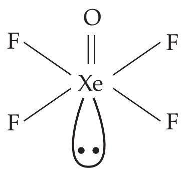
XeF_4 (sp^3d^2)
[Square Planar]



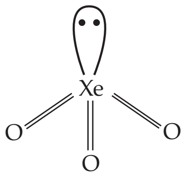
XeF_6 (sp^3d^3)
[Distorted Octahedral]



$XeOF_2$ (sp^3d)
[T-Shaped]



$XeOF_4$ (sp^3d^2)
[Square Pyramidal]



$XeO_3(sp^3)$
[Trigonal Pyramidal]

- **Uses :**

Helium	Neon	Argon	Krypton	Xenon
(i) To lift weather balloons and air ships.	For advertising.	To create an inert atmosphere.	For runway and approach lights in airports.	In electric flash bulbs for high speed photography.
(ii) As breathing mixture.	For filling sodium vapour lamps.	In geiger counters.	In high efficiency miner's cap lamps.	In gas filled lamps.
(iii) For inflating the tyres of aeroplanes.	In beacon light.	To date the age of rocks.		

❑❑

Chapter - 8 : The d-Block and f-Block Elements

TOPIC-1
d-Block Elements, their Properties and Compounds

Quick Review

- ***d*-block elements :** The elements in which last electron enters the *d* - sub-shell of penultimate shell and lies in the middle of the periodic table belonging to groups 3-12.
- **Transition elements :** The elements of *d*-block are known as transition elements as they posses properties that are transitional between the *s*-block and *p*-block elements. Transition elements are defined as elements which have incompletely filled *d*-orbitals in their ground states or in any of its oxidation state. Transition elements have four series :

(i) First transition series : These elements have incomplete 3*d*-orbitals and they are from Sc (21) to Zn (30).

(ii) Second transition series : These elements have incomplete 4*d*-orbitals and they are from Y (39) to Cd (48).

(iii) Third transition series : These elements have incomplete 5*d*-orbitals and they are La (57) and from Hf (72) to Hg (80).

(iv) Fourth transition series : This series is yet incomplete and these elements have incomplete 6*d*-orbitals. Known elements of this series are–actinium (89) and Rf to ununbium – 112 and three other elements.

3. **General electronic configuration of transition elements :** Valence shell electronic configuration is $(n–1)d^{1–10}$, $ns^{1–2}$, where *n* is the outermost shell.

Electronic configuration of *d*-block elements

Series	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12
3*d* series	Sc (21) $4s^2\,3d^1$	Ti (22) $4s^23d^2$	V (23) $4s^2\,3d^3$	Cr (24) $4s^1\,3d^5$	Mn (25) $4s^23d^5$	Fe (26) $4s^23d^6$	Co (27) $4s^23d^7$	Ni (28) $4s^2\,3d^8$	Cu (29) $4s^13d^{10}$	Zn (30) $4s^2\,3d^{10}$
4*d* series	Y (39) $5s^24d^1$	Zr (40) $5s^24d^2$	Nb (41) $5s^14d^4$	Mo (42) $5s^14d^5$	Tc (43) $5s^24d^5$	Ru (44) $5s^14d^7$	Rh (45) $5s^14d\ ^8$	Pd (46) $5s^04d^{10}$	Ag (47) $5s^14d^{10}$	Cd (48) $5s^24d^{10}$
5*d* series	La (57) $6s^25d'\,4f^0$	Hf (72) $6s^25d^24f^{14}$	Ta (73) $6s^25d^34f^{14}$	W (74) $6s^25d^4\,4f^{14}$	Re (75) $6s^25d^54f^{14}$	Os (76) $6s^25d^64f^{14}$	Ir (77) $6s^25d^74f^{14}$	Pt (78) $6s^15d^94f^{14}$	Au (79) $6s^15d^{10}4f^{14}$	Hg (80) $6s^25d^{10}4f^{14}$
6*d* series	Ac (89) $7s^25f^06d^1$	Rf (104) $7s^25f^{14}6d^2$	Db (105) $7s^25df^{14}6d^3$	Sg (106) $7s^25f^{14}6d^4$	Bh (107) $7s^25f^{14}6d^5$	Hs (108) $7s^25f^{14}6d^6$	Mf (109) $7s^25f^{14}6d^7$	Ds (110) $7s^25f^{14}6d^8$	Rg (111) $7s^15f^{14}6d^{10}$	uub (112) $7s^25f^{14}6d^{10}$

➢ **General characteristics of Transition Elements :**

Physical Properties :

(i) All are metals.

(ii) These are malleable and ductile except mercury which is liquid.

(iii) High thermal and electrical conductivity

(iv) Metallic lustre and sonorous.

(v) Atomic radii : Smaller than those of *s*-block elements, are larger than those of *p*-block elements in a period. In a transition series, as the atomic numbers increases, the atomic radii first decreases till the middle, becomes constant and then increases towards end of the period.

It usually increase down the group. The size of 4*d* elements is almost the same size of the 5*d* series elements. The filling of 4*d* before 5*d* orbitals results in regular decrease in atomic radii is called as lanthanoid contraction.

(vi) Ionic radii : The ionic radii decrease, with increase in oxidation state.

(vii) Density : From left to right in a period, density increases.

(viii) Ionisation enthalpy : Along the series from left to right, there is an increase in ionisation enthalpy. Irreglar trend in the Ist ionisation enthalpy of 3*d* metals is due to irregularity in electronic configuration of 4*s* and 3*d* orbitals. In a group IE decrease from 3*d* to 4*d*-series but increases from 4*d* to 5*d* series due to lanthnoid contraction.

(ix) Metallic bonding : In metallic bonding, regular lattice of positive ions is held together by a cloud of free electrons, which can move freely through the lattice. Transition metal atoms are held together by strong metallic bonds.

(x) Enthalpy of atomisation : Enthalpy of atomisation is the heat required to convert 1 mole of crystal lattice into free atoms. Transition elements have high enthalpy of atomisation. It first increases, becomes maximum in the middle of the series and then decreases regularly.

(xi) Variable oxidation state : Since the energies of *ns* and $(n–1)$ *d* electrons are almost equal, therefore the electrons of both these orbitals take part in the reactions, due to which transition elements show variable oxidation states. Transition metal ions show variable oxidation states except the first and last member of the series.

(xii) Electrode potential : The electrode potential develops on a metal electrode when it is in equilibrium with a solution of its ions, leaving electrons from the electrode. Transition metals have lower value of reduction potential. Variation in E_0 value is irregular due to the regular variation in ionisation enthalpies $(I.E_1 + I.E_2)$, sublimation and hydration enthalpies.

(xiii) Catalytic properties : Many of the transition metals and their compounds, particularly oxides act as catalysts for a number of chemical reactions. Iron, cobalt, nickel, platinum, chromium, manganese and their compounds are commonly used catalysts.

All transitional metals show multiple oxidation states and have large surface area so all metals work as a catalyst.

(xiv) **Magnetic properties :** On the basis of the behaviour of substances in magnetic field, they are of two types : **(i)** Diamagnetic, **(ii)** Paramagnetic.
Diamagnetic substances have paired electrons only. *e.g.,* Zn has only paired electrons.
In paramagnetic substances, it is necessary to have at least one unpaired electron. Paramagnetism increases with the increase in number of unpaired electrons.
Paramagnetism may be measured by magnetic moment.

Magnetic moment $(\mu) = \sqrt{n(n+2)}$ B.M.,

where n = number of unpaired electrons in atom or ion and B.M. = Bohr magneton (unit of magnetic moment) Diamagnetic and paramagnetic substances are repelled and attracted in the magnetic field respe tively (Magnetic properties of transition elements).

(xv) **Melting and boiling points :** Except zinc, cadmium and mercury all other transition elements have high melting and boiling points. This is due to strong metallic bonds and presence of partially filled *d*-orbitals in them.

(xvi) **Complex formation :** They have tendency to form complex ions due to high charge on the transition metal ions and the availability of *d*-orbitals for accommodating electrons donated by the ligand atoms.

(xvii) **Formation of coloured compounds :** Transition metals form coloured ions due to the presence of unpaired *d*-electrons. As a result, light is absorbed in the visible region to cause excitation of unpaired *d*-electrons ($d - d$ transition) and colour observed corresponds to the complementary colour of the light absorbed. Cu^+, Zn^{2+}, Cd^{2+} are colourless due to the absence of unpaired *d*-electron (d^{10}).

(xviii) **Formation of alloys :** Alloy formation is due to almost similar size of the metal ions, their high ionic charges and the availability of *d*-orbitals for bond formation. Therefore these metals can mutually subs tiute their position in their crystal lattice to form alloys. eg. steel, brass.

(xix) **Formation of interstitial compounds :** Interstitial compounds are known for transition metals as small sized atoms of H, B, C, N, etc. can easily occupy positions in the voids present in the crystal lattices of trans tion metals. Characteristics of interstitial compounds :

- High melting points.
- They are very hard.
- Chemically inert.
- Retain metallic conductivity.
- Non-stoichiometric.

➢ **Oxides of Transition metals :** They form oxides of the general composition MO, M_2O_3, MO_2, M_2O_5 and MO_6. Oxides in the lower oxidation states are generally basic while those in the higher oxidation states are amphoteric or acidic. For example,

+2	+3	+8, +3	+4	+7
MnO	Mn_2O_3	Mn_3O_4	MnO_2	Mn_2O_7
Basis	Amphoteric	Amphoteric	Amphoteric	Acidic

➢ **Potassium Dichromate ($K_2Cr_2O_7$)**

Preparation : It is prepared from chromate ore in the following steps :

(i) Chromate ore is fused with sodium carbonate in the presence of air to give sodium chromate.

$$2\,FeCr_2O_4 + 4Na_2CO_3 + 7/2O_2 \rightarrow Fe_2O_3 + \underset{\text{Sodium chromate}}{4Na_2CrO_4} + 4CO_2$$

(ii) Na_2CrO_4 is filtered and acidified with conc. H_2SO_4 to give $Na_2Cr_2O_7$.

$$Na_2CrO_4 + 2H_2SO_4 \rightarrow Na_2Cr_2O_7 + 2Na_2SO_4 + H_2O.$$

(iii) Sodium dichromate solution is treated with KCl to give $K_2Cr_2O_7$.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Properties :

(a) It is an orange, crystalline solid.

(b) With alkali :

$$Cr_2O_7^{2-} + 2OH^- \rightarrow \underset{\substack{\text{Chromate ion} \\ \text{(Yellow)}}}{2CrO_4^{2-}} + H_2O$$

(c) With acid :

$$Cr_2O_7^{2-} + 2H^+ \rightarrow \underset{\substack{\text{Dichromate ion} \\ \text{(orange red)}}}{Cr_2O_7^{2-}} + H_2O$$

(d) It is a powerful oxidising agent. For example,

(i) It oxidises ferrous to ferric.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$[Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 6$$

$$\overline{Cr_2O_7^{2-} + 6Fe^{2+}\ 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}$$

(ii) It oxidises stannous to stannic.

$$\begin{array}{r}
Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\
[Sn^{2+} \rightarrow Sn^{4+} + 2e^-] \times 3 \\
\hline
Cr_2O_7^{2-} + 3Sn^{2+}\ 14H^+ \rightarrow 2Cr^{3+} + 7H_2O \\
\hline
\end{array}$$

(iii) It oxidises sulphur dioxide to sulphuric acid.

$$\begin{array}{r}
Cr_2O_7^{2-} + 14H^+ t\,6e^- \rightarrow 2Cr^{3+} + 7H_2O \\
[SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-] \times 3 \\
\hline
Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O \\
\hline
\end{array}$$

(iv) It oxidises hydrogen sulphide to sulphur.

$$\begin{array}{r}
Cr_2O_7^{2-} + 14H + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\
[H_2S \rightarrow 2H^+ + S + 2e^-] \times 3 \\
\hline
Cr_2O_7^{2-} + 3H_2S + H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O \\
\hline
\end{array}$$

(v) It oxidises iodides to iodine.

$$\begin{array}{r}
Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\
[2I^- \rightarrow I_2 + 2e^-] \times 3 \\
\hline
Cr_2O_7^{2-} + I^- + 14H+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O \\
\hline
\end{array}$$

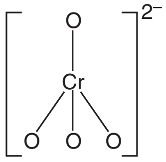
Uses :

(i) In leather industry for chrome tanning.

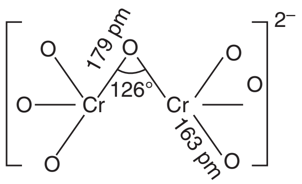
(ii) Preparation of azo compounds.

(iii) As a primary standard in volumetric analysis for the estimation of reducing agent.

Structure :



Chromate ion



Dichromate ion

➢ **Potassium permanganate ($KMnO_4$)**

Preparation :

(i) It is prepared from pyrolusite are with KOH in the presence of oxidising agent like KNO_3. The dark green potassium manganate undergoes electrolytic oxidation to produce potassium permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

(ii) Commercially, it is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of maganate (VI).

$$MnO_2 + 2e^- \xrightarrow[\text{Oxidised with air/KNO}_3]{\text{Fused with KOH}} MnO_4^{2-}$$

Manganate ion

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} MnO_4^- + 1e^-$$

Permanganate ion

(iii) In laboratory, by oxidation of manganese (II) ion salt by peroxodisulphate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Peroxodisulphate

Properties :

(i) Dark purple crystalline solid.

(ii) Sparingly soluble in water.

(iii) Decomposes on heating at 513 K.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

(iv) Acts as a powerful oxidising agent in acidic, alkaline and neutral medium. For Example :

1. **In acidic medium oxidises :**

(i) Iodide to iodine

$$\begin{array}{rl}
[MnO_4^- + 8H^+ + 5e^- & \rightarrow Mn^{2+} + 4H_2O] \times 2 \\
[2I^- & \rightarrow I_2 + 2e^-] \times 5 \\
\hline
2MnO_4^- + 10I^- + 16\,H^+ & \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O \\
\hline
\end{array}$$

(ii) Ferrous to ferric

$$\begin{array}{rl}
MnO_4^- + 8H^+ + 5e^- & \rightarrow Mn^{2+} + 4H_2O \\
[Fe^{2+*} & \rightarrow Fe^{3+} + e^-] \times 5 \\
\hline
MnO_4^- + 5Fe^2 + 8H^+ & \rightarrow Mn^{2+} + 5\,Fe^{3+} + 4H_2O \\
\hline
\end{array}$$

(iii) Oxalate to carbon dioxide :

$$\begin{array}{rl}
[MnO_4^- + 8H + 5e^- & \rightarrow Mn^{2+} + 4H_2O] \times 2 \\
[C_2O_4^{2-} & \rightarrow 2CO_2 + 2e^-] \times 5 \\
\hline
2MnO_4^- + 5C_2O_4^{2-} + 16H^+ & \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \\
\hline
\end{array}$$

(iv) Hydrogen sulphide to sulphur

$$\begin{array}{rl}
[MnO_4^- + 8H^+ + 5e^- & \rightarrow Mn^{2+} + 4H_2O\,] \times 2 \\
[S^{2-} & \rightarrow S + 2e^-] \times 5 \\
\hline
2MnO_4^- + 5S^{2-} + 16H^+ & \rightarrow 2Mn^{2+} + 5S + 8H_2O \\
\hline
\end{array}$$

(v) Sulphite to sulphate

$$\begin{array}{rl}
[MnO_4^- + 8H^+ + 5e^- & \rightarrow Mn^{2+} + 4H_2O] \times 2 \\
[SO_3^{2-} + H_2O & \rightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5 \\
\hline
5SO_3^{2-} + 2MnO_4^- + 6H^+ & \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O \\
\hline
\end{array}$$

(vi) Nitrite to nitrate

$$\begin{array}{rl}
[MnO_4^- + 8H^+ + 5e^- & \rightarrow Mn^{2+} + 4H_2O] \times 2 \\
[NO_2^- + H_2O & \rightarrow NO_3^- + 2H^+\ 2e^-] \times 5 \\
\hline
2\,MnO_4^- + 5NO_2^- + 6H^+ & \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O \\
\hline
\end{array}$$

2. In neutral alkaline medium :

(i) Iodide to iodate

$$\begin{array}{rl}
[MnO_4^- + 2H_2O + 3e^- & \rightarrow MnO_2 + 4OH^-] \times 2 \\
I^- + 6OH^- & \rightarrow IO_3^- + 3H_2O + 6e^- \\
\hline
2\,MnO_4^- + I^- + H_2O & \rightarrow IO_3^- + 2MnO_2 + 2OH^- \\
\hline
\end{array}$$

(ii) Manganous to manganese dioxide

$$3Mn^{2+} + 12OH^- \rightarrow 3MnO_2 + 6H_2O + 6e^-$$

Uses :

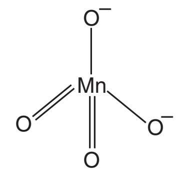
(i) Bleaching of silk, cotton etc.

(ii) Decolourisation of oils.

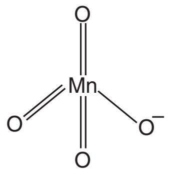
(iii) In analytical chemistry (titration)

(iv) In organic synthesis.

Structure :



Tetrahedral manganate ion (Green)



Tetrahedral permanganate ion (Purple)

Know the Terms

- **Oxidation state :** The measure of the electronic state of an atom in a particular compound, equal to the number of electron it has, more than or less than the number of electrons in free atom.
- **Ferromagnetic substances :** Substances which are attracted very strongly by the applied magnetic field. *e.g.,* Fe, Co, Ni etc.
- **Alloy :** A mixture of two elements, one of which is a metal. For example, brass (Cu + Zn), bronze (Cu + Sn).

TOPIC-2

f-Block Elements: Lanthanoids and Actinoids

Quick Review

- ***f*-block elements :** The elements in which filling of electrons takes place in (n–2) f - subshell which belongs to anti-penultimate (third to the outermost) energy shell. This block consists of two series of elements known as **Lanthanoids and Actinoids.** These elements also known as inner transition elements. The general electronic configuration of the f - block elements is

  $$(n-2)\,f^{1-14}\,(n-1)\,d^{0-1}\,ns^2$$

  For Lanthanoids, n is 6 while its value is 7 for Actinoids. There are many exceptions in the electronic configuration.
- **Lanthanoids :** The series involving the filling of 4f-orbitals following lanthanum La (Z = 57) is called the lanthanoid series. There are 14 elements in this series starting with Ce (Z = 58) to Lu (Z = 71).
  - **Electronic configuration :** [Xe] $4f^{1\text{-}14}\,5d^{0\text{-}1}\,6s^2$
  - **Physical properties :**

    (i) Highly dense metals, soft, malleable and ductile.

    (ii) High melting point.

    (iii) Form alloys easily with other metals.

    (iv) **Magnetic Properties :** Among lanthanoids, La^{3+} and Lu^{3+} which have $4f^0$ or $4f^{14}$ electronic configurations are diamagnetic and all other trivalent lanthanoid ions are paramagnetic due to presence of unpaired electrons.

    (v) **Atomic and ionic sizes :** With increasing atomic number, the atomic and ionic radii decreases from one element to the other but the decrease is very small.

    A steady decrease in the size of lanthanoids with increase in atomic number is known as **lanthanoid contraction.**

    Consequences of Lanthanoid contraction :

    (a) It leads to similar physical and chemical properties among lanthanoids.

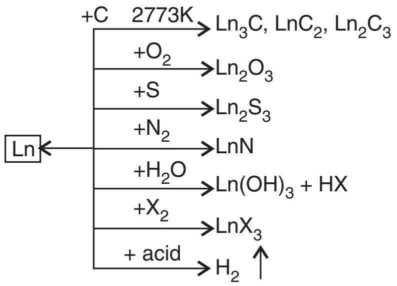
    (b) Zr and Hf have same properties, due to similar atomic radii.

    (c) Chemical separation of lanthanoids become difficult.

    (vi) **Oxidation state :** They mainly give + 3 oxidation state. Some elements show + 2 and + 4 oxidation states.

    (vii) **Colour :** Some of the trivalent ions are coloured. This happens due to the absorption in visible region of the spectrum resulting in f-f transitions.

    Chemical properties : All lanthanoids are highly electropositive metals and have almost similar chemical reactivity.



Uses :

(i) Misch-metals in the alloy of cerium (about 25%) and various other Lanthanoid elements. It contains iron upto 5% and traces of sulphur, carbon, silicon calcium and aluminium. It is a pyrophoric material, hence it is used in lighter flints.

(ii) Lanthanoid oxides are used for polishing glass.

(iii) Cerium salts are used in dyeing cotton and also as catalysts.

(iv) Lanthanoid compounds are used as catalyst for hydrogenated dehydrogenation and petroleum cracking.

(v) Pyrophoric alloys are used for making tracer bullets and shells.

- **Actinoids :** The series involving the filling of 5f orbitals from actinium, Ac (Z = 89) up to lawrencium, Lr (Z = 103) comprises of actinoids.
  - **Electronic configuration :** [Rn] $5f^{1\text{-}14}\,6d^{0\text{-}1}\,7s^2$
  - **Physical properties :**

    (i) Highly dense metals and form alloys with other metals.

(ii) Silvery white metals.
(iii) Highly electropositive.
(iv) High melting point.
(v) **Ionic and atomic radii :** The atomic and ionic size decreases with an increase in atomic size due to actinoid contraction. The electrons are added to 5*f* shell resulting in an increase in the nuclear charge causing the shell to shrink inwards. This is known as actinoid contraction.
(vi) **Colour :** Many actinoid ions are coloured.
(vii) **Magnetic properties :** Many actinoid ions are paramagnetic.
(viii) **Oxidation State :** The common oxidation state exhibited is + 3. They also exhibit oxidation state of + 4, + 5, + 6 and + 7.
(ix) Many elements are radioactive.

- **Chemical reactivity :** Less reactive towards acids.
- **Uses :**
  (i) Thorium is used in the treatment of cancer and in incandescent gas mantles.
  (ii) Uranium is used in the glass industry, in medicines and as nuclear fuel.
  (iii) Plutonium is used in atomic reactors and in atomic bombs.

- **Difference between Lanthanoids and Actinoids :**

S. No.	Lanthanoids	Actinoids
(i)	4*f* orbital is progressively filled.	5*f* orbital is progressively filled.
(ii)	+ 3 oxidation state is most common along with + 2 and + 4.	+ 3 oxidation state is most common, but exhibit higher oxidation state of + 4, + 5, + 6, + 7.
(iii)	Except promethium, all are non-radioactive.	All are radioactive.
(iv)	Less tendency of complex formation.	Strong tendency of complex formation.
(v)	Chemically less reactive than actinoids.	More reactive than lanthanoids.

Know the Terms

- **Coinage metals or currency metals :** Copper (Cu), silver (Ag) and gold (Au) present in group-11 are known as coinage metals or currency metals.
- **Transuranic elements :** All the elements beyond uranium known as transuranic or man made elements. These elements do not occur in nature because their half life periods are so short.
- **Occlusion :** It is the adsorption of H_2 by transitions metals such as Pt, Pd, Ni etc.
- **Platinum black :** It is the finely reduced form of platinum in the form of velvety black powder.

Chapter - 9 : Co-ordination Compounds

TOPIC-1

Co-ordination Compounds and their Properties, IUPAC Nomenclature of Mono Nuclear Co-ordination Compounds

Quick Review

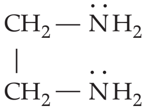
- **Co-ordination Compound :** A co-ordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. There is a co-ordinate bond between metal atom and these ions or molecules, *e.g.*, $[Cu(NH_3)_4]^{2+}$.
- **Double Salt :** When two or more salts are added to form a stable solid together and break into constituent ions when dissolved in water or any solvent salts. *e.g.*, $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt).
- **Properties of double salts :**
  (i) They give simple ions in aqueous solution because they are ionic compounds.
  (ii) They do not contain co-ordinate bonds.
  (iii) They exist only in solid state as double salt.
  (iv) They are soluble in water.

- **Co-ordinate Bonds :** A type of covalent bond in which one of the atoms supplies both the electrons. It can be considered as a combination of transfer and sharing of electrons. Co-ordinate bonds are also called semi polar bonds.
- **Central-metal atom or ion :** The metal atom or ion surrounded by fixed number of ions or molecules is called central metal atom or ion, *e.g.*, in $K_4[Fe\ (CN)_6]$, Fe^{2+} is central metal ion.
- **Ligand :** A ligand is an ion or a small molecule having at least one lone pair of electrons and capable of forming a co-ordinate bond with central atom/ion in the co-ordination entity. *e.g.*, Cl^-, OH^-, CN^-, CO, NH_3, H_2O etc. A ligand may be neutral or charged species. It always act as a lewis base.
  - **Types of ligands :**

  (a) On the basis of number of donor sites :

  (i) Unidentate ligands : Contain one donor atom. *e.g.*, $\ddot{N}H_3, H_2\ddot{O}:$

  (ii) Bidentate ligands : Contain two donor atom. *e.g.*, $(COO^-)_2$,



  (iii) Polydentate ligands : Contain several donor atoms. *e.g.*, EDTA.

  (b) On the basis of charge :

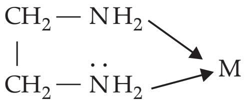
  (i) Cationic ligands : Carry positive charge. *e.g.*, NO_2^+, $N_2H_5^+$.

  (ii) Anionic ligands : Carry negative charge. *e.g.*, X^-(halo), CN^-(cyano).

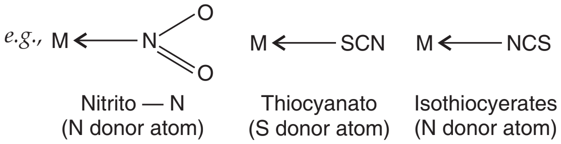
  (iii) Neutral ligands : Do not carry any charge. *e.g.*, $\ddot{N}H_3$ (amine), $H_2\ddot{O}:$ (aqua).

  (c) On the basis of charge :

  (i) Chelating ligands : A bidentate or polydentate uses its two or more donor atoms to bind a single metal ion, then a ring like structure is obtained. It is called chelate and the ligand is known as chelating ligand. *e.g.*,



  (ii) Ambidentate ligand : A ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal/ion is called ambidentate ligand.



- **Co-ordination Number :** Number of monodentate ligands attached to central metal ion in a complex is called co-ordination number. It may also be defined as total number of chemical bonds formed between central metal ion and donor atom of ligand *e.g.*, in $[Ni(NH_3)_6]^{2+}$, the coordination number of Ni^{2+} is 6.
- **Co-ordination Polyhedron :** The spatial arrangement of the ligand atoms which are directly attached to the central atoms or ions define a co-ordination polyhedron about the central atom *e.g.*, $[Pt\ Cl_4]^{2-}$ is square planar.
- **Charge on the complex ion :** The charge on the complex ion is equal to the algebric sum of the charges on all the ligands co-ordinated to the central metal ion.
- **Donor atom :** An atom in the Lewis base that forms the bond with the central atom / ion is called donor atom because it donates the pair of electrons.
- **Denticity :** The number of ligating groups or coordinating atoms in a ligand is called denticity *e.g.*, unidentate, didentate etc.
- **Applications of chelates :**

  (i) In the softening of hard water.

  (ii) In the separation of lanthanoids and actinoids.

  (iii) In the detection as well as estimation of some metal ions such as nickel (II) ion.
- **Co-ordination sphere :** The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as co-ordination sphere *e.g.*, in the complex $K_4[Fe(CN)_6]$, the co-ordination sphere is $[Fe(CN)_6]^{4-}$.
- **Flexidentate character of ligands :** Certain polydentate ligands have flexible character and are called flexidentates. *e.g.*, EDTA is hexadentate in nature but in some cases, it may act as pentadentate or tetradentate ligand.
- **Oxidation number of central atom :** It is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. It is represented by Roman numerical.
- **Homoleptic and Heteroleptic complexes :** Complexes in which the metal atom or ion is linked to only one type of ligands are called homoleptic complexes *e.g.*, $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$ etc. The complexes in which the metal atom or ion is linked to more than one kind of ligands are called heteroleptic complexes. *e.g.*, $[Co(NH_4)Cl_2]^+$ and $[Cr(en)_2Cl_2]^+$ etc.

- **Homonuclear and Polynuclear complexes :** Complexes in which only one metal atom is present are known as homonuclear complexes. *e.g.* $[Co(NH_3)_6]Cl_3$ and $[Cu(NH_3)_4]SO_4$. Complexes in which more than one metal atom is present are known as polynuclear complexes.
- **Counter ions :** The ions which are not included in the primary co-ordination sphere are known as counter ions. *e.g.*, in $K_4[Fe(CN)_6]$, K^+ ions are counter ions.
- **Coordination ions :** The coordination entity with charge is called as coordination ion.
- **Nomenclature of coordination compounds :**
  (i) The cation whether simple or complex is named first followed by anion.
  (ii) Ligands are named in alphabetical order.
  (iii) For indicating the number of each kind of ligand within the coordination entity, two kinds of numerical prefixes are used (di, tri, tetra etc.) For ligands containing any of these prefixes in their names, their numbers are indicated by prefixes bis, tris, tetrakis etc. Anionic ligands end in —O. Neutral retain their names while cationic end in -ium.
  (iv) The coordination sphere is written in square bracket.
  (v) In naming, ligands are named first in alphabetical order followed by metal atom and then the oxidation state of metal by a Roman numeral in parentheses.
  (vi) Name of coordination compounds starts with a small letter and the complex part is written as one word.
  (vii) Oxidation number of central atom is indicated in roman numerals. No space is left between the number and the rest of the name.
- **Isomers :** The compounds having same molecular formula but different structural formulae are known as isomers. *e.g.*, C_2H_6O can represent C_2H_5OH and CH_3OCH_3, which are isomers and this phenomenon is known as isomerism.
- **Types of isomerism :** Two types of isomerism observed in co-ordination compounds are :
  - **Structural isomerism is of following types :**

  (i) Ionisation isomerism : In this type of isomerism isomers have same molecular formula but gives different ions in solution. *e.g.*, $[Co(NH_3)_5Cl]^{2+}\ SO_4^{2-}$ and $[Co(NH_3)_5SO_4]^+\ Cl^-$.

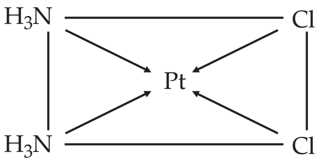
  (ii) Co-ordination isomerism : This type of isomerism is shown by those complexes in which both the cation and the anion are complex ions and they differ in the co-ordination of ligands. *e.g.*, $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6]\ [Co(C_2O_4)_3]$.

  (iii) Hydration isomerism : Isomers having the same molecular formula but different water molecules of hydration. *e.g.*, $[Cr(H_2O)_5Cl]Cl.H_2O$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

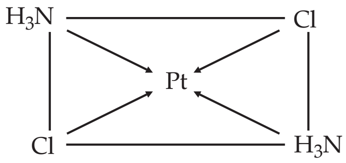
  (iv) Linkage isomerism : Isomers having the same molecular formula but different linking atom, this is due to the presence of ambident ligands. *e.g.*, $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$.

  - **Stereo isomerism is of following types :**

  (i) Geometrical isomerism or *cis-trans* isomerism : In tetra co-ordinated square planar complexes, the cis-isomer has the same groups on the same side whereas trans-isomer has same groups on opposite sides *e.g.*,

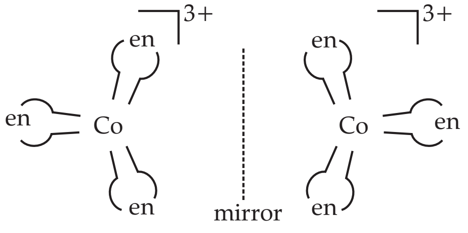


cis-diammine dichloro platinum (II)



trans-diammine dichloro platinum (II)

  (ii) Optical isomerism : Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral.* The two forms are called *dextro (d)* and *laevo (l)* depending upon the direction in which they rotate the plane of polarised light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving didentate ligands.



dextro　　laevo

Optical isomers (*d* and *l*) of $[Co(en)_3]^{3+}$

Know the Terms

- **Co-ordination Chemistry :** The study of the co-ordination compounds is known as co-ordination chemistry.
- **Labile Complex :** A complex in which ligand substitution is fast.
- **Inert Complex :** A complex in which ligand substitution is slow.
- **Synergic Bonding :** A ligand donates a pair of electrons to the metal atom or ion and then accepts a pair of electrons back in its vacant orbital also from *d*-orbitals of the metal or ion. This is called synergic bonding and the ligands involved are known as π-donor ligands.
- **Effective Atomic Number (EAN) :** It can be calculated for the metal atom or ion in the co-ordination complex by using following relation :

  EAN = Atomic no. (Z) of metal atom – Oxidation no + 2CN. where, C.N. is co-ordination number.
- **Facial or fac isomer :** When three ligands with donor atoms are on the same triangular face of the octahedron, the geometrical isomer is known as facial or fac isomer.
- **Meridional or mer isomer :** When three ligands with donor atoms are on the same equatorial plane of the octahedron or around the meridian of the octahedron, the isomer is called meridional or mer isomer.
- **Perfect or penetrating complexes :** These are the complexes in which complex ion is fairly stable and either completely or feebly dissociates in solution.
- **Imperfect or abnormal complexes :** These are the complexes in which the complex ion is less stable and is dissociated reversibly to give enough simple ions.

TOPIC-2

Werner's Theory Bonding in Co-ordination Compound, VBT, CFT and Importance of Co-ordination Compounds

Quick Review

- **Werner's Theory of Coordination Compounds :**

  Werner was able to explain the nature of bonding in complexes. The brief outlines of Werner's theory are as : metal shows two different kinds of valencies.
  - **(i)** Primary valency
  - **(ii)** Secondary valency.

  (i) Primary valencies are satisfied by anions and equal to the oxidation state of the metal.

  (ii) Secondary valencies are satisfied either by oppositely charged ions or neutral molecules and sometimes by cationic groups. Secondary valencies are equivalent to coordination number and they are directed in space in specific number around each central metal atom within the lattice.
- **Limitation of Werner's theory :** This theory does not explain the following queries—
  - **(i)** Why is the complex forming tendency limited to a few elements only ?
  - **(ii)** Why bonds in the co-ordination complexes are of directional nature ?
  - **(iii)** Why are certain complexes of magnetic nature and show geometrical and optical isomerism ?
- **Valence Bond theory :** It was developed by Pauling. The brief points are :
  - **(i)** A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of co ordinate bond with the ligands.
  - **(ii)** Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon tota number of ligands.
  - **(iii)** The hybridised orbitals are allowed to overlap with those ligands orbitals that can donate an electron pair for bonding.
  - **(iv)** The outer orbitals (high spin) or inner orbitals (low spin) complexes are formed depending upon whethe outer *d*-orbitals or inner *d*-orbitals are used.
- **Limitation of valence bond theory :** It fails to explain following facts about the co-ordination compounds :
  - **(i)** It cannot explain the detailed magnetic properties of complex compounds.
  - **(ii)** It cannot explain the optical absorption spectra of co-ordination compounds.
  - **(iii)** It cannot predict property whether a particular 4 co-ordinate complex is square planar or tetrahedral in nature.
  - **(iv)** It fails to make distinction between strong and weak ligands.
  - **(v)** It does not explain thermodynamic or kinetic stabilities of coordination compounds.
- **Crystal field theory (CFT) :**
  - **(i)** According to crystal field theory ligands are point charges.
  - **(ii)** On approaching ligands, *d*-orbitals of metal ion gets split.
  - **(iii)** e_g orbitals have higher energy in octahedral and lower energy in tetrahedral complexes.

(iv) t_{2g} orbitals have high energy in tetrahedral and complexes.

(v) Some ligands are able to produce strong fields in which case, the splitting will be large whereas others pro duce weak fields and consequently result in small splitting of *d*-orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below and called as spectrochemical series :

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$$

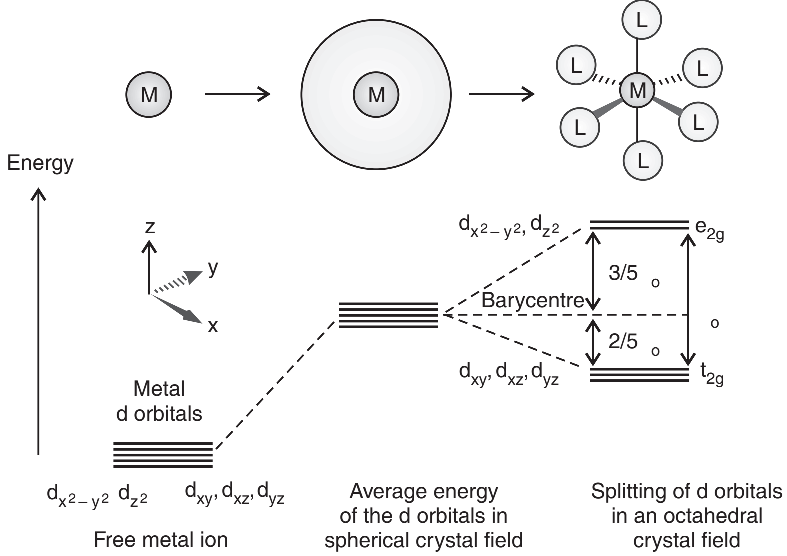


Fig. 1 : d orbital splitting in an octahedral crystal field

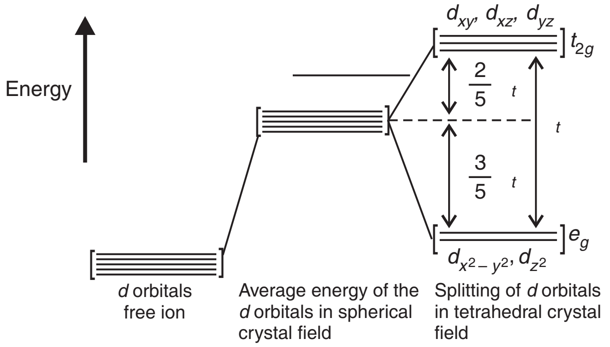
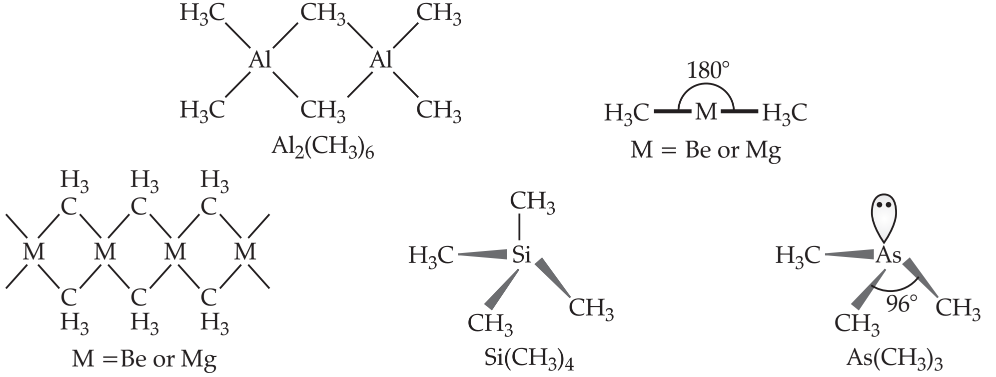


Fig. 2 : d orbital splitting in a tetrahedral crystal field

(vi) Explanation of colour and magnetic behaviour in complexes is possible by crystal field theory.

- **Classification of organometallic compounds :** The broad divisions of organometallic compounds are :

(i) Main group organometallics : The *s*-and *p*-block organometallics are called main group organometallics, *e.g.*,
$(CH_3)_4$ Sn, Tetramethyl stannane
$Si(CH_3)_4$ Tetramethyl silane
$B(CH_3)_3$ Trimethly borane
$As(CH_3)_3$ Trimethyl arsene
The structure of some representative main group organometallics are shown below :



$Al_2(CH_3)_6$ M = Be or Mg

M =Be or Mg $Si(CH_3)_4$ $As(CH_3)_3$

Structure of some representative main group organometallic compounds

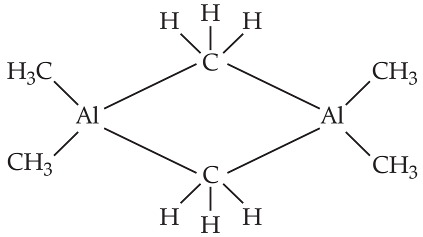
(ii) *d*-and *f*-block organometallics : The organometallics formed by *d* and *f*-block elements are called *d*-and *f* block organometallics, *e.g.*, $[PtCl_3(C_2H_4)^-]$, $[Ni(CO)_4]$, $(C_5H_5)_2Fe$. The first *f*-block organometallic compound,

$[ThH(OR)(C_5Me_5)_2]$ was prepared in late 1970s. Pentamethyl cyclopentadienyl ligand (C_5Me_5) forms stable *f*-block compounds.

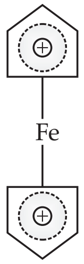
- **Metal carbonyls :** Homoleptic carbonyls are formed by *d*-block elements and contain carbonyl ligands only. *e.g.*, $V(CO)_6$, $Cr(CO)_6$, $[Mo(CO)_6]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Co_2(CO_8)]$, $[Co_4(CO)_{12}]$, $[Ni(CO)_4]$, etc. Metal carbonyls of outside the central part of *d*-block are unstable.

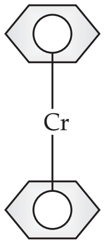
  Properties of metal carbonyls :

  (i) Metal carbonyls are mostly solids at room temperature and pressure. Exceptions being iron and nickel cabonyls which are liquids.
  (ii) The mononuclear carbonyls are volatile and toxic.
  (iii) Most of metal carbonyls are soluble in hydrocarbon solvents except $[Fe_2(CO)_9]$.
  (iv) Mononuclear carbonyls are either colourless or light coloured.
  (v) They are highly reactive due to metal centre and the CO ligands.
  (vi) Metal carbonyls are used as industrial catalyst and as precursor in organic synthesis.

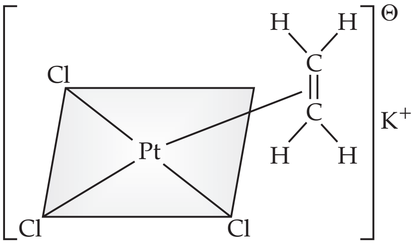


Dimer of trimethyl aluminium





$Cr(\eta_6–C_6H_6)_2$
Dibenzene chromium



$K[PtCl_3\text{-}n_2(C_2H_4)]$
Ziese's Salt
Potassium trichloroethy lene platinate (H)

- **Bonding in π-bonded complex :** It also involves both σ- and π-bond. σ-bond is formed by overlapping of π-electrons of alkene with vacant *d*-orbitals of transition metal. π-bond is formed by back donation of pair of electrons from *d*-orbital of transition metal to vacant antibonding orbital of carbon of alkene.
- **Bonding in metal carbonyls :** It also involves both σ- and π-bond. σ-bond is formed by overlapping of lone pair on CO to the vacant *d*-orbitals of metal whereas π-bond is formed by back donation of pair of *d*-electrons to vacant anitbonding orbital of carbonyl.
- **Factors affecting the stability of complexes :**

  (i) **Nature of the central ion :** Greater the charge density on the central metal ion, greater is the stability of the complex.
  (ii) **Nature of the ligand :** More basic ligands have a tendency to donate the electron pairs to central metal ion more easily resulting in a stable complex.
  (iii) **Chelate effect :** Entropy increases when chelation occurs and so the formation of the complex becomes more favourable.
- **Application of complex compounds :**

  (i) They are used in photography, *i.e.*, AgBr forms soluble complex with sodium thiosulphate in photography.
  (ii) $K[Ag(CN)_2]$ is used for electroplating of silver, $K[Au(CN)_2]$ is used for gold plating.
  (iii) Some of ligands oxidise Co^{2+} to Co^{3+} ion.
  (iv) EDTA is used for estimation of Ca^{2+} and Mg^{2+} in hard water.
  (v) Silver and gold are extracted by treating Zn with their cyanide complexes.
  (vi) Ni^{2+} is tested and estimated by DMG (dimethyl glyoxime).
  (vii) Cis-platin $[Pt(NH_3)_2Cl_2]$ is used as antitumor agent in treatment of cancer.
  (viii) EDTA is used to remove Pb by forming Pb-EDTA complex which is eliminated in urine.
  (ix) Haemoglobin contains Fe, chlorophyll contains (Mg) and vitamin B_{12} contain Co^{2+}.
  (x) Bauxite is purified by forming complex with NaOH.
  (xi) Coordination compounds are used as catalysts for many industrial processes.

Know the Terms

- **Homogeneous Catalysis :** Organometallic compounds or intermediates derived from soluble transition metal complexes catalyse a variety of reaction in solutions. This is known as homogeneous catalysis.
- **Macrocyclic effect :** Multidentate ligands happen to be cyclic in nature without causing any steric hindrance, the stability of the complexes is further increased. This is known as macrocyclic effect.
- **Stability constants (K) :** The relative stabilities of co-ordination complexes can be compared in terms of stability constant (K) also denoted by β (Beta).
- **Metal carbonyl :** Organometallic compounds in which carbon monoxide acts as the ligand.

❑❑

Chapter - 10 : Haloalkanes and Haloarenes

TOPIC-1

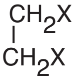
Haloalkanes and their Properties

Quick Review

- Hydrogen atom in aliphatic hydrocarbon replaced by halogen are called haloalkanes, while in benzene ring are called haloarenes.
- In haloalkane, halogen is attached with carbon through sp^3 hybridisation while in haloarenes it is attached with sp^2 hybridisation.
- **Classification :**
  - **On the basis of the number of halogen atom :** These may be classified as mono, di or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,

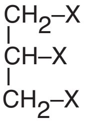
C_2H_5X

Monohaloalkane



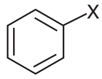
CH_2X-CH_2X

Dihaloalkane

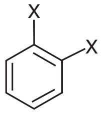


$CH_2X-CHX-CH_2X$

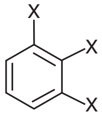
Trihaloalkane



Monohaloarene



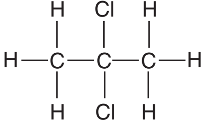
Dihaloarene



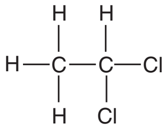
Trihaloarene

Dihalogen compounds may be further classified as :

(i) Geminal dihalides : Two hydrogen atoms are attached to the same carbon atom. For example,



Isopropylidene chloride
(2, 2–Dichloropropane)

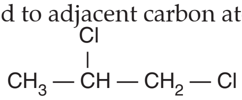


Ethylidene chloride
(1, 1–Dichloroethane)

(ii) Vicinal dihalides : Two halogen atoms are attached to adjacent carbon atoms. For example,

$Cl-CH_2-CH_2-Cl$

Ethylene dichloride
(1, 2-Dichloroethane)

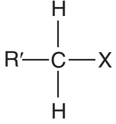


$CH_3-CH(Cl)-CH_2-Cl$

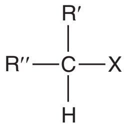
Propylene dichloride
(1, 2-Dichloropropane)

  - **On the basis of sp^3 hybridisation :**

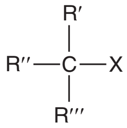
(i) Haloalkanes or alkylhalides (R—X) : General formula is $C_nH_{2n+1}X$. They are further classified as primary, secondary and tertiary haloalkanes.



Primary haloalkane



Secondary haloalkane

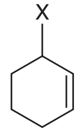


Tertiary haloalkane

(ii) Allylic halides : Halogen is bonded to allylic carbon.

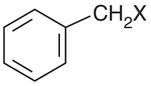
$CH_2 = CH - CH_2 - X$

Allyl halide
(3—Halo–1–propene)

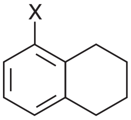


3—Halocylohex–1–ene

(iii) Benzylic halides : Halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.



Benzyl halide

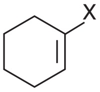


1 – Halo –1, 2, 3, 4
tetrahydro naphthalene

- **On the basis of sp^2 hybridisation :**
  - **(i) Vinylic halides :** Halogen is bonded to one of the carbon atoms of a vinylic carbon.

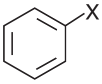
$CH_2 = CH - X$

Vinyl halide



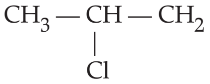
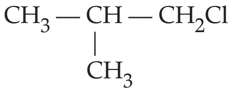
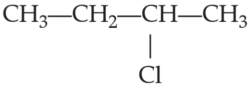
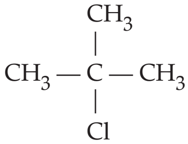
1–Halocylohex–1–ene

  - **(ii) Aryl halides :** Halogen atom is directly bonded to sp^2 hybridised carbon atom of an aromatic ring.

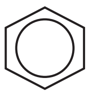


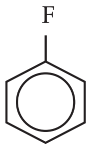
Halobenzene

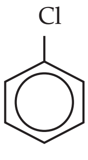
➢ **Common and IUPAC name of some halides :**

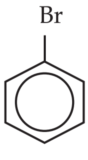
Structure	IUPAC Name	Common names
CH_3Cl	Chloromethane	Methyl chloride
CH_3CH_2Cl	Chloroethane	Ethyl chloride
$CH_3—CH_2—CH_2Cl$	1-Chloropropane	*n*-Propyl chloride
 $CH_3 - \underset{\underset{Cl}{\vert}}{CH} - CH_2$	2-Chloropropane	Isopropyl chloride
$CH_3—CH_2—CH_2—CH_2Cl$	1-Chlorobutane	*n*-Butyl chloride
 $CH_3 - \underset{\underset{CH_3}{\vert}}{CH} - CH_2Cl$	1-Chloro-2-methyl propane	Isobutyl chloride
 $CH_3—CH_2—\underset{\underset{Cl}{\vert}}{CH}—CH_3$	2-Chlorobutane	Sec. butyl chloride
 $CH_3 - \overset{\overset{CH_3}{\vert}}{\underset{\underset{Cl}{\vert}}{C}} - CH_3$	2-Chloro-2-methyl propane	Tertiary butyl chloride
CH_3F	Fluoromethane	Methyl fluoride
CH_3Br	Bromomethane	Methyl bromide
CH_3I	Iodomethane	Methyl iodide
CH_2Cl_2	Dichloromethane	Methylene dichloride
$CHCl_3$	Trichloromethane	Chloroform
CCl_4	Tetrachloromethane	Carbon tetrachloride
$CHBr_3$	Tribromomethane	Bromoform
CHI_3	Triiodomethane	Iodoform
$ClCH_2—CH_2Cl$	1, 2-Dichloroethane	Ethylene dichloride

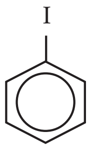
CH_3CHCl_2	1, 1-Dichloroethane	Ethylidene chloride
$CH_2 = CHCl$	Chloroethene	Vinyl chloride
$CH_2 = CH—CH_2Br$	3-Bromopropene	Allyl bromide
$(CH_3)_3CCH_2Br$	1-Bromo-2, 2-dimethylpropane	neo-pentylbromide
$CF_3CF_2CF_3$	Octafluoropropane	Perfluoropropane
CCl_2F_2	Dichlorodifluoromethane	Freon
$CHCl_2—CHCl_2$	1, 1, 2, 2-Tetrachloroethane	Acetylene tetrachloride
$CHCl = CCl_2$	1, 1, 2-Trichloroethene	Acetylene trichloride

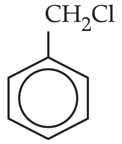
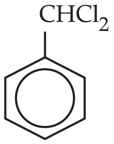
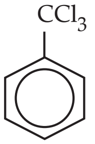
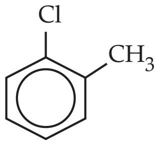

Benzene


Fluorobenzene


Chlorobenzene


Bromobenzene


Iodobenzene

				
IUPAC name	1–Chloro –1–phenylmethane	Dichlorophenyl methane	Trichlorophenyl methane	1–Chloro–2–methyl benzene
Common name	(Benzyl chloride)	(Benzylidene chloride) (Benzal chloride)	(Benzotrichloride)	(2–Chlorotoluene)

➢ **Methods of preparation of Haloalkanes :**

(a) From alcohols : Alkyl halides are prepared from alcohols, which are easily accessible.

$R – OH + HX \xrightarrow{ZnCl_2} R – X + H_2O$ (X = Cl, Br, I)

$R – OH + NaBr + H_2SO_4 \longrightarrow R – Br + NaHSO_4 + H_2O$

$3R – OH + PX_3 \longrightarrow 3R – X + H_3PO_3$ (X = Cl, Br)

$R – OH + PCl_5 \longrightarrow R – Cl + POCl_3 + HCl$

$R – OH \xrightarrow[X_2 = Br_2, I_2]{Red\ P/X_2} R – X$

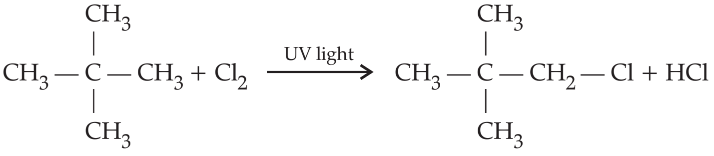
$R – OH + SOCl_2 \longrightarrow R – Cl + SO_2 + HCl$

The reaction of primary and secondary alcohols with HX require the presence of the catalyst $ZnCl_2$.

(b) From hydrocarbons : By free radical halogenation.

$CH_3CH_2CH_2CH_3 \xrightarrow[Or\ heat]{Cl_2/UV\ Light} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

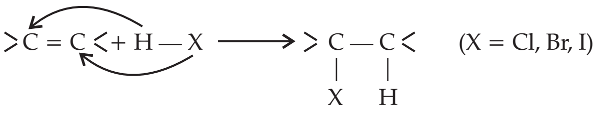
n-Butane *n*-Butyl chloride Sec.-Butyl chloride



$$CH_3 — \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} — CH_3 + Cl_2 \xrightarrow{UV\ light} CH_3 — \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} — CH_2 — Cl + HCl$$

neo-Pentane neo-pentyl chloride

(c) From alkenes : (i) Addition of hydrogen halide :

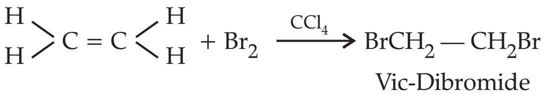


$$>C = C< + H — X \longrightarrow > \underset{\underset{X}{|}}{C} — \underset{\underset{H}{|}}{C} < \quad (X = Cl, Br, I)$$

$$R — CH = CH_2 + \overset{\delta+}{H} — \overset{\delta-}{X} \xrightarrow{Markovnikov's\ Rule} R — \underset{\underset{X}{|}}{CH} — CH_2$$

$R – CH = CH_2 + H – Br \xrightarrow[(Anti\ Markovnikov's\ addition)]{Benzoyl\ peroxide} R – CH_2 – CH_2 – Br$

(ii) Addition of Halogens :



$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2-CH_2Br$

Vic-Dibromide

(d) Halide Exchange : (i) By Finkelstein Reaction :

$R-X + NaI \xrightarrow{\text{Dry acetone}} R-I + NaX \qquad (X = Cl, Br)$

(ii) By Swarts Reaction :

$R-X \xrightarrow{AgF, Hg_2F_2, COF_2 \text{ or } SbF_3} R-F$

$CH_3-Br + AgF \longrightarrow CH_3-F + AgBr$

- **Nature of C-X bond in haloalkanes :** The carbon halogen bond is polarised. Carbon atom holds partial positive charge and halogen atom holds partial negative charge. This occurs due to difference in electronegativity. Halogens are more electronegative than carbon. Size of the halogen atoms increases down the group. Fluorine being the smallest and iodine being the largest. Carbon-halogen bond length also increases from C-F to C-I.
- **Physical properties of haloalkanes :** Haloalkanes are colourless when pure but compounds of bromine are coloured.

(i) Melting and boiling points : Haloalkanes, due to polar and strong dipole-interactions between their molecules, have high B.P. and M.P. This increase in B.P. and M.P. depends on size and mass of halogens, with weak van der Waals forces of attractions. The increasing order is RCl < RBr < RI. With respect to isomeric alkyl halides, B.P. decreases with increase in branching due to less surface area and weak inter-particle forces.

(ii) Density : It increases with increase in carbon atoms and halogen atoms.

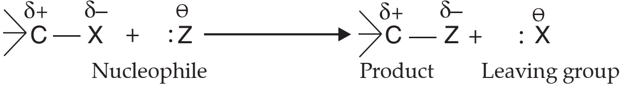
(iii) Solubility : Haloalkanes are insoluble in water but are soluble in organic solvents.

- **Chemical properties of haloalkanes :** Reactivity of haloalkanes, depends on the C-X bond cleavage. Higher the bond dissociation energy of C-X bond, lesser will be the reactivity. Dissociation energy of C-X bond decreases with increase in the halogen size, *i.e.,* C–Cl > C–Br > C–I. Reactivity order of haloalkanes would be :

Chlorides < Bromides < Iodides

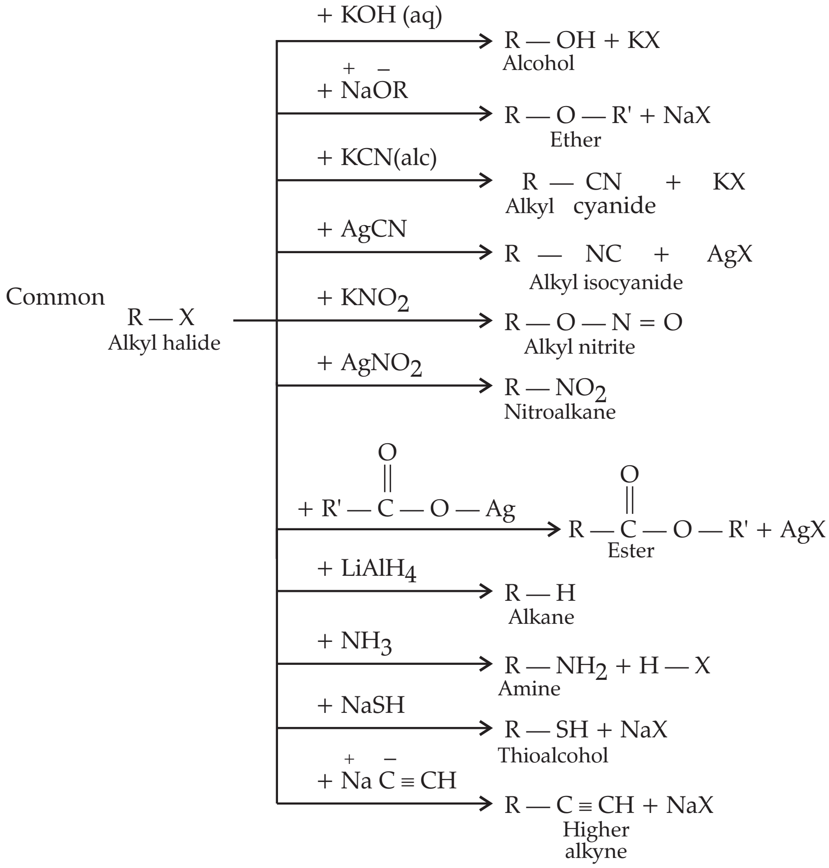
There are four types of chemical reactions with haloalkanes :

(a) Nucleophilic substitution reactions : When an atom or group of atoms is replaced by a *nucleophile,* the reaction is called nucleophilic substitution reaction, *e.g.,*



$\overset{\delta+}{>C}-\overset{\delta-}{X} + :\overset{\ominus}{Z} \longrightarrow \overset{\delta+}{>C}-\overset{\delta-}{Z} + :\overset{\ominus}{X}$

Nucleophile Product Leaving group



Common $R-X$ Alkyl halide

$+ KOH(aq) \longrightarrow R-OH + KX$ Alcohol

$+ \overset{+}{Na}\overset{-}{OR} \longrightarrow R-O-R' + NaX$ Ether

$+ KCN(alc) \longrightarrow R-CN + KX$ Alkyl cyanide

$+ AgCN \longrightarrow R-NC + AgX$ Alkyl isocyanide

$+ KNO_2 \longrightarrow R-O-N=O$ Alkyl nitrite

$+ AgNO_2 \longrightarrow R-NO_2$ Nitroalkane

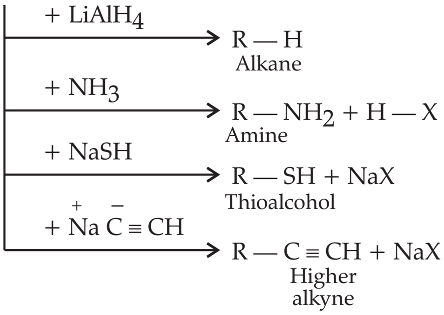
$+ R'-\overset{O}{\overset{\|}{C}}-O-Ag \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-R' + AgX$ Ester

$+ LiAlH_4 \longrightarrow R-H$ Alkane

$+ NH_3 \longrightarrow R-NH_2 + H-X$ Amine

$+ NaSH \longrightarrow R-SH + NaX$ Thioalcohol

$+ \overset{+}{Na}\overset{-}{C}\equiv CH \longrightarrow R-C\equiv CH + NaX$ Higher alkyne

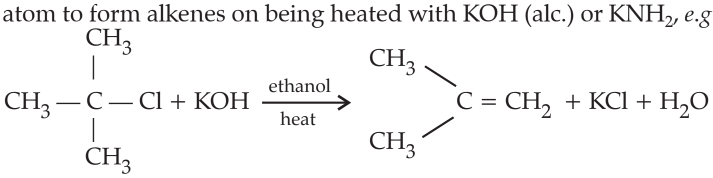


$$\xrightarrow{+ LiAlH_4} R—H \text{ (Alkane)}$$
$$\xrightarrow{+ NH_3} R—NH_2 + H—X \text{ (Amine)}$$
$$\xrightarrow{+ NaSH} R—SH + NaX \text{ (Thioalcohol)}$$
$$\xrightarrow{+ \overset{+}{Na}\overset{-}{C} \equiv CH} R—C \equiv CH + NaX \text{ (Higher alkyne)}$$

Alkyl halides undergo nucleophilic substitution reactions.

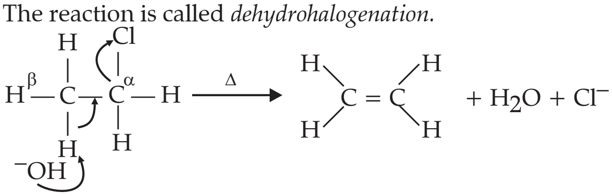
$$CH_3CH_2Br + :\ddot{\underset{..}{O}}H^- \longrightarrow CH_3CH_2OH + :\ddot{\underset{..}{Br}}:^-$$

(b) Elimination Reaction : Alkyl halide undergo β-elimination of hydrogen atom from β-carbon atom and halgen atom to form alkenes on being heated with KOH (alc.) or KNH_2, *e.g.*,



$$(CH_3)_3C—Cl + KOH \xrightarrow[\text{heat}]{\text{ethanol}} (CH_3)_2C = CH_2 + KCl + H_2O$$

The reaction is called *dehydrohalogenation.*



The following is order of reactivity :

$RCl < RBr < RI$

$RCH_2X < R_2CHX < R_3CX$

(c) Reaction with metals : (1) Reaction with magnesium :

$$\underset{\text{Alkyl halide}}{R–X} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Alkyl magnesium halide}\\ \text{(Grignard reagent)}}}{RMgX}$$

$$CH_3 – CH_2 – Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl magnesium bromide}}{CH_3 – CH_2 – MgBr}$$

(2) Reduction with sodium (Wurtz reaction) :

$$R – X + 2Na + X – R \xrightarrow{\text{Dry ether}} R – R + 2NaX$$

$$CH_3 – CH_2 – Cl + 2Na + Cl – CH_2 – CH_3 \xrightarrow{\text{Dry ether}} \underset{n\text{-Butane}}{CH_3 – CH_2 – CH_2 – CH_3} + 2NaCl$$

(d) Reduction :

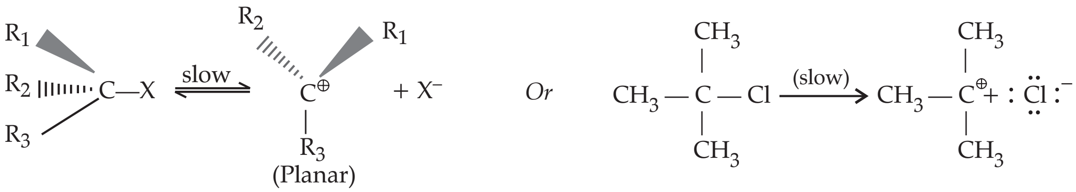
$$R – X + 2(H) \xrightarrow{Zn/HCl(conc.)} R – H + H – X$$

$$CH_3 – CH_2 – Cl + 2(H) \xrightarrow{Zn/HCl(conc.)} CH_3 – CH_3 + HCl$$

- **Mechanism of Nucleophilic substitution reaction :** Alkyl halide undergoes two types of nucleophilic substitution reactions.

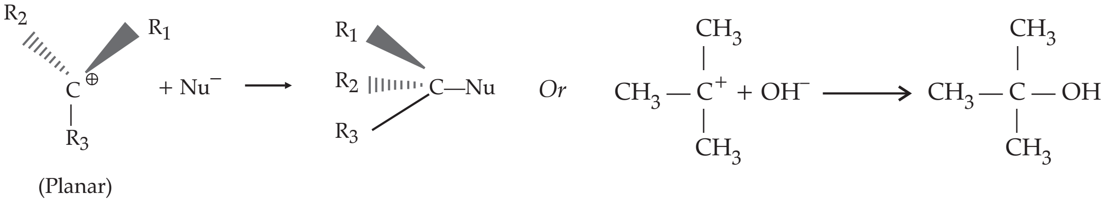
(i) Unimolecular nucleophilic substitution reaction (S_N1) : Those substitution reactions in which rate of reaction depends upon the concentration of only one of the reactants, *i.e.*, alkyl halides are called S_N1 reactions, *e.g.*, h drolysis of tertiary butyl chloride follows S_N1 reaction. This reaction takes place in two steps. The first step involves formation of carbocation.

STEP I :



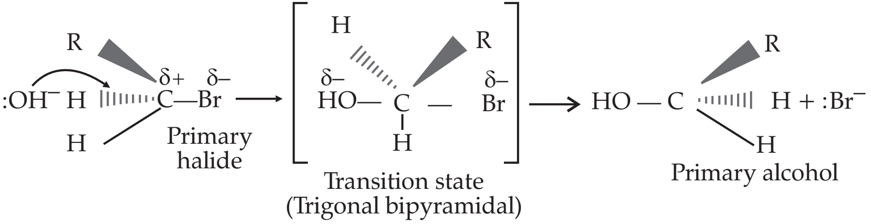
$$(CH_3)_3C—Cl \xrightarrow{\text{(slow)}} (CH_3)_3C^\oplus + :\ddot{\underset{..}{Cl}}:^-$$

STEP II :



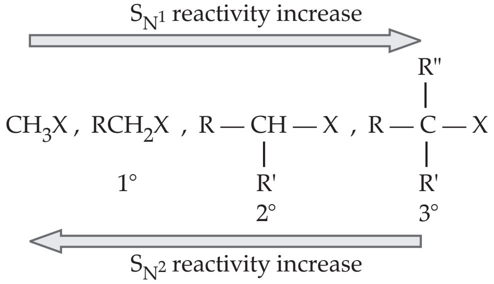
The slowest step is rate determining step which involves one species only. Therefore, rate of reaction depends only on the concentration of tertiary butyl chloride. Tertiary haldies follow S_N^1 mechanism. Polar protic solvents like water, alcohol favour S_N^1 because they stabilize carbocation by solvation. Tertiary halides follow S_N^1 mechanism.

(ii) Biomolecular nucleophilic substitution reaction (S_N^2) : The reaction whose rate depends on the concentration of two species, alkyl halide and nucleophile. They involve one step mechanism: back side attack of nucleophile and departing of leaving group take place simultaneously.



Non-polar solvents favour S_N^2 mechanism. Primary halides follow S_N^2 mechanism.

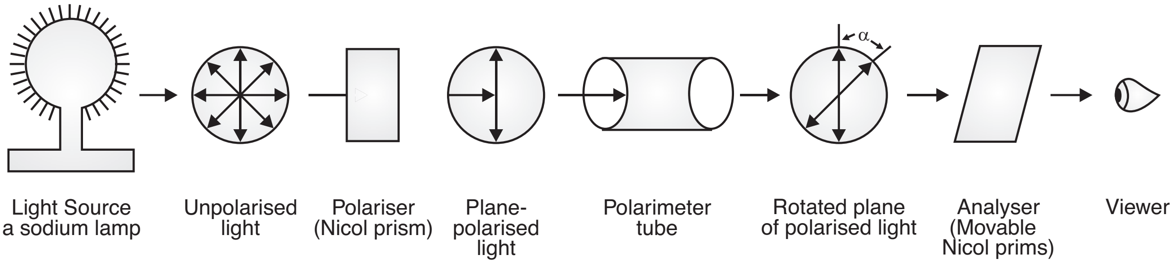
- **Reactivity of S_N^1 and S_N^2 mechanisms :** S = Substitution, N = Nucleophilic, 2 = Bimolecular, 1 = Unimolecular. Nucleophilic substitution seldom occurs exclusively by one mechanism only. With a given halogen, primary, secondary and tertiary halides show opposite order of reactivity in the two mechanisms.



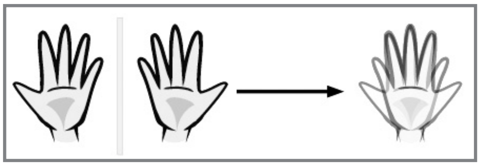
- **Stereoisomerism :** Isomerism exhibited by two or more compounds with the same molecular and structural formula, but different spatial arrangements of atoms or groups in space is called stereoisomerism.
- **Plane-polarised light :** The beam of light whose oscillations or vibrations are confined to one plane only is called plane-polarised light. It is obtained by passing a monochromatic light (light of single wavelength) through a nicol prism.
- **Nicol prism :** A nicol prism is a special type of prism made from calcite, a special crystalline form of calcium carbonate. It is a device for producing plane polarised light.
- **Optical rotation :** Property of rotating the plane of polarisation either towards left or right.
- **Dextrorotatory :** Those substances which rotate the plane of polarisation of light towards right, *i.e.*, in clockwise direction are called dextrorotatory. It is conventionally given a positive sign. It is denoted by '*d*' and positive (+) sign is placed before the degrees of rotation.
- **Laevorotatory :** Those substances which rotate the plane of polarisation of light towards the left, *i.e.*, in anticlockwise direction are called laevorotatory. It is denoted by '*l*' and a negative (–) sign is placed before the degrees of rotation.
- **Specific rotation :** The extent of experimentally observed angle of rotation (optical rotation, represented by α_{obs}) of a substance depends upon the following factors :
  - **(i)** nature of substance,
  - **(ii)** wavelength of the light used,
  - **(iii)** the number of optically active molecules in the path of light beam (which depends upon concentration of sample),
  - **(iv)** length of polarimeter tube,
  - **(v)** solvent used.

$$\text{Specific rotation } [\alpha] = \frac{\text{observed rotation } (\alpha_{obs})}{\text{length of tube } (d_m)} \times \text{concentration of solution (g mol}^{-1})$$

- **Optically active substances :** Those substances which rotate the plane of polarisation of plane-polarised light when it is passed through their solutions are called optically active substances. This phenomenon is called optical activity.
- **Polarimeter :** The angle of rotation by which the plane-polarised light is rotated, can be measured by using an instrument called polarimeter. A schematic diagram of a polarimeter is shown in figure below :

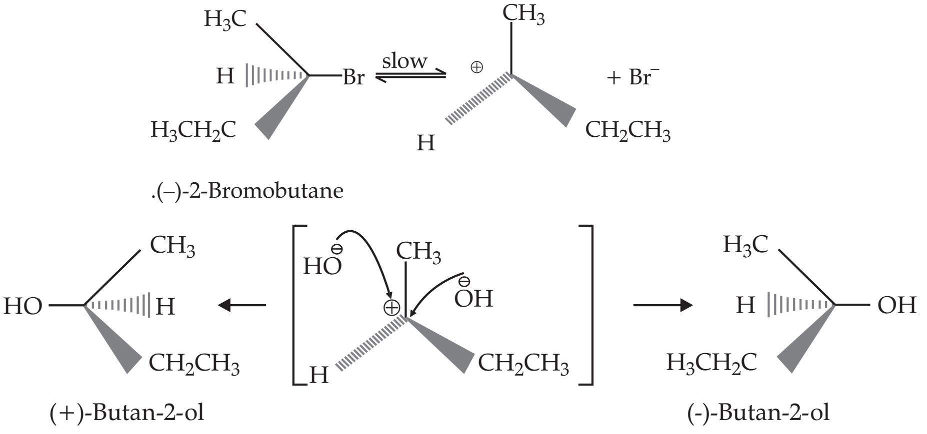


- **Enantiomers :** Those stereoisomers which are mirror images of each other but non-superimposable are called enantiomers, *e.g.*, *d*(+) glucose and *l*(–) glucose are enantiomers.
- **Asymmetric molecule :** If all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.
- **Symmetrical objects :** Those objects whose projections are superimposable on their mirror images are symmetrical objects, *e.g.*, a sphere, a cube, a cone, a tetrahedron are all identical to their mirror images and can thus be superimposed.
- **Chiral :** An object which is non-superimposable on its mirror image is said to be chiral. The property of being chiral is known as chirality. A chiral object is also called dissymmetric. e.*g.*,

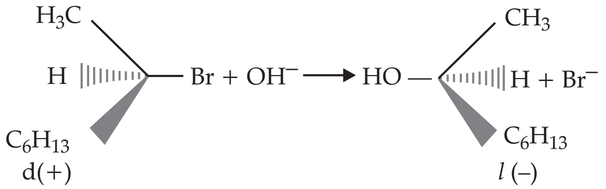


Non-superimposable left hands

- **Achiral :** Achiral objects are those objects which are superimposable on their mirror images.
- **Asymmetric carbon :** The carbon atom which is attached with four different groups of atoms is called asymmetric carbon atom.
- **Racemic mixture :** A mixture containing equal amounts of enantiomers which does not show any optical activity.
- **Racemisation :** The process of conversion of an enantiomer into racemic mixture is known as racemisation.
- **Absolute configuration :** The three dimensional structure of a molecule that has one or more centres of chirality is referred to its absolute configuration.
- **Diastereoisomers :** Those pair of stereo isomers which are not mirror images of each other and are non-superimposable.
  - **(i)** Diastereoisomers have different physical properties.
  - **(ii)** Diastereoisomers differ in magnitude of specific rotation.
  - **(iii)** A compound with two chiral centres does not always have four stereoisomers.
- **Example of racemisation in S_N^1 mechanism :** When optically active alkyl halide undergoes S_N^1 mechanism, it is accompanied by racemisation because intermediate carbocation formed is sp^2-hybridised and polar. Nucleophile (OH^-) has equal probability of attacking it from either side leading to formation of equal amount of dextro and laevo-rotatory alcohols. As the products of S_N^1 mechanism has both inversion as well as rotation the products formed by this reaction would be racemic mixture of alcohols.

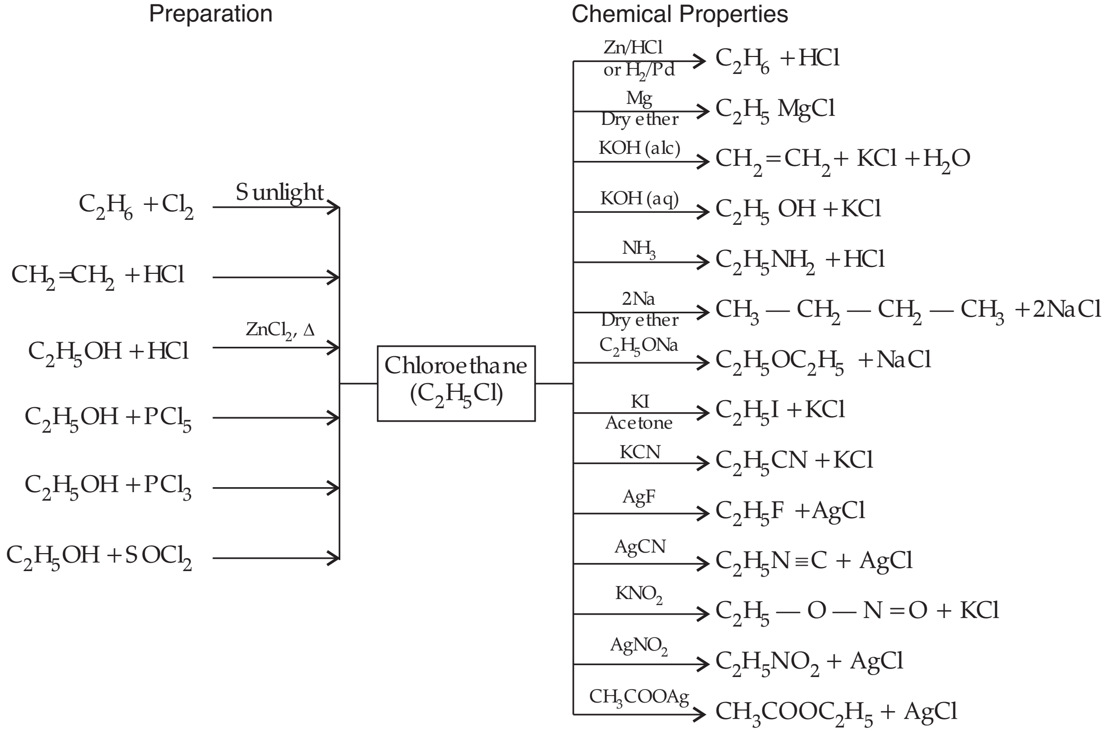


- **Meso compounds :** Those compounds which have two or more (even number) chiral carbon atoms and have an internal plane of symmetry are called meso compounds. They are optically inactive due to internal compensation.
- **Example of inversion in S_N^2 mechanism :** When optically active *d*(+) alkyl halide is treated with OH^-, we get optically active *l* (–) alcohol due to back side attack of nucleophile.



When *d*(+)-2-bromooctane is reacted with NaOH, *l*(–)-2-octanol is formed. Thus S_N^2 mechanism leads to inversion of configuration. This inversion is called Walden's inversion.

- **Important reactions of chloroethane :**

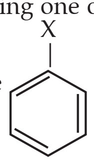


Know the Terms

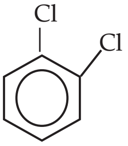
- **Walden Inversion :** S_N^2 mechanism in alkyl halides leads to inversion of configuration known as Walden inversion.
- **Synthetic tools :** Alkyl halides are regarded as synthetic tools in the hands of chemistry due to their highly reactive nature.
- **Relative configuration :** Arrangement of atoms in space of a stereoisomer of a compound relative to another compound chosen as arbitrary standard (like glyceraldehyde).

TOPIC-2
Haloarenes and Polyhalogen Compounds

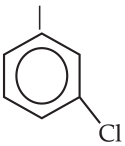
Quick Review

- **Haloarenes :** Haloarenes are the compounds formed by replacing one or more hydrogen atoms in an aromatic ring with halogen atoms. For example, monohalogen derivative  (X = F, Cl, Br, or I).

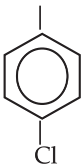
- When two halogens are at 1, 2- positions of benzene ring, it is called ortho substituted derivative. *e.g.*,



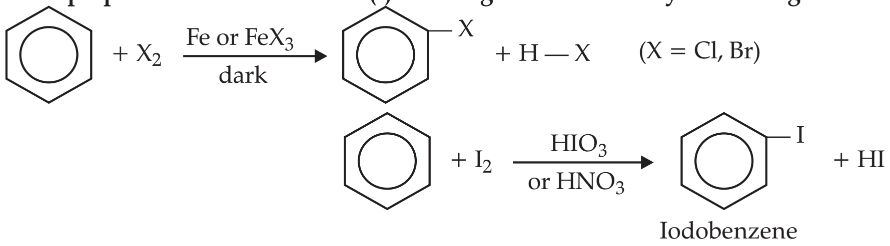
- When two halogens are at 1, 3-positions of benzene ring, it is called meta substituted derivative *e.g.*,



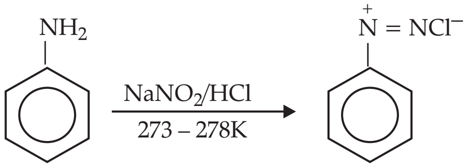
- When two halogens are at 1, 4-positions of benzene ring, it is called para substituted derivative. *e.g.*,



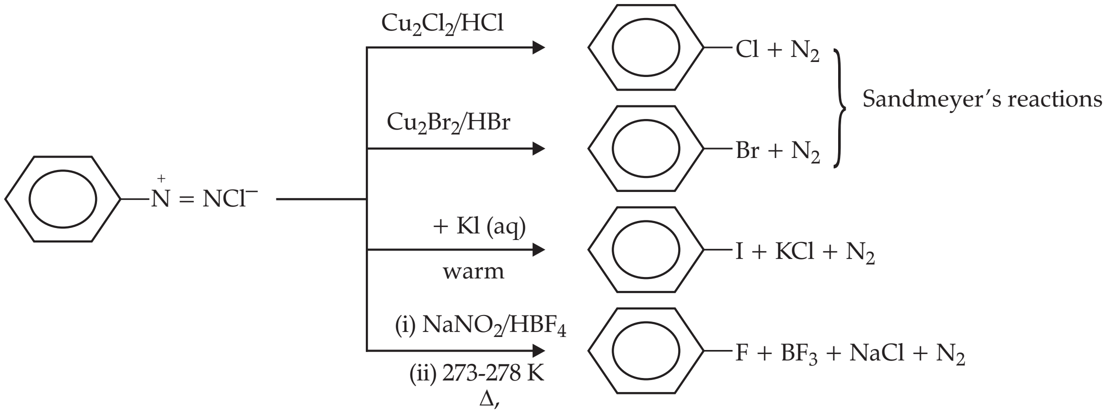
- **Methods of preparation of Haloarenes : (i) Reacting benzene directly with halogen :**



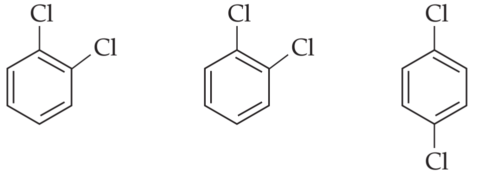
(ii) Starting with diazonium salts :



Benzene diazonium chloride



- **Physical properties of Haloarenes :** Isomeric haloarenes have similar boiling points. But *para* isomer have higher melting point than other two *i.e.*, meta and ortho because of the symmetry in *para* isomer which occupies the crystal lattice better than *ortho* and *meta* isomers.

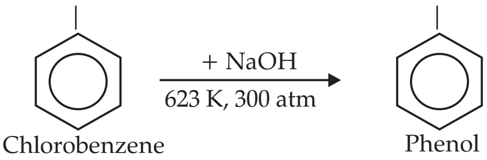


b.p. (*k*)	453	446	448
m.p. (*k*)	256	249	323

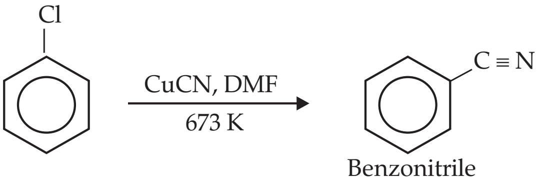
- **Chemical properties of Haloarenes :**

(a) Nucleophilic substitution reactions are very less possible with haloarenes as C—X bond attains partial double bond character because of resonance effect, difference in hybridization, instability of the formed phenyl cation. Due to these repulsions, it makes difficult for electron rich nucleophile to attack electron rich haloarenes. Under higher temperatures, some of the below mentioned nucleophilic reactions are possible.

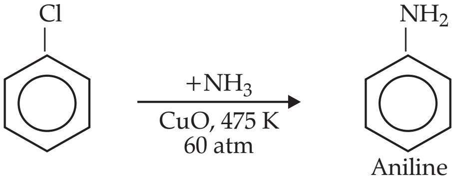
(i) Substitution by —OH group (Dow's process) :



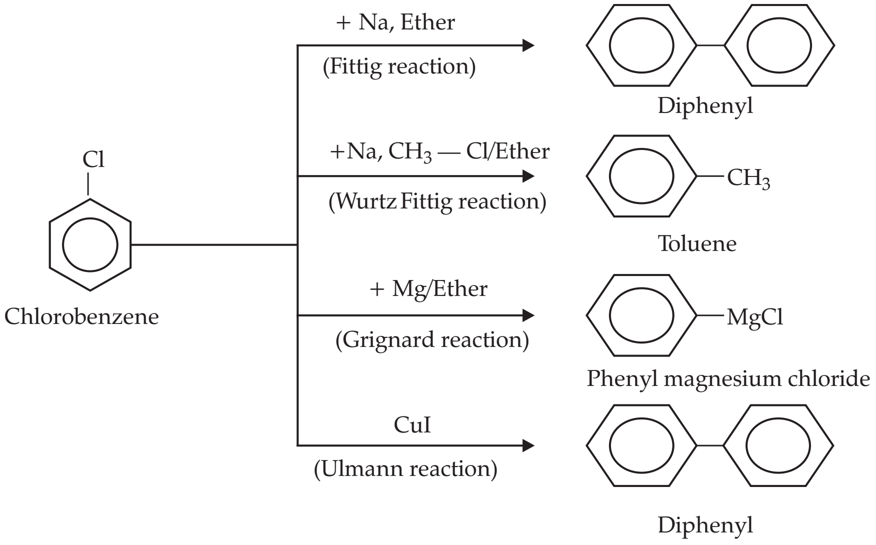
(ii) Substitution by —CN group :



(iii) Substitution by —NH_2 group :

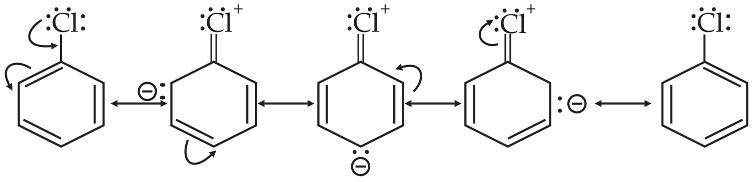


(iv) Reaction with metals :



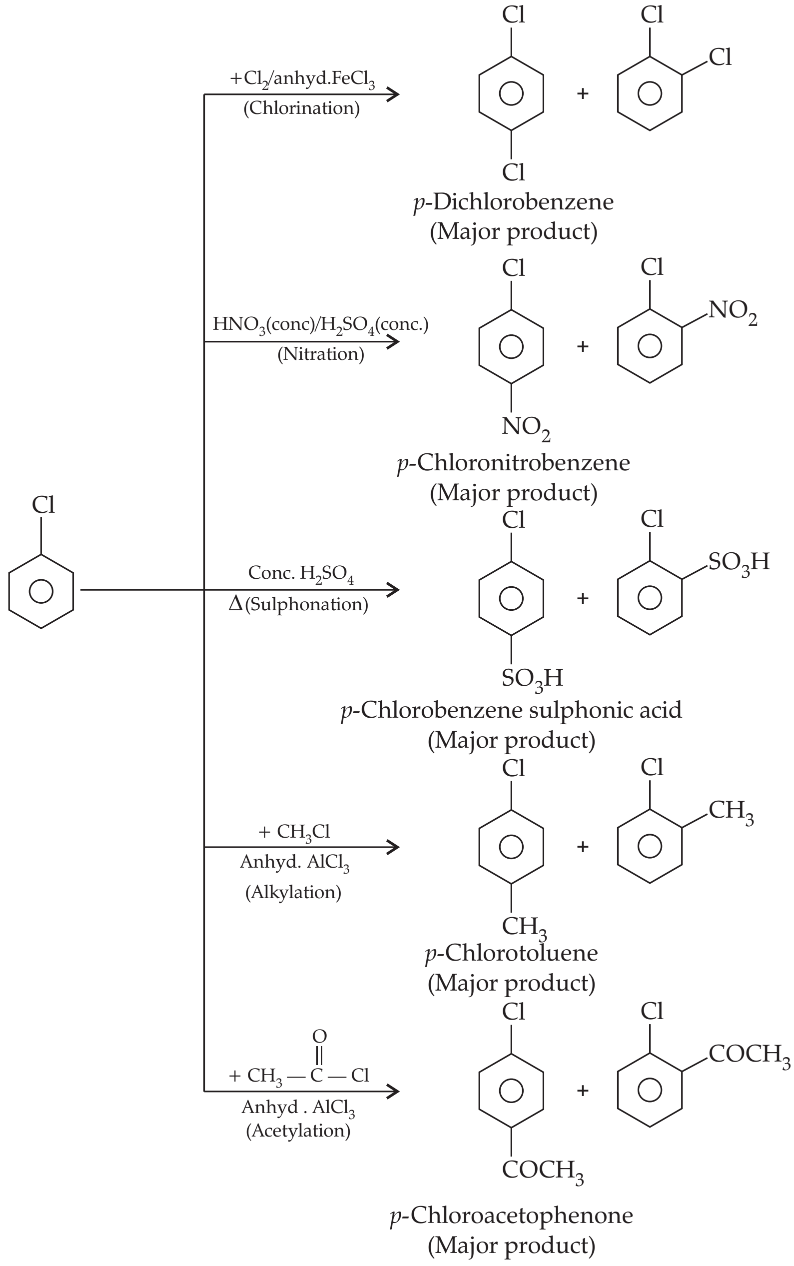
- **Nature of C—X bond in haloarene**—The C—X bond of aryl halide is less reactive than that of haloalkanes. One reason is that in aryl halide, halogen atom is attached to sp^2-hybrid carbon atom whereas in alkyl halides, it is attached to sp^3-hybrid carbon atom. Due to more electronegativity of sp^2-hybrid carbon in comparison to sp^3-carbon atom, there is less charge in separation of C—X bond in haloarene.

Secondly in aryl halides like chlorobenzene, the lone pair of electrons present on chlorine atom migrate towards the aromatic ring by + R effect due to conjugation of lone pair of electrons with π-electrons of the aromatic ring. As a result of which, the halogen atom is attached with the aromatic ring by partial double bond. The phenyl cation formed is highly unstable. The replacement of such a halogen atom by other nucleophiles becomes difficult.



(v) Electrophilic substitution reactions of haloarenes :

It take place at ortho and para positions :



- **Polyhalogen compounds :** Carbon compounds containing more than one halogen atoms are usually referred to as polyhalogen compounds. Many of those compounds are useful in industry and agriculture :

(i) Dichloromethane (Methylene chloride) : It is prepared industrially by the direct chlorination of methane.

$$CH_4 + 2Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + 2HCl$$

The mixture so obtained is separated by fractional distillation. It is widely used as solvent in pharmaceuticals and food industry.

(ii) Chloroform : It is manufactured by chlorination of methane followed by separation by fractional distillation.

$$CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{h\nu} CHCl_3 + 3HCl.$$

It is extensively used as solvent for waxes, resins, rubber, fats etc. It was earlier used as anaesthetic and swallowing agent, but due to formation of Phosgene gas, (Poisonous gas.) it is not used at present.

(iii) Iodoform (Triiodomethane) : It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or Na_2CO_3 and I_2 in water. It is insoluble in water, yellow precipitate of CHI_3 is formed. This reaction is called iodoform reaction :

$$CH_3CH_2OH + 6NaOH + 4I_2 \xrightarrow{\text{heat}} CHI_3 + 5NaI + HCOONa + 5H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{\text{heat}} CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

It is used as an antiseptic for dressing wounds.

(iv) Carbon tetrachloride (Tetrachloro-methane) : It is prepared by chlorination of methane and by action of chlorine on CS_2 in the presence of $AlCl_3$ as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + \underset{\text{(Sulphur dichloride)}}{SCl_2}$$

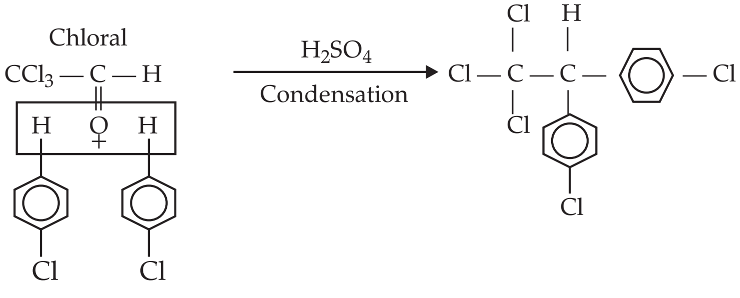
$$CH_4 + 4Cl_2 \xrightarrow{h\nu} CCl_4 + 4HCl$$

It is highly used as solvent for fats, resins etc. Its used in fire extinguisher.

(v) Perfluorocarbons (PFC's) : Perfluorocarbons C_nF_{2n+2} are obtained by controlled fluorination of vapourised alkanes diluted with N_2 gas in the presence of catalysts.

$$C_7H_{16} + 16F_2 \xrightarrow[\text{COF}_2\text{ (catalyst)}]{\text{vapour phase }N_2\ 300°C} \underset{\text{Perfluoroheptane}}{C_7F_{16}} + 16HF$$

(vi) DDT : It is used as an insecticide. It creates pollution due to its extreme stability. It is non-biodegradable. It is manufactured by the condensation of chlorobenzene with chloral (trichloroacetaldehyde) in the presence of sulphuric acid. It is also called *p, p′*-dichlorodiphenyltrichloroethane. It was earlier used to control malaria and typhoid. But it is highly toxic to fish and due to stability, it get deposited and stored in animal fat tissues. Thus was banned in USA and India but still used in other countries of the world.



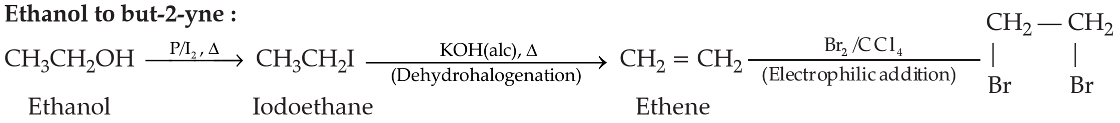
Chlorobenzene

➢ **Some Important Conversions :**

(i) Propene to propan-1-ol :

$$\underset{\text{Propene}}{CH_3CH = CH_2} \xrightarrow[\text{(Anti-Markvonikov, addition)}]{\text{HBr/peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(Hydrolysis)}]{\text{aq. KOH, }\Delta} \underset{\text{Propan-1 -ol}}{CH_3CH_2CH_2OH}$$

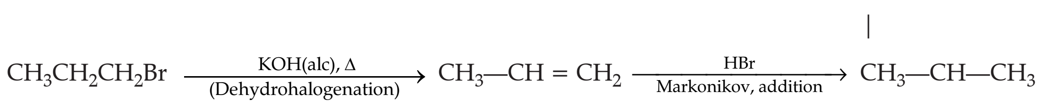
(ii) Ethanol to but-2-yne :



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{P/I_2,\ \Delta} \underset{\text{Iodoethane}}{CH_3CH_2I} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc), }\Delta} \underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow[\text{(Electrophilic addition)}]{Br_2/CCl_4} \underset{Br\quad\ \ Br}{\underset{|\qquad\ |}{CH_2 — CH_2}}$$

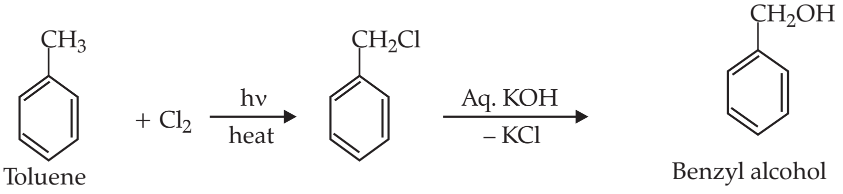
$$\xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc), }\Delta} HC \equiv CH \xrightarrow[196K]{NaNH_2,\text{liq.}NH_3} \xrightarrow[\text{(Nuclephilic substitution)}]{CH_3I\text{(excess)}} \underset{\text{But-2-yne}}{CH_3—C \equiv C—CH_3}$$

(iii) 1-Bromopropane to 2-bromopropane :

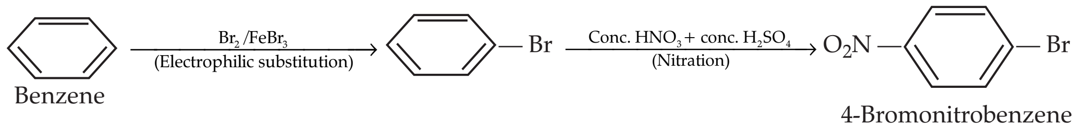


$$\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc), }\Delta} \underset{\text{1-Propene}}{CH_3—CH = CH_2} \xrightarrow[\text{Markonikov, addition}]{HBr} \underset{\text{2–Bromopropane}}{CH_3—\overset{\overset{Br}{|}}{CH}—CH_3}$$

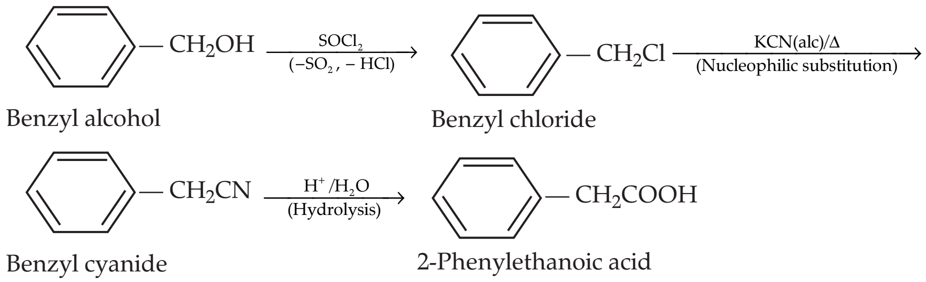
(iv) Toluene to benzyl alcohol :



(v) Benzene to 4-bromonitrobenzene :



(vi) Benzyl alcohol to 2-phenylethanoic acid :

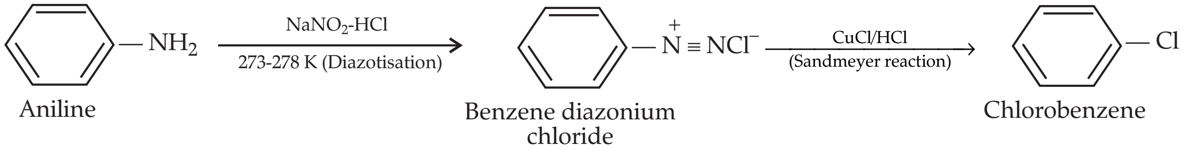


(vii) Ethanol to propanenitrile :

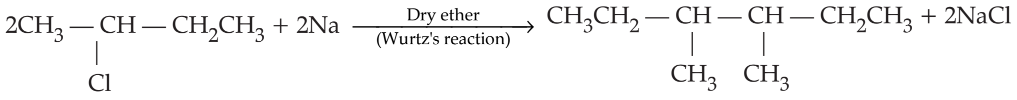
$$CH_3CH_2OH \xrightarrow{P/I_2,\,\Delta} CH_3CH_2I \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN (alc)}/\Delta} CH_3CH_2CN$$

Ethanol 1-Iodoethane Propane nitrile

(viii) Aniline to chlorobenzene :



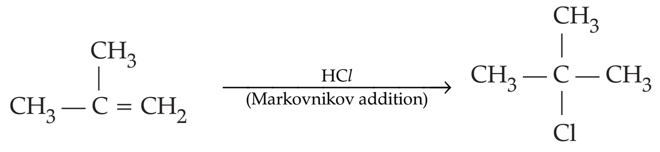
(ix) 2-Chlorobutane to 3, 4-dimethyl hexane :



$$2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2CH_3 + 2Na \xrightarrow[\text{(Wurtz's reaction)}]{\text{Dry ether}} CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3 + 2NaCl$$

2-chlorobutane 3, 4-Dimethyl hexane

(x) 2-Methyl-1-propene to 2-chloro-2-methyl propane :



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(Markovnikov addition)}]{\text{HC}l} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2-Methyl-1-propene 2-Chloro-2-methyl propane

(xi) Ethyl chloride to propanoic acid :

$$CH_3CH_2Cl \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN (alc)}/\Delta} CH_3CH_2CN \xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} CH_3CH_2COOH$$

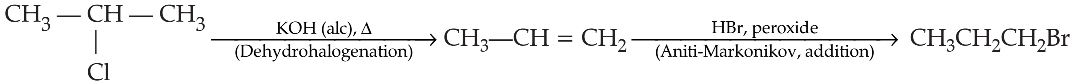
Ethyl chloride Ethyl cyanide Propanoic acid

(xii) But-1-ene to *n*-butyl iodide :

$$CH_3CH_2CH=CH_2 \xrightarrow[\text{(Anti-Markoinkov addition)}]{\text{HBr/peroxide}} CH_3CH_2CH_2CH_2Br \xrightarrow[\text{(Finkelstein reaction)}]{\text{NaI, acetone}} CH_3CH_2CH_2CH_2I$$

But-1-ene 1-Bromobutane *n*-Butyl iodide

(xiii) 2-Chloropropane to 1-propanol :



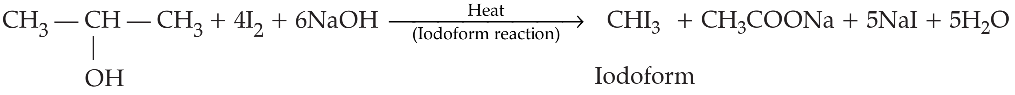
$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc)},\,\Delta} CH_3-CH=CH_2 \xrightarrow[\text{(Aniti-Markonikov, addition)}]{\text{HBr, peroxide}} CH_3CH_2CH_2Br$$

2-Chloropropane Propene 1-Bromopropane

$$\xrightarrow[\text{Nucleophilic substitution}]{\text{KOH(aq)}, \Delta} CH_3CH_2CH_2OH$$

1-Propanol

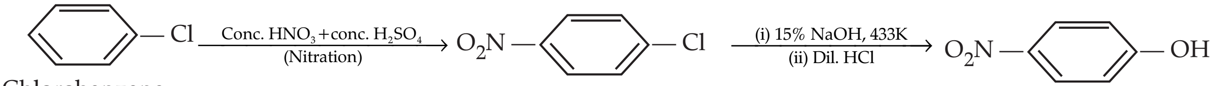
(xiv) Isopropyl alcohol to iodoform :



$$\underset{\underset{\text{OH}}{|}}{CH_3-CH-CH_3} + 4I_2 + 6NaOH \xrightarrow[\text{(Iodoform reaction)}]{\text{Heat}} CHI_3 + CH_3COONa + 5NaI + 5H_2O$$

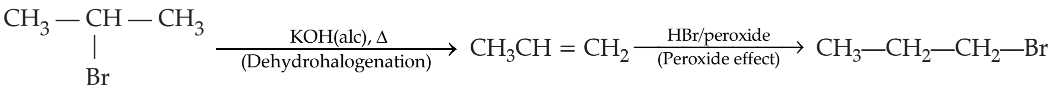
Isopropyl alcohol Iodoform

(xv) Chlorobenzene to *p*-nitrophenol :



Chlorobenzene *p*-Nitrochlorobenzene (*major isomer*) *p*-Nitrophenol

(xvi) 2-Bromopropane to 1-bromopropane :



$$\underset{\underset{\text{Br}}{|}}{CH_3-CH-CH_3} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}, \Delta} CH_3CH=CH_2 \xrightarrow[\text{(Peroxide effect)}]{\text{HBr/peroxide}} CH_3-CH_2-CH_2-Br$$

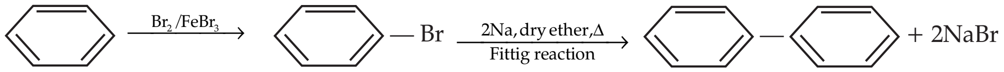
2-Bromopropane Propene 1-Bromopropane

(xvii) Chloroethane to butane :

$$2CH_3CH_2-Cl + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}, \Delta} CH_3CH_2-CH_2CH_3 + 2NaCl$$

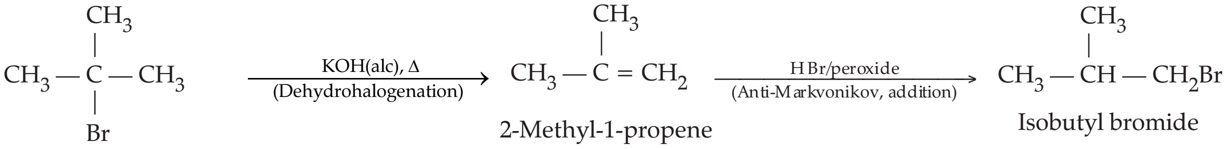
Chloroethane Butane

(xviii) Benzene to diphenyl :



Benzene Bromobenzene Diphenyl

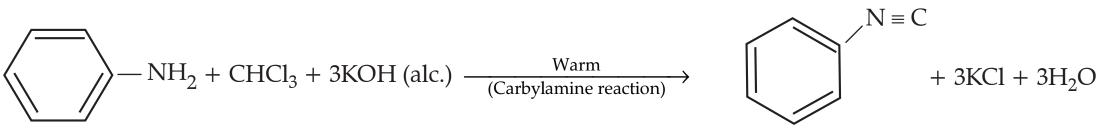
(xix) *tert*-Butyl bromide to iso-butyl bromide :



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}, \Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(Anti-Markvonikov, addition)}]{\text{HBr/peroxide}} CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2Br$$

tert-Butyl bromide 2-Methyl-1-propene Isobutyl bromide

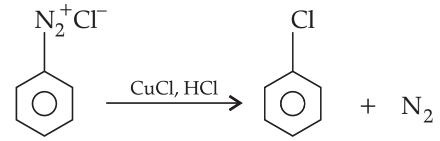
(xx) Aniline to phenyl isocyanide :



Aniline Phenyl isocyanide

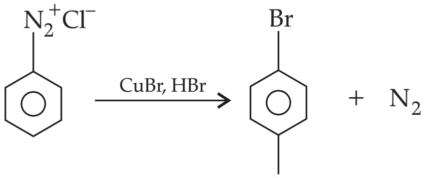
- **Important Name Reactions :**

(i) Sandmeyer's Reaction :

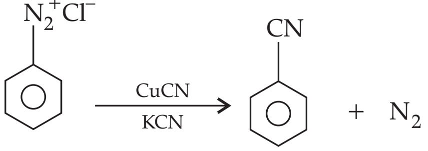


Benzene
diazonium chloride

Chlorobenzene



Bromobenzene



Cyanobenzene

(ii) Finkelstein Reaction :

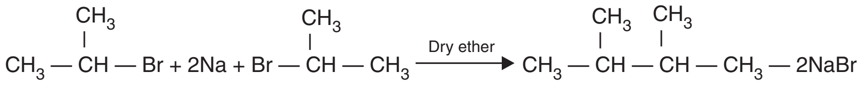
$$CH_3CH_2Cl + NaI \xrightarrow{\text{Dry acetone}} CH_3CH_2I + NaCl$$

Ethyl iodide

(iii) Wurtz Reaction :

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{Dry ether}} CH_3CH_3 + 2NaBr$$

Ethane

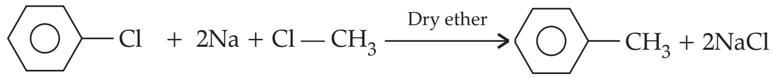


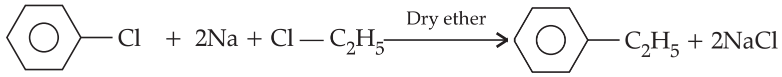
$$CH_3-\overset{CH_3}{\overset{|}{CH}}-Br + 2Na + Br-\overset{CH_3}{\overset{|}{CH}}-CH_3 \xrightarrow{\text{Dry ether}} CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3-2NaBr$$

Isopropyl bromide

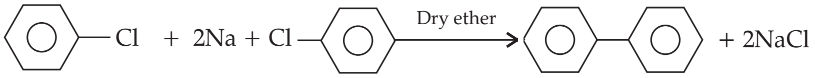
2, 3-Dimethyl butane

(iv) Wurtz-Fittig Reaction :

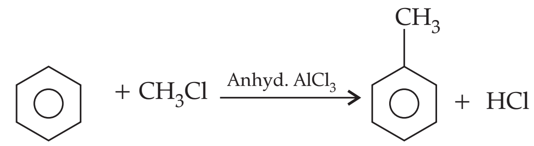




(v) Fittig's Reaction :

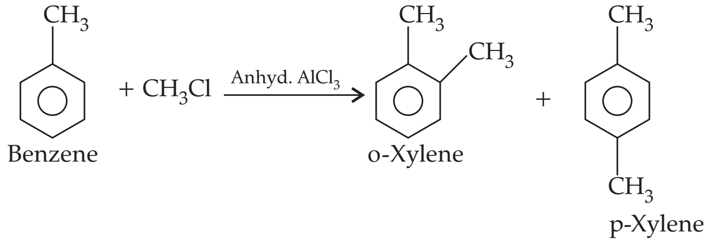


(vi) Friedel-Crafts Alkylation :

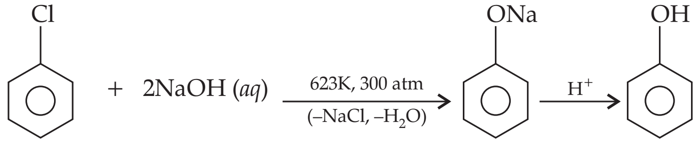


Benzene

Toluene



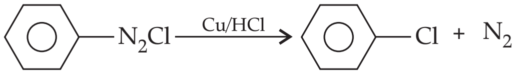
(vii) Dow's Process :



(viii) Hunsdiecker's Reaction :

$$R — COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} R — Br + AgBr + CO_2$$

(ix) Gattermann's Reaction :



Know the Term

- **Phosgene :** A poisonous gas formed on slow oxidation of chloroform in the presence of sunlight.

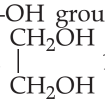
❑❑

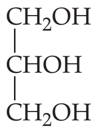
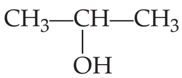
Chapter - 11 : Alcohols, Phenols and Ethers

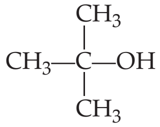
TOPIC-1

Methods of Preparation and Properties of Alcohols and Phenols

Quick Review

- **Alcohol :** When one hydrogen atom of alkane is replaced by —OH group, the compounds obtained are called alcohols having general formula $C_nH_{2n+1}OH$.
- **Classification of Alcohols : (a) mono, di, tri and hydric alcohols.**
  - **(i)** Those alcohols which contain one —OH group *e.g.,* CH_3OH, C_2H_5OH etc. are called monohydric alcohols.
  - **(ii)** Those alcohols which contain two —OH groups, are called dihydric alcohols. Their general formula is $C_nH_{2n}(OH)_2$. They are called diols. *e.g.,*  $\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$ 1, 2-ethanediol.
  - **(iii)** Those alcohols which contain three hydroxyl (—OH) groups, are called trihydric alcohols. They are also called triols.

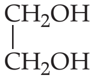
    Their general formula is $C_nH_{2n-1}(OH)_3$. *e.g.,*  $\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$ 1, 2, 3 propanetriol.
- **(b) 1°, 2° and 3° Alcohols :**
  - **(i)** The alcohol in which —OH group is attached to primary (1°) carbon atom is called primary alcohol *e.g.,* CH_3OH, C_2H_5OH etc.
  - **(ii)** The alcohol, in which —OH group is attached to secondary (2°) carbon atom is called secondary alcohol, *e.g.,*  $\begin{array}{c} CH_3—CH—CH_3 \\ | \\ OH \end{array}$ (2-propanol).
  - **(iii)** The alcohol in which —OH group is attached to tertiary (3°) carbon atom is called tertiary alcohol *e.g.,*



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$$ or $(CH_3)_3COH$ (2-methylpropan-2-ol).

(c) Allylic and vinylic alcohols :

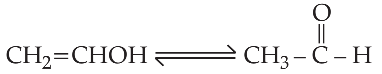
(i) Those alcohols which have more than one —OH groups are called polyhydric alcohols *e.g.,*



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$ Glycol.

(ii) Those alcohols in which —OH group is attached to single bonded sp^3-hybridised carbon next to carbon-carbon double bond, that is to allylic carbon are called allylic alcohols. *e.g.,* $CH_2 = CH—CH_2—OH$

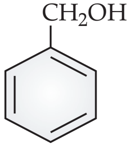
(iii) Those alcohols in which —OH group is attached to double bonded sp^2-hybridised carbon atom are called vinylic alcohols. They are highly unstable and get tautomerised to form aldehydes. *e.g.,*



$$CH_2{=}CHOH \rightleftharpoons CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(Vinyl alcohol) (Acetaldehyde)

(d) Benzyl Alcohol : Those alcohols in which —OH group is attached to single bonded sp^3-hydridised carbon atom attached to aromatic ring are called benzyl alcohols. *e.g.,*

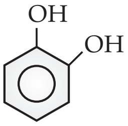


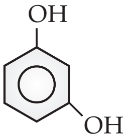
(Benzylalcohol)
Phenyl methanol

➢ **Common and IUPAC Names of Some Alcohols**

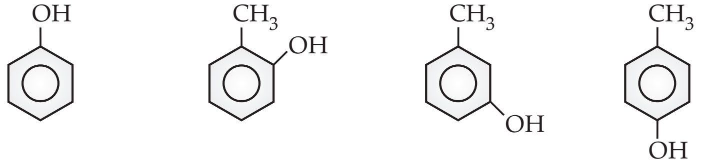
Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3CHOHCH_3$	*iso*-Propyl alcohol	Propan-2-ol
$(CH_3)_2CH—CH_2OH$	*iso*-Butyl alcohol	2-Methyl propan-1-ol
$CH_3CH_2CHOHCH_3$	*sec*- Butyl alcohol	Butan-2-ol
$(CH_3)_3C—OH$	*tert*- Butyl alcohol	2-Methyl propan-2-ol
$\begin{array}{ll}Ch_2 — & CH_2\\ \mid & \mid\\ OH & OH\end{array}$	Ethylene glycol	Ethane-1, 2-diol
$\begin{array}{lll}CH_2 — & CH — & CH_2\\ \mid & \mid & \mid\\ OH & OH & OH\end{array}$	Glycerol or Glycerine	Propane-1, 2, 3-triol

➢ **IUPAC names of some Phenols :**



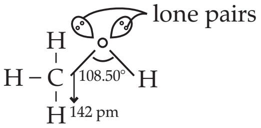


Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1, 2-diol	Benzene-1, 3-diol	Benzene-1, 4-diol



Common name	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	3-Methylphenol

- **Structure of alcohol :** The oxygen of the —OH group is attached to sp^3 hybridised carbon by a σ bond.



- **Methods preparation of Alcohols :**

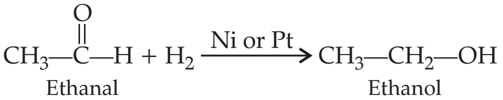
(1) From Haloalkanes : Haloalkanes are hydrolysed to the corresponding alcohols by treatment with aqueous alkali.

$$CH_3—Cl + KOH_{(aq)} \rightarrow CH_3—OH + KCl$$

(2) From Aldehydes and Ketones :

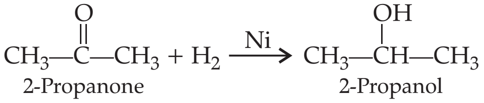
(i) Reduction : Aldehyde and ketones are reduced to primary and secondary alcohols respectively. The common reducing agents are lithium aluminium hydride ($LiAlH_4$), sodium borohydride ($NaBH_4$) or hydrogen gas in the presence of nickel or platinum as catalyst.

(a)



$$\underset{\text{Ethanal}}{CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—H} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Ethanol}}{CH_3—CH_2—OH}$$

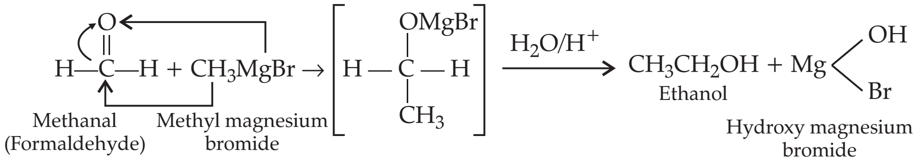
(b)



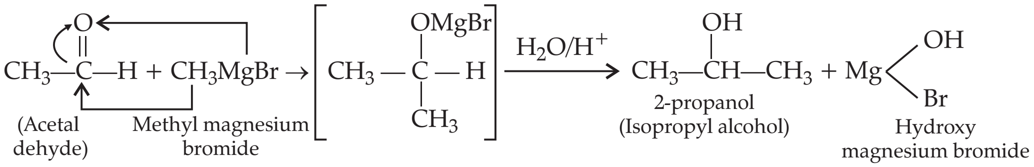
$$\underset{\text{2-Propanone}}{CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3} + H_2 \xrightarrow{\text{Ni}} \underset{\text{2-Propanol}}{CH_3—\overset{\overset{\displaystyle OH}{|}}{C}H—CH_3}$$

(ii) Using Grignard reagent : This method is used to get all three types of alcohols. Formaldehyde (HCHO) reacts with Grignard reagent to give primary alcohol whereas other aldehydes give secondary alcohols. Ketones give tertiary alcohols. *e.g.*,

(a)



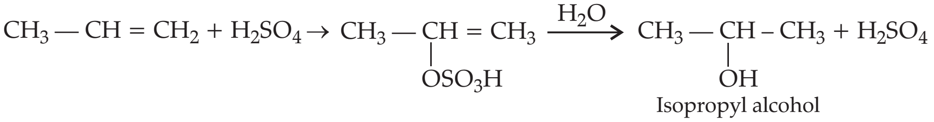
(b)



(3) From Alkenes :

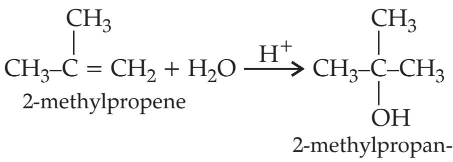
(i) $\underset{\text{Ethene}}{CH_2 = CH_2} + H_2SO_4 \rightarrow CH_3CH_2OSO_3H \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + H_2SO_4$

(ii)



$$CH_3 — CH = CH_2 + H_2SO_4 \rightarrow CH_3 — \underset{\underset{\displaystyle OSO_3H}{|}}{C}H = CH_3 \xrightarrow{H_2O} \underset{\text{Isopropyl alcohol}}{CH_3 — \underset{\underset{\displaystyle OH}{|}}{C}H – CH_3} + H_2SO_4$$

(iii)

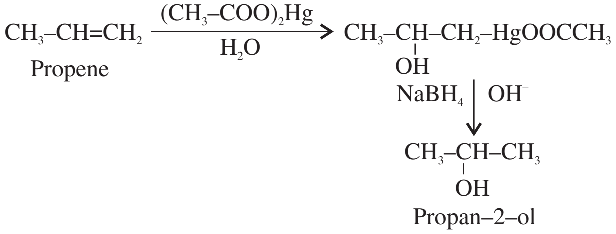


$$\underset{\text{2-methylpropene}}{CH_3–\overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2} + H_2O \xrightarrow{H^+} \underset{\text{2-methylpropan-2-ol}}{CH_3–\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}–CH_3}$$

(4) By hydroboration oxidation : As per anti-Markovnikov's rule -

$$R-CH=CH_2+\frac{1}{2}(BH_3)_2 \longrightarrow (R-CH_2-CH_2)_3B \xrightarrow[OH^-,H_2O]{H_2O_2} R-CH_2-CH_2-OH+H_3BO_3$$

(5) By oxymercuration-demercuration : As per Markovnikov's rule :



$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[H_2O]{(CH_3-COO)_2Hg} CH_3-\underset{OH}{CH}-CH_2-HgOOCCH_3 \xrightarrow{NaBH_4,\ OH^-} \underset{\text{Propan–2–ol}}{CH_3-\underset{OH}{CH}-CH_3}$$

(6) Reduction of carboxylic acids and esters : With the help of strong agent, lithium aluminium hydride, carboxylic acids are reduced to primary alcohols.

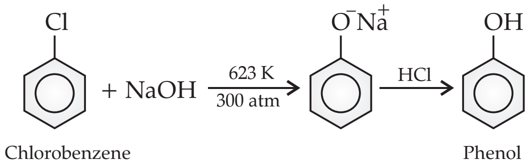
$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

Commercially, acids are reduced to alcohols by converting them to the esters, followed by catalytic hydrogenation.

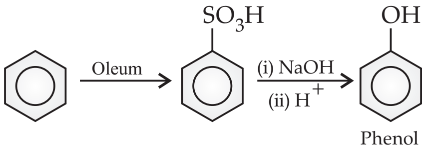
$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

- **Preparation of Phenols :**

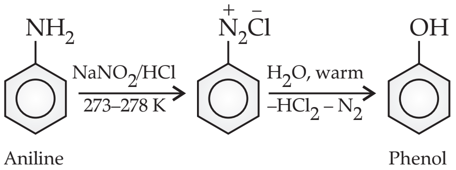
(i) From aryl halides



(ii) From benzene sulphonic acid



(iii) From diazonium salts

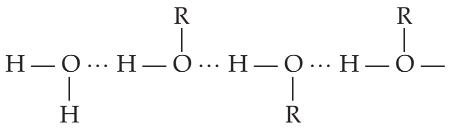


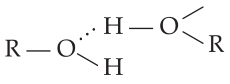
- **Physical and chemical properties of Alcohols and Phenols :**

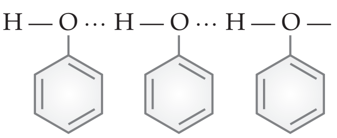
(a) Physical properties :

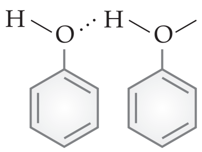
(i) Boiling points : The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding which is responsible for the high boiling point, which is lacking in ethers and hydrocarbons.

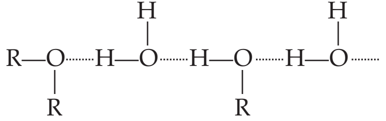






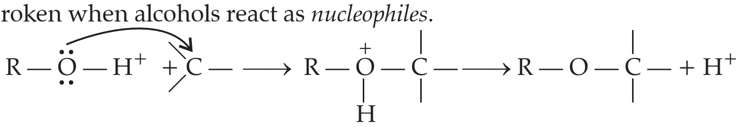


(ii) Solubility : Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.



$$\underset{R}{R-O}\cdots H-\overset{H}{O}\cdots H-\underset{R}{O}\cdots H-\overset{H}{O}\cdots$$

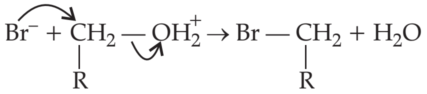
(b) Chemical properties : Alcohols and phenols react both as nucleophiles and electrophiles. The bond between O–H is broken when alcohols react as *nucleophiles*.



$$R-\ddot{O}-H^+ + \!>\!C- \longrightarrow R-\underset{H}{\overset{+}{O}}-\overset{|}{\underset{|}{C}}- \longrightarrow R-O-\overset{|}{\underset{|}{C}}- + H^+$$

The bond between C–O is broken when they react as *electrophiles*.

$$R-CH_2OH + H^+ \longrightarrow RCH_2\overset{+}{O}H_2$$



$$Br^- + \underset{R}{CH_2}-\overset{+}{O}H_2 \rightarrow Br-\underset{R}{CH_2} + H_2O$$

The reactions of alcohols can be classified into

(a) Reactions involving the cleavage of O–H bond :

(i) Reaction with metals :

$$2R-O-H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R-\overset{-}{O}\overset{+}{Na}} + H_2$$

$$CH_3-CH_2-OH + Na \longrightarrow \underset{\text{Sodium ethoxide}}{CH_3-CH_2-\overset{-}{O}\overset{+}{Na}} + \frac{1}{2}H_2$$

$$\underset{\text{3° Butyl alcohol}}{6(CH_3)_3-C-OH} + 2Al \longrightarrow \underset{\text{Aluminium tert-butoxide}}{2((CH)_3-C\text{–}O)_3\,Al} + 3H_2$$

(ii) Esterification :

$$\underset{\text{Carboxylic acid}}{R-COOH} + \underset{\text{Alcohol}}{R'-OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R\text{–}COOR'} + H_2O$$

$$\underset{\text{Acid anhydride}}{(R-CO)_2\,O} + R'-OH \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R\text{–}COOR'} + R-COOH$$

$$\underset{\text{Acid chloride}}{R-COCl} + R'-OH \xrightarrow{\text{Pyridine}} \underset{\text{Ester}}{R\text{–}COOR'} + HCl$$

(b) Reactions involving cleavage of C–O bond :

Order of reactivity in such type of reaction is

3° Alcohol > 2° Alcohol > 1° Alcohol

(i) Reaction with hydrogen halides :

$$R-OH + H-X \xrightarrow{\text{anhyd.}ZnCl_2} \underset{\text{Alkyl halide}}{R-X} + H_2O$$

(ii) Reaction with phosphorus halides :

$$R-OH + PCl_3 \longrightarrow R-Cl + POCl_3 + HCl$$

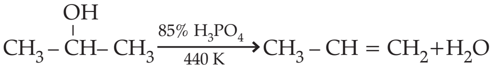
$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$

$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$$

(c) Reaction involving both the alkyl and hydroxyl group :

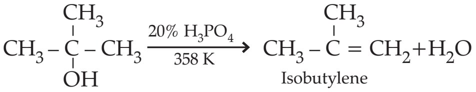
(i) Dehydration : 3° Alcohol > 2° Alcohol > 1° Alcohol

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2-OH} \xrightarrow[443\text{ K}]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$



$$CH_3-\overset{OH}{CH}-CH_3 \xrightarrow[440\text{ K}]{85\%\ H_3PO_4} CH_3-CH=CH_2+H_2O$$

Isopropyl alcohol Propylene



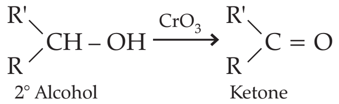
$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[358\text{ K}]{20\%\ H_3PO_4} CH_3-\overset{CH_3}{C}=CH_2+H_2O$$

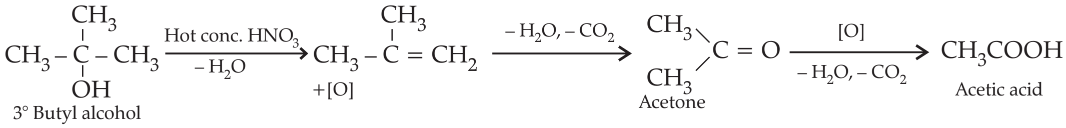
Isobutylene

(ii) Oxidation :

$$\underset{\text{1° Alcohol}}{R-CH_2-OH} + [O] \xrightarrow[\text{or alk.}KMnO_4]{K_2Cr_2O_7/H_2SO_4} R-CHO \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R-COOH}$$

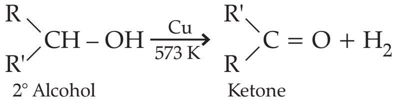
$-H_2O$

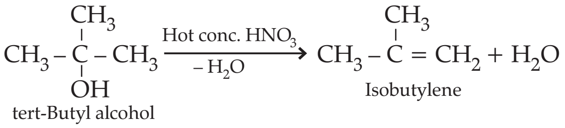




(iii) Dehydrogenation :

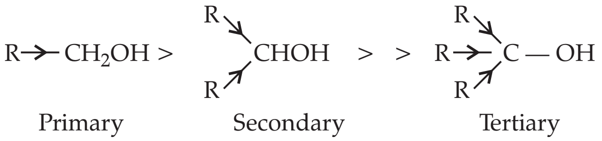
$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Aldehyde}}{R-CHO} + H_2$$





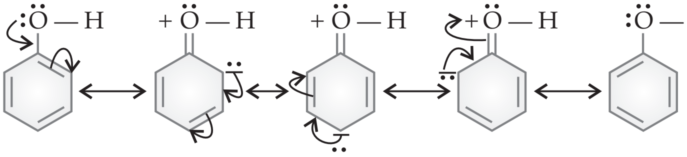
$$\underset{\text{tert-Butyl alcohol}}{CH_3-\overset{CH_3}{\overset{|}{C}}\underset{\underset{OH}{|}}{}-CH_3} \xrightarrow[-H_2O]{\text{Hot conc. }HNO_3} \underset{\text{Isobutylene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2} + H_2O$$

- **Acidity of alcohols and phenols :** The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O–H bond. This decreases the acid strength. For this reason, the acid strength of alcohol decreases in the order :

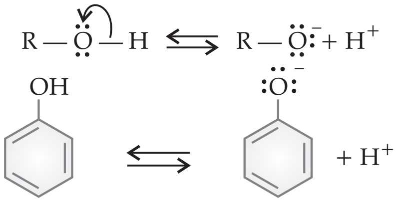


Alcohols can act as Bronsted acids as well as base due to donation of proton and presence of unpaired electron on oxygen respectively.

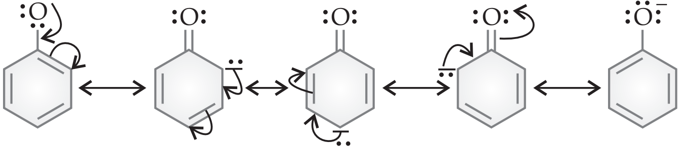
Phenols are more acidic than alcohols and water. The hydroxyl group in phenol is directly attached to the sp^2-hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.



The ionisation of an alcohol and a phenol takes place producing alkoxide and phenoxide ions as shown in equation.



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol.



- **Distinction between Primary, Secondary and Tertiary Alcohols :**

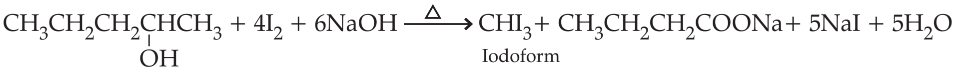
(i) Lucas Test : Alcohol is treated with Lucas reagent, and forms a clear solution. Alkyl chlorides are formed on reaction which being insoluble results in the turbidity in the solution.

$$\text{Alcohol} \xrightarrow[ZnCl_2]{HCl} \text{Alkyl chloride} + H_2O$$

Tertiary alcohol is indicated, if turbidity appears immediately. Secondary alcohol is indicated, if turbidity appears within five minutes.
Primary alcohol is indicated, if turbidity appears on heating.

(ii) Iodoform test : When ethanol or any alcohol containing the group $CH_3-\overset{\overset{OH}{|}}{CH}-$ is heated with iodine and aqueous NaOH or Na_2CO_3 Solution at 333 – 343 K, a yellow precipitate of iodoform is obtained.

$$CH_3OH + I_2 + NaOH \xrightarrow{\Delta} \text{No reaction}$$

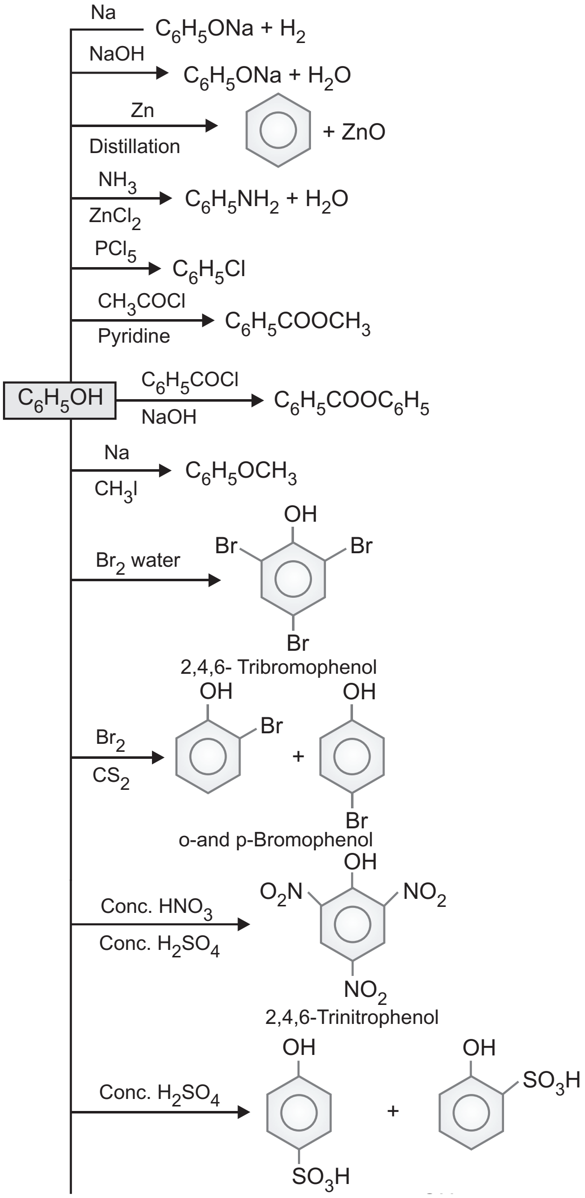


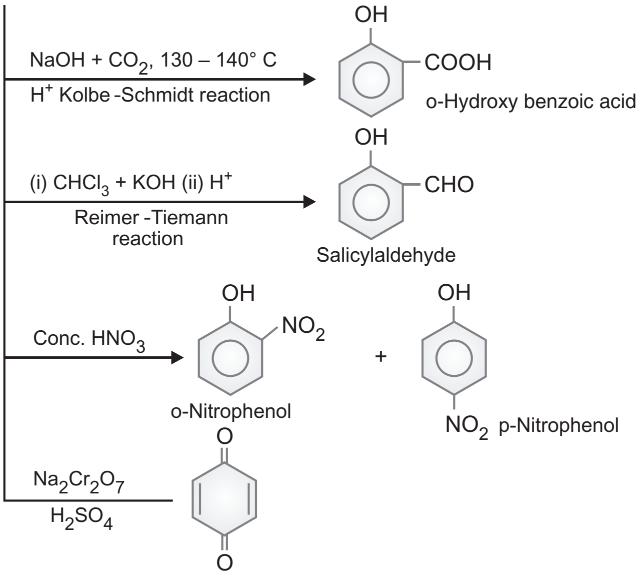
$$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + CH_3CH_2CH_2COONa + 5NaI + 5H_2O$$

(iii) Ferric chloride test or phenols : Phenols gives a violet coloured water soluble complex with ferric chloride.

$$6C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

- **Reactions of Phenol :**





Benzoquinone

- **Reactions of Ethanol :**

$C_2H_5OH \xrightarrow[\text{anhyd. } ZnCl_2]{HCl} C_2H_5Cl$

$C_2H_5OH \xrightarrow{HI + \text{Red P}} C_2H_6$

$C_2H_5OH \xrightarrow{NH_3/ThO_2 . 630K} C_2H_5NH_2$ + Secondary and tertiary amine

$C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl$

$C_2H_5OH \xrightarrow{SOCl_2} C_2H_5Cl$

$C_2H_5OH \xrightarrow[ZnCl_3 . 2NH_3]{NH_3} C_2H_5NH_2$

$C_2H_5OH \xrightarrow{Na} C_2H_5\overset{\ominus}{O}\,\overset{\oplus}{Na}$

$C_2H_5OH \xrightarrow[\text{or } (CH_3CO)_2O]{CH_3COOH \text{ or } CH_3COCl} C_2H_5OOCCH_3$

$C_2H_5OH \xrightarrow[520K]{Al_2O_3} C_2H_5OC_2H_5$

$C_2H_5OH \xrightarrow[620\text{ K}]{Al_2O_3} CH_2 = CH_2$

$C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$

$C_2H_5OH \xrightarrow[410K]{\text{Heat with } H_2SO_4,\ C_2H_5OH \text{ in excess}} C_2H_5\text{–}O\text{–}C_2H_5$

$C_2H_5OH \xrightarrow[440K]{H_2SO_4 \text{ in excess}} CH_2 = CH_2$

$C_2H_5OH \xrightarrow{Cu,\ 573K} CH_3CHO + H_2$

$C_2H_5OH \xrightarrow{Cl_2} CH_3CHO \xrightarrow{Cl_2} CCl_3CHO$

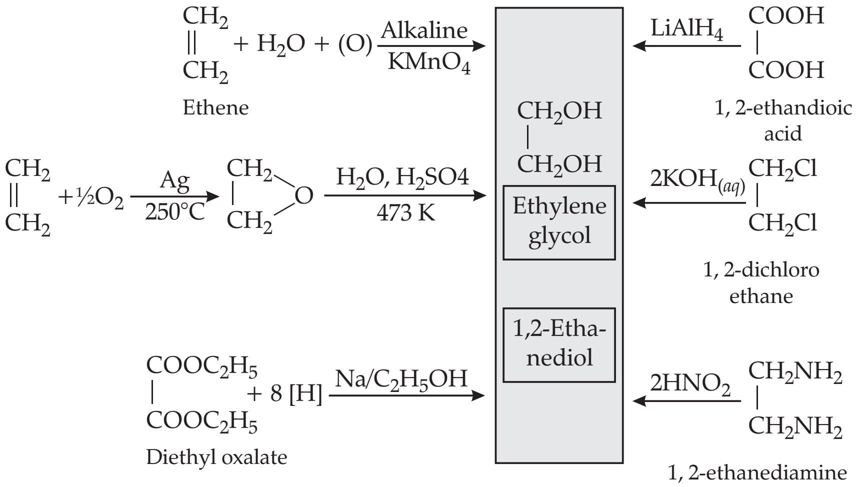
$C_2H_5OH \xrightarrow{I_2 + NaOH} CHI_3$

$C_2H_5OH \xrightarrow{CH_3MgI} CH_4 + Mg\begin{cases} I \\ OC_2H_5 \end{cases}$

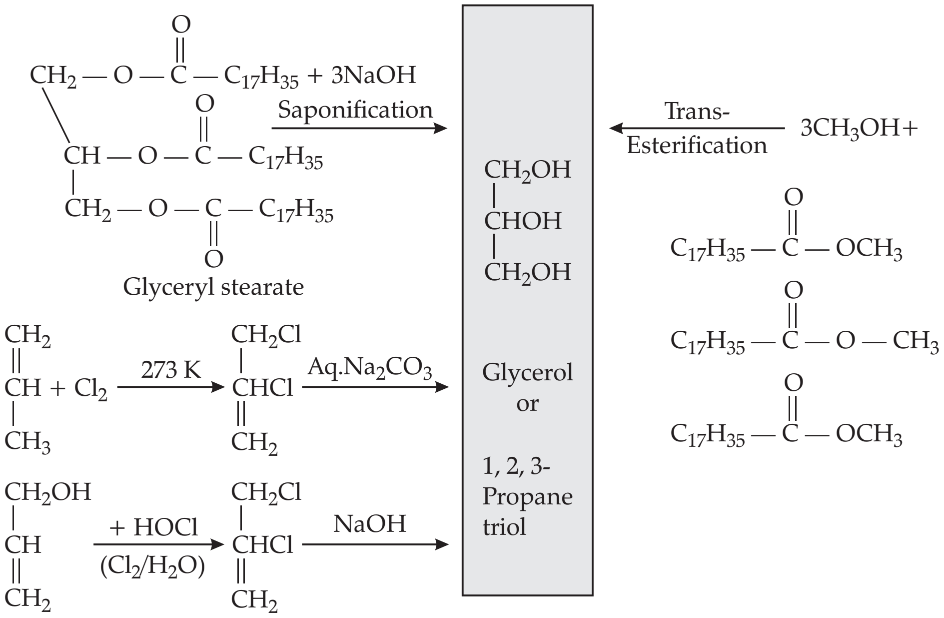
- **Differences between or Identification of Methyl Alcohol and Ethyl Alcohol :**

S.No.	Test	Methyl alcohol	Ethyl alcohol
(i)	Boiling point.	338K.	351.2K.
(ii)	On heating with I_2 and NaOH.	No reaction.	Iodoform is obtained.
(iii)	On heating with anhydrous sodium acetate and conc. sulphuric acid.	A specific odour of methyl acetate is produced.	Ethyl acetate is formed which has a sweet fruity odour.
(iv)	On heating with salicylic acid and conc. H_2SO_4.	Methyl salicylate (oil of winter green) is formed which has a characteristic odour.	No specific smell.
(v)	On heating with bleaching powder	No reaction.	Chloroform with sweet smell is formed.

- **Methods of preparation of Glycol :**



- **Methods of preparation of Glycerol :**



Know the Terms

- **Lucas reagent :** An equimolar mixture of HCl and $ZnCl_2$.
- **Wood spirit :** Methanol is known as wood spirit as it is prepared by destructive distillation of wood.

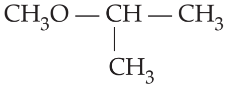
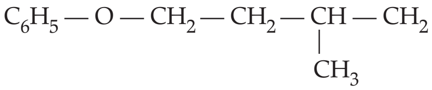
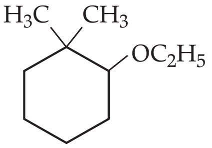
- **Methylated spirit :** Denatured ethyl alcohol which is unfit for drinking purpose is called methylated spirit.
- **Fusal oil :** In the fermentation of starch, ethyl alcohol is prepared but in small amount. Some higher alcohol also form like isopentyl alcohol or isoamyl alcohol. This mixture is quite often called fusel oil.
- **Power Alcohol :** It is the mixture of 20% alcohol, and 80% petrol with ether, benzene or tetralin. It is used as a substitute for petrol for running internal combustion, engines in cars, scooters etc.
- **Lederar Mannase reaction :** Phenol condenses with formaldehyde in presence of acid or base to give bakelite (polymer). The reaction is known as Lederar-Mannase reaction.
- **Rectified spirit :** It contains about 95.5 percent alcohol.

TOPIC-2

Methods of Preparation and Properties of Ethers

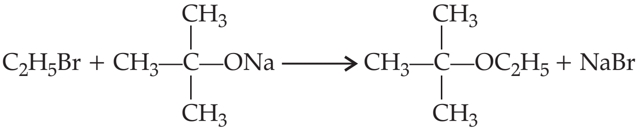
Quick Review

- **Ethers :** Compounds with general formula $C_nH_{2n+2}O$. They are represented by general structure, R–O–R'.
- **Nomenclature of Ethers :** Ethers are named from names of alkyl/aryl/groups written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix '*di*' is added before the alkyl group. For example, $C_2H_5OC_2H_5$ is diethyl ether. These types of ethers are called symmetrical ethers. If both the alkyl groups are the different, for example, $CH_3OC_2H_5$ is ethylmethyl ether. These types of ethers are called unsymmetrical ethers. During naming ethers, the larger alkyl group is chosen as the parent hydrocarbon.
- **Common and IUPAC names of some Ethers are :**

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_2CH_3$	Methyl *n*-butyl ether	1-Methoxybutane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_2H_5—O—C_6H_5$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6—CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
 $CH_3O—\underset{CH_3}{CH}—CH_3$	Methyl isopropyl ether	2-Methoxypropane
 $C_6H_5—O—CH_2—CH_2—\underset{CH_3}{CH}—CH_2$	Phenyl isopentyl ether	3-Methylbutoxybenzene
$CH_3—O—CH_2—CH_2—OCH_3$	—	1, 2-Dimethoxyethane
	—	2-Ethoxy-1, 1-dimethylcyclohexane

- **Methods of preparation of Ethers :**
  - **(i) Williamson's synthesis :** When alkyl halide reacts with sodium alkoxide, ethers are formed. *e.g.*,

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}-\overset{-}{O}-R'} \longrightarrow \underset{\text{Ether}}{R-O+R'} + NaX$$



$$C_2H_5Br + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-ONa \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OC_2H_5 + NaBr$$

2-ethoxy, 2-methyl propane

(ii) Dehydration of alcohols : Alcohols are dehydrated to ethers in presence of concentrated sulphuric acid at 413 K. The reaction involves the removal of one molecule of water from two moles of alcohols.

$$C_2H_5\boxed{OH+H}OC_2H_5 \xrightarrow[413\text{ K}]{\text{conc. }H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

Ethyl alcohol Diethyl ether (Ethoxy ethane)

Alcohols can also be dehydrated by heating with alumina at 523 K and high pressure. This method is not suitable for preparation of unsymmetrical ethers.

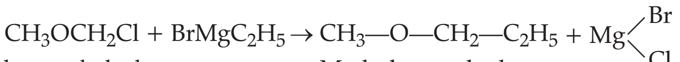
(iii) Heating alkyl halides with dry silver oxide : Ethers can be prepared by heating alkyl halides with dry silver oxide (Ag_2O).

$$2C_2H_5Cl + Ag_2O \xrightarrow{\text{heat}} C_2H_5—O—C_2H_5 + 2AgCl$$

$$CH_3Cl + Ag_2O + C_2H_5Cl \longrightarrow CH_3—O—C_2H_5 + 2AgCl$$

Mixed ethers or unsymmetrical ethers can be prepared by this method.

(iv) Reaction of lower halogenated ethers with Grignard reagent : Higher homologues ethers can be prepared by action of Grignard reagent on lower halogenated ethers.



$$CH_3OCH_2Cl + BrMgC_2H_5 \rightarrow CH_3—O—CH_2—C_2H_5 + Mg\begin{matrix}Br\\Cl\end{matrix}$$

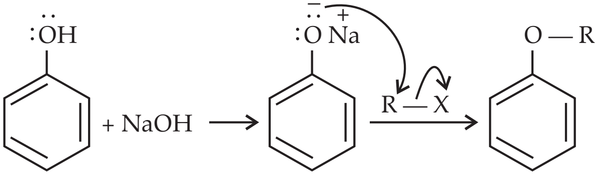
Chloromethyl ether Methyl propyl ether

(v) Action of diazomethane on alcohols : Methyl ethers can be prepared by action of diazomethane on alcohols in the presence of catalysts like BF_3.

$$C_2H_5OH + CH_2N_2 \xrightarrow{BF_3} C_2H_5OCH_3 + N_2$$

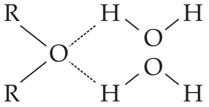
Methyl ethyl ether

(vi) Preparation of Aryl Ether :



➢ **Physical Properties :**

(i) Colourless, pleasant smelling and volatile liquids.
(ii) Lower boiling points than alcohols.
(iii) Solubility is comparable to those of corresponding alcohols due to the ability of their molecules of form hydrogen bond with water molecules.



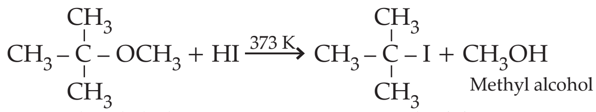
➢ **Chemical properties :**

(i) Cleavage with halogen acid :

$$\underset{\text{Ether}}{R-O-R} + HX \xrightarrow{373\text{ K}} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX} \; (X = Br, I)$$

$$C_2H_5OC_2H_5 + HI \xrightarrow{373\text{ K}} C_2H_5OH + C_2H_5I$$

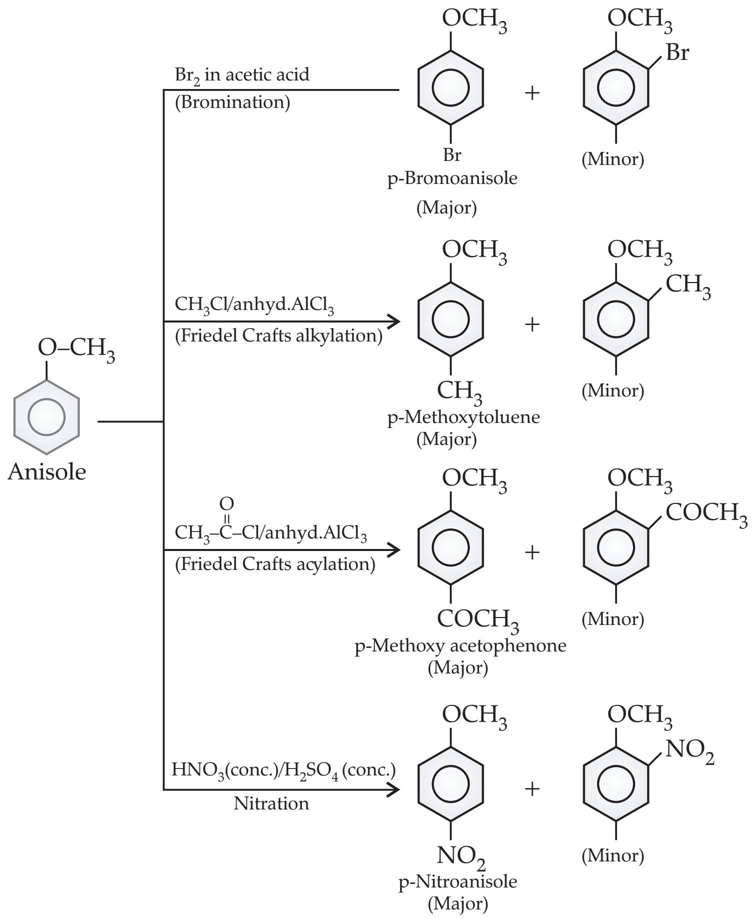
$$C_2H_5OC_2H_5 + \underset{\text{(Excess)}}{2HI} \xrightarrow{373\text{ K}} 2C_2H_5I + H_2O$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3 + HI \xrightarrow{373\text{ K}} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-I + \underset{\text{Methyl alcohol}}{CH_3OH}$$

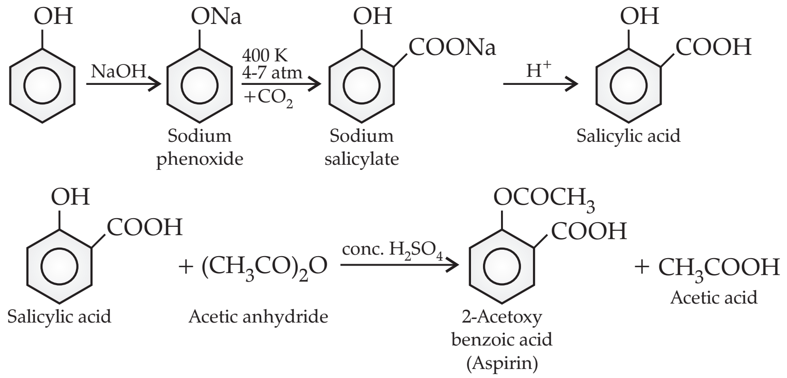
tert-Butyl methyl ether tert-Butyl iodide

(ii) Ring substitution in aromatic ethers :

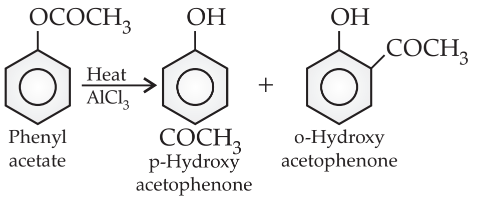


- **Some important name reactions :**

(i) Kolbe's reaction :



(ii) Fries Rearrangement :



(iii) Williamson synthesis :

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}-\overset{-}{O}-R'} \longrightarrow \underset{\text{Ether}}{R-O} + R' + NaX$$

Know the Term

- **Alkoxyalkanes :** Ethers are named as alkoxyalkanes. The larger alkyl group forms the part of parent chain while smaller alkyl group constitutes the alkoxy group.

❑❑

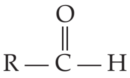
Chapter - 12 : Aldehydes Ketones and Carboxylic Acids

TOPIC-1

Aldehydes and Ketones

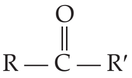
Quick Review

- **Carbonyl group :** The functional group >C=O is called carbonyl group. Organic compounds containing carbonyl group are aldehydes, ketones, carboxylic acids and their derivatives. The general formulae of these compounds are



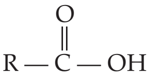
$\mathrm{R-\overset{O}{\overset{\|}{C}}-H}$

Aldehyde
(Where R=H or
any alkyl, aryl or
aralkyl group)



$\mathrm{R-\overset{O}{\overset{\|}{C}}-R'}$

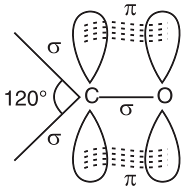
Ketone
(where R and R'
may be same or
different alkyl, aryl
or aralkyl group)

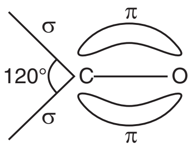


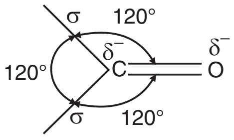
$\mathrm{R-\overset{O}{\overset{\|}{C}}-OH}$

Carboxylic acid
(where R=H or any
alkyl, aryl or
aralkyl group)

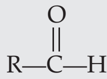
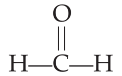
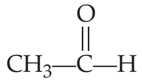
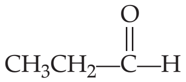
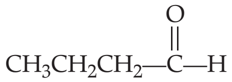
- **Structure of Carbonyl Group :**

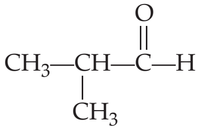
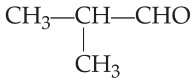
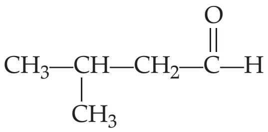
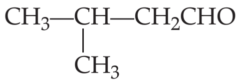
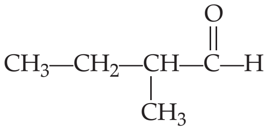
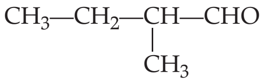




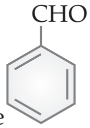
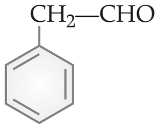
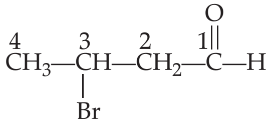
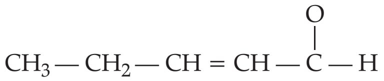
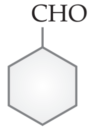
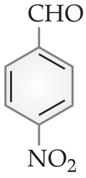
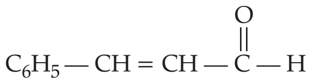
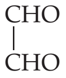
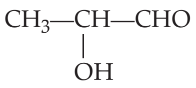
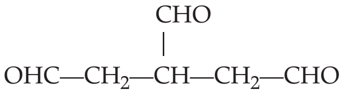
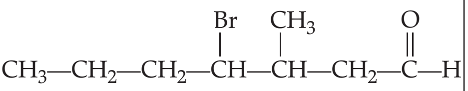
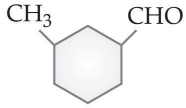
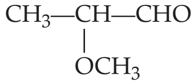
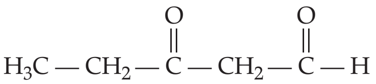


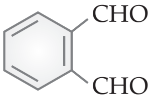
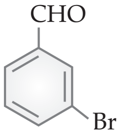
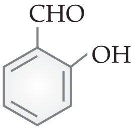
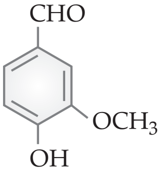
- Aldehydes are those compounds in which carbonyl group is attached to either two hydrogen atoms or one hydrogen atom and one carbon containing group such as alkyl or aryl group with hydrogen atom. *e.g.*, CH_3CHO, C_2H_5CHO, C_6H_5CHO etc.
- Ketones are those compounds in which carbonyl group is attached with two alkyl or two aryl or one alkyl and one aryl group *e.g.*, CH_3COCH_3, $CH_3COC_6H_5$, $C_6H_5COC_6H_5$ etc.
- **Nomenclature of Aldehydes and Ketones :**

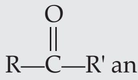
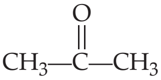
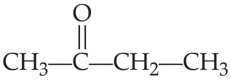
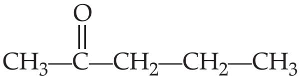
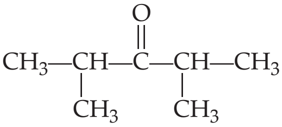
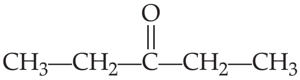
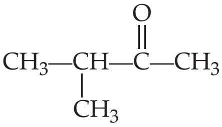
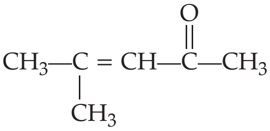
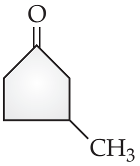
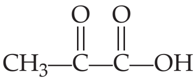
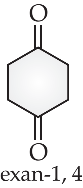
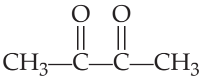
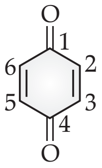
Aldehydes	 **General formula :** $\mathrm{R-\overset{O}{\overset{\|}{C}}-H}$, where R = C_nH_{2n+1}		
Structural formula	**Condensed formula**	**Common name**	**IUPAC name**
 $\mathrm{H-\overset{O}{\overset{\|}{C}}-H}$	HCHO	Formaldehyde	Methanal
 $\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-H}$	CH_3CHO	Acetaldehyde	Ethanal
 $\mathrm{CH_3CH_2-\overset{O}{\overset{\|}{C}}-H}$	CH_3CH_2CHO	Propionaldehyde	Propanal
 $\mathrm{CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-H}$	$CH_3CH_2CH_2CHO$	Butyraldehyde	Butanal

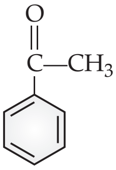
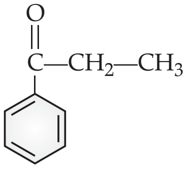
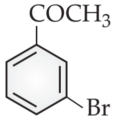
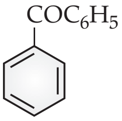
 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-\overset{\overset{O}{\|}}{C}-H$	 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CHO$	Isobutyraldehyde	2-Methylpropanal
 $CH_3CH_2CH_2CH_2-\overset{\overset{O}{\|}}{C}-H$	$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$	 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CH_2CHO$	Isovaleraldehyde	3-Methylbutanal
 $CH_3-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-\overset{\overset{O}{\|}}{C}-H$	 $CH_3-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-CHO$	α-Methylbutyraldehyde	2-Methylbutanal

Nomenclature of Some Important Aldehydes (With Common Names)

C_6H_5CHO or  Benzaldehyde	 Phenylacetaldehyde (2-Phenylethanal)	 $\overset{4}{CH_3}-\underset{\underset{Br}{\mid}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{\overset{O}{1\|}}{C}-H$ β-Bromobutyraldehyde (3-Bromobutanal)
$CH_2=CH-CHO$ Acrolein (Prop-2-en-1-al)	$CH_3-CH=CH-CHO$ Crotonaldehyde (But-2-en-1-al)	 $CH_3-CH_2-CH=CH-\overset{\overset{O}{\mid}}{C}-H$ Pent-2-enal
 (Cyclohexanecarbaldehyde)	 4-Nitrobenzaldehyde (4-Nitrophenylcarbaldehyde)	 $C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-H$ Cinnamaldehyde (3-Phenylprop-2-en-l-al)  $\begin{array}{l}CHO\\ \mid\\ CHO\end{array}$ Glyoxal (Ethane-1, 2-dial)
 $CH_3-\underset{\underset{OH}{\mid}}{CH}-CHO$ 2-Hydroxypropanal	 $OHC-CH_2-\overset{\overset{CHO}{\mid}}{CH}-CH_2-CHO$ Propan- 1, 2, 3-tricarbaldehyde	 $CH_3-CH_2-CH_2-\overset{\overset{Br}{\mid}}{CH}-\overset{\overset{CH_3}{\mid}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$ 4-Bromo-3-methylheptanal
 γ-Methylcyclohexanecarbaldehyde 3-Methylcyclohexanecarbaldehyde	 $CH_3-\underset{\underset{OCH_3}{\mid}}{CH}-CHO$ α- Methoxypropionaldehyde 2- Methoxypropanal	 $H_3C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$ 3-Oxopentanal

 Phthaldehyde Benzene-1, 2-dicarbaldehyde	 *m*- Bromobenzaldehyde 3- Bromobenzaldehyde	 (Salicylaldehyde) 2-Hydroxybenzaldehyde
 4-Hydroxy -3- methoxy benzaldehyde		

Ketones	**General formula :** $R-\overset{\overset{O}{\parallel}}{C}-R'$ and $R' = C_{n'}H_{2n'+1}$ ($n = n'$, $n \neq n'$)		
Structural Formula	**Condensed formula**	**Common name**	**IUPAC name**
$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$	CH_3COCH_3	Acetone	Propanone
$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_3$	$CH_3COCH_2CH_3$	Ethyl methyl ketone	Butan-2-one
$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_2-CH_3$	$CH_3COCH_2CH_2CH_3$	Methyl *n*-Propyl ketone	Pentan-2-one
$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\overset{\overset{O}{\parallel}}{C}-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2, 4-Dimethyl pentan-3-one
$CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_3$	$CH_3CH_2COCH_2CH_3$	Diethyl Ketone	Pentan-3-one
$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\overset{\overset{O}{\parallel}}{C}-CH_3$	$(CH_3)_2CHCOCH_3$	Isopropyl methyl ketone	3-Methylbutan-2-one
$CH_3-\underset{\underset{CH_3}{\vert}}{C}=CH-\overset{\overset{O}{\parallel}}{C}-CH_3$	$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one
 β-Methylcyclopentanone (3-Methylcyclopentanone)	$CH_3-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-OH$ Pyruvic acid (2-Oxopropanoic acid)  Cyclohexan-1, 4-dione	$CH_3-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-CH_3$ Diacetyl (Butane-2-3-dione)	 p-Benzoquinone Cyclohexan-2, 5-diene-1, 4-dione

 Acetophenone (Phenylethanone)	 1-Phenylpropan-l-one	 *m*-Bromoacetophenone 1-(3-Bromophenyl) ethanone	 benzophenone (Diphenylmethanone)

- **Methods of preparation of Aldehydes and Ketones :**

(a) Preparation of Aldehydes :

(i) By oxidation of primary alcohols : Aldehydes can be prepared by the oxidation of primary alcohols.

$$\underset{\text{1° Alcohol}}{RCH_2OH} + [O] \xrightarrow[\text{or } KMnO_4]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Aldehyde}}{R-CHO} + H_2O$$

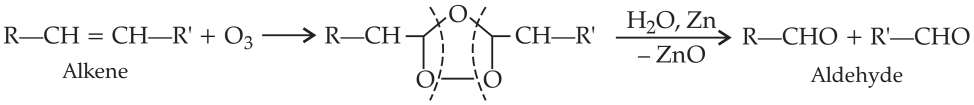
$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{Aldehyde}}{R-CHO}$$

(ii) By dehydrogenation of alcohols :

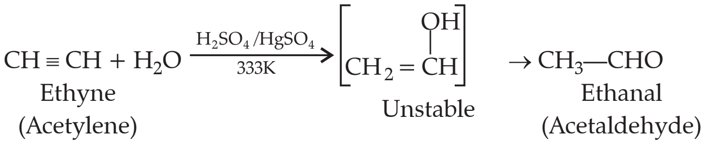
$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow[573K]{Cu} \underset{\text{Aldehyde}}{RCHO + H_2}$$

(iii) From hydrocarbons : From hydrocarbons aldehydes can be prepared either by ozonolysis or by hydration of alkenes.

(a) By Ozonolysis of alkenes :

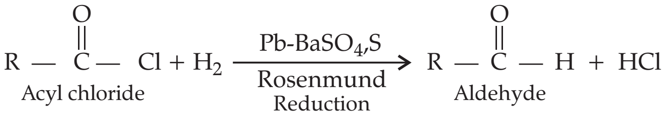


(b) By hydration of alkynes :

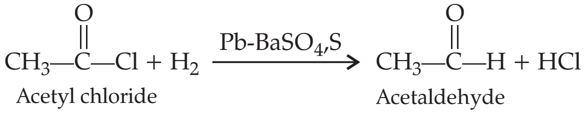


$$\underset{\substack{\text{Ethyne}\\ \text{(Acetylene)}}}{CH \equiv CH} + H_2O \xrightarrow[333K]{H_2SO_4/HgSO_4} \underset{\text{Unstable}}{\left[CH_2 = \overset{\overset{\displaystyle OH}{|}}{CH}\right]} \rightarrow \underset{\substack{\text{Ethanal}\\ \text{(Acetaldehyde)}}}{CH_3-CHO}$$

(iv) From acyl chloride :



$$\underset{\text{Acyl chloride}}{R-\overset{\overset{\displaystyle O}{||}}{C}-Cl} + H_2 \xrightarrow[\substack{\text{Rosenmund}\\ \text{Reduction}}]{Pb\text{-}BaSO_4, S} \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{||}}{C}-H} + HCl$$



$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-Cl} + H_2 \xrightarrow{Pb\text{-}BaSO_4, S} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H} + HCl$$

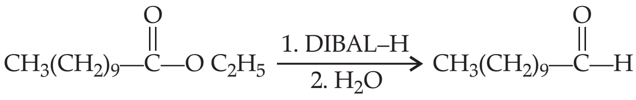
(v) From nitriles and esters :

$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2(H)$

$$R-C \equiv N + HCl + 2(H) \longrightarrow R-CH = NH.\,HCl \xrightarrow[-NH_4Cl]{+H_2O} \underset{\text{Aldehyde}}{RCHO}$$

$$R-CN \xrightarrow[2.\ H_2O]{1.\ AlH\ (i.Bu)_2} \underset{\text{Aldehyde}}{R-CHO}$$

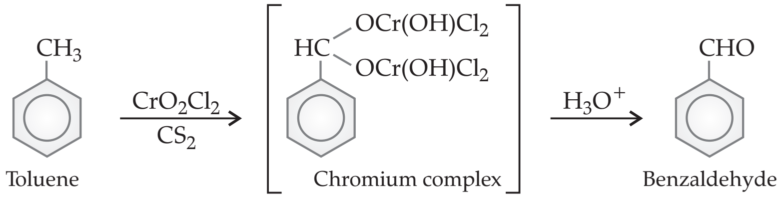
$$CH_3-CH = CH-CH_2-CH_2-CN \xrightarrow[2.\ H_2O]{AlH\ (i.Bu)_2} CH_3-CH = CH-CH_2-CH_2-CHO$$



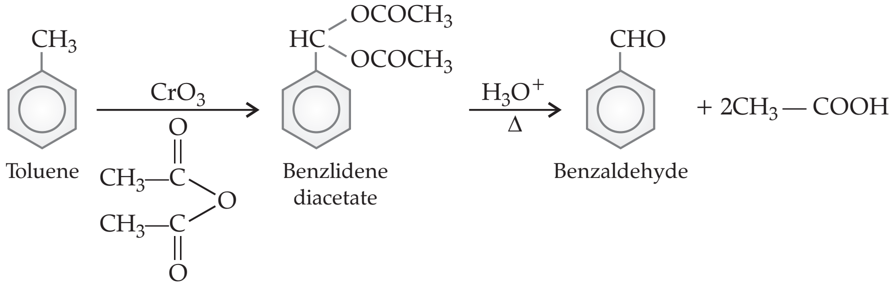
$$CH_3(CH_2)_9-\overset{\overset{\displaystyle O}{||}}{C}-O\,C_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{–}H} \underset{\text{Aldehyde}}{CH_3(CH_2)_9-\overset{\overset{\displaystyle O}{||}}{C}-H}$$

(b) Preparation of Benzaldehyde :

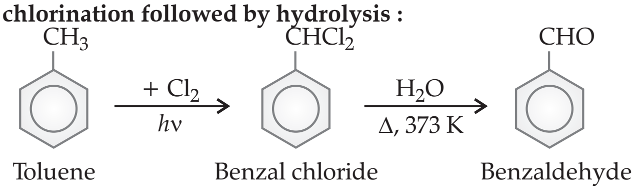
(i) By oxidation of toluene :



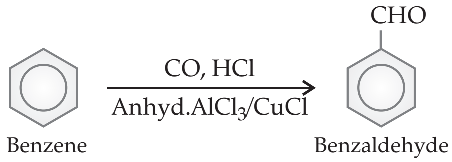
This reaction is called *Etard reaction.*



(ii) By side chain chlorination followed by hydrolysis :

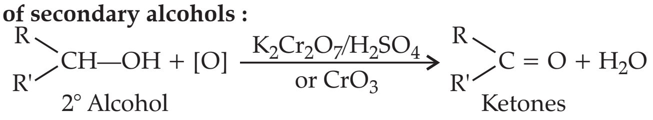


(iii) By Gattermann - Koch reaction :

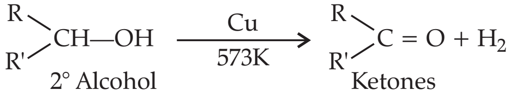


(c) Preparation of Ketones :

(i) By oxidation of secondary alcohols :

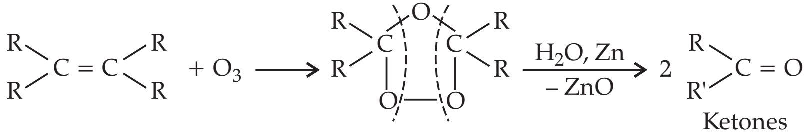


(ii) By dehydrogenation of secondary alcohols :

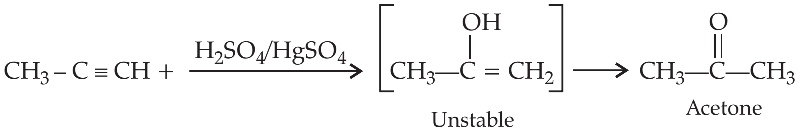


(iii) From Hydrocarbons : From hydrocarbons, Ketones can be prepared either by or by hydration of alkynes.

(1) By ozonolysis of alkynes :



(iv) By hydration of alkynes :

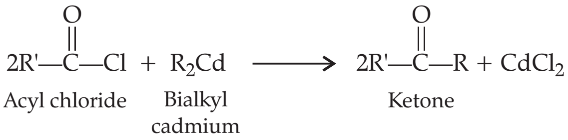


$$CH_3-C\equiv CH + \xrightarrow{H_2SO_4/HgSO_4} \left[CH_3-\overset{\overset{\large OH}{|}}{C}=CH_2 \right] \longrightarrow CH_3-\overset{\overset{\large O}{||}}{C}-CH_3$$

Unstable Acetone

(v) From acyl chlorides :

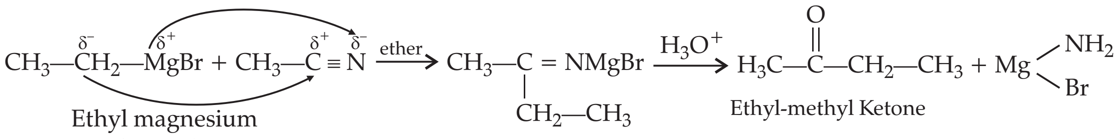
$$2R - MgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$$



$$2R'-\overset{\overset{\large O}{||}}{C}-Cl + R_2Cd \longrightarrow 2R'-\overset{\overset{\large O}{||}}{C}-R + CdCl_2$$

Acyl chloride Bialkyl cadmium Ketone

(vi) From nitriles :



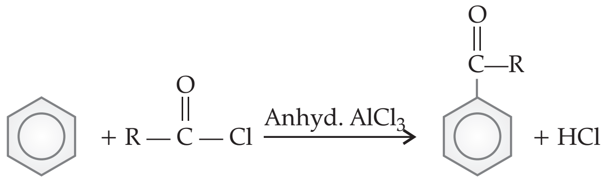
$$CH_3-\overset{\delta^-}{C}H_2-\overset{\delta^+}{Mg}Br + CH_3-\overset{\delta^+}{C}\equiv\overset{\delta^-}{N} \xrightarrow{ether} CH_3-\underset{\substack{|\\CH_2-CH_3}}{C}=NMgBr \xrightarrow{H_3O^+} H_3C-\overset{\substack{O\\||}}{C}-CH_2-CH_3 + Mg\begin{smallmatrix}NH_2\\Br\end{smallmatrix}$$

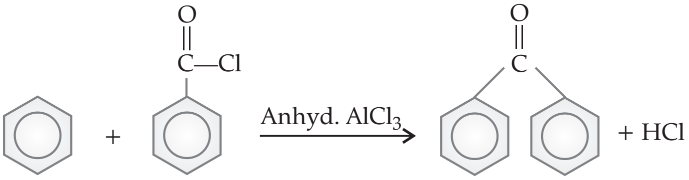
Ethyl magnesium bromide

Ethyl-methyl Ketone

(d) Preparation of Aromatic ketones :

(i) By Friedel Crafts acylation :

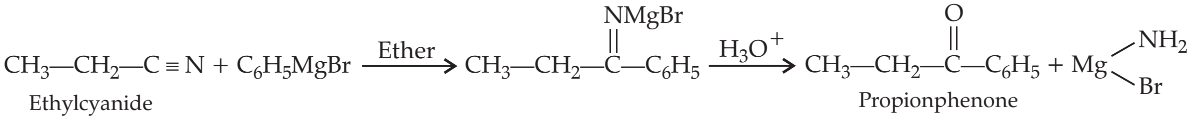




Benzoyl chloride

Benzophenone

(ii) From nitriles :



$$CH_3-CH_2-C\equiv N + C_6H_5MgBr \xrightarrow{Ether} CH_3-CH_2-\overset{\substack{NMgBr\\||}}{C}-C_6H_5 \xrightarrow{H_3O^+} CH_3-CH_2-\overset{\substack{O\\||}}{C}-C_6H_5 + Mg\begin{smallmatrix}NH_2\\Br\end{smallmatrix}$$

Ethylcyanide

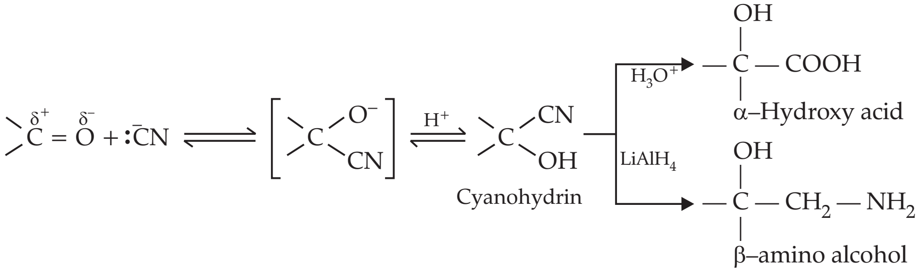
Propionphenone

- **Physical properties of Aldehydes and Ketones :**
  - **(i)** Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have a pleasant smell.
  - **(ii)** Both of these have relatively high b.p. as compared to hydrocarbons of comparable molecular masses due to presence of polar carbonyl group. But they have lower b.p. than alcohols of comparable molecular masses.
  - **(iii)** The lower members of aldehydes and ketones (up to four carbon atoms) are soluble in water due to hydrogen bonding capacity.
- **Chemical properties of Aldehydes and Ketones** : Aldehydes and ketones are highly reactive compounds. Both undergo nucleophilic addition reaction.

Some important nucleophilic Addition reactions :

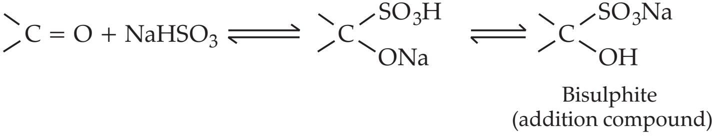
(i) Addition of hydrogen cyanide (HCN) :

$$HCN + OH^- \rightleftharpoons :\bar{C}N^- + H_2O$$



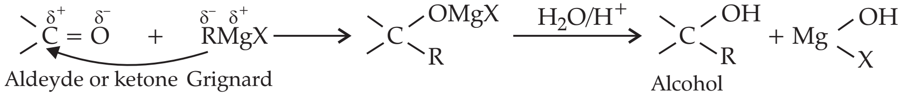
Cyanohydrin

(ii) Addition to sodium hydrogen sulphite :



Bisulphite
(addition compound)

(iii) Addition of Grignard reagent :

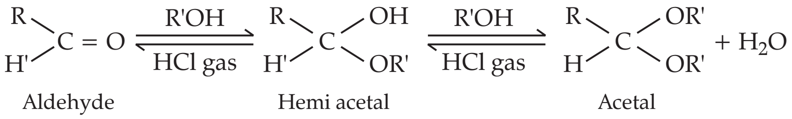


Aldeyde or ketone compound

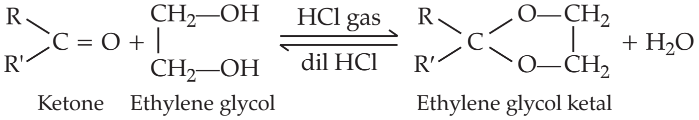
Grignard reagent

Alcohol

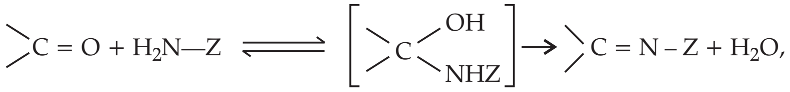
(iv) Addition of Alcohols :



Ketones do not react with monohydric alcohols but react with dihydric alcohols to give ketals.



(v) Addition of ammonia and its derivatives :

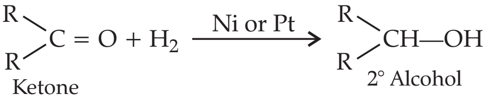


where Z = Alkyl, aryl, OH, NH_2 C_6H_5NH, NH_2CONH_2 etc.

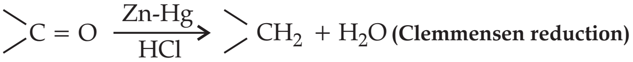
- **Reduction :**

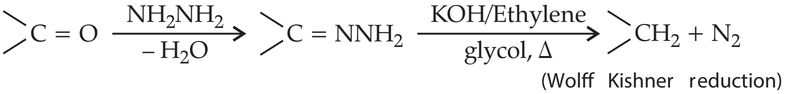
(i) Reduction to alcohols :

$$\underset{\text{Aldehyde}}{R-CHO} + 2[H] \xrightarrow[\text{or } BH_4]{LiAlH_4} \underset{1^\circ \text{ Alcohol}}{R-CH_2-OH}$$



(ii) Reduction to hydrocarbons :

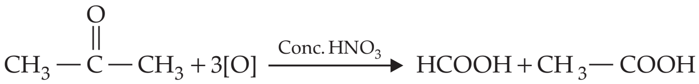




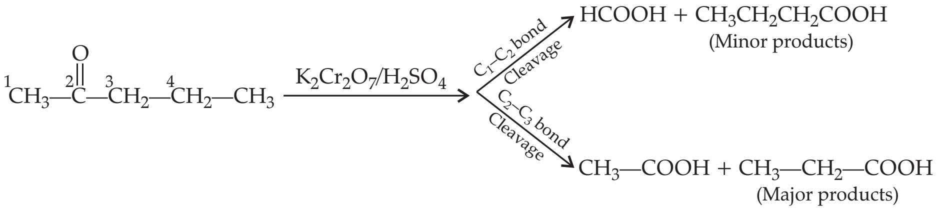
- **Oxidation :** Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents or mild oxidising agent like Tollen's reagent or Fehling's solution.

$$\underset{\text{Aldehyde}}{R-CHO} + [O] \xrightarrow[KMnO_4/H_2SO_4]{K_2Cr_2O_7/H_2SO_4 \text{ or}} \underset{\text{Carboxylic acid}}{R-COOH}$$

Ketones undergo oxidation under vigorous conditions with cleavage of carbon bond.

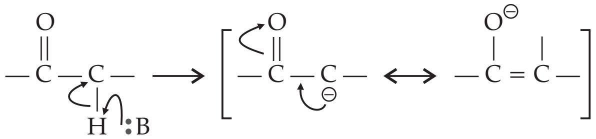


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3[O] \xrightarrow{\text{Conc. } HNO_3} HCOOH + CH_3-COOH$$

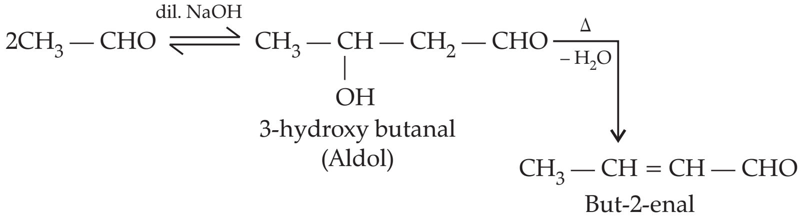


- **Reaction due to α-hydrogen:**

α-hydrogen in aldehydes and ketones is acidic in nature due to strong electron withdrawing effect of carbonyl group. As a result aldehydes and ketones undergo a number of reactions.



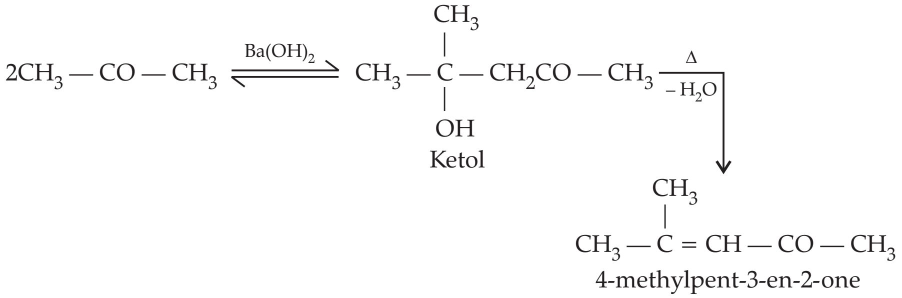
(i) Aldol condensation : Aldehydes and ketones having at least one α-hydrogen react in presence of dilute alkali to form β-hydroxy aldehyde (aldol) or β-hydroxy ketones (Ketol).



$$2CH_3-CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

3-hydroxy butanal (Aldol)

But-2-enal

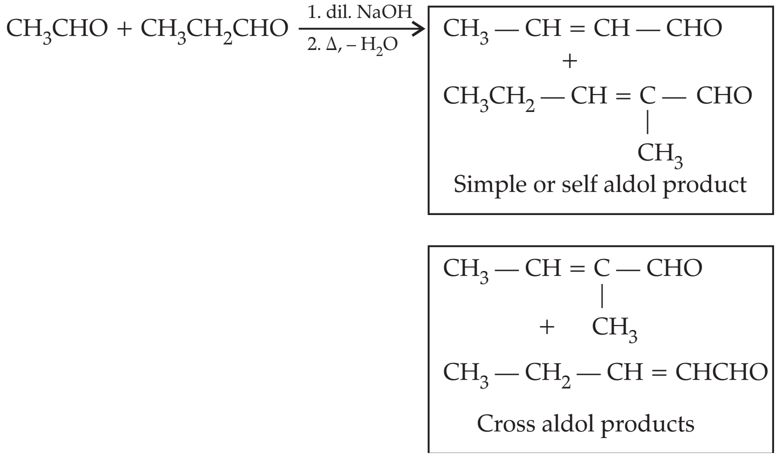


$$2CH_3-CO-CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2CO-CH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CO-CH_3$$

Ketol

4-methylpent-3-en-2-one

(ii) Cross aldol condensation : When two different aldehydes and/or ketones undergo aldol condensation, it is called cross aldol condensation.

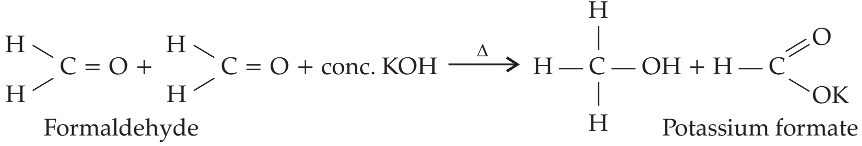


$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta,\ -H_2O]{1.\ \text{dil. NaOH}} \boxed{\begin{array}{c} CH_3-CH=CH-CHO \\ + \\ CH_3CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CHO \end{array}} + \boxed{\begin{array}{c} CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CHO \\ + \\ CH_3-CH_2-CH=CHCHO \end{array}}$$

Simple or self aldol product

Cross aldol products

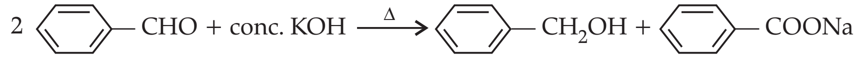
(iii) Cannizzaro Reaction : Aldehydes undergo self oxidation and reduction on heating with conc. alkali. The aldehydes which do not α-hydrogen undergo this reaction.



Formaldehyde

Methyl alcohol

Potassium formate

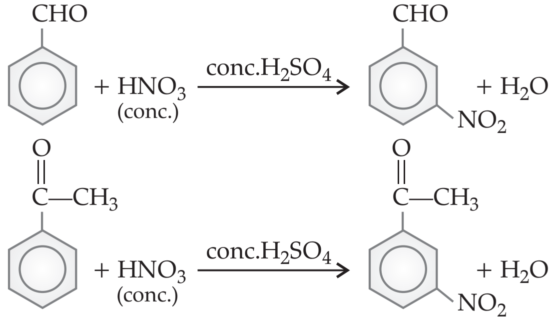


Benzaldehyde

Benzyl alcohol

Sodium benzoate

(iv) Electrophilic substitution reaction :



➢ **Test for aldehydes and ketones :**

(i) Both form coloured compounds with 2, 4-dinitrophenylhydrazine.

(ii) Both gives iodofom test when have one α-hydrogen.

(iii) Aldehydes restore pink colour of Schiff base. Ketones does not give any colour.

(iv) **Fehling's test :** Aliphatic aldehydes reduce the Fehling solution to red cuprous oxide.

$$R - CHO + 2CuO + 5OH^- \longrightarrow R - COOH + \underset{\text{(red ppt.)}}{Cu_2O \downarrow} + 3H_2O$$

Ketones does not give any precipitate.

(v) Ketones are not oxidised by Tollen's reagent

Aldehydes form silver mirror with ammonical silver nitrate (Tollen's reagent) solution

$$R - CHO + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} R - COOH + \underset{\text{(Silver mirror)}}{2Ag} + H_2O + 4NH_3$$

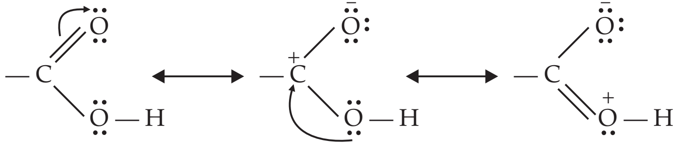
Know the Terms

- **Hydroformylation :** In this process, alkenes give aldehydes by the reaction of hydrogen and CO.
- **Colin's Reagent :** This reagent can be prepared by mixing pyridine (C_5H_5N), CrO_3. and HCl in the presence of dichloromethane. This reagent is used to prepare aldehydes by controlled oxidation process.
- **Baeyer-Villiger Oxidation :** In this process, when ketones are treated with peroxyacids (per acetic acid) *e.g.,* in the presence of an acid catalyst give carboxylic esters by insertion of esters.
- **MPV-Reduction :** It is Meerwein Ponndorf Verily reduction. In this process ketones are reduced to secondary alcohols with isopropyl alcohol in the presence of aluminium isopropoxide.

TOPIC-2
Carboxylic Acids

Quick Review

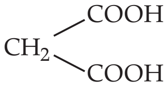
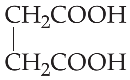
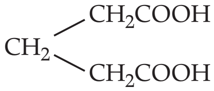
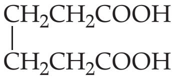
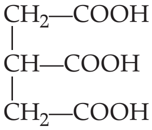
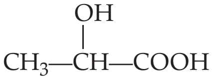
- Carboxylic acids are those compounds which have $-\overset{\overset{O}{\|}}{C}-OH$ group. The carboxyl group is made up of carboxyl, >C=O and hydroxyl, –OH group, hence, its name is carboxyl group.
- Structure of carboxyl group : The bonds to the carboxyl carbon lie in one plane separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon due to possible resonance structure.

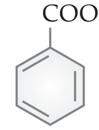
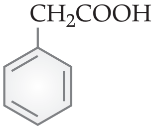
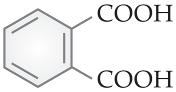
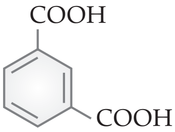
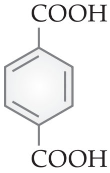


- **Nomenclature of carboxylic acids :** Derived by replacing terminal 'e' of the alkane with 'aic acid'.

Carboxylic acids **Structural formula**	**General formula :** $R-\overset{\overset{O}{\|}}{C}-OH$, where $R = C_nH_{2n+1}$		
	Condensed formula	**Common name**	**IUPAC name**
$R-\overset{\overset{O}{\|}}{C}-OH$	HCOOH	Formic acid	Methanoic acid
$CH_3-\overset{\overset{O}{\|}}{C}-OH$	CH_3COOH	Acetic acid	Ethanoic acid
$CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH$	CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH$	$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\overset{\overset{O}{\|}}{C}-OH$	$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid

Dicarboxylic Acids

 $HOOC—COOH$ (Oxalic acid) Ethane-1, 2-dioic acid	 $CH_2(COOH)_2$ (Malonic acid) Propane-1, 3-dioic acid	 $CH_2COOH—CH_2COOH$ (Succinic acid) Butane-1, 4-dioic acid	 $CH_2(CH_2COOH)_2$ (Glutaric acid) Pentane-1, 5-dioic acid
 $CH_2CH_2COOH—CH_2CH_2COOH$ (Adipic acid) Hexane-1, 6-dioic acid	 $CH_2(COOH)—CH(COOH)—CH_2(COOH)$ Propane-1, 2- 3-tricarboxylic acid	$CH_3—CH = CH—COOH$ Crotonic acid But-2-enoic acid	 $CH_3—CH(OH)—COOH$ Lactic acid 2-Hydroxypropanoic acid

 Benzoic acid or Benzene carboxylic acid	 Phenylacetic acid or 2-Phenylethanoic acid	 Phthalic acid or Benzene-1, 2-dicarboxylic acid	 Isophthalic acid or Benzene-1, 3-dicarboxylic acid	 Terephthalic acid or Benzene-1, 4-dicarboxylic acid

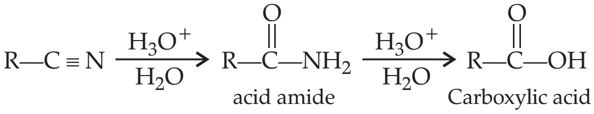
➢ **Methods of preparation of Carboxylic acids :**

(i) By oxidation of primary alcohols and aldehydes :

$$\underset{\text{1° Alcohol}}{R — CH_2 — OH} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Alk.}KMnO_4} \underset{\text{Carboxylic acid}}{R — COOH}$$

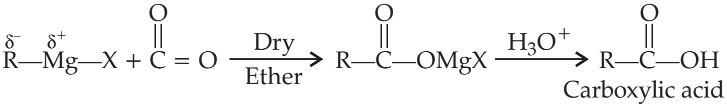
$$\underset{\text{Aldehyde}}{R — CHO} + [O] \xrightarrow{K_2CrO_7/H_2SO_4} \underset{\text{Carboxylic acid}}{R — COOH}$$

(ii) From alkyl cyanides and amides :



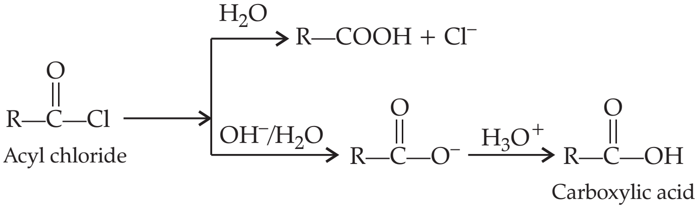
$$R—C \equiv N \xrightarrow[H_2O]{H_3O^+} \underset{\text{acid amide}}{R—\overset{O}{\overset{\|}{C}}—NH_2} \xrightarrow[H_2O]{H_3O^+} \underset{\text{Carboxylic acid}}{R—\overset{O}{\overset{\|}{C}}—OH}$$

(iii) From Grignard reagent :



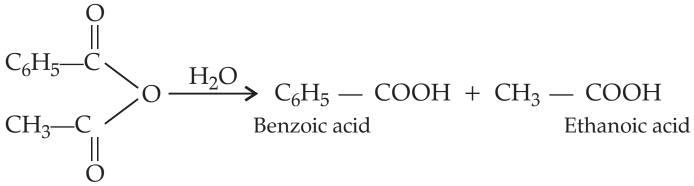
$$\overset{\delta^-}{R}—\overset{\delta^+}{Mg}—X + \overset{O}{\overset{\|}{C}} = O \xrightarrow[\text{Ether}]{\text{Dry}} R—\overset{O}{\overset{\|}{C}}—OMgX \xrightarrow{H_3O^+} \underset{\text{Carboxylic acid}}{R—\overset{O}{\overset{\|}{C}}—OH}$$

(iv) From hydrolysis of acyl halide and acid anhydrides :



$$\underset{\text{Acyl chloride}}{R—\overset{O}{\overset{\|}{C}}—Cl} \longrightarrow \begin{cases} \xrightarrow{H_2O} R—COOH + Cl^- \\ \xrightarrow{OH^-/H_2O} R—\overset{O}{\overset{\|}{C}}—O^- \xrightarrow{H_3O^+} \underset{\text{Carboxylic acid}}{R—\overset{O}{\overset{\|}{C}}—OH} \end{cases}$$

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2C_6H_5 — COOH}$$



$$\underset{\text{Benzoic ethanoic anhydride}}{C_6H_5—\overset{O}{\overset{\|}{C}}—O—\underset{\underset{O}{\|}}{C}—CH_3} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5 — COOH} + \underset{\text{Ethanoic acid}}{CH_3 — COOH}$$

(v) By hydrolysis of esters :

$$\underset{\text{Ethyl butanoate}}{CH_3—CH_2—CH_2—COOCH_2—CH_3} \xrightleftharpoons{NaOH} CH_3—CH_2—CH_2—COONa + CH_3CH_2—OH \xrightarrow{H_3O^+} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

- **Physical properties of Carboxylic acids :**
  - **(i)** Lower members are colourless liquid with pungent smell, while higher members are odourless waxy solid. Benzoic acid is crystalline solid.
  - **(ii)** First four members are water miscible due to tendency to form hydrogen bond. Higher acids are insoluble.
  - **(iii)** Carboxylic acids have higher boiling point due to their ability to form intermolecular hydrogen bonding.
  - **(iv)** Carboxylic acid with even number of carbon atoms have higher melting points than those with odd number of carbon atoms above or below it.
- **Chemical Properties :** Chemical properties of carboxylic acids are classified as follows :
  - **(i) Reaction involving cleavage of O — H bond :** Reactions with metal alkalies :

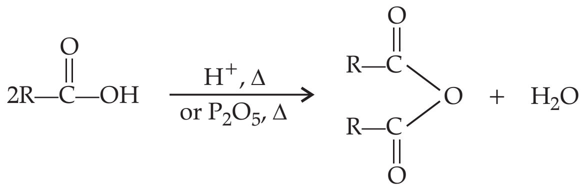
$$2R — COOH + 2Na \longrightarrow \underset{\text{Sodium Carboxylate}}{2R — COONa} + H_2$$

$$R — COOH + NaOH \longrightarrow R — COONa + H_2O$$

$$R — COOH + NaHCO_3 \longrightarrow R — COONa + H_2O + CO_2\uparrow$$

(ii) Reactions involving cleavage of C — OH Bond :

(a) Formation of anhydride :



Acid anhydride

(b) Esterification :

$$R — COOH + R' — OH \xrightleftharpoons{H^+} R — COOR' + H_2O$$

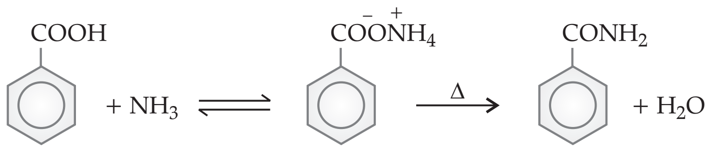
(c) Reaction with PCl_5, PCl_3 and $SOCl_2$

$$R — COOH + PCl_5 \longrightarrow \underset{\text{acyl chloride}}{RCOCl} + POCl_3 + HCl$$

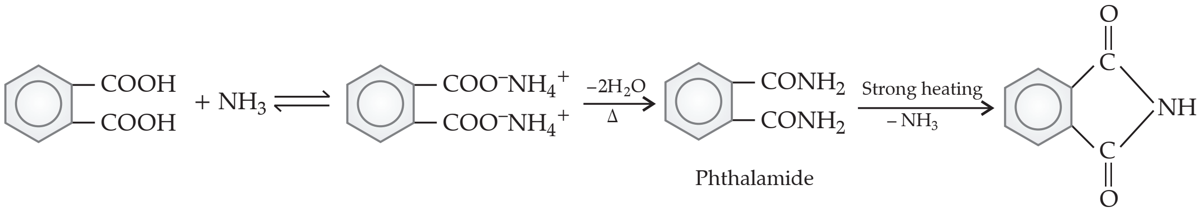
$$R — COOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$$

(d) Reaction with ammonia :

$$\underset{\text{Carboxylic acid}}{R — COOH} + NH_3 \rightleftharpoons R — COO – NH_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Acid amide}}{R — CONH_2}$$



Benzoic acid   Ammonium benzoate   Benzamide



Phthalamide

Phthalimide

(iii) Reduction involving –COOH group :

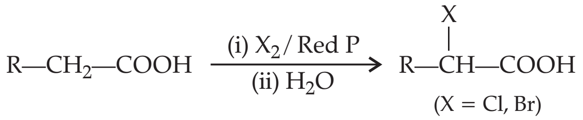
(a) Reduction :

$$R — COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4 \text{ / ether or } B_2H_6} \underset{1° – \text{Alcohol}}{R — CH_2 — OH}$$

(b) Decarboxylation :

$$\underset{\text{Sodium carboxylate}}{R - COONa} \xrightarrow[\Delta]{\text{NaOH and CaO}} R - H + Na_2CO_3$$

(c) Halogenation :

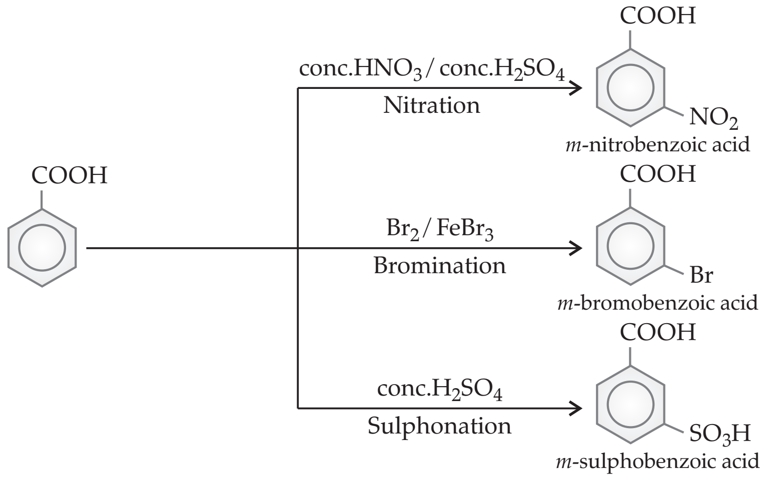


$$R{-}CH_2{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}} R{-}\overset{\overset{X}{|}}{C}H{-}COOH$$

(X = Cl, Br)

This reaction is known as Hell-Volhard Zelinsky reaction.

(iv) Ring Substitution Reaction :



- **Test for Carboxylic acid :**
  - **(i) Litmus test :** It turns blue litmus to red.
  - **(ii) Sodium bicarbonate test :** When they react with $NaHCO_3$, evolve CO_2 gas with brisk effervescence.

    $$\underset{\text{Carboxylic acid}}{RCOOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium carboxylate}}{RCOONa} + H_2O + CO_2\uparrow$$

  - **(iii) Ester formation test :** On heating with ethanol (alcohol) in the presence of conc. H_2SO_4, they give fruity smell of ester.

    $$\underset{\text{Acid.}}{R - COOH} + R' - OH \xrightarrow{H_2SO_4} \underset{\text{(Ester)}}{\underset{\text{Fruity smell}}{RCOOR'}} + H_2O$$

- **Test to distinguish between formic acid and acetic acid :**
  - **(i) Tollens' reagent test :** Formic acid reduces Tollens' reagent to metallic silver but acetic acid does not.

    $$HCOOH + 2\,[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow \underset{\text{(Silver mirror)}}{2Ag\downarrow} + CO_2\uparrow + 2H_2O + 4NH_3$$

  - **(ii) $HgCl_2$ Test :** Formic acid reduces $HgCl_2$ to give white ppt. of Hg_2Cl_2 while acetic acid does not give this test.

    $$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Mercuric chloride}}{2HgCl_2} \longrightarrow \underset{\text{Mercurous chloride (white ppt)}}{Hg_2Cl_2\downarrow} + 2HCl + CO_2\uparrow$$

Chapter - 13 : Amines

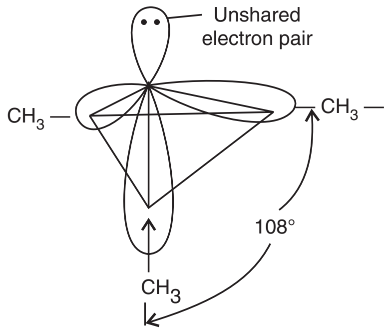
Quick Review

- **Amines :** Amines are considered as amino derivatives of hydrocarbons or alkyl derivatives of ammonia. In these compounds, one, two or three hydrogen atoms are replaced by alkyl or aryl groups. Aliphatic amino compounds are called amino alkanes and aromatic amines are called amino arenes. *e.g.*, CH_3NH_2, $C_2H_5NH_2$, $C_6H_5NH_2$ etc.

- **Classification of amines :**

$-NH_2$	$-\overset{\mid}{N}H$	$-\overset{\mid}{N}-$
Primary	Secondary	Tertiary
(1°)	(2°)	(3°)

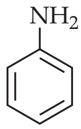
- **Structure of amines :**

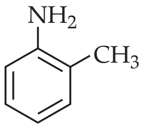
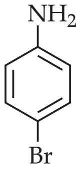
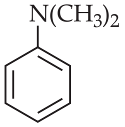


Pyramidal shape of trimethylamine

Nitrogen orbitals in amines are sp^3 hybridised and the geometry is pyramidal. Due to the presence of unshared pair of electrons, the angle C—N—E is less than 109.5°.

- **Nomenclature of Some Alkylamines and Arylamines :**

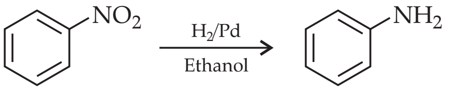
Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-Propylamine	Propan-1-amine
$CH_3-\underset{\substack{\mid\\NH_2}}{CH}-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-\underset{\substack{\mid\\H}}{N}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3-\underset{\substack{\mid\\CH_3}}{N}-CH_3$	Trimethylamine	N, N-Dimethylmethanamine
$C_2H_5-\underset{\substack{\mid\\C_2H_5}}{N}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N, N-Diethylbutylamine	N, N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1, 6-diamine
	Aniline	Aniline or Benzenamine

	*o*-Toluidine	2-Aminotoluene
	*p*-Bromoaniline	4-Bromobenzylamine or 4-Bromoaniline
	N, N-Dimethylaniline	N, N-Dimethylbenzenamine

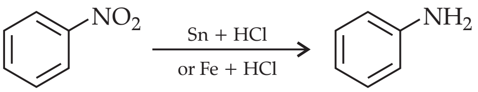
- **Preparation of Amines :**

(i) By reduction of nitro compounds :

(a)



(b)



(c)

$$R-NO_2 + 3H_2 \xrightarrow{Ni} R-NH_2 + 2H_2O$$

1° amine

(ii) By ammonolysis of alkyl halides :

$$R\text{–}X + NH^3 \rightarrow RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

(1°) (2°) (3°) Quaternary ammonium salt

The free amine can be obtained from the ammonium salt by treatment with a strong base :

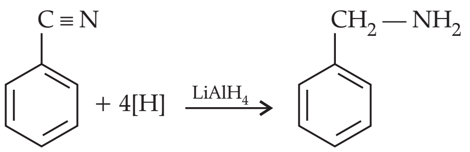
$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \rightarrow R-NH_2 + H_2O + \overset{+}{N}a\overset{-}{X}$$

(iii) By reduction of nitriles :

$$2H_2 + R-C \equiv N \xrightarrow{Ni} R-CH_2-NH_2$$

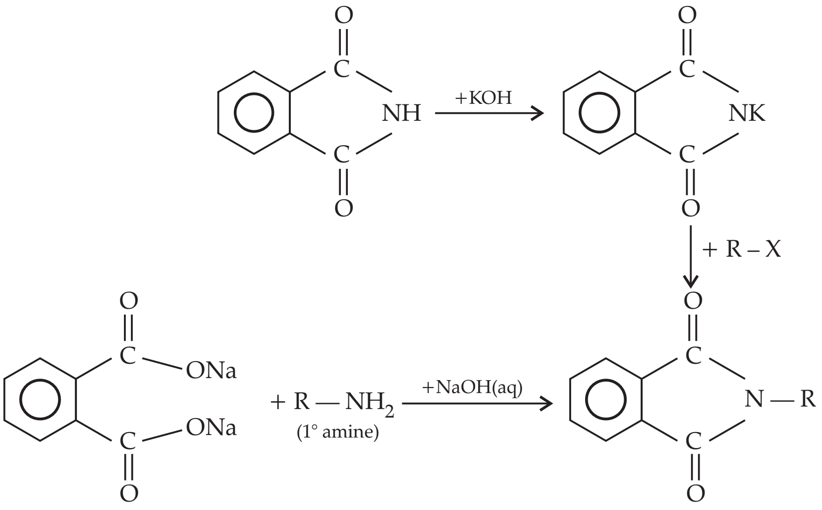
$$R-C \equiv N + 4\,[H] \xrightarrow[\text{or } LiAlH_4]{Na(Hg)\,/\,C_2H_5OH} R-CH_2-NH_2$$

1° amine

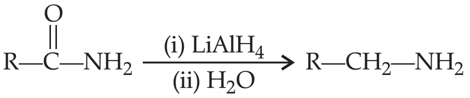


Benzyl amine

(iv) Gabriel phthalimide synthesis :



(v) By reduction of amides :



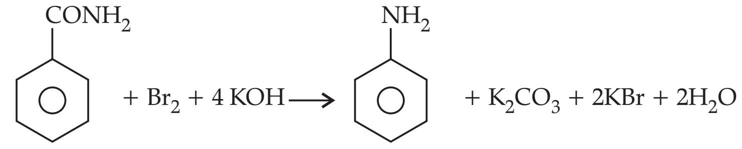
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R-CH_2-NH_2$$

Amine

(vi) By Hoffmann bromamide degradation reaction :

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

1° amine



Benzamide Aniline

- **Physical properties :**

(i) Lower members are combustible gases, members from C_3 to C_{11} are volatile liquids and C_{12} onwards are gaseous. Lower aromatic amines are liquids.

(ii) Pure amines are colourless but develop colour on keeping in air for long time.

(iii) Boiling point increases with an increase in molecular weight. The order of boiling points of isomeric amines :

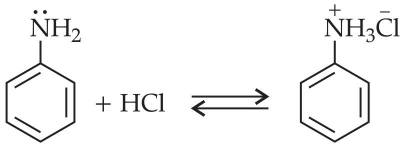
Primary > Secondary > Tertiary.

(vi) Lower members are readily soluble in water which decreases in water and increases in organic solvents with an increase in molecular weight.

- **Chemical properties :**

Reactions due to alkyl group :

$$R-\ddot{N}H_2 + \underset{\text{acid}}{HX} \rightleftharpoons R-\overset{+}{N}H_3\overset{-}{X} \text{ (Salt)}$$



Aniline Anilinium chloride

$$\underset{\text{Amine salts}}{R\overset{+}{N}H_3\overset{-}{X}} + \underset{\text{base}}{\overset{-}{O}H} \longrightarrow \underset{\text{parent}}{R\ddot{N}H_2} + \underset{\text{amine}}{H_2O} + \overset{-}{X}$$

Due the alkyl group, reaction of amines with proton helps to share the proton of the acid and the ammonium ion formed is stabilized by dispersal of positive charge by +I effect of alkyl group. Thus, alkylamines are stronger bases than ammonia. The basic nature of aliphatic amines should increase with increase in the number of alkyl groups. The order of basicity of amines in the gaseous phase follows the expected order :

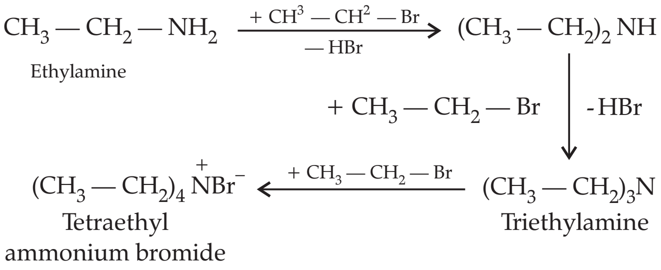
Tertiary amine > Secondary amine > Primary amine > NH_3.

The inductive effect, solvation effect and steric hindrance of the alkyl group decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows :

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

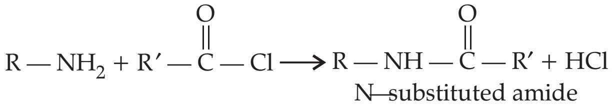
As the $—NH_2$ group is attached directly to the benzene ring in aryl amines, which results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. Thus, proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like $—OCH_3$, $—CH_3$ increase basic strength whereas electron withdrawing groups like $—NO_2$, $—SO_3H$, —COOH, —X decrease it.

(i) Alkylation :



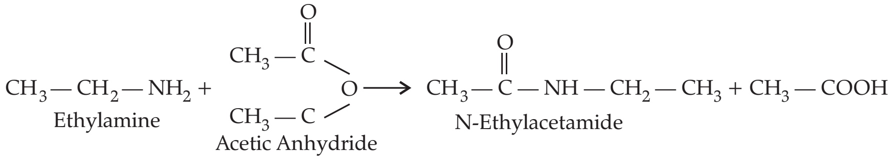
$$CH_3—CH_2—NH_2 \xrightarrow[—HBr]{+CH^3—CH^2—Br} (CH_3—CH_2)_2NH \xrightarrow[-HBr]{+CH_3—CH_2—Br} (CH_3—CH_2)_3N \xrightarrow{+CH_3—CH_2—Br} (CH_3—CH_2)_4\overset{+}{N}Br^-$$

(ii) Acylation :

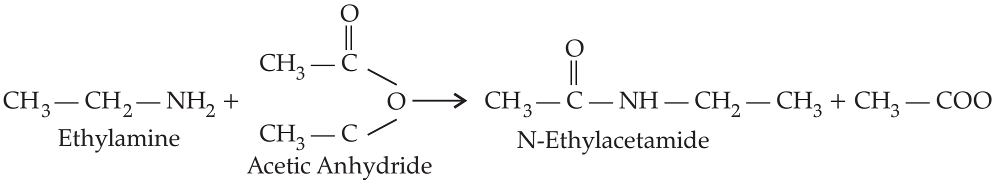


$$R—NH_2 + R'—\overset{O}{\overset{\|}{C}}—Cl \longrightarrow R—NH—\overset{O}{\overset{\|}{C}}—R' + HCl$$

N–substituted amide

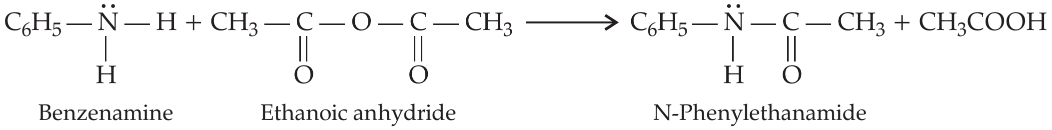


$$CH_3—CH_2—NH_2 + (CH_3CO)_2O \longrightarrow CH_3—\overset{O}{\overset{\|}{C}}—NH—CH_2—CH_3 + CH_3—COOH$$



$$CH_3—CH_2—NH_2 + (CH_3CO)_2O \longrightarrow CH_3—\overset{O}{\overset{\|}{C}}—NH—CH_2—CH_3 + CH_3—COOH$$

Ethylamine Acetic Anhydride N-Ethylacetamide



$$C_6H_5—\underset{H}{\underset{|}{\ddot{N}}}—H + CH_3—\underset{O}{\underset{\|}{C}}—O—\underset{O}{\underset{\|}{C}}—CH_3 \longrightarrow C_6H_5—\underset{H}{\underset{|}{\ddot{N}}}—\underset{O}{\underset{\|}{C}}—CH_3 + CH_3COOH$$

Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

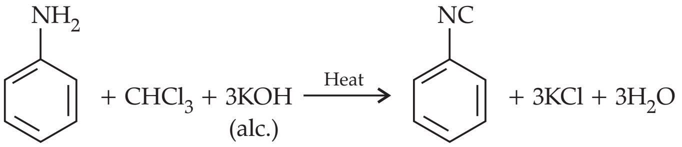
Benzoylation :

$$CH_3NH_2 + C_6H_5COCl \rightarrow CH_3NHCOC_6H_5 + HCl$$

Methlamine Benzoyl chloride N–Methylbenzamide

(iii) Carbylamine reaction : Secondary and tertiary amines do not give this reaction. This reaction is used as a test for primary amines.

$$R—NH_2 + CHCl_3 + \underset{(alc.)}{3KOH} \xrightarrow{Heat} R—NC + 3KCl + 3H_2O$$



(iv) Reaction with nitrous acid :

$$\underset{1^\circ \text{ amine}}{R-NH_2} + HNO_2 \xrightarrow{NaNO_2+HCl} [R-\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

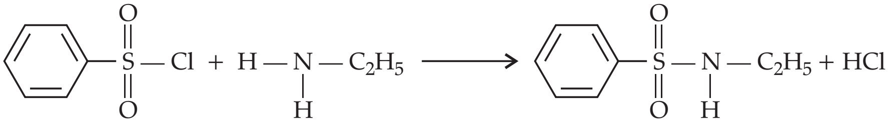
$$\underset{2^\circ \text{ amine}}{R_2NH} + HNO_2 \longrightarrow \underset{\text{N-Nitrosamine}}{R_2N-N=O} + H_2O$$

$$\underset{3^\circ \text{ amine}}{R_3N} + HNO_2 \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{R_3NHNO_2}$$

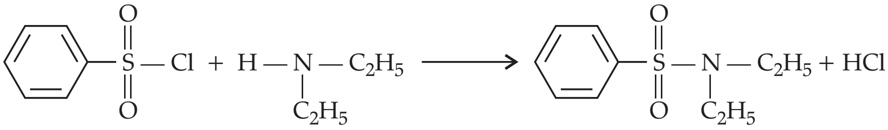
$$\underset{\text{Aromatic amine}}{C_6H_5-NH_2} \xrightarrow[273-278K]{NaNO_2+2HCl} \underset{\text{Benzenediazonium chloride}}{C_6H_5-\overset{+}{N_2}\overset{-}{Cl}} + NaCl + 2H_2O$$

Secondary and tertiary amines react with nitrous acid in a different manner.

(v) Reaction with arylsulphonyl chloride :



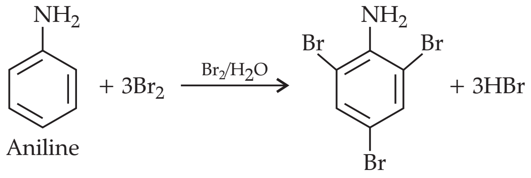
Benzenesulphonyl chloride (Hinsberg's reagent)
Primary amine
N-Ethylbenzenesulphonamide (soluble in alkali)



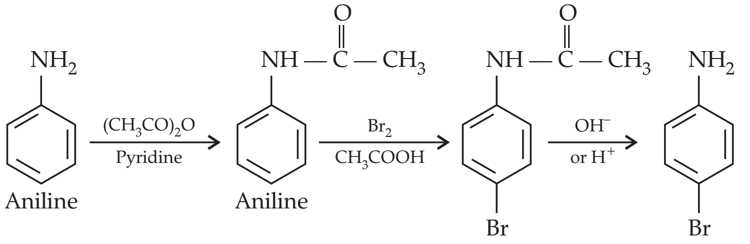
Secondary amine
N- N-Diethylbenzenesulphonamide

Tertiary amines do not react with benzenesulphonyl chloride.

(vi) Bromination :

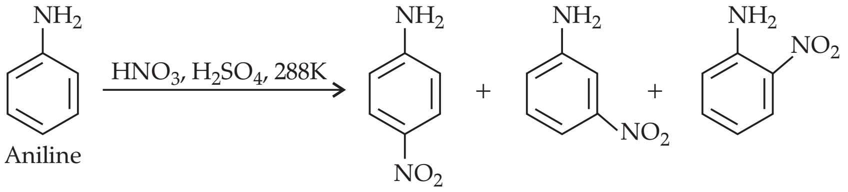


Aniline
2, 4, 6-Tribromoaniline



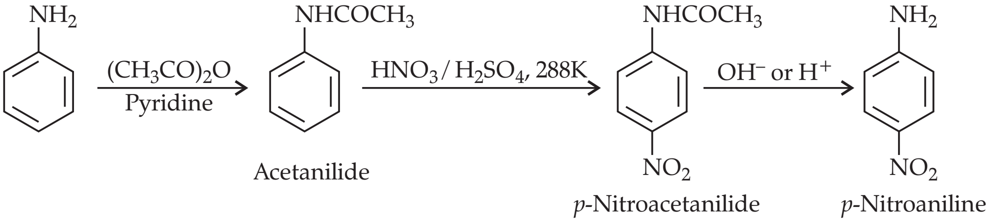
Aniline
Aniline
(Major)
p-Bromoaniline

(vii) Nitration :

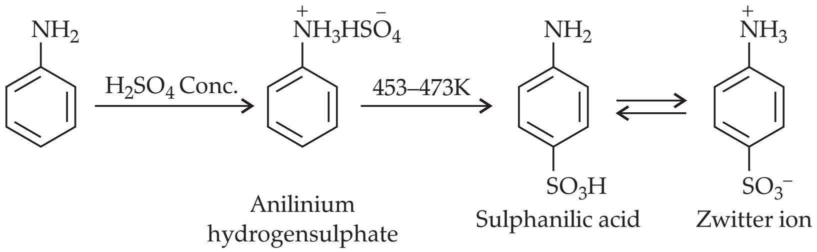


Aniline
(51%) p-nitroaniline
(47%) m-nitroaniline
(2%) o-nitroaniline

(viii) Preparation of monosubstituted aniline derivative by acetylation of —NH_2 group :



(ix) Sulphonation :

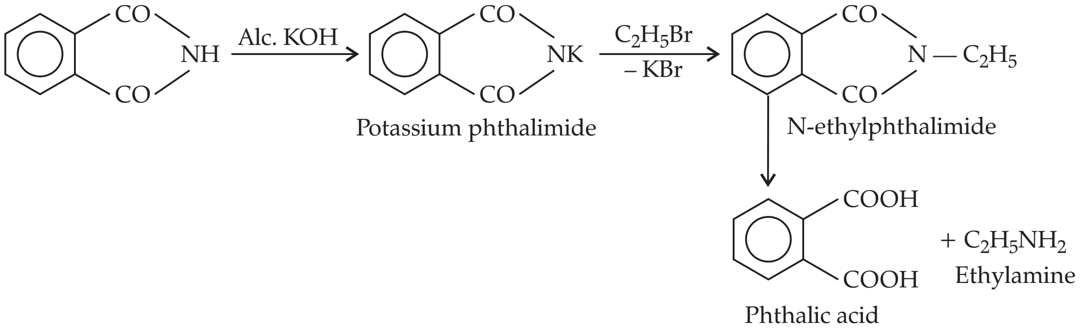


Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride.

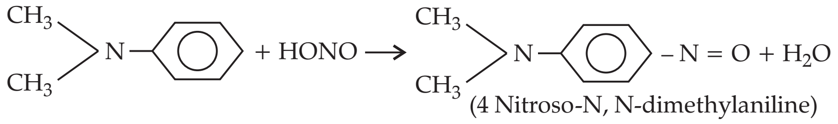
(x) Ammonolysis : Alkyl halide reacts with ammonia to form primary amine. The reaction of ammonia with alkyl halide is known as ammonolysis.

$$C_2H_5I \xrightarrow[-HI]{NH_3/343K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2NH \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3N \xrightarrow[C_2H_5I]{} [(C_2H_5)_4N^+]I^-$$

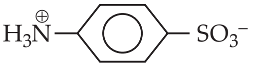
(xi) Gabriel Phthalimide Synthesis : In Gabriel phthalimide synthesis, pure primary aliphatic amines can be prepared by this process. In this process, phthalimide is reacted with alcoholic KOH to get potassium phthalimide which reacts with alkyl halide to form N-alkyl phthalimide which on basic hydrolysis gives primary amine and phthalic acid. Phthalic acid can be reused to get phthalimide.



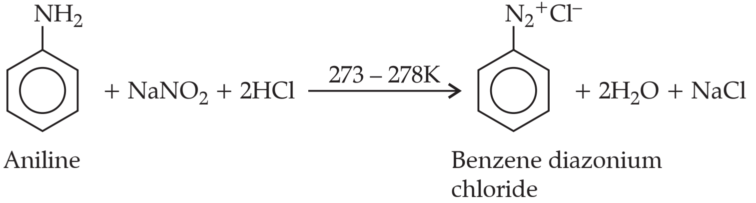
(xii) Nitrosation : Nitrosation is a process of reacting aromatic amines with nitrous acid to introduce nitroso group in it *e.g.*,



(xiii) Zwitter ion formation : Zwitter ion is the ion which contains both positive and negative ions. It contains acidic as well as basic groups in the same molecule e.g.,



(xiv) Diazotisation : Diazotisation is a process of treating primary aromatic amines with nitrous acid at 273 – 278 K to get diazonium salts which are very useful compounds.

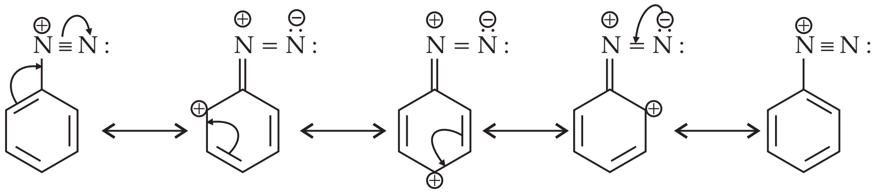


(xv) Friedel-Crafts reaction : Aniline does not undergo Friedel-Crafts reaction as it forms a salt with $AlCl_3$ which is a Lewis acid.

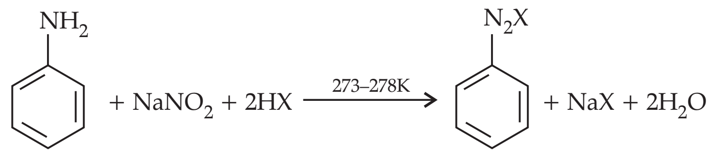
- **Diazonium salts :**

(i) General formula : $R\overset{+}{N_2}\overset{-}{X}$ where R stands for an aryl group and X^- ion may be Cl^-, Br^-, HSO_4^-, BF_4^- etc.

(ii) Stability of diazonium salts : Arenediazonium salts are more stable than alkyl diazonium salts due to the dispersal of the positive charge over the benzene ring.



(iii) Preparation of diazonium salts :



Aniline

Benzene diazonium salt

(iv) Chemical properties :

(a) Reactions involving displacement of nitrogen :

(i) Replacement by halide or cyanide ion–

$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{CuCl/HCl} ArCl + N_2$$
$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{CuBr/HBr} ArBr + N_2$$
$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{CuCN/KCN} ArCN + N_2$$

Sandmeyer's reaction

$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

Gatterman's reaction

(ii) Replacement by iodide ion–

$$Ar\overset{+}{N_2}\overset{-}{Cl} + KI \longrightarrow ArI + KCl + N_2$$

Benzene diazonium chloride Iodobenzene

(iii) Replacement by fluoride ion–

(a) $ArN_2^+Cl^- + HBF_4 \longrightarrow ArN_2^+BF_4^-$

(b) $Ar\overset{+}{N_2}\overset{-}{BF_4} \xrightarrow{\Delta} Ar — F + BF_3 + N_2$

(iv) Replacement by H—

(a) $Ar\overset{+}{N_2}\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

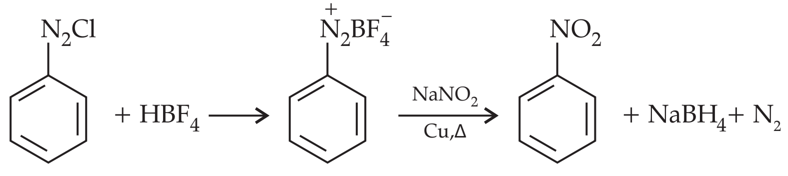
(b) $Ar\overset{+}{N_2}\overset{-}{Cl} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$

(v) Replacement by hydroxyl group–

$$Ar\overset{+}{N_2}\overset{-}{Cl} + H_2O \xrightarrow{\Delta} ArOH + N_2 + HCl$$

Phenol

(vi) Replacement by — NO_2 group—

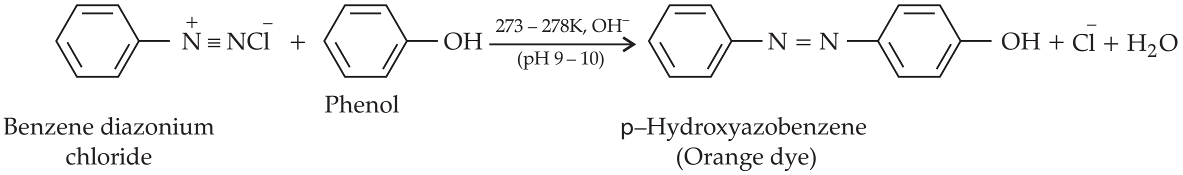


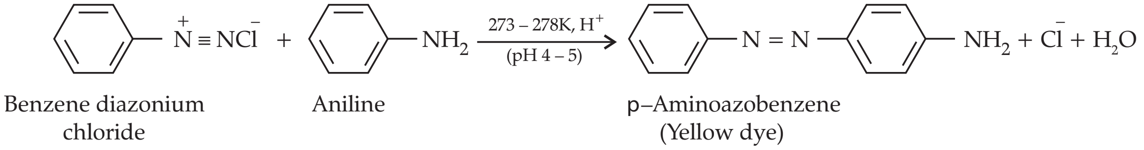
Fluoroboric acid

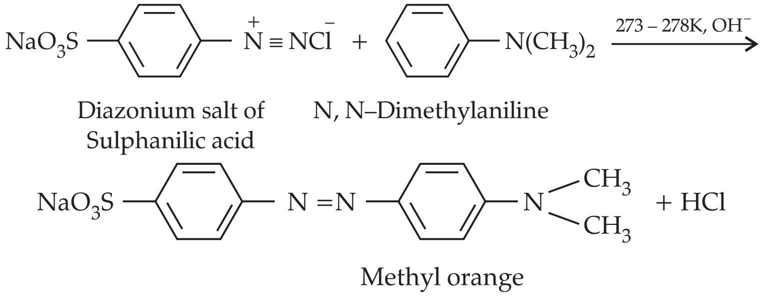
Nitrobenzene

(b) Reactions involving retention of diazo group :

(i) Coupling reaction : The reaction of diazonium salts with phenols and aromatic amines to form azo compounds with the general formula, Ar — N = N — Ar is known as coupling reaction.

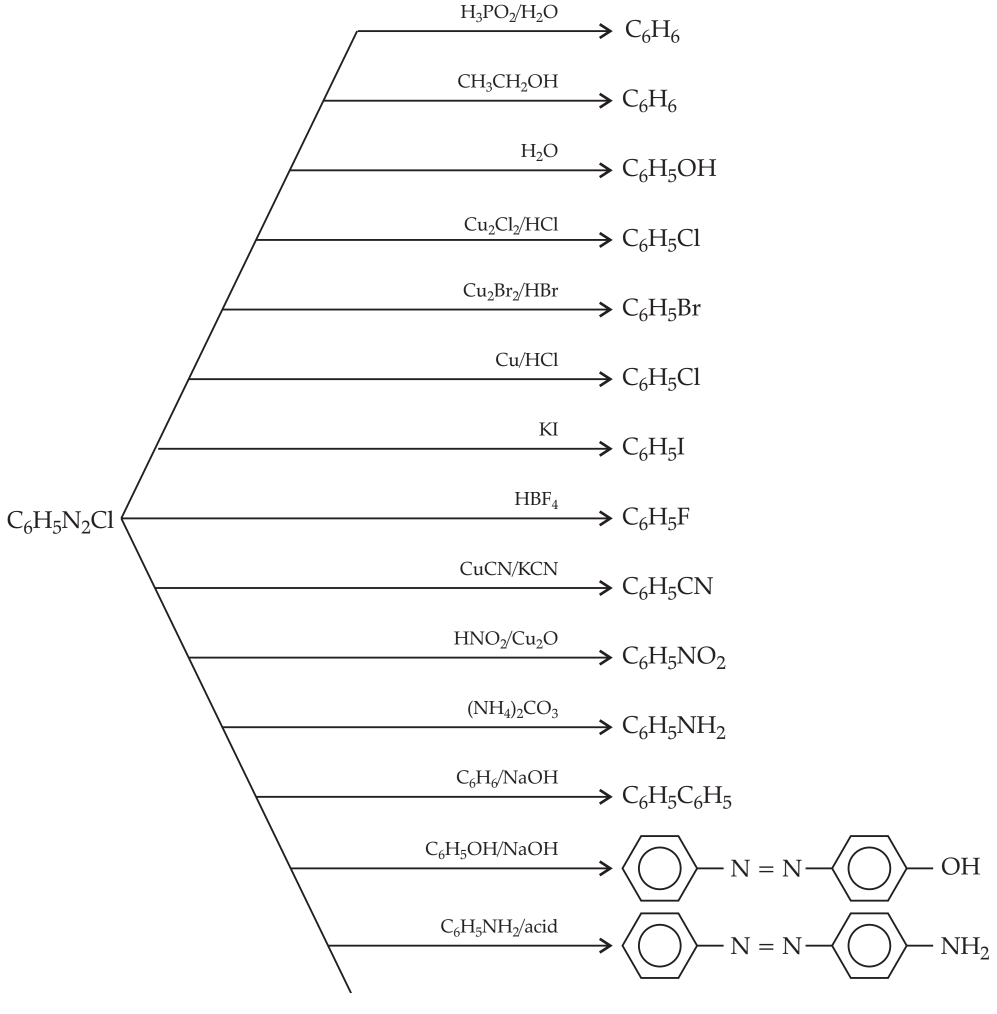


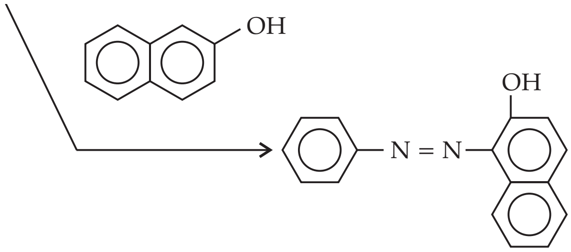




(v) Importance of Diazonium salts : They are very good intermediates for the introduction of – F, – Cl, – Br, – I, – CN, – OH, – NO_2 groups into aromatic ring. Cyanobenzene can be prepared from diazonium salts.

- **Synthesis of organic compounds form diazonium salts :**

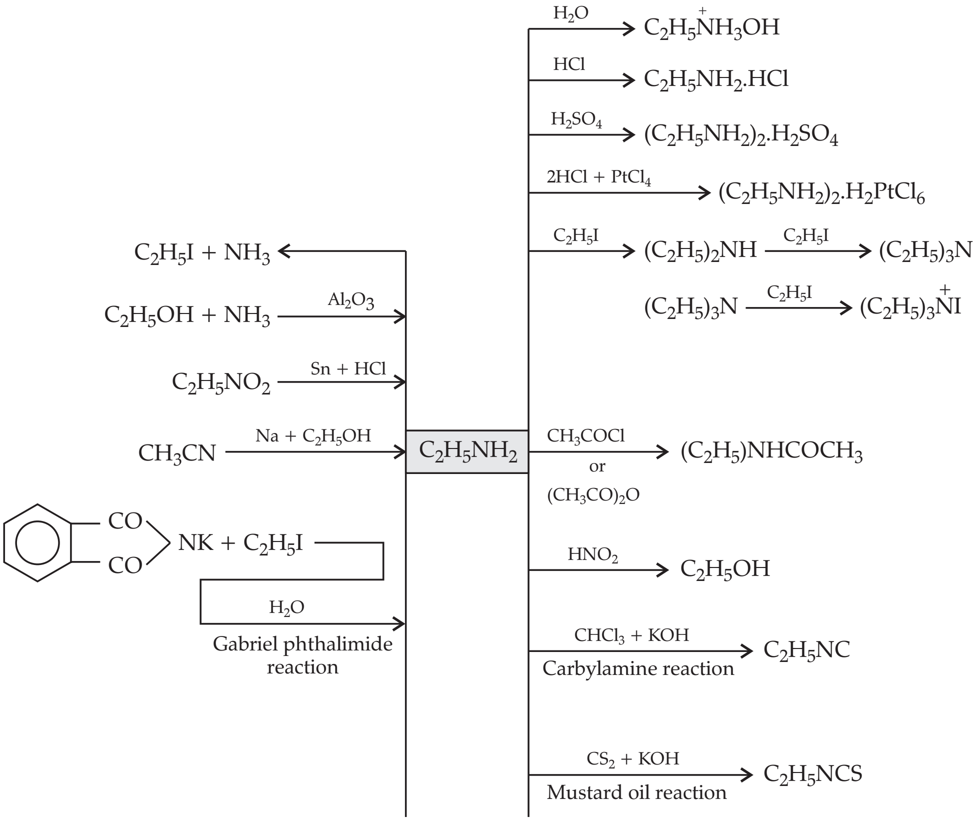


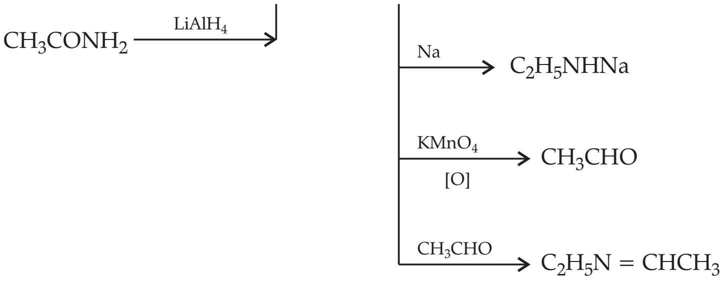


- **Identification of primary, secondary and tertiary amines :**

S.No.	Test	Primary amine	Secondary amine	Tertiary amine
(i)	Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives oily nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold soluble in water and on heating gives nitrososamine.
(ii)	Reaction with benzene sulphonyl chloride (Hinsberg's reagent).	Gives N-alkyl benzenesulphonamide which is soluble in alkali.	Gives N, N-dialkyl benzene sulphonamide which is insoluble in alkali.	No reaction.
(iii)	**Carbylamine test :** Reaction with chloroform and alcoholic KOH.	Forms carbylamine or isocyanide (RNC) with characteristic unpleasant odour.	No reaction	No reaction.
(iv)	**Hoffman's mustard oil reaction :** Reaction with CS_2 and $HgCl_2$.	Forms N-substituted isothiocyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.

- **Methods of preparation and reactions of ethylamine :**





Know the Terms

- **Gomberg-Bachmann reaction :** In the alkaline medium of sodium hydroxide, benzene diazonium chloride reacts with aromatic compound like benzene. When the diazo group is replaced by phenyl or aryl group. The reaction is called Gomberg-Bachmann reaction.
- **Baker-Mulliken test :** The hydroxyl amines when warmed with Tollen's reagent convert it to metallic silver. This reaction is used as a test for nitro compound and known as Baker-Mulliken test.
- **Schotten Baumann reaction :** Benzoylation of amines with benzoyl chloride is known as Schotten Baumann reaction.
- **Cope Elimination :** It is quite useful to determine the structure of tertiary amines. It involves the treatment of a tertiary amine in which one of the alkyl group contains at least one β-hydrogen atom with hydrogen peroxide to get an amine oxide which later upon heating forms an alkane and a dialkyl hydroxyl amine.

❑❑

Chapter - 14 : Biomolecules

TOPIC-1

Carbohydrates, their Classification and Importance

Quick Review

- **Biomolecules :** Biomolecules are the naturally occurring organic compounds present as essential constituents of living organism in different cells. Examples : polysaccharides, proteins etc.
- **Carbohydrates :** Carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or compound which produce such units on hydrolysis. *e.g.,* cellulose, glycogen, starch etc.
- **Classification of carbohydrates :** On the basis of the molecular size, carbohydrates have been classified into following four types :

(i) **Monosaccharides :** Monosaccharides include non-hydrolysable carbohydrates. They are soluble in water. Those containing aldehydic group are called aldoses while other containing a ketonic group are called ketoses. Some monosaccharides with example are given in the table as shown below :

Class	Molecular Formula	Structural formula	Example
		Aldoses	
Aldotriose	$C_3H_6O_3$	$CH_2OH.CHOH.CHO$	Glycerol aldehyde
Aldotetrose	$C_4H_8O_4$	$CH_2OH.(CHOH)_2.CHO$	Arithriose, Thriose
Aldopentose	$C_5H_{10}O_5$	$CH_2OH.(CHOH)_3\ CHO$	Arabinose, Ribose, Xylose, Lixose
Aldohexose	$C_6H_{12}O_6$	$CH_2OH.(CHOH)_4CHO$	Glucose, Mannose, Galactose, Talose, Idose, Alose, Altrose

		Ketoses	
Ketotriose	$C_3H_6O_3$	$CH_2OH.CO.CH_2OH$	Dihydroxy acetone
Ketotetrose	$C_4H_8O_4$	$CH_2OHCO\ CHOH\ CH_2OH$	Erythrulose
Ketopentose	$C_5H_{10}O_5$	$CH_2OH.CO(CHOH)_2CH_2OH$	Ribulose, Xylulose
Ketohexose	$C_6H_{12}O_6$	$CH_2OHCO\ (CHOH)_3.CH_2OH$	Fructose, Sorbose, Tagatose etc.

(ii) Disaccharides : Those carbohydrates, which on hydrolysis yields two molecules of monosaccharides are called disaccharides. They are crystalline, soluble in water and sweet in taste. *e.g.*, cane sugar, maltose etc.

(iii) Oligosaccharides : Those carbohydrates which yields 2 to 10 monosaccharide molecules on hydrolysis are called oligosaccharides. *e.g.*, raffinose on hydrolysis gives glucose, fructose and galactose.

(iv) Polysaccharides : Those carbohydrates, which produce large number of monosaccharide units on hydrolysis are called polysaccharides. They are formed by linking together a large number of monosaccharide units through glycosidic linkage. *e.g.*, starch, amylose and cellulose.

➢ **Sugar :** In general, monosaccharides and oligosaccharides are crystalline solids, soluble in water, sweet in taste. They are collectively called sugar. *e.g.*, glucose, fructose, sucrose etc. They are of two types :

(i) Reducing sugars : Those carbohydrates which contain free aldehydic or ketonic group and reduce Fehling's solution and Tollen's reagent are known as reducing sugars. *e.g.*, all mono-saccharides, maltose.

(ii) Non-reducing sugars : Those carbohydrates which do not have free aldehydic or ketonic group and do not reduce Fehling's solution or Tollen's reagent are known as non-reducing sugars. *e.g.*, sucrose.

➢ **Glucose :** Glucose occurs in nature in free as well as in combined form. It is present in sweet fruits and honey.

- **Methods of preparation of Glucose :**

(i) From sucrose :

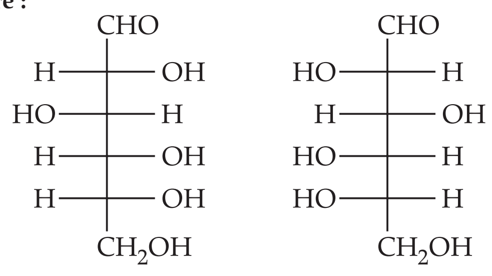
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) From starch : Commercially, glucose is obtained by hydrolysis of starch by boiling it with dil H_2SO_4 at 393 K under pressure.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{393 K, 2-3 bar}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

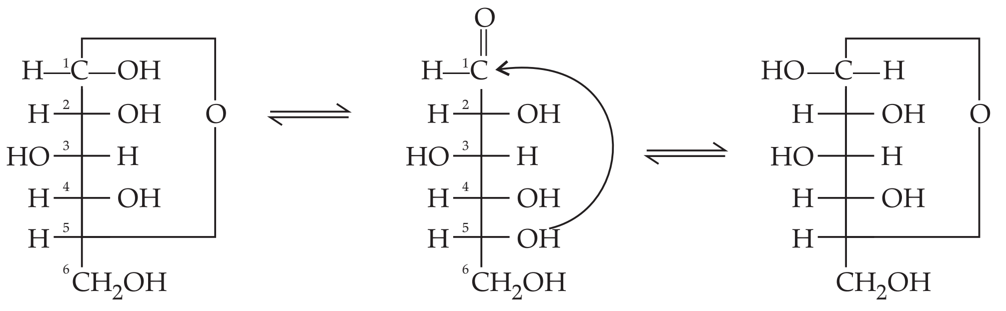
- **Structure of Glucose :** It is a six carbon straight chain aldose which has one aldehydic group (–CHO), one primary hydroxyl group (–CH_2OH) and four secondary hydroxyl groups (–CHOH).

(a) Open chain structure :



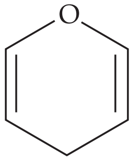
D–(+)–Glucose L–(–)–Glucose

(b) Cyclic structure :

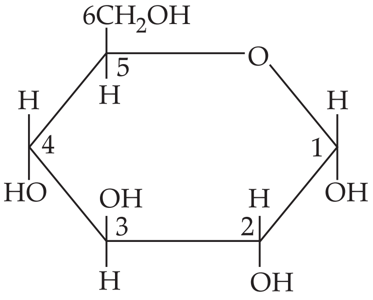


α-D-(+)–Glucose β-D–(+)–Glucose

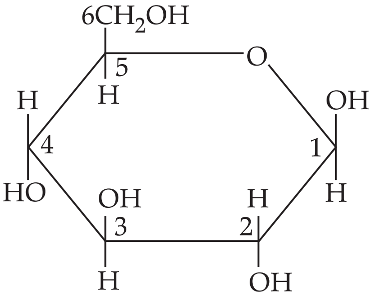
(c) Haworth structure :



Pyran



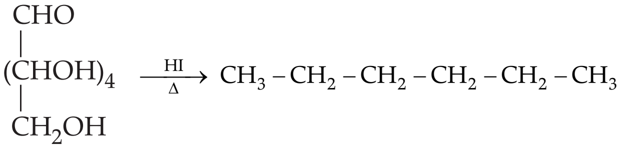
α-D–(+)–Glucopyranose



β-D –(+)–Glucopyranose

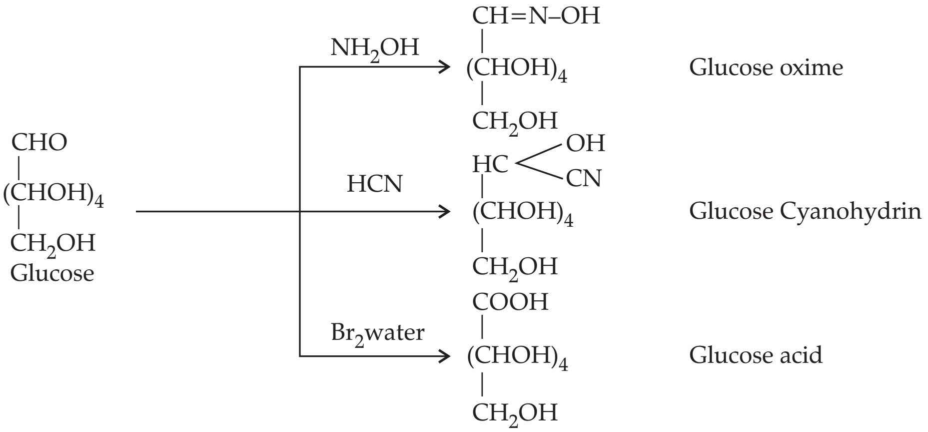
- **Reactions of Glucose :**

(i) With HI :

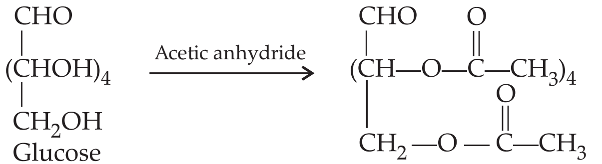


$$\underset{\text{Glucose}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}\xrightarrow[\Delta]{HI}CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

(ii) Reactions showing the presence of carbonyl group (> C = 0) :

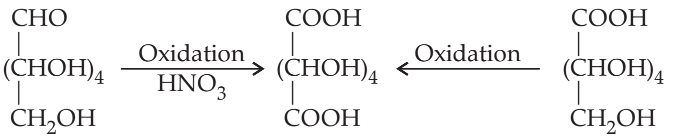


(iii) Acetylation of glucose :



$$\underset{\text{Glucose}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}\xrightarrow{\text{Acetic anhydride}}\underset{\text{Glucose pentaacetate}}{\begin{array}{l}CHO\\|\\(CH-O-\overset{\overset{O}{\|}}{C}-CH_3)_4\\|\\CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3\end{array}}$$

(iv) Reaction showing the presence of alcoholic (– OH) group :

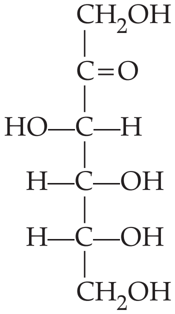


$$\underset{\text{Glucose}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}\xrightarrow[HNO_3]{\text{Oxidation}}\underset{\text{Saccharic acid}}{\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\COOH\end{array}}\xleftarrow{\text{Oxidation}}\underset{\text{Gluconic acid}}{\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}$$

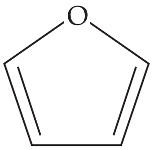
➢ **Fructose : It is a ketohexose obtained by hydrolysis of disaccharide.**

- **Structure of Fructose :**

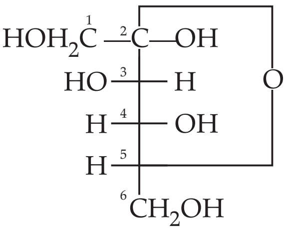
(a) Open chain structure



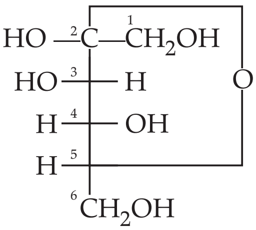
(b) Cyclic structure :



Furan

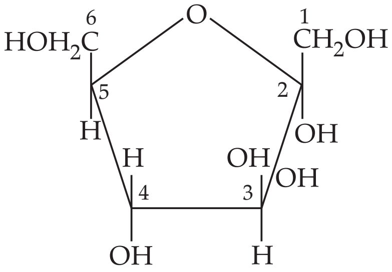


α-D–(+)–Fructofuranose

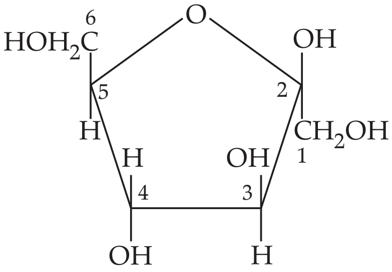


β-D–(–)Fructofuranose

(c) Haworth structure :



α-D–(–)–Fructofuranose

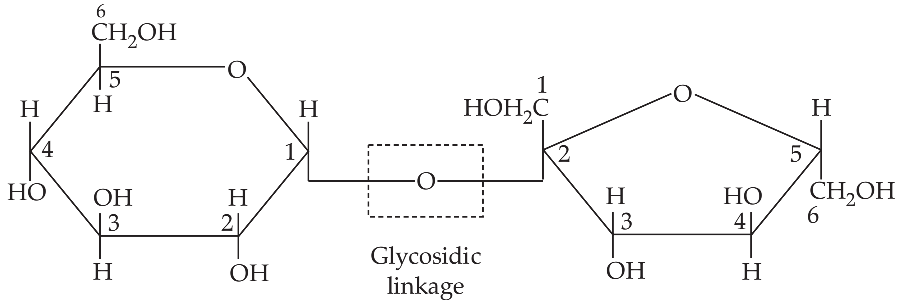


β-D–(–)–Fructofuranose

- **Sucrose :**

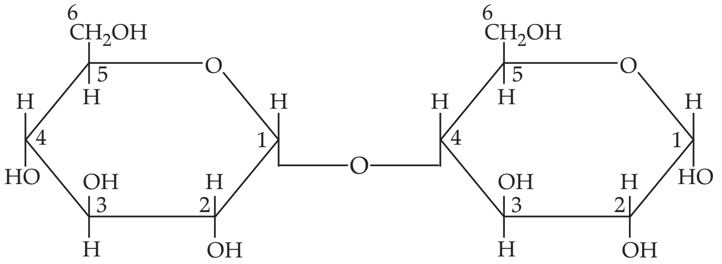
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{D–(+)–Glucose}}{C_6H_{12}O_6} + \underset{\text{D–(–)–Glucose}}{C_6H_{12}O_6}$$

- **Structure :**



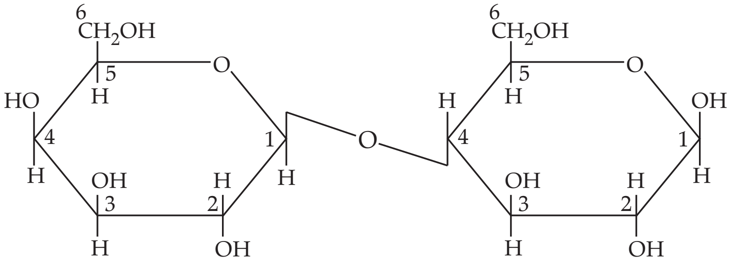
α – D–Glucose β –D–Fructose

- Maltose molecule is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II).



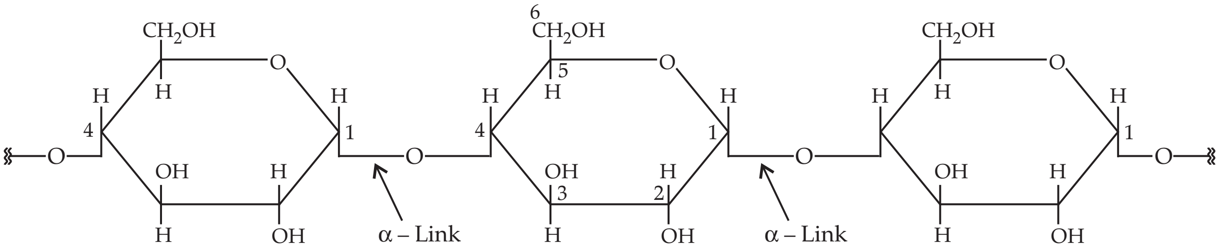
α – D–Glucose I β – D–Glucose II

- Lactose is a reducing sugar



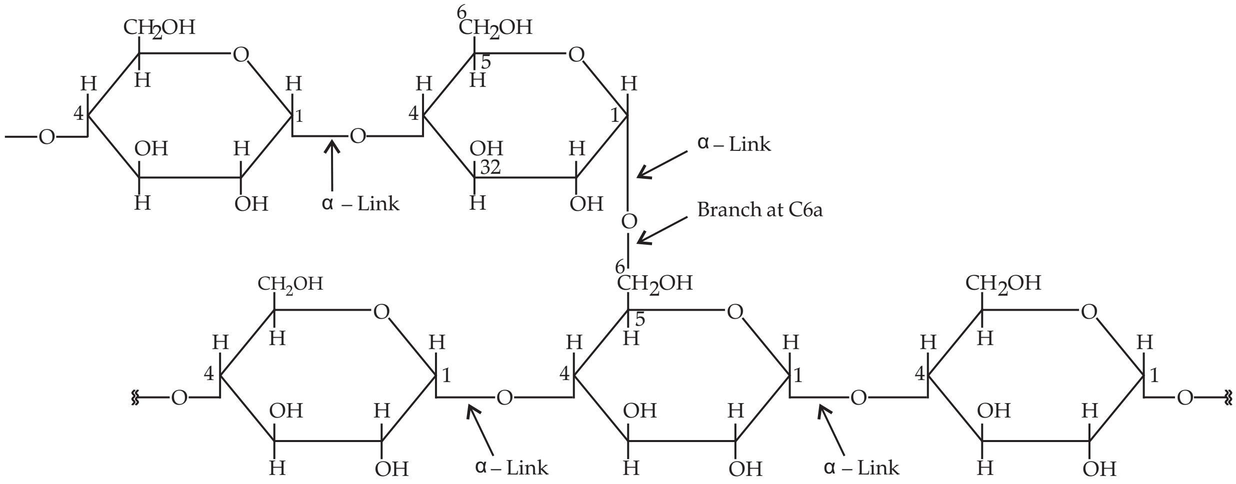
α – D–Galactose β – D–Glucose

- **Polysaccharides :** Carbohydrates which contain a large number of monosaccharide units joined together by glycosidic linkages.
  - **(a)** Starch is a polymer of α-glucose and consists of two components – amylose and amylopectin. Amylose is a long unbranched chain with 200 – 1000 α-D-(+)-glucose units held by Cl – C4 glycosidic linkage.



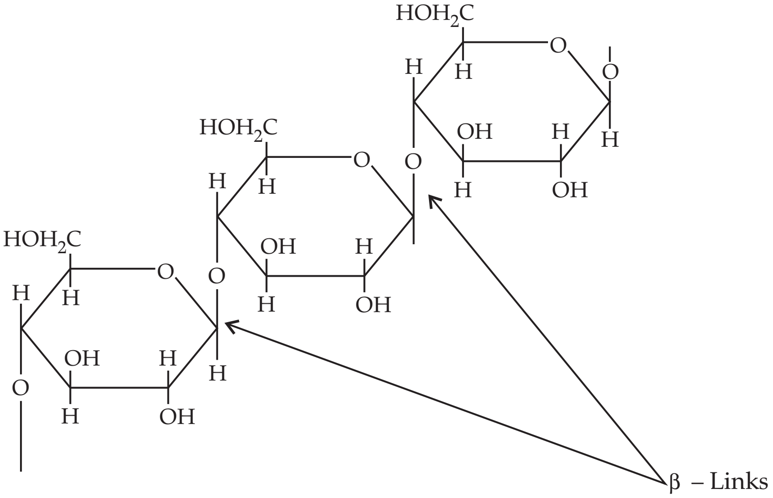
Amylose

Amylopectin is a branched chain polymer of α-D-glucose units in which the chain is formed by C1 – C6 glycosidic linkage whereas branching occurs by C1 – C6 glycosidic linkage.∝



Amylopectin

  - **(b)** Cellulose is a polysaccharide whose fundamental structural unit is β-D-glucose joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.



(c) Glycogen is an animal starch with structure similar to amylopectin and has more branches.

- **Importance of Carbohydrates :**
  - **(i)** They are essential for plants and animals as a source of energy.
  - **(ii)** They form structural materials for cells.
  - **(iii)** They provide raw materials for textile, paper and alcohol industry.
  - **(iv)** Monosaccharides are also present in nucleic acids which control the transmission of hereditary effects from one generation to other and biosynthesis of proteins as well.
- **Distinction between Glucose (monosaccharide), Sucrose (disaccharide) and Starch (polysaccharide) :**

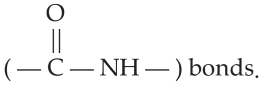
S. No.	**Test**	**Glucose (Monosaccharide)**	**Sucrose (Disaccharide)**	**Starch (Polysaccharide)**
1.	On heating with Fehling's solution	Red precipitate is obtained.	No precipitate.	No precipitate.
2.	On heating with Tollens' reagent (ammonical $AgNO_3$)	Silver mirror is formed.	No Silver mirror is formed.	No Silver mirror is formed.
3.	On heating with phenyl hydrazine	Yellow coloured crystals of osazone are formed.	No osazone is formed.	No osazone is formed.
4.	On heating with resorcinol and HCl	No colour.	Wine red colour.	No colour.
5.	On adding NaOH solution and 1-2 drops of cobalt nitrate	No colour.	Violet colour.	No colour.
6.	On adding I_2 solution in aqueous solution	No colour.	No colour.	Blue-violet colour.
7.	On heating in a dry test tube	Melts into brown coloured substance and smells of burnt sugar. Turns black on heating further.	Melts at 463 K, becomes brown at 473 K, chars at high temperature.	Chars on heating strongly.

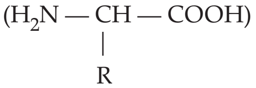
Know the Terms

- **Aldoses :** Monosaccharides which contain an aldehyde (—CHO) group are called aldoses.
- **Ketoses :** Monosaccharides which contain a keto (>C=O) group are called ketoses.
- **Invert Sugar :** An equimolar mixture of glucose and fructose which is formed as a result of hydrolysis of sucrose is known as Invert sugar.
- **Anomers :** Diastereomers of cyclic forms of sugar differing in configuration at the aromatic carbon, generally found in 2 forms α and β .
- **Glycosidic linkage** : It is an oxide linkage between two or more monosaccharide units in polysaccharides.

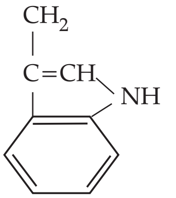
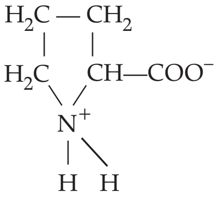
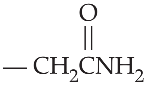
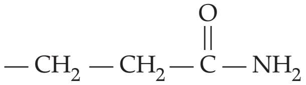
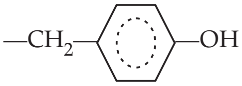
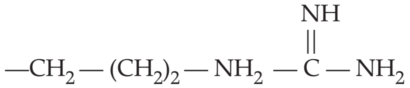
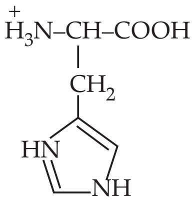
TOPIC-2
Proteins, Hormones, Vitamins and Nucleic Acids

Quick Review

- **Proteins :** Proteins are complex polyamides formed from amino acids. They are essential for proper growth and maintenance of body. They have many peptide  $(-\overset{\overset{O}{||}}{C}-NH-)$ bonds.
- **Amino Acids :** The compounds which contain carboxylic acid (–COOH) group and amino group ($-NH_2$) are called amino acids. Amino acids form proteins.
- **α-Amino Acids :** Those amino acids in which—NH_2 group and —COOH group are attached to same carbon are called α-amino acids. These are obtained by hydrolysis of proteins *e.g.*, glycine.
- **Types of Amino Acids :**

  Acidic, Basic and Neutral Amino Acids : Amino acids are acidic, basic or neutral depending upon the relative number of amino and carbonyl group in their molecule, if equal number of amino and carboxyl group is present. It is neutral. More number of amino than carbonyl group makes it basic and more carboxyl group as compared to amino makes it acidic.
- **Essential and Non-essential Amino Acids :** The amino acids, which can be synthesised in the body, are known as non-essential amino acids. *e.g.,* glycine, alanine, glutamine etc. On the other hand, those which can not be synthesised in the body and must be obtained by diet are known as essential amino acids.
- **Classification of Proteins :** Proteins are classified as follows :
  - **(a) Based on molecular shape :**
    - **(i) Fibrous proteins :** They have thread like molecules which tend to lie side by side to form fibres. *e.g.,* keratin, collagen etc.
    - **(ii) Globular proteins :** They have molecules which are folded into compact units that often approach spheroidal shape. *e.g.,* insulin, albumin, haemoglobin etc.
  - **(b) Based on structure and shape :**
    - **(i) Primary structure :** Each polypeptide in a protein has amino acids linked with each other in a specific sequence. This sequence of amino acids is called as primary structure of proteins.
    - **(ii) Secondary structure :** It refers to the shape in which a long polypeptide chain exists. They are of two types :
      1. α-helix in which polypeptide chain forms intramolecular hydrogen bonds by twisting into a right handed helix with the — NH group of each amino acid residue hydrogen bonded to the >C = O of an adjacent turn of the helix. *e.g.*, keratin in hair, nails.
      2. β-pleated sheet has all peptide chains stretched to nearly maximum extension and then arranged side by side held together with intermolecular hydrogen bonding. *e.g.*, silk.
    - **(iii) Tertiary structure :** It represents overall folding of polypeptide chains by H-bonds, disulphide linkages, van der Waals' and electrostatic form of attraction. *e.g.*, Fibrous and globular proteins.
    - **(iv) Quaternary structure :** The spatial arrangement of two or more polypeptide chains with respect to each other is known as quaternary structure.
- **Name and Structure of Some Naturally Occurring α-Amino Acids :**  $(H_2N-\underset{\underset{R}{|}}{CH}-COOH)$

S. No.	Amino acids	Isoelectric point (Hydrophobic)	One alphabet code	Three alphabet code	—R (Side chain)
1.	**Non-polar** Glycine	5.97	G	Gly	—H
2.	Alanine	6.02	A	Ala	$-CH_3$
3.	Valine*	5.97	V	Val	$-CH(CH_3)_2$
4.	Leucine*	5.90	L	Leu	$-CH_2-CH(CH_3)_2$

5.	Isoleucine*	6.02	I	Ile	$—CH(CH_3)—CH_2—CH_3$
6.	Phenylalanine*	5.84	F	Phe	$—CH_2—Ph$
7.	Methionine*	5.06	M	Met	$—CH_2—CH_2—S—CH_3$
8.	Tryptophan*	5.88	W	Trp	
9.	Proline	6.30	P	Pro	
10.	Polar (Neutral) Serine	5.68	S	Ser	$—CH_2OH$
11.	Cysteine	5.02	C	Cys	$—CH_2—SH$
12.	Asparagine	5.41	N	Asn	 $—CH_2\overset{\overset{O}{\|}}{C}NH_2$
13.	Glutamine	5.70	Q	Gln	 $—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—NH_2$
14.	Threonine*	5.60	T	Thr	$—CH(OH)—CH_3$
15.	Tyrosine	5.67	Y	Tyr	
16.	Acidic Aspartic acid	2.98	D	Asp	$—CH_2—COOH$
17.	Glutamic acid	3.22	E	Glu	$—CH_2CH_2COOH$
18.	Basic Lysine*	9.47	K	Lys	$—CH_2—(CH_2)_3—NH_2$
19.	Arginine*	10.76	R	Arg	 $—CH_2—(CH_2)_2—NH_2—\overset{\overset{NH}{\|}}{C}—NH_2$
20.	Histidine*	7.59	H	His	

* These are essential amino acids.

- **Different Proteins and their Functions :**

S. No.	Type of Protein	Example	Function
1.	Enzyme	Trypsin, Pepsin	As a catalyst in biochemical reactions.
2.	Structural	Collagen, Keratin	Structural and protective action in teeth, nails and hairs.

3.	Transport	Haemoglobin	Transport of oxygen from lungs by blood stream to different tissues.
4.	Motion	Myosin, Actin	For motion of muscles.
5.	Storage	Myoglobin	Storage of oxygen in muscles.
6.	Storage house	Albumin, Casein	Food for chick, complete food for new born baby.

- **Denaturation of Proteins :** When a protein in its native form is subjected to change, like change in temperature or pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. It is called denaturation of protein. *e.g.* coagulation of egg white on boiling, curding of milk etc.
- **Enzymes :** Enzymes are essential biological catalysts which are needed to catalyse biochemical reactions *e.g.*, maltase, lactase, invertase etc. Almost all enzymes are globular proteins.
- **Some specific Enzymes and the Reactions catalysed by them :**

Enzyme	Reaction catalysed
Maltase	Maltose $\rightarrow$ Glucose
Lactase	Lactose $\rightarrow$ Glucose + Galactose
Amylase or Ptyalin	Starch $\rightarrow$ Glucose
Invertase	Sucrose $\rightarrow$ Glucose + Fructose
Urease	Urea $\rightarrow$ $NH_3 + CO_2$
Trypsin, Pepsin	Protein $\rightarrow$ Amino acid

- **Vitamins :** Vitamins are group of organic compounds which are required in very small amount for the healthy growth and functioning of animal organism. They cannot be made by organism and so have to be part of our diet.
- **Types of Vitamins :**

(i) Fat soluble vitamins : Vitamins A, D, E and K are fat soluble but insoluble in water.

(ii) Water soluble vitamins : Vitamins belonging to group B (B_1, B_2, B_6, B_{12} etc.) and vitamin C are soluble in water.

- **Different Vitamins :**

Vitamin	Name and Formula	Sources	Function	Deficiency Diseases
Vitamin A	Retinol or Excerophytol $C_{20}H_{30}O$	Milk, butter, egg, fish, spinach, green vegetables, carrot etc.	Essential for vision and growth. Develops resistance against diseases.	Night blindness, xerophthalmia, retarded growth and decreases the immunity of body towards various diseases.
Vitamin B_1	Thiamine or Aneurin $C_{12}H_{17}N_4OS$	Egg, fish, meat, rice, wheat, yeast etc.	For proper functioning of nervous system.	Beri-beri, anaemia, weakness of muscles, etc.
Vitamin B_2	Riboflavin or Lactoflavin $C_{17}H_{20}N_4O_6$	Milk, cheese, egg, meat, green vegetables, liver etc.	Essential for growth of body.	Cracking skin particularly at the corners of mouth (Cheilosis), glossitis, dermatitis.
Vitamin B_6	Pyridoxine $C_8H_{11}O_3N$	Wheat, maize, husk of rice, meat, fish, egg etc.	In blood formation	Convulsions, paralysis.
Vitamin B_{12}	Cyanocobalamin $C_{63}H_{88}CoN_{14}O_{14}P$	Liver, egg, fish, meat etc.	In blood formation	Macrocytic anaemia or pernicious anaemia.
Vitamin C	Ascorbic acid $C_6H_8O_6$	Citrus fruits such as lemon, orange, tomatoes, amla etc.	For bones, teeth and healing of wounds, healthy skin.	Scurvy, pyria, pain in joints, loosening of teeth, mental depression, anaemia, bleeding of gums.

Vitamin D	Calciferol or Ergocalciferol or Vitamin D_2, $C_{27}H_{44}O$	Egg, meat, fish, liver oil, butter etc.	Control of metabolism of calcium and phosphorus in the formation of bones.	Rickets, osteomalacia.
Vitamin E	α-Tocopherol $C_{29}H_{50}O_2$	Milk, egg, meat, pulses, green vegetables, seeds, beans etc.	Anti sterility or reproduction.	Loss of reproductive ability or infertility.
Vitamin K (Vitamin K_1 or K_2)	Vitamin K_1 or Phylloquinone $C_{31}H_{46}O_2$, Vitamin K_2, $C_{41}H_{56}O_2$	Cabbage, spinach, green vegetables, egg, fish etc.	Helps in clotting of blood.	Delay in blood clotting (Haemophilia).

- **Hormones :** Hormones are the chemical substances produced by ductless glands called endocrine glands such as thyroid, adrenals etc. They find their way into the blood stream and influence and regulate the functions of the other organs of the body. Hormonal deficiency leads to specific biological disorders which can be cured by the administration of the specific hormones.
- **Steroid hormones :** Those hormones which have structure similar to steroids. *e.g.*, cortisone, testosterone, estrogen and progesterone.
- **Various hormones, gland of secretion and their functions :**

S. No.	Hormones	Gland	Function
1.	**Steroid hormones :**		
	(i) Testosterone (androgens)	Testes	Responsible for development of male sex organs.
	(ii) Estrogen and progesterone	Ovary	Influences development of sex organs maintains pregnancy.
	(iii) Cortisone	Adrenal cortex	Regulates metabolism of water, mineral salts.
2.	**Amine hormones :**		
	(i) Adrenalin	Adrenal medulla	Increases blood pressure and pulse rate. It also releases glucose from glycogen and fatty acids from fats.
	(ii) Thyroxine	Thyroid	Stimulates rate of oxidative metabolism and regulates general growth and development.
3.	**Peptide hormones :**		
	(i) Oxytocin	Posterior pituitary	Causes constriction of some smooth muscles. It causes contraction of uterus during child birth.
	(ii) Vasopressin (ADH)	Posterior pituitary	Controls the reabsorption of water in kidneys.
	(iii) Insulin	Pancreas	Controls blood glucose level.
	(iv) Glucagon	Pancreas	Increases blood glucose level.

- **Nucleic acid :** The polymers of nucleotides help in synthesis of protein and transfer genetic traits.

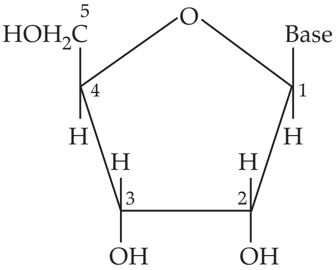
  Nucleic acids are of two types :

  (i) Deoxyribonucleic acid (DNA)

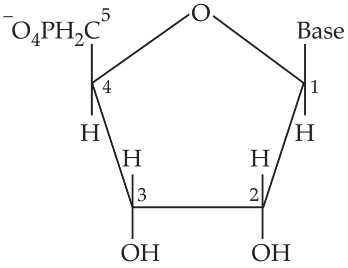
  (ii) Ribonucleic acid (RNA)

(a) Constituents of nucleic acids : Pentose sugar, phosphoric acid and nitrogenous bases.

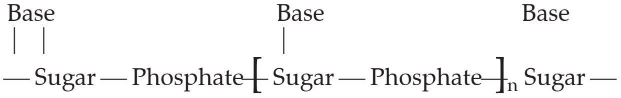
- **Nitrogen containing bases :**
  - **Pyrimidines :** These are three bases derived from pyrimidines. These are cytosine (C), thymine (T) and uracil (U). In DNA, T is present but in RNA, U is present.
  - **Purines :** There are two bases derived from purine. These are adenine (A) and guanine (G).
  - **Nucleoside :** A unit formed by the attachment of a base to 1′-position of sugar is known as nucleoside.



- **Nucleotide :** When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, the unit obtained is called nucleotide.



- **Simple structure of nucleic acid chain :**



$$-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}-\left[\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}-\right]_n\text{Sugar}-$$

- **DNA :** James Watson and Francis Crick gave double helix structure of DNA.

Nucleic acid (DNA)

↓ hydrolysis

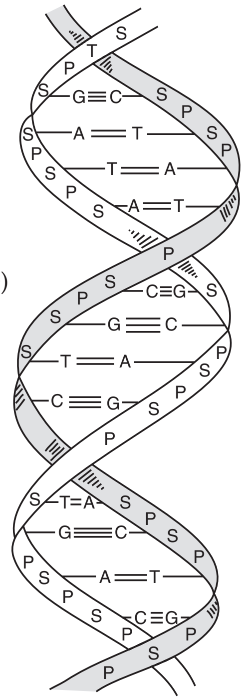
Nucleotide

↓ hydrolysis

Phosphoric acid + Nucleoside

↓ hydrolysis

Sugar (2-deoxy ribose)	Purine base (Adenine + Guanine)	Pyrimidine base (Cytosine + Thymine)



Double helix structure of DNA molecule

- **RNA : (i)** *m*-RNA (Messenger RNA)

  (ii) *r*-RNA (Ribosomal RNA)

  (iii) *t*-RNA (Transfer RNA)

Nucleic acid (RNA)

↓ hydrolysis

Nucleotide

↓ hydrolysis

Phosphoric acid | Nucleoside

Nucleoside

↓ hydrolysis

Sugar (Ribose)	Purine base (Adenine + Guanine)	Pyrimidine base (Cytosine + Uracil)

- **Properties of Nucleic Acids :**

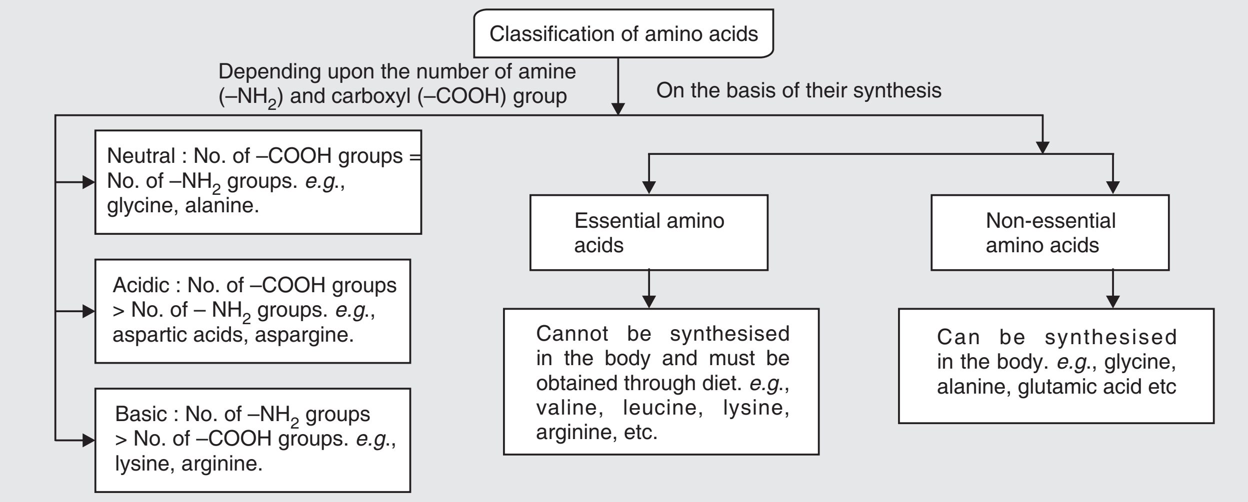
(i) Nucleic acids are very important constituents (polynucleotide) found in nucleus of cell which help in biosynthesis of protein and act as carriers for transfer of hereditary characters.

(ii) A molecule formed by the combination of one pentose sugar unit, a purine or pyrimidine base and a phosphate nucleotides combine among themselves to manufacture polynucleotide (nucleic acid).

(iii) A polynucleotide (DNA) which has a thiamine base but not a uracil base. It contains deoxyribose sugar but not ribose sugar. It has double helix structure.

(iv) A polynucleotide (RNA) which contains uracil base and ribose sugar but thiamine base and deoxy-ribose sugar are absent. It has single stranded structure.

- **Flowchart for the Classification of Amino Acids :**



Know the Terms

- **N-Terminal end :** There is a free amino group at one end of molecule of amino acid which is known as N-Terminal end.
- **C-Terminal end** : There is a free carboxyl group at the end of amino acid molecule which is known as C-Terminal end.
- **Conjugated** proteins : In this case, a protein part is linked to a non protein part called prosthetic group which is mostly concerned with the special biological function of protein.
- **Derived protein**s : These are the proteins formed by the partial hydrolysis of simple conjugated proteins such as proteases, peptones, peptides etc.
- **Enzyme inhibitors** : These are the chemical substances which tend to reduce the activity of a particular enzyme instead of increasing it.
- **Transcription** : Process of synthesis of RNA.
- **Replication** : Process by which a single DNA molecule produces two identical copies of itself.
- **Native protein** : Protein found in biological system with a unique 3-dimensional structure and biological activity.
- **Gene** : Sequence of bases or nucleotides in the DNA molecule which regulates the synthesis of a specific protein.

❑❑

Chapter - 15 : Polymers

Quick Review

- **Polymers :** Polymers are defined as the high molecular mass macromolecules, which consists of repeating structural units derived from the corresponding monomers.

- **Polymerisation :** The process by which monomers are converted into polymers is called polymerisation.

$$nCH_2 = CH_2 \xrightarrow[\text{Traces of } O_2]{350 - 570\text{ K}, 100 - 200\text{ atm}} \left(CH_2 - CH_2 \right)_n$$

Ethene (Monomer) Polythene (Polymer)

- **Classification of Polymers :** Polymers are classified on the basis of their sources, structure and mode of polymerisation.

(i) Classification based on sources :

(a) Natural Polymers : They are found in nature, mostly in plants and animals are called natural polymers. *e.g.*, proteins, natural rubber etc.

(b) Semisynthetic Polymers : They are obtained by making some modifications in natural polymers by artificial means. *e.g.*, nitrocellulose, cellulose acetate etc.

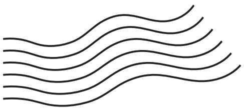
(c) Synthetic Polymers : These are man-made polymers prepared in the laboratory. *e.g.*, polythene, teflon, nylon etc.

(ii) Classification based on structure of polymer :

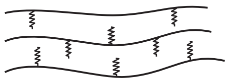
(a) Linear Polymers : These polymers consist of long and straight chains. *e.g.*, high density polythene, nylon, polyvinyl chloride etc.

(b) Branched chain Polymers : These polymers contain linear chains having some branches. *e.g.*, low density polythene, glycogen etc.

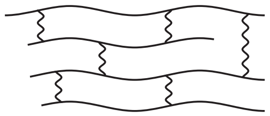
(c) Cross linked or Network Polymers : These polymers are usually formed from bifunctional and trifunctional monomers and contain strong covalent bonds between various linear polymer chain. *e.g.*, bakelite, melamine. etc.



(a) Linear Chain



(b) Branched Chain



(b) Cross Chain

(iii) Classification based on mode of polymerisation :

(a) Addition Polymers : These polymers are formed by the repeated addition of same or different monomer molecules possessing double or triple bonds. *e.g.*, polythene, buna-S, buna-N etc.

- **Homopolymers :** The addition polymer formed by the polymerisation of a single monomer species.

$$nCH_2 = CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2 - CH_2 \right]_n$$

Ethene Polythene

- **Copolymers :** The polymers made by addition polymerisation from two different monomers.

$$nCH_2 = CH - CH = CH_2 + nC_6H_5CH = CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2 - CH = CH - CH_2 - CH_2 - C_6H_5 - CH \right]_n$$

1, 3-Butadiene Styrene Butadiene-styrene (Buna-S)

(b) Condensation Polymers : These polymers are formed by the repeated condensation reactions between different bifunctional or trifunctional monomer units usually with elimination of small molecules such as water, alcohol, hydrogen chloride etc. *e.g.*, nylon 6, 6 and nylon, terylene etc.

$$nH_2N(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \longrightarrow \left[NH(CH_2)_6NHCO(CH_2)_4CO \right]_n + n2H_2O$$

Hexamethylenediamine Adipic acid Nylon 6, 6

(iv) Classification based on molecular forces :

(a) Elastomers : In these polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces allow the polymer to be stretched. A few 'cross links' when introduced in between the chains helps the polymer to retract to its original position after the stretching force is removed. *e.g.*, buna-S, buna-N etc.

(b) Fibres : These are the polymers which have strongest intermolecular forces such as hydrogen bond or dipole-dipole interactions. These polymers can be used for making fibre as their molecules are long and thread like. *e.g.*, nylon 6, 6 and terylene etc.

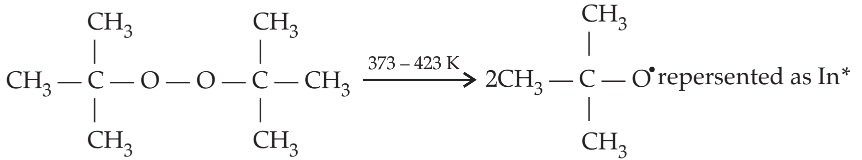
(c) Thermoplastics : These polymers possess intermolecular force of attraction intermediate between elastomers and fibres. These are linear or slightly branched chain polymers capable of repeatedly softening on heating and hardening on cooling. *e.g.*, polythene, polypropylene, polyvinyl chloride etc.

(d) Thermosetting polymers : These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reshaped. *e.g.*, bakelite, urea-formaldehyde resins etc.

(v) Classification based on growth polymerisation : The addition and condensation polymers referred as chain growth polymers and step growth polymers depending on the type of mechanism.

➢ **Mechanism of Polymerisation :**

(i) Free Radical Polymerisation : It is initiated by molecules like tert.-butyl peroxide.



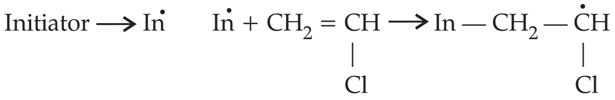
$$CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-O-O-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-CH_3 \xrightarrow{373-423\ K} 2CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-\dot{O}\ \text{repersented as In}^*$$

(Tert. butoxy free redical)

$$In + CH_2=CH_2 \longrightarrow In-CH_2-\dot{C}H_2 \xrightarrow{CH_2=CH_2} In-CH_2-CH_2-CH_2-\dot{C}H_2 \xrightarrow{n\,CH_2=CH_2} In-(CH_2-CH_2)_n$$

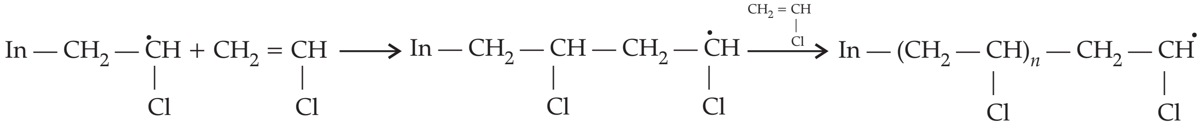
(ii) Vinyl Polymerisation :

(a) Chain initiation step :



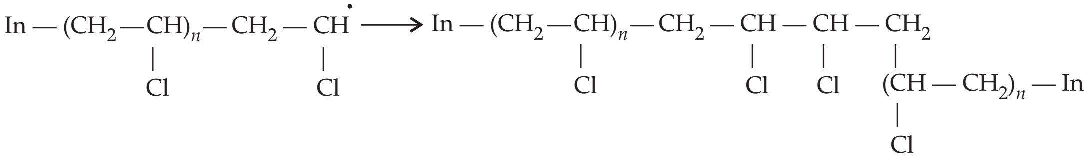
$$\text{Initiator} \longrightarrow \dot{In} \qquad \dot{In} + CH_2=\underset{Cl}{\underset{|}{CH}} \longrightarrow In-CH_2-\underset{Cl}{\underset{|}{\dot{C}H}}$$

(b) Chain propagation step :



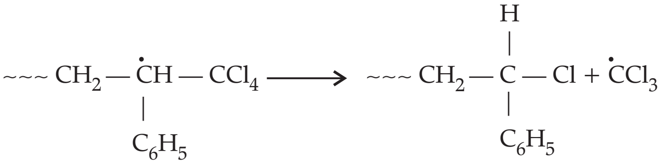
$$In-CH_2-\underset{Cl}{\underset{|}{\dot{C}H}} + CH_2=\underset{Cl}{\underset{|}{CH}} \longrightarrow In-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{\dot{C}H}} \xrightarrow{CH_2=\underset{Cl}{\underset{|}{CH}}} In-(CH_2-\underset{Cl}{\underset{|}{CH}})_n-CH_2-\underset{Cl}{\underset{|}{\dot{C}H}}$$

(c) Chain termination step : (Head – Head)

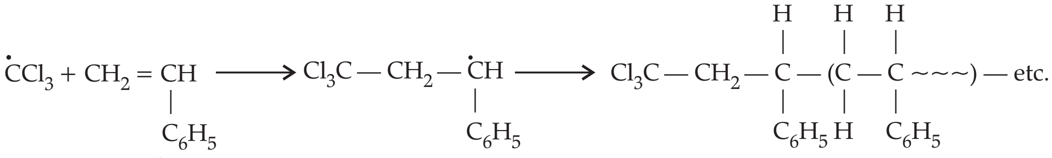


$$In-(CH_2-\underset{Cl}{\underset{|}{CH}})_n-CH_2-\underset{Cl}{\underset{|}{\dot{C}H}} \longrightarrow In-(CH_2-\underset{Cl}{\underset{|}{CH}})_n-CH_2-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-\underset{(\underset{Cl}{\underset{|}{CH}}-CH_2)_n-In}{\underset{|}{CH_2}}$$

(iii) Chain Transfer Agents : Those reagents which generate free radicals and lead to lowering of the average molecular mass of the polymer and enter the chain, *e.g.*, CCl_4.



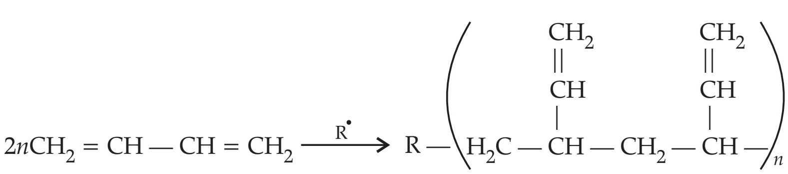
$$\sim\sim\sim CH_2-\underset{C_6H_5}{\underset{|}{\dot{C}H}}-CCl_4 \longrightarrow \sim\sim\sim CH_2-\underset{C_6H_5}{\underset{|}{\overset{\overset{H}{|}}{C}}}-Cl + \dot{C}Cl_3$$



$$\dot{C}Cl_3 + CH_2=\underset{C_6H_5}{\underset{|}{CH}} \longrightarrow Cl_3C-CH_2-\underset{C_6H_5}{\underset{|}{\dot{C}H}} \longrightarrow Cl_3C-CH_2-\underset{C_6H_5}{\underset{|}{\overset{\overset{H}{|}}{C}}}-(\underset{H}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\underset{C_6H_5}{\underset{|}{\overset{\overset{H}{|}}{C}}}\sim\sim\sim)-\text{etc.}$$

Styrene

(vi) 1, 2-Polymerisation :

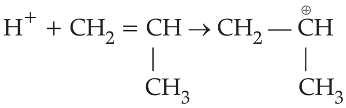


$$2nCH_2=CH-CH=CH_2 \xrightarrow{\dot{R}} R-\left(H_2C-\underset{}{\overset{\overset{\overset{CH_2}{||}}{CH}}{\overset{|}{CH}}}-CH_2-\overset{\overset{\overset{CH_2}{||}}{CH}}{\overset{|}{CH}}-\right)_n$$

trans - 1, 4-structure

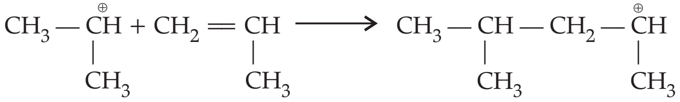
(v) Cationic addition polymerisation : When initiator is cationic in nature, on addition to the double bond it would generate carbocation. If functional group attached to vinyl group is electron releasing, it will undergo cationic polymerisation, *e.g.*, propene will undergo cationic polymerisation.

(a) Chain initiation step :



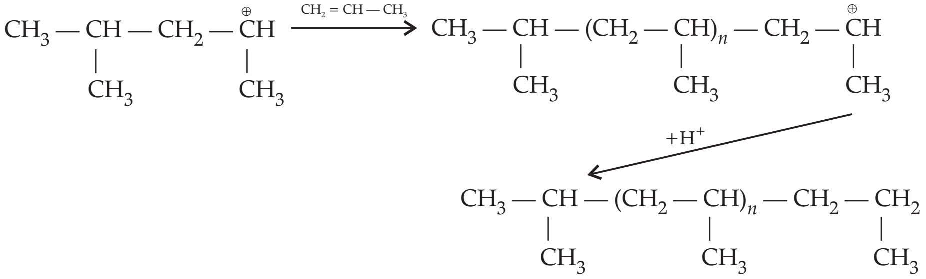
$$H^+ + CH_2=\underset{\substack{|\\ CH_3}}{CH} \rightarrow CH_2-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}H}$$

(b) Chain propagation step :



$$CH_3-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}H} + CH_2=\underset{\substack{|\\ CH_3}}{CH} \longrightarrow CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}H}$$

(c) Chain termination step :



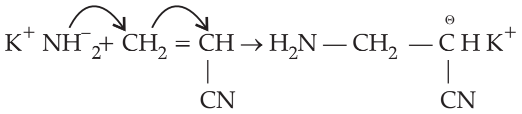
$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}H} \xrightarrow{CH_2=CH-CH_3} CH_3-\underset{\substack{|\\ CH_3}}{CH}-(CH_2-\underset{\substack{|\\ CH_3}}{CH})_n-CH_2-\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}H}$$

$$\xrightarrow{+H^+} CH_3-\underset{\substack{|\\ CH_3}}{CH}-(CH_2-\underset{\substack{|\\ CH_3}}{CH})_n-CH_2-\underset{\substack{|\\ CH_3}}{CH_2}$$

Polymer

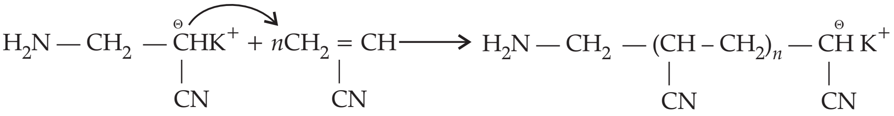
(vi) Anionic polymerisation : When initiator is *n*-butyl lithium or KNH_2,on addition to double bond, it would generate carbanion. If functional group attached to vinyl group is electron withdrawing such as —CN, —Cl, —$COOCH_3$, —C_6H_5, it will undergo anionic polymerisation.

(a) Chain initiation setp :



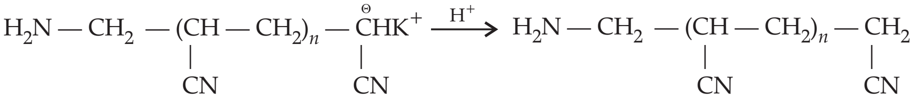
$$K^+\,\overset{-}{N}H_2 + CH_2=\underset{\substack{|\\ CN}}{CH} \rightarrow H_2N-CH_2-\underset{\substack{|\\ CN}}{\overset{\ominus}{C}H}\,K^+$$

(b) Chain propagation step :



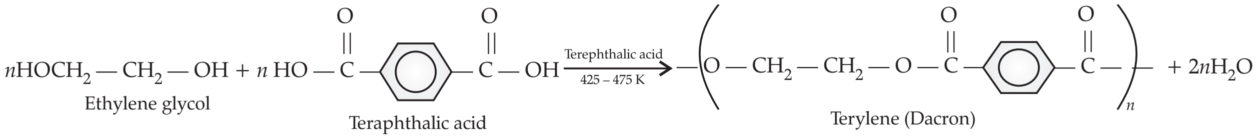
$$H_2N-CH_2-\underset{\substack{|\\ CN}}{\overset{\ominus}{C}HK^+} + nCH_2=\underset{\substack{|\\ CN}}{CH} \longrightarrow H_2N-CH_2-(\underset{\substack{|\\ CN}}{CH}-CH_2)_n-\underset{\substack{|\\ CN}}{\overset{\ominus}{C}H}\,K^+$$

(c) Chain termination step :

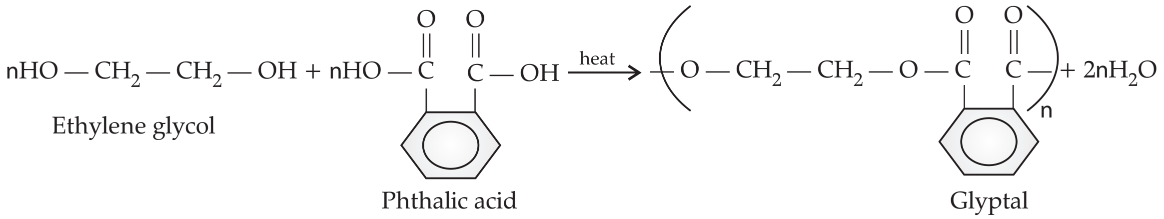


$$H_2N-CH_2-(\underset{\substack{|\\ CN}}{CH}-CH_2)_n-\underset{\substack{|\\ CN}}{\overset{\ominus}{C}HK^+} \xrightarrow{H^+} H_2N-CH_2-(\underset{\substack{|\\ CN}}{CH}-CH_2)_n-\underset{\substack{|\\ CN}}{CH_2}$$

- **Condensation Polymers :**
  - **(a) Polyesters :** These are polymers having large number of ester linkages, *e.g.*,
    - **(i) Terylene :** It is resistant to action of chemical and solvent. It has a low moisture absorbing power. It is also called **dacron.** It is used in dress materials like sarees. It is used as a blend with cotton and wool to give terycot and terywool.

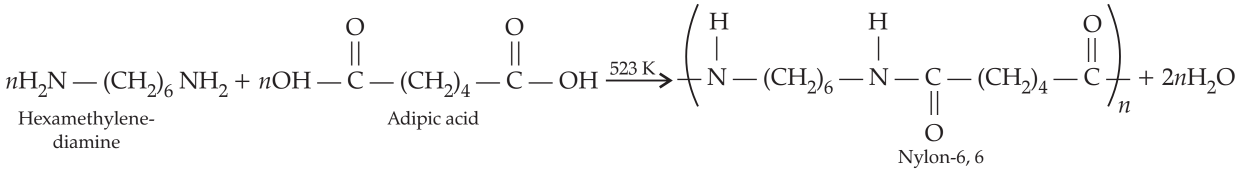


    - **(ii) Glyptal or Alkyd resin :** These are three dimensional cross-linked polymers. It is tough and flexible. It is used in adherent paints, lacquers and building materials like asbestos and cement.



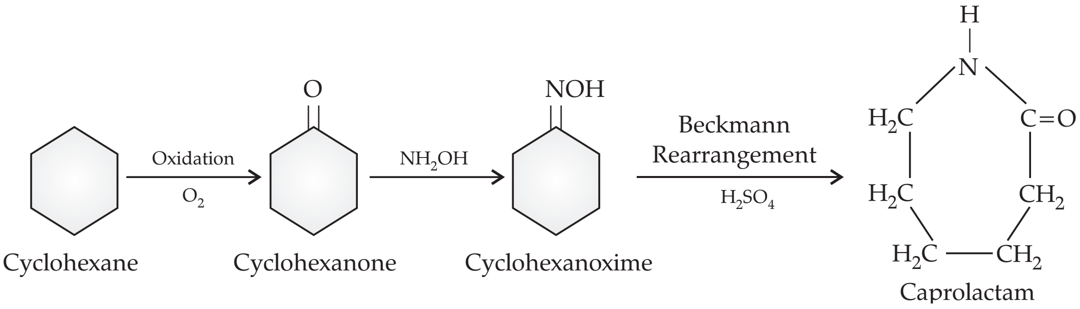
  - **(b) Polyamides :** Those polymers which have large number of amide linkages are called polyamides, *e.g.*,
    - **(i) Nylon-6, 6 :** It can be cast into sheets or fibres. Nylon fibres have high tensile strength. They are tough and resistance to abrasion. They are also elastic in nature. It is used to make bristles of toothbrush, climbing

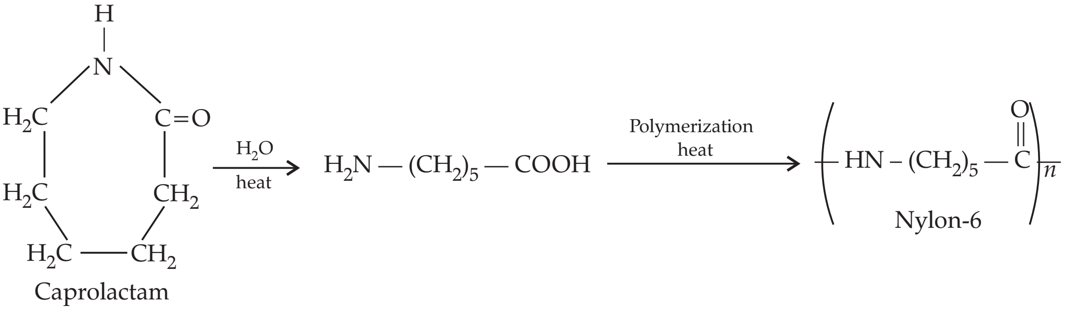
ropes, fishing nets and parachute fabrics. It is a condensation polymer of adipic acid and hexamethylenediamine.



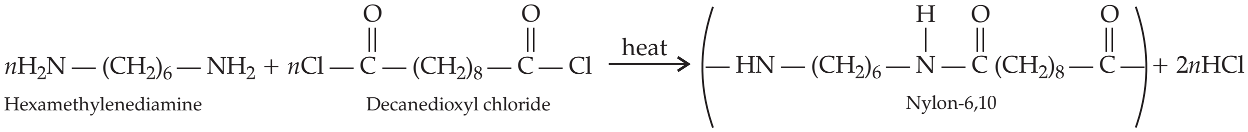
$$\underset{\text{Hexamethylene-diamine}}{nH_2N-(CH_2)_6\,NH_2} + \underset{\text{Adipic acid}}{nOH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{523\text{ K}} \underset{\text{Nylon-6, 6}}{\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n} + 2nH_2O$$

(ii) Nylon-6 : It can be cast into sheets and fabrics. It is tough and strong.



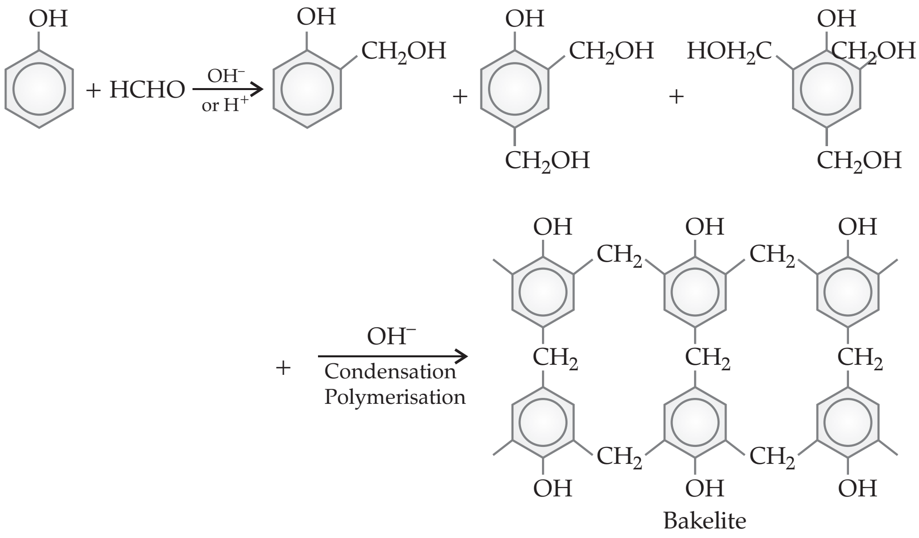


(iii) Nylon-6, 10 : It is a polymer of hexamethylene diamine and decanedioyl chloride (sebacoyl chloride).

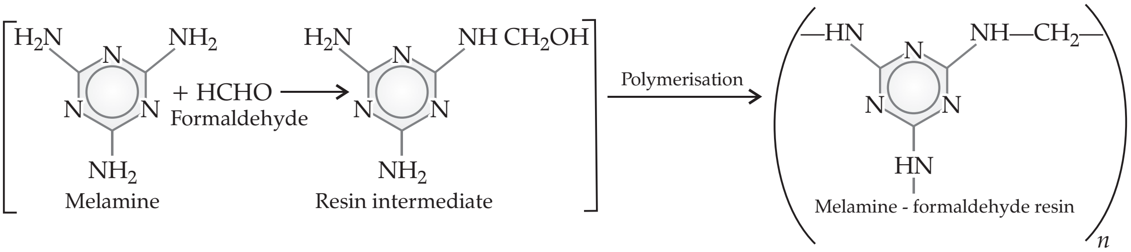


$$\underset{\text{Hexamethylenediamine}}{nH_2N-(CH_2)_6-NH_2} + \underset{\text{Decanedioxyl chloride}}{nCl-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow{\text{heat}} \underset{\text{Nylon-6,10}}{\left(-HN-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}\,(CH_2)_8-\overset{O}{\overset{\|}{C}}-\right)} + 2nHCl$$

(c) Phenol-formaldehyde resin (Bakelite) : It is heat resistant thermosetting plastic.



(d) Melamine-formaldehyde resin : It is thermosetting plastic which is unbreakable.



- **Differences between chain growth and step growth polymerisation :**

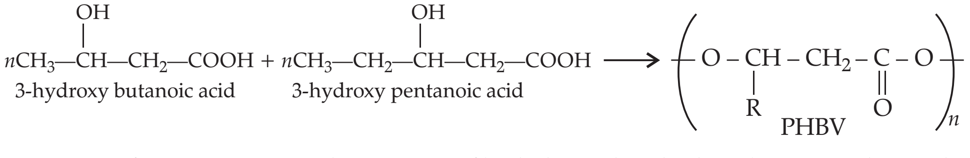
S. No.	Chain Growth Polymerisation	Step Growth Polymerisation
(i)	Concentration of monomers disappears early in the reaction.	Concentration of monomers decreases steadily throughout the reaction.
(ii)	Reaction is fast and polymer is formed at once.	The polymer is formed in gradual steps.
(iii)	There is very little change in the molecular mass throughout the reaction.	The molecular mass of polymer increases throughout the reaction.
(iv)	Increase in reaction time increases the yield but molecular weight is affected a little.	Long reaction time is required to get high molecular mass polymer.
(v)	Only one repeating unit is added at a time.	Any two species present can react.
(vi)	Reaction mixture contains only monomer, polymer and growing chain.	All molecular species are present at any stage.

- **Differences between addition and condensation polymerisation :**

S. No.	Addition Polymerisation	Condensation Polymerisation
(i)	They are formed by adding monomers to a growing polymer chain without loss of any molecule.	Monomers combine together with the loss of small molecules like H_2O, NH_3, CO_2, CH_3OH, etc.
(ii)	They are formed from unsaturated compounds.	Monomers have di or poly functional groups.
(iii)	It involves chain reaction. *e.g.,* polyethene, polypropene, PVC, teflon, etc.	It does not involve chain reaction. *e.g.,* nylon-66, nylon-6, terylene, glyptal, bakelite, etc.

- **Low density polyethene :** It is produced by free radical polymerisation at high temperature (200°C) and high pressure about 1000 atm. It is branched chain.
- **High density polyethene :** It is produced by polymerisation of ethene in presence of Ziegler-Natta catalyst at temperature below 100°C and pressure less than 100 atmosphere. It is linear polymer.
- **Biodegradable polymers :** Those polymers which are biodegradable, *i.e.,* decomposed by micro-organisms and do not cause water pollution, *e.g.,* PHBV, Poly (Glycolic acid) and Poly (Lactic acid) etc.

(i) PHBV (Poly-β-hydroxybutyrate-co-β-hydroxy valerate) : It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid in which the monomers are connected by ester linkages.



$$\underset{\text{3-hydroxy butanoic acid}}{n\mathrm{CH_3{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_2{-}COOH}} + \underset{\text{3-hydroxy pentanoic acid}}{n\mathrm{CH_3{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_2{-}COOH}} \longrightarrow \underset{\text{PHBV}}{\left(\mathrm{O-\underset{\underset{\displaystyle R}{|}}{C}H-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-O}\right)_n}$$

The properties of PHBV vary according to ratio of both the acids. 3-hydroxybutyric acid provides stiffness and 3-hydroxypentanoic acid provides flexibility to copolymer. It is used in speciality packaging, orthopaedic devices and even in controlled drug release. It is biodegradable.

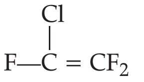
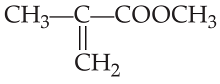
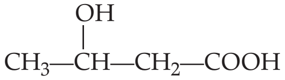
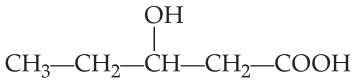
(ii) Poly (Glycolic acid) and Poly (Lactic acid) are biodegradable polymers and used in sutures. Dextron was the first bioabsorbable suture made from biodegradable polyesters for post operation.

- **Natural, Synthetic and Condensation Polymers :**

Natural Polymers

S. No.	Polymer	Monomer	Class	Uses
(i)	Cellulose	β-Glucose	Biopolymer	Occurs in cotton, cell wall
(ii)	Starch	α-Glucose	Biopolymer	Food material storage in plants
(iii)	Proteins	Amino acids	Biopolymer	Essential for growth
(iv)	Nucleic acid	Nucleotides	Biopolymer	Essential for life perpetuation
(v)	Rayon (Artificial silk)	β-Glucose	Processed cellulose	Fabrics, surgical dressings
(vi)	Natural rubber	*cis*-Isoprene (cis-2-methyl-1, 3-butadiene)	Natural polymer Elastomer	Used for tyres after vulcanisation
(vii)	Gutta percha	*trans*-Isoprene	″	Rubber like material

Synthetic Polymers

S. No.	Polymer	Monomer	Class	Uses
(i)	Polyethene	Ethene ($CH_2 = CH_2$)	Addition and Chain growth	Electrical insulator, packing materials, films, bottles etc.
(ii)	Polypropene	Propene ($CH_3—CH=CH_2$)	Addition and Chain growth	Storage battery tanks
(iii)	Polystyrene	Styrene ($C_6H_5–CH=CH_2$)	Addition and Chain growth	In combs, plastic handles, toys
(iv)	Polyvinyl chloride (PVC)	$CH_2 = CHCl$ Vinyl chloride	Addition and Chain growth	Pipes, raincoats, vinyl floorings
(v)	Polytetrafluoroethene PTFE (Teflon)	$CF_2 = CF_2$ Tetrafluoroethene	Addition and Chain growth	Non-stick kitchenwares, electrical insulator
(vi)	Polymonochlorotrifluoroethene	 $F—\overset{\overset{Cl}{\vert}}{C} = CF_2$ Monochlorotrifluoroethene	Addition and Chain growth	Non-stick kitchenwares
(vii)	Polymethyl methacrylate (PMMA) (Perspex, Lucite or Acrylite)	 $CH_3—\underset{\underset{CH_2}{\Vert}}{C}—COOCH_3$ Methyl methacrylate	Addition and Chain growth	Substitute of glass and decorative material
(viii)	Polyethyl acrylate	$CH_2 = CH—COOC_2H_5$ Ethyl-2-propenoate	Addition and Chain growth	Lacquers, films, house piping
(ix)	Polyvinyl acetate	$CH_2 = CH—O—COCH_3$	Addition and Chain growth	Floor coverings and fibres
(x)	Vinylite	Vinyl chloride and Vinyl acetate	Addition and Chain growth	Vinyl floorings
(xi)	Polyacrylonitrile or Acrylane (orlon)	$CH_2 = CH—C \equiv N$ Vinyl cyanide (Acrylonitrile)	Addition and Chain growth	It closely resembles wool
(xii)	Buna-S	1, 3-Butadiene and styrene	Addition and Chain growth	Automobile tyres
(xiii)	Buna-N	1, 3-Butadiene and Acrylonitrile	Addition and Chain growth	Used for storing oil and solvents
(xiv)	Neoprene	2-Chloro-1, 3-butadiene (Chloroprene)	Addition and Chain growth	Insulation, conveyor belt
(xv)	Thiokol	1, 2-Dichloroethene and sodium polysulphide	Condensation polymer	Rocket propellent
(xvi)	Poly-β-hydroxybutyrate-co-β-hydroxyvalerate (PHBV)	 $CH_3—\overset{\overset{OH}{\vert}}{CH}—CH_2—COOH$  $CH_3—CH_2—\overset{\overset{OH}{\vert}}{CH}—CH_2—COOH$	Condensation Polymer	As packaging, orthopaedic and in controlled drug release.

(xvii)	Nylon-2-Nylon-6	Glycine (H_2NCH_2COOH) and aminocaproic acid $H_2N(CH_2)_5COOH$	Condensation polymer	Biodegradable polymer

Condensation Polymers

S. No.	Polymer	Monomer	Class	Uses
1.	Polyesters (Terylene) Dacron	Terephthalic acid and ethylene glycol	Condensation and step growth	Ropes, safety belts, tyre cards.
2.	Glyptal (Alkyd resin)	Phthalic acid and ethylene glycol	Condensation and step growth	Binding material, paints and Lacquers
3.	Nylon-6	Caprolactam (cyclic amide)	Condensation and step growth	Fibre, plastic, tyre-cords and ropes
4.	Nylon-6, 6	Adipic acid and hexamethylenediamine	Condensation and step growth	Stockings, shirts, ropes
5.	Bakelite	Phenol and formaldehyde	Condensation and step growth	Electric switches and switch-boards
6.	Melamine formaldehyde resin	Melamine and HCHO	Condensation and step growth	Crockery
7.	Urea formaldehyde resin	Urea and HCHO	Condensation and step growth	Crockery and laminated sheets

Know the Terms

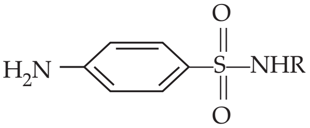
- **Plasticizers :** These are the substances which are added in the formation of polymers in order to alter their physical properties.
- **PMMA :** It represents polymethylmethacrylate polymer.
- **PAN :** It represents polyacrylonitrile polymer.
- **PTFE :** It represents polytetrafluoroethylene polymer.
- **PCTFE :** It represents polymonochlorotrifluoroethene polymer.

❑❑

Chapter - 16 : Chemistry in Everyday Life

Quick Review

- **Drugs :** Drugs are the chemical substances of low molecular mass, interacting with macromolecular targets and produce a biological response.
- **Medicines :** Drugs which produce a therapeutic and useful response.
- **Chemotherapy :** It is the science in which chemicals are used in the treatment of diseases due to bacterial invasion. These chemicals destroy the micro-organisms without affecting any material extent (the tissues of the host).
- **Classification of Drugs :**
  - **(i) On the basis of pharmacological effect :** Most useful for doctors as it provides the whole range of drugs available for the treatment of a particular type of problem. *e.g.*, analgesics have pain killing effect, antiseptics kill or arrest the growth of microorganisms.
  - **(ii) On the basis of drug action :** It is based on the action of a drug on a particular biochemical process. *e.g.*, all histamines inhibit the action of the compound histamines, which causes inflammation of the body.
  - **(iii) On the basis of chemical structure :** Drugs which have common structural features and often have similar pharmacological activity. *e.g.*, sulphonamides have common structural feature.



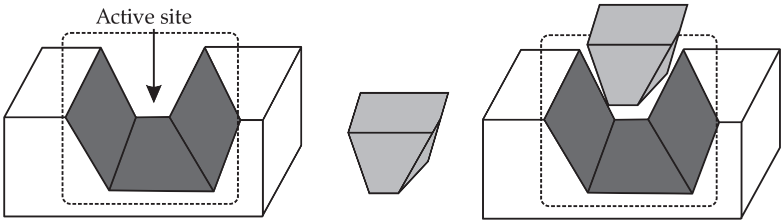
  - **(iv) On the basis of molecular targets :** Drugs generally interact with biological macromolecules such as carboh drates, proteins, lipids and nucleic acids called target molecules. This classification is based upon the type of the molecular target with which the drug interacts.

- Enzymes are the proteins which perform the role of biological catalysts in the body. Carrier proteins carry polar molecules across the cell membrane.

- **Catalytic action of enzymes :**

(i) The prime function of an enzyme is to hold the substrate for a chemical reaction. Active sites of enzymes hold the substrate molecule in a suitable position, such that it can be attacked by the reagents effectively. Substrates bind to the active site of the enzymes through many kinds of interactions like ionic bonding, hydrogen bonding, van der Waals' or dipole-dipole interactions.

(ii) The second function of an enzymes is to provide functional groups that will attack the substrate and carry out chemical reaction.



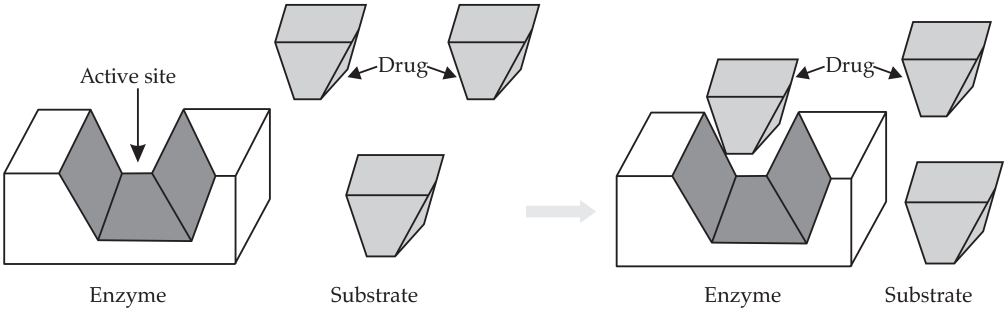
(a) (b) (c)

Fig. 1 : (a) Active site of an enzyme, (b) Substrate.
(c) Enzyme holding the substrate

- **Drug-enzyme interactions :** Drugs can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme. Such drugs are called enzyme inhibitors.

Drugs inhibit the attachment of substrate on active site of enzymes in two ways :

(i) Drugs compete with natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors.



Drug and substrate competing for active site of enzymesite of enzyme **Drug blocks the active**

Fig. 2 : Drug and substrate competing for active site

(ii) Instead of joining to the enzyme's active site, some drugs bind to a different site of enzyme which is called allosteric site. This can change the shape of the active site in such a way that the substrate can't recognize it. If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme Inhibitor complex and synthesises the new enzyme.

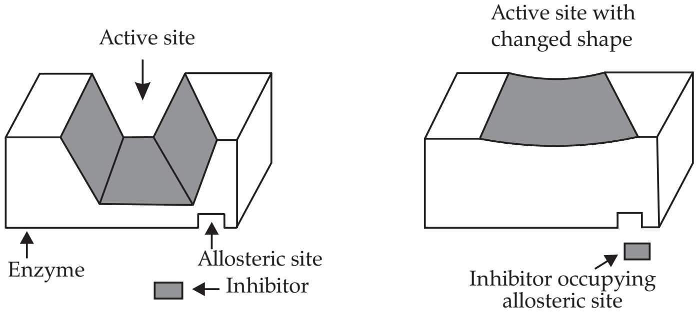


Fig. 3 : Non-competitive inhibitor changes the active site of enzyme after binding all allosteric site

- **Receptors as drug targets :** Proteins that are crucial to body's communication process are called as receptors. They are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.

  Message between two neurons and that between neurons to muscles is communicated through chemical receptors. To accommodate a messenger, shape of the receptor site changes. This brings about the transfer of message into the cell. Thus, chemical messenger gives message to the cell without entering the cell.
- **Antagonists :** Drugs that bind to the receptor site and inhibit its natural function are called antagonists. These are useful when blocking of message is needed.
- **Agonists :** Drugs that mimic the natural messenger by switching on the receptor are called agonists. These are useful when there is lack of natural chemical messenger.
- **Types of drugs on the basis of therapeutic action :**

(i) **Analgesics :** These are the medicines which give relief from pain. They are of two types :

(a) **Non-narcotic (non-addictive) analgesics :** Aspirin (2-acetoxy benzoic acid), paracetamol, phenylbutazone or butazolidine etc. are the common examples of this group. Aspirin is the most common analgesic with antipyretic properties. also has anti blood clotting action. It also reduces body temperature in fever.

(b) **Narcotic analgesics :** These are the drugs which produce sleep and unconsciousness *e.g.*, opium, alkaloids like morphine, codeine, heroine (morphine diacetate) etc. These are, however, addictive drugs, hence used in severe pain only.

(ii) **Antiseptic :** These are the chemicals which prevent the growth of micro-organisms or kill them but are not harmful to human beings. These are applied externally to the living tissues such as wounds, cuts and diseased skin surfaces. Dettol (chloroxylenol + α-terpineol), bithional, furacin, dilute solution of boric acid are common example of antiseptics.

(iii) **Disinfectant :** These are chemicals which kill micro-organisms or prevent their growth but are not safe for human beings. These are applied to inanimate objects such as floors, drainage systems. Some substances can act as an antiseptic as well as disinfectant by varying the concentration. For example, 0.2% solution of phenol is an antiseptic while its one percent solution is disinfectant.

(iv) **Tranquillizers :** It is a group of chemical substances which is used in the treatment of stress, and severe mental stress. These are essential component of sleeping pills and psychotherapeutic drugs. These are of two types :

(a) **Barbiturates :** (Derivatives of barbituric acid)—These are sleep inducing and hence also called hypnotics. *e.g.*, veronal, amytal, nembutal, luminal and seconal.

(b) **Non-hypnotic tranquilizers :** Chlordiazepoxide and meprobamate are relatively mild tranquilizers which are used for relieving tension. Equanil is another non hypnotic tranquilizer which is used for controlling depression and hypertension. Valium, serotonin, reserpine etc. are some other tranquilizers.

(v) **Antimicrobials :** These are drugs which are used to cure diseases caused by a variety of microbes such as bacteria, fungi, virus etc. Antibiotic, antiseptic and disinfectants etc. are all antimicrobials.

(vi) **Antibiotics :** These are the chemical substances (prepared wholly or partially by chemical synthesis) which in low concentration, either kill or inhibit the growth of micro-organisms. Penicillin is a narrow spectrum ant biotic whereas ampicillin and amoxicillin are wide spectrum antibiotic which exerts antimicrobial activity on more than one type of micro-organisms.

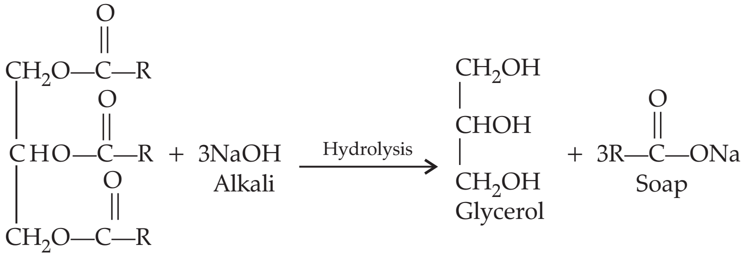
(vii) **Sulpha drugs :** These are derivatives of sulphanilamide. These have antibacterial powers and are used as medicines for various diseases. These are also used as antibiotics. Sulpha drugs used against diseases like pneumonia, tuberculosis, diphtheria, etc. *e.g.* sulphadiazine, sulphathiazole.

(viii) **Antifertility drugs :** These are the chemical substances used to control the pregnancy in woman. *e.g.*, norethindrone and ethinylestradiol etc.

(ix) **Antihistamines :** These drugs are also called as anti allergy drugs and are used to treat allergy. *e.g.*, skin rashes, conjunctivitis, inflammation of conjunctiva of eye, and rhinitis (inflammation of nasal mucosa). *e.g.*, diphenlhydramine, chlorpheniramine.

- **Antioxidants :** These are the other important and necessary food additives. These compounds retard the action of oxygen on the food and thereby help in its preservation. They also reduce the rate of involvement of free radicals in the aging process. *e.g.*, butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA) are used as antioxidants.

- **Antacid :** An antacid is a substance that removes the excess of acid and raise the pH of stomach to appropriate level. The most commonly used antacids are magnesium hydroxide, magnesium carbonate and sodium bicarbonate etc.
- **Chemicals in food :** Chemicals are added to food for various purposes like, for preservation, for enhancing their appeal and for adding nutritive value etc. Some uses are discussed below :
  - **(i) Artificial Sweeteners :** These are the chemical compounds which are non-nutritive in nature and used as substituent for sugar in foods and beverages specially soft drinks. Some common artificial sweeteners are :
  - **(a) Saccharin :** It is useful as a sugar substitute for diabetic persons and those who need to control their calorie intake.
  - **(b) Aspartame :** It is methyl ester of dipeptide formed from aspartic acid and phenylalanine. Aspartame is used only in cold foods and soft drinks as it is unstable at cooking temperature.
  - **(c) Alitame :** It is a high potency sweetener. The control of sweetness of food is difficult while using alitame.
  - **(d) Sucralose :** It is trichloro derivative of sucrose. It is stable at cooking temperature.
- **Food preservatives :** Food preservatives are the substances which are capable of inhibiting or arresting the process of fermentation, acidification of the food. *e.g.*, sodium benzoate, sodium metabisulphite.
- **Soaps :** Soaps are sodium or potassium salts of long chain fatty acids and are prepared by a process called saponification, in which fat reacts with alkali.
- **Synthetic detergent :** These are soapless soap and are of three types :
  - **(a) Anionic detergents :** These are sodium salts of sulphonated long chain alcohols or hydrocarbons. *e.g.*, sodium dodecylbenzene sulphonate these are used in toothpaste and household works.
  - **(b) Cationic detergents :** These are quaternary ammonium salts of amines with acetates, chlorides or bromides *e.g.*, cetyltrimethyl ammonium bromide and are expensive.
    These have germicidal property and are expensive.
  - **(c) Non-ionic detergents :** They do not contain any ion in their constitution. *e.g.*, liquid dishwash detergents.
- **Biodegradable and non-biodegradable detergents :** Detergents which contain straight chain hydrocarbons are biodegradable. On the other hand, detergents which have branched chain hydrocarbons are non-biodegradable and this leads to environmental pollution.
- **Saponification :** The process of manufacturing soap by the hydrolysis of oils and fats with aqueous alkalis.



$$\begin{array}{l} CH_2O-\overset{O}{\overset{\|}{C}}-R \\ | \\ CHO-\overset{O}{\overset{\|}{C}}-R \\ | \\ CH_2O-\overset{O}{\overset{\|}{C}}-R \end{array} + \underset{\text{Alkali}}{3NaOH} \xrightarrow{\text{Hydrolysis}} \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\text{Soap}}{3R-\overset{O}{\overset{\|}{C}}-ONa}$$

Know the Terms

- **Neurologically active drugs :** The drugs which are used to cure tension and anxiety.
- **Hypnotics :** These are sleep inducing medicines.
- **Salting out of soap :** This is the process by which soap is separated from glycerol.
- **Fillers :** The chemical substances which are added to laundry soaps. *e.g.*, sodium silicate, borax etc.
- **Spectrum :** The full range of micro-organism attacked by an antibiotic.
- **Hard soaps :** Sodium salts of fatty acids.
- **Soft soaps :** Potassium salts of fatty acids.