

CHAPTER-1

SOLID STATE

Revision Notes

Classification of Solids, Unit Cells and Packing in Solids

➤ **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 given below:**

- (i) Solids have definite mass, shape and volume.
- (ii) The intermolecular distance is minimum in solids and intermolecular forces are strong.
- (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.

➤ **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.

➤ **Characteristics of Crystalline solids**

- (i) Constituent particles are regularly arranged.
- (ii) They possess strong melting point.
- (iii) Their outer surface also show a regular arrangement during the formation of crystals.
- (iv) These are anisotropic in nature.
- (v) Crystalline solids have a definite geometric shape with flat faces and sharp edges.
- (vi) Crystalline solids have 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 not have ordered arrangement (short range order) are amorphous solids. These have a range of melting point. For example, plastic, glass, etc.

Characteristics of Amorphous solids:

- (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) They have short range order of arrangement of constituent particles.

➤ **Isotropy and Anisotropy:**

- Solids whose value of any physical property would be same along any direction. This property is called isotropy.
- Amorphous solids are isotropic in nature.
- 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.

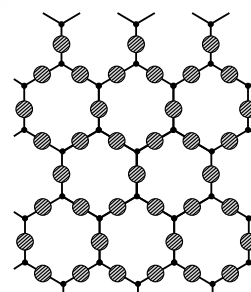


Fig. 1 : Two - dimensional representation of structure of crystalline solid (SiO₂) Quartz

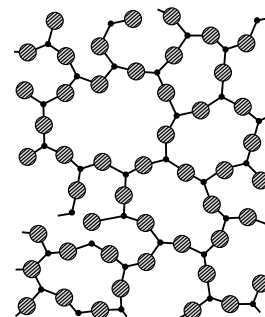


Fig. 2 : Two - dimensional representation of structure of amorphous solid (SiO₂) Quartz Glass

- Crystalline solids are anisotropic 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	Molecules										
	(i) Non-polar							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 ₂ O (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 delocalized 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 a 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:
 - Axial lengths a , b and c of the three edges along the three axis *i.e.*, axial distances.
 - Axial angles α , β and γ between the pairs of edges (b , c), (c , a) and (a , b) respectively.
 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.

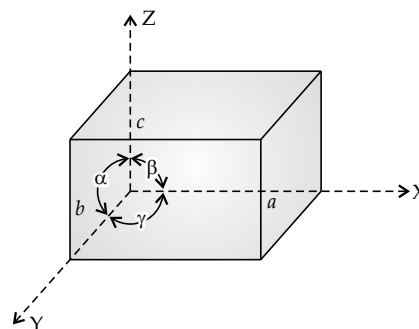
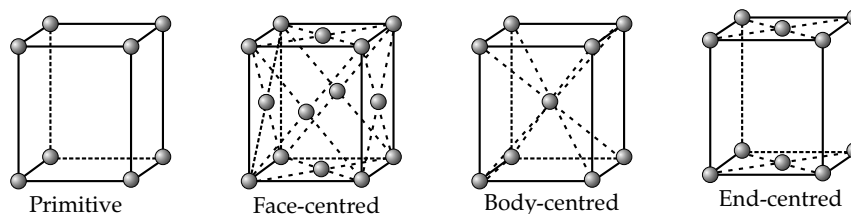


Fig. 3 : Characteristic parameters of a unit cell

**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	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	9 planes, 13 axis	3	NaCl, KCl, ZnS, Diamond
4. 5.	Primitive Body-centred	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	5 planes, 5 axis	2	TiO ₂ , SnO ₂ , PbSO ₄ , NH ₄ Br
6. 7. 8. 9.	Primitive Body-centred Face-centred End-centred	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	3 planes, 3 axis	4	KNO ₃ , BaSO ₄ , K ₂ SO ₄
10.	Primitive	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	7 planes, 7 axis	1	ZnO, CdS
11.	Primitive	Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	7 planes, 7 axis	1	NaNO ₃ , HgS
12. 13.	Primitive End-centred	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	7 planes, 10 axis	2	Monoclinic sulphur, PbCrO ₄
14.	Primitive	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	No planes, No axis	1	CuSO ₄ ·5H ₂ O, K ₂ Cr ₂ O 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.

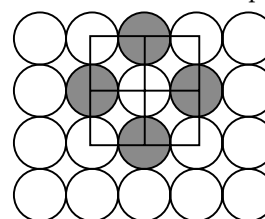
Number of atoms per unit cell

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

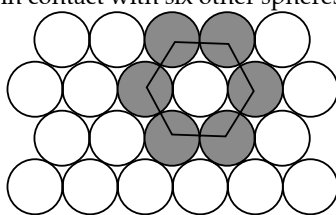


Fig. 6: Hexagonal close packing of spheres in two dimensions

- (c) **Close-packing in three dimensions:** All solids exist 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*' = $\frac{a}{2\sqrt{2}}$.

Voids, Packing Efficiency, Calculations Related to Unit Cell Dimensions

- **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.

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

- **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,

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

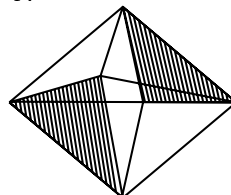
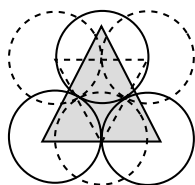


Fig. 8: Octahedral void

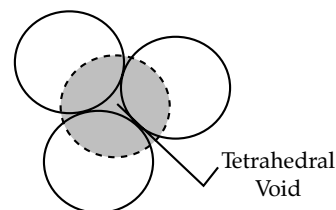


Fig. 7 : Tetrahedral void

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.

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

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

(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 hcp and bcc. For simple cubic lattice $a = 2r$.

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

$$= \frac{\frac{4}{3} \pi r^3 \times 100}{(2r)^3} = 52.4\%$$

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

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

$$\begin{aligned} \text{Mass of the unit cell} &= \text{Number of atoms in the unit cell} \times \text{Mass of each atom} \\ &= Z \times m \end{aligned}$$

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

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

$$m = \frac{M}{N_A}$$

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

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

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

Defects in Solids

➤ Defects in solids:

- It is also known as 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

- Point defect.
- 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.

(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. Also called dislocation defect, it creates vacancy defect at the original site and interstitial defect at the new site.

Consequences of Frenkel defect:

- Crystal becomes conductor of electricity.
- Stability of crystal decreases.
- Dielectric constant increases.

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

Positive symbols represent cations (*i.e.*, Na^+) and the negative symbols represent 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+} ion 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.

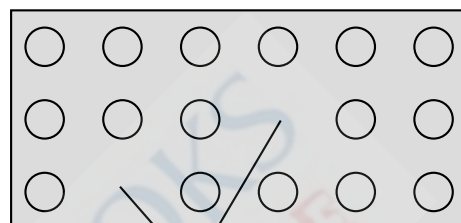


Fig. 9 : Crystalline solid showing vacancy defect

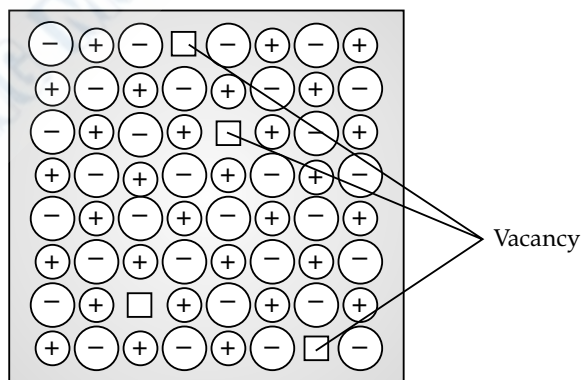


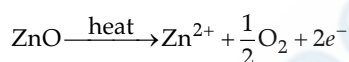
Fig. 10 : Frenkel defect

(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.



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.

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.

Know the Formulae

$$\text{Density of the unit cell } (d) = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}} = \frac{Z \times M}{N_A \times a^3}$$

➤ **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 ₂ O 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

CHAPTER-2 SOLUTIONS

Revision Notes

Types of Solutions, Expression of Concentration of Solutions and Solubility

- **Solution:** A homogeneous mixture of two or more 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:**
- Solute:** A substance that is dissolved in another substance in lesser amount, forming a solution. For example: Sugar, salt, etc.
 - 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 substances 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 adsorbed 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 is known as unsaturated solution.
- **Solubility:** Solubility can be defined as the maximum amount of solute that can be dissolved in 100 g of 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.

- **Factors affecting Solubility:**

- (i) **Nature of Solute and Solvent:** "Like dissolves 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 reaction.

- (iii) **Pressure:** The solubility of solid in liquid is not affected significantly by pressure because solids and liquids cannot be compressed.

- (iv) **Hydration Energy:** It is the amount of energy released when ions formed by 1 mole of ion 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 $\frac{w}{W}$:** 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 $\frac{v}{V}$:** 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 $\frac{v}{V}$:** 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.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in Litres)}}$$

$$M = \frac{W_B \times 1000}{M_B \times V}$$

where, W_B = Weight of solute, V = Volume of solution in ml, M_B = Molar mass of solute.
Unit is mol L⁻¹ or M (molar).

And
$$\frac{\text{Weight of solute (} W_B \text{)}}{\text{Molar mass of solute (} M_B \text{)}} = \text{Moles of solute}$$

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

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$m = \frac{W_B \times 1000}{M_B \times W}$$

where, W_B = Weight of the solute, M_B = Molar mass of solute, W = Mass of solvent in g
Unit is mol kg⁻¹ or molal (m). Molality and mole fraction do not change with change in temperature.

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

$$\text{Normality} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in Litre}}$$

$$N = \frac{W_B \times 1000}{E_B \times V}$$

where, W_B = Mass of solute, E_B = Equivalent weight of solute, V = Volume of solution in ml

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

$$\frac{1}{m} = \frac{d}{M} - \frac{M_B}{1000}$$

where, m = Molality of solution, M = Molarity of solution,

M_B = Molar mass of solute, d = Density of solution in g ml⁻¹

➤ **Relationship between Mole fraction of solute (χ_B) and Molality (m):**

$$m = \frac{\chi_B \times 1000}{(1 - \chi_B) \times M_A}$$

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

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 (p) in vapour phase is proportional to the mole fraction of the gas (χ) in the solution.

$$p = K_H \chi,$$

where K_H = Henry's constant.

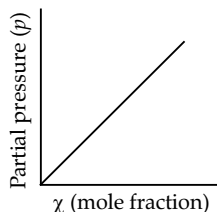


Fig. 1: The slope of the line is Henry's constant, (K_H)

- **Applications of Henry's law:**
 - To increase the solubility of CO_2 in soda water and soft drinks, the bottle is sealed under high pressure.
 - To avoid the toxic effects of high concentration of nitrogen in blood, the tanks used by scuba divers are filled with air diluted with helium (11.7%), nitrogen (56.2%) and oxygen (32.1%).
 - 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:
 - The pressure of gas is not too high and temperature is not too low.
 - The gas should not undergo any chemical change.
 - The gas should not undergo association or dissociation in the solution.

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

- Vapour pressure is the pressure exerted by vapours over a liquid at equilibrium state at constant temperature.
- Vapour pressure depends on the following factors:
 - Nature of the liquid.
 - 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 respectively in the solution at a particular temperature.

If p_A^0 and p_B^0 are their vapour pressures in the pure state respectively, 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 γ_A and γ_B are the mole fractions of components A and B respectively in the vapour phase, then

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

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

and

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,

$p_A^0 - p_A$ = Lowering of vapour pressure.

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

(i) Raoult's law is obeyed. $p_A = p_A^0 \chi_A$, $p_B = p_B^0 \chi_B$

(ii) $\Delta_{\text{mix}}H = 0$,

(iii) $\Delta_{\text{mix}}V = 0$,

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

(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) $\Delta_{\text{mix}}H \neq 0$,

(iii) $\Delta_{\text{mix}}V \neq 0$,

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

Some examples of non-ideal solutions 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-A 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.

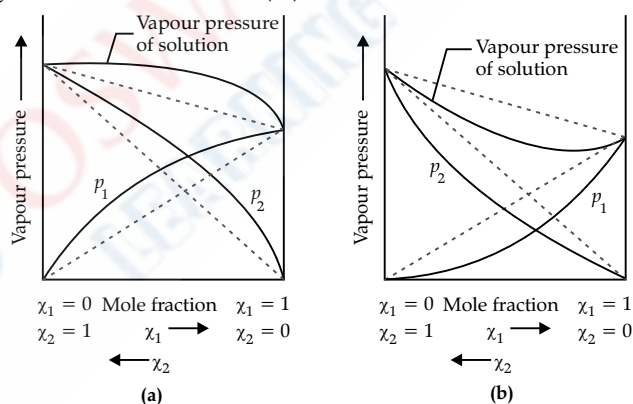


Fig. 2: The vapour pressures of two component systems as a function of composition:

(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 at a specific composition. 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 .

Colligative Properties, Determination of Molecular Mass

- **Colligative properties:** Certain properties of solutions depend only on the number of particles of the solute (molecules 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.

$$\text{Vapour pressure of pure solvent} = p_A^{\circ}$$

$$\text{Lowering of vapour pressure} = p_A^{\circ} - p_A$$

Relative lowering of vapour pressure

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

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.

$$\text{Boiling point of pure solvent} = T_b^{\circ}$$

$$\text{Boiling point of solution} = T_b$$

Increase in boiling point $\Delta T_b = T_b - T_b^{\circ}$ is known as elevation of boiling point for dilute solution.

$$\Delta T_b \propto \frac{\Delta p}{p^{\circ}} = x_B$$

$$\Delta T_b = K \chi_B$$

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

Where,

w_2 = weight of solute in g

M_2 = Molar mass of solute

w_1 = weight of solvent in g

$$\Delta T_b = K_b m$$

K_b = Boiling point elevation constant or molal elevation constant or **Ebullioscopic constant**.

- **Depression of freezing point:** According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and 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.

$$\text{The freezing point of pure solvent} = T_f^{\circ}$$

$$\text{The freezing point when non-volatile solute is dissolved in it} = T_f \text{ (Freezing point of solution)}$$

The decrease in freezing point $\Delta T_f = T_f^{\circ} - T_f$ is known as depression in freezing point.

For dilute solution,

$$\Delta T_f = K \chi_B$$

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

$$\Delta T_f = K_f m.$$

We know,

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

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

K_f = Freezing point depression constant or molal depression constant or **Cryoscopic constant**.

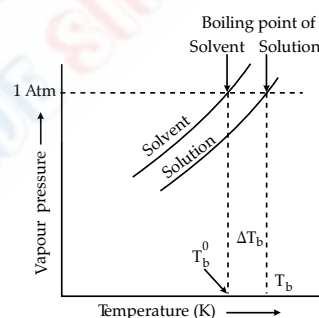


Fig. 3 : The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

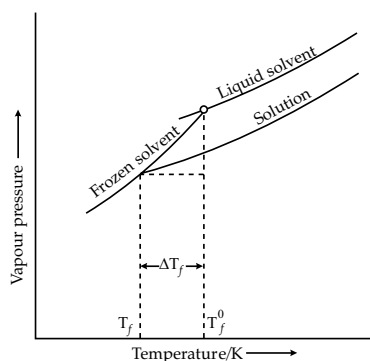


Fig. 4: Diagram showing ΔT_f , depression of the freezing point of a solvent in a solution.

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

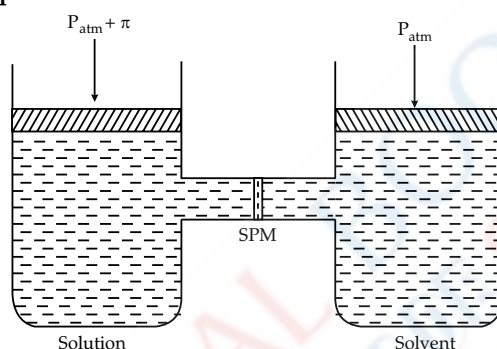


Fig. 5: The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.

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

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

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

- **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 semipermeable membrane. This phenomenon is called reverse osmosis.

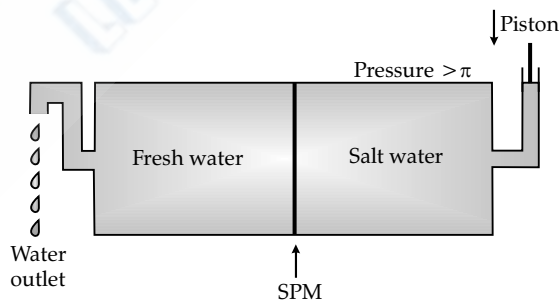


Fig. 6: Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

Know the Formulae

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

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

- Molarity (M) = $\frac{\text{Number of moles of solute}}{\text{Volume of solution in Litre}}$
- Molality (m) = $\frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$
- Normality (N) = $\frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in Litre}}$
- Mass percentage $\left(\frac{w}{W}\right) = \frac{\text{Mass of solute in the solution}}{\text{Total mass of the solution}} \times 100$
- Volume percentage $\left(\frac{v}{V}\right) = \frac{\text{Volume of solute}}{\text{Total volume of the solution}} \times 100$
- Mass by volume percentage $\left(\frac{w}{V}\right) = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$
- $p = K_H \cdot x$
where K_H = Henry's law constant
 p = partial pressure of the gas in vapour phase
 x = mole fraction of the gas in the solution
- ppm of component A = $\frac{\text{Mass of component A}}{\text{Total mass of solution}} \times 10^6$

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

$$p_A = p_A^{\circ} \chi_A$$

$$p_B = p_B^{\circ} \chi_B$$

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

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

- **Modified equations for colligative properties:**

- (i) Relative lowering of vapour pressure of solvent

$$\frac{p_A^{\circ} - p_A}{p_A^{\circ}} = \frac{n}{N + n}$$

- (ii) Elevation of boiling point

$$\Delta T_b = i K_b m$$

- (iii) Depression of freezing point

$$\Delta T_f = i K_f m$$

- (iv) Osmotic pressure of solution

$$\pi = \frac{i n R T}{V}$$

or

$$\pi = i C R T \quad \left[\because \frac{m}{V} = C \right]$$

- **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:**

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

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

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

(iii) Depression of freezing point:

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

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

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

(iv) Osmotic pressure:

$$\pi = CRT,$$

$$\Rightarrow \pi = \frac{\text{No. of moles}}{\text{Volume of solution}} \times R \times T$$

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

- Strength = Molarity × Mol. wt.
= Normality × Eq. wt.

••

CHAPTER-3

p-BLOCK ELEMENTS

Revision Notes

Group-15 Elements, Properties and Some Important Compounds

➤ **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:** ${}_7\text{N}$, ${}_{15}\text{P}$, ${}_{33}\text{As}$, ${}_{51}\text{Sb}$, ${}_{83}\text{Bi}$

(ii) **Atomic radii:** Smaller than the corresponding elements of group 14. Down the group, they increase due to addition of new shells.

(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 solids.

(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:**

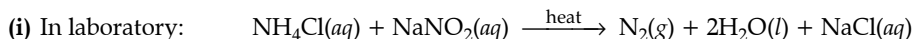
(i) **Towards hydrogen:** All the elements form hydrides of the type EH_3 where $\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$. The stability decreases from NH_3 to BiH_3 . Reducing character increases down the group. Basic character decreases down the group. Boiling point of NH_3 is greater than PH_3 because of intermolecular hydrogen bonding. Boiling point increases from PH_3 onwards.

- (ii) **Towards oxygen:** Form two types of oxides E_2O_3 and E_2O_5 . The acidic character decreases down the group.
 (iii) **Towards halogens:** Directly combine with halogens to form trihalides (EX_3) and pentahalides (EX_5).

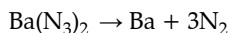
- (iv) **Towards metals:** All the elements react with metals to form their binary compounds exhibiting -3 oxidation state.
 ➤ **Anomalous properties of nitrogen:** N does not form pentahalides because of non-availability of d -orbitals in its valence shell. It has ability to form $p\pi-p\pi$ multiple 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.

➤ **Dinitrogen (N_2):**

Preparation:



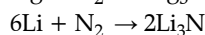
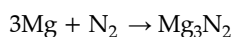
(ii) By thermal decomposition:



Properties:

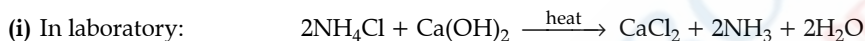
(i) N_2 has very little reactivity at ordinary temperature.

(ii) Forms nitrides with highly electropositive metals like



➤ **Ammonia (NH_3):**

Preparation:



(ii) By Haber's process:



Properties:

(i) Extremely soluble in water.

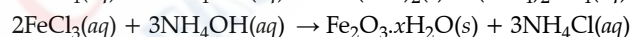
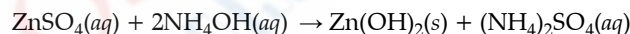
(ii) Acts as Lewis base



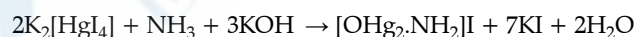
Deep blue



(iii) Forms salts with acids

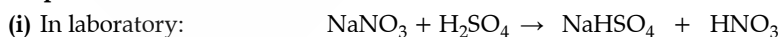


(iv) Reaction with Nessler's reagent:



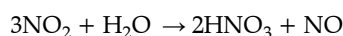
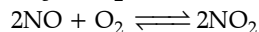
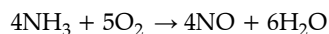
➤ **Nitric Acid (HNO_3):**

Preparation:



(conc.) (Brown ppt.)

(ii) By Ostwald's process:

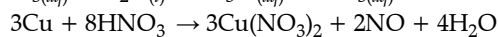
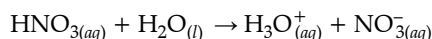


Properties:

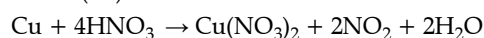
(i) Colourless liquid.

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

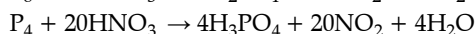
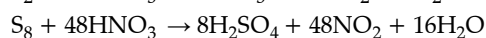
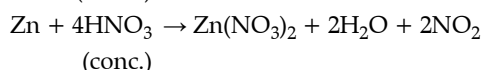
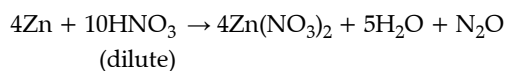
(iii) **Reactions:**



(dil)



(conc.)

**Uses:**

- (i) In the manufacturing of nitrates used in explosives (nitroglycerine, trinitrotoluene etc), fertilisers (ammonium nitrate) etc.
- (ii) As a reagent in laboratory.
- (iii) In preparing aqua-regia.

Group-16 Elements, Properties and Some Important Compounds

➤ **Oxygen family:** ${}_8\text{O}$, ${}_{16}\text{S}$, ${}_{34}\text{Se}$, ${}_{52}\text{Te}$, ${}_{84}\text{Po}$

➤ **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 becomes 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 are metalloids and polonium is a metal.
- (vi) **Melting and boiling points:** Increase regularly from O to Te due to increase in size and hence greater van der Waals forces. 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 OF₂ and H₂O₂). All other elements show +2, +4 and +6 oxidation states.

➤ **Chemical properties:**

(1) **With hydrogen:** Form hydrides of type H₂E (E = O, S, Se, Te and Po).

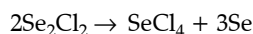
Properties of hydrides:

- (i) **Thermal stability:** Decreases down the group.
- (ii) **Acidic character:** Increases down the group.
- (iii) **Reducing nature:** All are reducing agents except H₂O.
- (iv) **Boiling point:** From H₂O to H₂S there is a sudden drop which increases from H₂S to H₂Te.

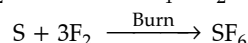
(2) **With halogens:** Form halides of type EX₂, EX₄ and EX₆ where E is an element of group and X is a halogen.

Properties of halides:

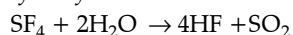
- (i) Only hexafluorides are the only stable halides.
- (ii) All elements except selenium form dichlorides and dibromides. These dihalides are sp³ hybridised and have tetrahedral structure.



(a) **Preparation of SF₄ and SF₆:**



(b) **Properties of SF₄:** SF₄ is readily hydrolysed.



(c) SF₆ is sp³d² hybridised and octahedral whereas SF₄ is sp³d hybridised and is trigonal bipyramidal with one position occupied by a lone pair of electrons.

(3) **With oxygen:** Form oxides of EO₂ and EO₃.

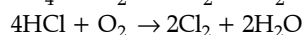
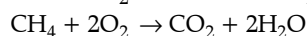
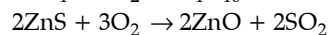
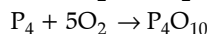
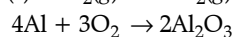
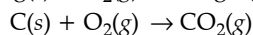
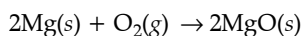
➤ **Dioxygen (O₂)**

Preparation:



Properties:

- (i) Slightly soluble in water and appreciably soluble in alkaline pyrogallol solution.
- (ii) Paramagnetic.
- (iii) Forms oxides with metals and non-metals.

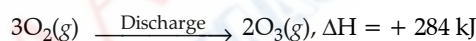


➤ **Classification of oxides:** On the basis of chemical nature,

- (i) **Basic:** Na₂O, CaO, etc. basic oxides.
- (ii) **Acidic:** CO₂, SO₂, etc. acidic oxides.
- (iii) **Amphoteric:** SnO₂, Al₂O₃, etc. are amphoteric oxides.
- (iv) **Neutral:** H₂O, CO, etc. are neutral oxides.
- (v) **Poly-oxide:** Oxides having oxygen more than required oxygen such as peroxide (Na₂O₂), super oxide (KO₂), dioxide (PbO₂), higher oxide (Mn₂O₇).
- (vi) **Sub-oxide:** Oxides having oxygen less than required, e.g., C₃O₂.

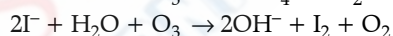
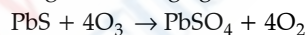
➤ **Ozone (O₃)**

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



Properties:

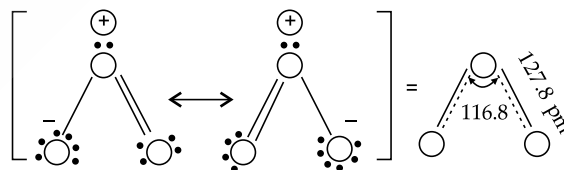
- (i) Poisonous in nature
- (ii) Powerful oxidising agent. It is a stronger oxidising agent than O₂.



Uses:

- (i) As bleaching agent
- (ii) As disinfectant and germicide
- (iii) For purification of air in hospitals, railway tunnels, cinema house
- (iv) For bleaching oils, ivory flour, starch, etc

Structure:



➤ **Allotropes of Sulphur:**

(a) **Rhombic Sulphur (α-Sulphur):**

- (i) Yellow in colour, melting point 385.8 K and specific gravity 2.06.
- (ii) Formed by evaporating the solution of roll sulphur in CS₂.
- (iii) Insoluble in water but dissolves to some extent in benzene, alcohol and ether.
- (iv) Readily soluble in CS₂.

(b) **Monoclinic Sulphur (β-Sulphur):**

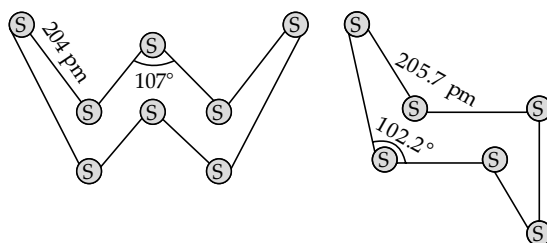
- (i) Melting point is 393 K and specific gravity 1.98.
- (ii) Soluble in CS₂.

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

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

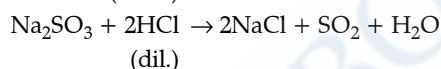
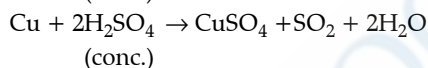
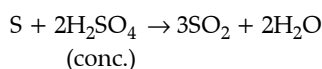
Both rhombic and monoclinic sulphur have S_8 molecules.

Shape of S_8 and S_6 molecules:



➤ Sulphur dioxide (SO_2):

Preparation:

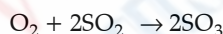
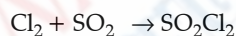
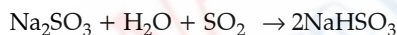
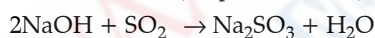
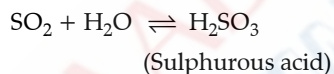


Properties:

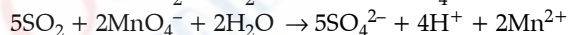
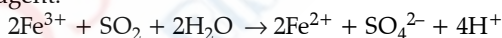
(i) Colourless gas with pungent, suffocating odour

(ii) Highly soluble in water

(iii)



(iv) SO_2 acts as reducing agent.



Uses:

(i) Used in refining petroleum and sugar.

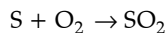
(ii) As bleaching agent for wool and silk.

(iii) As anti-chlor, disinfectant and preservative.

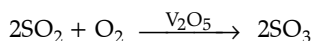
➤ Sulphuric acid (H_2SO_4)

Preparation: By contact process which involves 3 steps:

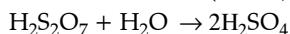
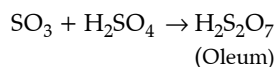
(i) Burning of sulphur or sulphide ores in air:



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



(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.



Properties:

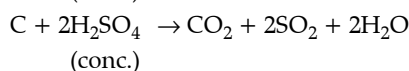
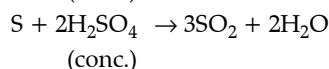
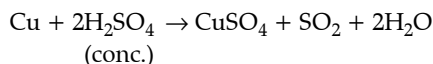
(i) Colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K

(ii) Low volatility

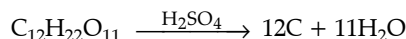
(iii) Strong acidic character

(iv) Strong affinity for water

(v) Acts as an oxidising agent



(vi) Acts as a dehydrating agent.



Uses:

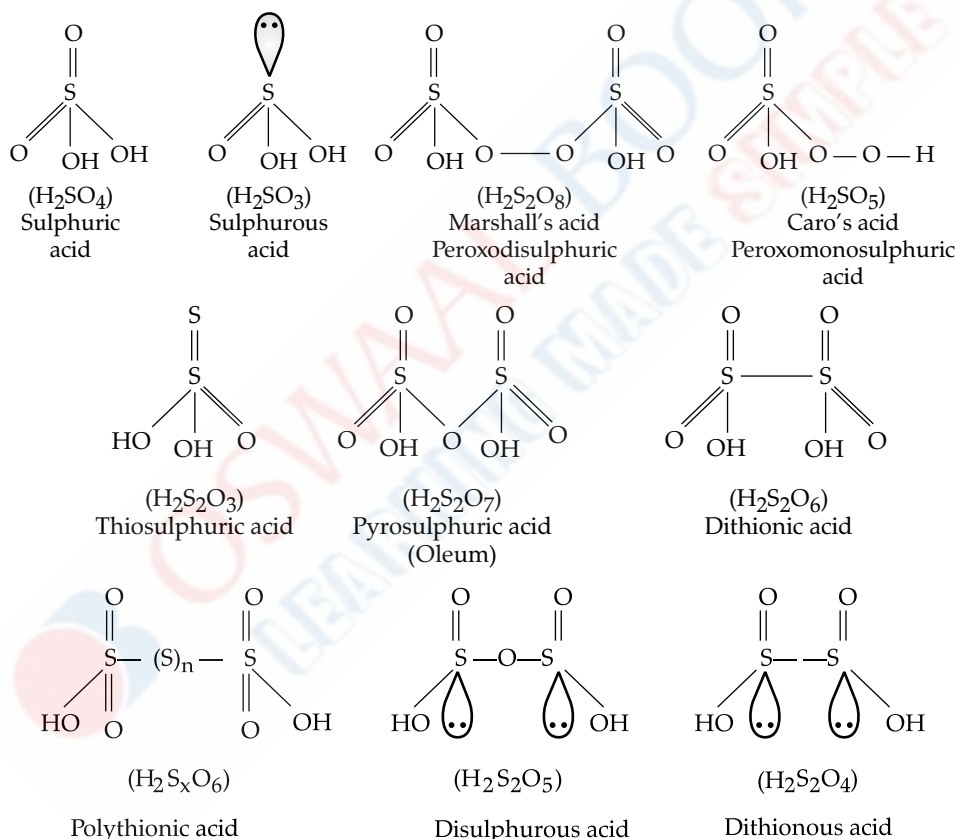
(i) In petroleum refining

(ii) Manufacture of pigments, paints and dye stuff

(iii) Detergent industry

(iv) In storage batteries

➤ **Oxoacids of Sulphur:**



Group-17 Elements, Properties and Some Important Compounds

➤ **Halogen family:** ${}_{9}\text{F}$, ${}_{17}\text{Cl}$, ${}_{35}\text{Br}$, ${}_{53}\text{I}$, ${}_{85}\text{At}$.

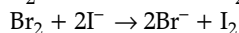
➤ **Physical Properties:**

- (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 oxidation state 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 character:** Due to very high ionisation enthalpies they are non-metals. The last element I, shows some metallic character as it can form I^+ by loss of electrons.

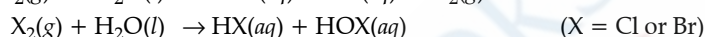
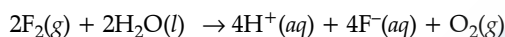
- (vi) **Electronegativity:** These are the most electronegative elements in their respective periods. Down the group, electronegativity decreases.
- (vii) F_2 and Cl_2 are gases, Br_2 is a liquid while I_2 is solid.
- (viii) All halogens are coloured.
- (ix) **Melting point and boiling point:** Increase 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 i.e., $Cl_2 > Br_2 > F_2 > I_2$.

➤ **Chemical Properties:**

- (a) **Highly reactive:** The reactivity decreases down the group. Fluorine is the strongest oxidising halogen. A halogen oxidises halide ions of higher atomic number.



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



- (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.

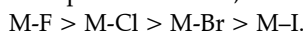
(iii) **Reducing character:** It increases from HF to HI due to decrease of stability.

(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



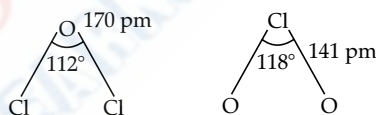
(ii) With metals having low I.E., halides are ionic.

(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.

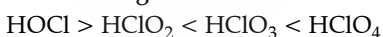
- (e) **Towards oxygen:** Halogens form many binary compounds with oxygen, but most of them are unstable. Cl, Br and I form oxides in their oxidation state +1 to +7. Their stability decreases in the order $I > Cl > Br$.



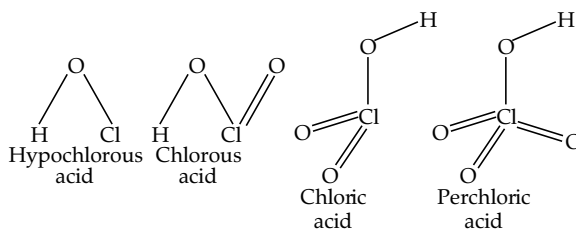
- (f) **Oxoacids:** Because of high electronegativity and small size, fluorine forms only one oxoacid, HOF (hypofluorous acid). The other halogens form acid of the type HOX —hypohalous acid, $HOXO$ —halous acid, $HOXO_2$ —halic acid and $HOXO_3$ —perhalic acid.

Acidic strength: $HClO > HBrO > HIO$

Acidic strength of oxoacids containing the same halogen:



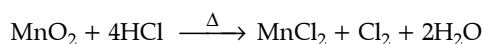
- (g) **Structure of oxoacids of Chlorine:**



➤ **Chlorine (Cl_2)**

Preparation:

In laboratory,



- (i) $4\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}_2} 2\text{Cl}_2 + 2\text{H}_2\text{O}$ (Deacon's process)
 (ii) $4\text{NaCl} + \text{MnO}_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{MnCl}_2 + 4\text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$

(iii) **Electrolytic process:** By electrolysis of brine.

At cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$; $\text{Na}^+ + \text{OH}^- \rightarrow \text{NaOH}$

At anode: $\text{Cl}^- \rightarrow \text{Cl} + \text{e}^-$; $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$

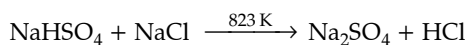
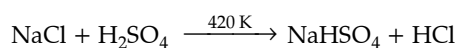
Properties:

- (i) It is a greenish yellow gas with a pungent suffocating smell
 (ii) It is soluble in water
 (iii) About 2.5 times heavier than air
 (iv) With metals and non-metals form chlorides
 $2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$; $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$
 $2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$; $\text{S}_8 + 4\text{Cl}_2 \rightarrow 4\text{S}_2\text{Cl}_2$
 $\text{P}_4 + 6\text{Cl}_2 \rightarrow 4\text{PCl}_3$; $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
 (v) Reacts with compounds containing hydrogen to form HCl
 $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$; $\text{C}_{10}\text{H}_{16} + 8\text{Cl}_2 \rightarrow 16\text{HCl} + 10\text{C}$
 $\text{NH}_3 + 3\text{Cl}_2 \rightarrow \text{NCl}_3 + 3\text{HCl}$; $8\text{NH}_3 + 3\text{Cl}_2 \rightarrow 6\text{NH}_4\text{Cl} + \text{N}_2$
 (excess) (explosive) (excess)
 (vi) With cold and dilute alkalis
 $2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$
 (cold and dilute)
 (vii) With hot and concentrated alkalis
 $6\text{NaOH} + 3\text{Cl}_2 \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$
 (hot and conc.)
 (viii) With dry slaked lime, it gives bleaching powder.
 $2\text{Ca}(\text{OH})_2 + 2\text{Cl}_2 \rightarrow \text{Ca}(\text{OCl})_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$
 (ix) Chlorine water on standing loses its yellow colour. HOCl formed gives nascent oxygen.
 $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$
 $\text{HOCl} \rightarrow \text{HCl} + \text{O}$
 (x) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.
 $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{HCl}$
 $\text{Na}_2\text{SO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$
 $\text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HCl}$
 $\text{I}_2 + 6\text{H}_2\text{O} + 5\text{Cl}_2 \rightarrow 2\text{HIO}_3 + 10\text{HCl}$

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):**

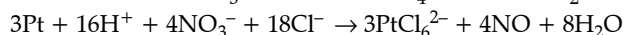
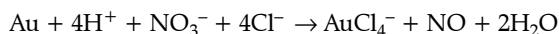
Preparation: In laboratory



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

Properties:

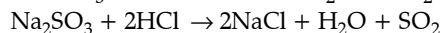
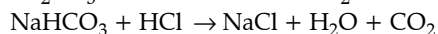
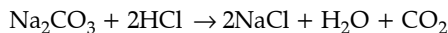
- (i) Colourless and pungent smelling gas.
 (ii) Extremely soluble in water.
 (iii) When three parts of conc. HCl and one part of conc. HNO_3 are mixed, aqua-regia is formed which is used for dissolving noble metals e.g., gold, platinum.



- (iv) Reacts with NH_3 giving white fumes of NH_4Cl



(v) Decomposes salts of weaker acids.



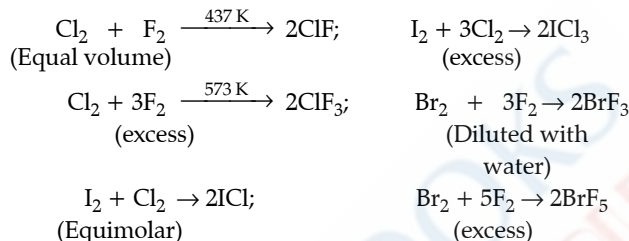
Uses:

(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 formulae 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:



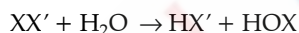
Properties:

(i) Covalent compounds.

(ii) Diamagnetic in nature.

(iii) More reactive than halogens.

(iv) Undergo hydrolysis.



- **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 .

Group-18 Elements, Properties and Some Important Compounds

- **Noble gases:** ${}^2\text{He}$, ${}^{10}\text{Ne}$, ${}^{18}\text{Ar}$, ${}^{36}\text{Kr}$, ${}^{54}\text{Xe}$, ${}^{86}\text{Ra}$.

- 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 increase down the group and highest in their respective periods.

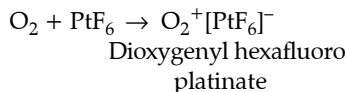
(iii) Highest ionisation enthalpy in their respective periods. Down the group, it decreases due to increase in atomic size.

(iv) Large positive values of electron gain enthalpy as noble gases have stable electronic configuration and no tendency to accept electron.

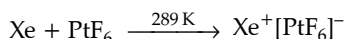
(v) Low melting points and boiling points due to weak dispersion forces. Down the group they increase because of increase in van der Waals forces.

(vi) **Liquefaction:** They are difficult to liquify. Down the group, the ease of liquefaction increases.

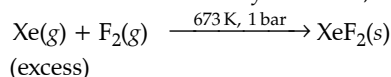
- In 1962, Bartlett studied the given reaction:

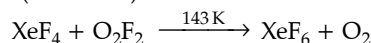
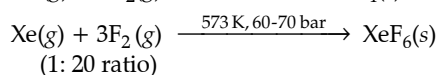
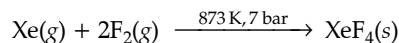


As ionisation enthalpy of molecular oxygen was almost similar to xenon, following reaction was also found to occur:

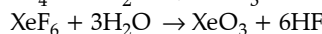


- **Preparation of Xenon fluorides:** Xenon forms three binary fluorides, XeF_2 , XeF_4 and XeF_6 .

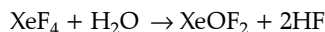




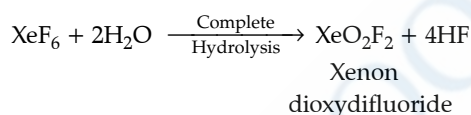
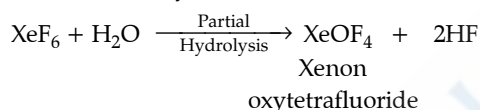
➤ **Preparation of Xenon trioxide (XeO₃):**



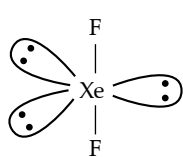
➤ **Preparation of Xenon oxyfluorides:**



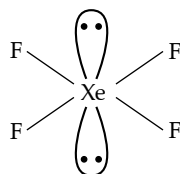
Xenon
oxydifluoride



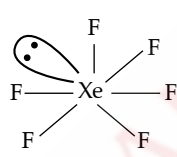
➤ **Structures of Xenon-fluorine compounds:**



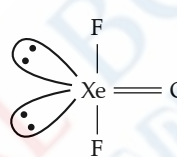
XeF₂ (sp³d)
[Linear]



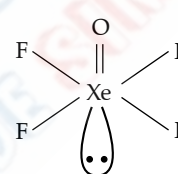
XeF₄ (sp³d²)
[Square Planar]



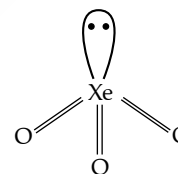
XeF₆ (sp³d³)
[Distorted
Octahedral]



XeOF₂ (sp³d)
[T-Shaped]



XeOF₄ (sp³d²)
[Square
Pyramidal]



XeO₃ (sp³)
[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.		

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 valence 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 NO₂ is known as fuming nitric acid. It can be obtained by distilling concentrated HNO₃ 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.
- **Chalcogens:** Group-16 elements are also known as chalcogens which means ore forming elements.

- **Oil of vitriol:** Pure sulphuric acid is highly viscous due to the presence of intermolecular hydrogen bonding. It is known as oil of vitriol.
- **Oxide:** A binary compound of oxygen with another element.
- **Pseudohalide ions:** CN^- , SCN^- and OCN^- ions are called pseudohalide ions while $(\text{CN})_2$, $(\text{SCN})_2$ and $(\text{OCN})_2$ are known as pseudohalogens.
- **Bleaching powder:** $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{CaOCl}_2 + \text{H}_2\text{O}$
Bleaching Powder

••

CHAPTER-4

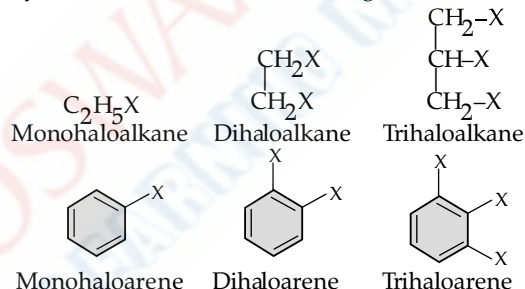
HALOALKANES AND HALOARENES

Revision Notes

Haloalkanes and their Properties

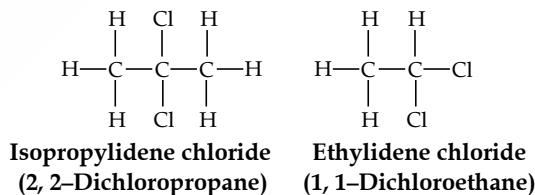
- Haloalkanes are aliphatic hydrocarbons where a hydrogen atom is replaced by halogen, while haloarenes are aromatic hydrocarbons where hydrogen in the benzene ring is replaced with halogen atom.
- Halogen atom is attached to sp^3 hybridised carbon atom in haloalkanes while in haloarenes it is attached to sp^2 hybridised carbon atom of the aryl group.
- **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,



Dihalogen compounds may be further classified as:

- (i) **Geminal dihalides:** Two halogen atoms are attached to the same carbon atom. For example,

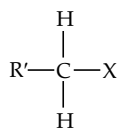


- (ii) **Vicinal dihalides:** Two halogen atoms are attached to adjacent carbon atoms. For example,

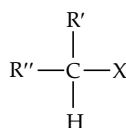


- **On the basis of sp^3 hybridisation:**

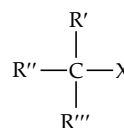
- (i) **Haloalkanes or alkyl halides ($\text{R}-\text{X}$):** General formula is $\text{C}_n\text{H}_{2n+1}\text{X}$. They are further classified as primary, secondary and tertiary haloalkanes.



Primary haloalkane

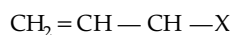


Secondary haloalkane



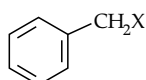
Tertiary haloalkane

(ii) **Allylic halides:** Halogen is bonded to allylic carbon.

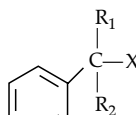
Allyl halide
(3-Halo-1-propene)

3-Halocyclohex-1-ene

(iii) **Benzylic halides:** Halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.

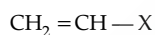


Benzyl halide (1°)

Here, $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$ (2°)
or $\text{R}_1 = \text{R}_2 = \text{CH}_3$ (3°)

● **On the basis of sp^2 hybridisation:**

(i) **Vinyl halides:** Halogen is bonded to one of the carbon atoms of a vinylic carbon.



Vinyl halide



1-Halocyclohex-1-ene

(ii) **Aryl halides:** Halogen atom is directly bonded to sp^2 hybridised carbon atom of an aromatic ring.

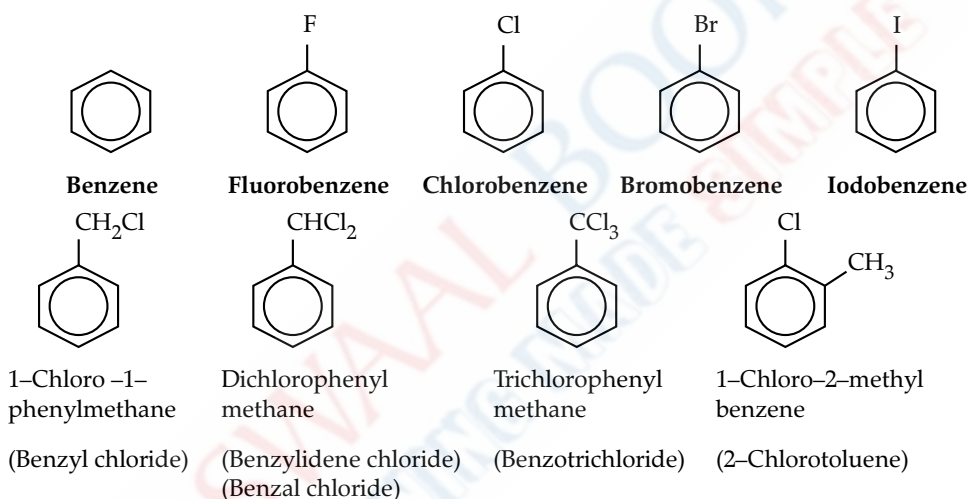


Halobenzene

➤ **Common and IUPAC name of some halides:**

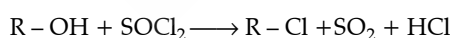
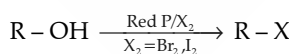
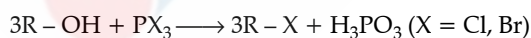
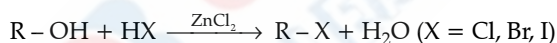
Structure	IUPAC Name	Common names
CH_3Cl	Chloromethane	Methyl chloride
$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane	Ethyl chloride
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Cl}$	1-Chloropropane	<i>n</i> -Propyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chloropropane	Isopropyl chloride
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{Cl}$	1-Chlorobutane	<i>n</i> -Butyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	1-Chloro-2-methyl propane	Isobutyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chlorobutane	Sec. butyl chloride
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chloro-2-methyl propane	Tertiary butyl chloride
CH_3F	Fluoromethane	Methyl fluoride
CH_3Br	Bromomethane	Methyl bromide
CH_3I	Iodomethane	Methyl iodide

CH ₂ Cl ₂	Dichloromethane	Methylene dichloride
CHCl ₃	Trichloromethane	Chloroform
CCl ₄	Tetrachloromethane	Carbon tetrachloride
CHBr ₃	Tribromomethane	Bromoform
CHI ₃	Triiodomethane	Iodoform
ClCH ₂ —CH ₂ Cl	1, 2-Dichloroethane	Ethylene dichloride
CH ₃ CHCl ₂	1, 1-Dichloroethane	Ethylidene chloride
CH ₂ = CHCl	Chloroethene	Vinyl chloride
CH ₂ = CH—CH ₂ Br	3-Bromopropene	Allyl bromide
(CH ₃) ₃ CCH ₂ Br	1-Bromo-2, 2-dimethylpropane	neo-pentylbromide
CF ₃ CF ₂ CF ₃	Octafluoropropane	Perfluoropropane
CCl ₂ F ₂	Dichlorodifluoromethane	Freon
CHCl ₂ —CHCl ₂	1, 1, 2, 2-Tetrachloroethane	Acetylene tetrachloride
CHCl = CCl ₂	1, 1, 2-Trichloroethene	Acetylene trichloride



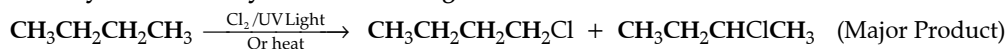
➤ **Methods of preparation of Haloalkanes:**

(a) **From alcohols:** Alkyl halides are prepared from alcohols, which are easily accessible.



The reactions of primary and secondary alcohols with HX require the presence of the anhydrous ZnCl₂.

(b) **From hydrocarbons: By free radical halogenation.**

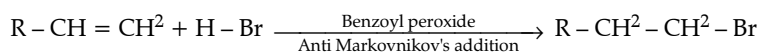
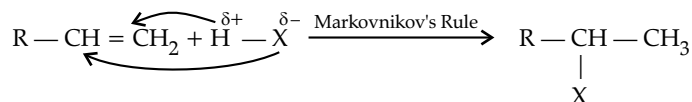
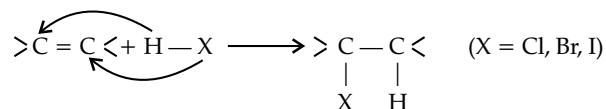
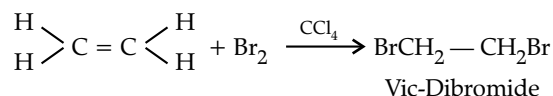
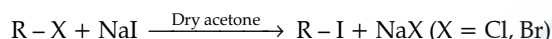
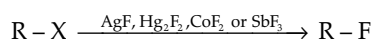


n-Butane

n-Butyl chloride

Sec.-Butyl chloride

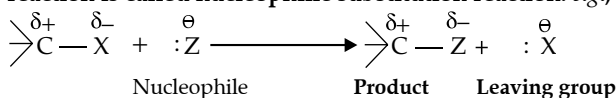
(c) **From alkenes:**

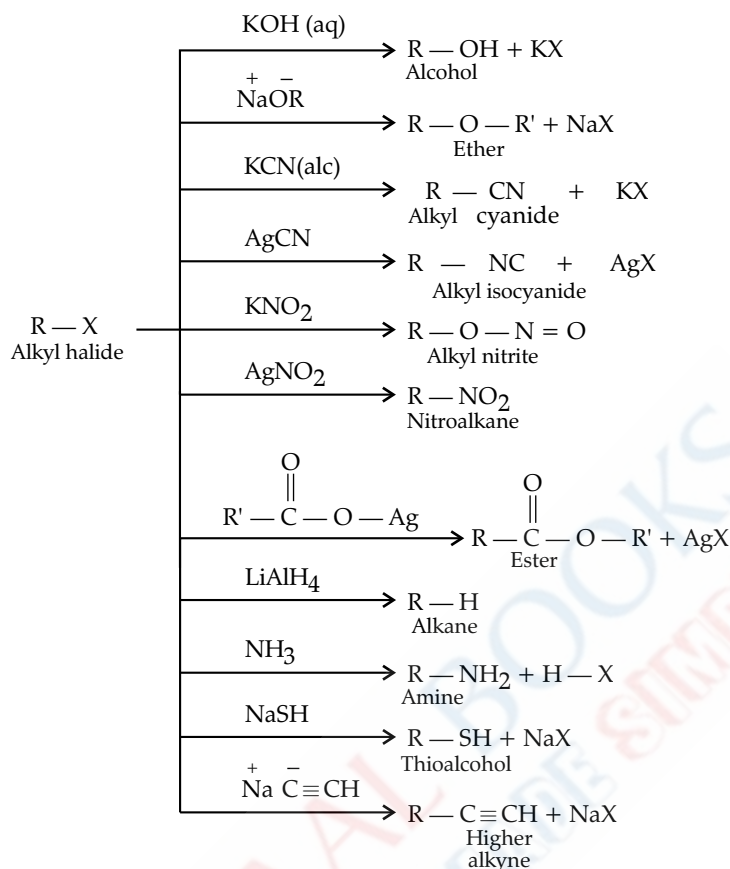
(c) From alkenes:**(i) Addition of hydrogen halide:****(ii) Addition of Halogens:****(d) Halide Exchange:****(i) By Finkelstein Reaction:****(ii) By Swarts Reaction:**

- **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 is the smallest and iodine is 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 increasing size, mass of halogens and magnitude of van der Waals forces of attractions. The increasing order is $\text{RF} < \text{RCl} < \text{RBr} < \text{RI}$. 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, halogen atoms and atomic mass of the 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., $\text{C}-\text{Cl} > \text{C}-\text{Br} > \text{C}-\text{I}$. Reactivity order of haloalkanes would be:

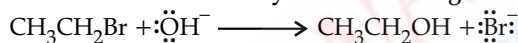


There are four types of chemical reactions with haloalkanes:

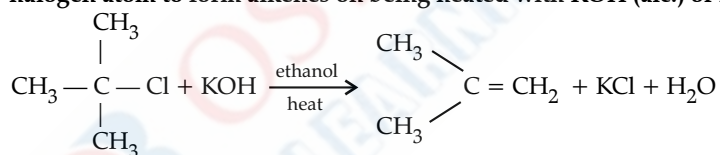
(a) Nucleophilic substitution reactions: When an atom or group of atoms is replaced by a nucleophile, the reaction is called nucleophilic substitution reaction. e.g.,



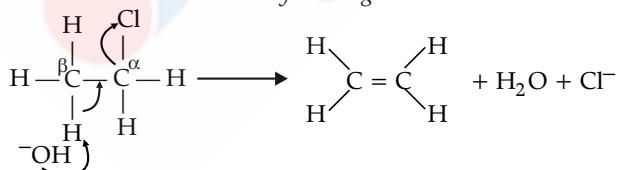
Alkyl halides undergo nucleophilic substitution reactions.



- (b) **Elimination reaction:** Alkyl halides undergo β -elimination of hydrogen atom from β -carbon atom and halogen atom to form alkenes on being heated with KOH (alc.) or KNH₂. e.g.,



The reaction is called *dehydrohalogenation*.

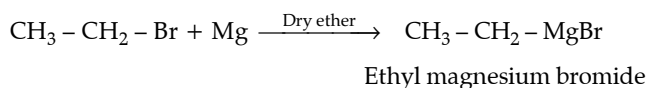
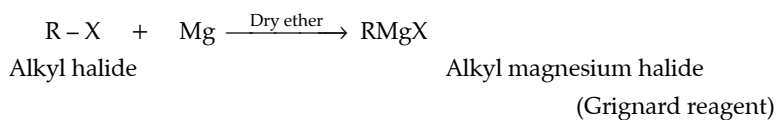


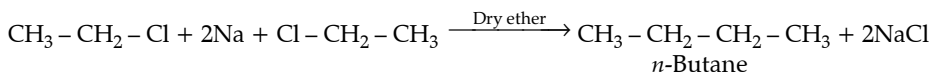
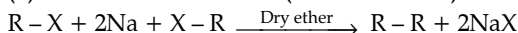
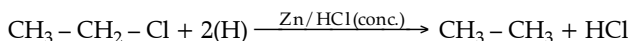
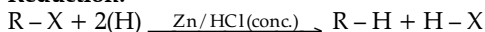
The following is order of reactivity:



- (c) **Reaction with metals:**

(1) **Reaction with magnesium:**

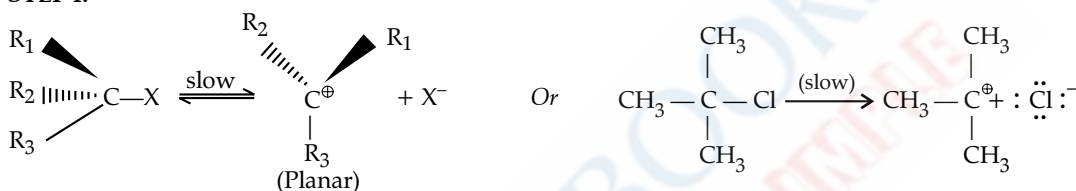


(2) Reaction with sodium (Wurtz reaction):**(d) Reduction:**

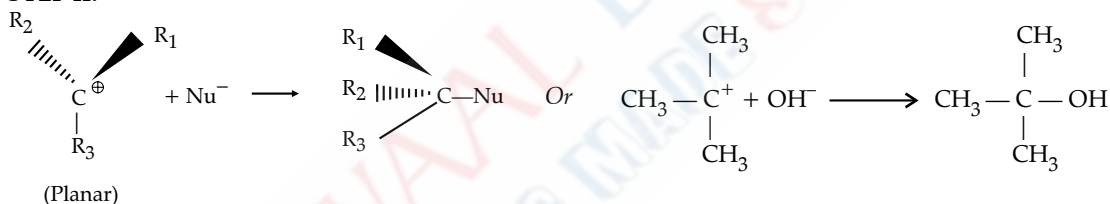
➤ **Mechanism of Nucleophilic substitution reaction:** Alkyl halides undergo two types of nucleophilic substitution reactions.

(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.*, hydrolysis of tertiary butyl chloride follows S_N1 reaction. This reaction takes place in two steps:

STEP I:

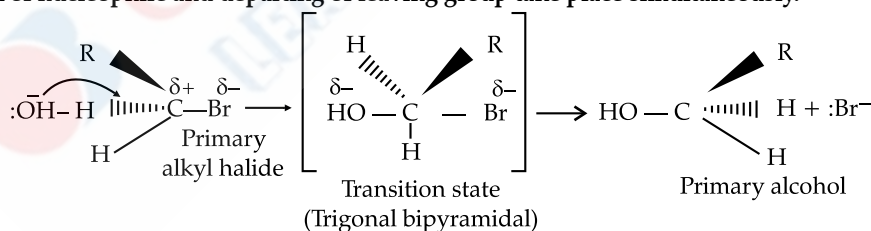


STEP II:



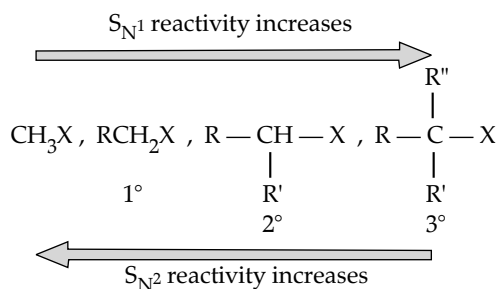
The slowest step is rate determining step which involves one species only. Therefore, rate of reaction depends only on the concentration of tertiary butyl chloride. Polar protic solvents like water, alcohol favour S_N1 because they stabilize carbocation by solvation. Tertiary alkyl halides follow S_N1 mechanism.

(ii) **Bimolecular nucleophilic substitution reaction (S_N2):** 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_N2 mechanism. Primary alkyl halides follow S_N2 mechanism.

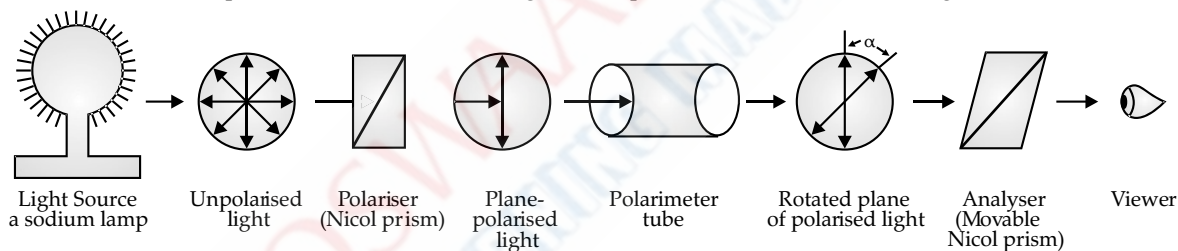
➤ **Reactivity of S_N1 and S_N2 mechanisms:** S = Substitution, N = Nucleophilic, 2 = Bimolecular, 1 = Unimolecular. Nucleophilic substitution seldom occurs exclusively by one mechanism only. With a given halogen, primary, secondary and tertiary halides show opposite order of reactivity in the two mechanisms.



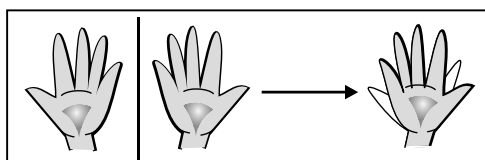
- **Stereoisomerism:** Isomerism exhibited by two or more compounds with the same molecular and structural formula, but different spatial arrangements of atoms or groups in space is called stereoisomerism.
- **Plane-polarised light:** The beam of light whose oscillations or vibrations are confined to 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 a positive (+) sign is placed before the degree 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 degree 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.

$$\text{Specific rotation } [\alpha]_D^{t^\circ C} = \frac{\text{observed rotation } (\alpha_{obs})}{\text{length of tube } (d_m) \times \text{concentration of solution } (\text{g mol}^{-1})}$$

- **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 the figure below:



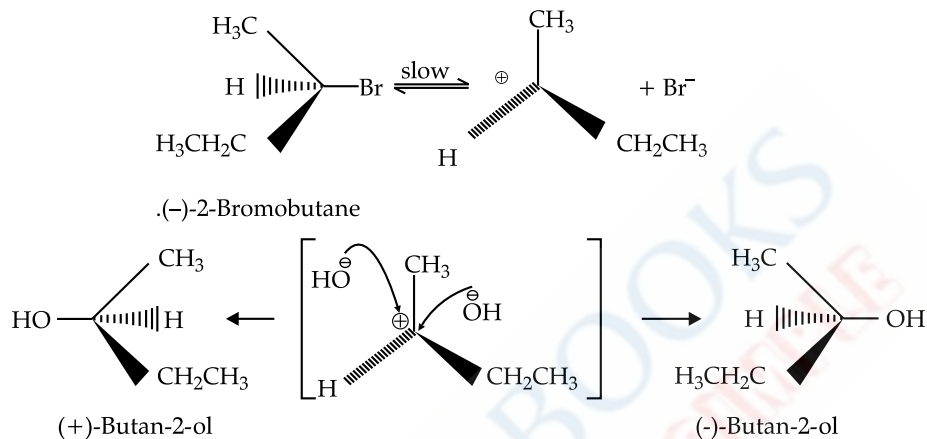
- **Enantiomers:** Those stereoisomers which are mirror images of each other but non-superimposable are called enantiomers, *e.g.*, *d*(+) glucose and *l*(–) glucose are enantiomers.
- **Asymmetric molecule:** If all the four substituents attached to carbon are different, the resulting molecule will 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.*,



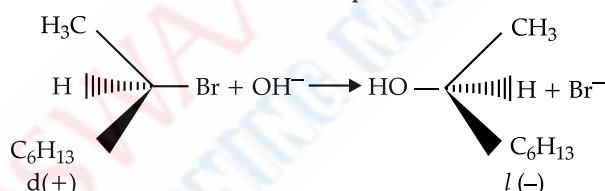
Non-superimposable hands

- **Achiral:** Achiral objects are those objects which are superimposable on their mirror images.
- **Asymmetric carbon (Chiral carbon):** The carbon atom which is attached with four different groups of atoms is called asymmetric or chiral carbon atom.
- **Racemic mixture:** A mixture containing equal amounts of enantiomers which does not show any optical activity. It is optically inactive due to external compensation.
- **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 pairs of stereoisomers which are not mirror images of each other and are non-superimposable.
 - Diastereoisomers have different physical properties.**
 - Diastereoisomers differ in magnitude of specific rotation.**
 - A compound with two chiral centres does not always have four stereoisomers.**
- **Example of racemisation in S_N1 mechanism:** When optically active alkyl halide undergoes S_N1 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_N1 mechanism has both inversion as well as rotation, the products formed by this reaction would be racemic mixture of alcohols.



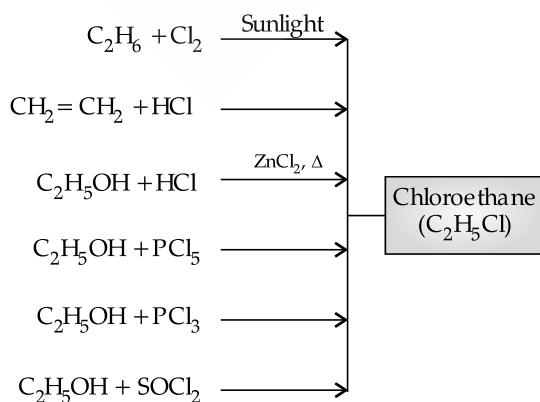
- **Meso compounds:** Those compounds which have two or more (even number) chiral carbon atoms and have an internal plane of symmetry are called meso compounds. They are optically inactive due to internal compensation.
- **Example of inversion in S_N2 mechanism:** When optically active *d* (+) alkyl halide is treated with OH^- , we get optically active *l* (-) alcohol due to back side attack of nucleophile.



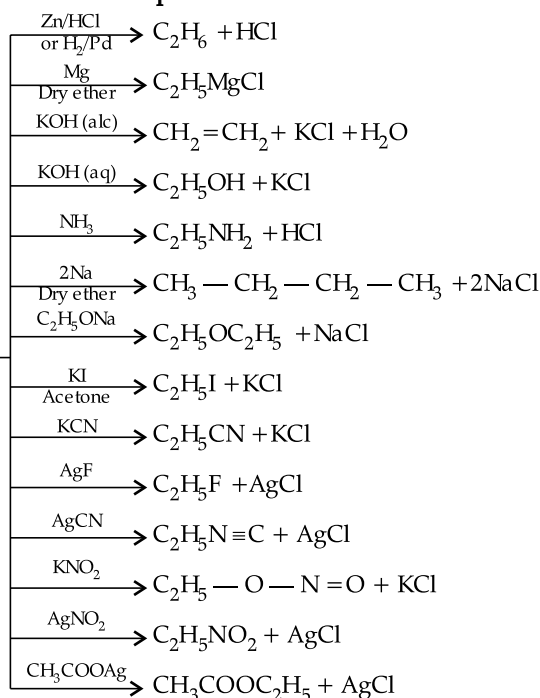
When *d*(+)-2-bromooctane is reacted with NaOH, *l*(-)-2-octanol is formed. Thus, S_N2 mechanism leads to inversion of configuration. This inversion is called Walden's inversion.

● Important reactions of chloroethane:

Preparation

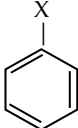


Chemical Properties

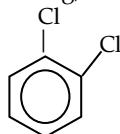


Haloarenes and Polyhalogen Compounds

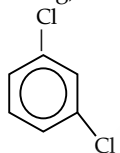
- **Haloarenes:** Haloarenes are the compounds formed by replacing one or more hydrogen atoms in an aromatic

ring with halogen atoms. For example, monohalogen derivative  (X = F, Cl, Br, or I).

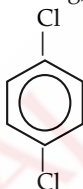
- When two halogens are at 1, 2- positions of benzene ring, it is called ortho substituted derivative. *e.g.*,



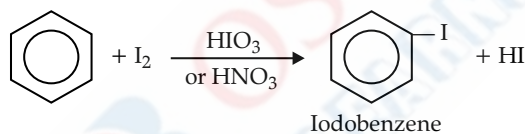
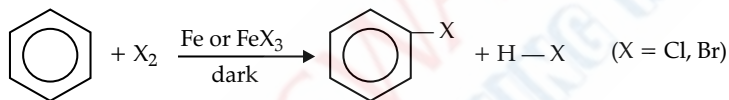
- When two halogens are at 1, 3- positions of benzene ring, it is called meta substituted derivative. *e.g.*,



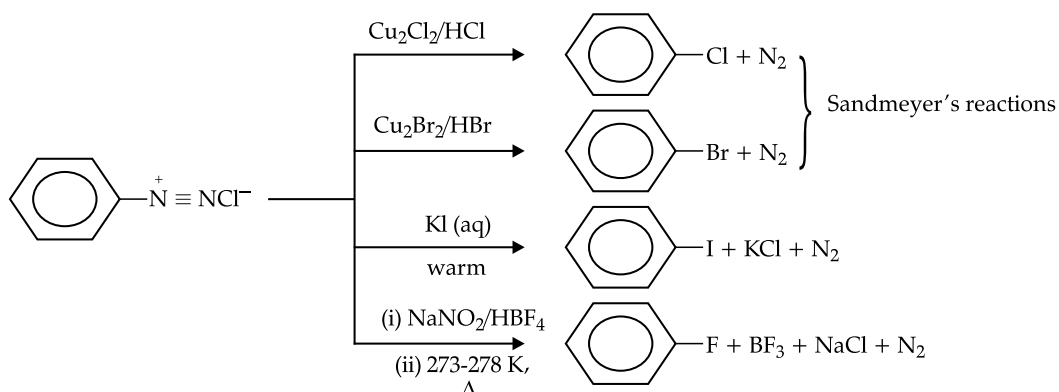
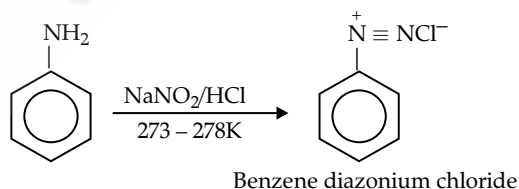
- When two halogens are at 1, 4- positions of benzene ring, it is called para substituted derivative. *e.g.*,



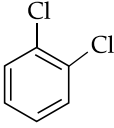
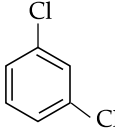
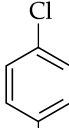
- **Methods of preparation of Haloarenes: (i) Reacting benzene directly with halogen:**



- (ii) **Starting with diazonium salts:**



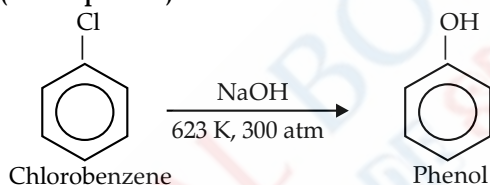
- **Physical properties of Haloarenes:** Isomeric haloarenes have similar boiling points. But *para* isomer has higher melting point than other two *i.e.*, *ortho* and *meta* because of the symmetry in *para* isomer which occupies the crystal lattice better than *ortho* and *meta* isomers.

		
<i>o</i> -	<i>m</i> -	<i>p</i> -
b.p. (K) 453	446	448
m.p. (K) 256	249	323

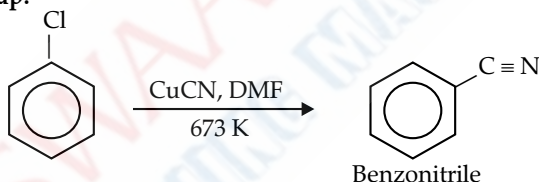
- **Chemical properties of Haloarenes:**

(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.

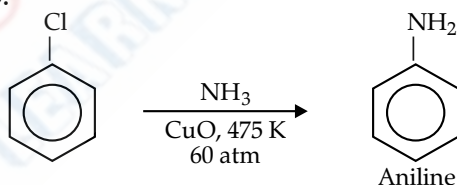
(i) Substitution by —OH group (Dow's process):



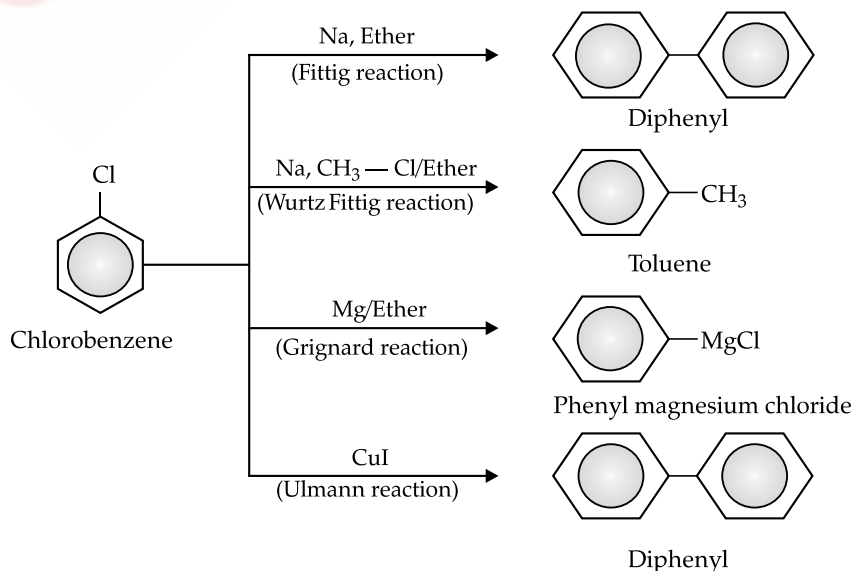
(ii) Substitution by —CN group:



(iii) Substitution by —NH₂ group:

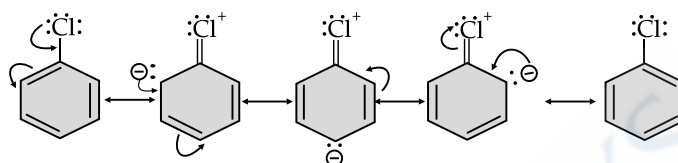


(iv) Reaction with metals:



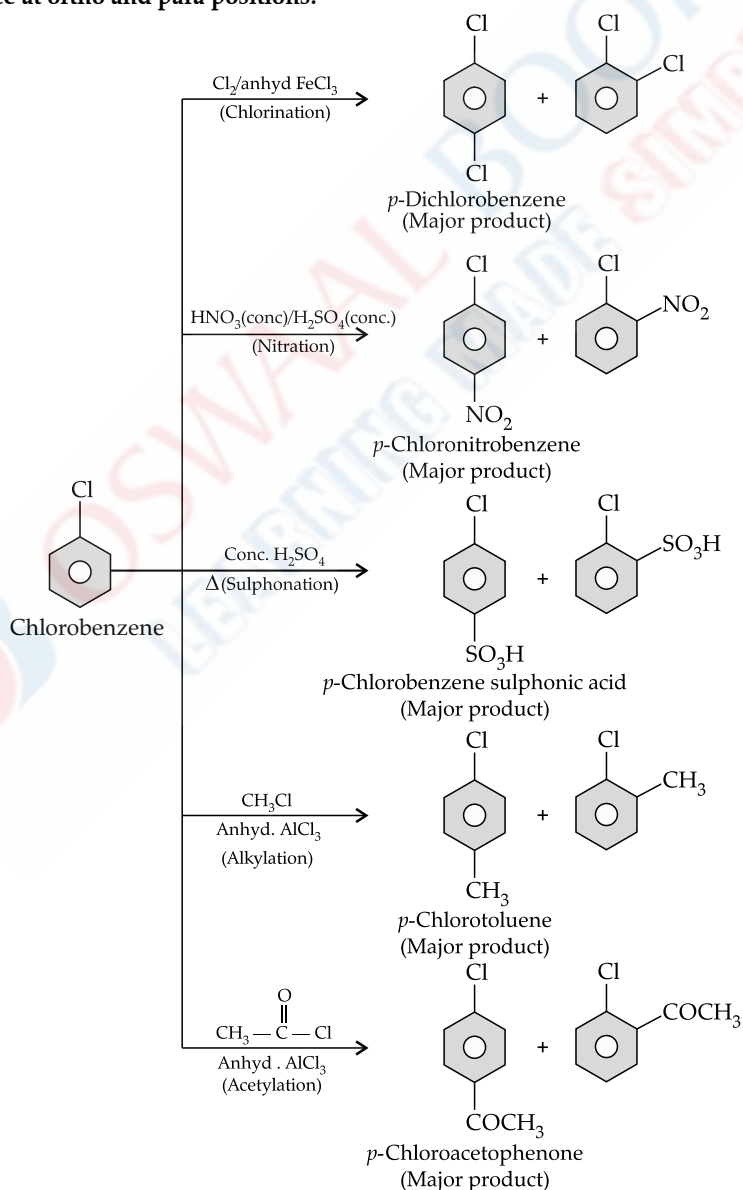
- **Nature of C—X bond in haloarene:** The C—X bond of aryl halide is less reactive than that of haloalkanes. One reason is that in aryl halide, halogen atom is attached to sp^2 -hybrid carbon atom whereas in alkyl halides, it is attached to sp^3 -hybrid carbon atom. Due to more electronegativity of sp^2 -hybrid carbon in comparison to sp^3 -carbon atom, there is less charge in separation of C—X bond in haloarene.

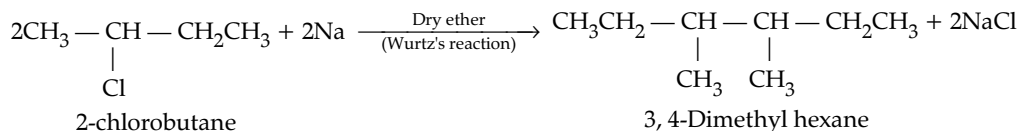
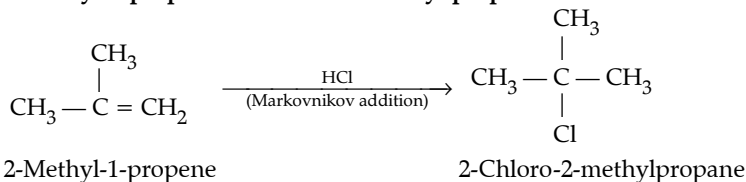
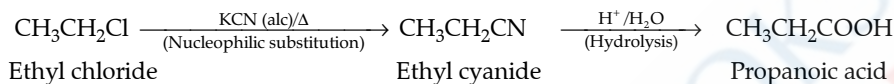
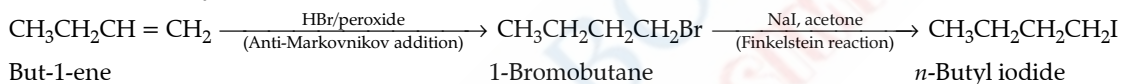
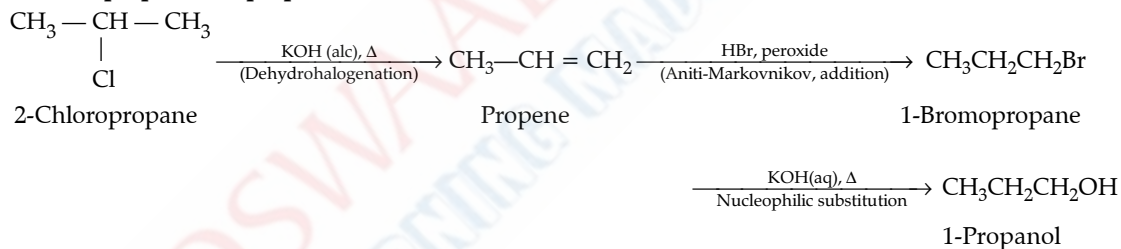
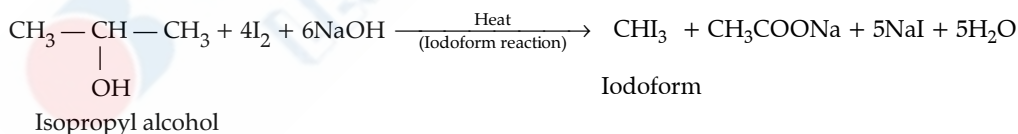
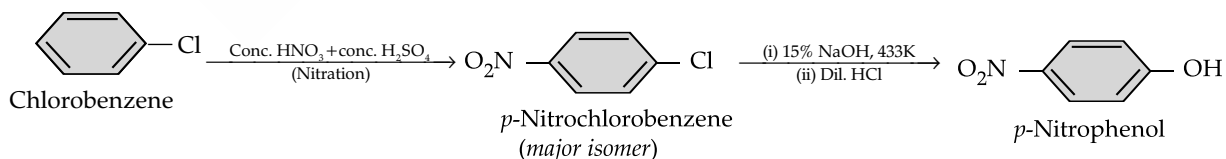
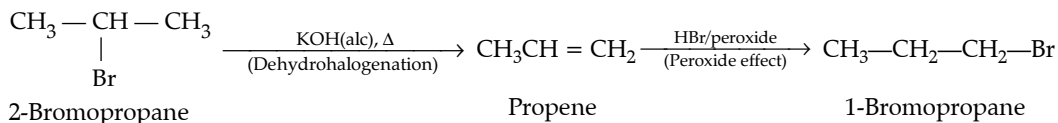
Secondly in aryl halides like chlorobenzene, the lone pair of electrons present on chlorine atom migrate towards the aromatic ring by +R effect due to conjugation of lone pair of electrons with π -electrons of the aromatic ring. As a result of which, the halogen atom is attached with the aromatic ring by partial double bond. The phenyl cation formed is highly unstable. The replacement of such a halogen atom by other nucleophiles becomes difficult.

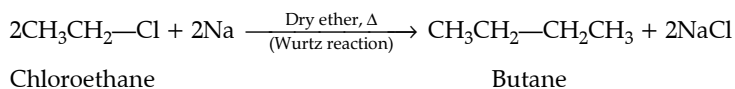
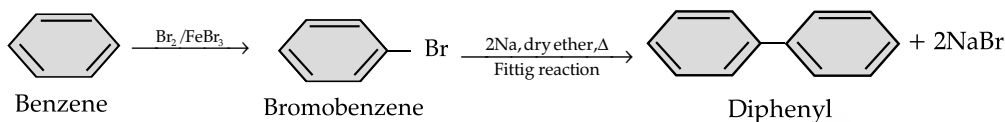
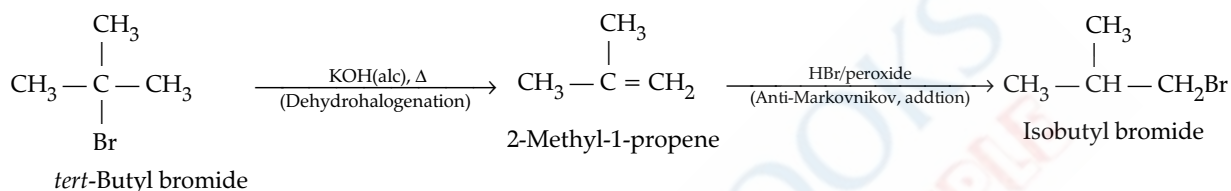
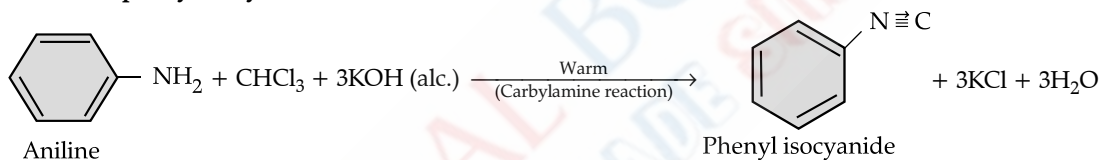
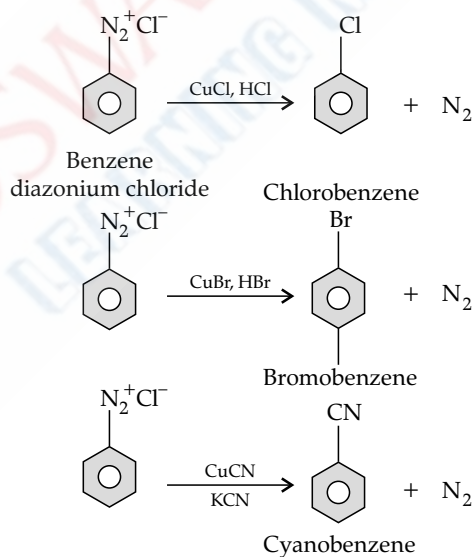
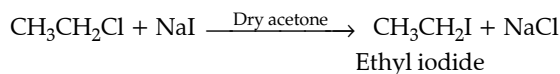
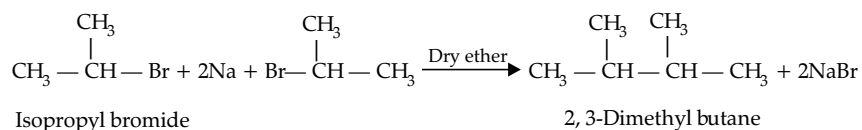
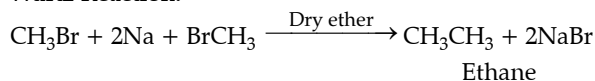


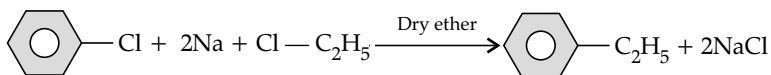
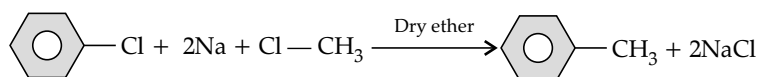
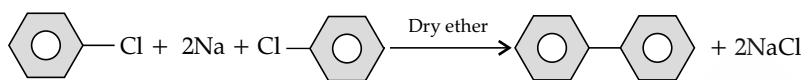
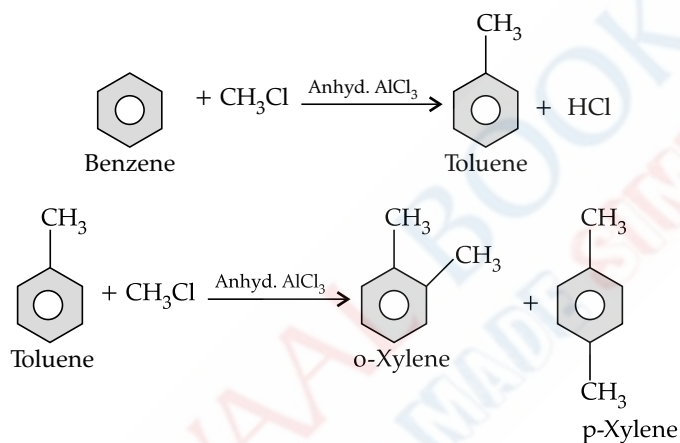
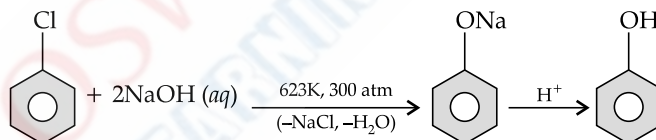
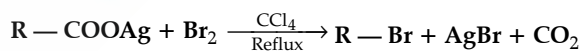
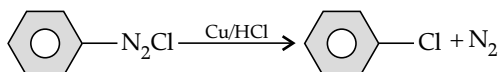
(v) **Electrophilic substitution reactions of haloarenes:**

It takes place at ortho and para positions:

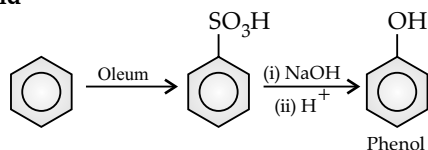
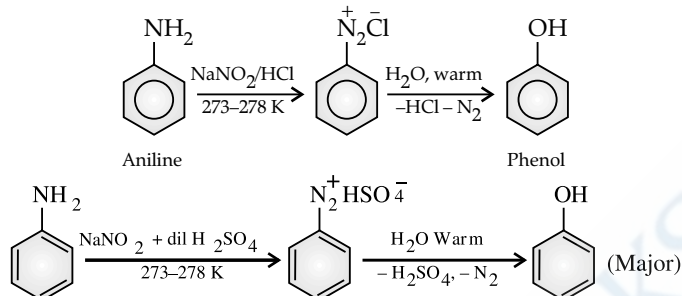


(ix) 2-Chlorobutane to 3, 4-dimethyl hexane:**(x) 2-Methyl-1-propene to 2-chloro-2-methyl propane:****(xi) Ethyl chloride to propanoic acid:****(xii) But-1-ene to *n*-butyl iodide:****(xiii) 2-Chloropropane to 1-propanol:****(xiv) Isopropyl alcohol to iodoform:****(xv) Chlorobenzene to *p*-nitrophenol:****(xvi) 2-Bromopropane to 1-bromopropane:**

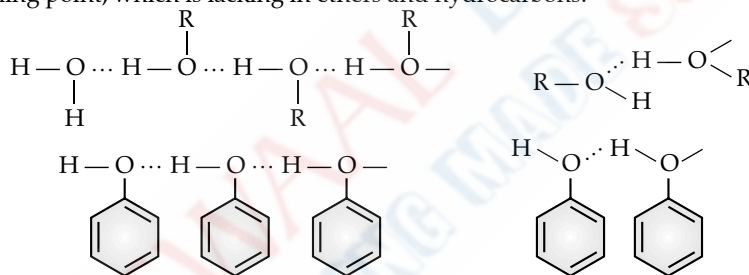
(xvii) Chloroethane to butane:**(xviii) Benzene to diphenyl:****(xix) *tert*-Butyl bromide to iso-butyl bromide:****(xx) Aniline to phenyl isocyanide:****➤ Important Name Reactions:****(i) Sandmeyer's Reaction:****(ii) Finkelstein Reaction:****(iii) Wurtz Reaction:**

(iv) Wurtz-Fittig Reaction:**(v) Fittig's Reaction:****(vi) Friedel-Crafts Alkylation:****(vii) Dow's Process:****(viii) Hunsdiecker's Reaction:****(ix) Gattermann's Reaction:****Know the Terms**

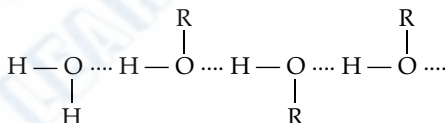
- **Synthetic tools:** Alkyl halides are regarded as synthetic tools in the hands of chemistry due to their highly reactive nature.
- **Relative configuration:** Arrangement of atoms in space of a stereo isomer of a compound relative to another compound chosen as arbitrary standard (like glyceraldehyde).

(ii) From benzene sulphonic acid**(iii) From diazonium salts****➤ Physical and Chemical properties of Alcohols and Phenols:****(1) Physical properties:**

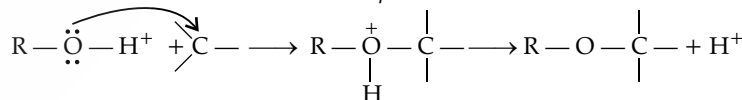
- (i) **Boiling points:** The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area). The -OH group in alcohols and phenols is involved in intermolecular hydrogen bonding resulting in high boiling point, which is lacking in ethers and hydrocarbons.



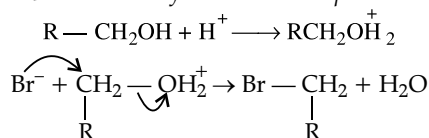
- (ii) **Solubility:** Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.



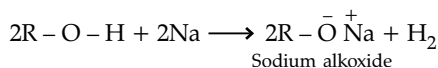
- (2) **Chemical properties:** Alcohols and phenols react both as nucleophiles and electrophiles. The bond between O-H is broken when alcohols react as *nucleophiles*.

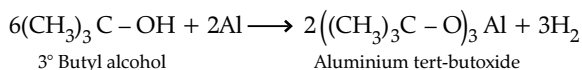
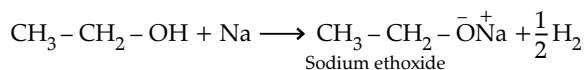
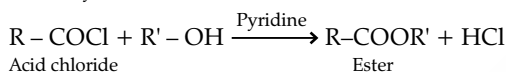
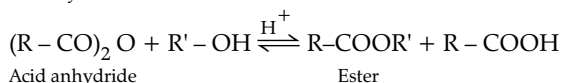
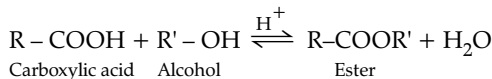


The bond between C-O is broken when they react as *electrophiles*.

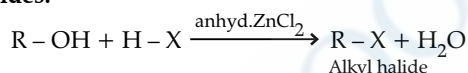
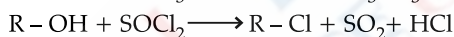
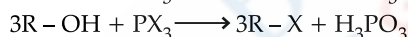
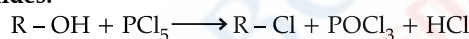
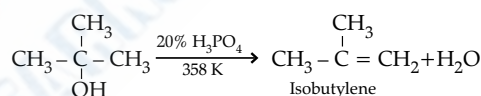
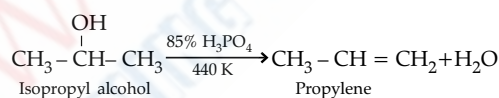
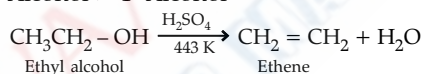
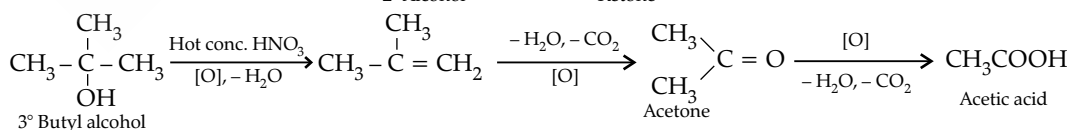
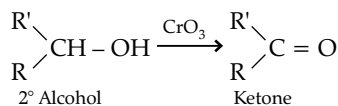
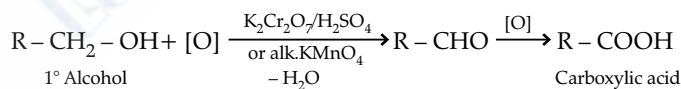
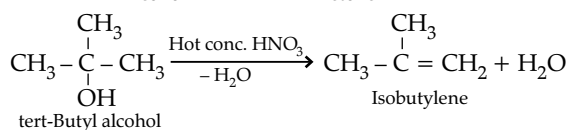
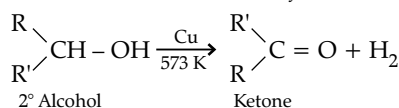
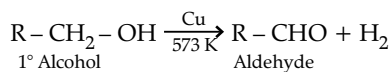


The reactions of alcohols can be classified into:

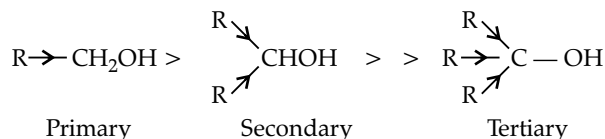
(a) Reactions involving the cleavage of O-H bond:**(i) Reaction with metals:**

**(ii) Esterification:****(b) Reactions involving cleavage of C–O bond:**

Order of reactivity in such type of reaction is

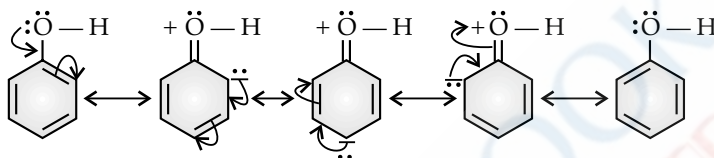
**(i) Reaction with hydrogen halides:****(ii) Reaction with phosphorus halides:****(c) Reactions involving both the alkyl and hydroxyl group:****(i) Dehydration:** 3° Alcohol > 2° Alcohol > 1° Alcohol**(ii) Oxidation:****(iii) Dehydrogenation:**

- **Acidity of alcohols and phenols:** The acidic character of alcohols is due to the polar nature of O–H bond. An electron releasing group (–CH₃, –C₂H₅) 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:

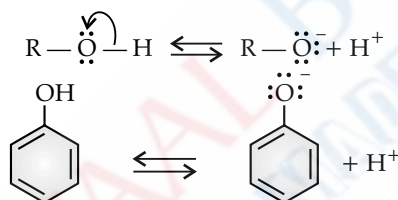


Alcohols can act as Bronsted acids as well as bases due to donation of proton and presence of unpaired electron on oxygen respectively.

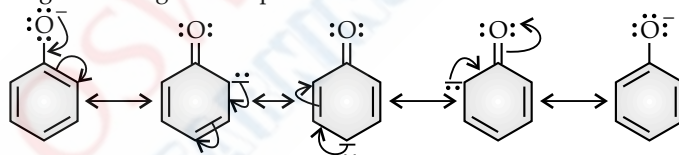
Phenols are more acidic than alcohols and water. The hydroxyl group in phenol is directly attached to the *sp*²-hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.



The ionisation of an alcohol and a phenol takes place producing alkoxide and phenoxide ions as shown in following 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.



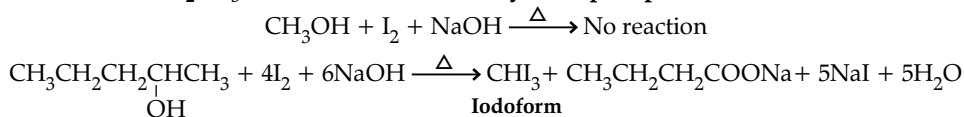
- **Distinction between Primary, Secondary and Tertiary Alcohols:**

- (i) **Lucas Test:** Alcohol on treating with Lucas reagent forms a clear solution. Alkyl chlorides are formed on reaction which being insoluble results in the turbidity in the solution.

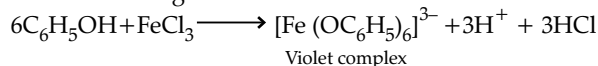


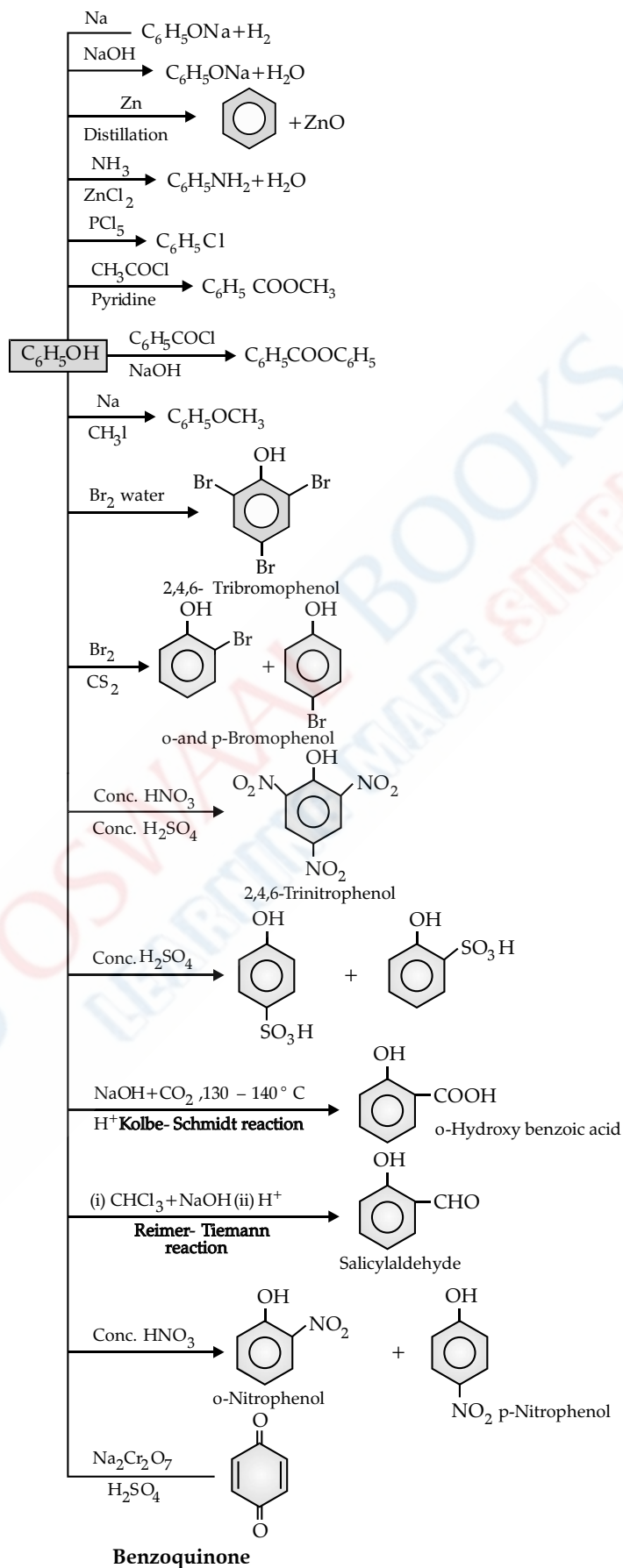
Tertiary alcohol is indicated, if turbidity appears immediately. Secondary alcohol is indicated, if turbidity appears within five minutes. Primary alcohol is indicated, if turbidity appears on heating.

- (ii) **Iodoform test:** When ethanol or any alcohol containing the group $\text{CH}_3 - \overset{\text{OH}}{\text{CH}} -$ is heated with iodine and aqueous NaOH or Na₂CO₃ solution at 333 – 343 K, a yellow precipitate of iodoform is obtained.

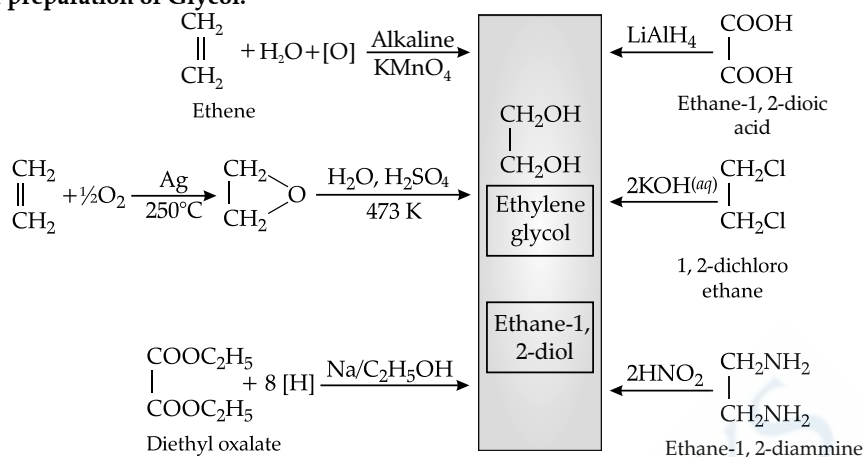


- (iii) **Ferric chloride test of phenols:** Phenol gives a violet coloured water soluble complex with ferric chloride.

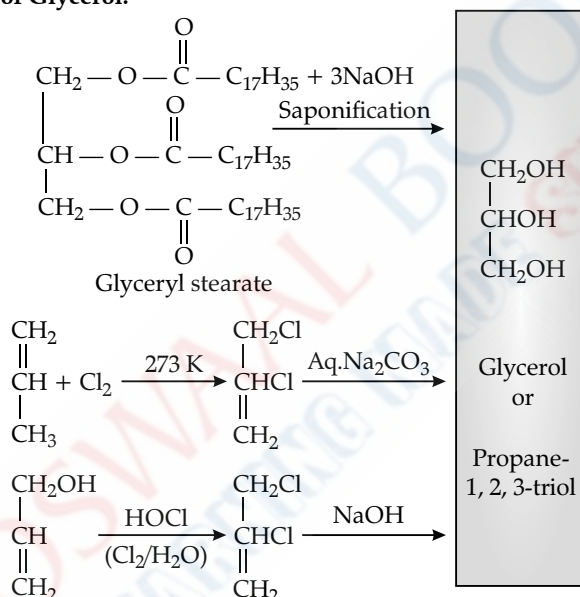


➤ **Reactions of Phenol:**

➤ **Methods of preparation of Glycol:**



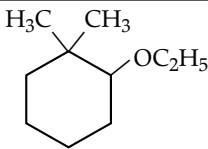
➤ **Methods of preparation of Glycerol:**



Methods of Preparation and Properties of Ethers

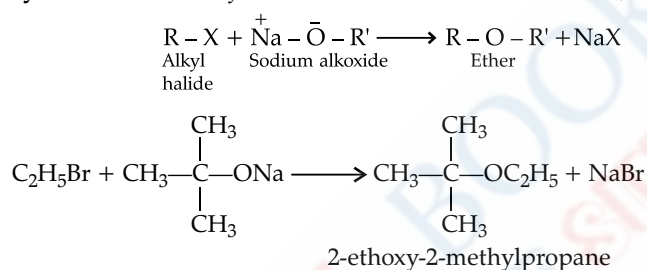
- **Ethers:** Compounds with general formula $\text{C}_n\text{H}_{2n+2}\text{O}$. They are represented by general structure, $\text{R}-\text{O}-\text{R}'$.
- **Nomenclature of Ethers:** Ethers are named from names of alkyl/aryl/groups written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group. For example, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ is diethyl ether. These types of ethers are called symmetrical ethers. If both the alkyl groups are different, for example, $\text{CH}_3\text{OC}_2\text{H}_5$ 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
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Methyl <i>n</i> -butyl ether	1-Methoxybutane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene
$\text{C}_2\text{H}_5-\text{O}-\text{C}_6\text{H}_5$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6-\text{CH}_3$	Heptyl phenyl ether	1-Phenoxyheptane

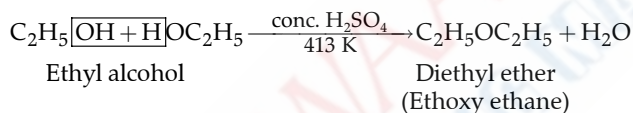
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2$	Phenyl isopentyl ether	3-Methylbutoxybenzene
$\text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	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.*,

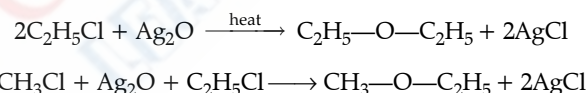


(ii) **Dehydration of alcohols:** Alcohols are dehydrated to ethers in presence of concentrated sulphuric acid at 413 K. The reaction involves the removal of one molecule of water from two moles of alcohols.



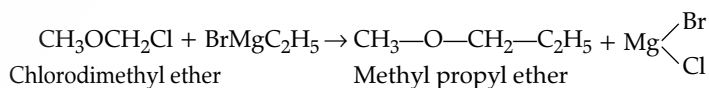
Alcohols can also be dehydrated by heating with alumina at 523 K and high pressure. This method is not suitable for preparation of unsymmetrical ethers.

(iii) **Heating alkyl halides with dry silver oxide:** Ethers can be prepared by heating alkyl halides with dry silver oxide (Ag_2O).

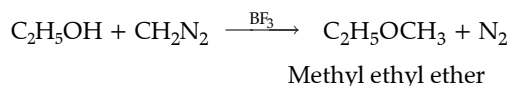


Mixed ethers or unsymmetrical ethers can be prepared by this method.

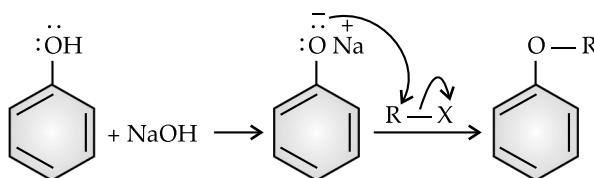
(iv) **Reaction of lower halogenated ethers with Grignard reagent:** Higher homologous ethers can be prepared by action of Grignard reagent on lower halogenated ethers.



(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 .

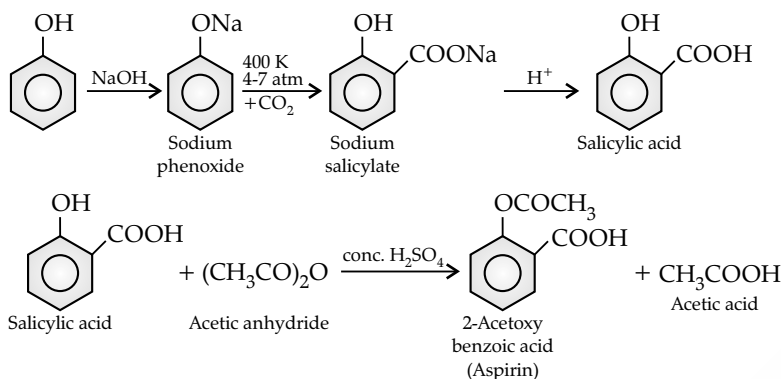


(vi) **From phenol:**

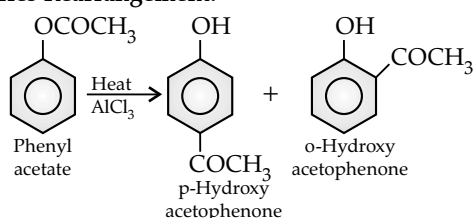


➤ **Some important name reactions:**

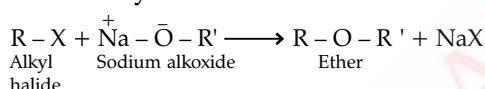
(i) **Kolbe's reaction:**



(ii) **Fries Rearrangement:**



(iii) **Williamson synthesis:**



Know the Terms

- **Lucas reagent:** An equimolar mixture of HCl and ZnCl₂.
- **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 purposes is called methylated spirit.
- **Fusel oil:** In the fermentation of starch, ethyl alcohol is prepared but in small amount. Some higher alcohols 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.
- **Lederer-Mannase reaction:** Phenol condenses with formaldehyde in presence of acid or base to give bakelite (polymer). The reaction is known as Lederer-Mannase reaction.
- **Rectified spirit:** It contains about 95.5% Ethyl alcohol + 4.5% water.

••

CHAPTER-6 BIOMOLECULES

Revision Notes

Carbohydrates, their Classification and Importance

- **Biomolecules:** Biomolecules are the naturally occurring organic compounds present as essential constituents of living organism in different cells. e.g., polysaccharides, proteins, etc.
- **Carbohydrates:** Carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or compounds 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 ₃ H ₆ O ₃	CH ₂ OH.CHOH.CHO	Glyceraldehyde
Aldotetrose	C ₄ H ₈ O ₄	CH ₂ OH.(CHOH) ₂ .CHO	Erythrose, Threose
Aldopentose	C ₅ H ₁₀ O ₅	CH ₂ OH.(CHOH) ₃ .CHO	Arabinose, Ribose, Xylose, Lyxose
Aldohexose	C ₆ H ₁₂ O ₆	CH ₂ OH.(CHOH) ₄ .CHO	Glucose, Mannose, Galactose, Talose, Idose, Ilose, Altrose
Ketoses			
Ketotriose	C ₃ H ₆ O ₃	CH ₂ OH.CO.CH ₂ OH	Dihydroxyacetone
Ketotetrose	C ₄ H ₈ O ₄	CH ₂ OH.CO.CHOH.CH ₂ OH	Erythrulose
Ketopentose	C ₅ H ₁₀ O ₅	CH ₂ OH.CO.(CHOH) ₂ .CH ₂ OH	Ribulose, Xylulose
Ketohexose	C ₆ H ₁₂ O ₆	CH ₂ OH.CO.(CHOH) ₃ .CH ₂ OH	Fructose, Sorbose, Tagatose, etc.

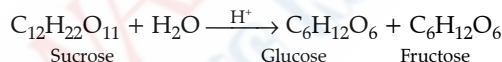
➤ **Sugar:** In general, monosaccharides and oligosaccharides are crystalline solids, soluble in water, sweet in taste. They are collectively called sugars. *e.g.*, glucose, fructose, sucrose etc. They are of two types:

- (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 monosaccharides, 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.

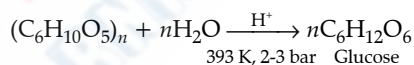
➤ **Glucose:** Glucose occurs in nature in free as well as in combined form. It is present in sweet fruits and honey.

- **Methods of preparation of Glucose:**

(i) **From sucrose:**

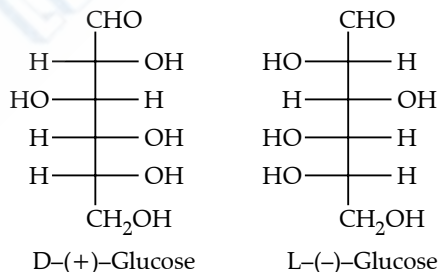


(ii) **From starch:** Commercially, glucose is obtained by hydrolysis of starch by boiling it with dil H₂SO₄ at 393 K under pressure.

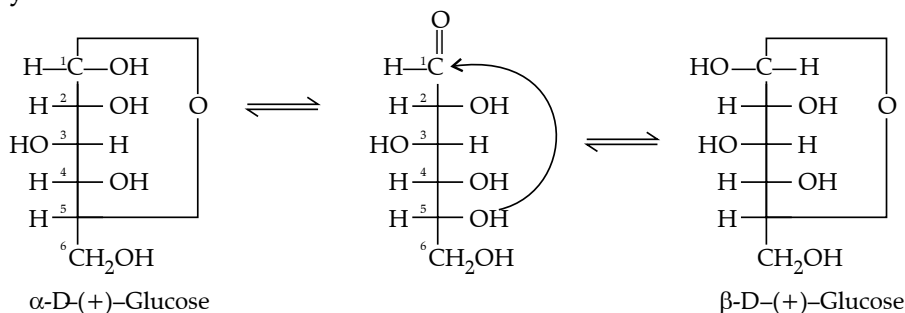


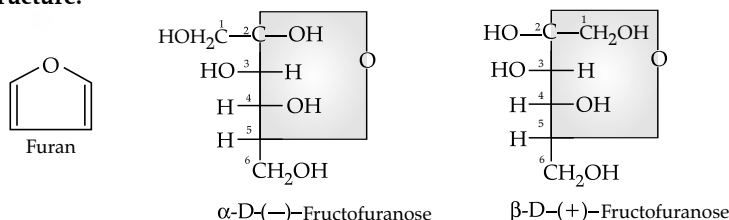
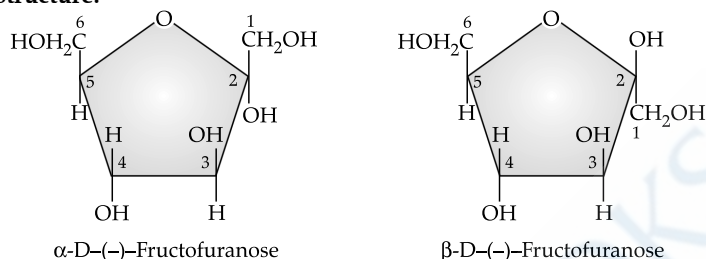
- **Structure of Glucose:** It is a six carbon straight chain aldose which has one aldehydic group (–CHO), one primary hydroxyl group (–CH₂OH) and four secondary hydroxyl groups (–CHOH).

(a) **Open chain structure:**



(b) **Cyclic structure:**



(b) Cyclic structure:**(c) Haworth structure:****➤ 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.

Proteins and Nucleic Acids

➤ **Proteins:** Proteins are complex polyamides formed from amino acids. They are essential for proper growth and

$$\text{O}$$

$$\parallel$$

$$\text{— C — NH —}$$

maintenance of body. They have many peptide (— C — NH —) bonds.

➤ **Amino Acids:** The compounds which contain carboxylic acid (—COOH) group and an amino group (—NH₂) are called amino acids. Amino acids form proteins.

➤ **α -Amino Acids:** Those amino acids in which —NH₂ 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 carboxyl groups in their molecule. If equal number of amino and carboxyl groups are present, it is neutral. More number of amino than carboxyl groups makes it basic and more carboxyl groups 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 cannot 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:**

- Fibrous proteins:** They have thread like molecules which tend to lie side by side to form fibres. *e.g.*, keratin, collagen, etc.
- 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:**

- 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.
- 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.
- 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.
- 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:** $(H_2N - CH - COOH)$
 $\begin{array}{c} | \\ R \end{array}$

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	$\begin{array}{c} CH_2 \\ \\ C=CH \\ \quad \\ \text{Benzene ring} \quad NH \end{array}$
9.	Proline	6.30	P	Pro	$\begin{array}{c} H_2C - CH_2 \\ \quad \\ H_2C \quad CH - COOH \\ \diagdown \quad / \\ N^+ \\ \\ H \end{array}$
10.	Polar (Neutral) Serine	5.68	S	Ser	—CH ₂ OH

11.	Cysteine	5.02	C	Cys	$-\text{CH}_2-\text{SH}$
12.	Asparagine	5.41	N	Asn	$-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$
13.	Glutamine	5.70	Q	Gln	$-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$
14.	Threonine*	5.60	T	Thr	$-\text{CH}(\text{OH})-\text{CH}_3$
15.	Tyrosine	5.67	Y	Tyr	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$
16.	Acidic Aspartic acid	2.98	D	Asp	$-\text{CH}_2-\text{COOH}$
17.	Glutamic acid	3.22	E	Glu	$-\text{CH}_2\text{CH}_2\text{COOH}$
18.	Basic Lysine*	9.47	K	Lys	$-\text{CH}_2-(\text{CH}_2)_3-\text{NH}_2$
19.	Arginine*	10.76	R	Arg	$-\text{CH}_2-(\text{CH}_2)_2-\text{NH}-\overset{\text{NH}}{\parallel}{\text{C}}-\text{NH}_2$
20.	Histidine*	7.59	H	His	$\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{COOH} \\ \\ \text{CH}_2 \\ \\ \text{HN} \quad \text{NH} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$

* 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.	Hormone	Insulin	Regulate body metabolism.
	Storage	Ferritin, Casein	Store nutrients.

➤ **Denaturation of Protein:** 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 gets uncoiled and protein loses its biological activity. It is called denaturation of protein. *e.g.* coagulation of egg white on boiling, curdling of milk etc.

➤ **Nucleic acid: The polymers of nucleotides help in synthesis of protein and transfer genetic traits.**

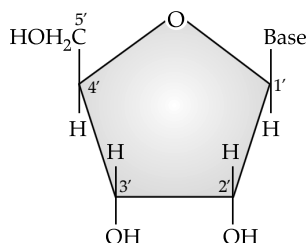
Nucleic acids are of two types:

- (i) Deoxyribonucleic acid (DNA)
- (ii) Ribonucleic acid (RNA)

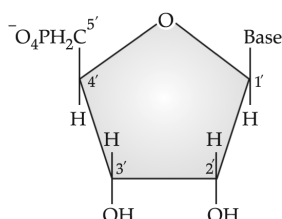
Constituents of nucleic acids: Pentose sugar, phosphoric acid and nitrogenous bases.

➤ **Nitrogen containing bases:**

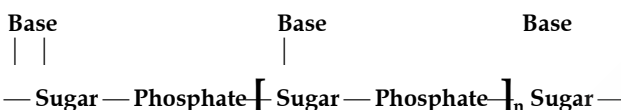
- **Pyrimidines:** These are three bases derived from pyrimidines. These are cytosine (C), thymine (T) and uracil (U). In DNA, T is present but in RNA, U is present.
- **Purines:** There are two bases derived from purine. These are adenine (A) and guanine (G).
- **Nucleoside:** A unit formed by the attachment of a base to 1'-position of sugar is known as nucleoside.



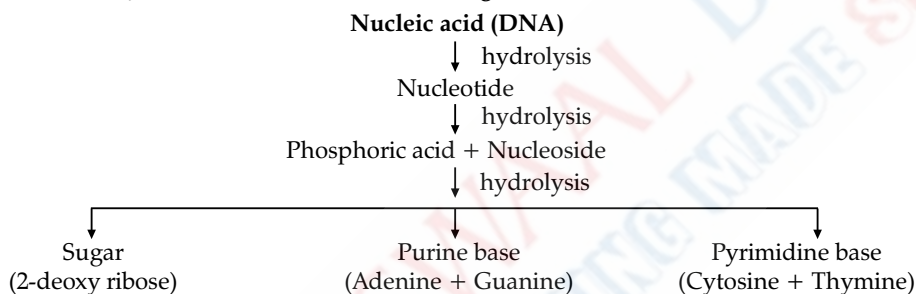
- **Nucleotide:** When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, the unit obtained is called nucleotide.



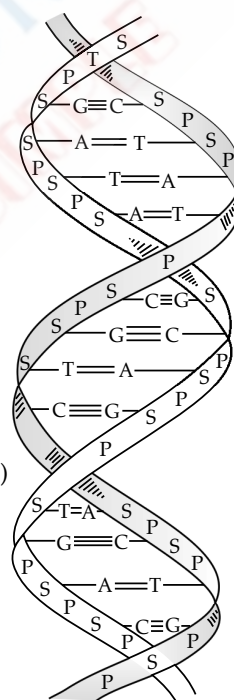
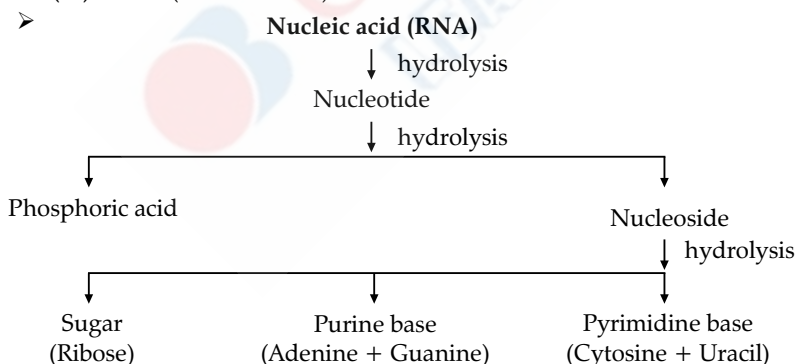
➤ **Simple structure of nucleic acid chain:**



➤ **DNA:** James Watson and Francis Crick gave double helix structure of DNA.



- **RNA:** (i) *m*-RNA (Messenger RNA)
 (ii) *r*-RNA (Ribosomal RNA)
 (iii) *t*-RNA (Transfer RNA)



Double helix structure of DNA molecule

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 form polynucleotide (nucleic acid).
- (iii) A polynucleotide (DNA) which has a thymine 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 thymine base and deoxyribose sugar are absent. It has single stranded structure.

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 anomeric carbon, generally found in two forms α and β .
- **Glycosidic linkage:** It is an oxide linkage between two or more monosaccharide units in polysaccharides.
- **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 proteins:** 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.

●●

