## Chapter 1

## The Solid State

### Solids

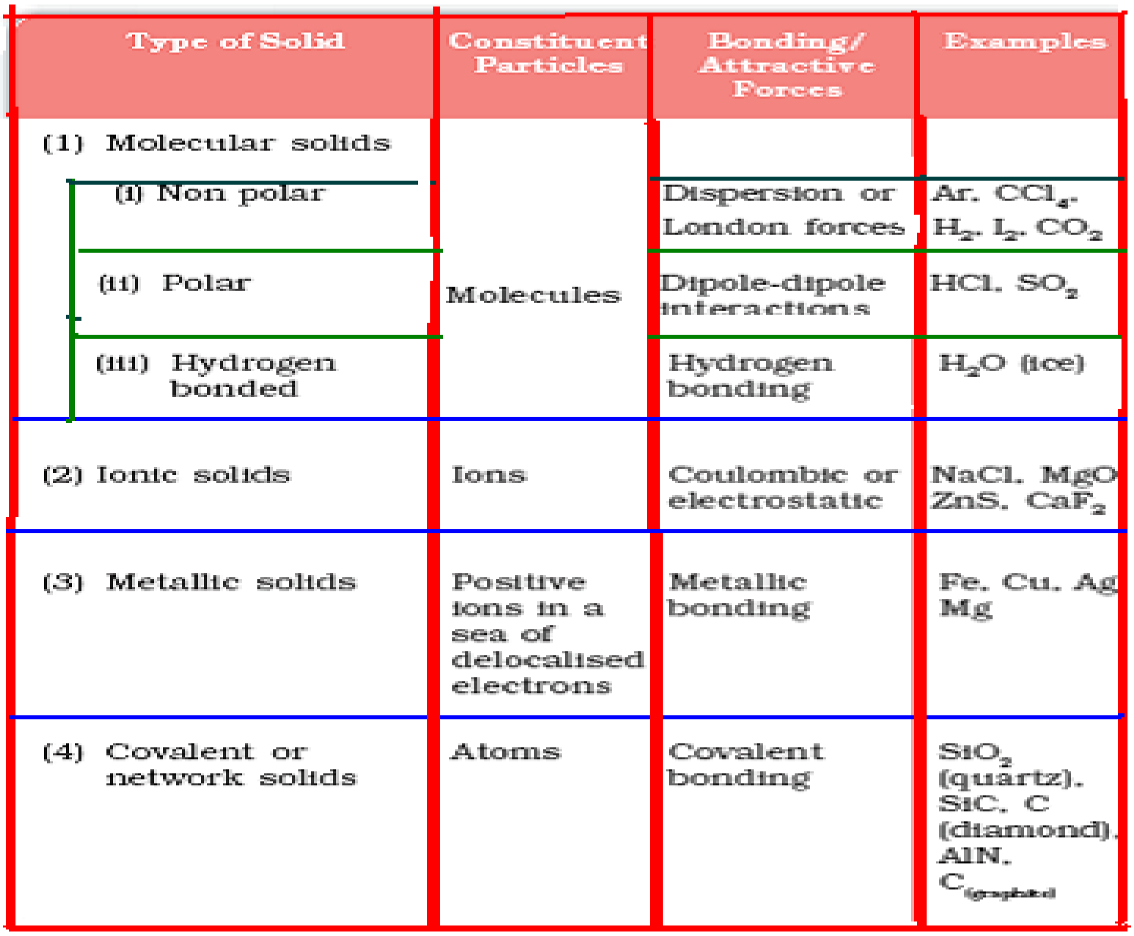
Solids are the chemical substances which are characterised by define shape and volume, rigidity, high density, low compressibility. The constituent particles (atoms, molecules or ions) are closely packed and held together by strong interparticle forces

### Types of Solids

The solids are of two types : Crystalline solids and amorphous solids.

### Distinction Between Crystalline and Amorphous Solids

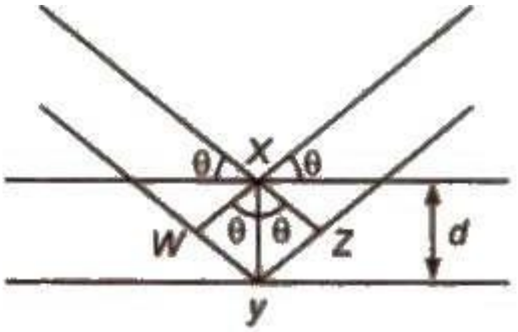
| | Crystalline solid | Amorphous solids |
|---|---|---|
| 1. | These have definite and regular arrangement of the constituent particles in space. | These doesn’t have any regular arrangement of the constituent particles in space. |
| 2 | These are true solids. | These are super cooled liquids or pseudo soilds.. |
| 3 | These have long order arrangement of the particles. | These have short order arrangement of particle. |
| 4 | These are anisotropic in nature, i.e., their physical properties are different in different directions. | These are isotropic in nature i.e., their physical properties are same in all the directions. |
| 5 | They have sharp melting points. | They melt over a certain range of temperature. |
| 6 | They undergo a clean cleavage when cut. | They undergo irregular cleavage when cut. |



| Type of Solid | Constituent Particles | Bonding/ Attractive Forces | Examples |
|---|---|---|---|
| (1) Molecular solids | | | |
| (i) Non polar | Molecules | Dispersion or London forces | Ar, $CCl_4$, $H_2$, $I_2$, $CO_2$ |
| (ii) Polar | | Dipole-dipole interactions | HCl, $SO_2$ |
| (iii) Hydrogen bonded | | Hydrogen bonding | $H_2O$ (ice) |
| (2) Ionic solids | Ions | Coulombic or electrostatic | NaCl, MgO, ZnS, $CaF_2$ |
| (3) Metallic solids | Positive ions in a sea of delocalised electrons | Metallic bonding | Fe, Cu, Ag, Mg |
| (4) Covalent or network solids | Atoms | Covalent bonding | $SiO_2$ (quartz), SiC, C (diamond), AlN, $C_{(graphite)}$ |

**Structure Determination by X-ray Diffraction** (Bragg’s Equation)

When a beam of X-rays falls on a crystal plane composed of regularly arranged atoms or ions, the X-rays are diffracted. If the waves are in phase after reflection, the difference in distance travelled by the two rays ti.e., path difference) must be equal to an integral number of Wavelength, nλ for constructive.



Thus, path difference = WY + YZ

= XY sin θ + xy sin θ
2 XY sin θ = 2d sin θ

∴ nλ = 2d sin θ

This equation is called Bragg’s equation. Where,

n = 1. 2, 3… (diffraction order)

λ = wavelength of X·rays incident on crystal d =

distance between atomic planes

θ = angle at which interference occurs.

**Unit Cell**

The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

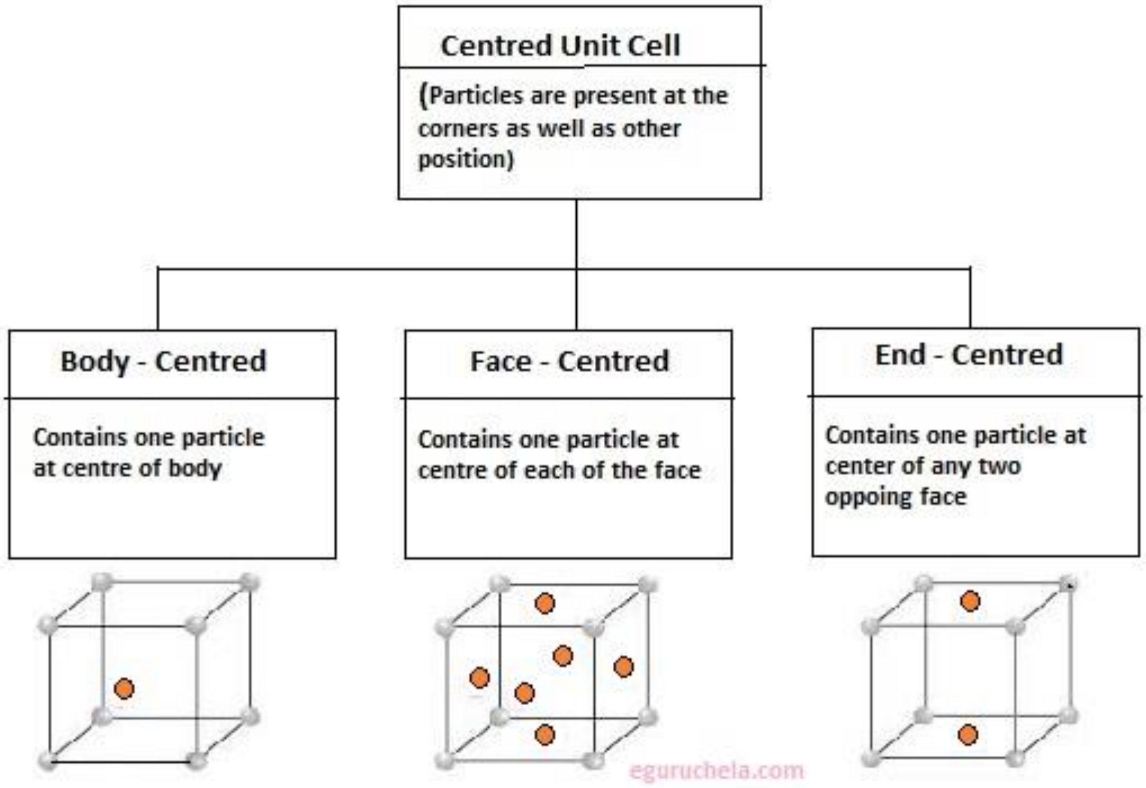
**Types of Unit Cell**

**(i)Simple or primitive Unit cell** In which the particles are present at the corners only.

(ii) **Face centred unit cell** In which the particles are present at the corners as well as at the centre of each of six faces.

(iii)**Body centred unit cell** In which the particles are present at the corners as well as at the centre of the unit cell.

(iv) **End centred unit cell** In which the particles are present at the corners and at the centre of two opposite faces.



**Centred Unit Cell**

(Particles are present at the corners as well as other position)

**Body - Centred**

Contains one particle at centre of body

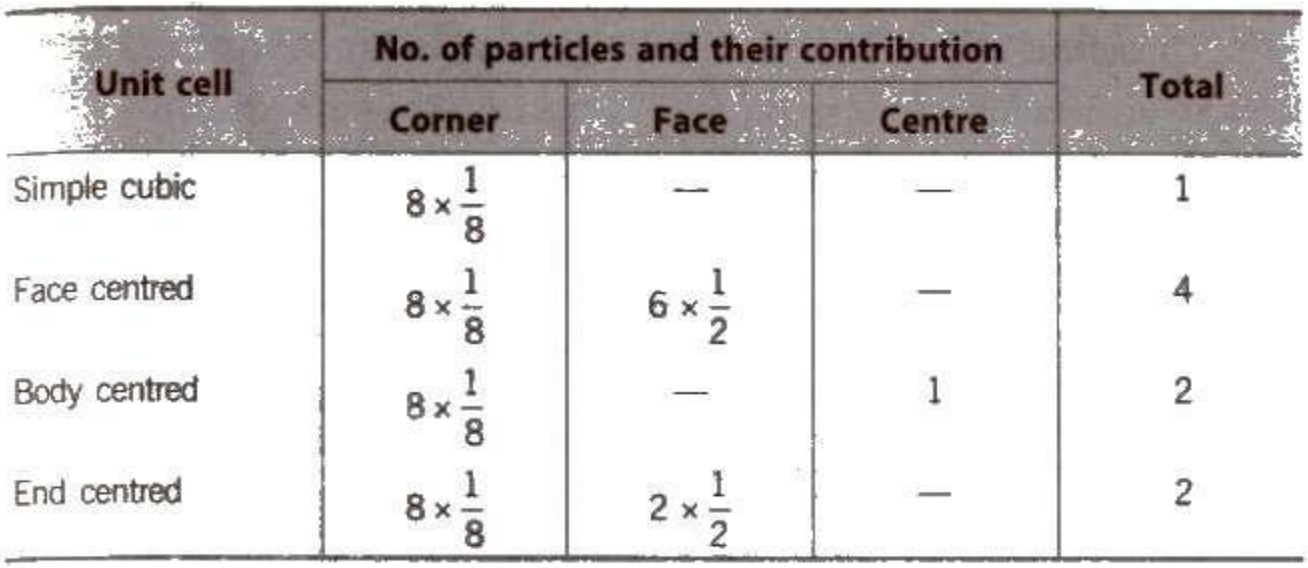
**Face - Centred**

Contains one particle at centre of each of the face

**End - Centred**

Contains one particle at center of any two opposing face

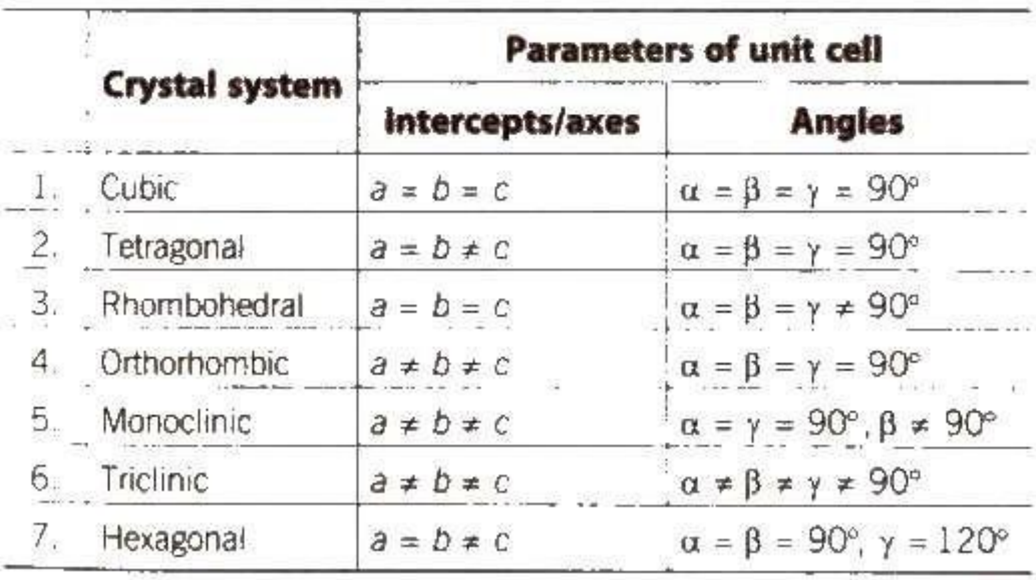
**Number of Particles Per Unit Cell**



| Unit cell | No. of particles and their contribution | | | Total |
|---|---|---|---|---|
| | Corner | Face | Centre | |
| Simple cubic | $8 \times \frac{1}{8}$ | — | — | 1 |
| Face centred | $8 \times \frac{1}{8}$ | $6 \times \frac{1}{2}$ | — | 4 |
| Body centred | $8 \times \frac{1}{8}$ | — | 1 | 2 |
| End centred | $8 \times \frac{1}{8}$ | $2 \times \frac{1}{2}$ | — | 2 |

**Seven Crystal Systems**

There are about 230 crystal forms, which have been grouped into 14 types of space lattices, called Bravais Lattices, on the basis of their symmetry and seven different crystal systems on the basis of interfacial angles and axes.



| | Crystal system | Parameters of unit cell | |
|---|---|---|---|
| | | Intercepts/axes | Angles |
| 1. | Cubic | $a = b = c$ | $\alpha = \beta = \gamma = 90^\circ$ |
| 2. | Tetragonal | $a = b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ |
| 3. | Rhombohedral | $a = b = c$ | $\alpha = \beta = \gamma \neq 90^\circ$ |
| 4. | Orthorhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ |
| 5. | Monoclinic | $a \neq b \neq c$ | $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ |
| 6. | Triclinic | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^\circ$ |
| 7. | Hexagonal | $a = b \neq c$ | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ |

**Packing Fraction**

It is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the volume of the unit cell.

(i) **Primitive cubic unit cell** Atoms touch each other along edges.

Hence, d = a or r = a / 2

(r = radius of atom and a = edge length) Therefore, PF = 4 /

3 $\pi r^3$ / $(2r)^3$ = 0.524 or 52.4%

(ii) **Face centred cubic unit cell** Atoms touch each other along the face diagonal.

Hence, d = a / √2 or

r = √2a / 4

Therefore; PF = 4 * 4 / 3 $\pi r^3$ / (4r / √2)$r^3$ = 0.74 or 74%

(iii) **Body centred cubic unit** cell Atoms touch each other along the body diagonal.

Hence, √3a / 2 or

r = √3a / 4

Therefore; PF = 2 * 4 / 3 $\pi r^3$ / (4r / √3)$r^3$ = 0.68 or 68%

**Coordination Number**

It is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

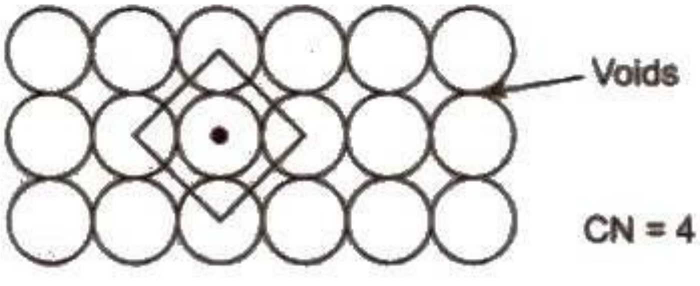
[In simple cubic lattice, CN is 6, in body centred lattice, CN is 8 and in face centred cubic lattice, CN is 12].

High pressure increases CN and high temperature decreases the CN.

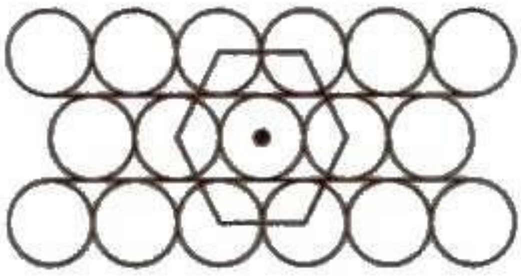
**Close Packing in Crystals**

**Two Dimensional Packing of Constituent Particles**

(i) **Square close packing** Space occupied by spheres is 52.4%.



(ii) **Hexagonal close packing** Space occupied by spheres is 60.4%.Hence. It is more efficient.



CN = 6

**Three Dimensional Packing of Constituent Particles**

(i) ABAB arrangement gives hexagonal close packing (hcp).

(ii) ABCABC arrangement gives cubic close packing or face centred CUbIC packing (ccp or fcc).

- In both these arrangements 740/0 space is occupied
- Coordination number in hop and ccp arrangement is 12 while in bcc arrangement, it is 8.
- Close packing of atoms in cubic structure = fcc > bcc > sc.
- All noble gases have ccp structure except He (hcp structure).

**Void or Space or Holes**

- Empty or vacant space present bet veen spheres of a unit cell, is called void or space or hole or interstitial void. When particles are closed packed resulting in either cpp or hcp structure, two types of voids are generated:
- **Tetrahedral voids** are holes or voids surrounded by four spheres Present at the corner of a tetrahedron. Coordination number of a tetrahedral void is 4.

$r_{\text{void}} = 0.225 \times r_{\text{sphere}}$ (for tetrahedral voids)

- **Octahedral voids** are holes surrounded by six spheres located on a regular tetrahedron. Coordination number of octahedral void is 6.

$r_{\text{void}} = 0.414 \times r_{\text{sphere}}$ (for octahedral voids)

[The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids present in a lattice is twice to the number of close packed particles.]

**Density of Unit Cell** (d)

Density of unit ce11 = mass of unit cell / volume of unit cell $d = Z * M / a^3$

$= ZM / a^3 * N_A$

(The density of the unit cell is same as the density of the substance.) where, d =

density of unit cell.

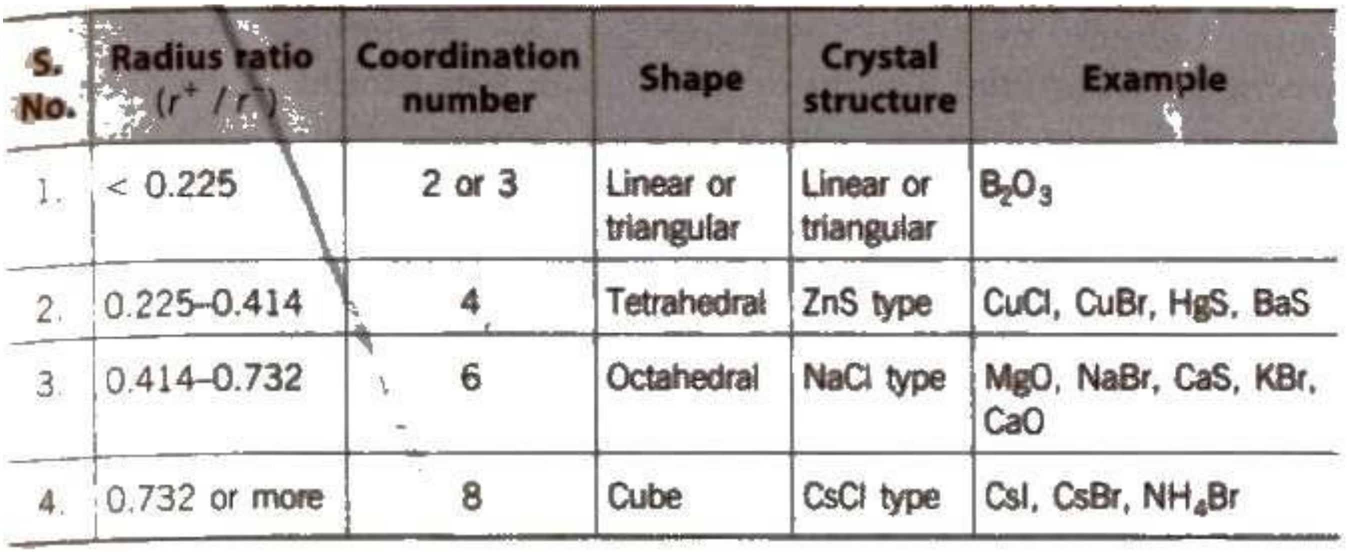
M = molecular weight Z = no. of atoms per unit cell $N_A$ = Avogadro number

a = edge length of unit cell.

### The Structure of Ionic Crystals

The ionic radius ratios of cation and anion, play a very important role in giving a clue to the nature of the crystal structure of ionic substances.

Radius Ratio and Crystal Structure



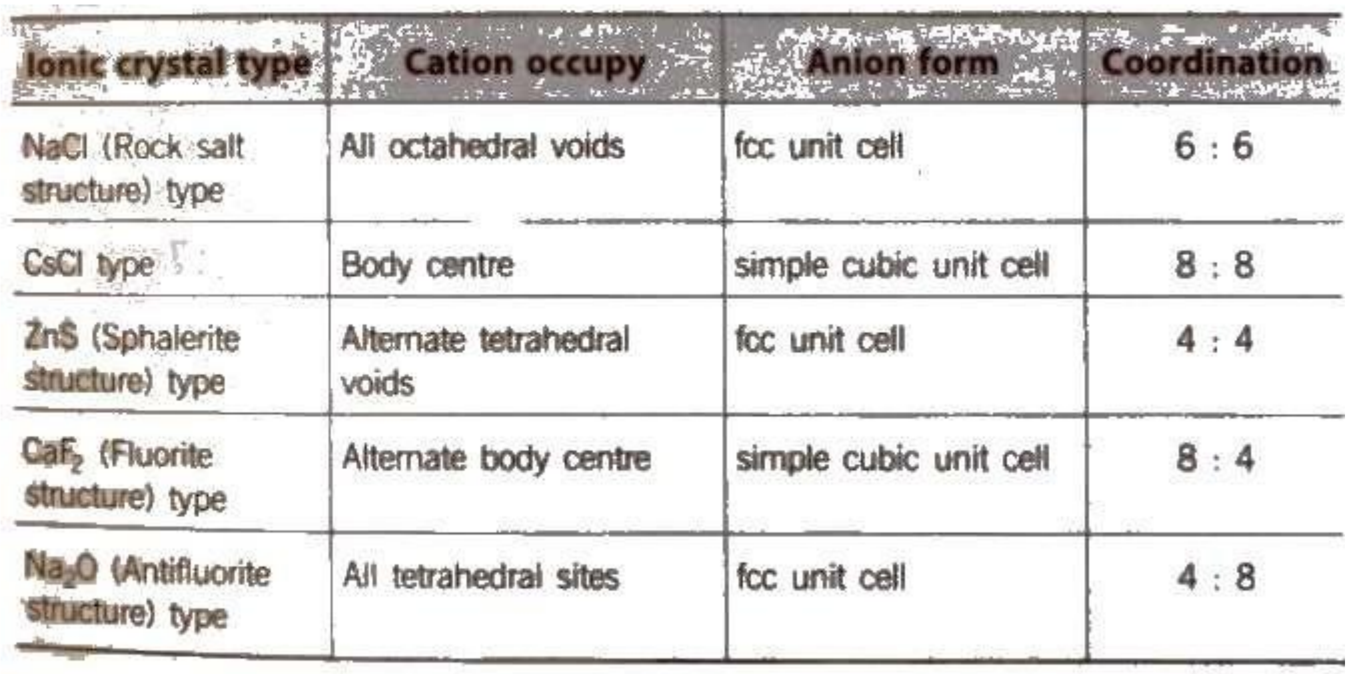
| S. No. | Radius ratio ($r^+ / r^-$) | Coordination number | Shape | Crystal structure | Example |
|---|---|---|---|---|---|
| 1. | < 0.225 | 2 or 3 | Linear or triangular | Linear or triangular | $B_2O_3$ |
| 2. | 0.225–0.414 | 4 | Tetrahedral | ZnS type | CuCl, CuBr, HgS, BaS |
| 3. | 0.414–0.732 | 6 | Octahedral | NaCl type | MgO, NaBr, CaS, KBr, CaO |
| 4. | 0.732 or more | 8 | Cube | CsCl type | CsI, CsBr, $NH_4Br$ |

Ionic crystals may be of two types (i)AB

type and

(ii) $A_2B$ or $AB_2$

**Structure of Ionic Crystals**



| Ionic crystal type | Cation occupy | Anion form | Coordination |
|---|---|---|---|
| NaCl (Rock salt structure) type | All octahedral voids | fcc unit cell | 6 : 6 |
| CsCl type | Body centre | simple cubic unit cell | 8 : 8 |
| ZnS (Sphalerite structure) type | Alternate tetrahedral voids | fcc unit cell | 4 : 4 |
| $CaF_2$ (Fluorite structure) type | Alternate body centre | simple cubic unit cell | 8 : 4 |
| $Na_2O$ (Antifluorite structure) type | All tetrahedral sites | fcc unit cell | 4 : 8 |

On applying pressure NaC} structure (6 : 6 coordination) changes into CsCI structure (8 : 8 coordination) and reverse of this occur at high temperature (760 K).

**Imperfections in Solids**

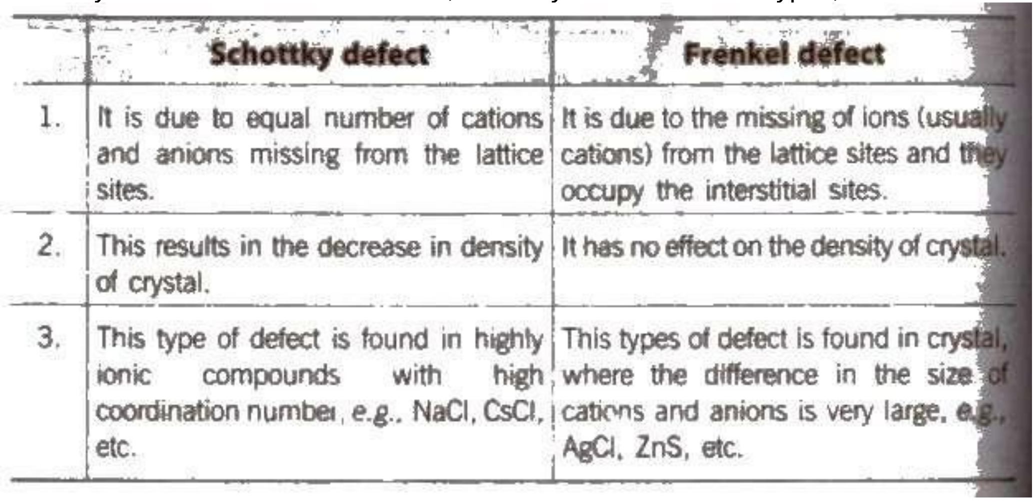
- In a crystalline solid, the atoms, ions and molecules are arranged in a Definite repeating pattern, but some defects may occur in the pattern. derivations from perfect arrangement may occur due to rapid cooling or presence of additional particles.
- The defects are of two types, namely point defects and line defects.

**Point Defects**

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance Point defects can be classified into three types : (1) psychometric defects (2) impurity defects (3) non–stoichiometric defects

### 1. Stoichiometric Defect

These are point defects that do not disturb' the -stoichiometric of the solid. They are also called intrinsic or thermodynamic defects. In ionic solids, basically these are of two types, Frankel defect and Schottky defect.



| | Schottky defect | Frenkel defect |
|---|---|---|
| 1. | It is due to equal number of cations and anions missing from the lattice sites. | It is due to the missing of ions (usually cations) from the lattice sites and they occupy the interstitial sites. |
| 2. | This results in the decrease in density of crystal. | It has no effect on the density of crystal. |
| 3. | This type of defect is found in highly ionic compounds with high coordination number, e.g., NaCl, CsCl, etc. | This types of defect is found in crystal, where the difference in the size of cations and anions is very large, e.g., AgCl, ZnS, etc. |

AgBr has both Schottky and Frenkel defects. Frenkel defects are not found in pure alkali metal halides because cations are of large size.

## 2. Impurity Defect

- It arises when foreign atoms or ions aloe present in the lattice. In case of ionic compounds, the impurity 1S also ionic in nature. When the impurity has the same charge as the host ion. it just substitutes some of the host ions.
- Impurity defects can also be introduced by adding impurity ions having different charge than host ions. e.g. molten NaCl containing a little amount of $SrCl_2$ is crystallised. In such cases,
- Cationic vacancies produced = [number of cations of higher valence * Difference in valence of the host cation and cation of higher valence

## 3. Non-Stoichiometric Defect

Non-stoichiometric crystals are those which do not obey the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. However, the crystal as a whole in neutral.

Types of n-stoichiometric defects are as follows:

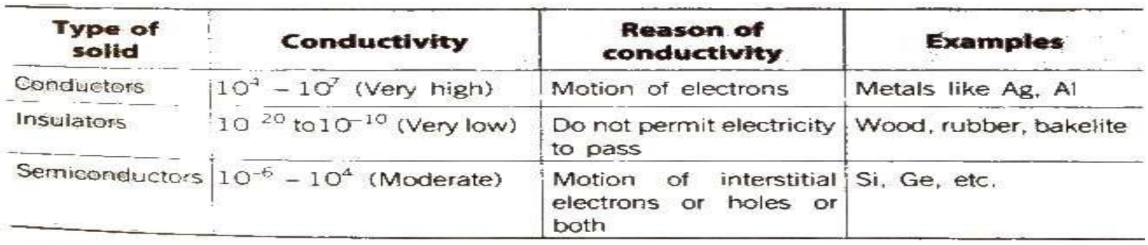
(i) **Met excess defect** Metal excess defect due to anionic vacancies: Alkyl halides like NaC1 and KCl show this type of defect. centres ale the sites from where anions are missing and the vacant sites are occupied by electrons. F-centres contribute colour and paramagnetic nature of the crystal [F stands for German wo\d Farbe meaning colour).

**Metal excess defect due to presence of extra cations at interstitial sites**, e.g., zinc oxide is white in colour at room temperature. On beating, it loses oxygen and turns yellow.

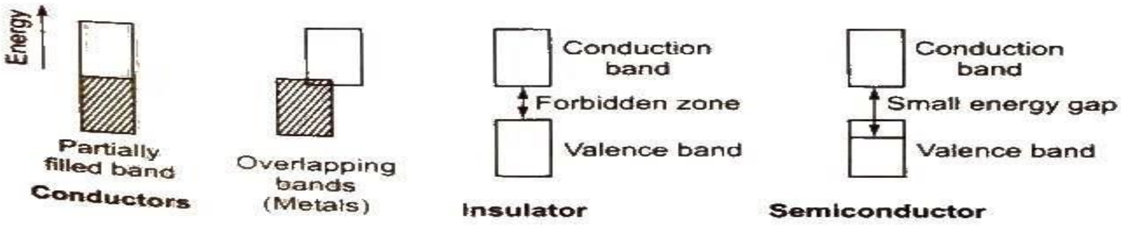
$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

(ii)Metal deficiency defect due to cation vacancy It is due to the absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge. Transition metals exhibit this defect, e.g., FeO, which is found in the composition range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystal of FeO, some $Fe^{2+}$ cations are missing and the loss of positive charge is made up by the presence of required number of $Fe^{3+}$ ions.

### Classification of Solids on the Basis of Electrical Conductivity



| Type of solid | Conductivity | Reason of conductivity | Examples |
|---|---|---|---|
| Conductors | $10^4 - 10^7$ (Very high) | Motion of electrons | Metals like Ag, Al |
| Insulators | $10^{20}$ to $10^{-10}$ (Very low) | Do not permit electricity to pass | Wood, rubber, bakelite |
| Semiconductors | $10^{-6} - 10^4$ (Moderate) | Motion of interstitial electrons or holes or both | Si, Ge, etc. |



## Classification of Solids on the Basis of Electrical Conductivity

[The electricity produced on heating a polar crystal is called ‘pyroelectricity’.]

When mechanical stress is applied on polar crystals, electricity produced due to displacement of ions is called ‘piezoelectricity’

### Semiconductors

Electronic conductors having electrical conductivity in the range of $10^4 – 10^7\ \Omega^{-1}\ cm^{-1}$ are known as semiconductors. Examples Si, Ge Sn (grey), $Cu_2O$, SiC and GaAs.

### Intrinsic Semiconductors

Pure substances that are semiconductors are known as Intrinsic Semiconductors e.g., Si, Ge

### Extrinsic Semiconductors

Their conductivity is due to the presence of impurities. They are formed by doping. It is defined as addition of impurities to a semiconductor to increase the conductivity. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

(i) **n·type semiconductors** Silicon doped with 15 group elements like phosphorus is called n- type semiconductor. The conductivity is due to the presence of negative charge (electrons),

(ii) **p·type semiconductors** Silicon doped with 13 group element like gallium is called p-type semiconductor. The conductivity is due to the presence of positive holes.

- Some typical 13-15 compounds are InSb, AlP and GaAs and SOme typical 12-16 compounds are ZnS, CdS. CdSe and HgTe.
- These exhibit electrical and optical properties of great use in electronic industry.

### Magnetic Properties of Solids

Solids can be divided into different classes depending on their response to magnetic field.

1. **Diamagnetic Substances**

These are weakly repelled by the magnetic field and do not have any unpaired electron, e.g., $TiO_2$, $V_2O5$, $C_6H_6$, NaCl, etc.

2. **Paramagnetic Substances**

These are attracted by the magnetic field and have unpaired electrons These lose magnetism in the absence of magnetic field, e.g., $O_2$, $Cu^{2+}$, $Fe^{3+}$, etc.

3. **Ferromagnetic Substances**

These are attracted by the magnetic field and show permanent magnetism even ill the absence of magnetic field e.g., Fe, Co and Ni.

4. **Anti-ferromagnetic Substances**

These substances have net magnetic moment zero due to compensatory alignment of magnetic . moments, e.g., MnO, $MnO_2$, FeO, etc.

5. **Ferrimagnetic Substances**

These substances have a net dipole moment due to unequal parallel and anti-parallel alignment of magnetic moments, e.g., $Fe_3O_4$, ferrites, etc.

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## Cheapter-2 Solution

A Solution is a homogenous mixture of two or more components. It is defined by using the terms *solute* and *solvent*.
***Solvent:*** The component that is present in largest quantity is called solvent. It determines the physical state of solution.
***Solute****:* One or more components present in solution other than solvent is called solute.
***Binary solutions***: Solution consisting of two components only.

**Types of Solutions**

According to the phase of solvent, a binary solution can be classified in following types:

| Types of Solutions | Solute | Solvent | Examples |
|---|---|---|---|
| **Gaseous solutions** | Gas | Gas | Mixture of $O_2$ and $N_2$ |
| | Liquid | Gas | Chloroform mixed with $N_2$ Gas |
| | Solid | Gas | Camphor in nitrogen gas |
| | | | |
| **Liquid Solutions** | Gas | Liquid | Oxygen dissolved in water |
| | Liquid | Liquid | Ethanol dissolved in water |
| | solid | Liquid | Glucose dissolved in water |
| | | | |
| **Solid Solutions** | Gas | solid | Solution of $H_2$ and Pd |
| | Liquid | solid | Amalgam of Hg with Na |
| | Solid | solid | Alloy |

In this chapter we are mainly focusing on binary solutions (solution made up of two components) of liquid known as **liquid solutions**.

### Different Methods of Expressing Concentration of Solutions

The composition of solution is defined in terms of concentration. There are several ways to define concentration of solution as follows:

(A) **Mass percentage (w/w)**:

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

(B) **Volume percentage (V/V)** =

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

(C) **Mass by volume percentage (w/V)** = $\dfrac{\text{Mass of the component}}{\text{100 mL solution}}$

(D) **Part per million (ppm)**:

$$\text{ppm} = \frac{\text{Number of parts of compnent}}{\text{Total number of parts of all components of solution}} \times 10^6$$

(E) **Mole fraction**:

$$\text{Mole fraction of component} = \frac{\text{Moles of component}}{\text{Total number of moles of all the component}}$$

(F) **Molarity** = $\dfrac{\text{Moles of solute}}{\text{Volume of solution in Litre}}$

(G) **Molality** = $\dfrac{\text{Moles of solute}}{\text{Mass of solution in Kg}}$

**NOTE**- Related numerical see in book.

**Solubility**

Solubility of a substance is the maximum amount that can be dissolved in given amount of solvent at specific temperature. Factors affecting the solubility:

- **Nature of solute**
- **Nature of solvent**
- **Temperature**
- **Pressure**

***Nature of solute and solvent*****:** If the nature of solute and solvent is same, the intermolecular force of interaction would be same. That helps in solubility of solute in solvent.

Polar solute dissolves in polar solvent. For example: NaCl and sugar dissolves in water. Non-polar solute dissolves in non-polar solvent. For example: Naphthalene and anthracene dissolves in benzene not in water.

***Saturated solution:*** If the concentration of solute in solution remain constant at given set of temperature and pressure is called saturated solution. If we add more solute in it, it would precipitate out.

***Un-Saturated solution****:* If the concentration of solute in solution can increase at given set of temperature and pressure is called un-saturated solution. If we add more solute in it, it would get dissolve and increase the concentration of solution.

***Effect of temperature****:*

The solubility of solute in solvent always follows the dynamic equilibrium.

Solute + Solvent → Solution.

It follows the Le Chateliers principle for the change in temperature at dynamic equilibrium.If the solution is formed by giving heat means dissolution is endothermic. By increasing the temperature,the reaction will proceed in forward direction and solubility of solute increases.If the heat is released in formation of solute means dissolution is exothermic. By increasing the temperature, the reaction will proceed in backward direction and solubility of solute decreases.

***Effect of pressure****:*

Pressure has no significant effect on solubility of solid in liquid.

**Solubility of Gas in a Liquid**
**Nature of solute and solvent:**
Solubility of gas in liquid is also somewhat affected by nature of solute and solvent. Oxygen dissolves only a small extent in water but HCl is highly soluble in water because of polar nature of solute and solvent.
**Effect of pressure***:*
Solubility of gas in liquid is highly affected by temperature and pressure. As the pressure of the gas above the surface of the liquid increases, it increases the solubility of gas in liquid. The quantitative relation of this equation is given by Henry's Law.
**Henry's Law:**
It states that, "*At constant temperature, the solubility of gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of the liquid or solution."*
If we consider mole fraction of gas in a solution to measure its solubility then it can be said that, "Mole *fraction of gas in a liquid is proportional to the partial pressure of gas above the liquid or solution*."
Now the Henry's Law can be stated as , " *The partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of gas(x) in solution*."
Expression for Henry's Law:
$p_x$
$p = K_H . x$
$K_H$ is Henry's Law constant
Important point regarding Henry's Law:

- Different gases have different $K_H$ values at the same temperature. That is $K_H$ depends on the nature of gas.
- Higher the value of $K_H$ at given pressure, lower is the solubility of gas in given liquid.
- $K_H$ value of particular gas increases with increasing temperature. It indicates that solubility of gas decreases with increasing temperature.

**Effect of temperature:**
Dissolution of gas in a liquid is an exothermic process. As dissolution process involves dynamic equilibrium, it follows Le Chaterlier's principle. Hence the solubility of gas in liquid, decreases with increase in temperature.
**Vapour Pressure of a Liquid Solution**
Liquid solution are formed when solvent is in liquid phase. Solute may be solid, liquid or gas. On the basis of solute, the liquid solution is classified in 3 types as:

(*i*) Solid in liquid
(*ii*) Liquid in liquid
(*iii*) Gas in liquid
We will discuss the various properties of liquid in liquid solution and solid in liquid solutions.

**Vapour Pressure of a Liquid-Liquid Solution**
Let us take a binary solution made up of two volatile liquids 1 and 2. As the liquid start evaporating; a stage will come when the vapour pressure of liquid will be in equilibrium with the corresponding liquid. As we know that vapour pressure of liquid is proportional to its mole fraction. The quantitative relationship between the vapour pressure and mole fraction in binary solution is given by *Roult's Law*.

**Roult's Law:**
It states that for the solutions of volatile liquid, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

For component 1,

$p_1 \propto x_1$
$p_1 = p_1° x_1$...(1)
$p_1$ = Vapour pressure of component 1 in solution.
$p_1°$ = Vapour pressure of pure liquid component 1at the same temperature
$x_1$ = Mole fraction of component 1 in solution.

Similarly for component 2 :

$P_2 = p_2^\circ x_2$ ...(2)

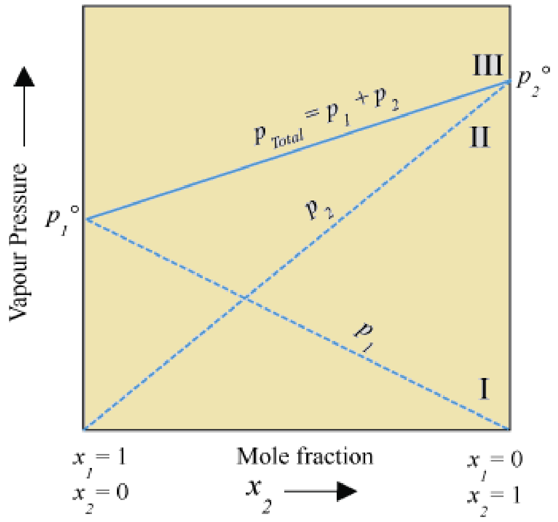
According to **Dalton's Law of partial pressure**, The total pressure ($p_{total}$ ) over the solution phase in the container will be the sum of partial pressure of the components in solution. If the solution is made up of two volatile liquids then total pressure above the solution is:

$p_{total} = p_1 + p_2$ ...(3)
$p_{total}$ = Total pressure over the solution phase
$p_1$ = Vapour pressure of component 1 in solution
$p_2$ = Vapour pressure of component 1 in solution
Substituting the values of $p_1$ and $p_2$ in eq...(3)
we get:
$p_{total} = p_1^\circ x_1 + p_2^\circ x_2$ ...(4)
As, total mole fraction of components in any solution is 1. Therefore,

$x_1 + x_2 = 1$
$x_1 = (1 - x_2)$...(5)
Putting the value of $x_1$ in eq (4) we get:
$p_{total} = p_1^\circ(1 - x_2) + p_2^\circ x_2$
$p_{total} = p_1^\circ - p_1^\circ x_2 + p_2^\circ x_2$
**$p_{total} = p_1^\circ + (p_2^\circ - p_1^\circ) x_2$ ...(6)**
The equation ...(6) is known as the mathematical expression for Roult's Law for the solution made up of two volatile liquids.From this equation ...(6) we can conclude the following points :

- $p_{total}$ can be related to mole fraction of any of the one component.
- $p_{total}$ varies linearly with $x_2$.
- $p_{total}$ increases or decreases with increase of $x_1$

This can be represents on graph as follows assuming $p_1^\circ < p_2^\circ$:



**Conclusion from graph:**

- Plot of $p_1^\circ$ vs $x_1$ is linear
- Plot of $p_2^\circ$ vs $x_2$ is linear
- Maximum value of $p_{total} = p_2^\circ$
- Minimum value of $p_{total} = p_1^\circ$

Composition of vapour phase at equilibrium is determined by using Dalton's Law. Let $y_1$ and $y_2$ be the mole fraction of liquid 1 and 2 in solution then partial vapour pressure of each component is written as:
**$p_1 = y_1 p_{total}$... (7)**
Equation ...(7) gives you the value of partial vapour pressure of each component in vapour phase.

**Vapour Pressure of a Solid-Liquid Solution**

When a non-volatile solid is added to the solvent to form a solution, then the vapour pressure of solution is found lower than vapour pressure of the pure solvent at same temperature. The decrease in the vapour pressure of the solution is solely depends on the quantity of non-volatile solute present in solution.

The vapour pressure of such solution is given by using general equation of Roult's Law. Assume that water is component 1 and non-volatile component is component 2, then vapour pressure of the solution will be equal to the vapour pressure of solvent in solution. Vapour pressure of solvent $p_1$ is proportional to its mole fraction in solution and given as :

$p_1 \propto x_1$
$p_1 = p_1^{\circ} x_1$...(1)
$p_1$ = Vapour pressure of component 1 in solution.
$p_1^{\circ}$ = Vapour pressure of pure liquid component 1at the same temperature
$x_1$ = Mole fraction of component 1 in solution.

**Ideal and Non Ideal Solutions**
Liquid-liquid solutions can be classified as ideal and non-ideal on the basis of certain properties.

**Ideal Solution**

- Obeys the Roult's Law over the entire range of concentration.
- $\Delta H_{mixing} = 0$
- $\Delta V_{mixing} = 0$
- Example : solution of n-hexane and n-heptane, solution of bromoethane or chloroethane.
  It can be summarised as: If a Solution formed by mixing the two components A and B, in which intermolecular force of attraction between A and B (A–B) is nearly equal to intermolecular force of attraction between pure components (A–A and B–B) then no heat would be evolved or absorbed in forming the solution. Also volume of the solution will be equal to the total volume of the individual component taken to form the solution.

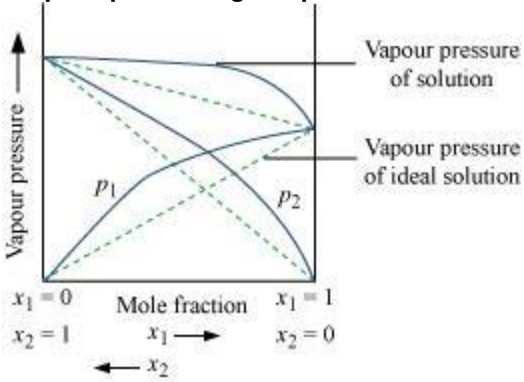
**Non-Ideal Solution**

- Does not obey the Roult's Law over the entire range of concentration.
- $\Delta H_{mixing} \neq 0$
- $\Delta V_{mixing} \neq 0$
- Example: Solution of chloroform and acetone
  It can be summarised as: If a Solution formed by mixing the two components A and B , in which intermolecular force of attraction between A and B (A–B) is not equal to intermolecular force of attraction between pure components (A–A and B–B). This new interaction (A–B) is either less than or more than the interaction of the pure components (A–A and B–B). This leads to the positive or negative deviations from Roult's Law.

**Positive Deviation from Roult's Law**

- The vapour pressure of solution formed by mixing two components is **higher** than predicted from Roult's Law
- The new intermolecular interactions formed by mixing the component A and B (A–B) are **weaker** than the intermolecular interactions of pure component (A–A and A–B)
- Example: mixture of ethanol and acetone, solution of carbon disulphide and acetone.

**Graph representing the positive deviation:**

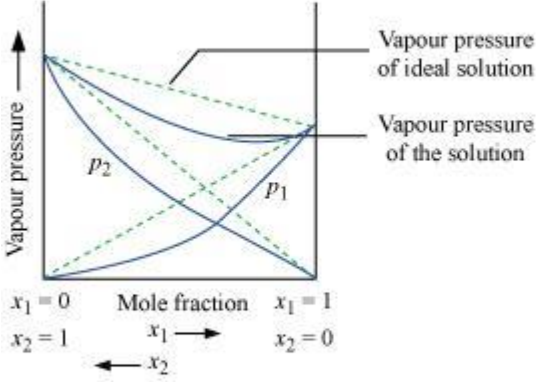


**Negative Deviation from Roult's Law**

- The vapour pressure of solution formed by mixing two components is lower than predicted from Roult's Law

- The new intermolecular interactions formed by mixing the component A and B (A-B) are stronger than the intermolecular interactions of pure component (A-A and A-B)
- Example: solution of phenol and aniline, chloroform and acetone.

**Graph representing the negative deviation:**



**Azeotropes**

These are mixture of two liquids having same composition in liquid as well as vapour phase and boil at the constant temperature. This liquid mixture cannot be separated into pure component even on fractional distillation.

**Types of Azeotropes**

**Minimum boiling azeotrope:** The solution which show large positive deviation from Raoult's Law. Example: solution of 95% ethanol in water.

**Maximum boiling azeotropes:** The solution which show large negative deviation from Raoult's Law. Example: solution of 68% nitric acid and 32% water by mass.

**Colligative properties** are properties of a solution which depend only on the number of particles like ions or molecules of the solute in a definite amount of the solvent but not on the nature of the solute.

These are as follows**:**

1. Relative lowering of vapour pressure
2. Osmotic pressure
3. Elevation in boiling point
4. Depression in freezing point

**Relative Lowering of Vapour Pressure**

When a non-volatile solute is added in a volatile solvent, the V.P of solution becomes less than the V.P. of pure solvent. It is due to increase in density which decreases rate of evaporation.

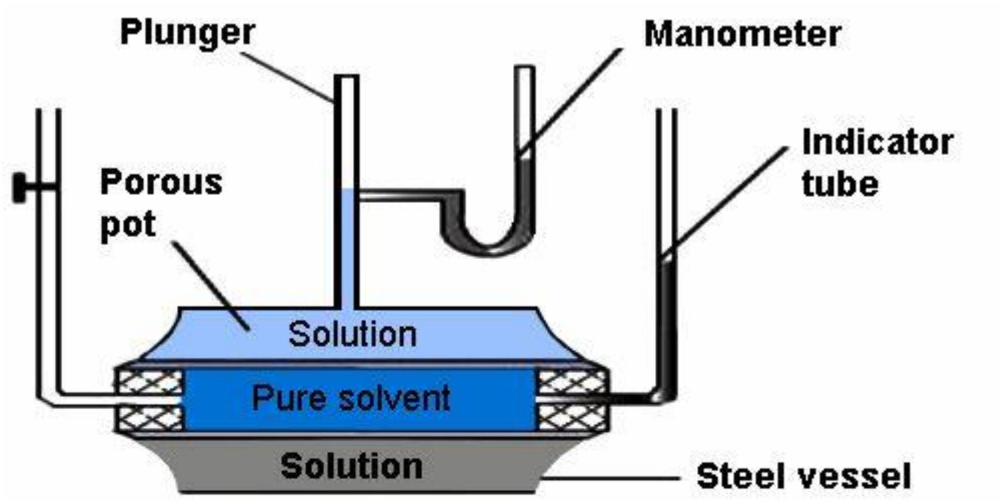
If $p^0$ = vapour pressure of pure solvent
p = vapour pressure of solvent in solution

- The lowering of vapour pressure
  $\Delta p = (p^0 - p)$
- The relative lowering of vapour pressure is defined as the ratio between lowering of vapour pressure and the vapour pressure of pure solvent.
  $$\frac{\Delta p}{p0} = \frac{p0 - p}{p0} = \text{Realtive lowering of vapour pressure}$$
- When a solution is prepared by mixing the non-volatile solute B and solvent A
  $x_A + x_B = 1$
  $x_B = 1 - x_A$
  Here, $x_B$ is the mole fraction of solute.
  As $\frac{p_A}{p^0_A} = x_A$
  $$1 - \frac{p_A}{p^0_A} = 1 - x_A = x_B \quad 1 - x_A = x_B$$
  $$\frac{p^0_A - p_A}{p^0_A} = x_B = \frac{\Delta p}{p^0_A} = \frac{n}{n + N}$$
  Here, n = Number of moles of the solute
  N = Number of moles of the solvent

- In a dilute solution, N is far greater than n, and hence,
  $$x_B = \frac{n}{N} = \frac{w/m}{W/m} = \frac{wM}{Wm}$$
  Here, w = Weight of solute
  W = Weight of solvent
  m = Molecular weight of solute
  M = Molecular weight of solvent
  So, $$\frac{p^0_A - p_A}{p^0_A} = \frac{\Delta p}{p^0} = \frac{wM}{Wm} = \frac{m \times M}{1000}$$
- The molecular weight of a solute can be determined with the help of the relative lowering of vapour pressure method.

**Osmosis**
In osmosis, there is a net flow of solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution across a semipermeable membrane (membranes of animal origin, membranes made from $Cu_2$ [Fe (CN) $_6$], $Ca_3$ (PO4)$_2$ etc.)Osmosis was first observed by Abbe Nollet in 1748.

**Osmotic Pressure**
Osmotic pressure is the equilibrium hydrostatic pressure of the column set up as a result of osmosis. It is the minimum pressure that must be applied on the solution to prevent the entry of the solvent into the solution through the semi-permeable membrane. It is the minimum pressure needed to apply on a solution to make its vapour pressure equal to vapour pressure of the solvent.



**Measurement of Osmotic Pressure:** Different methods are in use for the measurement of osmotic pressure in the laboratory but Berkley and Hartley's method gives the preeminent results. The apparatus consists of an absorbent pot containing copper ferrocyanide deposited in its wall (acts as a semi-permeable membrane) and fixed into a bronze cylinder to which is fixed a piston and a pressure determine (to read the applied pressure).

**Procedure –** The porcelain tube is filled with pure solvent and the metallic jacket with a solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.

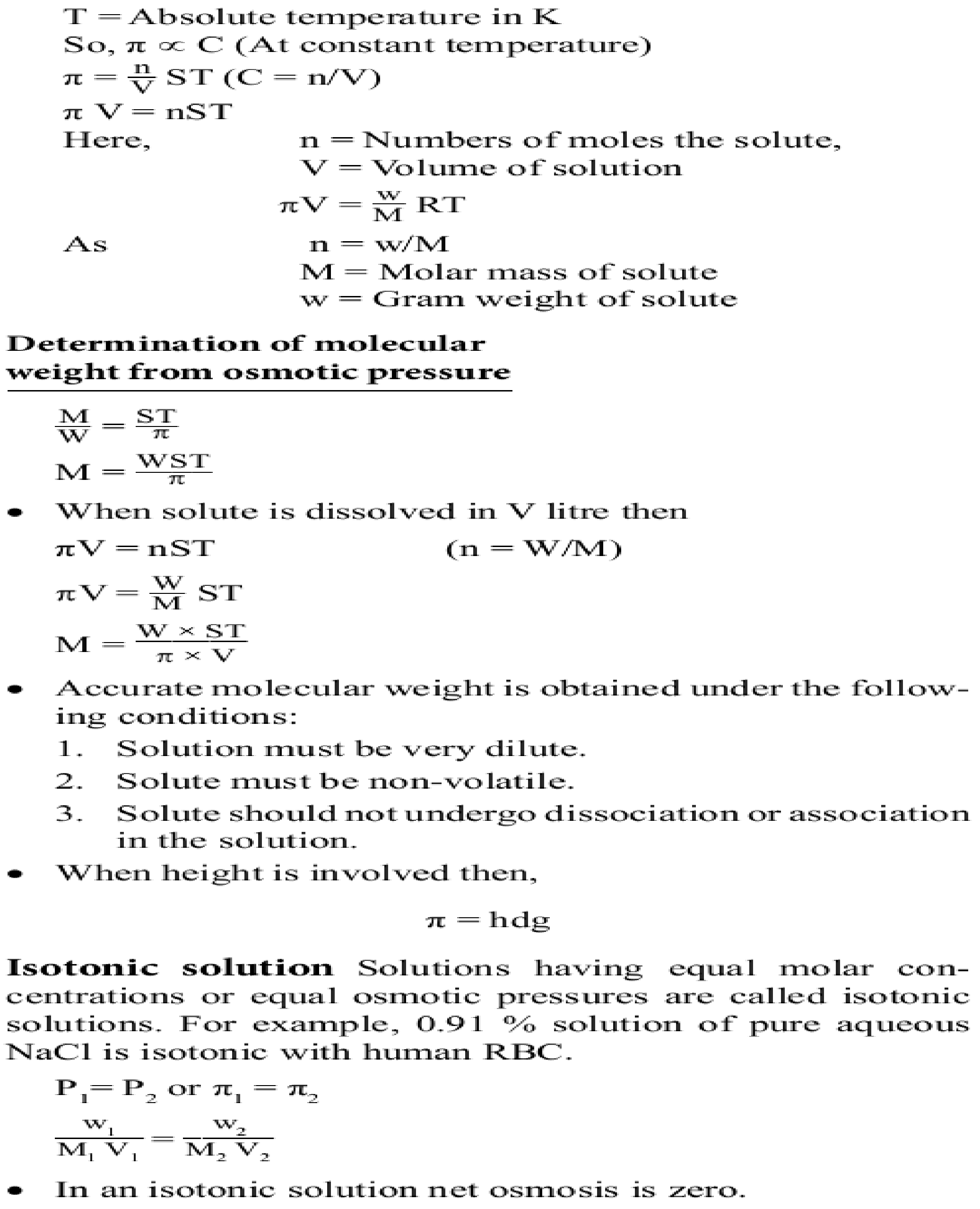
The pot is fixed with a tube indicator on left and water reservoir on right. Pot is filled with water while the cylinder is filled with a solution whose osmotic pressure is to be measured. Water tends to pass into the solution through the semipermeable membrane with the result that the water level in the indicator falls down. External pressure is now applied with the piston so as to preserve a constant level in the indicator. This external pressure is osmotic pressure.

Due to osmosis the water from tube A flows to the solution in B and causes a movement in the liquid meniscus in D. Berkeley and Hartley prevented the inflow of water on tube B by applying an external pressure through C and maintained the liquid meniscus in at the position until equilibrium. The excess pressure thus applied to the solution side to prevent water inflow gave the osmotic pressure at the temperature of the experiment. The apparatus is capable of giving good results in a relatively short time compared to other methods where the solvent is allowed to flow into the solution. In this method, there is no change in the concentration of the solution because no solvent is allowed to enter the solution tube. Pressure up to 150 atmospheres can be measured by this method.

- It is denoted by P or π.
- It is measured by Pfeiffer's method, BerkelyHartley's method, Townsend's method.

**Van't Hoff equation of osmotic pressure**

$\pi = CST$
Here, $\pi$ = Osmotic pressure
C = Concentration of solution in mol/L
S or R = Solution constant



T = Absolute temperature in K
So, $\pi \propto C$ (At constant temperature)
$\pi = \frac{n}{V} ST$ $(C = n/V)$
$\pi V = nST$
Here, n = Numbers of moles the solute,
V = Volume of solution

$$\pi V = \frac{w}{M} RT$$

As n = w/M
M = Molar mass of solute
w = Gram weight of solute

**Determination of molecular weight from osmotic pressure**

$$\frac{M}{W} = \frac{ST}{\pi}$$

$$M = \frac{WST}{\pi}$$

- When solute is dissolved in V litre then

$$\pi V = nST \qquad (n = W/M)$$

$$\pi V = \frac{W}{M} ST$$

$$M = \frac{W \times ST}{\pi \times V}$$

- Accurate molecular weight is obtained under the following conditions:
  1. Solution must be very dilute.
  2. Solute must be non-volatile.
  3. Solute should not undergo dissociation or association in the solution.
- When height is involved then,

$$\pi = hdg$$

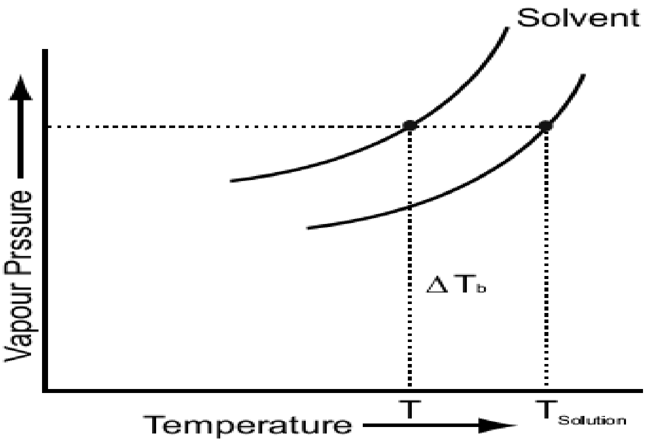
**Isotonic solution** Solutions having equal molar concentrations or equal osmotic pressures are called isotonic solutions. For example, 0.91 % solution of pure aqueous NaCl is isotonic with human RBC.

$P_1 = P_2$ or $\pi_1 = \pi_2$

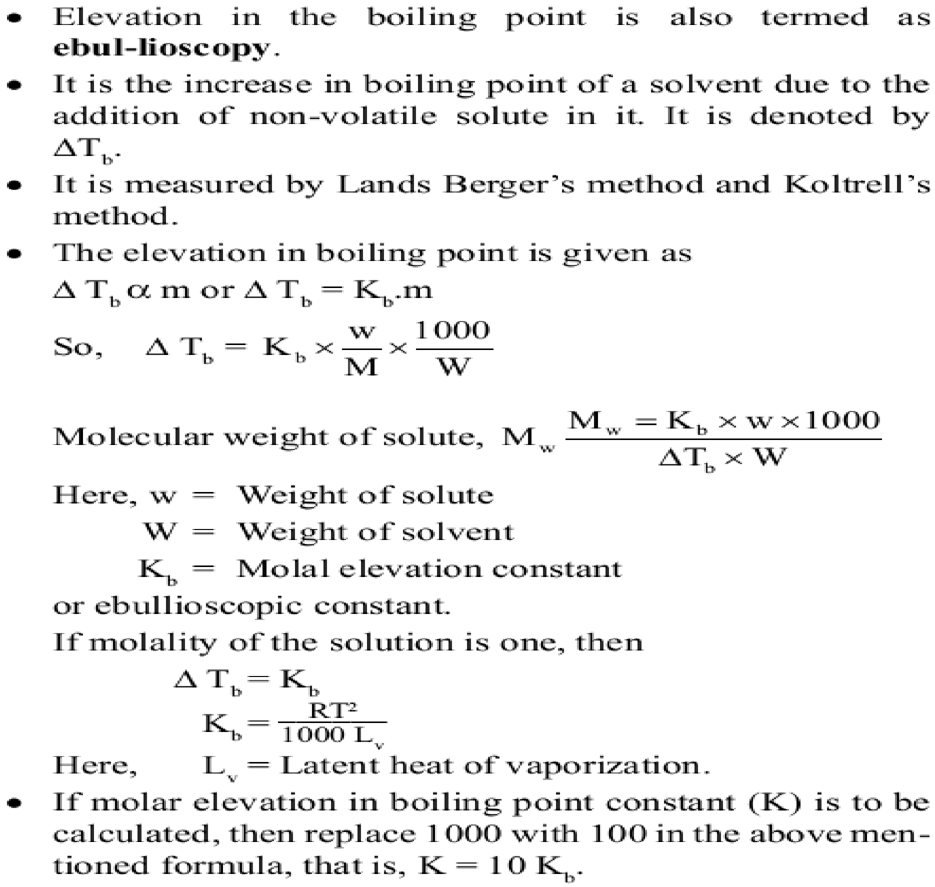
$$\frac{w_1}{M_1 V_1} = \frac{w_2}{M_2 V_2}$$

- In an isotonic solution net osmosis is zero.

**Elevation in Boiling Point**
Boiling point is the temperature of a liquid at which its vapour pressure becomes equal to the atmospheric pressure.



Elevation in Boiling Point



- Elevation in the boiling point is also termed as **ebul-lioscopy**.
- It is the increase in boiling point of a solvent due to the addition of non-volatile solute in it. It is denoted by $\Delta T_b$.
- It is measured by Lands Berger's method and Koltrell's method.
- The elevation in boiling point is given as

  $\Delta T_b \alpha m$ or $\Delta T_b = K_b.m$

  So, $\Delta T_b = K_b \times \frac{w}{M} \times \frac{1000}{W}$

  Molecular weight of solute, $M_w \frac{M_w = K_b \times w \times 1000}{\Delta T_b \times W}$

  Here, w = Weight of solute

  W = Weight of solvent

  $K_b$ = Molal elevation constant

  or ebullioscopic constant.

  If molality of the solution is one, then

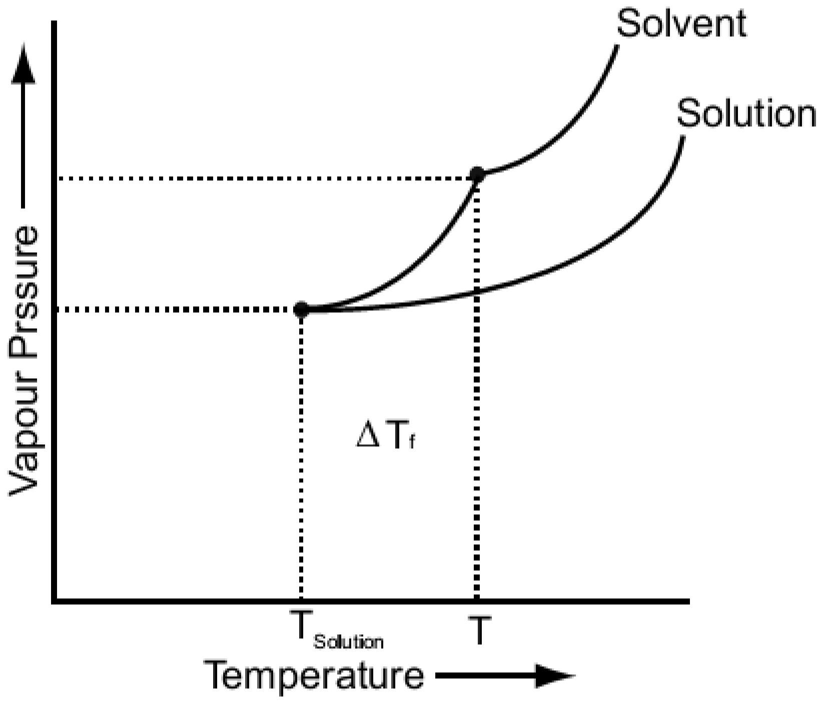
  $$\Delta T_b = K_b$$

  $$K_b = \frac{RT^2}{1000 L_v}$$

  Here, $L_v$ = Latent heat of vaporization.
- If molar elevation in boiling point constant (K) is to be calculated, then replace 1000 with 100 in the above mentioned formula, that is, $K = 10 K_b$.

**Depression in Freezing Point**

Freezing point is the temperature at which the liquid and the solid form of the same substance are in equilibrium and have the same vapour pressure. Due to lower vapour pressure of the solution, solid form of a solution separates out at a lower temperature. lid form of a solution separates out at a lower temperature.



Depression in Freezing Point

- It is the decrease in freezing point of a solvent due to the addition of a non volatile solute.
- This is also termed as **cryoscopy**.
- Depression in freezing point ($\Delta T_f$) = Freezing point of pure solvent – Freezing point of solution
- It is measured by Beckmann's thermometer method and Rast's method.

  $\Delta T_f = K_f.m.$

- $\Delta T_f = K_f \ \frac{w}{m_w} \times \frac{1000}{W}$
- $M \text{ or } m_w = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$

  Here, w = Weight of solute
  W = Weight of solvent
  $K_f$ = Molal depression constant or cryoscopic constant

- If molality of the solution is one, then

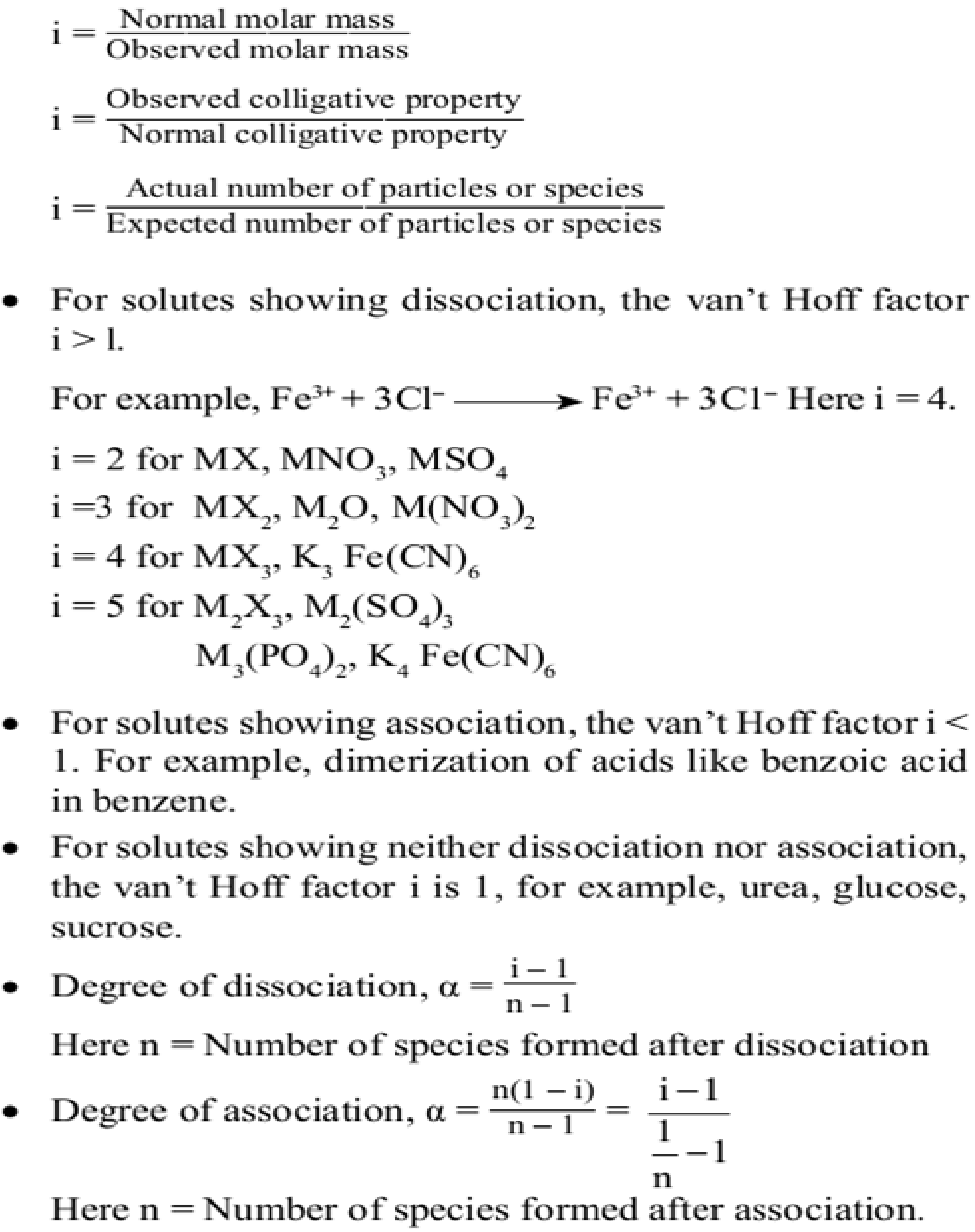
  $\Delta T_f = K_f$

- $K_f = \frac{RT^2}{1000 \ L_f}$

  Here, $L_f$ = Latent heat of fusion.

**Van’t Hoff Factor**

Certain solutes which undergo dissociation or association in solution are found to show abnormal molecular mass. Due to this, the colligative property becomes abnormal which can be explained by van’t Hoff factor.



$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$i = \frac{\text{Actual number of particles or species}}{\text{Expected number of particles or species}}$$

- For solutes showing dissociation, the van’t Hoff factor $i > 1$.

  For example, $Fe^{3+} + 3Cl^- \longrightarrow Fe^{3+} + 3C1^-$ Here $i = 4$.

  $i = 2$ for $MX$, $MNO_3$, $MSO_4$
  $i = 3$ for $MX_2$, $M_2O$, $M(NO_3)_2$
  $i = 4$ for $MX_3$, $K_3\,Fe(CN)_6$
  $i = 5$ for $M_2X_3$, $M_2(SO_4)_3$
  $M_3(PO_4)_2$, $K_4\,Fe(CN)_6$
- For solutes showing association, the van’t Hoff factor $i < 1$. For example, dimerization of acids like benzoic acid in benzene.
- For solutes showing neither dissociation nor association, the van’t Hoff factor i is 1, for example, urea, glucose, sucrose.
- Degree of dissociation, $\alpha = \frac{i-1}{n-1}$

  Here n = Number of species formed after dissociation
- Degree of association, $\alpha = \frac{n(1-i)}{n-1} = \frac{i-1}{\frac{1}{n}-1}$

  Here n = Number of species formed after association.

**Chapter -3** **Electrochemistry**

Electrochemistry is that branch of chemistry which deals with the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Importance of Electrochemistry

1. Production of metals like Na, Mg. Ca and Al.
2. Electroplating.
3. Purification of metals.

4. Batteries and cells used in various instruments.

**Conductors**

Substances that allow electric current to pass through them are known as conductors.

**Metallic Conductors or Electronic Conductors**

Substances which allow the electric current to pass through them by the movement of electrons are called metallic conductors, e.g.. metals.

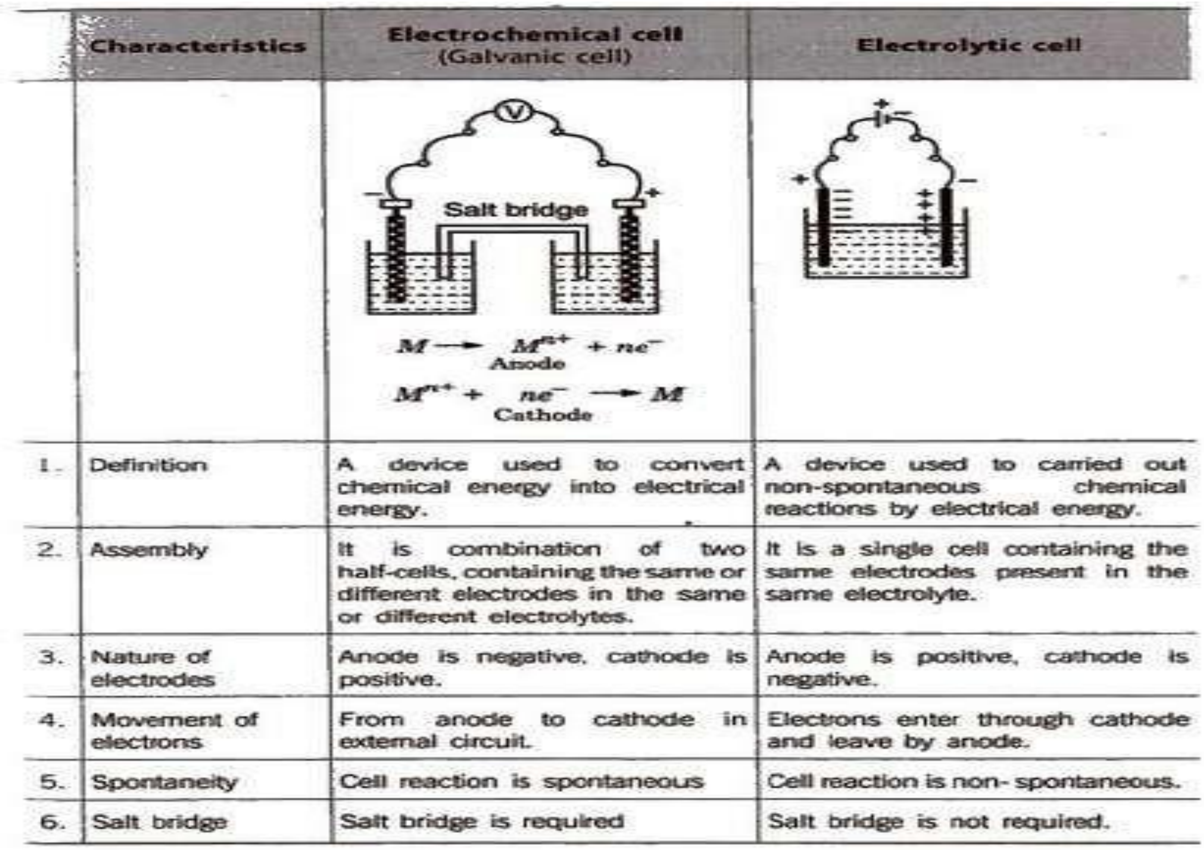
**Electrolytic Conductors or Electrolytes**

Substances which allow the passage of electricity through their fused state or aqueous solution and undergo chemical decomposition are called electrolytic conductors, e.g., aqueous solution of acids. bases and salts.

**Electrolytes are of two types:**

1. **Strong electrolytes** The electrolytes that completely dissociate or ionise into ionsare called strong electrolytes. e.g., HCl, NaOH, $K_2SO_4$
2. **Weak electrolytes** The electrolytes that dissociate partially (ex < 1) are called weak electrolytes, e.g., $CH_3COOH$, $H_2CO_3$, $NH_4OHH_2S$, etc.

**Electrochemical Cell and Electrolytic**

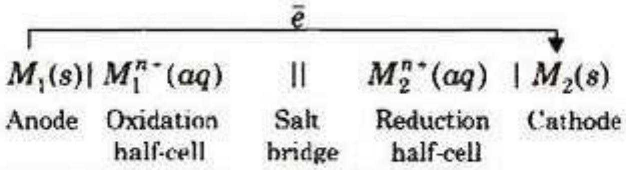


| | Characteristics | Electrochemical cell (Galvanic cell) | Electrolytic cell |
|---|---|---|---|
| | | Salt bridge<br>$M \longrightarrow M^{n+} + ne^-$ Anode<br>$M^{n+} + ne^- \longrightarrow M$ Cathode | |
| 1. | Definition | A device used to convert chemical energy into electrical energy. | A device used to carried out non-spontaneous chemical reactions by electrical energy. |
| 2. | Assembly | It is combination of two half-cells, containing the same or different electrodes in the same or different electrolytes. | It is a single cell containing the same electrodes present in the same electrolyte. |
| 3. | Nature of electrodes | Anode is negative, cathode is positive. | Anode is positive, cathode is negative. |
| 4. | Movement of electrons | From anode to cathode in external circuit. | Electrons enter through cathode and leave by anode. |
| 5. | Spontaneity | Cell reaction is spontaneous | Cell reaction is non- spontaneous. |
| 6. | Salt bridge | Salt bridge is required | Salt bridge is not required. |

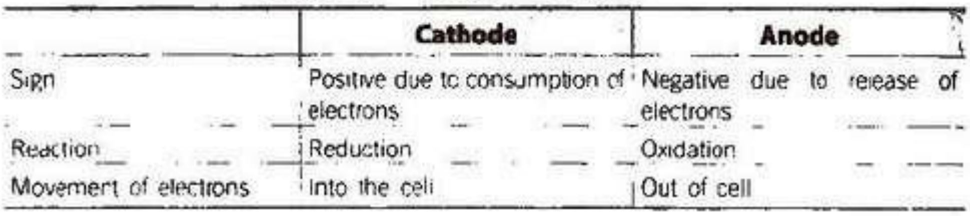
A cell of almost constant emf is called standard cell. The most common is Weston standard cell.

Galvanic cell is also called voltaic cell.

**General Representation of an Electrochemical Cell**



$$M_1(s) | M_1^{n+}(aq) \;||\; M_2^{n+}(aq) \;|\; M_2(s)$$



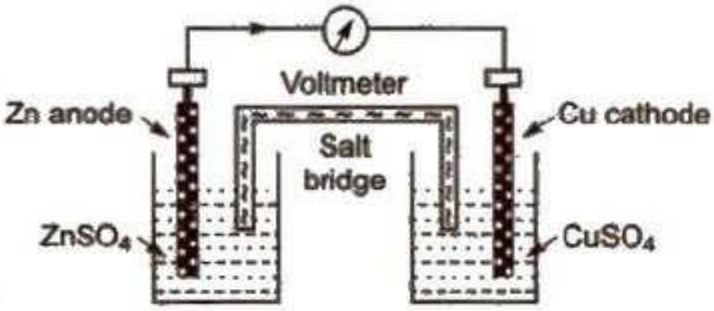
| | Cathode | Anode |
|---|---|---|
| Sign | Positive due to consumption of electrons | Negative due to release of electrons |
| Reaction | Reduction | Oxidation |
| Movement of electrons | Into the cell | Out of cell |

**Other features of the electrochemical cell are**

1. There is no evolution of heat.
2. The solution remains neutral on both sides.
3. The reaction and now of electrons stops after sometime.

## Daniell Cell

An electrochemical cell of zinc and copper metals is known as Daniell cell. It is represented as



**Cell diagram,**

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$

$$\text{LHS oxidation,} \qquad Zn \longrightarrow Zn^{2+} + 2e^-$$

$$\text{RHS reduction,} \qquad Cu^{2+} + 2e^- \longrightarrow Cu$$

$$\text{Overall reaction,} \quad Zn + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu$$

By convention cathode is represented on the RHS and anode on the LHS. Function of salt bridge

1. It completes the circuit and allows the flow of current.
2. It maintains the electrical neutrality on both sides. Salt-bridge generally contains solution of strong electrolyte such as $KNO_3$, KCL etc. KCI is preferred because the transport numbers of $K^+$ and $Cl^-$are almost same.

**Transport number or Transference number** The current flowing through an electrolytic solution is carried by the ions. The fraction of the current carried by an ion is called its transport number or transference number. Thus.Transport number of cation. $n_c$ = (current carried by cation/totalcurrent) Transport number of cation. $n_a$ = (current carried by anion/total current) Evidently $n_c + n_a = 1$

## Electrode Potential

When an electrode is in contact with the solution of its ions in a half-cell, it has a tendency to lose or gain electrons which is known as electrode potential. It is expressed in volts. It is an intensive property, i.e., independent of the amount of species in the reaction.

**Oxidation potential** The tendency to lose electrons in the above case is known as oxidation potential. Oxidation potential of a half-cell is inversely proportional to the concentration of ions in the solution.

**Reduction potential** The tendency to gain electrons in the above case is known as reduction potential. According to IUPAC convention, the reduction potential alone be called as the electrode potential unless it is specifically mentioned.

$E^\circ_{red} = -E^\circ_{oxidalion}$

It is not possible to determine the absolute value of electrode potential. For this a reference electrode [NHE or SHE] is required. The electrode potential is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell.

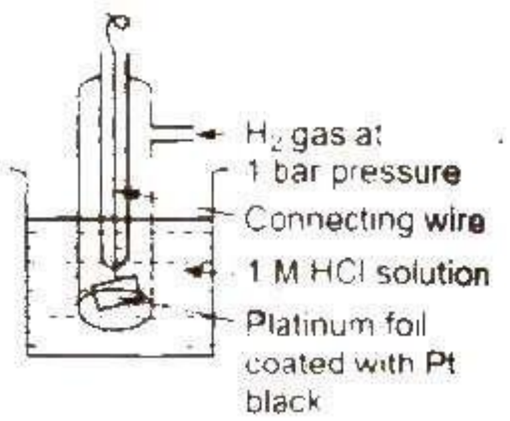
**Standard electrode potential** The potential difference developed between metal electrode and solution of ions of unit molarity (1M) at 1 atm pressure and 25°C (298 K) is called standard electrode potential.

It is denoted by E°.

**Reference Electrode**

The electrode of known potential is called reference electrode. It may be primary reference electrode like hydrogen electrode or secondary reference electrode like calomel electrode.

Standard hydrogen electrode (SHE) Standard hydrogen electrode (SHE). also known as normal hydrogen electrode (NHE), consists of platinum wire, carrying platinum foil coated with finely divided platinum black. The wire is sealed into a glass tube. placed in beaker containing 1 M HCl. The hydrogen gas at 1 atm pressure is bubbled through the solution at 298K. Half-cell is pt $H_2$ (1 atm) $H^+$ (1 M)



In SHE. at the surface of plantinum, either of (he following reaction can take place .

$2H^+(ag) + 2e^- \rightarrow H_2G$ Reduction
$H_2(g) \rightarrow 2H^+(ag) + 2e^-$ Oxidation

The electrode potential of SHE has been fixed as zero at all temperatures. Its main drawbacks are

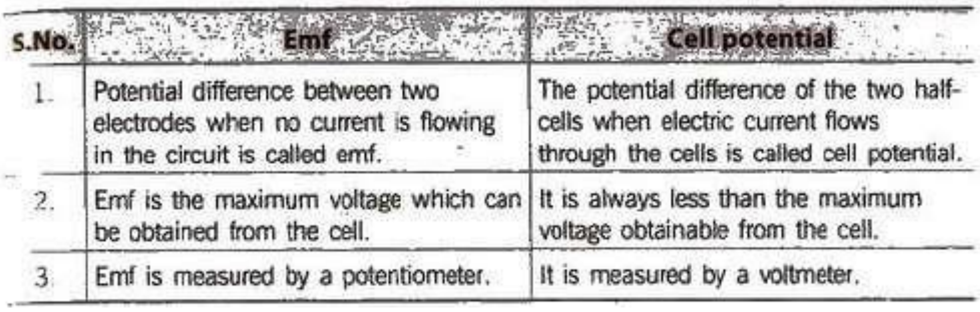
1. It is difficult to maintain 1 atm pressure of $H_2$ gas.
2. It is difficult to maintain $H^+$ ion concentration 1 M.
3. The platinum electrode is easily poisoned by traces of impurities.

Hence, calomel electrodes are conveniently used as reference electrodes, It consists of mercury in contact with $Hg_2\,Cl_2$ (calomel) paste in a solution of KCl.

**Electromotive Force (emf) of a Cell**

It is the difference between the electrode potentials of two half-cells and cause flow of current from electrode at higher potential to electrode at lower potential. It is also the measure of free energy change. Standard emf of a cell,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{right} - E^\circ_{left} = E^\circ_{red} + E^\circ_{oxi}$$



| S.No. | Emf | Cell potential |
|---|---|---|
| 1. | Potential difference between two electrodes when no current is flowing in the circuit is called emf. | The potential difference of the two half-cells when electric current flows through the cells is called cell potential. |
| 2. | Emf is the maximum voltage which can be obtained from the cell. | It is always less than the maximum voltage obtainable from the cell. |
| 3 | Emf is measured by a potentiometer. | It is measured by a voltmeter. |

**Electrochemical Series**

It is the arrangement of electrodes in the increasing order of their standard reduction potentials. Standard Electrode Potential at 298 K . table see in book

Applications of Electrochemical Series (ECS)

1. The lower the value of E°, the greater the tendency to form cation.

$M \rightarrow M^{n+} + ne^-$

Metals placed below hydrogen in ECS replace hydrogen from di1 acids but metals placed above hydrogen cannot replace hydrogen from dil acids.

$$Ca + dil.\,H_2SO_4 \longrightarrow CaSO_4 + H_2\uparrow$$

possible, $(Ca + 2H^+ \longrightarrow Ca^{2+} + H_2)$

$$Cu + dil.\,H_2SO_4 \longrightarrow CuSO_4 + H_2\uparrow$$

not possible, $(Cu + 2H^+ \longrightarrow Cu^{2+} + H_2)$

3. Oxides of metals placed below hydrogen are not reduced by $H_2$ but oxides of iron and metals placed above iron are reduced by $H_2$·

- SnO, PbO, CuO are reduced by $H_2$
- CaO, $K_2O$ are not reduced by $H_2$·

4. Reducing character increases down the series.

5. Reactivity increases down the series.

6. Determination of emf; emf is the difference of reduction potentials of two half-cells.

- $E_{emf} = E_{RHS} - E_{LHS}$

If the value of emf is positive. then reaction take place spontaneously, otherwise not.

7. Greater the reduction potential of a substance, oxidising power. (e.g.. $F_2 > Cl_2 > Br_2 > I_2$)

8. A negative value of standard reduction potential shows that it is the site of oxidation.

9. Oxides of metals having $E°_{red} \geq 0.79$ will be decomposed by heating to form $O_2$ and metal.

**Nernst Equation**

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

$$M^{n+} + ne^- \longrightarrow M$$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{2.303\,RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.0591}{n} \log \left[\frac{1}{M^{n+}}\right]$$

For a electrochemical cell,

$$aA + bB \longrightarrow cC + dD$$

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

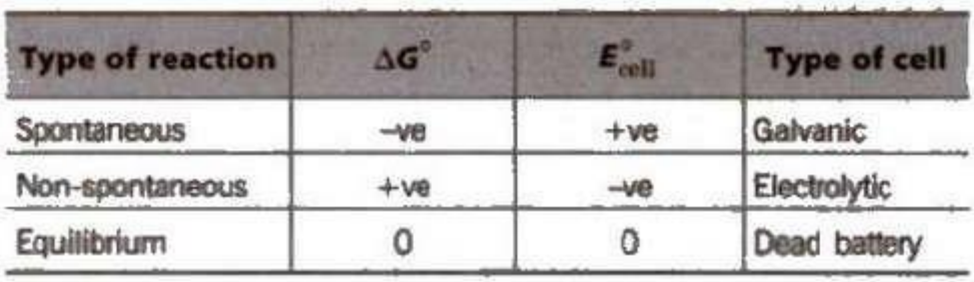
Concentration of pure solids and liquids is taken as unity. Nernst equation and $K_c$ At equilibrium

$$\because \text{ At equilibrium, } E_{\text{cell}} = 0$$

$$E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K_c \text{ at 298K}$$

$$\Delta G^\circ = -\,nFE^\circ_{\text{cell}}$$

Here, ΔG° is the standard Gibbs free energy change.



| Type of reaction | $\Delta G^\circ$ | $E^\circ_{\text{cell}}$ | Type of cell |
|---|---|---|---|
| Spontaneous | –ve | +ve | Galvanic |
| Non-spontaneous | +ve | –ve | Electrolytic |
| Equilibrium | 0 | 0 | Dead battery |

Relationship between free energy change and equilibrium constant $\Delta G^\circ = -\,2.303RT \log K_c$

**Concentration Cells**

(i) Electrode concentration cells Two hydrogen electrodes or different pressures are dipped in the same solution of electrolyte,

e.g..

$$\text{Pt}, \text{H}_2(p_1)|\text{H}^+|\text{H}_2(p_2)\text{Pt}, \; p_1 > p_2$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$$

(ii) Electrolyte concentration cells Electrodes are the same but electrolyte solutionshave different concentrations, e.g..

$$\text{Zn}|\text{Zn}^{2+}(C_1)||\text{Zn}^{2+}(C_2)|\text{Zn}, \; C_2 > C_1$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Conductance (G)

It is the ease of flow of electric current through the conductor. It is reciprocal of resistance (R). G = (1/R), units ohm$^{-1}$ mhos or $\Omega^{-1}$

**Specific Conductivity (K)**

It is the reciprocal of specific resistance.

$$\kappa = \frac{1}{\rho} = \frac{l}{R.a} = G \times \frac{l}{a} = G \times \text{cell constant } (G^*)$$

$$\left(\frac{l}{a} = \text{cell constant}\right)$$

$$\text{Units of } \kappa = \Omega^{-1}\text{cm}^{-1}$$

$$= \text{S cm}^{-1} (\Omega^{-1} = \text{S } i.e., \text{ Siemens})$$

Unit of cell constant is cm$^{-1}$ or m$^{-1}$.

Specific conductivity decreases on dilution. This is because concentration of ions per cc decreases upon dilution.

## Molar Conductivity ($\Lambda_m$)

The conductivity of all the ions produced when 1 mole of an electrolyte is dissolved in V mL of solution is known as molar conductivity.
It is related to specific conductance as
$\Lambda_m = (k \text{ x } 1000/M)$
where. M = molarity.

It units are $\Omega^{-1}$ cm$^2$ mol$^{-1}$ or S cm$^2$ mol$^{-1}$.

## Equivalent conductivity ($\Lambda_m$)

The conducting power of all the ions produced when 1 g-equivalent of an electrolyte is dissolved in V mL of solution, is called equivalent conductivity. It is related to specific conductance as

$\Lambda_m = (k \text{ x } 1000/N)$
where. N = normality.
Its units are ohm$^{-1}$ cm$^2$ (equiv$^{-1}$) or mho cm$^2$ (equiv$^{-1}$) or S cm$^2$ (g-equiv$^{-1}$).

**Debye-Huckel Onsagar equation** It gives a relation between molar conductivity, $\Lambda_m$ at a particular concentration and molar conductivity $\Lambda_m$ at infinite dilution.

$\Lambda_m = \Lambda^0{}_m - \sqrt{C}$

## Factors Affecting Conductivity

**(i) Nature of electrolyte** The strong electrolytes like $KNO_3$ KCl. NaOH. etc. are completely ionised in aqueous solution and have high values of conductivity (molar as well as equivalent).

The weak electrolytes are ionised to a lesser extent in aqueous solution and have lower values of conductivity (molar as well as equivalent) .

**ii) Concentration of the solution** The concentrated solutions of strong electrolytes have Significant interionic attractions. which reduce the speed of ions and lower the value of $\Lambda_m$. and $\Lambda_{eq}$. The dilution decreases such attractions and increase the value of $\Lambda_m$ and $\Lambda_{eq}$.
(iii) **Temperature** The increase of temperature decreases inter-ionic attractions and increases kinetic energy of ions and their speed. Thus, $\Lambda_m$ and $\Lambda_{eq}$ increase with temperature.

## Kohlrausch's Law

At infinite dilution, the molar conductivity of an electrolyte is the sum of the ionic conductivities of the cations and anions, e.g., for $A_xB_y$.

$$\Lambda^0_m\,(A_xB_y) = x\Lambda^0_{A^+} + y\Lambda^0_{B^-}$$

$$\Lambda^0_{eq} = \Lambda^0_{A^+} + \Lambda^0_{B^-}$$

**Applications**

(i) Determination of equivalent/molar conductivities of weak electrolytes at infinite dilution, e.g.,

$$\Lambda^{\infty}_{CH_3COOH} = \Lambda^{\infty}_{CH_3COONa} + \Lambda^{\infty}_{HCl} - \Lambda^{\infty}_{NaCl}$$

$$\Lambda^{\infty}_{NH_4OH} = \Lambda^{\infty}_{NH_4Cl} + \Lambda^{\infty}_{NaOH} - \Lambda^{\infty}_{NaCl}$$

(ii) Determination of degree of dissociation (α) of an electrolyte at a given dilution.

$$\alpha = \frac{\text{molar conductance at concentration ‘}C\text{’}}{\text{molar conductance at infinite dilution}} = \frac{\Lambda^{C}_{m}}{\Lambda^{\infty}_{m}}$$

The dissociation constant (K) of the weak electrolyte at concentration C of the solution can be calculated by using the formula

$k_c = (C\alpha^2/1 - \alpha)$

where, α is the degree of dissociation of the electrolyte.

(iii) Salts like $BaSO_4$ .., $PbSO_4$‘ AgCl, AgBr and AgI which do not dissolve to a large extent in water are called sparingly soluble salts.

The solubility of a sparingly soluble salt can be calculated as

$$\Lambda^{\circ}_{m} = \frac{\kappa \times 1000}{\text{solubility (in mol L}^{-1})}$$

$$\text{Solubility (in mol L}^{-1}) = \frac{\kappa \times 1000}{\Lambda^{\circ}_{m}}$$

**Electrolysis**

It is the process of decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten state,

1. In electrolytic cell both oxidation and reduction takes place in the same cell.
2. Anode is positively charged and cathode is negatively charged, In electrolytic cell.
3. During electrolysis of molten electrolyte, cations are liberated at cathode. while anionsat the anode.
4. When two or more ions compete at the electrodes. the ion with higher reduction potential gets liberated at the cathode while the ion with lower reduction potential at the anode.

**Discharge potential** is defined as the minimum potential that must be applied across the electrodes to bring about the electrolysis and subsequent discharge of the ion on the electrode.

## Faraday’s Laws of Electrolysis

### 1. First law

The amount of the substance deposited or liberated at cathode directly proportional to the quantity of electricity passed through electrolyte.

$W \propto I \times t = I \times t \times Z = Q \times Z$

- I current in amp, t = time in sec,
- Q = quantity of charge (coulomb)
- Z is a constant known as electrochemical equivalent.

When I = 1 amp, t = 1 sec then Q = 1 coulomb, then w = Z.

Thus, electrochemical equivalent I” the amount of the substance deposited or liberated by passing 1A current for 1 sec (i.e.. 1 coulomb, I x t = Q)

### 2. Second law

When the same quantity of electricity is passed through different electrolytes. the amounts of the substance deposited or liberated at the electrodes arc directly proportional to their equivalent weights, Thus,

$$\frac{\text{Mass of } A}{\text{Mass of } B} = \frac{\text{eq. wt. of } A}{\text{eq. wt. of } B}$$

$$\frac{\omega_1}{\omega_2} = \frac{E_1}{E_2} \Rightarrow \frac{Z_1 Q}{Z_2 Q} = \frac{E_1}{E_2}$$

Hence, electrochemical equivalent ∝ equivalent weight.

**Batteries**

These are source of electrical energy which may have one or more cells connected in series. For a good quality battery it should be reasonably light. compact and its voltage should not vary appreciably during its use.

**Primary Batteries**

In the primary batteries. the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again.

**(i) Dry cell or Leclanehe cell**

Anode-Zinc container Cathode-Graphite rod surrounded by $MnO_2$powderElectrolytePasteof $NH_4Cl + ZnCl_2$

Cathode reaction,

$2MnO_2(s) + 2\ NH^+_4(aq) + 2e^- \rightarrow Mn_2O^3(s) + 2NH_3(g) + H_2O(l)$
Anode reaction,

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ Cell potential 1.25 V to 1.5 V

**(ii)** Mercury cell

Anode-Zn-Hg amalgam
Cathode-Paste of (HgO + C)
Electrolyte-Moist paste of KOH-ZnO

Cathode reaction,

$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$$

Anode reaction,

$$Zn\,(Hg) + 2OH^-\,aq \longrightarrow ZnO(s) + H_2O(l) + 2e^-$$

Net reaction,

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

Cell potential 1.35 V

**Secondary Batteries**

These cells can be recharged and can be used again and again, e.g.,

**(i) Lead Storage battery**

Anode-Spongy lead
Cathode-Grid of lead packed with $PbO_2$
Electrolyte 38% $H_2SO_4$ by mass

Anode reaction,

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

Cathode reaction,

$$\underline{PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)}$$

Net reaction,

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

When recharged the cell reactions are reversed.

**(ii) Nickel-cadmium storage cell**
AnodeCadmium
Cathode-Metal grid containing $NiO_2$
Electrolyte-KOH solution

Anode reaction,

$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode reaction,

$$\underline{NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)}$$

Net reaction,

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

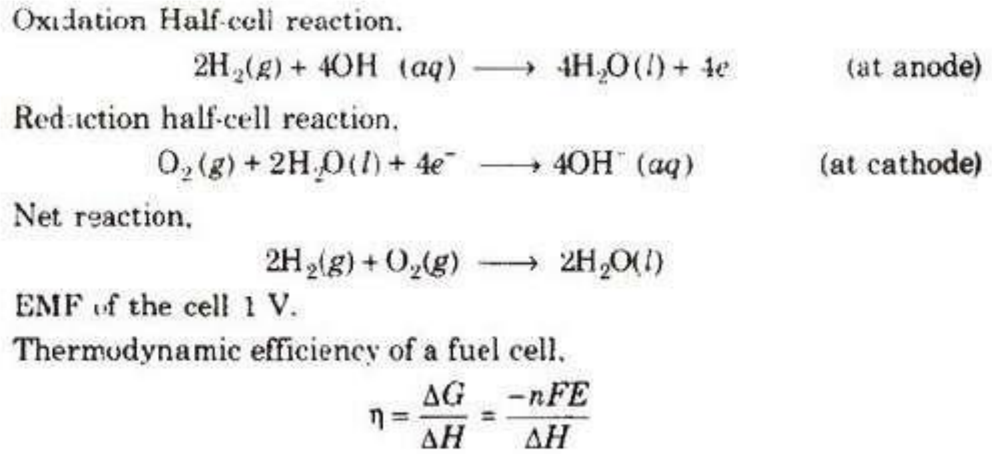
Cell potential = 1.4 V

**Fuel Cells**

Galvanic cells which use energy of combustion of fuels like $H_2$, $CH_4$, $CH_3OH$, etc., as the source to produce electrical energy are called fuel cells. The fuel cells are pollution free and have high efficiency.

**Hydrogen-Oxygen Fuel Cell**

Electrodes-Made of porous graphite impregnated with catalyst (Pt, Ag or a metal oxide). Electrolyte-Aqueous solution of KOH or NaOH
Oxygen and hydrogen are continuously fed into the cell.



Oxidation Half-cell reaction.

$$2H_2(g) + 4OH\ (aq) \longrightarrow 4H_2O(l) + 4e \qquad \text{(at anode)}$$

Reduction half-cell reaction.

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq) \qquad \text{(at cathode)}$$

Net reaction.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

EMF of the cell 1 V.

Thermodynamic efficiency of a fuel cell.

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H}$$

**Corrosion**

Slow formation of undesirable compounds such as oxides, sulphides or carbonates at the surface of metals by reaction with moisture and other atmospheric gases is known as corrosion.

**Factors Affecting Corrosion**

1. Reactivity of metals
2. Presence of moisture and atmospheric gases like $CO_2$, $SO_2$, etc.
3. Presence of impurities
4. Strains in the metal
5. Presence of electrolyte

**Rusting of Iron-Electrochemical Theory**

An electrochemical cell, also known as corrosion cell, is developed at the surface of iron. Anode- Pure iron
Cathode-Impure surface

Electrolyte,

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

Anode reaction,

$$2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 4e^-$$

Cathode reaction,

$$\underline{O_2(g) + 4H^+(aq) + 4e^-(l) \longrightarrow 2H_2O(l)}$$

Net reaction,

$$2Fe(s) + 4H^+(aq) + O_2(g) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

At surface,

$$4Fe^{2+}(aq) + O_2(g) + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+(aq)$$

$$Fe_2O_3(s) + xH_2O(l) \longrightarrow Fe_2O_3 \cdot xH_2O \text{ (Rust)}$$

Rusting of iron can be prevented by the following methods :

1. Barrier protection through coating of paints or electroplating.
2. Through galvanisation or coating of surface with tin metal.
3. By the use of antirust solutions (bis phenol).
4. By cathodic protection in which a metal is protected from corrosion by connecting it to another metal that is more easily oxidised.

## Chapter -4

## Chemical Kinetics

The branch of chemistry, which deals with the rate of chemical reactions. the factors affecting the rate of reactions and the mechanism of the reaction. is called **chemical kinetics.**

### Chemical Reactions on the Basis of Rate of Reaction

1. **Fast/instantaneous reactions** Chemical reaction which completes in less than Ips ($10^{-12}$ s) time, IS known as fast reaction. It IS practically impossible to measure the speed of such reactions, e.g., ionic reactions. organic substitution reactions.
2. **Slow reactions** Chemical re actions which completes in a long time from some minutes to some years are called slow reactions. e.g., rusting of iron. transformation of diamond etc.
3. **Moderately** slow reactions Chemical reactions which are intermediate between slow and fast reactions are called moderately slow reactions.

### Rate of Reaction

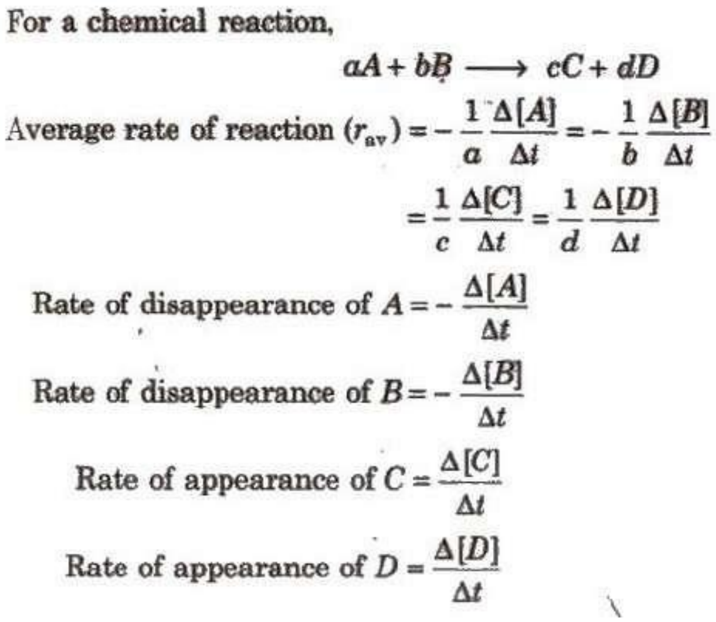
Rate of a chemical reaction IS the change in the concentration of any one of the reactants or products per unit time. It is expressed in mol $L^{-1}$ $s^{-1}$ or $Ms^{-1}$ or atm $time^{-1}$ units.

### Rate of reaction

= (decrease/increase in the concentration of reactant/product/time taken)

This rate of reaction is known as average rate of reaction ($r_{av}$).($r_{av}$ can be calculated by dividing the concentration difference by the time interval).

For a chemical reaction,



For a chemical reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\text{Average rate of reaction } (r_{av}) = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

$$\text{Rate of disappearance of } A = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Rate of disappearance of } B = -\frac{\Delta[B]}{\Delta t}$$

$$\text{Rate of appearance of } C = \frac{\Delta[C]}{\Delta t}$$

$$\text{Rate of appearance of } D = \frac{\Delta[D]}{\Delta t}$$

## Instantaneous Rate of Reaction

Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.

For reaction,

For reaction, $R \longrightarrow P$

$$r_{ins} = -\frac{\Delta[R]}{\Delta t} \text{ or } \frac{\Delta[P]}{\Delta t} \text{ as } \Delta \to d$$

$$\Rightarrow \quad r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Methods for measuring reaction rate (i) pH measurement, (ii) change in optical activity, (iii) change in pressure, (iv) change in conductance.

Slowest step of a reaction was called rate determining step by van’t Hoff.

## Factors Affecting Rate of Reaction

1. Nature and concentration of reactant
2. Temperature
3. Surface area of reactant
4. Radiations and catalyst
5. Pressure of gas

## Rate Law Expressions

According to the law of mass action, For a

chemical reaction,

$aA + bB \rightarrow$ Products

Rate $\alpha$ $[A]^a [B]^b = k[A]^a [B]^b$

But experimentally, it is observed that the rate of reaction is found to depend upon ‘α’ concentration terms of A and ‘β’ concentration terms of B Then,

Rate $\alpha$ $[A]^\alpha [B]^\beta = k[A]^\alpha [B]^\beta$

where, [A] and [B] molar concentrations of A and B respectively and k is the velocity constant or rate constant. The above expression is known as rate law.

Rate Constant

In the above expression, k is called rate constant or velocity constant.

Rate constant may be defined as the specific rate of reaction when the molar concentrations of the reactants is taken to be unity, i.e.,

Rate = k, if [A] = [B] = 1

Units of rate constant or specific reaction rate for a nth order reaction is given as K = (1/Time) x

$(1/[\text{Conc.}]^{n-1})$

**Characteristics of rate constant**

1. Greater the value of rate constant, faster is the reaction.
2. Each reaction has a particular value of rate constant at a particular temperature.
3. The value of rate constant for the same reaction changes with temperature.
4. The value of rate constant for a reaction does't depend upon the concentration of the reactants.

**Difference between rate of reaction and reaction rate constant .**

RATE OF REACTION

Rate of reaction in the change in concentration of a reactant or product in a unit interval of time.

The rate of reaction at any instant of time depends upon the molar concentration of the reactants at that time.

Its units are always mol $\text{litre}^{-1}$ $\text{time}^{-1}$

REACTION RATE CONSTANT

It is the rate of reaction when the molar concentration of each of the reactants is unity.

The rate constant does not depend upon the concentration of the reactants.

Its units depend upon the order of reaction.

| | Order of reaction | Molecularity of reaction |
|---|---|---|
| 1. | Order of reaction is the sum of the concentration terms on which rate of reaction actually depends.<br>Or<br>It is also defined as sum of the exponents of the molar concentrations in the rate law equation. | Molecularity of a reaction is the number of atoms, ions or molecules that must collide with one another to form products in a chemical reaction. |
| 2. | It can be fractional as well as zero. | It cannot be zero or fractional. |
| 3. | It is an experimentally determined term. | It is theoretically determined term. |
| 4. | Order of reaction is applicable to elementary as well as complex reactions. | Molecularity is applicable only to elementary reactions. |
| 5. | Negative order reaction is also possible, e.g.,<br>$2O_3 \longrightarrow 3O_2$ Rate = $k[O_3]^2[O_2]^{-1}$<br>Order w.r.t to $O_2$ is –1. | Molecularity can never be negative. |
| 6. | Types of reactions depending upon orders | Types of reactions depending upon molecularity |
| | (i) Zero order reaction<br>(I) $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl$<br>(II) $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$ | (i) Unimolecular reaction,<br>$N_2O_4(g) \longrightarrow 2NO_2(g)$ |
| | (ii) First order reaction<br>(I) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$<br>(II) Radioactive disintegration<br>(III) Inversion of cane sugar. | (ii) Bimolecular reactions,<br>$2HI(g) \longrightarrow H_2(g) + I_2(g)$<br>(iii) Termolecular reactions,<br>$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ |
| | (iii) Second order reaction<br>(I) $2HI \longrightarrow H_2 + I_2$<br>(II) Alkaline hydrolysis of ester (saponification) | |
| | (iv) Third order reaction<br>$2NO + O_2 \longrightarrow 2NO_2$ | |

**Integrated Rate Equation for Zero Order Reactions**

$$k_0 = \frac{1}{t}\{[A]_0 - [A]\}$$

[where, $[A]_0$ is initial concentration and $[A]$ is final concentration]

$$t = t_{1/2} \text{ when } [A] = \frac{[A]_0}{2}$$

Half-life period, $t_{1/2} = \frac{[A]_0}{2k_0}$

Units of rate constant, $k_0 = \text{mol L}^{-1}\text{s}^{-1}$ = units of rate

For zero order gaseous reactions,

$$k_0 = \frac{1}{t}[p_0 - p] \quad \text{and} \quad t_{1/2} = \frac{p_0}{2k_0}$$

**Integrated Rate Equation for First Order Reactions**

$$k_1 = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$[A] = [A]_0 e^{-k_1 t}$$

Half-life period ($t_{1/2}$) : It is concentration independent term.

$$t = t_{1/2}, [A] = \frac{[A]_0}{2}$$

Amount of a substance after $n$ half-lives $= \frac{[A]_0}{2^n}$

$$t_{1/2} = \frac{0.693}{k_1}$$

For such reactions, $t_{75\%} = 2 \times t_{50\%}$

$$t_{99.9\%} = 10 \times t_{1/2}$$

All radioactive changes follow the first order kinetics.

Integrated rate equation for first order gaseous reactions,

$$A(g) \longrightarrow B(g) + C(g)$$

| | $A(g)$ | $B(g)$ | $C(g)$ |
|---|---|---|---|
| Initial pressure | $p_0$ atm | 0 | 0 |
| Pressure at $t$ | $[p_0 - p]$ atm | $p$ atm | $p$ atm |

$$k_1 = \frac{2.303}{t}\log\frac{p_0}{(2p_0 - p_t)}$$

**For first order chemical reactions,**

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$k_1 = \frac{2.303}{t} \log\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

($V_o$, $V_t$, and $_\infty$ are the volumes of NaOH solution used for the titration of same volume of the reaction mixture after times 0, t and ∞ respectively.)

**Pseudo First Order Reaction**

Chemical reactions which appear to be of higher order but actually are of the lower order are called pseudo order reactions. In case of pseudo first order reaction, chemical reaction between two substances takes place and one of the reactant is present in execess. e.g., hydrolysis of ester.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

So, in this reaction,

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$

For chemical reaction,

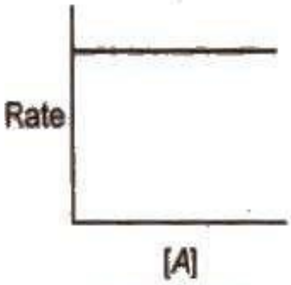
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$k = \frac{2.303}{t} \log\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$$

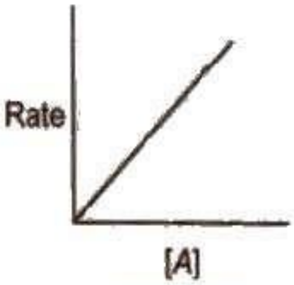
[$r_O$ $r_t$, and $r_\infty$.. are the polarimetric readings at t = 0, t and ∞, respectively.]

**Methods to Determine Order of Reaction**

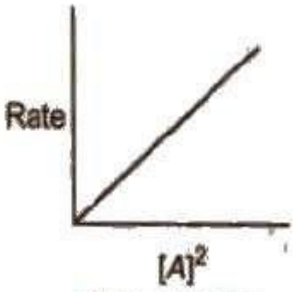
**(i) Graphical method**



Zero order



First order



Second order

**(ii) Initial rate method** In this method, the order of a reaction is determined by varying the concentration of one of the reactants while others are kept constant
**(iii) Integrated rate law method** In this method out different integrated rate equation which gives the most constant value for the rate constant corresponds to a specific order of reaction.

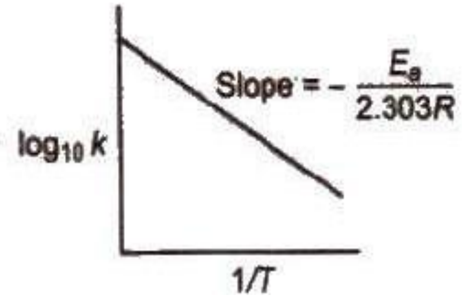
## Arrhenius Equation

Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature, and the expression is

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

or $$\ln k = \ln A - \frac{E_a}{RT}$$

or $$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

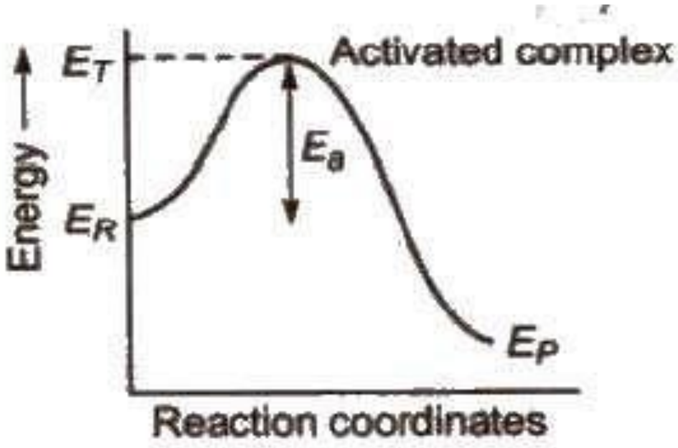


where, A = frequency or Arrhenius factor. It is also called pre-exponential factor.
R = gas constant

$E_a$ = activation energy

## Activated complex (or transition state)

Activated complex is the highest energy unstable intermediate between the reactants and products and gets decomposed immediately (having very short life), to give the products. In this state, bonds of reactant are not completely broken while the bonds of products are not completely formed.



**Threshold energy ($E_T$)** The minimum amount of energy which the reactant must possess in order to convert into products is known as threshold energy.

Activation energy ($E_a$) The additional amount of energy, required by the reactant so that their energy becomes equal to the threshold value is known as activation energy.

$\Rightarrow E_a = E_T - E_R$

Lower the activation energy, faster is the reaction.

Different reactions have different rates because their activation energies are different.

Larger the value of Eo, smaller the value of rate constant and greater is the effect of a given temperature rise on K

Important points about Arrhenius equation

(i) If $\Re_2$ and $\Re_1$ are rate constant at temperature $T_2$ and $T_1$; then

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\, R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

ii) Fraction of molecules with energy equal to or greater than the activation energy is called Boltzmann factor and is given by

$$x = \frac{n}{N} = e^{-E_a/RT}$$

$$\log x = \frac{-E_a}{2.303\, RT}$$

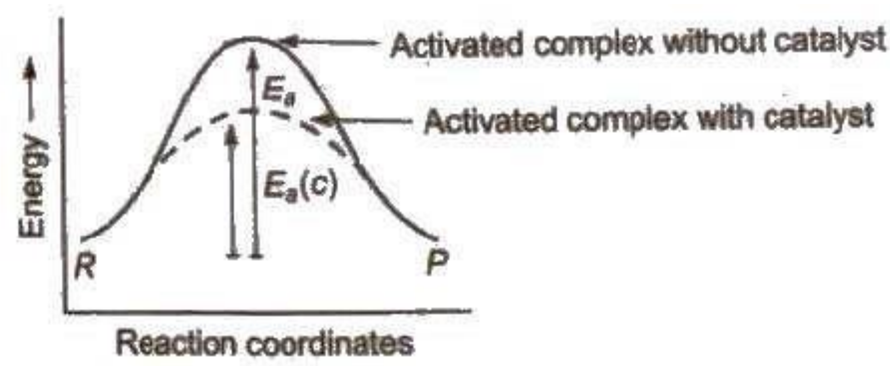
(iii) $E_a$ is constant for a particular reaction.

(iv) $E_a$ does't depend on temperature, volume, pressure, etc., but gets affected by catalyst.
In the Arrhenius equation, when $T \rightarrow \infty$ then $\Re = Ae^\circ = A$ when $E_a = 0, k = A$ and the rate of reaction becomes independent temperatur

## Role of Catalyst in a Chemical Reaction

A catalyst is a chemical substance which alters the rate of a reaction WIthout itself undergoing any permanent chemical change.

In the chemical reactions, catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence. lowering the potential energy barrier as shown.



In the presence of catalyst, activation energy decreases and hence.

$$\frac{k_P}{k_a} = e^{(E_a - E_P)\,RT} = e^{\Delta E/RT}$$

where, P denotes presence of catalyst and a denotes absence of catalyst.

## Theory of Reaction Rates

Collision Theory -According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur, when molecules collide with each other.The number of collisions between the reacting molecules taking place per second per unit volume is known as collision frequency ($Z_{AB}$)·But only those collisions in which the colliding species are associated with certain minimum amount of energy and collide in proper orientation result in the product formation, such collisions are called **fruitful collisions or effective collision.**

Here, rate = – (dv/dt) = collision frequency x fraction of effective collision

= $Z_{AB}$ x f = $Z_{AB}$ x $e^{-E_a/RT}$

where, $Z_{AB}$ represents the collision frequency of reactants, A and B $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than $E_a$.

So, to account for effective collisions, another factor, P called the probability or steric factor is introduced.

So, rate = $PZ_{AB}e^{-E_a/RT}$

## The Activated Complex Theory or Transition State Theory

Reactants ⇔ Activated complex → Products

This theory is based on the fact that bond cleavage and bond formation, involved in a chemical reaction, must occur simultaneously. Hence, the reactants are not converted directly into the products. There is an energy barrier or activated complex [intermediate product with partially formed bond] between the reactants and products. The reactants must cross this energy barrier before converting into products. The height of the barrier determines the threshold energy.

## Photochemical Reactions

Chemical reactions, that occur on exposure to visible radiation are called photochemical reactions.

1. The rate of a photochemical reactions is affected by the the intensity of light.
2. Temperature has little effect on photochemical reactions.

Quantum yield or quantum efficiency of a photochemical reaction,

φ = (number of reactant molecules reacting in a given time / number of photons (quanta) of light absorbed ill the same time).

## Fractional order

In fractional order reactions, the order is a non-integer, which often indicates a chemical chain reaction or other complex reaction mechanism. For example, the pyrolysis of acetaldehyde ($CH_3CHO$) into methane and carbon monoxide proceeds with an order of 1.5 with respect to acetaldehyde: $r = k[CH_3CHO]^{3/2}$.The decomposition of phosgene ($COCl_2$) to carbon monoxide and chlorine has order 1 with respect to phosgene itself and order 0.5 with respect to chlorine: $v = k[COCl_2]\ [Cl_2]$

The order of a chain reaction can be rationalized using the steady state approximation for the concentration of reactive intermediates such as free radicals. For the pyrolysis of acetaldehyde, the Rice-Herzfeld mechanism is

**Initiation**

$CH_3CHO \rightarrow \bullet CH_3 + \bullet CHO$

**Propagation**

$\bullet CH_3 + CH_3CHO \rightarrow CH_3CO\bullet + CH_4$

$CH_3CO\bullet \rightarrow \bullet CH_3 + CO$

**Termination**

$2\ \bullet CH_3 \rightarrow C_2H_6$

where • denotes a free radical.

To simplify the theory, the reactions of the •CHO to form a second $\bullet CH_3$ are ignored.

In the steady state, the rates of formation and destruction of methyl radicals are equal, so that the concentration of methyl radical satisfies.

The reaction rate equals the rate of the propagation steps which form the main reaction products $CH_4$ and CO:

# Chapter -5 Surface Chemistry

Surface Chemistry is the branch of chemistry which deals with the phenomenon that occurs on the surfaces or interfaces, such phenomenon includes corrosion. catalysis, crystallisation, etc

## Adsorption

Due to unbalanced attraction forces, accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption. The molecular species accumulates at the surface is termed as adsorbate and the material on the surface of which the adsorption takes place is called adsorbent, e.g..

(i) $O_2$, $H_2$, $C1_2$, $NB_3$ gases are adsorbed on the surface of charcoal.
(ii) Silica gels adsorb water molecules from air.

Charcoal, silica gel, metals such as Ni, Cu, Ag, Pt and colloids are some adsorbents.

## Important Characteristics of Adsorption

1. It is specific and selective in nature.
2. Adsorption is spontaneous process, therefore change in free energy ($\Delta G$)is negative.

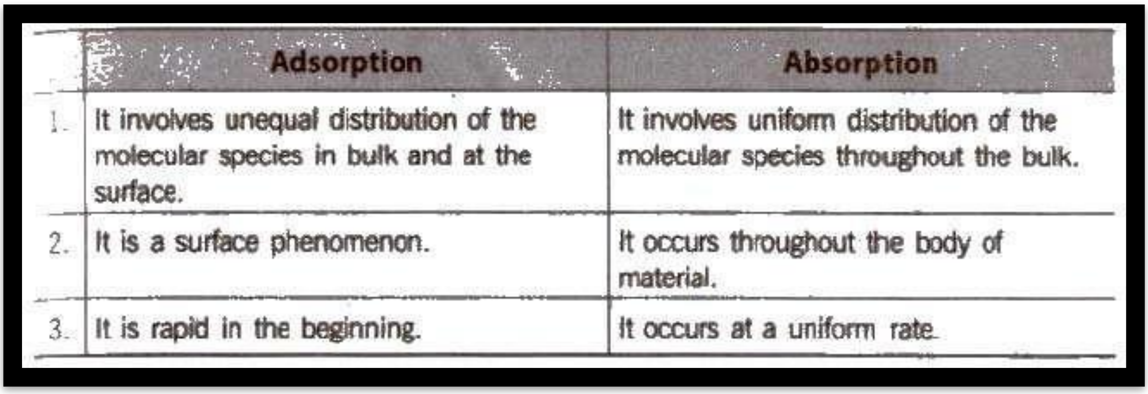
$\Delta G = \Delta H - T\Delta S$,

For the negative value of $\Delta G$,in a system, in which randomness decreases, $\Delta H$ must be negative. Hence, adsorption is always exothermic. Adsorption of hydrogen over Pt is called **occlusion**.

## Desorption

It is a process of removing an adsorbed substance from a surface on which it is adsorbed, is known as desorption.

## Distinction between Adsorption and Absorption



| | Adsorption | Absorption |
|---|---|---|
| 1. | It involves unequal distribution of the molecular species in bulk and at the surface. | It involves uniform distribution of the molecular species throughout the bulk. |
| 2. | It is a surface phenomenon. | It occurs throughout the body of material. |
| 3. | It is rapid in the beginning. | It occurs at a uniform rate. |

### Sorption

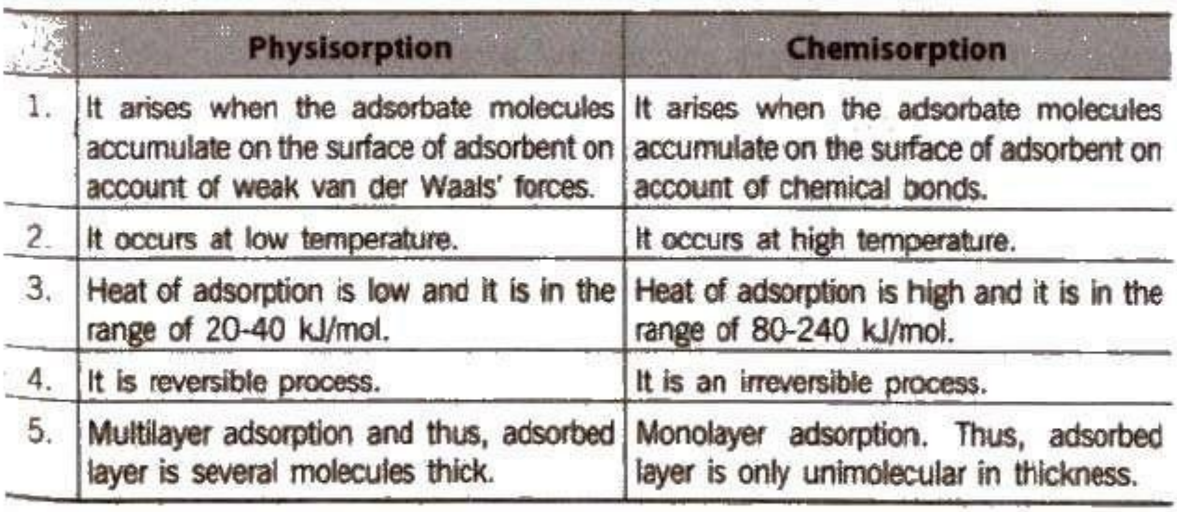
It is a process in which both adsorption and absorption take place simultaneously, the term sorption is simply used.

### Positive and Negative Adsorption

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

On the other hand, if the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption, e.g., when a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption.

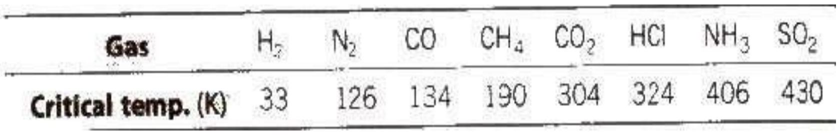
### Distinction between Physisorption and Chemisorption



| | Physisorption | Chemisorption |
|---|---|---|
| 1. | It arises when the adsorbate molecules accumulate on the surface of adsorbent on account of weak van der Waals' forces. | It arises when the adsorbate molecules accumulate on the surface of adsorbent on account of chemical bonds. |
| 2. | It occurs at low temperature. | It occurs at high temperature. |
| 3. | Heat of adsorption is low and it is in the range of 20-40 kJ/mol. | Heat of adsorption is high and it is in the range of 80-240 kJ/mol. |
| 4. | It is reversible process. | It is an irreversible process. |
| 5. | Multilayer adsorption and thus, adsorbed layer is several molecules thick. | Monolayer adsorption. Thus, adsorbed layer is only unimolecular in thickness. |

### Factors Affecting Adsorption

**(a) Nature of adsorbent** Same gas may be adsorbed to different extents on different adsorbent.



| Gas | $H_2$ | $N_2$ | CO | $CH_4$ | $CO_2$ | HCl | $NH_3$ | $SO_2$ |
|---|---|---|---|---|---|---|---|---|
| Critical temp. (K) | 33 | 126 | 134 | 190 | 304 | 324 | 406 | 430 |

(b) **Surface area of the adsorbent** Greater the surface area, greater is the extent of adsorption.

**(c) Nature of the gas being adsorbed** Greater is the critical temperature of a gas, greater are the van der Waals' forces of attraction and thus, greater is the adsorption.

**(d) Temperature** Adsorption is an exothermic process involving the equilibrium : Gas (adsorbate) + Solid (adsorbent) ⇔ Gas adsorbed on solid + Heat

Applying Le-Chatelier principle, increase of temperature decreases the adsorption and vice- versa.

**(e)Pressure** Adsorption increases with pressure at constant temperature. The effect is large if temperature is kept constant at low value.

**(f) Activation of the solid adsorbent** Activation means increasing the adsorbing power of the solid adsorbent. This can be done by subdividing the solid adsorbent or by removing the gases already adsorbed by passing superheated steam

**Adsorption Isotherms**

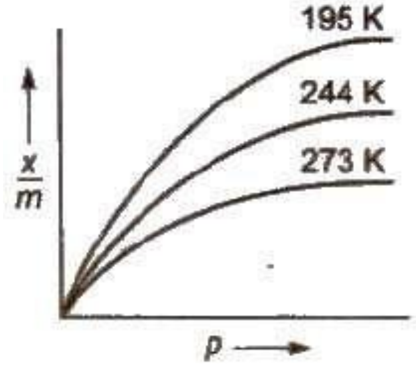
It is the plot of the mass of gas adsorbed per gram of adsorbent (x / m) versus equilibrium pressure at constant temperature.

**Freundlich Adsorption Isotherm**

It gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. It can be expressed by the equation.

$x / m = kp^{1/n}$ …(i)

Where, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.



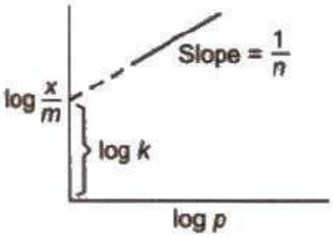
At low pressure, n = 1, i.e., x / m = kp

At high pressure, n > 1, i.e., x / m = k (independent of p) Taking logarithm of Eq. (i)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Plot of $\log \frac{x}{m}$ *vs* $\log p$ is a straight line with slope $\frac{1}{n}$ and intercept on $y$-axis = $\log k$.

The factor $\frac{1}{n}$ can have values between 0 and 1.



**Freundlich Adsorption Equation for Solutions**

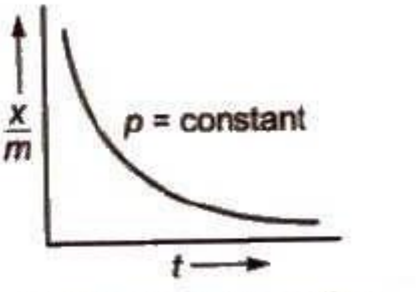
$x / m = kC^{1/n}$

where, C is the equilibrium concentration. On taking logarithm of the above equation, we have

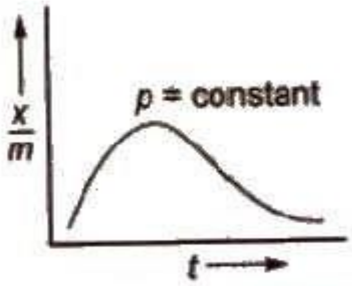
$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

## Adsorption Isobars

These are plots of x / m us temperature t at constant pressure. For physical and chemical adsorption, they are shown below.



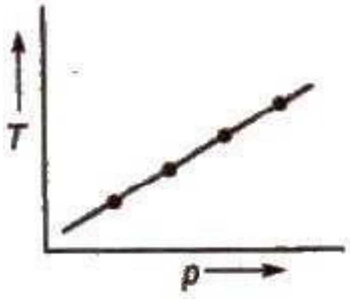
(a) Physical adsorption



(b) Chemical adsorption

## Adsorption Isostere

These are the plot of temperature versus pressure for a given amount of adsorption

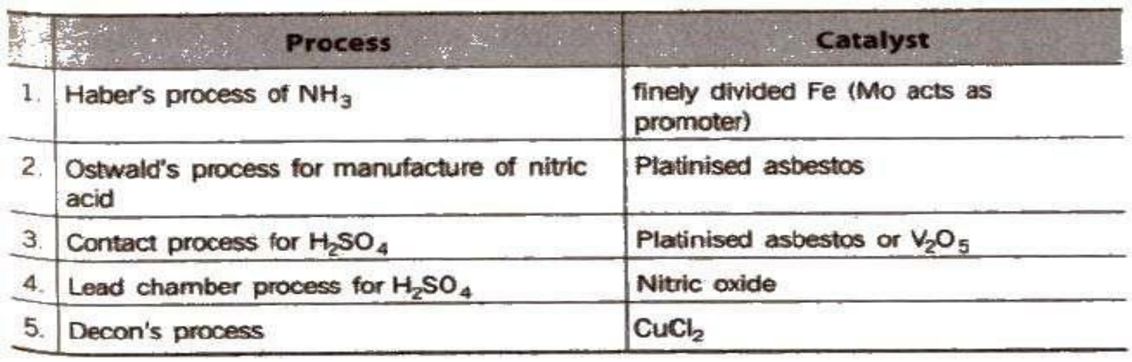


## Applications of Adsorption

1. For production of high vacuum.
2. Gas masks containing activated charcoal is used for breathing in coalmines. They adsorb poisonous gases.
3. Silica and aluminium gels are used as adsorbents for controlling humidity.
4. Removal of colouring matter from solutions.
5. It is used in heterogeneous catalysis.
6. In separation of inert gas.
7. As adsorption indicators.
8. In chromatographic analysis.
9. Qualitative analysis, e.g., lake test for $Al^{3}$+.

## Catalysis

Catalyst is a chemical substance which can change the rate of reaction without being used up in that reaction and this process is known as catalysis



|  | Process | Catalyst |
|---|---|---|
| 1. | Haber's process of $NH_3$ | finely divided Fe (Mo acts as promoter) |
| 2. | Ostwald's process for manufacture of nitric acid | Platinised asbestos |
| 3. | Contact process for $H_2SO_4$ | Platinised asbestos or $V_2O_5$ |
| 4. | Lead chamber process for $H_2SO_4$ | Nitric oxide |
| 5. | Decon's process | $CuCl_2$ |

A catalyst may be positive (i.e., increases rate of reaction) or negative (i.e., decreases rate of reaction).

**Types of Catalysis**

(a) **Homogeneous catalysis** In this catalysis, and the catalyst reactants are in the same physical state [phase], e.g.,

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(b) **Heterogeneous catalysis** In heterogeneous catalysis, catalyst is present in a different phase than that of reactants, e.g.,

$$2KClO_3(s) \xrightarrow{MnO_2} 2KCl(s) + 3O_2(g)$$

(c) **Autocatalysis** When one of the product of a reaction acts as catalyst, the process is called autocatalysis.

**Characteristics of Catalysts**

1 The catalyst remains unchanged in mass and chemical composition.
2. In case of reversible reactions, the catalyst does not influence the composition of reaction mixture at equilibrium. It only helps to attain the equilibrium quickly.

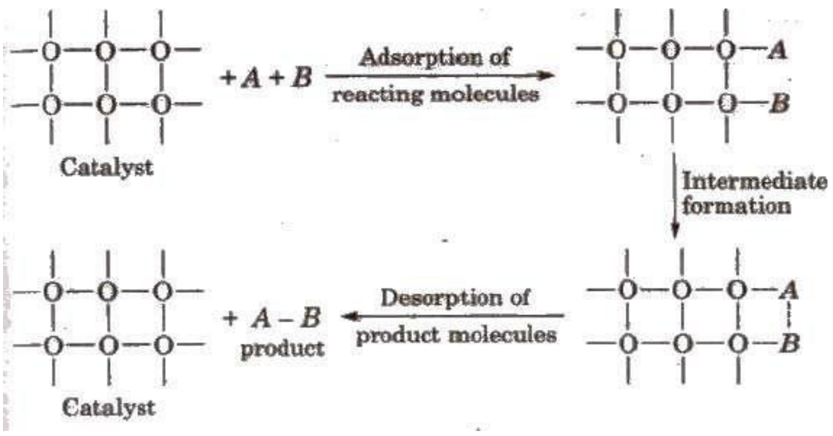
**Promoters and Poisons**

Promoters are chemical substances that enhance the activity of a catalyst while poisons decreases the activity of a catalyst

**Adsorption Theory of Heterogeneous Catalysis**

The mechanism involves five steps:

(i) Diffusion of reactants to the surface of the catalyst
(ii) Adsorption of reactant molecules on the surface of the catalyst.
(ill) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.
(iv) Desorption of reaction products from the catalyst surface.
(v) Diffusion of reaction products away from the catalyst's surface



**Important Features of Solid Catalysts**

(i) **Activity** The activity of a catalyst depends upon the strength of chemisorption to a large extent. The adsorption should be reasonably strong but not so strong that they become immobile and no space is available for other reactants to get adsorbed.

(ii) **Selectivity** The selectivity of a catalyst is its ability to direct a reaction to yield a particular product, e.g., starting with Hz and CO using different catalysts, we get different products.

$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

$$CO(g) + 2H_2(g) \xrightarrow{Cu,\ ZnO\text{-}Cr_2O_3} CH_3OH(l)$$

$$CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$$

**Shape–selective catalysis** The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis.

Cracking Isomerization of hydrocarbons in the presence of zeolites is an example of shape- selective catalysis.
An important zeolite catalyst used in the petroleum industry is ZSM-S.lt converts alcohols directly into gasoline

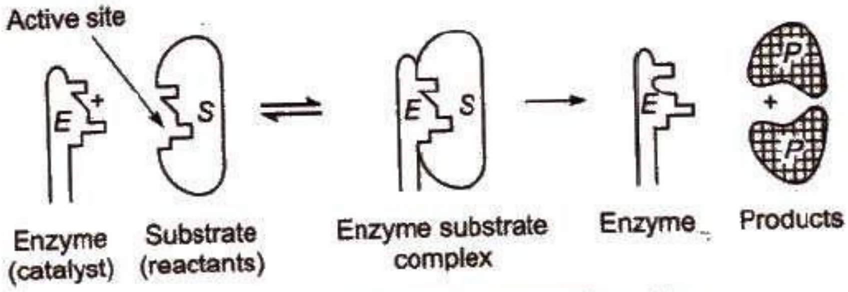
**Enzyme Catalysis**

Enzymes are complex nitrogenous organic compounds which are Produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water.
They are also known as biochemical catalysis.

**Mechanism of Enzyme Catalysis**

**Step I** $E + S \longrightarrow ES$

**Step II** $ES \longrightarrow E + P$



**Mechanism of enzyme catalysed reaction**

(i) $\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$

(ii) $\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

(iii) $\underset{\text{starch}}{n(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}} \xrightarrow{\text{Maltose}} \text{Glucose}$

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

(Source of invertase, zymase and maltose is yeast and that of diastase is malt. Soybean is the source of urease.)

(v) In stomach, the pepsin enzyme converts proteins into peptides while in intestine,the pancreatic trypsin converts proteins into amino acids by hydrolysis.

(vi) Lactobacilli is used to convert milk into curd.

**Characteristics of Enzyme Catalysis**

- **High efficiency** One molecule of an enzyme may transform one million molecule of reactant per minute.
- **Highly specific nature** Each enzyme catalyst cannot catalyse more than one reaction.
- **Optimum temperature** Enzyme catalyst gives higher yield at optimum temperature i.e., at 298-310 K. Human body temperature, i.e., at being 310 K is suited for enzyme catalysed reactions.
- **Optimum pH** The rate of an enzyme catalysed reaction is maximum at optimum pH range 5 to 7.
- **Activators** Activators like ions such as $Na^+$ ,$Ca^{2+}$, $Mn^{2+}$ help in the activation of enzymes which cannot act on their own strength.
- **Co-enzyme** Co-enzymes are the substance having nature similar to the enzyme and their presence increases the enzyme activity. Mostly vitamins act as co-enzymes.
- **Effect of Inhibitors** Inhibitors slow down the rate of enzymatic reaction. The use of many drugs is based on enzyme inhibition action of those drugs in the body

## colloid

A colloid is one of the three primary types of mixtures, with the other two being a solution and suspension. A colloid is a mixture that has particles ranging between 1 and 1000 nanometers in diameter, yet are still able to remain evenly distributed throughout the solution. These are also known as colloidal dispersions because the substances remain dispersed and do not settle to the bottom of the container. In colloids, one substance is evenly dispersed in another. The substance being dispersed is referred to as being in the dispersed phase, while the substance in which it is dispersed is in the continuous phase.

To be classified as a colloid, the substance in the dispersed phase must be larger than the size of a molecule but smaller than what can be seen with the naked eye. This can be more precisely quantified as one or more of the substance's dimensions must be between 1 and 1000 nanometers. If the dimensions are smaller than this the substance is considered a solution and if they are larger than the substance is a suspension.

### Classifying Colloids

A common method of classifying colloids is based on the phase of the dispersed substance and what phase it is dispersed in. The types of colloids includes sol, emulsion, foam, and aerosol.

1. **Sol** is a colloidal suspension with solid particles in a liquid.
2. **Emulsion** is between two liquids.
3. **Foam** is formed when many gas particles are trapped in a liquid or solid.
4. **Aerosol** contains small particles of liquid or solid dispersed in a gas.

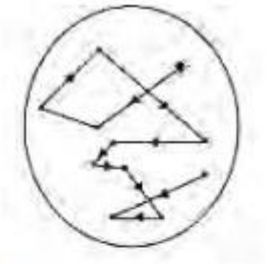
### PROPERTIES OF COLLOIDS

The properties of colloids are discussed under three types

i. Kinetic property
ii. Optical property
iii. Electrical property

### (i) Kinetic property

When sol is examined with an ultramicrosope, the suspended particles are seen as shining specks of light. By following an individual particle, it is observed that the particle is undergoing a constant rapid motion. It moves in a series short straight line paths in the medium, changing direction abruptly.



'Brownian movement

The continuous rapid zig-zag chaotic random and ceaseless movement executed by a colloidal particle in the dispersion medium is called brownian movement. This is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium.

### (ii) Optical property

When a strong beam of light is passed through a sol and viewed at right angles, the path of light shows up as a hazy beam. This is due to the fact that sol particles absorb light energy and then emit it in all directions. This scattering of light illuminates the path of the beam. The phenomenon of the scattering of light by the sol particles is called Tyndall effect.

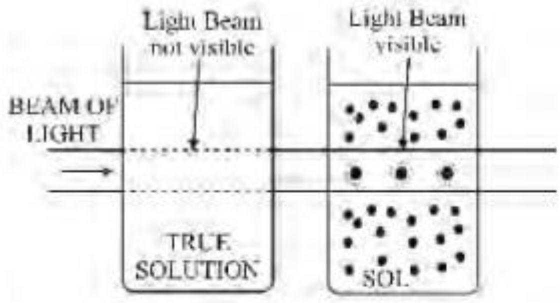


Fig. Tyndall effect

**(iii). Electrical Properties**

**(i) Charge on Colloidal particles**

The important property of colloidal dispersions is that all the suspended particles possess either a positive or negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol.

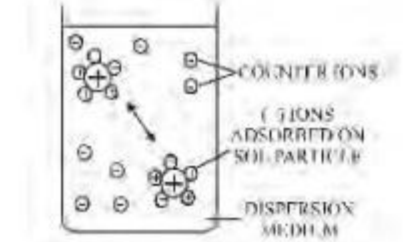


Fig. Adsorption of ions from dispersion medium gives charge to sol particles which do not settle on account of mutual repulsions

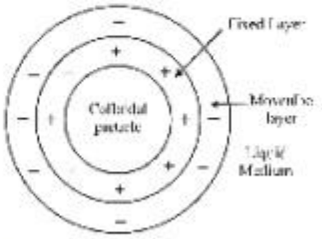


Fig. Helmholtz Double layer

The surface of colloidal particle acquires a positive charges by selective adsorption of a layer of positive ions around it. This layer attracts counterions from the medium which form a second layer of negative charges. The combination of the two layers of charges around the sol particle is called **Helmholtz double layer.**

**(ii) Electrophoresis**

If electric potential is applied across two platinum electrodes immersed in a hydrophilic sol, the dispersed particles move toward one or the other electrode. The movement of sol particles under an applied electric potential is called electrophoresis or cataphoresis. If the sol particles here negatively charged, they migrate toward the positive electrode. On the other hand, if they have positively charged they move toward the negative electrode. From the direction of movement of the sol particles, we can determine the charge of the sol particles.

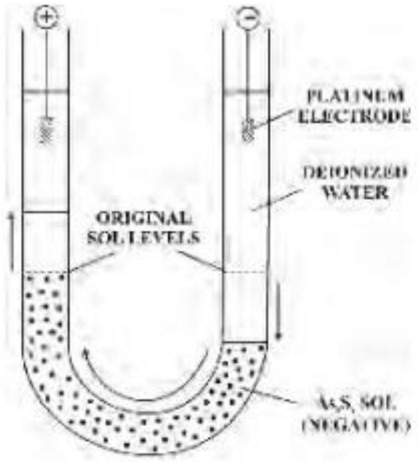


Fig. Electrophoresis of a sol

The phenomenon of electrophoresis can be demonstrated by placing a layer of $As_2S_3$ sol under two limbs of a U-tube. When a potential difference of about 100 volts is applied across the two platinum electrodes dipping in deionised water, it is observed that the level of the sol drops on the negative electrode side and rises on the positive electrode side (Fig.) This shows that $As_2S_3$ sol has migrated to the positive electrode, indicating that the particles are negatively charged.

**(iii) Electro osmosis**

In a sol, the dispersion medium carries an equal but opposite charge to that of the dispersed particles. Thus, the medium will move in opposite direction to the dispersed phase under the influence of applied electric potential. The movement of the dispersion medium under the influence of applied potential is known as electro-osmosis.

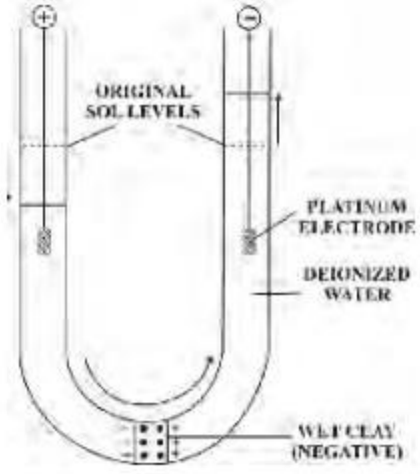


Fig. Electro-osmosis

The phenomenon of electro-osmosis can be demonstrated by using a U-tube in which a plug of wet clay (a negative colloid) is fixed. The two limbs of the tube are filled with water to the same level. The platinum electrodes are immersed in water and potential applied across them. It will be observed that water level rises on the cathode side and falls on anode side. This movement of the medium towards the negative electrode, shows that the charge on the medium is positive. Similarly, for a positively charged colloid electro-osmosis will take place in the reverse direction.

Protective colloid:

Lyophobic sols like those of metals (Au, Ag etc) are unstable and are easily coagulated by addition of electrolyte. However, it is observed that when certain lyophilic colloids such as gum, geletin, Agar – Agar etc. are added to a lyophobic sol, the stability of the lyophobic colloids is markedly increased i.e. the addition of small amount of electrolytes does not cause coagulation of lyophobic colloids. This action of lyophilic colloids to prevent the coagulation of lyophobic colloid by addition of electrolyte is called Protection of Colloidal Soland the lyophilic colloid is called Protective Colloid. Explanation :

The Particles of protective colloid is believed to be adsorbed by lyophobic colloidal particles and thus forms a covering over the surface of lyophobic colloidal particles. The lyophobic colloid thus behaves as lyophilic colloid and is precipitated less easily by electrolytes.

It may be noted that protective colloid not only increases stability of lyophobic colloids but it also makes them reversible. The protecting power of different protective (lyophilic)colloids is different. The efficiency of any protective colloid is expressed interms of gold number.

Gold number : Zsigmondy introduced a term called gold number todescribe the protective power of different colloids. This is defined as,“weight of the dried protective agent in milligrams, which when added to 10 mlof a standard gold sol (0.0053 to 0.0058%) is just sufficient to prevent acolour change from red to blue on the addition of 1 ml of 10 % sodium chloridesolution, is equal to the gold number of that protective colloid.”

Thus, smaller is the gold number, higher is the protectiveaction of the protective agent.

Protective power ∝ 1/Gold number

Table : 14.4 Gold numbers of some hydrophilic substances

Hydrophilic substance
Hydrophilic substance
Gold number
Hydrophilic substance
Gold number
Gelatin 0.005 - 0.01
Sodium oleate 0.4 – 1.0
Sodium caseinate 0.01
Gum tragacanth 2
Hamoglobin 0.03 – 0.07
Potato starch 25
Gum arabic 0.15 – 0.25

Mechanism of solution protection

(i) The actual mechanism of sol protection is very complex.However it may be due to the adsorption of the protective colloid on thelyophobic sol particles, followed by its solvation. Thus it stabilises the solvia solvation effects.

(ii) Solvation effects contribute much towards the stability oflyophilic systems. For example, gelatin has a sufficiently strong affinity forwater. It is only because of the solvation effects that even the addition ofelectrolytes in small amounts does not cause any flocculation of hydrophilicsols. However at higher concentration, precipitation occurs. This phenomenon iscalled salting out.

(iii) The salting out efficiency of an electrolyte depends uponthe tendency of its constituents ions to get hydrated i.e, the tendency tosqueeze out water initially fied up with the colloidal particle.

(iv) The cations and the anions can be arranged in thedecreasing order of the salting out power, such an arrangement is calledlyotropic series.

Cations : Mg2+ > Ca2+ > Sr2+ > Ba2+ > Li+ > Na+> K+ > NH4+ > Rb+ > Cs+

Anions : Citrate3– > SO42– > Cl– > NH3– > I– >CNS–

Ammonium sulphate, due to its very high solubility in water, isoftenly used for precipitating proteins from aqueous solutions.

(v) The precipitation of lyophilic colloids can also be affectedby the addition of organic solvents of non-electrolytes. For example, theaddition of acetone or alcohol to aqueous gelatin solution causes precipitationof gelatin. Addition of petroleum ether to a solution of rubber in benzenecauses the precipitation of rubber.

## Chapter 6

## General Principles and Processes of Isolation of Elements

Earth crust is the source of many elements. Out of these elements, 70% are metals. Aluminium is the most abundant metal of earth crust and iron comes second. The percentage of different elements in earth crust are

O-49%, Si-26%, Al-7.5%, Fe-4.2%, Ca-3.2%, Na-2.4%, K-2.3%, Mg-2.3%, H-l%

Metals occur in two forms in nature (i) in native state (ii) in combined state, depending upon their chemical reactivities.

**Native State**

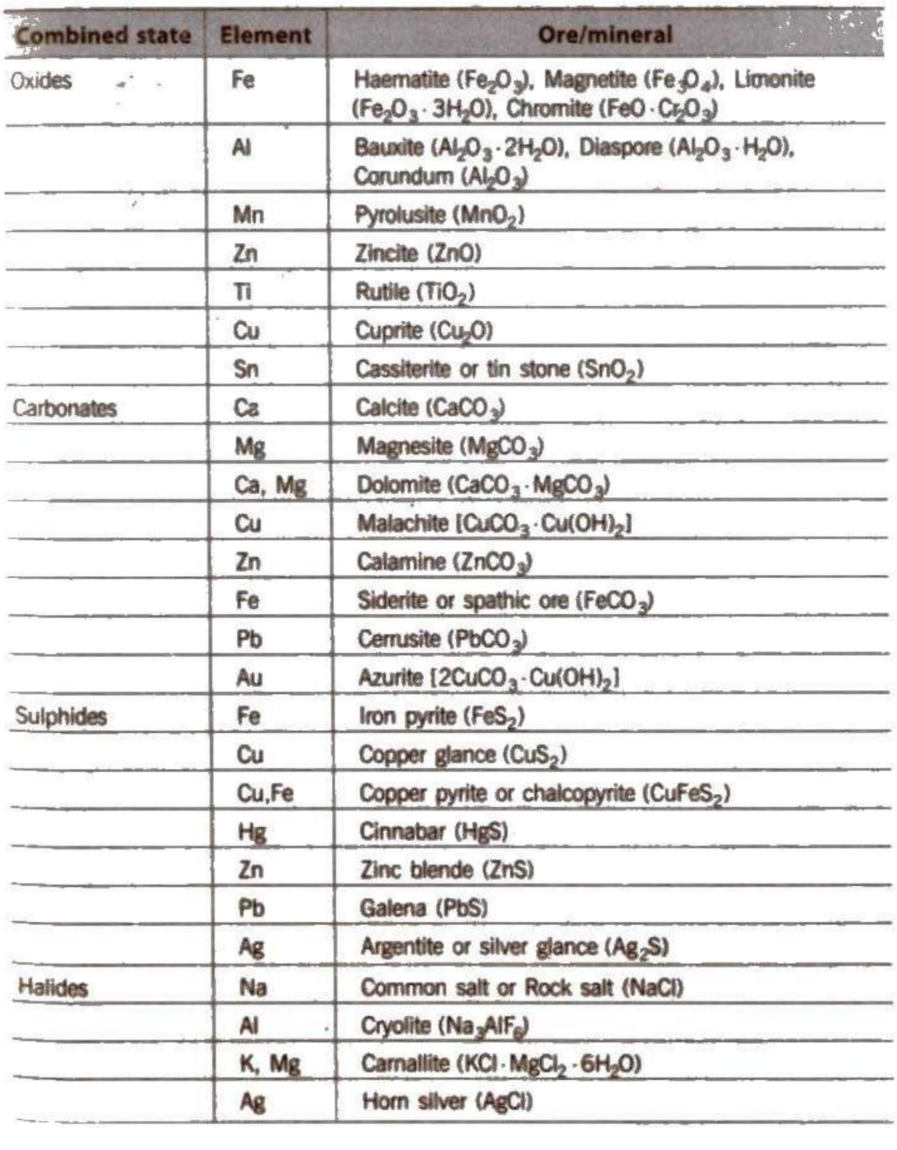
Elements which have low chemical reactivity or noble metals having least electropositive character are not attacked by oxygen. moisture and $CO_2$ of the air. These elements, therefore, occur in the free state or in the native state, e.g., Au, Ag, Pt, S, O, N, noble gases, etc.

**Combined State**

Highly reactive elements such as F, CI, Na, K, etc., occur in nature combined form as their compounds such as oxides, carbonates sulphides. halides, etc.Hydrogen is the only non-metal which exists in oxidised form only.

**Minerals and Ores**

The naturally occurring substances in the form of which the metals occur in the earth crust are called minerals. Every mineral is not suitable for the extraction of the metal. The mineral from which the metal is economically and conveniently extracted is called an ore.Thus, all ores are minerals but all minerals are not ores.



| Combined state | Element | Ore/mineral |
|---|---|---|
| Oxides | Fe | Haematite ($Fe_2O_3$), Magnetite ($Fe_3O_4$), Limonite ($Fe_2O_3 \cdot 3H_2O$), Chromite ($FeO \cdot Cr_2O_3$) |
| | Al | Bauxite ($Al_2O_3 \cdot 2H_2O$), Diaspore ($Al_2O_3 \cdot H_2O$), Corundum ($Al_2O_3$) |
| | Mn | Pyrolusite ($MnO_2$) |
| | Zn | Zincite ($ZnO$) |
| | Ti | Rutile ($TiO_2$) |
| | Cu | Cuprite ($Cu_2O$) |
| | Sn | Cassiterite or tin stone ($SnO_2$) |
| Carbonates | Ca | Calcite ($CaCO_3$) |
| | Mg | Magnesite ($MgCO_3$) |
| | Ca, Mg | Dolomite ($CaCO_3 \cdot MgCO_3$) |
| | Cu | Malachite [$CuCO_3 \cdot Cu(OH)_2$] |
| | Zn | Calamine ($ZnCO_3$) |
| | Fe | Siderite or spathic ore ($FeCO_3$) |
| | Pb | Cerrusite ($PbCO_3$) |
| | Au | Azurite [$2CuCO_3 \cdot Cu(OH)_2$] |
| Sulphides | Fe | Iron pyrite ($FeS_2$) |
| | Cu | Copper glance ($CuS_2$) |
| | Cu,Fe | Copper pyrite or chalcopyrite ($CuFeS_2$) |
| | Hg | Cinnabar ($HgS$) |
| | Zn | Zinc blende ($ZnS$) |
| | Pb | Galena ($PbS$) |
| | Ag | Argentite or silver glance ($Ag_2S$) |
| Halides | Na | Common salt or Rock salt ($NaCl$) |
| | Al | Cryolite ($Na_3AlF_6$) |
| | K, Mg | Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) |
| | Ag | Horn silver ($AgCl$) |

### Gangue or Matrix

Impurities associated with ores are called gangue or matrix.

### Metallurgy

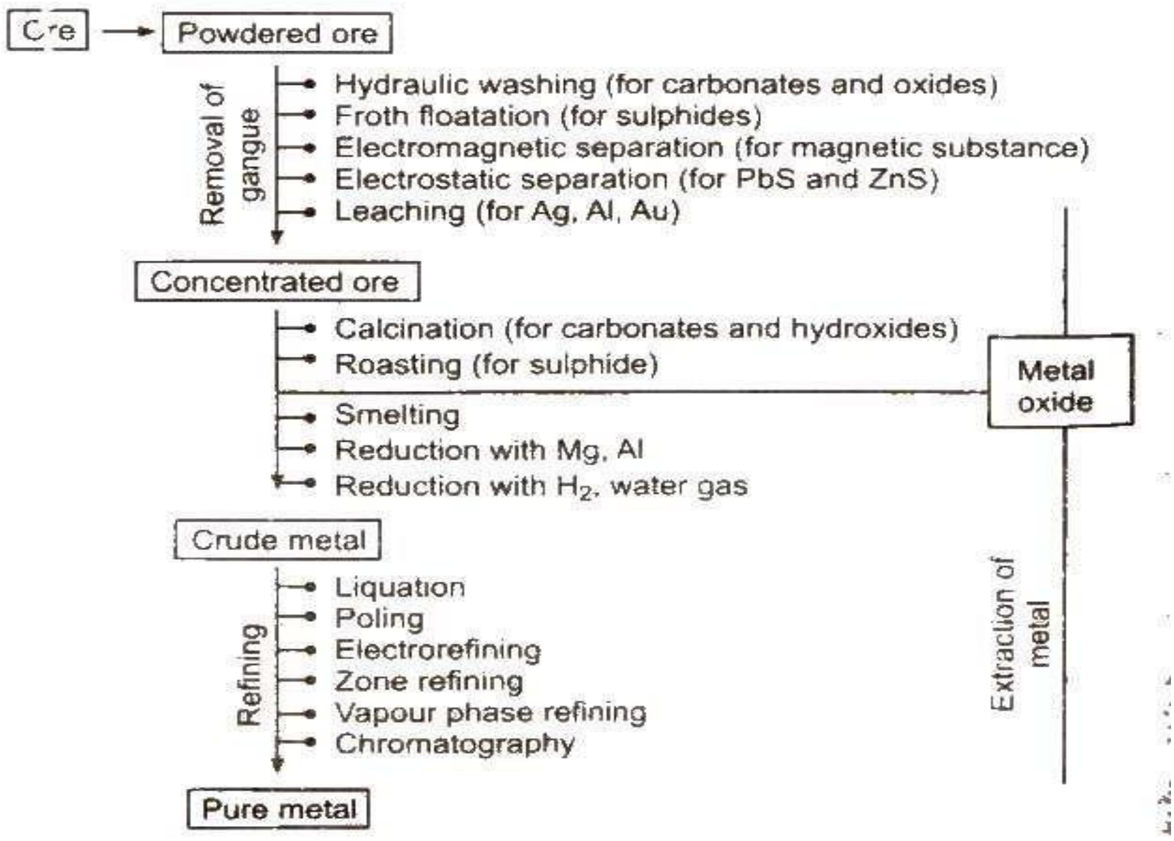
The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

### Types of Metallurgical Processes

1. Pyrometallurgy Extraction of metals takes place at very high temperature. Cu, Fe, Zn, Sn, etc .. are extracted by this method.
2. Bydrometallurgical process In this method, metals are extracted by the use of their aqueous solution. Ag and Au are extracted by this method.
3. Electrometallurgical process Na, K, Li, Ca, etc., are extracted from their molten salt solution through electrolytic method.

### Steps Involved in Metallurgy

Following steps are involved in the metallurgy :



## Crushing of the Ore

The big lumps of ore are crushed into smaller pieces with the help of jaw-crushers. The process of grinding the crushed ore into fine powder with the help of the stamp mills is called pulverisation.

## Concentration of Ores

Removel of unwanted materials (e.g., sand. clays, etc.) from the ore is known as ore concentration, ore dressing or ore benefaction. It can be carried out by various ways depending upon the nature of the ore.

### Hydraulic Washing/Gravity Separation/Levigation

The process by which lighter earthy impurities are removed from the heavier ore particles by washing WIth water is called levigation. The lighter impurities are washed away. Thus. this method is based on the difference in the densities (specific gravities) of ore and gangue.This method is commonly used for oxide ores such as haematite, tin stone and native orcs of Au, Ag, etc.

### Froth Floatation

This method is used for the concentration of sulphide ores. This method is based on the preferential wetting of ore particles by oil and that of gangue by water .. As a result. the ore particles become light and rise to the top in the form of froth while the gangue particles become heavy and settle down. Thus. adsorption is involved in this method.

The froth can be stabilised by the addition of stabilisers (aniline or cresols).

**Activator** They activate the floating property of one of the component of the ore I and help in the separation of different minerals present in the same ore ($CuSO_4$ is used as activator.

**Depressants** These are used to prevent certain types of particles from forming the froth with air bubbled, e.g., NaCN can be used as a depressant in the separation of ZnS and PbS ores.

KCN is an another depressant.

**Collectors** It increases the non-wettability of ore particles by water, e.g., pine oils, xanthates and fatty acids.

### Electromagnetic Separation

This method of concentration is employed when either the ore or the lmpurities associated with it are magnetic in nature. e.g., chromite, $FeCr_2O_4$, containing magnetic SiliCIOUS gangue and wolframite $FeWO_4$, Containing cassiterite, $8nO_4$ (non-magnetic impurities) can be separated by this method.

### Electrostatic Separation

This method is used for the separation of lead sulphide (good conductor) which is charged immediately in an electrostatic field and is thrown away from the roller from zinc sulphide (poor conductor) which is not charged and hence, drops vertically from the roller.

### Chemical Method-Leaching

Leaching is the process in which the ore is concentrated by chemical reaction with a suitable reagent which dissolves the ore but not the impurities, e.g., bauxite is leached with a hot concentrated solution of NaOH which dissolves aluminium while other oxides ($Fe_2O_3$, $TiO_2$, $SiO_2$), remain undissolved and noble metals (Ag and Au) are leached with a dilute aqueous solution of NaCN or KCN in the presence of air.

.

$$\underset{\text{bauxite}}{Al_2O_3 \cdot 2H_2O} + 2NaOH \longrightarrow \underset{\text{sod. meta aluminate}}{2NaAlO_2} + 3H_2O$$

and $$\underset{\text{argentite}}{Ag_2S} + 4NaCN \longrightarrow \underset{\text{sod. argento cyanide}}{2Na[Ag(CN)_2]} + Na_2S$$

**Extraction of Crude Metals from Concentrated Ore**

The concentrated ore is usually converted to oxide before reduction, as oxides are easier to reduce. Thus, isolation of crude metal from concentrated ore involves two major steps:

1. Conversion to oxide.
2. Reduction of the oxides to metal.

**Conversion to Oxides**

**(i) Calcination** It is the process of converting an ore into its oxides by heating it strongly, below its melting point in a limited supply of air or in absence of air.

During calcination, volatile impurities as well as organic matter and moisture are removed.

$$Al_2O_3 \cdot 2H_2O \xrightarrow{\text{Heat}} \underset{\text{alumina}}{Al_2O_3} + 2H_2O$$

$$\underset{\text{limestone}}{CaCO_3} \xrightarrow{\text{Heat}} CaO + CO_2$$

$$\underset{\text{dolomite}}{CaCO_3 \cdot MgCO_3} \xrightarrow{\text{Heat}} CaO + MgO + 2CO_2$$

Calcination is used for metal carbonates and hydroxides and is carried out in reverberatory furnace.

**(ii) Roasting** It is the process of converting an ore into its metallic oxide by heating it strongly. below its melting point m excess of air. This process is commonly used for sulphide ores and is carried out in blast furnace or reverberatory furnace. Roasting helps to remove the non-metallic impurities and moisture.

$$2ZnS + 2O_2 \longrightarrow 2ZnO + 2SO_2\uparrow$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2\uparrow$$

The furnaces used in calcination and roasting employ refractory materials which resist high temperature and do not become soft.

- Acidic refractories : $SiO_2$ and $SiO_2 + Al_2O_3$
- Basic refractories : CaO and MgO
- Neutral refractories : Graphite, chromites. etc.

Heavy metals like Cu. Zn, Fe. So, etc., arc obtained by roasting and smelting.

**Reduction of the Oxides to Metal**

The roasted or the calcined ore is then converted to the free metal by reduction. Reduction method depends upon the activity of metal.Metals which are low in the activity series (like Cu, Hg, Au) are obtained by heating their compounds lD air: metals which are in the middle of the activity “cries (like Fe. Zn, Ni, Sn) are obtained by heating their oxides with carbon while metals which are very high in the activity series (e.g., Na, K, Ca, Mg, Al) are obtained by electrolvtic reduction method.

**(i) Smelting** (reduction with carbon) The process of extracting the metal by fusion of its oxide ore with carbon (C) or CO is called smelting. It is carried out in a reverberatory furnace.

*e.g.,*

$$ZnO + C \longrightarrow Zn + CO\uparrow$$

$$Fe_2O_3 + CO \xrightarrow{823\ K} 2FeO + CO_2$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO\uparrow$$

During smelting a substance. called flux is added which removes the non-fusible impurities as fusible slag. This slag is insoluble in the molten metal and is lighter than the molten metal. So, it floats over the molten metal and is skimmed off.

**Acidic flux** For basic impurities, acidic flux is added. e.g.,

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$FeO + \underset{\text{acidic flux}}{SiO_2} \longrightarrow \underset{\text{fusible slag}}{FeSiO_3}$$

**Basic flux** For acidic impurities, basic flux is added.

*e.g.,*

$$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2\uparrow$$

$$SiO_2 + \underset{\text{basic flux}}{MgCO_3} \longrightarrow \underset{\text{fusible slag}}{MgSiO_3} + CO_2\uparrow$$

In the extraction of Cu and Fe, the slag obtained are respectively $FeSiO_3$ and $CaSiO_3$.

The obtained slag is used in road making as well as in the manufacturing of cement and fertilizers.

**(ii) Reduction by hydrogen** It is done for W or Mo oxide.

$$WO_3 + 3H_2 \xrightarrow{Heat} W + 3H_2O$$

**(iii) Reduction** by aluminium It is known as alumino thermic reduction or Gold Schmidt thermite process. Aluminium powder is used for this purpose.

e.g., $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

Mixture of the oxide and Al i.n the ratio of 3 : 1 is known as thermite and mixture of $BaO_2$ + Mg powder acts as ignition powder.

**(iv) Auto reduction** This is used for reduction of sulphide ores of Pb, Hg, Cu, etc. The sulphide ore is heated in a supply of air at 770-970 K when the metal sulphide is partially oxidised to form its oxide or sulphate which then reacts with the remaining sulphide to give the metal.

*e.g.,*

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

**(v) Reduction by Mg**

$TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti$ (Kroll's process)

vi) Electrolytic reduction or electrometallurgy It is the process of extracting highly electropositive (active) metals such as Na, K, Ca, Mg, Al, etc by electrolysis of their oxides, hydroxides or chlorides in fused state, e.g., Mg is prepared by the electrolysis of fused salt of $MgCl_2$ (Dow's process).

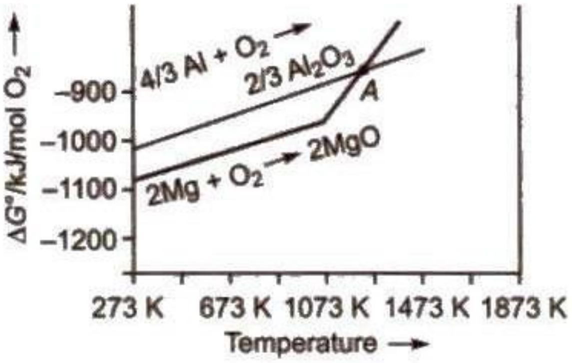
**Thermodynamic Principle in Extraction of Metals**

The free energy change ($\Delta G$) occurring during the reduction processes help in deciding the suitable method for reduction.For the spontaneous reduction of an oxide, halide or sulphide by an element, the essential condition is that there is a decrease in the free energy of the system (-ve $\Delta G$).More the negative value of $\Delta G$, the higher is the reducing power of an element. $\Delta G$ can be given as

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

- where, $\Delta H$ = enthalpy change;
- $\Delta G$ = Gibbs free energy
- T = temperature;
- $\Delta S$ = entropy change

For the reduction of a metal oxide with a reducing agent, the plot of $\Delta G°$ against temperature is studied, which is called **Ellingbam diagram.**



**Gibbs energy ($\Delta G°$) vs $T$ plots (Ellingham diagram)**

**Characteristics of Ellingham Diagram**

1. All the plots slope upwards since ΔG° becomes more positive when temperature increases, i.e., stability of oxides decreases.

2. A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, i.e., the metals for which the free energy of formation ($\Delta G°_f$) of their oxides is more negative can reduce those metal oxides which has less negative $\Delta G°_f$

3. The decreasing order of the negative values of $\Delta G°_f$ of metal oxides is Ca > Mg (below 1773 K) > AI > Ti > Cr > C > Fe > Ni> Hg > Ag .Thus, AI reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773 K.Mg can reduce $A1_2O_3$ below 162 K but above 1023 K, Al can reduce MgO.

4. CO is more effective reducing agent below 1073 K and above 1073 K. coke is more effective reducing agent, e.g., CO reduces $F_2O_3$ below 1073 K but above it, coke reduces $Fe_2O_3$.

Coke reduces ZnO above 1270 K

## Refining or Purification of Crude Metals

### Physical Methods

**(i) Liquation** This method is used for refining the metals having low melting points (such as Sn. Pb, Hg, Bi) than the impurities, The impure metal is placed on the sloping hearth and is gently heated. The metal melts and flows down leaving behind the non-fusible impurrties.

**(ii) Distillation** This is useful for low boiling metals such as Zn, Hg. The impure liquid metal is evaporated to obtain the pure metal as distillate.

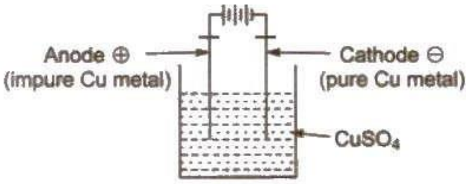
**(iii) Cupellation** This method is used when impure metal contains impurities of other metals which form volatile oxides.**e.g., traces of lead ore removed from silver (as volatile PbO) by this process.**

### Chemical Methods

**(i) Poling** This method is used when the impure metal contains impurities of Its own oxide, e.g., $CU_2O$ in blister copper and $SnO_2$ in impure Sn. The molten impure metal is stirred with green wood poles. At this high temperature. wood liberates gases such as $CH_4$ which reduces any oxides present in the metal.

**(ii) Electro-refining**

In this method, impure metal forms the anode while the cathode is a rod or sheet of pure metal. The electrolytic solution consists of a soluble salt of the metal.



Anode, $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode, $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

On passing electricity, the pure metal gets deposited on the cathode while the insoluble impurities settle down below the anode as anode mud or anode sludge. Metals like Cu, Ag, Au, Cr, Zn, Ni, etc are purified by this method.

**(iii) Zone-refining** This method is based upon the principle of fractional crystallisation, i.e., difference in solubilities of impurities in molten and solid state of metal. Semiconductors like silicon, germanium, gallium arsenide and indium antimonide are purified by this method. Elements of very high purity are obtained by this method.

**(iv) Vapour phase refining** In this method, crude metal is made free from impurities by first convertmg it Into its volatile compound by heating with a chemical reagent at low temperature. After this, the volatile compound is decomposed by heating to some higher temperature to give pure metal.

(a) van Arkel method This method is used for preparing ultra-pure metal used in space technology (e.g., Ti, Zr, etc.)

$$\underset{\text{impure}}{Ti(s)} + 2I_2(s) \xrightarrow{523\text{ K}} TiI_4(g) \xrightarrow{1700\text{ K}} \underset{\text{pure}}{Ti(s)} + 2I_2(g)$$

$$\underset{\text{impure}}{Zr(s)} + 2I_2 \xrightarrow{870\text{ K}} ZrI_4(g) \xrightarrow{1800\text{ K}} \underset{\text{pure}}{Zr(s)} + 2I_2(g)$$

(b) **Mond's process** It is used for refining of nickel.

$$\underset{\text{impure}}{Ni} + 4CO \xrightarrow{330\text{–}350\text{ K}} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{450\text{–}470\text{ K}} \underset{\text{pure}}{Ni} + 4CO$$

**Chromatographic method** Adsorption chromatography is generally used. The impure metal is dissolved in a suitable solvent and the solution is allowed to run slowly into an adsorbent column packed with alumina ($Al_2O_3$). The metal and the impurities present are adsorbed at different rates. These are then eluted with suitable eluent (solvent). In this method.weakly adsorbed component is eluted first and the strongly adsorbed component is eluted afterwards.

**Occurrence and Extraction of Some Metals**

1. **Metal** Aluminium (AI)

**Occurrence**

1. Bauxite – $Al_2O_3.XH_2O$
2. Cryolite – $Na_3AlF_6$

**Common method of extraction** Electrolysis of $Al_2O_3$ dissolved in molten $Na_3A1F_6$(neutral flux).

Neutral flux is the neutral compound added to the ore to decrease its melting point and to make it conducting, e.g., $CaF_2$, cryolite ($Na_3AlF_6$) etc.

2. **Metal** Iron (Fe)

**Occurrence**

1. Haematite – $Fe_2O_3$
2. Magnetite – $Fe_3O_4$

3. **Common method of extraction** Reduction of the oxide with CO and coke in blast furnace.

4. The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn) and is known as **pig iron.**

5. **Cast iron** is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

**Wrought iron** or **malleable iron** is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide.

$Fe_2O_2 + 3C \rightarrow 2Fe + 3CO$

1. **Metal** Copper (Cu)

**Occurrence**

1. Copper pyrites – $CuFeS_2$
2. Copper glance – $Cu_2S$

**Common method of extraction** Roasting of sulphide partially and reduction.

$Cu_2S + FeS$ is called matte. Blister copper contains 96-98% copper with small amounts of Ag and Au as impurity.

2. **Metal** Zinc (Zn)

**Occurrence**

1. Zinc blen de or sphalerite-ZnS
2. Calamine – $ZnCO_3$
3. Zincite – ZnO

**Common method of extraction** Roasting followed by reduction with coke. The

metal may be purified by fractional distillation.

97-98% pure zinc is called spelter.

3. **Metal** Nickel (Ni)

**Occurrence**

1. Penta landite – (Ni, Cu, Fe)S
2. Kupfernickel – NiAs
3. Smaltite – (Fe, Co. Ni) As

**Common method of extraction** Roasting followed by Refining is done by Mond's Process. Water gas is used as a reducing agent for nickel oxide.

$$2NiO + \underbrace{CO + H_2}_{\text{water gas}} \longrightarrow 2Ni + CO_2 + H_2O$$

## Cheapter -7 p-block elements

**p-block elements**

The group number 13 to 18, in which the last electrons or the valence electrons enter in the *p*-orbital are called the *p*-block elements. The general electronic configuration of *p*-block elements is $ns^2\ np^{1-6}$

**Nitrogen family**

The elements of group 15: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) having general electronic configuration $ns^2\ np^3$, are known as the nitrogen family. The *s*-orbital in these elements is completely filled and *p*-orbitals are half-filled, making their electronic configuration extra stable.

**General properties of nitrogen family:**

***Atomic and ionic radii:*** Covalent and ionic radii increase down the group. There is appreciable increase in covalent radii from N to P. However, from As to Bi only a small increase in covalent radius is observed.due to presence of completely filled *d* or *f*-orbitals in heavy elements.

***Ionisation enthalpy:*** Ionisation enthalpy goes on decreasing down the group due to the increase in atomic size. Due to the stable electronic configuration with half filled *p*-orbital, group 15 elements have higher ionisation energy than group 16 elements. Also due to the smaller size of the elements, the group 15 elements have higher ionisation energy than group 14 elements.

***Oxidation states:*** The common oxidation states are +3, +5, –3. The tendency to show –3 oxidation state decreases down the group due to increased size and hence decreased electronegativity. The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect. Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionation.

For example: $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

**Anomalous properties of nitrogen**

Nitrogen has unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Thus nitrogen exists as diatomc molecule, $N_2$ with a triple bond between the two atoms. However, P cannot $p\pi - p\pi$ from bond, therefore P exists as $P_4$ – $P_4$ is highly strained and is chemically reactive while $N_2$ is chemically inert.

The behaviour of nitrogen differs from rest of the elements due to the following reasons:

**(i)** It has a small size
**(ii)** It does not have d – orbitals
**(iii)** It has high electronegativity
**(iv)** It has high ionization enthalpy

All the elements of Group 15 form trihydrides, $MH_3$ having $sp^3$ type hybridization.

**Stability:** The stability of hydrides decreases down the group due to decrease in bond dissociation energy down the group.

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

**Boiling point:** Boiling point of hydrides (except $NH_3$) increases down the group as with increase in size due to the Van der Waals forces also increase down the group. Boiling point of $NH_3$ is highest due to the presence of hydrogen bonding.

$$PH_3 < AsH_3 < SbH_3 < BiH_3$$

**Bond angle:** Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs. Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.

$$NH_3\ (107.8°) > PH3\ (93.6°) > AsH_3\ (91.8°) \approx SbH_3\ (91.3°) > BiH_3\ (90°)$$

**Basicity:** Basicity decreases down the group.

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

**Reactivity towards oxygen:** All the group 15 elements form two types of oxides: trioxides, $M_2O_3$ and pentaoxides, $M_2O_5$. The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group.

**Reactivity towards halogens:** Group 15 elements react to form two series of halides: trihalides, $MX_3$ and pentahalides, $MX_5$. Trihalides are $sp^3$ hybridised with pyramidal shape whereas pentahalides are $sp^3d$ hybridized with trigonal bipyramidal shape. Nitrogen does not form pentahalide due to non-availability of the *d*- orbitals in its valence shell. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only $NF_3$ is known to be stable.

**Reactivity towards metals:** All the group 15 elements react with metals to form binary compounds in –3 oxidation state.

**Dinitrogen, $N_2$**

**Preparation:** $N_2$ is produced commercially by the liquifaction of air followed by fractional distillation.

Liquid $N_2$ distills out first leaving behind liquid oxygen. In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl\ (aq) + NaNO_2\ (aq) \rightarrow N_2\ (g) + 2H_2O\ (l) + NaCl\ (aq)$$

Small amounts of NO and $HNO_3$ formed as impurities can be removed by passing the gas through aqueous $H_2SO_4$ containing $K_2Cr_2O_7$.

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4\ H_2O + Cr_2O_3$$

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide

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

**Properties:** Dinitrogen is a colourless, odourless gas, tasteless and non-toxic gas. It is chemically inert at room temperature due to the presence of triple bond with high bond dissociation energy.

At higher temperature, $N_2$ combines with Li and Mg to form $Li_3N$ and $Mg_3N_2$ respectively.

It also combines with $H_2$, $O_2$, $F_2$ to form $NH_3$, NO and $NF_3$ respectively.

$$6Li + N_2 \xrightarrow{Heat} 2Li_3\ N$$

$$3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$$

$$N_2 + 3H_2 \overset{773k}{\rightleftarrows} 2NH_3$$

$$N_2 + O_2 \overset{Heat}{\rightleftarrows} 2NO$$

**Uses:** Some important uses of dinitrogen are as follows:

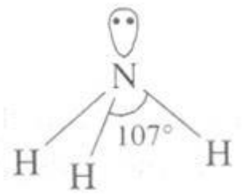
(i) Liquid $N_2$ is used as a refrigerant

(ii) It is used to provide inert atmosphere in iron and steel industry

(iii) It is used in the manufacture of $HNO_3$ and $NH_3$.

**Ammonia, $NH_3$**

Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is $sp^3$ hybridised.



Ammonia is highly soluble in water and is weakly basic.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

**Preparation:** Ammonia ($NH_3$) is manufactured on the commercial scale by Haber's process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \; \Delta_f H^\circ = -46.1 \text{ kJ mol}^{-1}$$

Pressure – 200 × $10^5$ Pa
Temperature – 773 K

Catalyst – Iron oxide with small amounts of $K_2O$ and $Al_2O_3$
In laboratory, ammonia is prepared by reacting $NH_4Cl$ with NaOH.

$$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3$$

**Properties:** Due to the presence of the lone pair of electrons on the nitrogen atoms, $NH_3$ is a Lewis base. It can form coordinate covalent bond with the transition metal ion and form complexes, e.g.

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

Aqueous $NH_3$ is also used in the precipitation of metal ions, e.g.

$$Fe^{3+} + 3NH_4OH \rightarrow \underset{\text{Reddish brown ppt}}{Fe(OH)_3} + 3NH_4^+$$

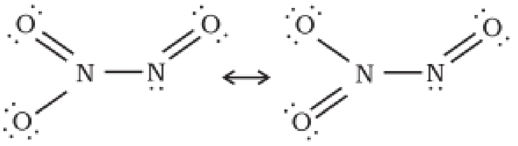
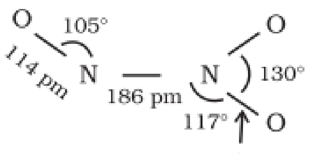
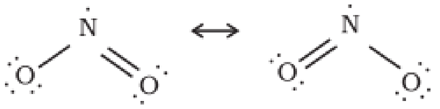
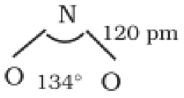
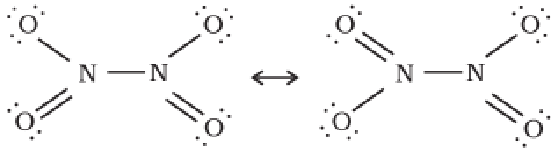
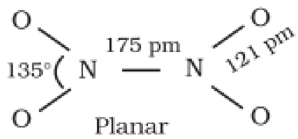
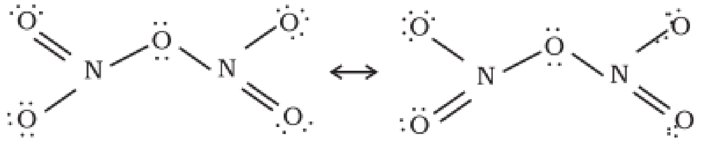
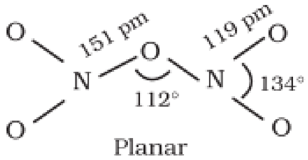
**Uses:** Some important uses of ammonia are:
(i) It is used as a refrigerant
(ii) It is used in the manufacture of nitric acid,
(iii) It is used in the production of nitrogenous fertilisers.

**Oxides of nitrogen**

Nitrogen forms a total of five oxides from +1 oxidation state to +5 oxidation state. The five oxides of nitrogen are: $N_2O$, NO, $N_2O_3$, $NO_2$ or $N_2O_4$, $N_2O_5$.
The following table gives the brief information of various oxides of nitrogen:

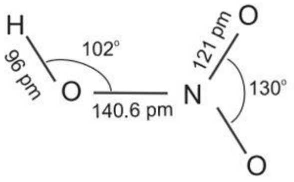
| Name | Formula | Oxidation state of nitrogen | Common methods of preparation | Physical appearance and chemical nature |
|---|---|---|---|---|
| Dinitrogen oxide [Nitrogen(I) oxide] | $N_2O$ | + 1 | $NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$ | colourless gas, neutral |
| Nitrogen monoxide [Nitrogen(II) oxide] | NO | + 2 | $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$ | colourless gas, neutral |
| Dinitrogen trioxide [Nitrogen(III) oxide] | $N_2O_3$ | + 3 | $2NO + N_2O_4 \xrightarrow{250\text{ K}} 2N_2O_3$ | blue solid, acidic |
| Nitrogen dioxide [Nitrogen(IV) oxide] | $NO_2$ | + 4 | $2Pb(NO_3)_2 \xrightarrow{673\text{ K}} 4NO_2 + 2PbO$ | brown gas, acidic |
| Dinitrogen tetroxide [Nitrogen(IV) oxide] | $N_2O_4$ | + 4 | $2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$ | colourless solid/ liquid, acidic |
| Dinitrogen pentoxide [Nitrogen(V) oxide] | $N_2O_5$ | +5 | $4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$ | colourless solid, acidic |

Table 7.4: Structures of Oxides of Nitrogen

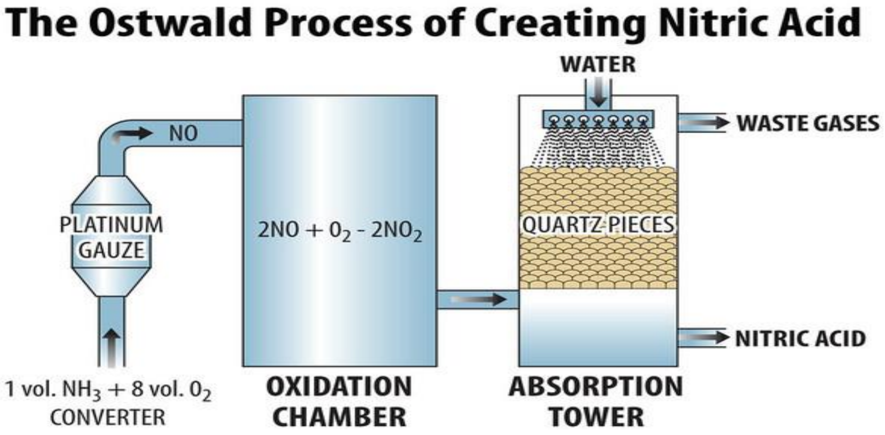
| Formula | Resonance Structures | Bond Parameters |
|---|---|---|
| $N_2O$ | $\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}=N=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \longleftrightarrow :N\equiv N-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$ | N — N — O<br>113 pm 119 pm<br>Linear |
| NO | $:N=\underset{\cdot}{\overset{\cdot\cdot}{O}}: \longleftrightarrow :\overset{\cdot}{N}=\overset{\cdot\cdot}{O}:$ | N — O<br>115 pm |
| $N_2O_3$ |  |  <br>Planar |
| $NO_2$ |  |  <br>Angular |
| $N_2O_4$ |  |  <br>Planar |
| $N_2O_5$ |  |  <br>Planar |

**Nitric acid, $HNO_3$**

Nitric acid is the most important oxoacid formed by nitrogen. It is a colourless liquid. In the gaseous state, $HNO_3$ exists as a planar molecule with the structure as shown below:



**Preparation:** Nitric acid is manufactured by the catalytic oxidation of ammonia in Ostwald process.
In the Ostwald process ammonia is converted to nitric acid in three stages. In the first stage ammonia is catalytically oxidized by atmospheric oxygen on a Platinum based gauze catalyst to form nitric oxide (NO). This step is strongly exothermic, making it a useful heat source once initiated. In the second stage this gas reacts with oxygen yet again to produce nitrogen dioxide. In the third and final stage, the gas is absorbed by water, yielding the desired product, while reducing a portion of it back to NO which is recycled and the acid is concentrated to the required strength by distillation.



First, the ammonia is oxidized at approximately 900°C over a platinum-rhodium catalyst to produce nitrogen monoxide.
4 NH3 (g) + 5 O2 (g) → 4 NO (g) + 6 H2O (g) (ΔH = −950 kJ/mol)

Then, the nitrogen monoxide cools and reacts with oxygen to produce nitrogen dioxide.
2 NO (g) + O2 (g) → 2 NO2 (g) (ΔH = −114 kJ/mol)

Lastly, the nitrogen dioxide reacts with water to create nitric acid.
3 NO2 (g) + H2O (l) → 2 HNO3 (aq) + NO (g) (ΔH = −117 kJ/mol)

Laboratorically, nitric acid can be prepared by the heating $NaNO_3$ or $KNO_3$ with conc. $H_2SO_4$.

$$MNO_3 + H_2SO_4 \rightarrow MHSO_4 + HNO_3$$

**Properties:** Concentrated $HNO_3$ is a strong oxidising agent and attacks most metals except noble metals. Cr, Fe and Al do not dissolve in conc. $HNO_3$ due to the formation of a passive film of oxide on the surface.
The oxidising action of $HNO_3$ is depends on its concentration and the nature of the reducing agent. The principal product of reduction of $HNO_3$ is NO when it is dilute but $NO_2$ when it is concentrated.
For example:

$3Cu + 8HNO_3$ (dil) → $3Cu(NO_3)_2 + 2NO + 4H_2O$
$Cu + 4HNO_3$ (conc) → $Cu(NO_3)_2 + 2NO_2 + 2H_2O$

**Brown ring test for the detection of nitrates:**
Addition of dilute ferrous sulphate solution ($Fe^{2+}$) to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube results in the formation of a brown coloured complex $[Fe(H_2O)_5(NO)]SO_4$.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$
$$NO + \left[Fe\,(H_2O)_6\right] SO_4 \rightarrow \underset{\text{(Brown complex)}}{\left[Fe\,(H_2O)_5\,(NO)\right] SO_4} + H_2O$$

**Uses:** Some important uses of nitric acid are:
**(i)** $HNO_3$ is used in the manufacture of fertilisers.
**(ii)** It is used in the formation of explosives, dynamites, TNT, etc.
**(iii)** It is also used in the etching of metals.

**Phosphorus**

Phosphorus is an essential constituent of elements and plants. It has many allotropic forms, the important ones are:

**(i)** White phosphorus

**(ii)** Red phosphorus

**(iii)** Black phosphorus

**Properties of white phosphorus:**

- Highly toxic and can ignite when exposed to air.
- Waxy, insoluble in $H_2O$
- More reactive than the other solid phases due to the angular strain in the $P_4$ molecule
- Glows in dark
- Discrete tetrahedral $P_4$ molecules.

**Properties of red phosphorus:**

- Prepared by heating white phosphorus at 573K in an inert atmosphere
- Odourless, nonpoisonous and insoluble in $H_2O$
- Less reactive than white phosphorus
- Polymeric structure consisting of chains of $P_4$ units linked together
- Higher meltng point and density

**Properties of black phosphorus:**

- Prepared by heating white phosphorus at 473 K under high pressure.
- Exists in two forms - α black P and β black P
- Thermodynamically most stable, i.e., least reactive
- Has an opaque monoclinic or rhombohedral crystals

**Uses:** Some important uses of phosphorus are:
(i) Used in the manufacture of fertilisers and food grade phosphates.

(ii) Elemental P is used the manufacture of organo-phosphorus compounds used as pesticides.

**Phosphine, $PH_3$**
Phosphine is a highly poisonous, colourless gas and has a smell of rotten fish.

**Preparation:** Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.
$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$
$Ca_3P_2 + 6HCl \rightarrow 2PH_3 + 3CaCl_2$
**Properties:** It is insoluble in water and is a weak base than ammonia. Like ammonia, it gives phosphonium compounds with acids.
For example: $PH_3 + HBr \rightarrow PH_4Br$
$PH_3$ is non-inflammable when pure but becomes inflammable owing to the presence of $P_2H_4$ or $P_4$ vapours.
In water, $PH_3$ decomposes in the presence of light to give red phosphorus and $H_2$.
**Phosphorus halides**
Phosphorus forms two types of halides, $PX_3$ (X = F, Cl, Br, I) and $PX_5$ (X = F, Cl, Br).
**Phosphorus trichloride, $PCl_3$**
It is a colourless oily liquid.

**Preparation:**
It is obtained by passing dry chlorine over heated white phosphorus or by the action of thionyl chloride with white phosphorus.

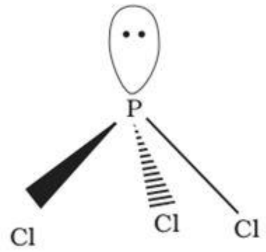
$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

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

**Properties:** It has a pyramidal shape, in which phosphorus is *sp*$^3$ hybridised.
It gets hydrolysed in the presence of moisture.

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
**Phosphorus pentachloride, PCl5**

It is molecular in gas and liquid phase, but in solid state exists as $[PCl_4]^+$ $[PCl_6]^-$ containing tetra and hexa-coordinated phosphorous species.



**Preparation:**

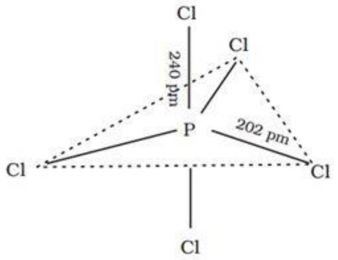
Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine or can be prepared by the action of $SO_2Cl_2$ on phosphorus.

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

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

**Properties:**

In gaseous and liquid phases, it has a trigonal bipyramidal structure.



$PCl_5$ is a yellowish white powder and in moist air, it hydrolyses to POCl3 and finally gets converted to phosphoric acid

$$PCI_5 + H_2O \rightarrow POCI_3 + 2HCI$$
$$POCI_3 + 3H_2O \rightarrow H_3PO_4 + 3HCI$$

When heated, it sublimes but decomposes on stronger heating.

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

**Oxygen family**

The elements of group 16: oxygen (O), sulphur (S), selenium(Se), tellurium (Te) and polonium (Po) having general electronic configuration $ns^2np^4$, are known as the oxygen family. All these elements collectively are also known as chalcogens. Polonium is a radioactive element.

**General properties of oxygen family**

***Atomic and ionic radii:*** Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group.

***Ionisation enthalpy:*** Due to the increase in size of the atoms the ionisation enthalpy decreases down the group. IE1of group 16 elements is less than the $IE_1$ of group 15. This is because group 15 elements have extrastability due to half-filled *p*-orbitals.

***Electron gain enthalpy:*** Due the compact nature of oxygen, it has less electron gain enthalpy than sulphur. After sulphur, the electron gain enthalpy decreases down the group.

***Electronegativity:*** The electronegativity decreases down the group. This implies that the metallic character increases down the group from oxygen to polonium.

***Melting and boiling point:*** The melting and boiling point increases with increase in atomic number down the group.

***Oxidation states:*** Group 16 elements show –2, +2, +4, +6 oxidation states. The stability of –2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity. O shows only –2 oxidation state except when it combines with the most electronegative F with which it shows positive oxidation states. S shows + 6 only with O and F.

### Anomalous behaviour of oxygen

Oxygen forms strong hydrogen bonding in $H_2O$ which is not found in $H_2S$. Also, the maximum covalency of oxygen is four, whereas in a case of other elements of the group, the valence shells can be expanded and covalency exceeds four.
Reasons for the anomalous behaviour of oxygen are:

- Small size and high electronegativity

- Absence of d-orbitals

***Reactivity towards hydrogen:*** All the elements of Group 16 form hydrides of the type $H_2E$ (E = S, Se, Te, Po).
***Thermal stability:*** Thermal stability of group 16 elements decreases down the group.

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

This is because the H-E bond length increases down the group, hence the bond dissociation enthalpy decreases down the group.

***Acidic nature:*** Due to the decreasing bond dissociation enthalpy, acidic character of group 16 elements increases down the group.

$$H_2O < H_2S < H_2Se < H_2Te$$

***Reducing character:*** The reducing character also decreases down the group due to the decreasing bond dissociation enthalpy.

$$H_2O < H_2S < H_2Se < H_2Te > H_2Po$$

***Reactivity towards oxygen:*** All group 16 elements form oxides of the type $EO_2$ and $EO_3$ Reducing character of dioxides decreases down the group. Acidity also decreases down the group. Besides $EO_2$ type, sulphur, selenium and tellurium also form $EO_3$ type oxides. Both types of oxides are acidic in nature.
***Reactivity with halogens:*** Elements of Group 16 form a large number of halides of the type, $EX_2$ $EX_4$ and $EX_6$, where X is a halogen. The stability of halides decreases in the order $F^- > Cl^- > Br^- > I^-$ . This is because E-X bond length increases with increase in size. Among hexa halides, hexafluorides are the most stable because of steric reasons. Dihalides are *sp*$^3$ hybridised and have tetrahedral geometry. $H_2O$ is a liquid while $H_2S$ is a gas. Because in water due to the small size and high electronegativity of O, strong hydrogen bonding is present there.

### Oxygen (O)

Oxygen is the first element of Group 16 with the electronic configuration of $1s^2\ 2s^2\ 2p^4$ in the ground state. Oxygen has two allotropes: dioxygen ($O_2$) and trioxygen or ozone ($O_3$).

### Dioxygen ($O_2$)

Oxygen usually exists in the form of dioxygen.

***Preparation:***
Dioxygen is prepared in the laboratory by thermal decompositions of oxygen rich compounds such as $KClO_3$,

$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KC1 + 3O_2$$

It is also prepared by the hydrolysis of sodium peroxide.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

Electrolysis of water also produces dioxygen in the pure state.

$$2H_2O \xrightarrow{Eelectrolysis} 2H_2 + O_2$$

***Properties:***
**(i)** Oxygen is a colourless, odourless and is a highly reactive tasteless gas.
**(ii)** Due to the presence of *pπ– pπ* bonding, $O_2$ is a discrete molecule and intermolecular forces are weak van der Waals forces, hence, $O_2$ is a gas.
**(iii)** Dioxygen combines with metals and non-metals to form binary compounds called oxides.
Examples are:

$$2Ca + O_2 \rightarrow 2CaO$$
$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

**Uses:**
**(i)** Dioxygen is used in making steel.

**(ii)** It is used in the production of oxygen containing organic chemicals.
**(iii)** Dioxygen is also used for sewage treatment, river revival and paper pulp bleaching.
**(iv)** It is used as an oxidiser in underwater diving and in space shuttles.

### Simple Oxides

Oxygen combines with majority of the elements of the periodic table to forms oxides ($O^{2-}$). There are three types of oxides:

$$S + O_2 \longrightarrow SO2$$

$SO_2 + H_2O \rightarrow H_2SO_3$

**(ii)** ***Basic oxides:*** Metallic oxides are mostly basic in nature. Basic oxides dissolve in water to give basic solution. For example, CaO combines with water to give $Ca(OH)_2$, a base.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

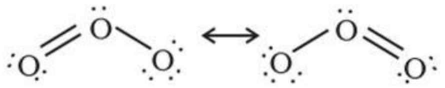
***(iii) Amphoteric oxides:*** Some metallic oxides show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. For example, $Al_2O_3$ reacts with acids as well as alkalies

$$\underset{\text{Base}}{Al_2O_3} + \underset{\text{Acid}}{6HCl} + 9H_2O \rightarrow 2\,[Al(H_2O)_6]^{3+} + 6\,Cl^-$$

$$\underset{\text{Acid}}{Al_2O_3} + \underset{\text{Base}}{6NaOH} + 3H_2O \rightarrow 2Na_3[Al(OH)_6]$$

### Ozone ($O_3$)

Ozone is an allotropic form of oxygen. Ozone has angular structure with a bond angle of about 117°. Both O = O bonds are of equal bond length due to resonance.



***Preparation:***
It is formed when dioxygen is irradiated with UV light or silent electric discharge.

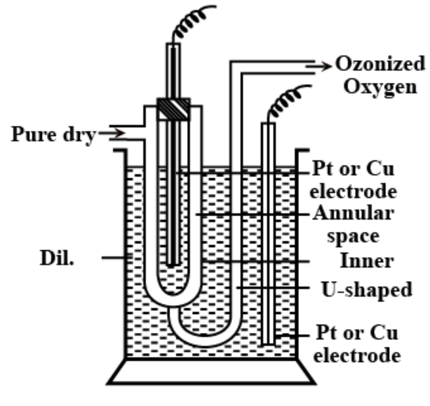


**Fig. Brodie's ozonizer**

$$3O_2\,(g) \rightarrow 2O_3\,(g)\ \Delta H^o = +142\ KJ/mol$$

***Properties:***
**(i)** Ozone is a pale blue gas with a characteristic pungent odour.
**(ii)** Ozone is diamagnetic in nature.
**(iii)** It is the second most powerful oxidising agent after fluorine. It liberates oxygen gas when acting as an oxidising agent.

$$2Fe^{2+} + O_3 + 2H^+ \rightarrow 2Fe^{3+} + H_2O + O_2$$

$$PbS + 4O_2 \rightarrow PbSO_4 + 4O_2$$

**Depletion of ozone layer:**

Thinning of the ozone layer is termed as depletion of ozone layer. The depletion of ozone layer in the stratosphere is caused by the presence of chlorofluoro carbons. CFCs decomposed by UV radiation to produce chlorine which reacts with ozone and this causes a de-crease in the concentration of ozone at a rate faster than its formation from dioxygen. Another cause of depletion of ozone layer is the release of nitrogen oxides into the stratosphere by supersonic jet aeroplanes.

$$NO + O_3 \rightarrow NO_2 + O_2$$

**Sulphur (S)**

Sulphur exhibits allotropy, two important allotropes of which are:

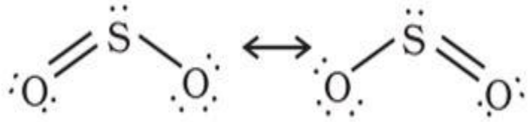
**(a)** Yellow Rhombic (α - sulphur)
**(b)** Monoclinic (β- sulphur)

$$\alpha - \text{Sulphur} \underset{\text{below 369 K}}{\overset{\text{above 369 K}}{\rightleftharpoons}} \beta - \text{Sulphur}$$

At 369 K both forms are stable. $S_8$ puckered shape in both forms and has crown shape.

**Sulphur Dioxide ($SO_2$)**

The molecule of $SO_2$ is angular. It is a resonance hybrid of the two canonical forms:



***Preparation:***

Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$$S\,(g) + O_2(g) \rightarrow SO_2(g)$$

In the laboratory it is readily generated by treating a sulphite with dilute sulphuric acid.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2$$

***Properties***:

(i) Colourless gas, pungent smell, highly soluble in $H_2O$

(ii) $SO_2 + H_2O \rightleftharpoons H_2SO_3$

(iii) $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

(iv) $SO_2 + CI_2 \rightarrow SO_2Cl_2$

(v) $SO_2$ is a reducing agent.
For example:

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

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

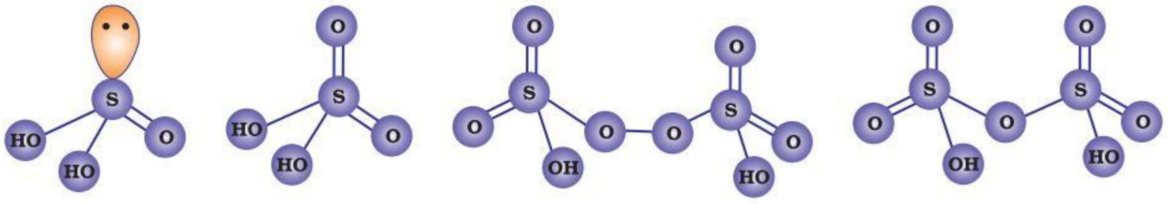
***Uses:***

**(i)** $SO_2$ is used in refining petroleum and sugar
**(ii)** It is used in bleaching wool and silk
**(iii)** It is also used as a disinfectant and preservative.
**(iv)** It is used in the manufacture of sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite.

**Oxoacids of sulphur**

Sulphur forms variety of oxoacids. All oxoacids of sulphur are dibasic.

Sulphur forms a number of oxoacids such as $H_2SO_3$, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2 to 5), $H_2SO_4$, $H_2S_2O_7$, $H_2SO_5$, $H_2S_2O_8$ . Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in figure given below



Sulphurous acid ($H_2SO_3$) Sulphuric acid ($H_2SO_4$) Peroxodisulphuric acid ($H_2S_2O_8$) Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Image Source: NCERT Books

**Sulphuric acid ($H_2SO_4$)**

***Preparation:***

Sulphuric acid is manufactured by the Contact Process as follows:

(i) $S + O_2 \rightarrow SO_2$ (Burning of sulphur)

(ii) $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

(ii) $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

(iv) $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

***Properties:***

**(i)** Sulphuric acid is a colourless, dense oily liquid.
**(ii)** It is dibasic acid or diprotic acid.
**(iii)** It is a strong dehydrating agent.
**(iv)** It is a moderately strong oxidizing agent.

***Uses:***

**(i)** $H_2SO_4$ is used in manufacture of fertilisers
**(ii)** It is also used in petroleum refining, manufacture of pigments, detergents, metallurgical application and storage batteries.

**Halogen family**

Group 17 elements are fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are collectively known as halogens and are having the general electronic configuration of $ns^2$, $np^5$.

**Atomic and ionic radii**

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. Atomic and ionic radii increases down the group due to the addition of a new shell at each step.

**Ionisation enthalpy**

Due to their small size halogens have little tendency to lose electron. Thus they have very high ionisation enthalpy. Ionisation enthalpy decreases down the group due to the increase in atomic size.

**Electron gain enthalpy**

Electron gain enthalpy of halogens is very high as they are short of only one electron to attain noble gas configuration. Electron gain enthalpy becomes less negative as we move down the group. However F has less electron gain enthalpy than Cl due to its small size and high electron density.

**Electronegativity**

Electronegativity decreases down the group. F is the most electronegative element in the periodic table.

**Melting and boiling point**

The melting and boiling points increases down the group.

**Bond dissociation enthalpy**

Bond dissociation enthalpy decreases as we move down the group. $F_2$ has less $\Delta H_{diss}$. Then $Cl_2$ due to small size and strong lone pair-lone pair repulsion.

**Colour**
All halogens exhibit colour due to the absorption of radiations in visible region of light due to which the electrons get excited to higher energy levels.

For example, $F_2$ has yellow, $Cl_2$ has greenish yellow, $Br_2$ has red and $I_2$ has violet colour.

**Oxidation state**
The most common oxidation state of halogens is −1. Cl, Br, I also shows positive oxidation states of +1, +3, + 5, + 7. F does not show positive oxidation states due to non-availability of *d*-orbitals.

**Reactivity**
All halogens are highly reactive and the reactivity decreases down the group.

**Anomalous behaviour of fluorine**
Fluorine is anomalous in many properties like, ionisation enthalpy, electronegativity, enthalpy of bond dissociation that are higher than expected from the regular trends among the halogens. Its ionic and covalent radii, melting and boiling points, and electron gain enthalpy is quite lower than expected.
Reasons for the anomalous behaviour of oxygen are:

- Small size and highest electronegativity

- Low F-F bond dissociation enthalpy

- Absence of d-orbitals

**Reactivity towards hydrogen**
All halogens reacts with $H_2$ to form hydrogen halides (HX) and the reactivity towards $H_2$ decreases down the group

**Acidic strength**
As the size of X increases and the strength of H─X bond decreases down the group, acidic strength dectreses down the group

$$HF < HCl < HBr < HI$$

**Stability**
As the bond dissociation enthalpy decreases down the group so the stability of hydrogen halides also decreases from HF to HI.

$$HF > HCl > HBr > HI$$

**Boiling point**
Due to the increase in size of halogens the van der Waals forces increases down the group resulting in the increase in boiling point from HCl to HI. HF has the highest boiling point due to the presence of strong intermolecular H bonding

$$HCl < HBr < HI < HF.$$

**Ionic character**
Due to the decrease in electronegativity down the group the ionic character of hydrogen halides also decreases down the group.

$$HF > HCl > HBr > HI$$

**Reducing power**
As the bond dissociation enthalpy decreases, so it becomes easier to give out the hydrogen atom causing the reducing power to increase from HF to HI.

$$HF < HCl < HBr < HI$$

**Reactivity towards metals**:
Halogens react with metals to form metal halides of the form MX, where M is a monovalent metal.

$2Na + Cl_2 \longrightarrow 2NaCl$

$Ca + Cl_2 \longrightarrow CaCl_2$

**Ionic character**

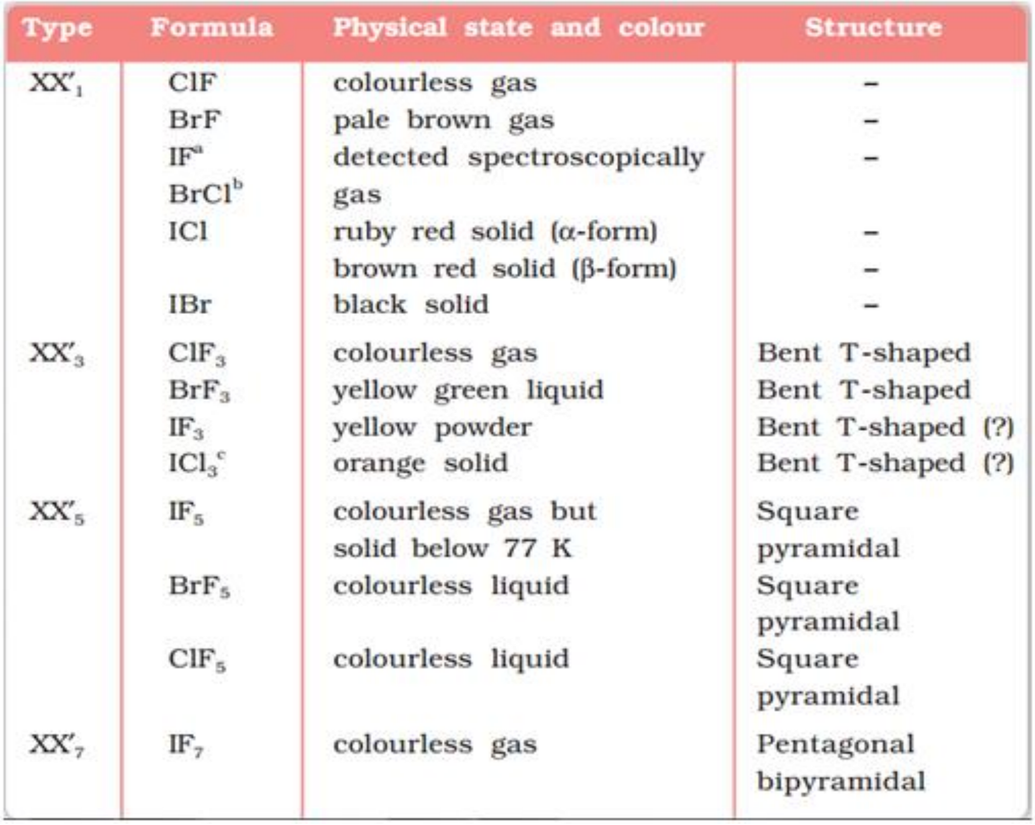
Due to the decrease in electronegativity down the group the ionic character of metal halides also decreases down the group

$$MF > MCl > MBr > MI$$

**Reactivity of halogens towards other halogens (Interhalogens):**

Binary compounds of two different halogen atoms of general formula $XX'_n$ are called interhalogen compounds where $n$ = 1, 3, 5, or 7. All the interhalogen compounds are covalent in nature.

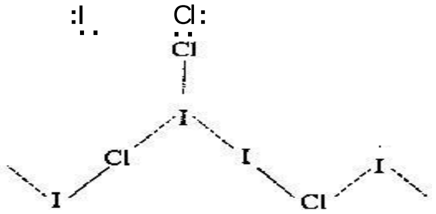
Some properties of interhalogen compounds are given in the following table:

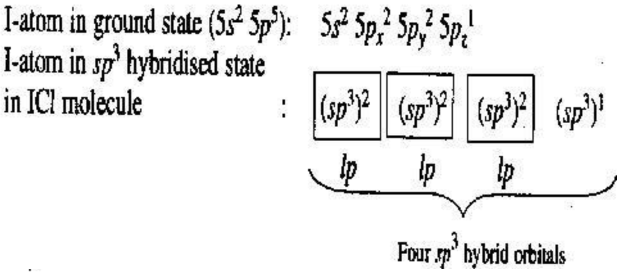


| Type | Formula | Physical state and colour | Structure |
|---|---|---|---|
| $XX'_1$ | ClF | colourless gas | – |
| | BrF | pale brown gas | – |
| | $IF^a$ | detected spectroscopically | – |
| | $BrCl^b$ | gas | |
| | ICl | ruby red solid (α-form) | – |
| | | brown red solid (β-form) | – |
| | IBr | black solid | – |
| $XX'_3$ | $ClF_3$ | colourless gas | Bent T-shaped |
| | $BrF_3$ | yellow green liquid | Bent T-shaped |
| | $IF_3$ | yellow powder | Bent T-shaped (?) |
| | $ICl_3^c$ | orange solid | Bent T-shaped (?) |
| $XX'_5$ | $IF_5$ | colourless gas but solid below 77 K | Square pyramidal |
| | $BrF_5$ | colourless liquid | Square pyramidal |
| | $ClF_5$ | colourless liquid | Square pyramidal |
| $XX'_7$ | $IF_7$ | colourless gas | Pentagonal bipyramidal |

## Structure and geometry of XY type Inter-halogen compounds:

Examples of such compounds are ClF, BrF, IF, BrCl, ICl abd IBr. Let us consider example of ICl molecule in which I-atom is the central atom. All these molecules have *linear geometry* which arises because of $sp^3$ hybridisation of the central halogen atom, iodine.





I-atom in ground state ($5s^2 5p^5$): $5s^2\,5p_x^2\,5p_y^2\,5p_z^1$

I-atom in $sp^3$ hybridised state in ICl molecule : $\underbrace{\boxed{(sp^3)^2}_{lp}\ \boxed{(sp^3)^2}_{lp}\ \boxed{(sp^3)^2}_{lp}\ (sp^3)^1}_{\text{Four } sp^3 \text{ hybrid orbitals}}$

I-Cl σ-bond results by the head-to-head overlap between the singly-filled $3p_z$ orbital of Cl-atom and singly filled $sp^3$ hybrid orbital on I-atom. Although the spatial arrangement of 4-electron pairs round I-atom is tetrahedral, due to the presence of three lone pairs of electrons, the shape of ICl molecule gets distorted and becomes linear. ICl molecule form zig-zag chains in both α and β-form. Both forms differ only whether Cl-branches are cis (α) or trans (β).

### Inter-halogen compounds of $XY_3$ type (Tetra-atomic inter-halogens): Preparation:

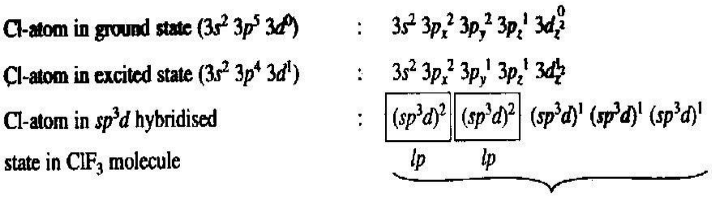
- These are generally prepared by direct combination of elements under suitable conditions.

$$Cl_2 + 3\,F_2\ (\text{excess}) \xrightarrow{200\text{-}300^0\ C} 2\,ClF_3\ ;$$

$$Br_2\ (\text{vapour}) + 3\,F_2 \xrightarrow{\text{In presence of } N_2} 2\,BrF_3\ ;$$

### Structure and geometry of $XY_3$ type Inter-halogen compounds:

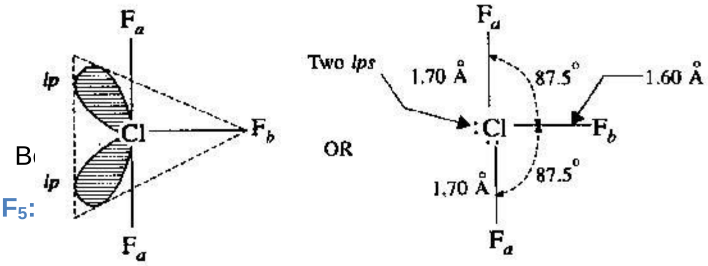
Examples of such compounds are $ClF_3$, $BrF_3$ and $IF_3$. All these molecules have bent *T-shaped structure* which is due to $sp^3d$ hybridization of the central bigger atom.Let us discuss the geometry of $ClF_3$ molecule in which Cl-atom is the central atom. Lewis structure of $ClF_3$ molecule shows that the central Cl-atom is surrounded by three σ-bps and two lone pairs of electrons and hence Cl-atom is $sp^3d$ hybridized in $ClF_3$ molecule.Each of the three Cl-F σ-bonds results by the overlap of singly-filled $sp^3d$ hybrid orbital on Cl-atom and singly-filled $2p_z$ orbital of F-atom.



Cl-atom in ground state ($3s^2\,3p^5\,3d^0$) : $3s^2\,3p_x^2\,3p_y^2\,3p_z^1\,3d_{z^2}^0$

Cl-atom in excited state ($3s^2\,3p^4\,3d^1$) : $3s^2\,3p_x^2\,3p_y^1\,3p_z^1\,3d_{z^2}^1$

Cl-atom in $sp^3d$ hybridised state in $ClF_3$ molecule : $\underbrace{\boxed{(sp^3d)^2}_{lp}\ \boxed{(sp^3d)^2}_{lp}\ (sp^3d)^1\ (sp^3d)^1\ (sp^3d)^1}$



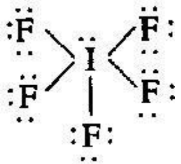
### 1. Iodine pentafluoride, $IF_5$:

**Preparation:**

- It is formed by direct combination of $I_2$ and $F_2$ (excess): $I_2 + 5\,F_2\ (\text{excess}) \rightarrow 2\,IF_5$
- By the action of $F_2$ on $I_2O_5$: $10\,F_2 + 2\,I_2O_5 \rightarrow 4\,IF_5 + 5\,O_2$
- By heating $I_2$ with AgF: $I_2 + 10\,AgF \rightarrow 2\,IF_5 + 10\,Ag$

Structure and geometry of $XY_5$ type Inter-halogen compounds:

Examples of such compounds are $ClF_5$, $BrF_5$ and $IF_5$. All these molecules have *distorted octahedral (square pyramidal) structure* which arises from $sp^3d^2$ hybridization of the central atom. Let us discu



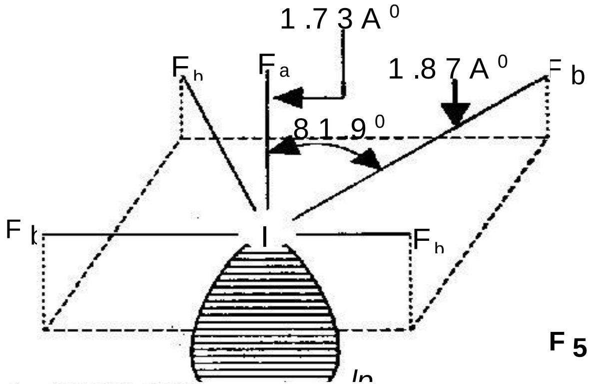
-ss the shape of $IF_5$ molecule in which bigger I-atom is the central atom. The Lewis structure of this molecule shows that the central I-atom is surrounded by five bps

and one lp of electrons hence I-atom is $sp^3d^2$ hybridized in $IF_5$ molecule.

Out of six $sp^3d^2$ hybrid orbitals, one axial hybrid orbital contains lone pair of electrons while remaining five orbitals are singly-filled. The lone pair occupies the axial orbital, since in this case (lp-lp) repulsion is minimum. Each of five F-I σ-bonds result by the overlap of singly-filled $sp^3d^2$ hybrid orbital in Cl-atom and singly-filled $2p_z$ orbital of F-atom.

Although the spatial arrangement of six electrons pairs round I-atom in space is octahedral, due to the presence of one lone pair electrons the shape of molecule gets distorted and hence $IF_5$ assumes square pyramidal shape.

A recent study of this molecule shows that all four basal F-atom are slightly displaced up wards from the base of the square pyramid and hence molecule assume the structure as shown in fig. 3.5



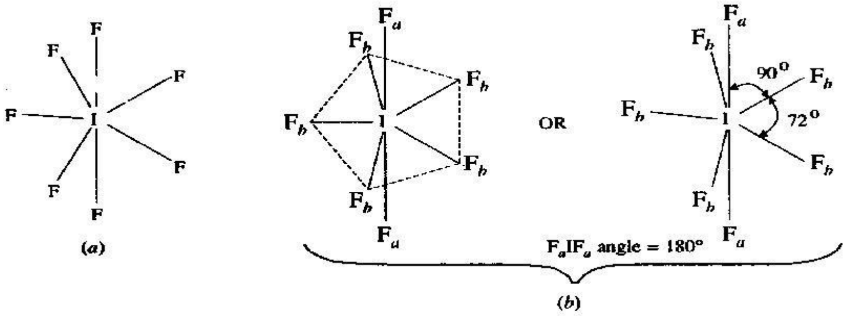
**$F_5$ molecule**

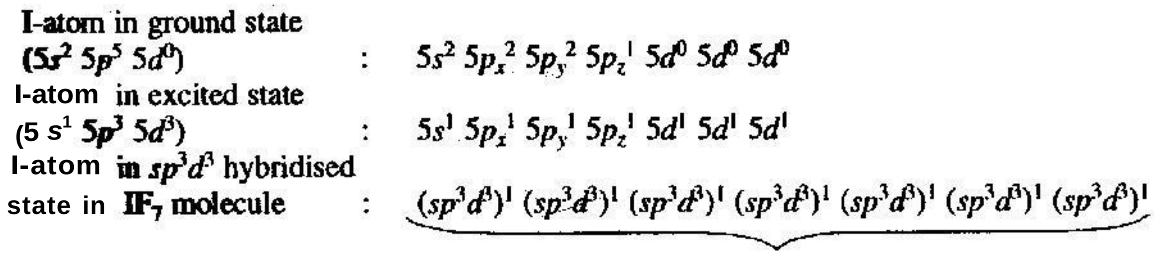
**I-atom in ground state**
**($5s^2\ 5p^3\ 5d^0$)** : $5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1\ 5d_{z^2}^0\ 5d_{x^2-y^2}^0$
**I-atom in the excited state**
**($5s^2\ 5p^3\ 5d^1\ 5d^1$)** : $5s^2\ 5p_x^1\ 5p_y^1\ 5p_z^1\ 5d_{z^2}^1\ 5d_{x^2-y^2}^1$
**I-atom in $sp^3d^2$ hybridised state**
**in $IF_5$ molecule** : $\underbrace{\underset{lp}{\boxed{(sp^3d^2)^2}}\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1\ (sp^3d^2)^1}_{\text{Six } sp^3d^2 \text{ hybrid orbitals}}$

## Structure and geometry of $XY_7$ type Inter-halogen compounds:

$IF_7$ is the only inter-halogen compound of this type. The Lewis structure of this molecule shows that the central I-atom is surrounded by seven σ-bps and hence I- atom in its excited state is $sp^3d^3$ hybridized in $IF_7$ molecule. Each of the seven I-F σ-bonds is formed by the overlap between the singly- filled $sp^3d^3$ hybrid orbital on I-atom and singly-filled $2p_z$ orbital in F-atom. Since there is no lone pair of electrons in any of the hybrid orbital, $IF_7$ molecule has expected pentagonal bipyramidal shape. $IF_7$ molecule has two equal axial, I-Fa bonds and

Fig. 3.8 (a) Lewis structure of $IF_7$ (b) Pentagonal bipyramida geometry of $IF_7$ molecule





I-atom in ground state ($5s^2\ 5p^5\ 5d^0$) : $5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1\ 5d^0\ 5d^0\ 5d^0$

I-atom in excited state ($5s^1\ 5p^3\ 5d^3$) : $5s^1\ 5p_x^1\ 5p_y^1\ 5p_z^1\ 5d^1\ 5d^1\ 5d^1$

I-atom in $sp^3d^3$ hybridised state in $IF_7$ molecule : $\underbrace{(sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1\ (sp^3d^3)^1}$

Seven $sp^3d^3$ hybrid orbitals

equal equatorial, I-Fb bonds. I-Fa bond length is longer than I-Fb bond length.

### Inter-halogen compounds of $XY_7$ type (Octa-atomic inter -halogens):

Only one compound, $IF_7$ of this type has been found and characterized. The reason is that an iodine atom has largest size among halogens, while F-atom has the smallest size.

## Iodine heptafluoride, $IF_7$:

**Preparation:**

It is prepared by the action of $F_2$ on $IF_5$, KI or $PbI_2$.

$F_2 + IF_5 \xrightarrow{250^0\text{-}300^0} CIF_7$; $4F_2 + KI \xrightarrow{250^0\ C} KF + IF_7$

$8F_2 + PbI_2 \longrightarrow PbF_2 + 2\ IF_7$

## Chlorine (Cl)

**Preparation:**
Chlorine can be prepared by any of the following processes:

(i) $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

(ii) $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

(iii) **Deacon's process**

$$4HCl + O_2 \xrightarrow[723K]{CuCl_2} 2H_2O + 2Cl_2$$

(iv) **Electrolytic process**

$$\underset{\text{Brine}}{\text{Conc. } NaCl} + H_2O \xrightarrow{\text{Electrolysis}} NaOH + \frac{1}{2}H_2 + \frac{1}{2}Cl_2$$

**Properties:**

- It is a greenish yellow gas with pungent and suffocating odour.

- It is soluble in $H_2O$
- Reaction with metals and non-metals: Chlorine reacts with a number of metals and non-metals to form chlorides.

  For example:

$$2\,Al + 3Cl_2 \rightarrow 2AlCl_3$$
$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

- Reaction with ammonia: When treated with excess ammonia, chlorine gives nitrogen and ammonium chloride whereas when excess chlorine reacts with ammonia, nitrogen trichloride is formed.

$$\underset{\text{Excess}}{8NH_3} + 3Cl_2 \rightarrow 6NH_4Cl + N_2$$

$$NH_3 + \underset{\text{Excess}}{Cl_2} \rightarrow NCl_3 + 3\,HCl$$

- Reaction with NaOH: Chlorine reacts differently with cold dilute NaOH and hot concentrated NaOH.

$$Cl_2 + \underset{\text{Cold dil.}}{2NaOH} \rightarrow NaCl + NaOCl + H_2O$$

$$Cl_2 + \underset{\text{Hot conc.}}{6NaOH} \rightarrow NaCl + NaOCl + H_2O$$

Reaction with slaked lime: $Cl_2$ when treated With dry slaked lime it gives bleaching powder:

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

$Cl_2$ acts as a powerful bleaching agent and its bleaching action is due to its oxidizing nature.

$$Cl_2 + H_2O \rightarrow 2HCl + O$$

**Uses:**

(i) Chlorine is used for bleaching woodpulp.

(ii) It is used in the extraction of gold and platinum

(iii) It is used in in sterilising drinking water.

(iv) It is used in the manufacture of dyes, drugs and organic compounds like $CCl_4$, DDT, refrigerants, etc.

## Hydrogen chloride (HCl)

**Preparation:**

It is prepared by heating sodium chloride with concentrated sulphuric acid.

$$2\ NaCl + H_2SO_4 + \text{Heat} \rightarrow Na_2SO_4 + HCl$$

**Properties:**
HCl is a colourless gas with pungent odour.

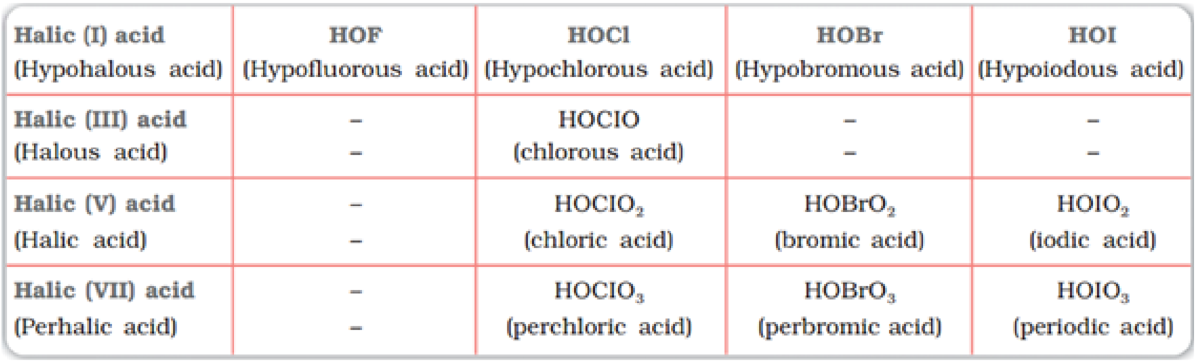
It is extremely soluble in water, $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
It decomposes salts of weaker acids, $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
When treated with $NH_3$, it gives white fumes of $NH_4Cl$, $NH_3 + HCl \rightarrow NH_4Cl$
3HCl : $1HNO_3$ is called aqua regia, which is used for dissolving noble metals.
$Au + 4\ H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2\ H_2O$

**Uses:**
(i) Hydrogen chloride is used in medicine and as a laboratory reagent.

(ii) It is used in the manufacture of chlorine, $NH_4Cl$ and glucose.

**Oxoacids of halogens**
Fluorine due to its small size and high electronegativity forms only one oxoacid HOF (Hypofluorous acid).

Other halogen form several oxoacids as given in the following table:



| **Halic (I) acid**<br>(Hypohalous acid) | **HOF**<br>(Hypofluorous acid) | **HOCl**<br>(Hypochlorous acid) | **HOBr**<br>(Hypobromous acid) | **HOI**<br>(Hypoiodous acid) |
|---|---|---|---|---|
| **Halic (III) acid**<br>(Halous acid) | –<br>– | HOCIO<br>(chlorous acid) | –<br>– | –<br>– |
| **Halic (V) acid**<br>(Halic acid) | –<br>– | $HOCIO_2$<br>(chloric acid) | $HOBrO_2$<br>(bromic acid) | $HOIO_2$<br>(iodic acid) |
| **Halic (VII) acid**<br>(Perhalic acid) | –<br>– | $HOCIO_3$<br>(perchloric acid) | $HOBrO_3$<br>(perbromic acid) | $HOIO_3$<br>(periodic acid) |

**Group 18, Noble gases**
Group 18 elements: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) having the electronic configuration $ns^2\ np^6$, are named as noble gases. All these are gases and chemically unreactive.

***General properties of noble gases***

**Atomic radii:**
Atomic radii of noble gases increases down the group due to the addition of a new shell at each step.

$$He < Ne < Ar < Kr < Xe < Rn$$

**Ionisation enthalpy:**
They have very high ionization enthalpy because of completely filled orbitals. Ionisation enthalpy decreases down the group because of increase in size.

$$He < Ne < Ar < Kr < Xe < Rn$$

**Electron gain enthalpy:**
Because of stable electronic configuration, noble gases have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

**Melting and boiling point:**
Due to the weak dispersion forces they have low melting and boiling point.

**Xenon-fluorine compounds**
Xenon forms three binary fluorides, $XeF_2$, $XeF_4$ and $XeF_6$ .

**Preparation:**

$$Xe(g) + F_2(g) \xrightarrow{673K, 1bar} XeF_2(s)$$

(Xenon in excess)

$$Xe(g) + 2F_2(g) \xrightarrow{873K, 7bar} XeF_4(s)$$

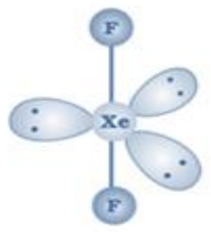
(1:5 ratio)

$$Xe(g) + 3F_2(g) \xrightarrow{573K, 60-70bar} XeF_6(s)$$

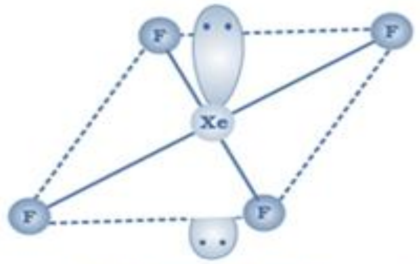
(1:20 ratio)

**Properties:**

$XeF_2$ is linear, $XeF_4$ is square planar and $XeF_6$ is distorted octahedral.



$XeF_2$ : Linear



$XeF_4$ : Square planar

$XeF_6$ : Distorted octahedral

$XeF_2$, $XeF_4$ and $XeF_6$ are colourless crystalline solids
They are readily hydrolysed

$$2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe(g) + HF(aq) + O_2(g)$$

They react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$XeF_2 + PF_5 \rightarrow [XeF] + [PF_6]^-$
$XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$
$XeF_6 + MF \rightarrow M^+ [XeF_7]^-$
[Where, M = Na, K, Rb or Cs]

**Xenon-oxygen compounds**

Xenon forms some important compounds with oxygen like $XeO_3$, $XeOF_4$ $XeO_2F_2$.

**Preparation:**

Various xenon-oxygen compounds are prepared as follows:

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

Partial Hydrolysis $XeOF_4$

$XeF_6 + H_2O \rightarrow XeOF_4 + 2 HF$

Partial Hydrolysis also gives $XeO_2F_4$

$XeF_6 + 2H_2O \rightarrow XeO_2F_4 + 4HF$

**Properties:**

$XeO_3$ is a colourless explosive solid having a trigonal pyramidal structure.
$XeOF_4$ is a colourless volatile liquid with a square pyramidal

$XeO_3$ : Pyramidal

$XeOF_4$ : Square pyramidal

**Uses of inert gases**

**Helium is used:**

- Gas cooled Nuclear reactors

- In filling balloons for meteorological observations.

- In the oxygen mixture of deep sea divers

- In inflating aeroplane tyres

- Used to provide an inert atmosphere in melting and welding of easily oxidizable metals.

**Neon is used:**
- In discharge tubes and fluorescent bulbs used for advertising purposes

- In beacon lights for the safety of air navigators as the light can easily pass through the fog for a clear view.

**Argon is used:**
- To provide an inert atmosphere in high-temperature metallurgical processes (arc welding of metals or alloys)

- For filling electric bulbs.

- In the laboratory for handling substances that are air-sensitive.

- Xenon and Krypton are also used in light bulbs.

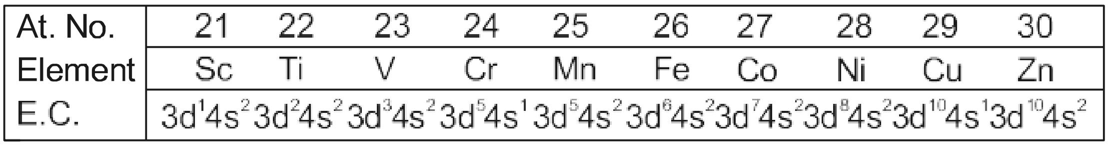
## *Cheapter-8 d-and f block elements*

***d* –Block elements and transition metals**

The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as *d* – block elements.

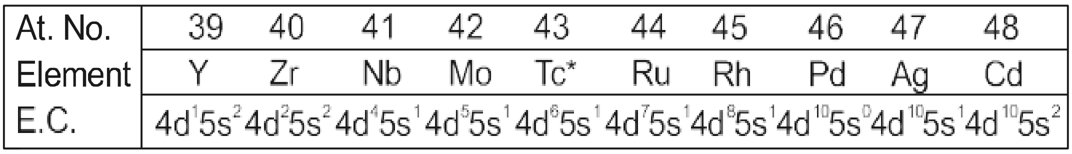
**Features of d-block elements:**
- The general electronic configuration of *d*-block elements is $(n-1)d^{1-10}\, ns^{1-2}$, where $(n-1)$ stands for the inner d orbitals.
- In *d*-block, each horizontal row consists of ten elements as *d*-subshell can accommodate maximum of 10 electrons.
- The *d*-block elements having incompletely filled *d*-subshell are called transition metals.
- Zinc, cadmium, mercury having the general electronic configuration as $(n-1)d^{10}\, ns^2$, are not regarded as transition metals due to completely filled *d* – orbital.
- There are mainly three series of the transition metals:

    - 3*d* series starts with Sc (Z = 21) and ends with Zn (Z = 30)



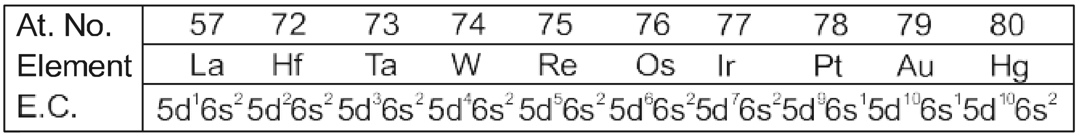
| At. No. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|---|---|---|
| Element | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| E.C. | $3d^1 4s^2$ | $3d^2 4s^2$ | $3d^3 4s^2$ | $3d^5 4s^1$ | $3d^5 4s^2$ | $3d^6 4s^2$ | $3d^7 4s^2$ | $3d^8 4s^2$ | $3d^{10} 4s^1$ | $3d^{10} 4s^2$ |

    - 4*d* series starts with Y (Z = 39) and ends with Cd (Z = 48)



| At. No. | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
|---|---|---|---|---|---|---|---|---|---|---|
| Element | Y | Zr | Nb | Mo | Tc* | Ru | Rh | Pd | Ag | Cd |
| E.C. | $4d^1 5s^2$ | $4d^2 5s^2$ | $4d^4 5s^1$ | $4d^5 5s^1$ | $4d^6 5s^1$ | $4d^7 5s^1$ | $4d^8 5s^1$ | $4d^{10} 5s^0$ | $4d^{10} 5s^1$ | $4d^{10} 5s^2$ |

    - 5*d* series starts with La (Z = 57) and ends with Hg (Z = 80)



| At. No. | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
|---|---|---|---|---|---|---|---|---|---|---|
| Element | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
| E.C. | $5d^1 6s^2$ | $5d^2 6s^2$ | $5d^3 6s^2$ | $5d^4 6s^2$ | $5d^5 6s^2$ | $5d^6 6s^2$ | $5d^7 6s^2$ | $5d^9 6s^1$ | $5d^{10} 6s^1$ | $5d^{10} 6s^2$ |

**General General Properties of transition elements:**

**Metallic character**

Almost all the transition elements display metallic properties such as metallic luster, high tensile strength, ductility, malleability and high thermal and electrical conductivity.In any row, the melting point of these metals rises to a maximum at $d^5$ and after that as the electrons start pairing up so the melting point decreases regularly as the atomic number increases with an exception of Mn and Tc are exception.

**Atomic and ionic radii**

Due to the addition of new electron to a *d*-orbital each time the effective nuclear charge increases which causes the atomic radii to decrease in a series of transition elements. However, the atomic size of Fe, Co, Ni is almost the same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increased in shielding effect. The size of the 4*d* series elements is almost the same as the size of the 5*d* series elements. This phenomenon is associated with the intervention of the 4*f* orbitals which must be filled before the filling starts in 5*d* subshell.

**Lanthanoid contraction**

The filling of the 4*f* before the 5*d* orbital results in a regular decrease in size called lanthanoid contraction. This compensates for the expected increase in the atomic size with increasing atomic number. The net result of the lanthanoid contraction is is that the 4*d* and 5*d* series elements exhibit similar radii and show similarity in their physical and chemical properties.

**Melting point**

Due to the strong interatomic bonding which involves both (*n*−1) *d* and *ns* electrons participation, transition metals have high melting points.

**Ionization enthalpy**

In a particular transition series, there is an increase in ionization enthalpy from left to right which is due to the increase in effective nuclear charge along a series. But the trend is not very regular. The exceptions are chromium and copper which have notably larger ionization enthalpy than their neighbours. These exceptions are due to the extra stability associated with the half-filled and fully-filled set of *d*-orbitals.

**Oxidation States**

Transition metals show variable oxidation states due to tendency of (*n*-1)*d* as well as *ns* electrons to take part in bond formation.

For example:- Oxidation states of the first row transition metals are:

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| | +2 | +2 | +2 | **+2** | **+2** | **+2** | **+2** | +1 | **+2** |
| +3 | +3 | +3 | **+3** | +3 | **+3** | **+3** | +3 | **+2** | |
| | **+4** | +4 | +4 | +4 | +4 | +4 | +4 | | |
| | | **+5** | +5 | +5 | | | | | |
| | | | **+6** | +6 | +6 | | | | |
| | | | | **+7** | | | | | |

**Enthalpy of atomization**

The transition elements have high enthalpy of atomization which is due to the presence of strong metallic bonding. The elements with highest enthalpy of atomization tend to be noble metals. The elements of 4*d* and 5*d* series have greater enthalpies of atomization than the elements of 3*d* series. That's why the elements of 4*d* and 5*d* series have more frequent metal-metal bonding in their compounds.

**Reactivity**

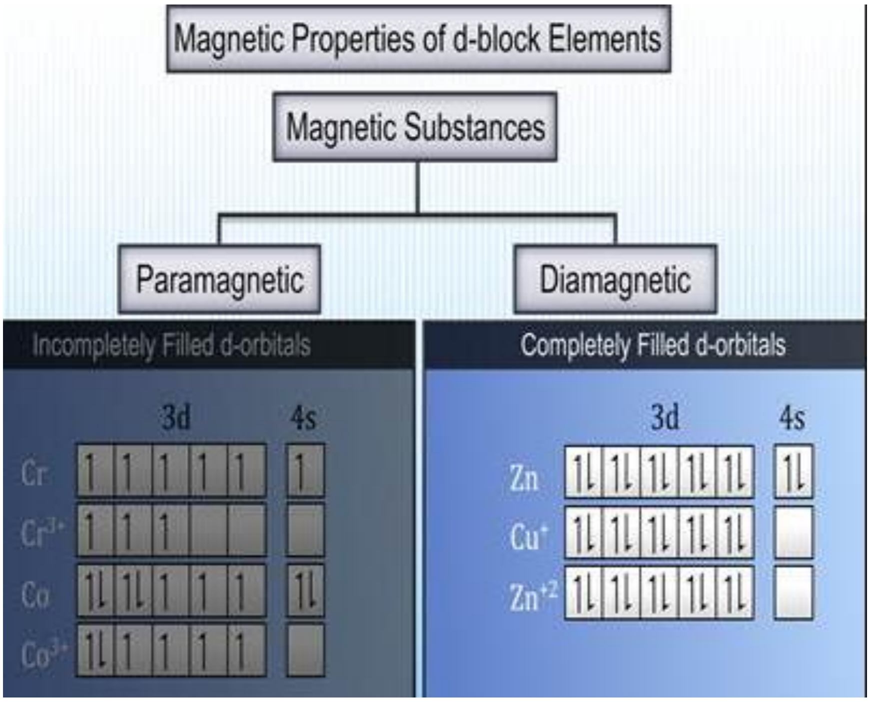
The metals of the 3*d* series are more reactive than the elements of the 4*d* or 5*d* series. All 3*d* series elements with the exception of Cu are highly reactive and are oxidized by 1 M $H^+$. The tendency to form divalent cation decreases along the 3*d* series as indicated by their $E°_{(M^{2+}/M)}$ values. The E° value does not follow a regular trend. This is due to irregularity in IE and the heat of atomisation.

**Magnetic properties**

Most of transition metals are paramagnetic in nature due to the presence of unpaired electrons. It increases from Sc to Mn due to the increased number of unpaired electrons and then starts decreasing as the number of unpaired electrons decreases.

$\mu_{eff} = \sqrt{n(n + 2)}$BM

n= no. of unpaired electrons.



**Formation of complexes**

The transition metals form a large number of complexes.

This is due to their

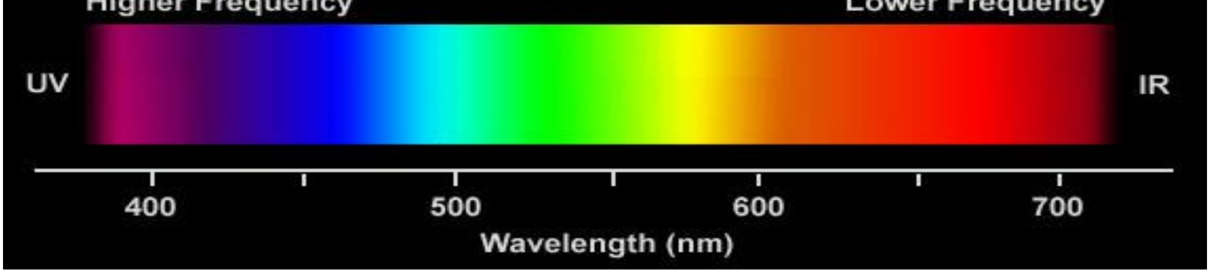
- Comparatively small sizes of the metal ions.
- High ionic charges.
- Availability of vacant d atomic orbitals

**Formation of coloured compounds**

Transition metals and their compounds show colour. The colour is due to the excitation of electron from one *d* atomic orbital to higher energy *d* atomic orbital in the same subshell. The frequency of the light absorbed generally lies in the visible region. The colour observed is due to the colour of the complementary light. The colour is due to the presence of unpaired electrons. All $Zn^{2+}$ compounds are white.

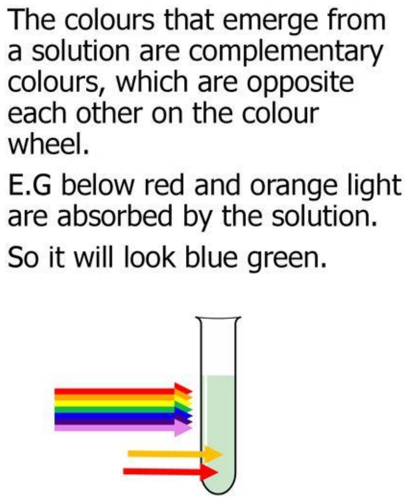
The d-orbitals of a free transition metal atom or ion are degenerate (all have the same energy.) However, when transition metals form coordination complexes, the d-orbitals of the metal interact with the electron cloud of the ligands in such a manner that the d-orbitals become non-degenerate (not all having the same energy.) The way in which the orbitals are split into different energy levels is dependent on the geometry of the complex. Crystal field theory can be used to predict the energies of the different d-orbitals, and how the d-electrons of a transition metal are distributed among them. When the d-level is not completely filled, it is possible to promote and electron from a lower energy d-orbital to a higher energy d-orbital by absorption of a photon of electromagnetic radiation having an appropriate energy. Electromagnetic radiations in the visible region of the spectrum often possess the appropriate energy for such transitions.

The sensors in our eyes detect only those wavelengths in the visible portion of the electromagnetic spectrum.



visible light appears "white", it is made up of a series of colors. White light consists of three primary colors (red, yellow and blue). These primary colors can be mixed to make three secondary colors (orange, green and violet).

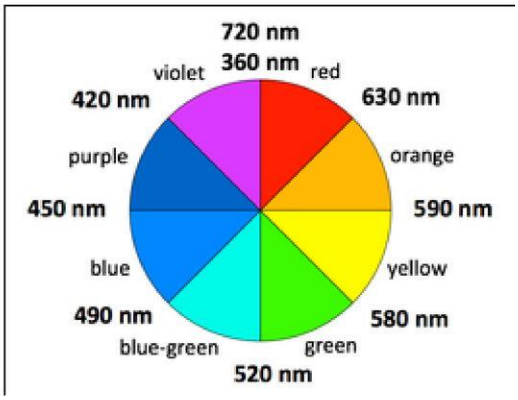
Red + Yellow makes Orange
Yellow + Blue makes Green
Blue + Red makes Violet trum.



The colours that emerge from a solution are complementary colours, which are opposite each other on the colour wheel.

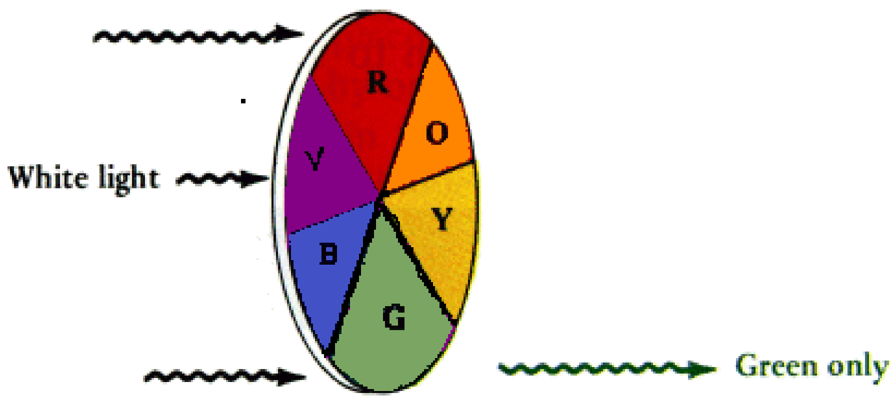
E.G below red and orange light are absorbed by the solution.

So it will look blue green.

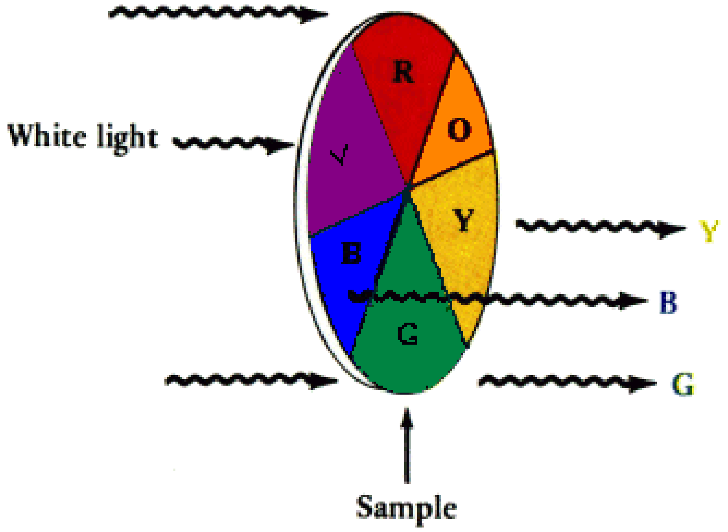


An "artist's" color wheel is a useful way show to these relationships. If you add the colors on opposite sides of the wheel together, white light is obtained. We only detect colors when one or more of the wavelengths in the visible spectrum have been absorbed, and thus removed, by interaction with some chemical species (see an animation of this here.) When the wavelengths of one or more colors is absorbed, it is the colors on the opposite side of the color wheel that are transmitted.

(a) Sample absorbs all but green light. Green is perceived.

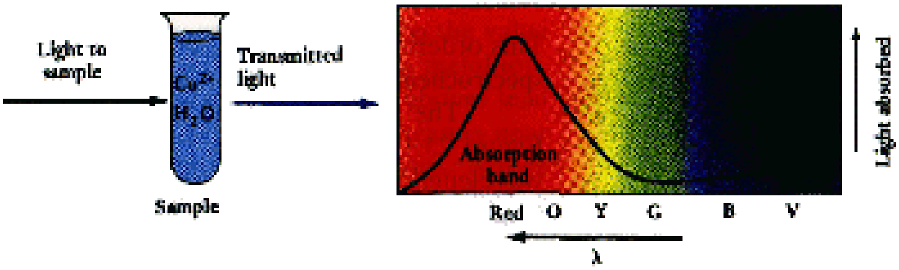


(b) Sample absorbs violet, red, and orange light. Blue, green, and yellow light are transmitted. Green light is perceived.

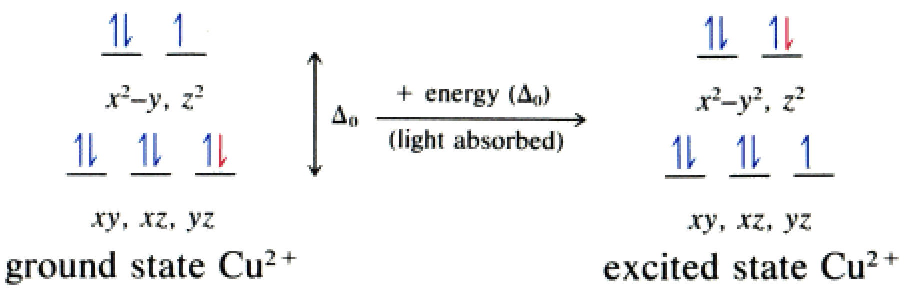


Transition Metal Complexes

When light passes through a solution containing transition metal complexes, we see those wavelengths of light that are transmitted. The solutions of most octahedral Cu (II) complexes are blue. The visible spectrum for an aqueous solution of Cu (II), [Cu(H2O6]2+, shows that the absorption band spans the red-orange-yellow portion of the spectrum and green, blue and violet are transmitted.



The absorption band corresponds to the energy required to excite an electron from the t2g level to the eg level.



Recall, the energy possessed by a light wave is inversely proportional to its wavelength. The Cu(II) solution transmits relatively high energy waves and absorbs the low energy wavelengths. This indicates that the band gap between the two levels is relatively small for this ion in aqueous solution.

d-Orbital Splitting

The magnitude of the splitting of the d-orbitals in a transition metal complex depends on three things:

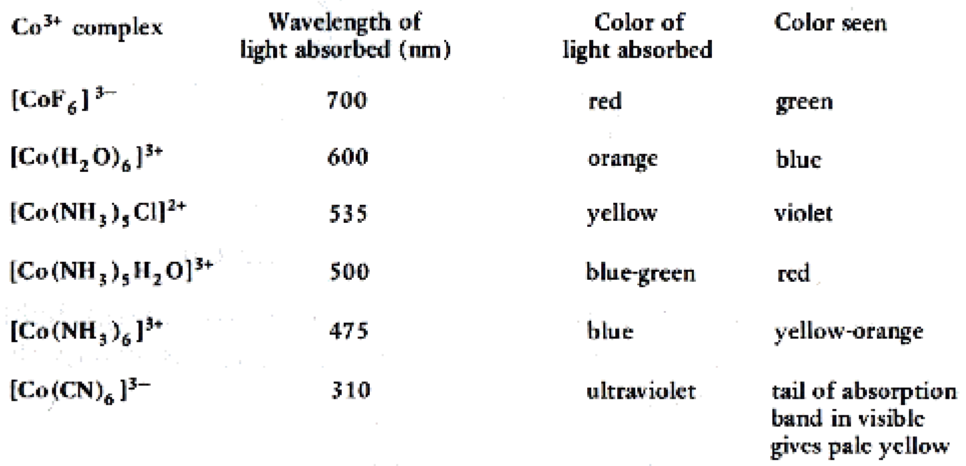
the geometry of the complex

the oxidation state of the metal

the nature of the ligands

The Nature of the Ligands

Some ligands only produce a small energy separation among the d-orbitals while others cause a wider band gap. Ligands that cause a small separation are called weak field ligands, and those that cause a large separation are called strong field ligands. The ordering of their splitting ability is called the spectrochemical



| $Co^{3+}$ complex | Wavelength of light absorbed (nm) | Color of light absorbed | Color seen |
|---|---|---|---|
| $[CoF_6]^{3-}$ | 700 | red | green |
| $[Co(H_2O)_6]^{3+}$ | 600 | orange | blue |
| $[Co(NH_3)_5Cl]^{2+}$ | 535 | yellow | violet |
| $[Co(NH_3)_5H_2O]^{3+}$ | 500 | blue-green | red |
| $[Co(NH_3)_6]^{3+}$ | 475 | blue | yellow-orange |
| $[Co(CN)_6]^{3-}$ | 310 | ultraviolet | tail of absorption band in visible gives pale yellow |

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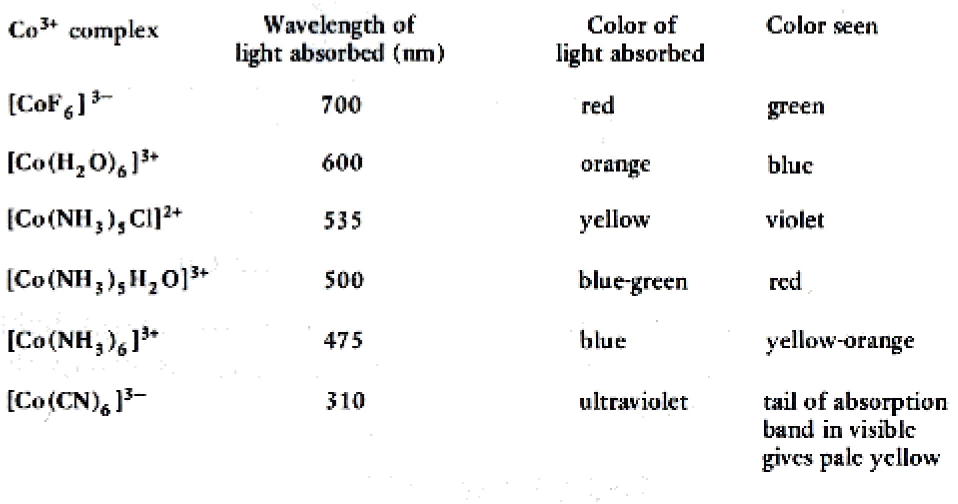
A comparison of the visible absorption maxima for a number of cobalt (III) complexes shows the effects of ligands on the d-orbital band gap.



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**Formation of interstitial compounds**

Transition metals have lattice structure in which the unoccupied space is called void or hole or interstices. Transition metals entrap smaller but highly electronegative elements in these interstices and results in the formation of interstitial compounds. Interstitial com-pounds have high melting points, hardness and retain metallic conductivity. The interstitial compounds are chemically inert. Examples are TiC, steel.

Some of their important characteristics are as follows:

(i) They are very hard and rigid, e.g., steel which is an interstitial compound of Fe and Cis quite hard. Similarly, some borides are as hard as diamond.

(ii) They have high melting points which are higher than those of the pure metals.

(iii) They show conductivity like that of the pure metal.

(iv) They acquire chemical inertness

**Formation of alloys**

Alloy is a homogeneous mixture of two or more metals. Due to the comparable size of transition metals, one metal can displace other metal in the crystal lattice and this results in the alloy formation. The alloys so formed are hard and have high melting points. The best known are ferrous alloys; chromium, vanadium, tungsten, manganese are used for the production of variety of steels and stainless steels.

**Catalytic properties**

Most of transition metals are used as catalysts.

This is due to the

(i) presence of incomplete or empty *d*-orbitals,
(ii) large surface area and

(iii) variable oxidation state. For example Fe, Ni, $V_2O_3$, Pt, Mo, Co, etc., are used as catalyst.

$$N_2(g)+3H_2(g)\xrightarrow{Fe}2NH_3(g)$$

$$C_2H_4(g)+H_2(g)\xrightarrow{Ni}C_2H_6(g)$$

**Formation of oxides**
Transition metals form oxides on reaction with oxygen at elevated temperature. Transition metal form oxide in oxidation state of + 1 (in $Ag_2O$) to + 7 ($Mn_2O_7$) to + 8 (in $OsO_4$). As the oxidation number increases in case of same elements,

(a) The covalent character of oxides increases.

(b) The acidic strength of the oxides increases.

(c) The oxidizing power of oxides increases.

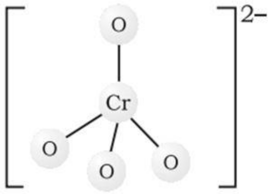
For example, $Cr_2O_3$ is amphoteric while CrO is basic and $CrO_3$ is acidic.

**Some Important Compounds of Transition Elements**
**Potassium dichromate, $K_2Cr_2O_7$**
**Preparation:**
It is prepared by fusion of chromate ore (FeCr2O4) with sodium carbonate in excess of air.

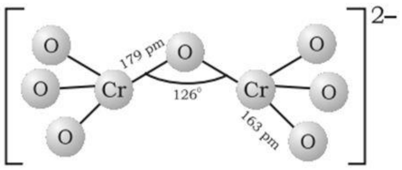
$8Na_2CO_3 + 4FeCr_2O_4 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
Yellow
$Na_2CrO_4$ produced in the above reaction is then acidified to get sodium dichromate, $Na_2Cr_2O_7$
$Na_2CrO_4$ produced in the above reaction is then acidified to get sodium dichromate, $Na_2Cr_2O_7$
$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$
Orange

Solution of sodium dichromate treated with potassium chloride to get the final product, $K_2Cr_2O_7$.
$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$
Orange Crystals

Structures of $CrO_4^{2-}$ and $Cr_2O_7^{2-}$ ions:



Chromate ion
(Tetrahedral)



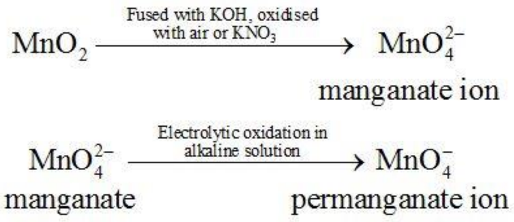
Dichromate ion
(Double tetrahedral)

**Uses:**
Potassium dichromate is used as a primary standard in volumetric analysis and as an oxidizing agent. In acidic medium, the oxidation state of Cr changes from + 6 in $Cr_2O_7^{2-}$ to + 3 in $Cr^{3+}$.
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
**Potassium permanganate, $KMnO_4$**
**Preparation:**
It is prepared by fusion of $MnO_4$ with alkali metal hydroxide (KOH) in presence of $O_2$ or oxidising agent like $KNO_3$. It produces dark green coloured compound , $K_2MnO_4$ which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

$$2KOH+\underset{\text{black}}{MnO_2}+\frac{1}{2}O_2\rightarrow\underset{\text{green}}{K_2MnO_4}+H_2O$$

$$3MnO_4^{2-}+4H^+\rightarrow 2MnO_4^-+MnO_2+2H_2O$$

Commercially it is prepared by the alkaline oxidative fusion of MnO2 followed by the electrolytic oxidation of manganate (VI).



**Uses:**
Potassium permanganate acts as a strong oxidizing agent in acidic, neutral or faintly basic medium.

**In acidic medium:**
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4\ H_2O$
Oxidises $Fe^{2+}$ to $Fe^{3+}$:
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
**In an alkaline medium:**
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$
Oxidises $I^-$ to iodate $IO_3^-$:
$6OH^- + I^- \rightarrow IO_3^- + 6e^- + 3H_2O$

### *f* –Block elements or Inner Transition elements

The elements in which the differentiating electron enters the penultimate energy level i.e. (n−2)*f*, are called *f*-block elements. Due to such electronic configuration where the last electron enters the 4*f* or 5*f* orbitals that are lower than the outermost electrons, *f*-block elements are also named as *inner transition elements*.
Depending upon the fact whether the last electron enters the 4*f* or 5*f*-orbitals, *f*-block elements are differentiated into lanthanoids and actinoids.

**1. Lanthanoids:** The 14 elements immediately following lanthanum, i.e., Cerium (58) to Lutetium (71) are called lanthanoids. They belong to first inner transition series. Lanthanum (57) has similar properties.
***General properties of lanthanoids:***

- **Electronic configuration:** The general electronic configuration of the lanthanoids is

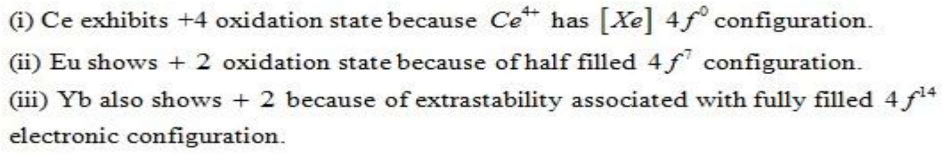
| | | | | | |
|---|---|---|---|---|---|
| | | | | | |
| Element | | Electronic Configuration | | Electronic Configuration of $M^3$ | Oxidation States |
| Lanthanum | | [Xe] $5d^1$ $6s^2$ | | [Xe] | |
| Cerium | Ce | [Xe] $4f^1$ $5d^1$ | $6s^2$ | [Xe] $4f^1$ | +3 |
| Praseodymium | Pr | [Xe] $4f^3$ | $6s^2$ | [Xe] $4f^2$ | +3, +4 |
| Neodymium | Nd | [Xe] $4f^4$ | $6s^2$ | [Xe] $4f^3$ | +2 ,+3 |
| Promethium | Pm | [Xe] 4f | $6s^2$ | [Xe] $4f^3$ | +2,+3 |
| Samarium | Sm | [Xe] $4f^6$ | $6s^2$ | [Xe] $4f^5$ | +2,+3 |
| Europium | Eu | [Xe] $4f^7$ | $6s^2$ | [Xe] $4f^6$ | +2,+3 |
| Gadolinium | Gd | [Xe] $4f^7$ $5d^1$ | $6s^2$ | [Xe] $4f^7$ | +3, |
| Terbium | Tb | [Xe] $4f^9$ | $6s^2$ | [Xe] $4f^8$ | +3, +4 |
| Dysprosium | Dy | [Xe] $4f^{10}$ | $6s^2$ | [Xe] $4f^9$ | +3, +4 |
| Holmium | Ho | [Xe] $4f^{11}$ | $6s^2$ | [Xe] $4f^{10}$ | +3 |
| Erbium | Er | [Xe] $4f^{12}$ | $6s^2$ | [Xe] $4f^{11}$ | +3 |
| Thulium | Tm | [Xe] $4f^{13}$ | $6s^2$ | [Xe] $4f^{12}$ | +2 +3 |
| Ytterbium | Yb | [Xe] $4f^{14}$ | $6s^2$ | [Xe] $4f^{13}$ | +2 +3 |
| Lutetium | Lu | [Xe] $4f^{14}$ $5d^1$ | $6s^2$ | [Xe] $4f^{14}$ | +3 |
| | | | | | |

- **Atomic and ionic Sizes:** The decrease in in atomic and ionic radii from lanthanum to lutetium is not quite regular but there is a regularity in the size of $M^{3+}$ ions. The regular decrease in size of $M^{3+}$ ion is attributed to the imperfect shielding of one electron by another in the same *4f* subshell. This regular decrease in size amongst lanthanides as atomic number increases is known as the *lanthanoid contraction*.
- As we move along the lanthanide series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell (viz., 4f). As a result, the attraction on the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the f-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these f-orbitals. This imperfect shielding is unable to counterbalance the effect of the increased nuclear charge. Hence, the net result is a contraction in the size though the decrease is very small. It is interesting to note that in lanthanides, the decrease in the atomic radius for 14 elements [Ce (58) to Lu (71)] is only 11pm (from 183 to 172 pm).
- Similarly, decrease in ionic radii from $Ce^{3+}$ to $Lu^{3+}$ is only 17 pm (103 to 86 pm)
- The contraction is similar to that observed in any transition series. The cause is also similar, just as in the transition series where the contraction is due to imperfect shielding of one d electron by another. But the shielding of one 4f electron by another is less than one d electron by another with increase in nuclear charge along the series.

| lement | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| tomic Radii (Ln) | 187 | 183 | 182 | 181 | 181 | 180 | 199 | 180 | 178 | 177 | 176 | 175 | 174 | 173 | 172 |
| onic Radii ($Ln^{3+}$) | 106 | 103 | 101 | 99 | 98 | 96 | 95 | 94 | 92 | 91 | 90 | 89 | 88 | 87 | 86 |

**Formation of coloured ions:** Lanthanide form ions which are coloured in both solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f-electron.Exception: $Lu^{3+}$ ions do not show any colour due to the absence of any unpaired electron in the *4f* subshell which is fully filled.

- **Magnetic character:** Lanthanide ions also show paramagnetism. In lanthanides, the magnetic moment is due to both spin magnetic moment as well as orbital magnetic moment.
- **Oxidation state:** The most common oxidation state of lanthanides is + 3 which is obtained by using two electrons in 6*s* and one electron from 5*d* subshell.
  Exception: Some elements show +2 and +4 oxidation states. This irregularity arises mainly from the extra stability of empty, half-filled or filled *f* subshell.
  For example:



(i) Ce exhibits +4 oxidation state because $Ce^{4+}$ has $[Xe]\ 4f^0$ configuration.

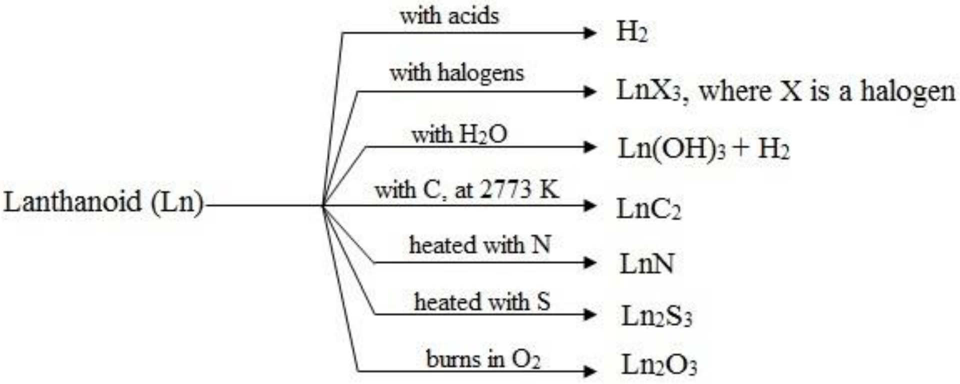
(ii) Eu shows + 2 oxidation state because of half filled $4f^7$ configuration.

(iii) Yb also shows + 2 because of extrastability associated with fully filled $4f^{14}$ electronic configuration.

**Physical properties of lanthanoids:**

- All the lanthanoids are silvery white soft metals and tarnish rapidly in air, the hardness increases with increasing atomic number.
- The melting points range between 1000 to 1200 K but samarium melts at 1623 K.
- They are also good conductors of heat and electricity.

**Chemical properties of lanthanoids:**
Some important chemical reactions of lanthenoids are:



**Formation of alloys:** Lanthanoids are all used in steel industry for making alloy steels. Important and well-known alloy is misch-metal and it con-sists of lanthanoid (90-95%), iron (4-5%) and trace amount of S, C Ca and Al.
***Uses:***
(i) Misch-metal is used in making tracer bullets, shell and lighter flint.

(ii) Mixed oxides of lanthanoids are used as a catalyst in petroleum cracking. Some individual oxides of lanthanoids are used as phosphors in television screens and similar fluorescing surface.

**2. Actinoids:** The 14 elements immediately following actinium (89), with atomic numbers 90 (Thorium) to 103 (Lawrencium) are called actinoids. They belong to second inner transition series. In actinoids the filling of electrons takes place in the anti-penultimate subshell.
***General properties of actinoids:***

- **Electronic configuration:** The general electronic configurations for the actinoids is $[Rn]5f^{1-14}6d^{0-1}7s^2$ , where Rn is the electronic configuration of the element Radium. The fourteen electrons are formally added to though not in Thorium but onwards from it and the 5f subshell is complete at Lr (Z = 103). The irregularities in the electronic con-figuration of the actinoids are releated to the stabilities of empty, half-filled or filled *f* subshell.

| Atomic | Element | Symbol | Outer electronic structure | Oxidation states* |
|---|---|---|---|---|
| 89 | Actinium | Ac | $6d^1 7s^2$ | +3 |
| 90 | Thorium | Th | $6d^2 7s^2$ | +3, +4 |
| 91 | Protactinium | Pa | $5f^2 6d^1 7s^2$ | +3, +4, +5 |
| 92 | Uranium | U | $5f^3 6d^1 7s^2$ | +3, +4, +5, +6 |
| 93 | Neptunium | Np | $5f^4 6d^1 7s^2$ | +3, +4, +5,+ 6, +7 |
| 94 | Plutonium | Pu | $5f^6 \quad 7s^2$ | +3, +4, +5, +6, +7 |
| 95 | Americium | Am | $5f^7 \quad 7s^2$ | +2, +3, +4, +5, +6 |
| 96 | Curium | Cm | $5f^7 6d^1 7s^2$ | +3, +4 |
| 97 | Berkelium | Bk | $5f^9 \quad 7s^2$ | +3, +4 |
| 98 | Californium | Cf | $5f^{10} \quad 7s^2$ | +2, +3 |
| 99 | Einsteinium | Es | $5f^{11} \quad 7s^2$ | +2, +3 |
| 100 | Fermium | Fm | $5f^{12} \quad 7s^2$ | +2, +3 |
| 101 | Mendelevium | Md | $5f^{13} \quad 7s^2$ | +2, +3 |
| 102 | Nobelium | No | $5f^{14} \quad 7s^2$ | +2 ,+3 |
| 103 | Lawrencium | Lr | $5f^{14} 6d^1 7s^2$ | +3 |
| 104 | Rutherfordium | Rf | $4f^{14} 6d^2 7s^2$ | |

- **Oxidation state:** The dominant oxidation state of actinoids is +3. However they also show variable oxidation states due to the comparable energy of 5*f*, 6*d* and 7*s* subshells.For example: The uranium shows oxidation states of and. The element neptunium (Z = 93) show an oxidation state upto +7.
- **Magnetic character:** Actinoids also show paramagnetism but their magnetic properties are much more complex than those of the lanthanoids.
- **Atomic and ionic sizes:** In actinides, the ionic radii decreases as we move down the series. This decrease in ionic radius is termed as actinide contraction. This effect is due to poor screening offered by 5*f* electrons.

- **Ionisation enthalpy:** The ionisation enthalpies of actinoids are lower than those of corresponding lanthanoids. This is because the orbitals in actinoids penetrate less into the inner core of electrons, and the electrons are more effectively shielded from the nuclear charge than are the electrons of the corresponding lanthanoids. As the outer electrons are less tightly held, less amount of energy is required to ionise an atom.
- **Metallic character:** The actinoids are all metals with silvery appearance. These metals are highly reactive when finely divided.

**Chemical properties:**

- They react with boiling water to give a mixture of oxide and hydride.
- All these metals are attacked by HCl but slightly affected by $HNO_3$ due to the formation of a protective oxide layer on their surface.
- They combine with most of the non-metals at moderate temperature.

Similarities :

As both Lanthanides and actinides involve filling of f- orbitals, they show similarities in many respects as follows :

(i) Both show mainly an oxidation state of +3.

(ii) Both are electropositive and very reactive.

(iii) Both exhibit magnetic and spectral properties.

Actinides exhibit Actinide contraction like Lanthanide contraction shown by Lanthanides

Differences :

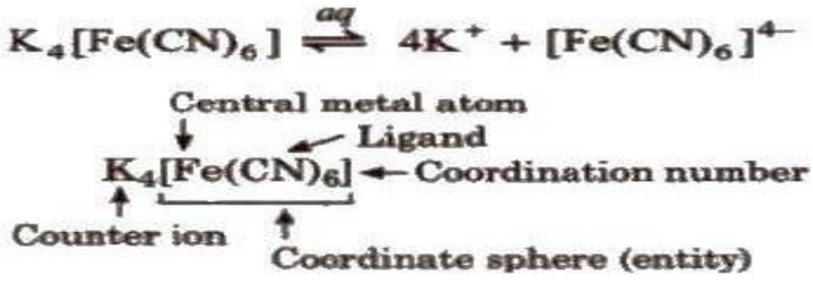
The show differences in some of their characteristics as follows :

| Lanthanides | Actinides |
|---|---|
| (i) Besides + 3 oxidation state they show + 2 and +4 oxidation states only in few cases. | (i) Besides +3 oxidation state, they show higher oxidation states of +4, +5, +6, + 7 also. |
| (ii) Most of their ions are colourless | (ii) Most of their ions are coloured |
| (iii) They have less tendency towards complex formation | (iii) They have greater tendency towards complex formation. |
| (iv) Lanthanides compounds are less basic. | (iv) Actinides compounds are more basic |
| (v) Do not form oxocation | (v) From oxocations e.g. $UO_2^{2+}$ , $PuO_2^{2+}$ and $UO^+$ |
| (vi) Except promethium, they are non-radioactive | (vi) They are radioactive. |
| (vii) Their magnetic properties can be explained easily can be explained easily. | (vii) Their magnetic properties cannot be explained easily, as they are more complex. |

## Chapter 9

## Coordination Compounds

Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds. the central metal atom or ion is linked by ions or molecules with coordinate bonds. e.g., Potassium ferrocyanide, $K_4$ [Fe(CN)$_6$].



**Double Salts**

These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr'S salt, [$FeSO_4 \cdot (NH_4)_2SO_4$ . $6H_2O$ get dissociated into $Fe^{2+}$, $NH_4^+$ and $SO_4^{2-}$ ions.

**Terms Related to Coordination Compounds**

### 1. Complex ion or Coordination Entity

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

(i) **Cationic complex entity** It is the complex ion which carries positive charge. e.g., $[Pt(NH_3)_4]^{2+}$

(ii) **Anionic complex entity** It is the complex ion which carries negative charge. e.g., $[Fe(CN)_6]^{4-}$

### 2. Central Atom or Ion

The atom or ion to which a fixed number of ions or groups are bound is .ned central atom or ion. It is also referred as Lewis acid. e.g., in $(NiCl_2(H_2O)_4]$. Ni is central metal atom. It is generally transition element or inner-transition element.

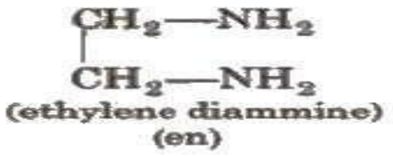
### 3. Ligands

Ligands is electron donating species (ions or molecules) bound to the Central atom in the coordination entity. These may be charged or neutral. LIgands are of the following types :

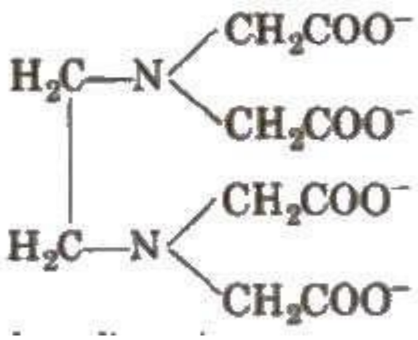
(i) **Unidentate** It is a ligand, which has one donor site, i.e., the ligand bound to a metal ion through a single donor site. e.g., $H_2O$, $NH_3$, etc.

(ii)**Didentate** It is the ligand. which have two donor sites.

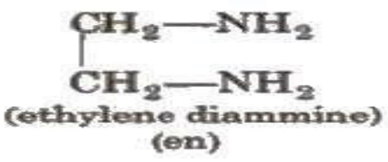

(oxalate ion)
(ox)


(ethylene diammine)
(en)

**(iii)Polydentate** It is the ligand, which have several donor sites. e.g., $[EDTA]^{4-}$ is hexadentate ligand.




(oxalate ion)
(ox)


(ethylene diammine)
(en)

(iii) **Ambidentate ligands** These are the monodentate ligands which can ligate through two different sites, e.g., $NO^{-2}$, $SCN^-$, etc.

(iv)**Chelating ligands** Di or polydentate ligands cause cyclisation around the metal atom which are known as chelate IS , Such ligands USes two or more donor atoms to bind a single metal ion and are known as chelating ligands.

More the number of chelate rings, more is the stability of complex.

The stabilisation of coordination compounds due to chelation is known as **chelate effect**.

π – acid ligands are those ligands which can form π – bond and n-bond by accepting an appreciable
amount of 1t electron density from metal atom to empty π or π – orbitals.

### 4. Coordination Number

It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

e.g., in $[PtCl_6]^{2-}$, Pt has coordination number 6.
In case of monodentate ligands, Coordination number = number of ligands In polydentate ligands.
Coordination number = number of ligands * denticity.

### 5. Coordination Sphere

The central ion and the ligands attached to it are enclosed in square bracket which is known as coordination sphere. The ionisable group written outside the bracket is known as counter ions.

### 6. Coordination Polyhedron

The spatial arrangement of the ligands which are directly attached to the central atom or ion, is called coordination polyhedron around the central atom or ion.

### 7. Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called oxidation number of central atom.

e.g., $[CU(CN_4)_{3-}$, oxidation number of copper is +1, and represented as Cu(I).

**Types of Complexes**

1. **Homoleptic complexes**

Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes e.g., $[Co(NH_3)_6]^{3+}$

**2.Heteroleptic complexes**

Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g., $[Co(NH_3)_4Cl_2]^+$

**3.Labile and Inert complexes**

Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow, are known as inert complexes.

**Effective Atomic Number** (EAN)

This concept was proposed by Sidgwick. In a complex, the EAN of metal atom is equal to the total number of electrons present in it.

EAN = Z – ON of metal + 2 * CN (where, Z =

atomic number of metal atom ON = oxidation

number of metal

and CN = coordination number of complex)

An ion with central metal atom having EAN equal to next inert gas will be more stable.

**IUPAC Naming of Complex Compounds**

Naming is based on set of rules given by IUPAC.

1. Name of the compound is written in two parts (i) name of cation, and (ii) name of anion.

2. The cation is named first in both positively and negatively charged coordination complexes.

3. The dissimilar ligands are named in au alphabetical order before the name of central metal atom or ion.
4. For more then one similar ligands. the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.

5. If the complex part is anion, the name of the central metal ends with suffix ‘ate’.

6. Names of the anionic ligands end in ‘0’, names of positive ligands end with ‘ium’ and names of neutral ligands remains as such. But exception are there as we use aqua for $H_2O$, ammine for $NH_3$, carbonyl for CO and nitrosyl for NO.

7. Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses.

8. The name of the complex part is written as one word.

9. If the complex ion is a cation, the metal is named same as the element.

10. The neutral complex molecule is named similar to that of the complex cation.

Some examples are

(i) $[Cr(NH_3)_3(H_2O)_3]Cl_3$

triamminetrichlorochromium (III) chloride

(ii) $[Co(H_2CH_2CH_2H_2)_3]_2(SO_4)_3$

tris (ethane-l,2-diamine) cobalt (III) sulphate

(iii) $Ag(NH_3)_2]$ $[Ag(CN)_2]$

diamminesilver (I) dicyanoargentate(I)

(iv) $K_4$ $[Fe(CN)_6]$

potassium hexacyanoferrate (II)

## Isomerism in Coordination Compounds

Coordination compounds exhibit the following types of isomerism: 1.**Structural Isomerism**

In this isomerism. isomers have different bonding pattern.

Different types of structural isomers are

1. **Linkage isomerism** This type of isomerism is shown by the coordination compounds having ambidentate ligands. e.g.,$[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$ or pentaammine nitrito- N Cobalt (III) chloride and pentaammine nitrito-O'Cobalt (III) chloride.
2. **Coordination isomerism** This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex, e.g.,$[Cr(NH_3)_6)$ $[CO(CN)_6]$and $[CO(NH_3)_6]$ $[Cr(CN)_6]$
3. **Ionisation isomerism** This isomerism arise due to exchange of ionisable anionwith anionic ligand. e.g..

$$\underset{\text{(red)}}{[Co(NH_3)_5SO_4]Br} \quad \text{and} \quad \underset{\text{(violet)}}{[Co(NH_3)_5Br]SO_4}$$

(i) **Solvate isomerism** This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside it. e.g..

$[Co(H_2O)_6]Cl_3$, $[Co(H_2O)_4C1_2]Cl\cdot 2H_2O$, $[Co(H_2O)_3Cl_3]$. $3H_2O$

2. **Stereoisomerism**

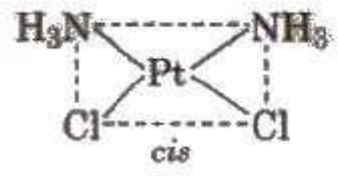
Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. These are of two types :

(i) **Geometrical isomerism** Geometrical isomers are of two types i.e., cis and trans isomers. This isomensm is common in complexes with coordination number 4 and 6.

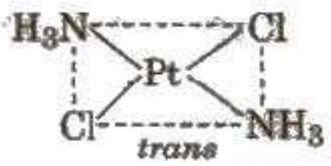
**Geometrical isomerism in complexes with coordination number 4**

(i) Tetrahedral complexes do not show geometrical isomerism.

(ii) Square planar complexes of formula [$MX_2L_2$] (X and L are unidentate) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer, e.g.,



cis



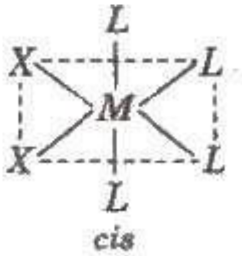
trans

(iii) Square planar complex of the type [MABXL] (where A, B, X, L, are unidentateligands) shows three isomers, two cis and one trans.

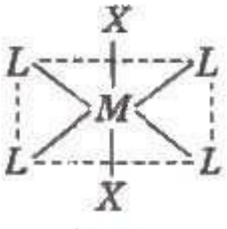
e.g., [$Pt(NH_3)$ (Br)(Cl)(Py)].

**Geometrical isomerism in complexes with coordination number 6**

Octahedral complexes of formula [$MX_2L_4$], in which the two X ligands may be oriented cis or trans to each other, e.g., $[Co(NH_3)_4Cl_2)^+$.



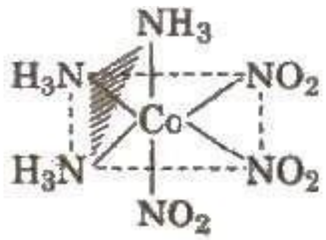
cis



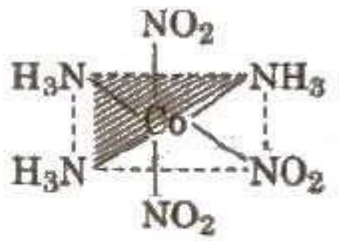
trans

Octahedral complexes of formula [$MX_2A_2$], where X are unidentate ligands and A are bidentate ligand. form cis and trans isomers, e.g., [$CoC1_2(en)_2$]’

In octahedral complexes of formula [$MA_3X_3$], if three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face. it is known as facial (fae) isomer, when the positions are around the meridian of the octahedron, it is known as meridional (mer) isomer. e.g., [$Co(NH_3)_3(NO_2)_3$]



*fac*



*mer*

(ii) **Optical isomerism** These are the complexes which have chiral structures. It arises when mirror images cannot be superimposed on one another. These mirror images are called enantiomers. The two forms are called dextro (d) and laevo (l) forms.

Tetrahedral complexes with formula [M(AB)$_2$] show optical isomers and octahedral complexes (cis form) exhibit optical isomerism.

**Bonding in Coordination Compounds**

**Werner's Theory**

Metals exhibit two types of valencies in the formation of complexes. These are

primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.

2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

**Valence Bond Theory** (VBT)

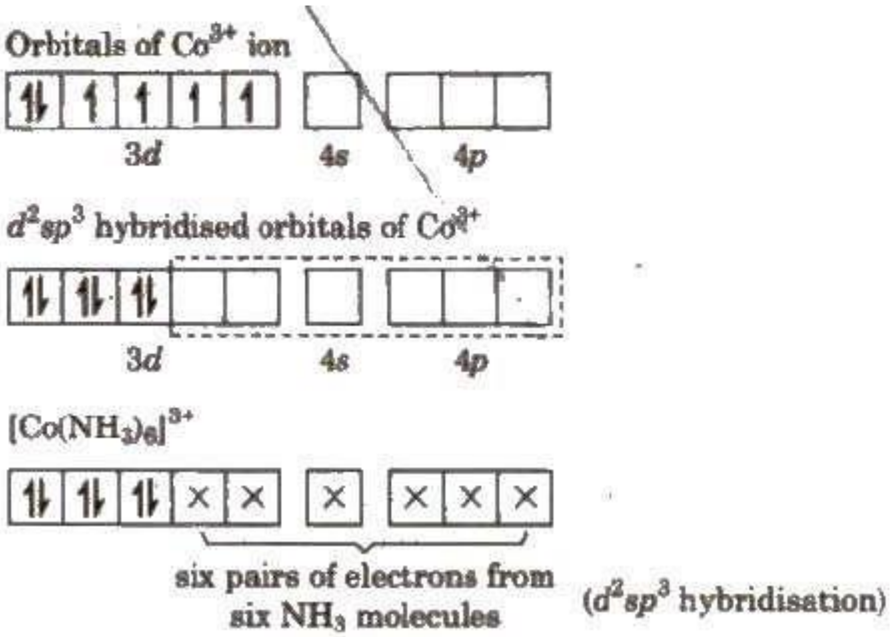
This theory was proposed by L. Pauling in 1930 s. According to this theory, when a complex is formed, the metal ion/atom provides empty orbitals to the surrounding ligands. Coordination number shows the number of such empty orbitals, i.e., number of empty orbitals is equal to the coordination number. These empty orbitals hybridised before participation in bonding and the nature of hybridisation depends on the nature of metal and on the nature of approaching ligand.

**Inner orbital complexes or outer orbital complexes**

When outer d-orbital are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation is $sp^3d^2$. They have octahedral shape.When d-orbitals of (n – 1) shell are used, these are known as inner orbital complex, they are formed due to strong field ligands or low spin ligands and hybridisation is $d^2sp^3$. They are also octahedral in shape.

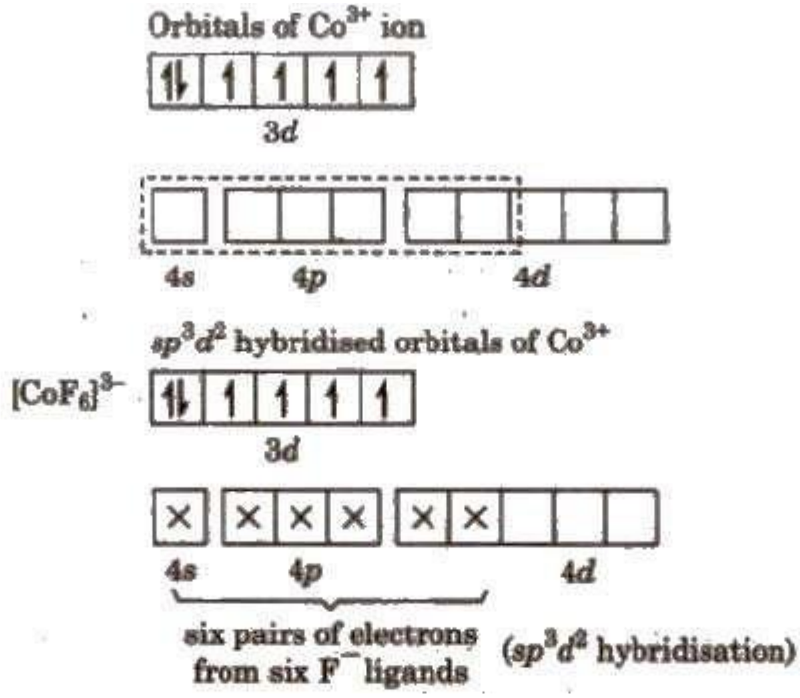
1. **6 – ligands** (unidentate), **octahedral entity.**

(i) **Inner orbital complex** $[Co(NH_3)_6]^{3+}$



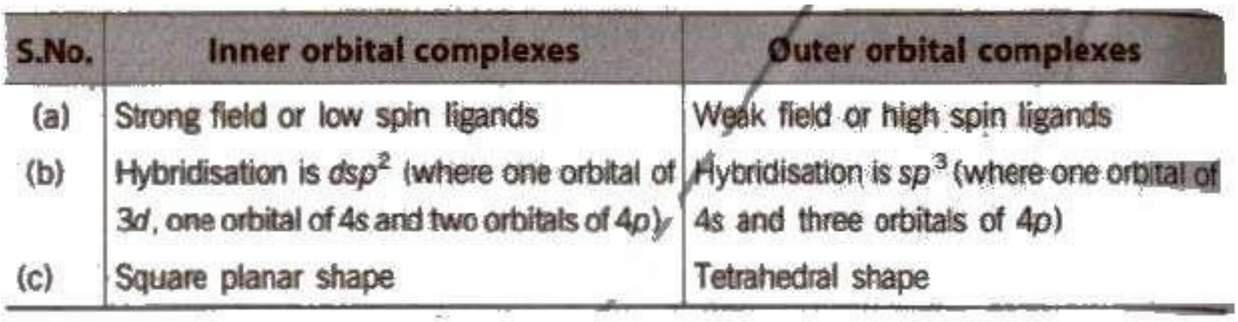
All electrons are paired, therefore complex will be diamagnetic in nature.

(ii) **Outer orbital complex,** $[CoF_6]^{3-}$



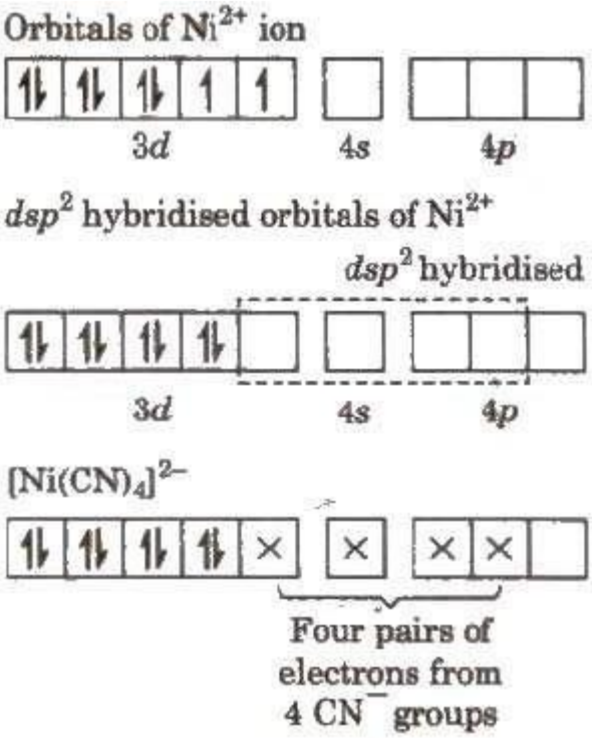
Complex has unpaired electrons, therefore, it will be paramagnetic in nature.

2. **4-ligands** (unidentate) **tetrahedral entity**.



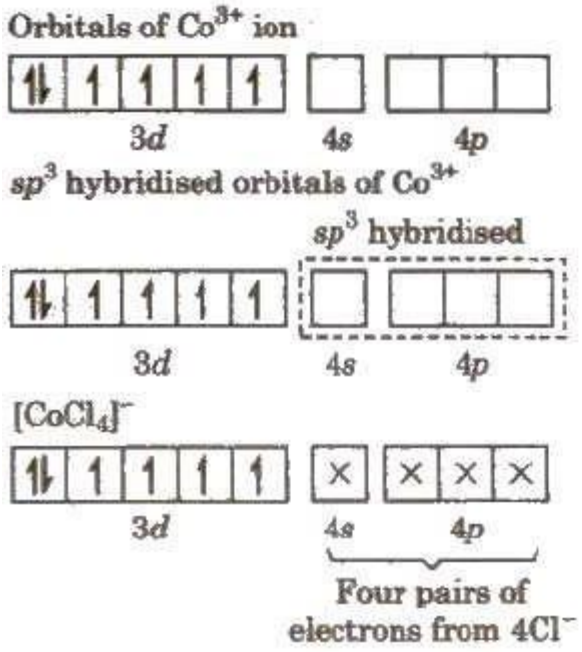
| S.No. | Inner orbital complexes | Outer orbital complexes |
|---|---|---|
| (a) | Strong field or low spin ligands | Weak field or high spin ligands |
| (b) | Hybridisation is $dsp^2$ (where one orbital of 3$d$, one orbital of 4$s$ and two orbitals of 4$p$) | Hybridisation is $sp^3$ (where one orbital of 4$s$ and three orbitals of 4$p$) |
| (c) | Square planar shape | Tetrahedral shape |

(i) **Inner orbital complex,** $[Ni(CN)_4]^{2-}$



All electrons are paired so complex will be diamagnetic in nature.

(ii) **Outer orbital complex,** $[CoCl_4]^-$



Since, complex has unpaired electrons. so it will be paramagnetic in nature.

**Limitations of VBT**

This theory could not explain the quantisation of the magnetic data, existence of inner orbital and outer orbital complex, change of magnetic moment with temperature and colour of complexes.

**Crystal Field Theory** (eFT)

This theory was proposed by H. Bethe and van Vleck. Orgel. in 1952, applied this theory to coordination compounds. In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

The five d-orbitals are classified as

(i) Three d-orbitals i.e., $d_{xy}$, $d_{yz}$ and $d_{zx}$ are oriented in between the coordinate axes and are called $t_{2g}$ – orbitals.

(ii) The other two d-orbitals, i.e., $d_{x^2-y^2}$ and $d_{z^2}$ oriented along the x – y % axes are called $e_g$ – orbitals.

Due to approach of ligands, the five degenerate d-orbitals split. Splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between $t_{2g}$ and $e_g$ level is designated by Δ and is called **crystal field splitting energy.**]

By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO.$$

**Crystal field splitting in octahedral complexes**

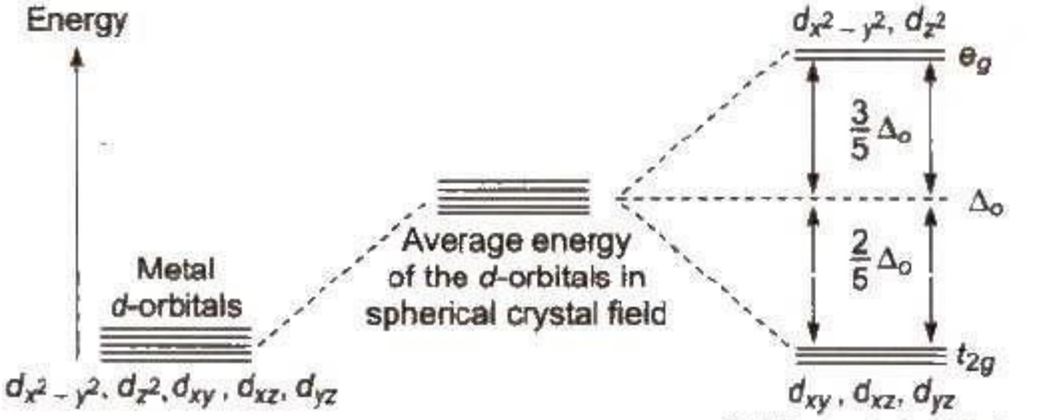
In case of octahedral complexes, energy separation is denoted by $\Delta_o$ (where subscript 0 is for octahedral).

In octahedral complexes, the six-ligands approach the central metal ion along the axis of $d_{x^2-y^2}$ and $d_{z^2}$ orbitals.

Energy of $e_g$ set of orbitals > energy of $t_{2g}$ set of orbitals.
The energy of $e_g$ orbitals will increase by (3/5) $\Delta_o$ and $t_{2g}$ will decrease by (2/5) $\Delta_o$.

If $\Delta_o < P$, the fourth electron enters one of the $e_g$ orbitals giving the configuration $t^3_{2g}\ e^1_g$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a $t_{2g}$ orbital with configuration $t^4_{2g}\ e^o_g$. (where, P = energy required for $e^-$ pairing in an orbital).
Ligands which produce this effect are known as strong field ligands and form low spin complexes.



Splitting of d-orbitals in octahedral crystal field

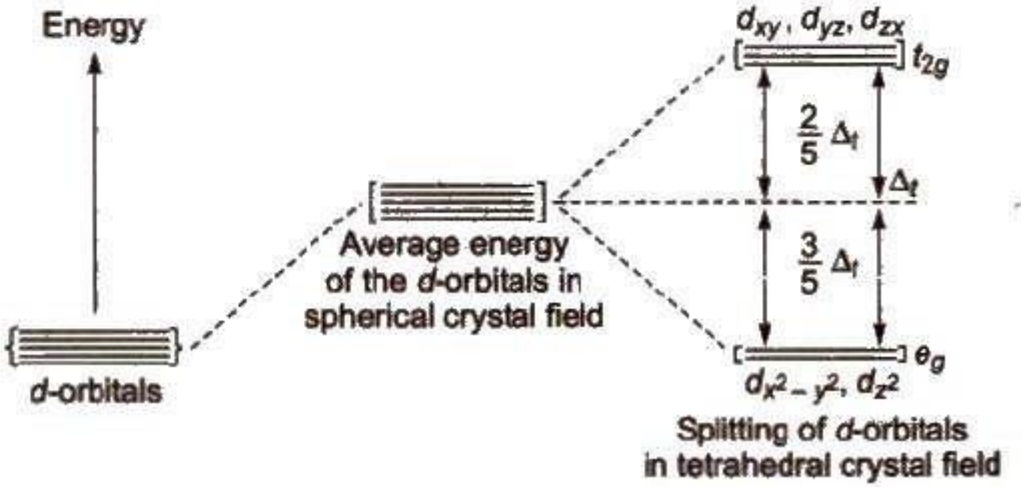
**Crystal field splitting in tetrahedral complexes**

In tetrahedral complexes, four ligands may be imagined to occupy the alternate comers of the cube and the metal ion at the center of the cube.

Energy of $t_{2g}$ set of orbitals > Energy of $e_g$ set of orbitals.

In such complexes d – orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Orbital splitting energies are so low that pairing of electrons are not possible so these are high spin complexes.



### Colour in Coordination Compounds

The crystal field theory attributes the colour of the coordination compounds to dod transition of the electron, i.e., electron jump from $t_{2g}$ level to higher $e_g$ level.

In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless.

$[Ti(H_2O]_6]^{3+}$ — Violet in colour

$[Cu(H_2O)_4]^{2+}$ — Blue in colour, etc.

### Limitations of CFT

1. It does not consider the formation of 7t bonding in complexes.
2. It is also unable to account satisfactorily for the relative strengths of ligands e.g., it does not explain why $H_2O$ is stronger ligand than $OH^-$.
3. It gives no account of the partly covalent nature of metal-metal bonds.

### Ligand Field or Molecular Orbital Theory

This theory was put forward by Hund and Mulliken. According to this theory, all the atomic orbitals of the atom participating in molecule formation get mixed to give rise an equivalent number of new orbitals, called the molecular orbitals. The electrons are now under the influence of all the nuclei.

### Stability of Coordination Compounds

The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as stability constant (K).

e.g.,

$$M^+ + nL^{x-} \rightleftharpoons [ML_n]^{y-}; \qquad K = \frac{[(ML_n)^{y-}]}{[M^+]\,[L^{x-}]^n}$$

The factors on which stability of the complex depends :

(i) **Charge on the central metal atom** As the magnitude of charge on metal atom increases, stability of the complex increases.

(ii) **Nature of metal ion** The stability order is 3d < 4d < 5d series.

(iii) **Basic nature of ligands** Strong field ligands form stable complex.

The instability constant or the dissociation constant of compounds is defined as the reciprocal of the formation or stability Constant.

### Importance and Applications of Coordination Compounds

1. They are used in many qualitative and quantitative analysis.
2. Hardness of water is estimated by simple titration with $Na_2$ EDTA.
3. Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.
4. They have great importance in biological systems.
5. They are used as catalyst for many industrial processes.
6. In medicinal chemistry, there is a growing interest of chelating therapy.

### Organometallic Compounds

They contain one or more metal-carbon bond in their molecules. They are of the following types:

#### 1. Sigma (σ) bonded compounds

Metal-carbon bond is sigma bond, e.g., $(C_2H_5)_4$ Pb, $Zn(C_2H_5)_2$ R – Mg – X, etc.

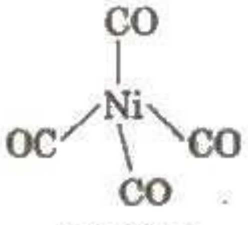
P In which molecules/ions containing π bonds act as a ligand. e.g., Ferrocene, Dibenzene chromium and Zeise's salt.

Zeise's salts is $K[PtCl_3(\eta^2 - C_2H_4)]$ In which ethylene acts as a ligand which do not have a lone pair oi electron.

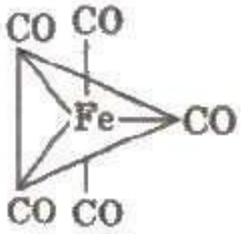
In ferrocene, $Fe(\eta^5 - C_5H_5)_2$ represents the number of carbon atoms with which metal ion is directly attached.

#### 2. σ and π bonded compounds

Metal carbonyls are their examples. Metal-carbon bond of metal carbonyls have both σ and π – bond character. They have CO molecule as ligand, e.g.,



$[Ni(CO)_4]$



$Fe(CO)_5$

Wilkinson's catalyst $(Rh(PPh_3)_3Cl]$ is used as homogeneous catalyst in the hydrogenation of alkenes. Zeigler-Natta catalyst
[Ti $Cl_4$ + $(C_2H_5>_3Al]$ acts as heterogeneous catalyst in the polymerisation of ethylene
i(π) bonded compounds.

## Chapter 10

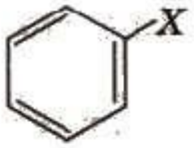
## Haloalkanes and Haloarenes

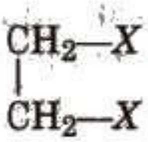
The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

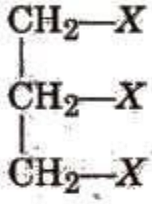
### Classification of Halogen Derivatives

On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,

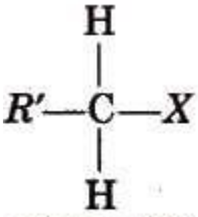
$C_2H_5X$
monohaloalkane

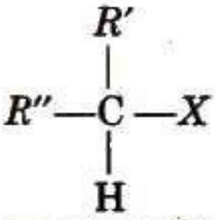

monohaloarene

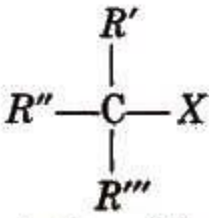

$$\begin{array}{l}CH_2-X\\ |\\ CH_2-X\end{array}$$
dihaloalkanes

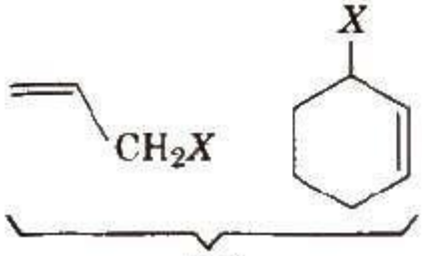

$$\begin{array}{l}CH_2-X\\ |\\ CH_2-X\\ |\\ CH_2-X\end{array}$$
trihaloalkane

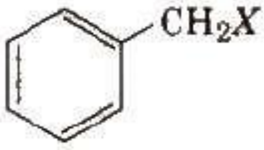
On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3°, allylic, benzylic, vinylic and aryl derivatives, e.g.,


$$\begin{array}{c}H\\ |\\ R'-C-X\\ |\\ H\end{array}$$
primary (1°)

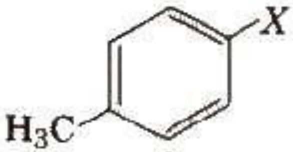

$$\begin{array}{c}R'\\ |\\ R''-C-X\\ |\\ H\end{array}$$
secondary (2°)


$$\begin{array}{c}R'\\ |\\ R''-C-X\\ |\\ R'''\end{array}$$
tertiary (3°)


allylic

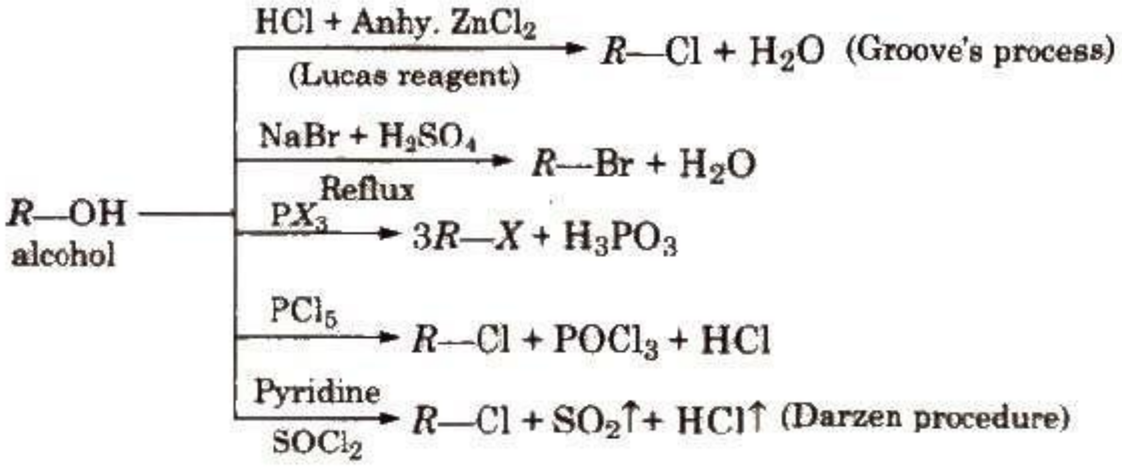

benzylic


vinylic


aryl

**General Methods of Preparation of Haloalkanes**

## 1. From Alcohols

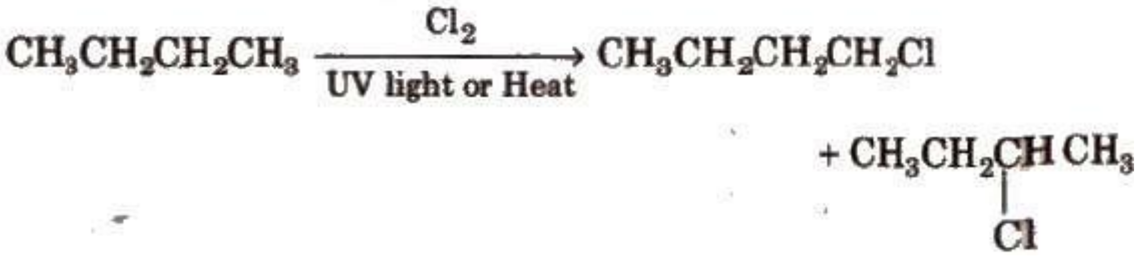


In Groove’s method, $ZnC1_2$ is used to weaken the C-OH bond. In case of 3° alcohols, $ZnC1_2$ is not required.

The reactivity order of halogen acids is HI > HBr > HCl.

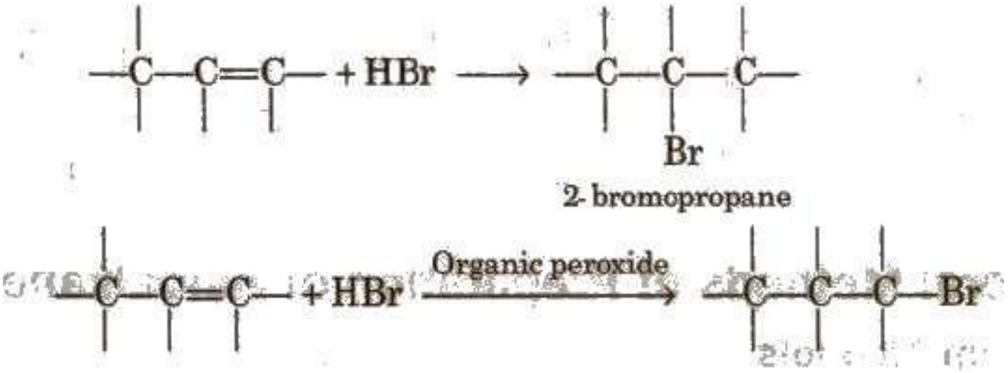
Darzen procedure is the best method for preparing alkyl halides from alcohols since both the by products ($SO_2$ and HCl) are gaseous and escape easily.

## 2. Free Radical Halogenation of Alkanes



$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{UV light or Heat}]{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{CH}}CH_3$$

**Addition of Hydrogen Halides on Alkenes**



1. **Finkelstein Reaction**

$$\underset{(X = Cl,\ Br)}{R—X} + NaI \xrightarrow{\text{Acetone}} R—I + NaX$$

2. **Swarts Reaction**

**$H_3C – Br + AgF \rightarrow H_3C – F + AgBr$**

$Hg_2F_2$, $COF_2$ and $SbF_3$ can also be used as a reagent for Swarts reaction.

3. **Hunsdiecker Reaction**

$$CH_3COOAg + Br_2 \xrightarrow[CCl_4]{} CH_3Br + AgBr + CO_2$$

**Physical Properties of Haloalkanes**

1. **Boiling point orders**

   1. R – I > R – Br > R – Cl > R – F
   2. $CH_3 – (CH_2)_2 – CH_2Br > (CH_3)_2\ CHCH_2Br > (CH_3)_3CBr$
   3. $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$

**2.** Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is

$CH_3F > CR_3Cl > CR_3Br > CH_3I$

**3.** Dipole moment decreases as the electronegativity of the halogen decreases.

**4.** Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

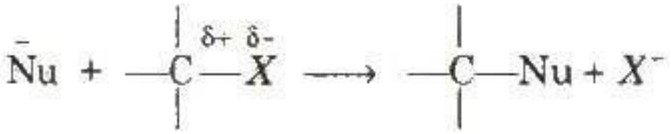
**5.** Density order is

RI > RBr > RCl > RF (For the same alkyl group) $CH_3I$ >

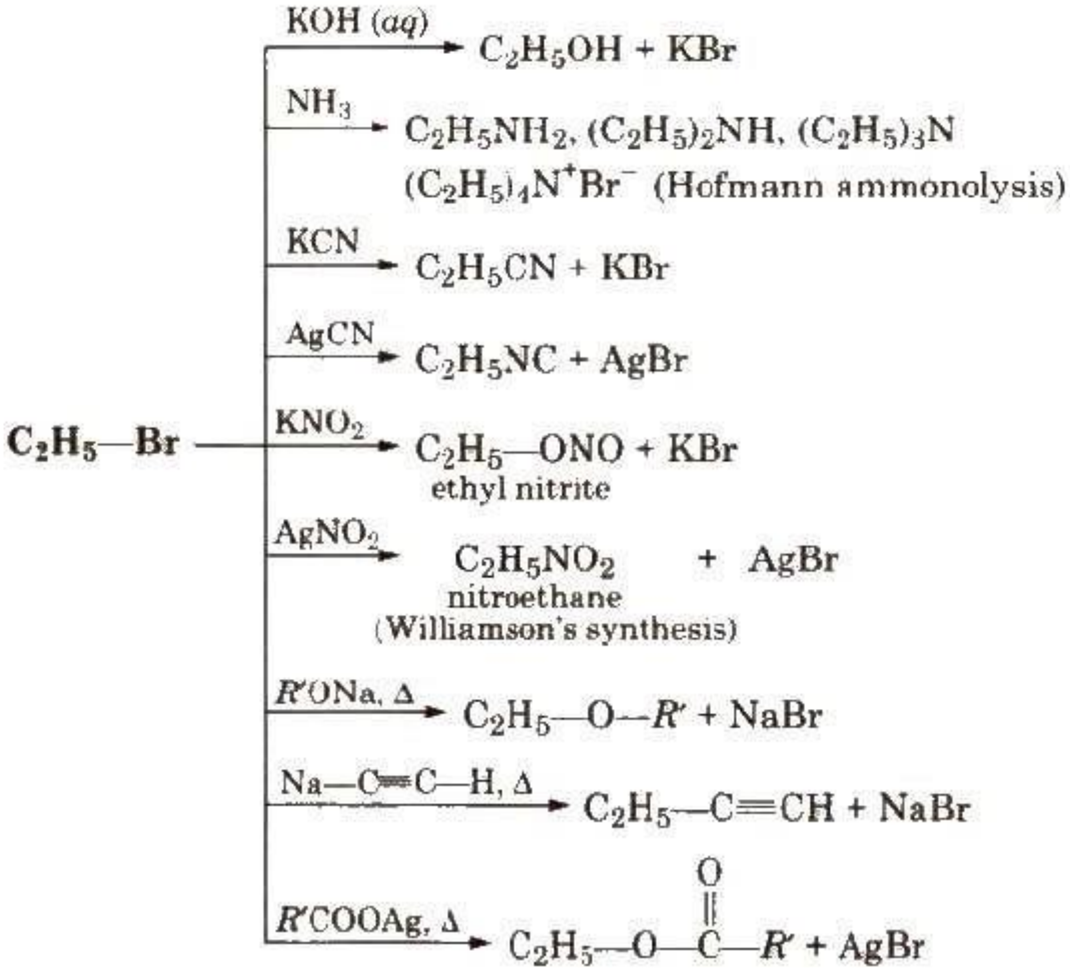
$C_2H_5I > C_3H_7I$

**Chemical Reactions of Haloalkanes**

1. **Nucleophilic Substitution Reactions ($S_N$ reactions)**



$$\overset{-}{Nu} + -\overset{|}{\underset{|}{C}}\overset{\delta+\ \delta-}{-}X \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^-$$

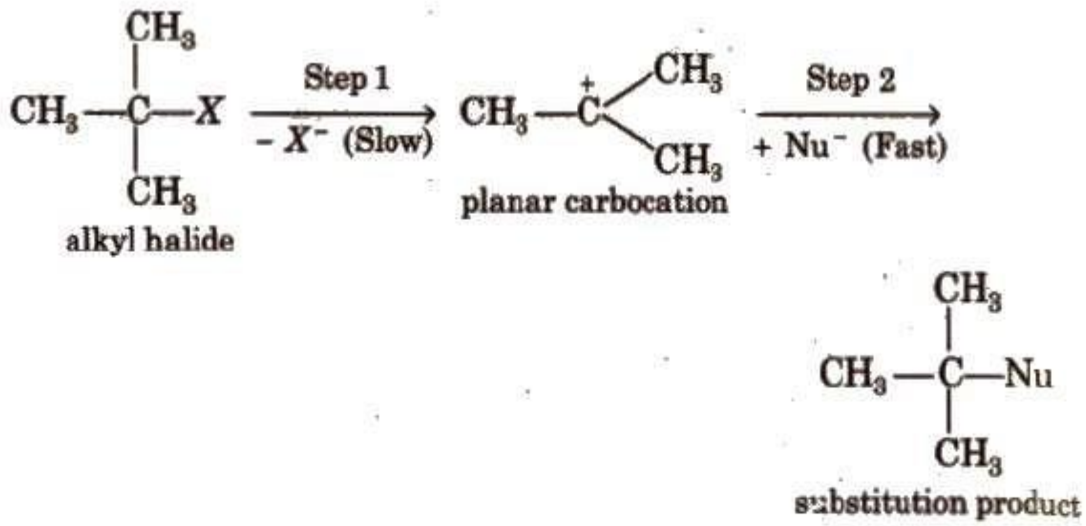


kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, $KNO_2$ form R-ONO while $AgNO_2$ produces R-$NO_2$ as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types;

**(a)** **$S_N1$ type** (Unimolecular nucleophilic reactions proceed in two steps:



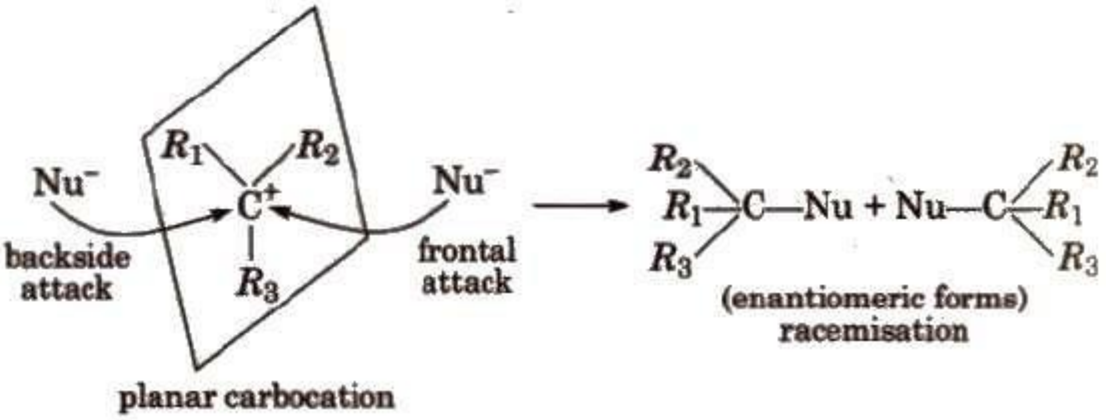
Rate, r = k [RX). It is a first order reaction.

Reactivity order of alkyl halide towards $S_N1$ mechanism 3° > 2° > 1°

Polar solvents, low concentration of nucleophiles and weak

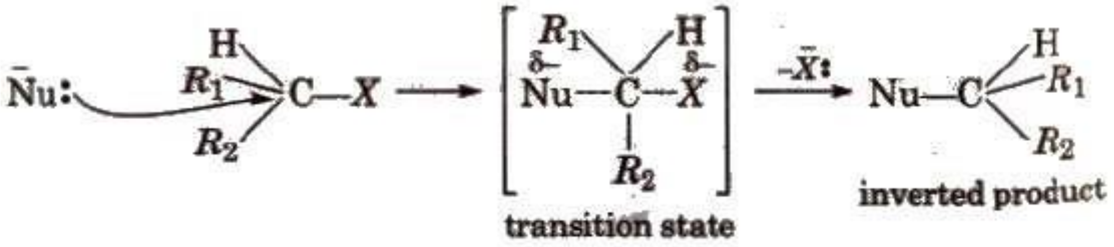
nucleophiles favour $S_N1$ mechanism.

In $S_N1$ reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



**(b)** $S_N2$ type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with r = k[RX] [Nu].

During $S_N2$ reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,



Reactivity of halides towards $S_N2$ mechanism is 1°>2°

> 3°

Rate of reaction in $S_N2$ mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

$:CN^- > : I^- > : OR^- > : OH^- > CH^3COO: > H_2O > F^-$

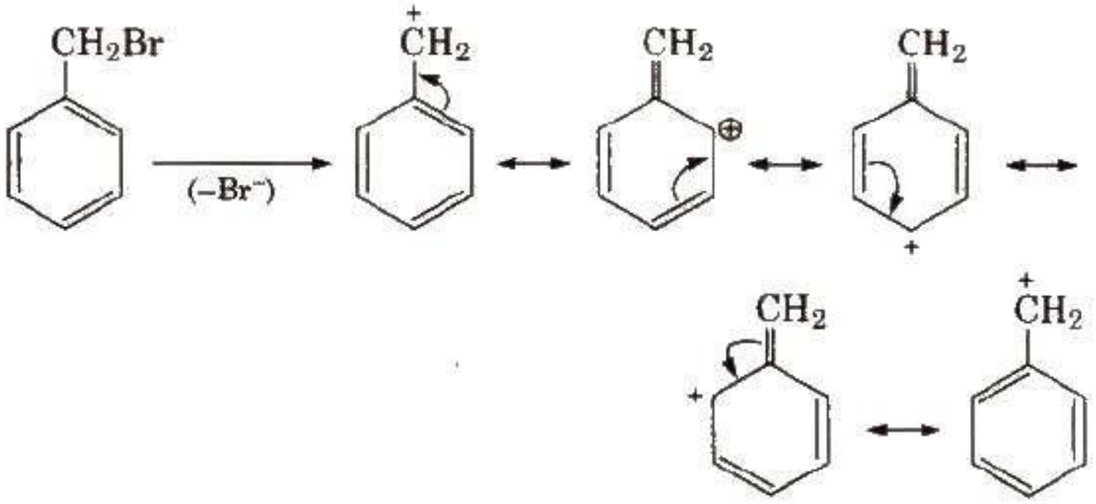
Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour $S_N2$ mechanism.

Relative rates of some alkyl halides in $S_N1$ and $S_N2$ reactions are in the order

$$S_N1 : (CH_3)_3CX > C_6H_5—CH_2—X > CH_2{=}CH—CH_2X > (CH_3)_2CHX > CH_3CH_2X > CH_3X$$

$$S_N2 : \underbrace{C_6H_5CH_2X > CH_2{=}CH—CH_2X}_{\text{resonance stabilised}} > CH_3X > CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$$

Resonating structure of benzyl carbocations are

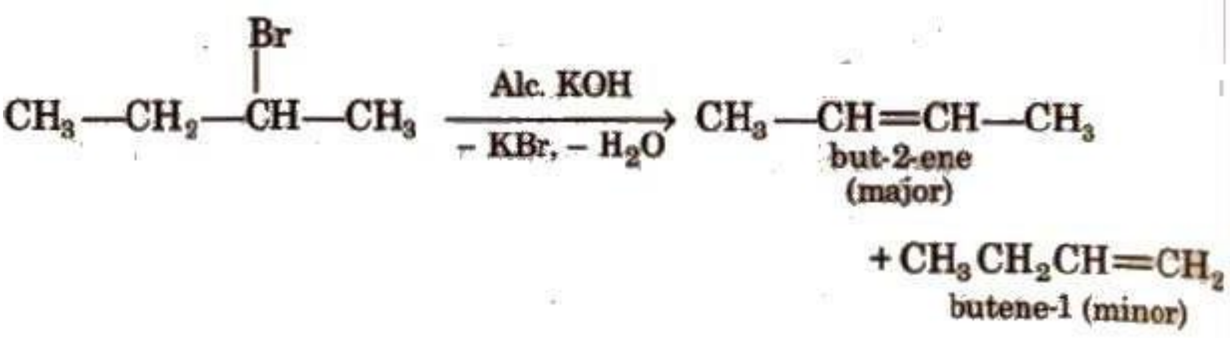


Relative reactivity of alkyl halides for same alkyl group is RI>RBr>

RCl > RF

## 2. Elimination Reactions

Dehydrohalogenation is a β – elimination reaction in which halogen is from α-carbon atom and the hydrogen from the α-carbon according to Saytzeff rule, e.g.,



$$CH_3-CH_2-\underset{}{\overset{Br}{\overset{|}{CH}}}-CH_3 \xrightarrow[-\,KBr,\,-\,H_2O]{Alc.\ KOH} \underset{\substack{\text{but-2-ene}\\ \text{(major)}}}{CH_3-CH=CH-CH_3} + \underset{\text{butene-1 (minor)}}{CH_3CH_2CH=CH_2}$$

Ease of dehydrohalogenation among halide 3°>2° >

1°

*i.e.,* $(CH_3)_3CCl > (CH_3)_2CHCl > CH_3CH_2Cl$

## 3. Reduction

$$C_2H_5-Br + H_2 \xrightarrow{Ni,\ 575\ K} C_2H_6 + HBr$$

$$C_2H_5I + HI \xrightarrow{Red\ P,\ 420\ K} C_2H_6 + I_2$$

## 4. Reaction with Metals

(i) **Wurtz reaction**

$$RX + 2Na + XR \xrightarrow{Dry\ ether} R-R\,(\text{alkane}) + 2NaX$$

(ii) **Wurtz-Fittig reaction**

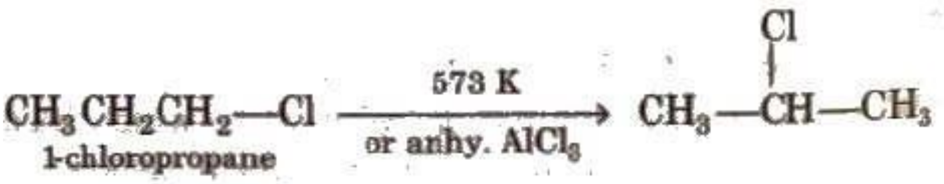
$$C_6H_5\boxed{-Cl + 2Na + Cl}\,CH_3 \xrightarrow{Dry\ ether} C_6H_5-CH_3 + 2NaCl$$

(iii) **Reaction with Mg**

$$C_2H_5Br + Mg \xrightarrow{Dry\ ether} \underset{\text{(Grignard's reagent)}}{C_2H_5-Mg-Br}$$

Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used as ethereal solution.

### 5. Isomerisation



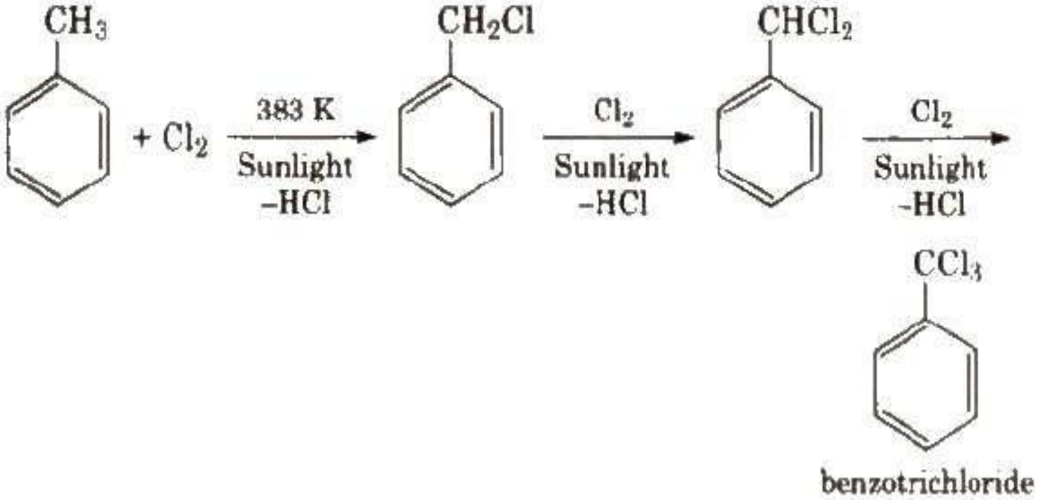
$$CH_3CH_2CH_2-Cl \xrightarrow[\text{or anhy. } AlCl_3]{573\text{ K}} CH_3-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_3$$

## General Methods of Preparation of Aryl Halides

### 1. By Halogenation of Aromatic Hydrocarbons

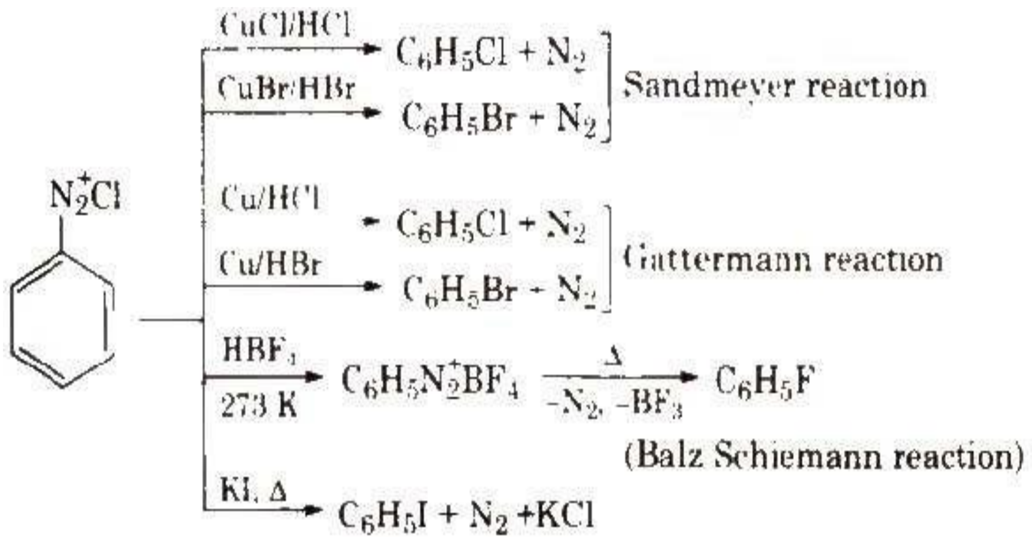
It is an electrophilic substitution reaction.

### 2. By Side Chain Halogenation

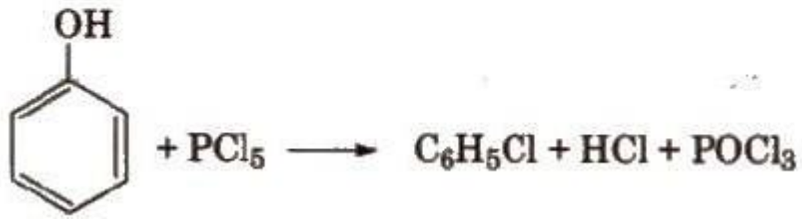


(It involves free radical mechanism.)

3. **From Benzene Diazonium Salt**



4. From Phenol



**Physical Properties of Aryl Halides**

1. Aryl halides are colourless liquids or colourless solids with characteristic odour.
2. Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order . Ar – I > Ar – Br > Ar – Cl > Ar – F
3. The melting point of p -isomer is more than 0- and m-isomer.This is because of more symmetrical nature of p-isomer.
4. Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that ofcyclohexylchloride.

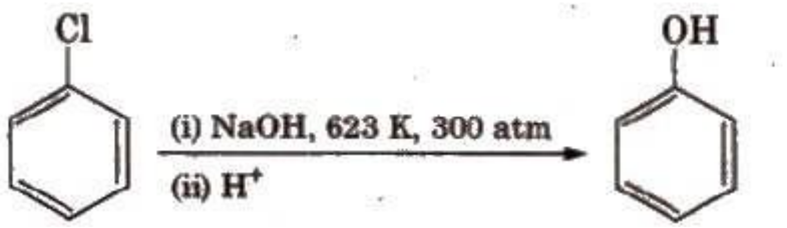
## Chemical Properties of Aryl Halides

### 1. Nucleophilic Substitution Reaction

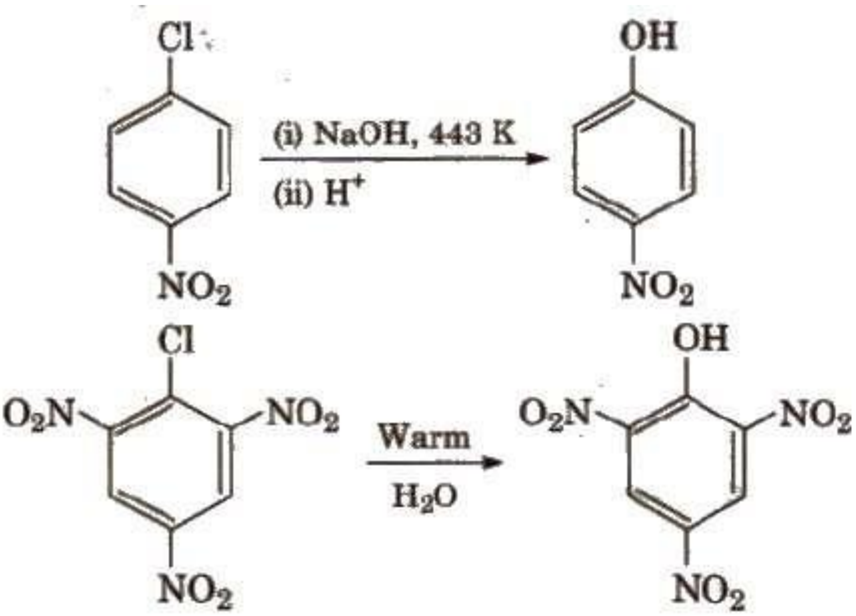
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

1. Due to resonance, C-X bond has partial double bond character.
2. Stabilisation of the molecule by delocalisation of electrons.
3. (Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like – $NO_2$, -$SO_3H$, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.



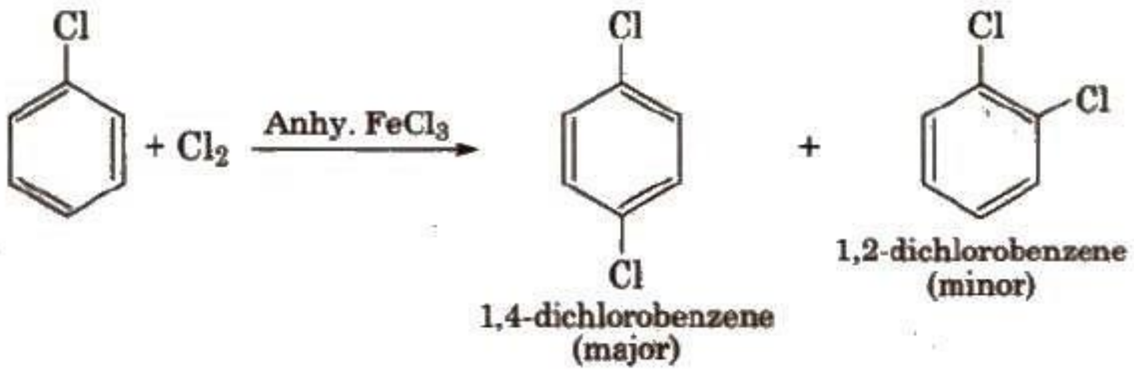
Presence of electron withdrawing group (-$NO_2$) increases the reactivity.



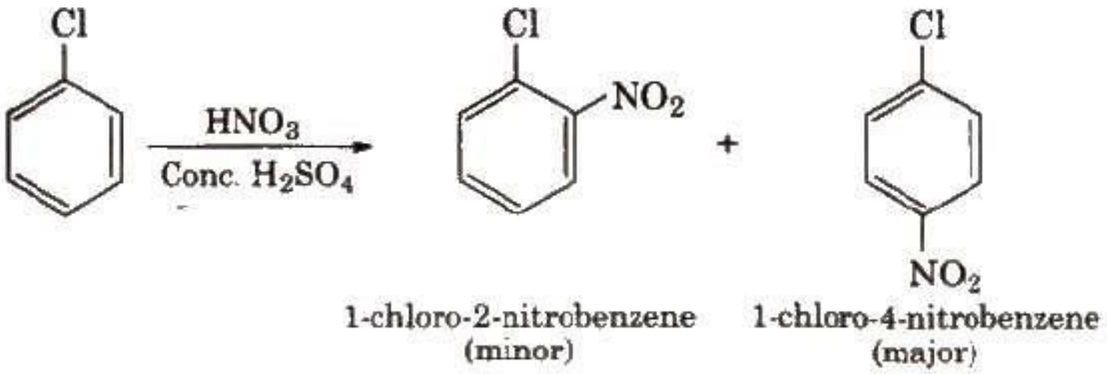
## 2. Electrophilic Substitution Reactions

Halogens are deactivating but O, p-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft's reaction give a mixture of o- and P- chloro substituted derivatives.

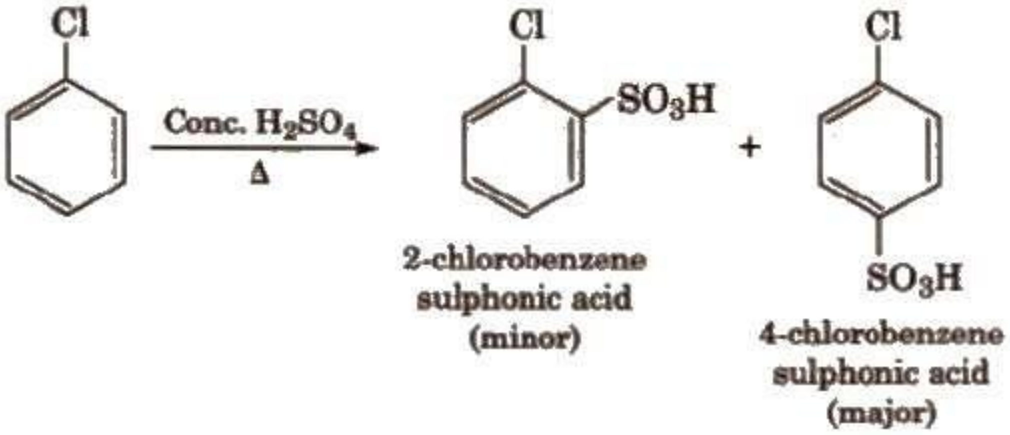
### (i) Halogenation



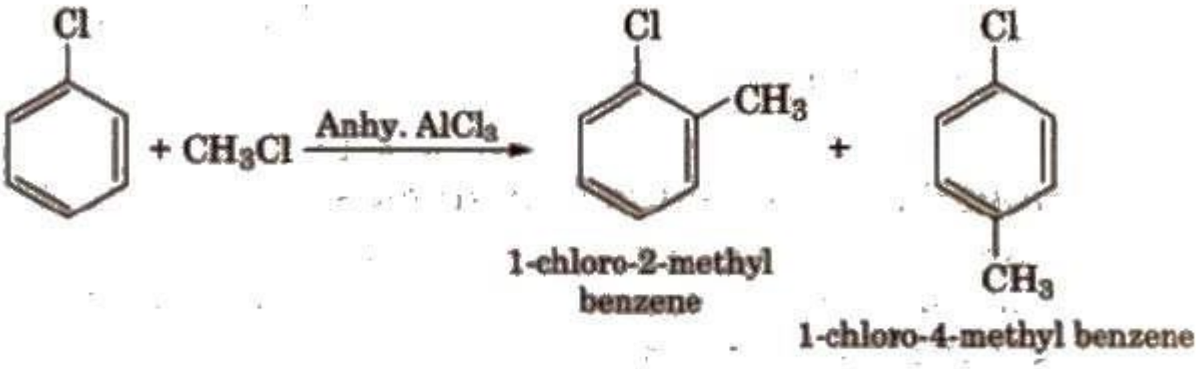
### (ii) Nitration

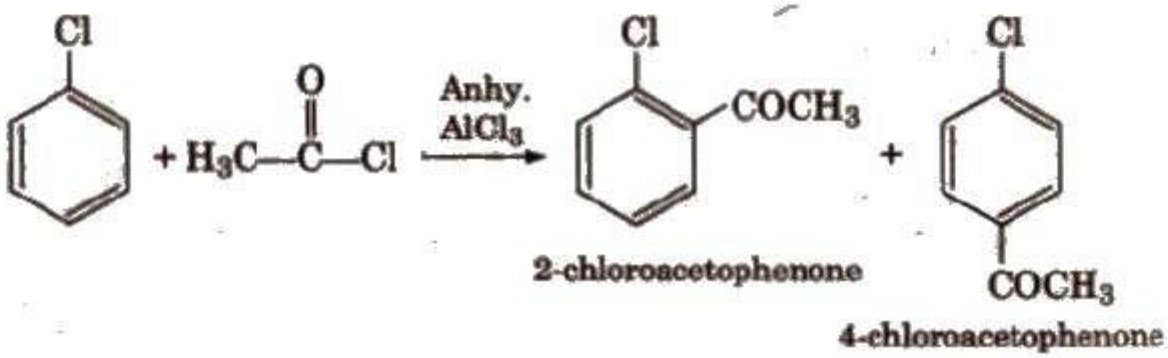


### Sulphonation



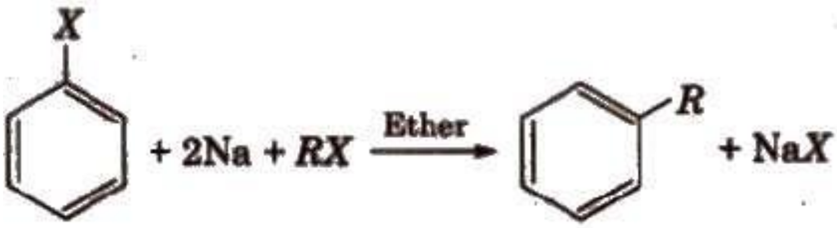
### (i) Friedel-Crafts reaction



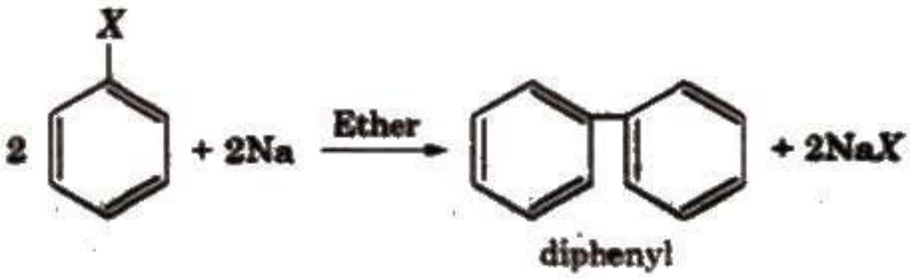


## 3. Reaction with Metals

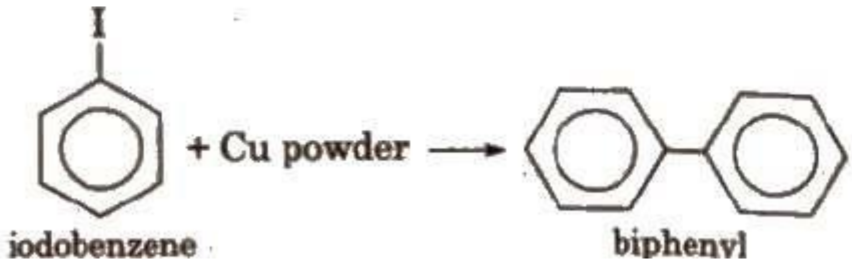
### (i) Wurtz Fittig reaction



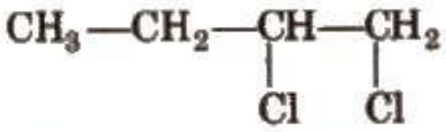
### (i) Fitting reaction



(ii) Ullmann reaction

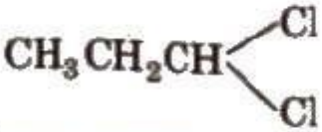


**DIhalogen Derivatives**



$CH_3-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH_2}$

*(Vic* or *vicinal*-dihalide)



(*Gem* or *geminal*-dihalide)

$ClCH_2-CH_2-CH_2-CH_2-Cl$

(Isolated dihalides)

Dichloromethane ($CH_2Cl_2$) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and milk redness of the skin.

**Trihalogen Derivatives**

1. Chloroform [Trichloromethane, $CHCl_3$]

**Methods of preparation**

(i) $CH_4 + 3Cl_2 \xrightarrow[\text{Controlled chlorination}]{\text{Sunlight}} CHCl_3 + 3HCl$

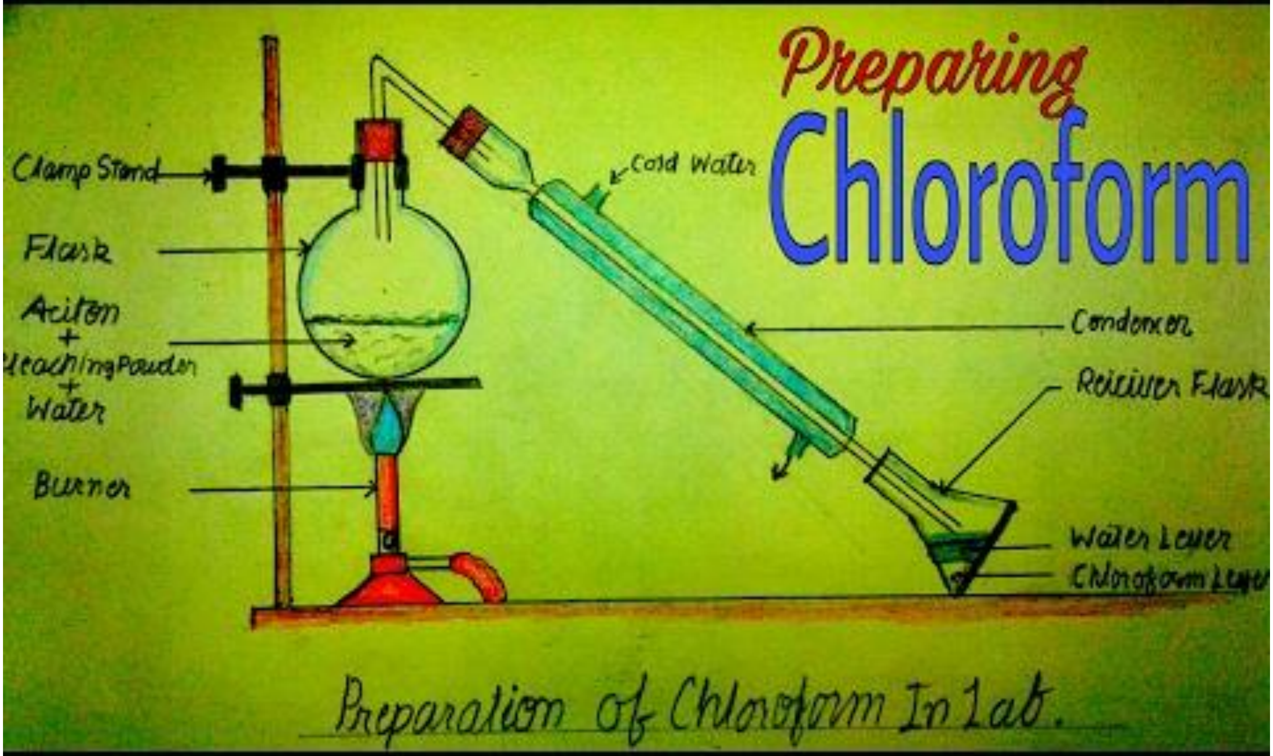
**(ii) Haloform reaction**

$$C_2H_5OH + Cl_2 \longrightarrow CH_3CHO + 2HCl \text{ [Oxidation]}$$

$$CH_3CHO + 3Cl_2 \longrightarrow CCl_3 \cdot CHO + 3HCl \text{ [Chlorination]}$$

$$2CCl_3 \cdot CHO + Ca(OH)_2 \longrightarrow 2CHCl_3 + (HCOO)_2Ca$$

[Hydrolysis]


Preparing
Chloroform
Clamp Stand
Flask
Aciton
+
leachingPowder
+
Water
Burner
Cold Water
Condenser
Reiciver Flask
Water Leyer
Chloroform Leyer
Preparation of Chloroform In lab.

**Properties**

1. Oxidation of $CHCl_3$ gives poisonous gas phosgene (carbonyl chloride).

$$2CHCl_3 + O_2 \xrightarrow{\text{Light}} \underset{\text{phosgene}}{2COCl_2} + 2HCl$$

To avoid this oxidation $CHCl_3$ il .toreci in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

2. $CHCl_3$ is widely used in the production of freon refrigerant R-22.

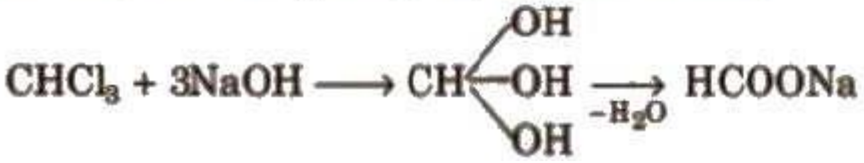
3. On nitration, it gives tear producing insecticide substance chloropicrin.

$$CHCl_3 + HONO_2\,(\text{conc.}) \longrightarrow \underset{\text{chloropicrin}}{NO_2\cdot CCl_3} + H_2O$$

4. **On dehalogenation, it gives $C_2H_2$ (acetylene).**

$$CHCl_3 + 6Ag + CHCl_3 \xrightarrow[\Delta]{} CH{\equiv}CH + 6AgCl$$

5. **When subjected to hydrolysis, it gives formate.**



$$CHCl_3 + 3NaOH \longrightarrow CH(OH)_3 \xrightarrow[-H_2O]{} HCOONa$$

**2. Iodoform (tri-iodornethane, $CHI_3$)**

Iodoform is prepared by iodoform reaction.

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

Compounds containing either $CH_3CO$- or $CH_3CH(OH)$ group form yellow colour iodoform with $I_2$ and NaOH. Iodoform when comes in contact with organic matter, decomposes easily to free iodine, an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

## Polyhalogen Derivatives

### 1. Tetrachloromethane (Carbon Tetrachloride, $CCl_4$ )

**Preparation**

(i) $CH_4 + 4Cl_2 \xrightarrow{\text{Sunlight}} CCl_4 + 4HCl$

(ii) $CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + 2HCl$

$CCl_4$ is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

**Uses**

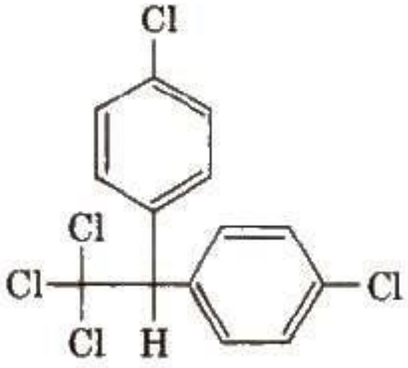
Carbon tetrachloride is used

1. as a solvent for oils, fats, resins
2. in dry cleaning
3. as fire extinguisher under the name ‘pyrene’.

### 2. Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Carbon tetra chloride when reacts with antimony trifluoride in the presence of $SbCl_5$ as catalyst, dichlorofluromethane (freon) is obtained.

### 3. **DDT** (p, p’-Dichlorodiphenyltrichloroethane)



2,2- bis (4-chlorophenyl) -1,1,1- trichloroethane

DDT is the first chlorinated organic insecticide. Its stability and fat solubility’is a great problem. It is prepared from chloral and chlorobenzene in the presence of conc. $H_2SO_4$·

### 4. Perchloroethane ($C_2Cl_6$)

It is used as moth repellant and is also known as artificial camphor.

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## Chapter 11

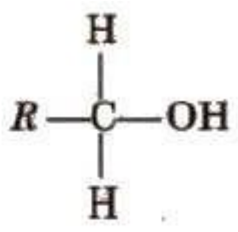
## Alcohols, Phenols and Ethers

## Alcohols and Phenols

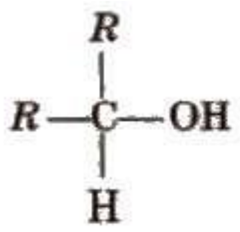
Alcohols and phenols are formed when a hydrogen atom in hydrocarbon, aliphatic and aromatic respectively, is replaced by hydroxyl group (-OR group).

### Classification of Alcohols and Phenols

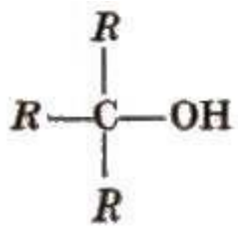
In alcohols, -OR group is attached to Sp3 hybridised carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.



primary (1°)



secondary (2°)



tertiary (3°)

Alcohols may be

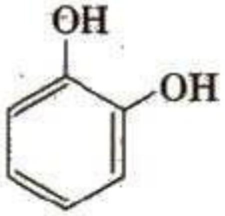
(i) monohydric-containing one – OR group,

(ii) dihydric-containing two – OR groups and

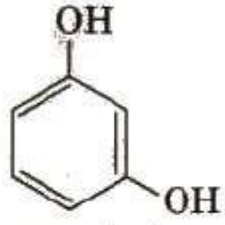
(iii) polyhydric-containing three or more -OR groups.

In phenols, -OR group is attached to Sp$^2$ hybridised carbon. These may also be monohydric, dihydric, etc. The dihydric phenol further rosy be ortho, meta’ or para derivative.

phenol



catechol



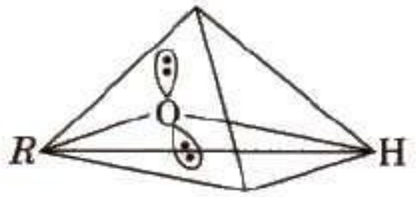
resorcinol

quinol or hydroquinone

In allylic alcohols, – OH group is attached to sp$^3$ hybridised carbon but next to C=C bond.e.g., $CH_2 = CH – CH_2OH$, Benzylic alcohol.($C_6H_5CH_2OH$)

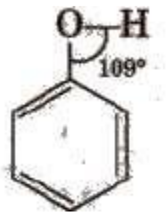
**Structure of Alcohols and Phenols**

The oxygen atom of alcohols is $Sp^3$ hybridised and they have tetrahedral position of hybrid atomic orbitals .



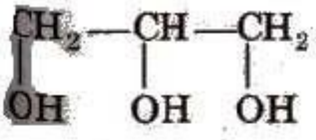
The value of LROH bond angle depends upon the R group. For methyl alcohol, it is (∠C – O – H) 108.9° due to repulsion of lone pairs.

In phenols, the – OH group is attached to $Sp^2$ hybridised carbon and thus, the C – O bond acquires a partial double bond character.



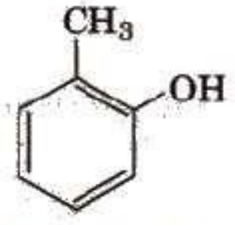
**Nomenclature of Alcohols and Phenol**

In IUPAC, system, alcohol or alkanols are named by replacing the last word ‘e’ of the corresponding alkane by ‘ol’. e.g.,

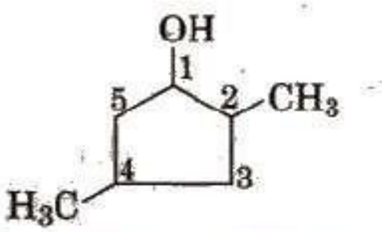


$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

propan-1,2,3-triol



2-methyl phenol

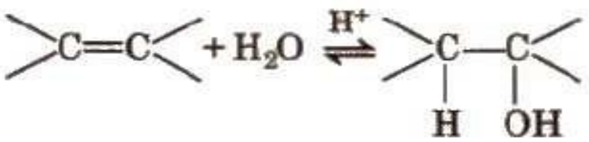


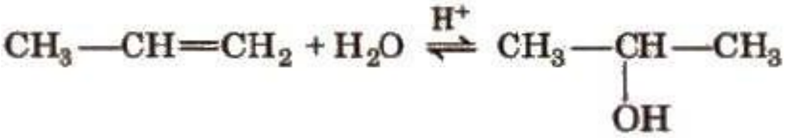
2,4-dimethylcyclopentanol

1. **Preparation of Alcohols**

**(i) From alkenes**

**(a )**By acid catalysed hydration in accordance with Markownikoff’s rule.

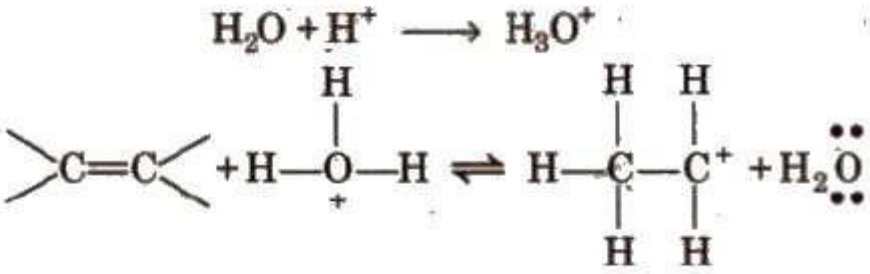




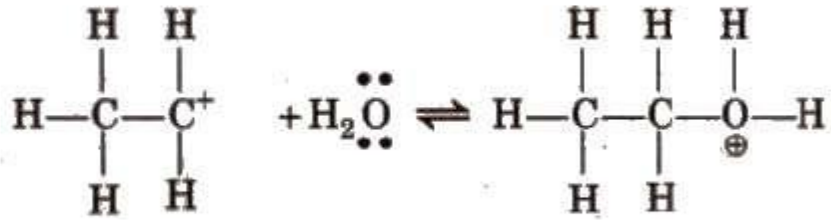
$$CH_3-CH=CH_2+H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

**Mechanism**

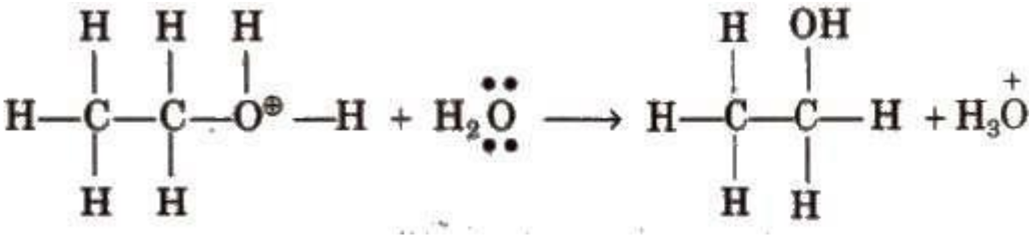
**Step I** Protonation of alkene by attack of $H_3O^+$



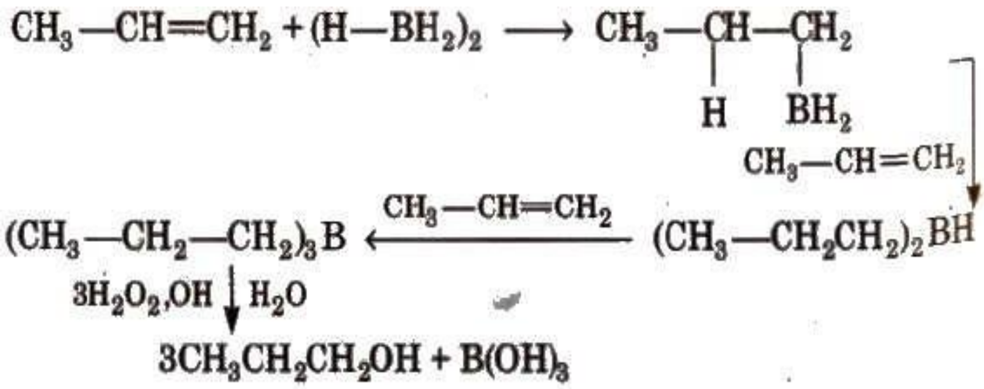
**Step II** Nucleophilic attack



**Step III** Deprotonation to form an alcohol

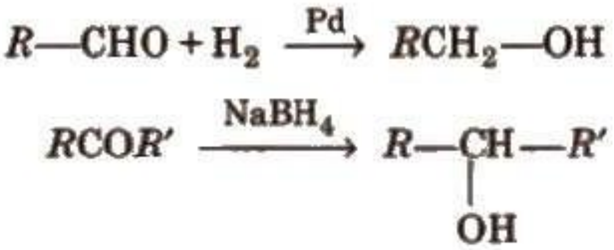


**(a) By hydroboration-oxidation**



**(ii)From carbonyl compounds**

(a) By reduction of aldehydes and ketones



$$R\text{—CHO} + H_2 \xrightarrow{\text{Pd}} RCH_2\text{—OH}$$

$$RCOR' \xrightarrow{\text{NaBH}_4} R\text{—}\underset{\displaystyle\text{OH}}{\underset{|}{\text{CH}}}\text{—}R'$$

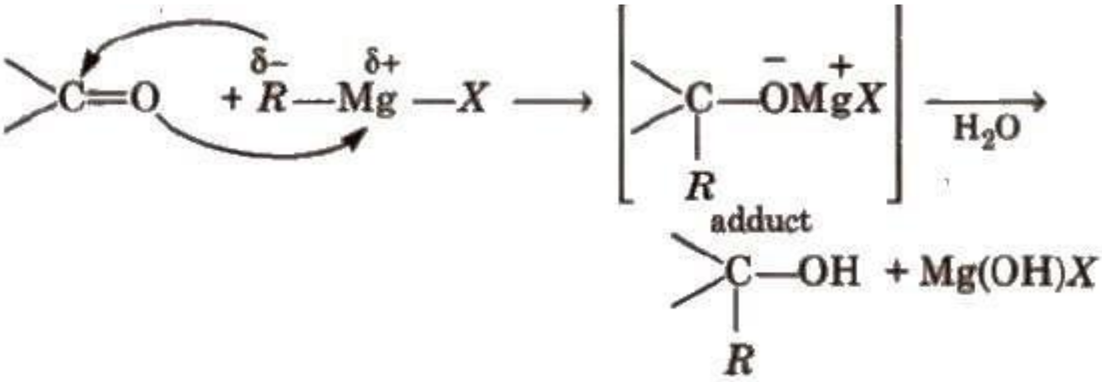
Aldehydes yield primary alcohols whereas ketones give secondary alcohols, when subjected to reduction.

(b) By reduction of carboxylic acids and ester

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) LiAlH}_4} RCH_2OH$$

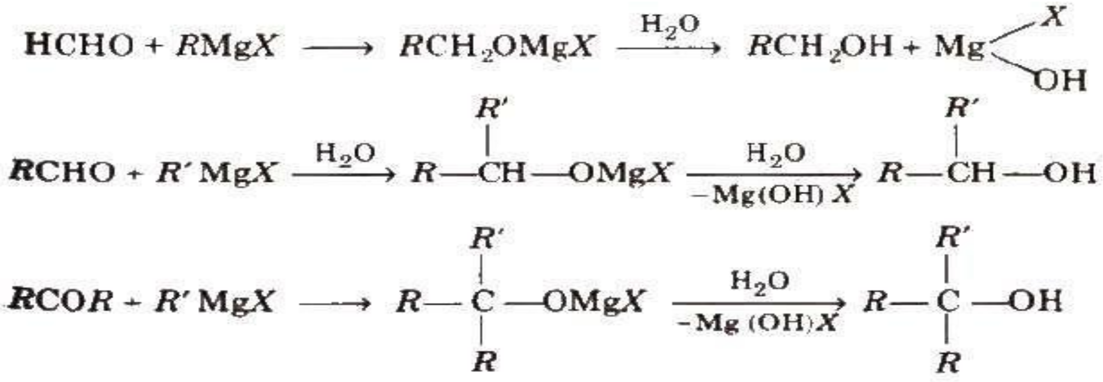
$$RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

Reduction of aldehyde, ketones and esters with No Alcohol iscalled Bouveault-blanc reduction.



$$\gt C{=}O + \overset{\delta-}{R}\text{—}\overset{\delta+}{\text{Mg}}\text{—}X \longrightarrow \left[\gt \underset{\displaystyle R}{\underset{|}{C}}\text{—}\overset{-}{O}\overset{+}{\text{Mg}}X\right] \xrightarrow{H_2O} \gt \underset{\displaystyle R}{\underset{|}{C}}\text{—OH} + \text{Mg(OH)}X$$

The reaction produces a primary alcohol with methanol, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones.



$$\text{HCHO} + R\text{Mg}X \longrightarrow RCH_2O\text{Mg}X \xrightarrow{H_2O} RCH_2OH + \text{Mg}\begin{matrix} X \\ OH \end{matrix}$$

$$RCHO + R'\text{Mg}X \xrightarrow{H_2O} R\text{—}\overset{\displaystyle R'}{\overset{|}{\text{CH}}}\text{—OMg}X \xrightarrow[-\text{Mg(OH)}X]{H_2O} R\text{—}\overset{\displaystyle R'}{\overset{|}{\text{CH}}}\text{—OH}$$

$$RCOR + R'\text{Mg}X \longrightarrow R\text{—}\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}\text{—OMg}X \xrightarrow[-\text{Mg (OH)}X]{H_2O} R\text{—}\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}\text{—OH}$$

(iv)**Hydrolysis of alkyl halides**

R – X + KOH(aq) → ROH + KX

To avoid dehydrohalogenation of RX, mild alkalies like moist. Ease of hydrolysis of alkyl halides RI > R – Br > RCI > and t > s > p alkyl halides.

(iv)**Hydrolysis of ethers**

$$R{-}\ddot{O}{-}R + H_2O \xrightarrow{H_2SO_4} 2ROH$$

(v) **From primary amines** By treatment with nitrous acid.

$$RNH_2 + HONO \xrightarrow{(NaNO_2 + HCl)} ROH + N_2 + H_2O$$

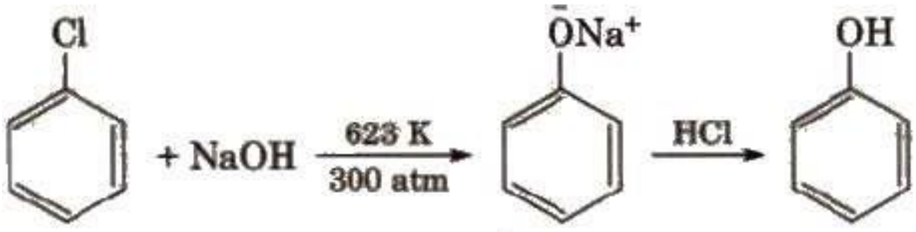
Methylamine does not give methyl alcohol when treated with $HNO_2$. It gives $CH_3OCH_3$ and $CH_3ONO$.

(vi) **By alcoholic fermentation**

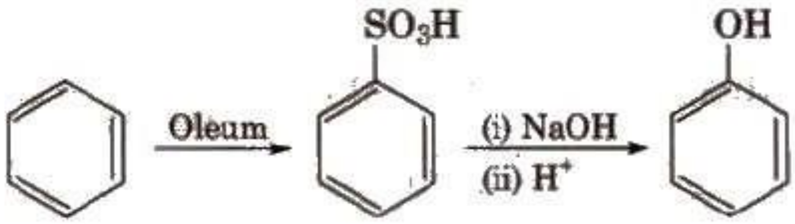
$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose and fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2(g)$$

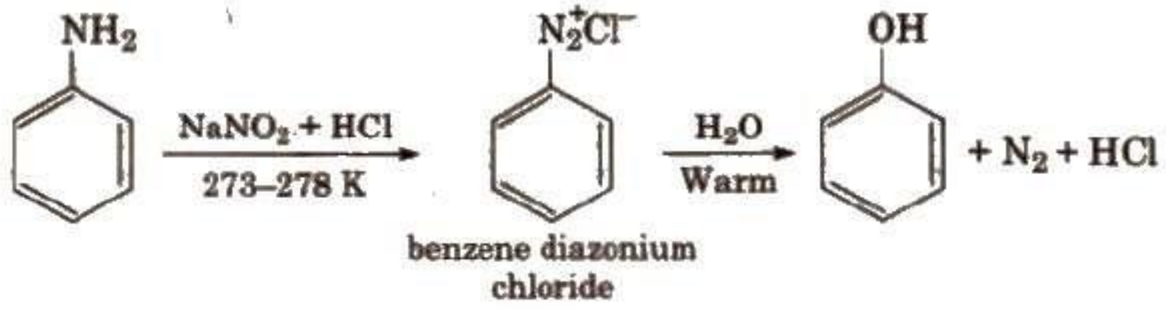
2. **Preparation of Phenols**



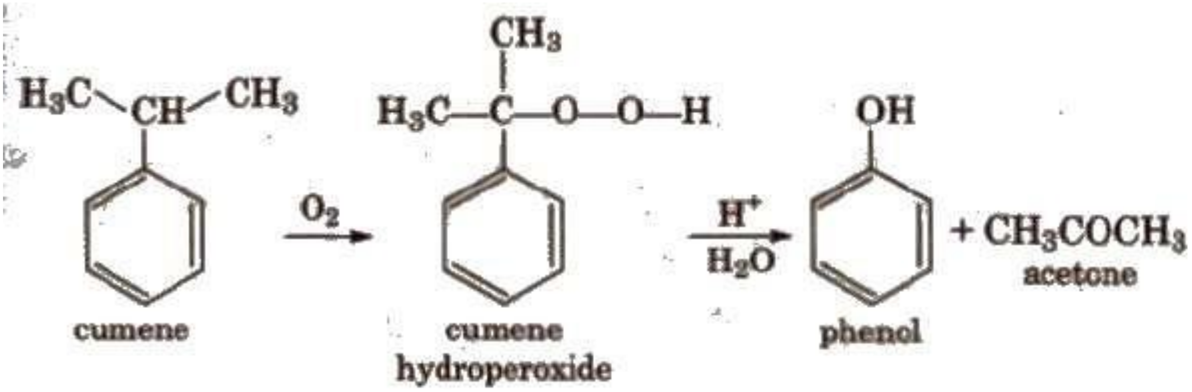
(i)**From benzene sulphonic acid**



**(ii)From diazonium salts**

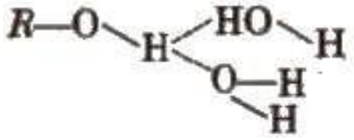


**(iii)From cumene**



**Physical Properties of Alcohols**

1. Lower alcohols are colourless liquids, members from $C_5$ – $C_{11}$ are oily liquids and higher members are waxy solids.
2. The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass.



3. Boiling points of alkanes are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules.[The boiling point decreases in the order 1° > 2° > 3° as the van der Waals' forces of attraction decreases]

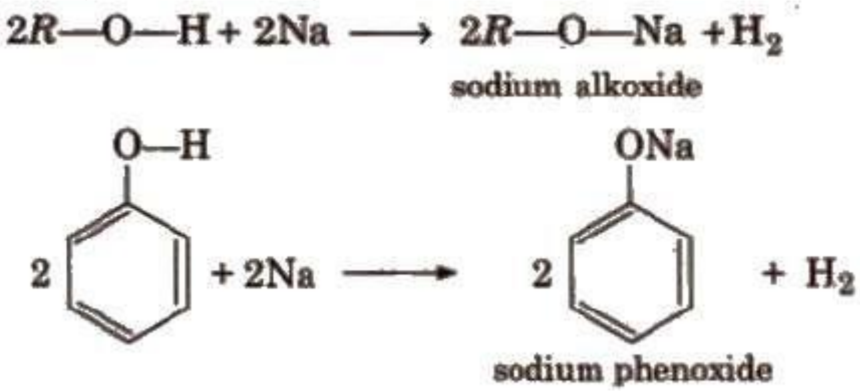
**Physical Properties of Phenols**

1. These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.
2. Phenol is also called carbolic acid.
3. Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

**Chemical Reactions of Alcohols and Phenols**

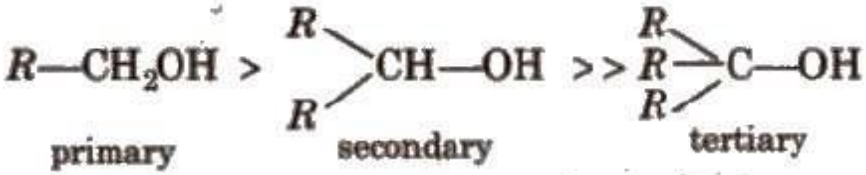
**(i) Reactions involving cleavage of O – H Bond**

(a) Acidity of alcohols and phenols



Alcohols are weaker acids than water due to +I group present in alcohols, which decreases the polarity of -O-H bond.

Acid strength of alcohols



Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond. Order of acidity is

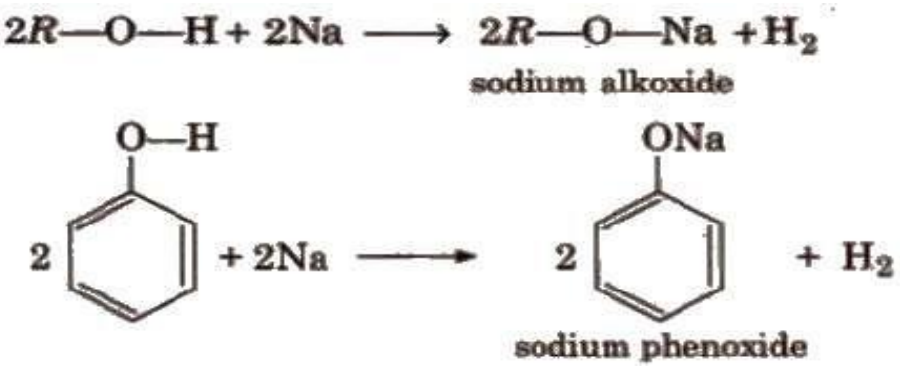
$RCOOH > H_2CO_3 > C_6H_5OH > H_2O > R – OH$.

Phenol is more acidic than alcohols due to stabilisation of phenoxide ion through resonance. Presence of electron withdrawing group increases the acidity of phenol by , stabilising phenoxide ion while presence of electron releasing group decreases the acidity of phenol by destabilising phenoxide ion.Thus. increasing acidic strength is

o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4. 6.trinitrophenol (picric acid) Higher $K_a$

and lower $pK_a$ value corresponds to the stronger acid.

(b) **Esterification**

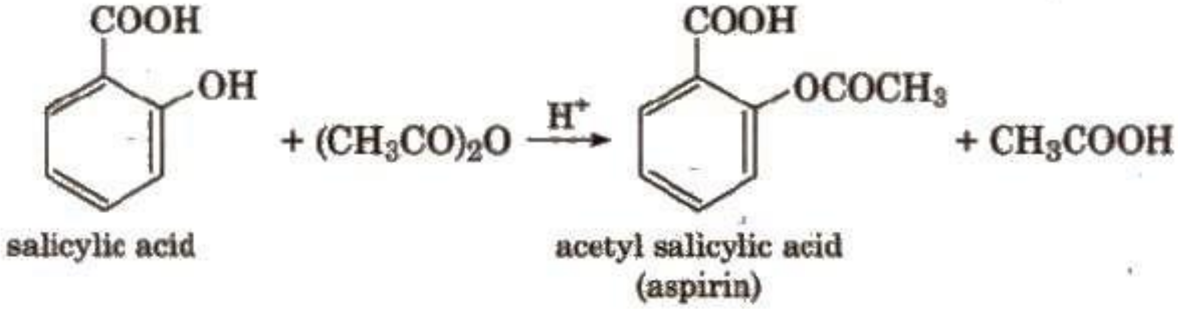


$$\mathrm{Ar}/R\text{—O—H} + R'\mathrm{COOH} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{Ar}/R - \mathrm{OCO}R' + \mathrm{H_2O}$$

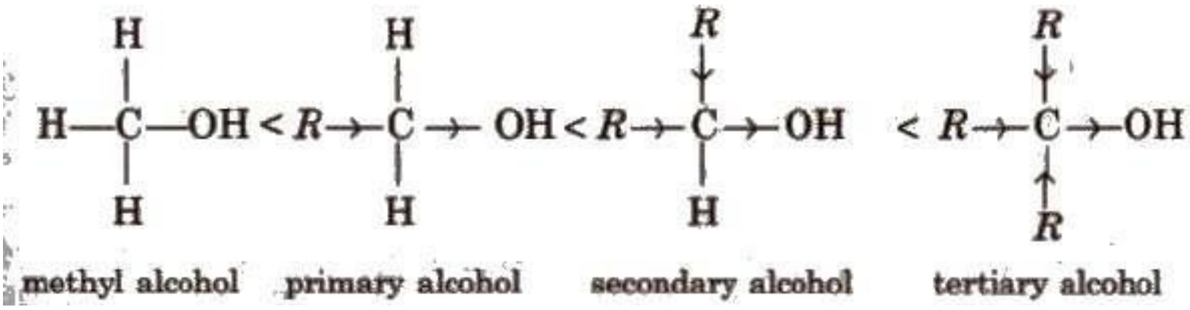
$$\mathrm{Ar}/R\text{—OH} + (R'\mathrm{CO})_2\mathrm{O} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{Ar}/R - \mathrm{OCO}R' + R'\mathrm{COOH}$$

$$R/\mathrm{Ar} - \mathrm{OH} + R'\mathrm{COCl} \xrightarrow[\text{Pyridine}]{} R/\mathrm{Ar} - \mathrm{OCO}R' + \mathrm{HCl}$$

The reaction with R’COOH and (R’ CO)$_2$O is reversible, so conc, $H_2SO_4$ is used to remove water.The reaction with R’ COCl is carried out in the presence of pyridine so as to neutralise HCl which is formed during the reaction.The introduction of acetyl ($CH_3CO$-) group in phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



(ii) **Reaction involving cleavage of C-O bond in alcohols** In these reactions, the reactivity order of different alcohols :



$$\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH} < R\rightarrow\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\rightarrow\mathrm{OH} < R\rightarrow\overset{R\downarrow}{\underset{\mathrm{H}}{\mathrm{C}}}\rightarrow\mathrm{OH} < R\rightarrow\overset{R\downarrow}{\underset{R\uparrow}{\mathrm{C}}}\rightarrow\mathrm{OH}$$

Alkyl group due to +I effect increases the electron density on the carbon and oxygen atom of C-OH bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present, more will be the reactivity of alcohol. Thus, the relative order of reactivity of the alcohols is justified.

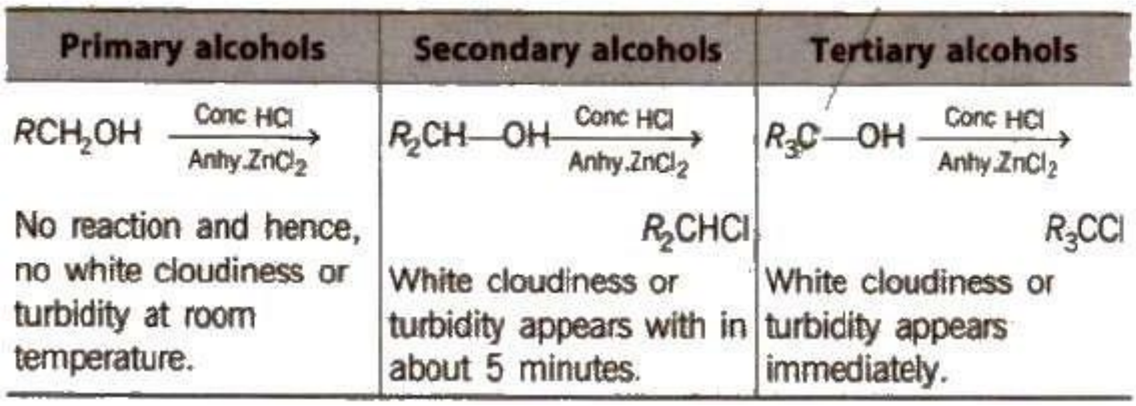
(a) **Reaction with halogen acids** Alcohols can be converted into haloalkanes by the action of halogen acids.

R – OH + HX (HCl, HBr, HI) → R-X +$H_2O$For a given alcohol order of reactivity of HX is H-I > H-Br > H-Cl

For a given halogen acid order of reactivity of alcohol.

Tertiary > Secondary > Primary

**Lucas test**



| Primary alcohols | Secondary alcohols | Tertiary alcohols |
|---|---|---|
| $RCH_2OH \xrightarrow[\text{Anhy.}ZnCl_2]{\text{Conc HCl}}$<br>No reaction and hence, no white cloudiness or turbidity at room temperature. | $R_2CH{-}OH \xrightarrow[\text{Anhy.}ZnCl_2]{\text{Conc HCl}} R_2CHCl$<br>White cloudiness or turbidity appears with in about 5 minutes. | $R_3C{-}OH \xrightarrow[\text{Anhy.}ZnCl_2]{\text{Conc HCl}} R_3CCl$<br>White cloudiness or turbidity appears immediately. |

**(b) Reaction with phosphorus halides**

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

$$3ROH + PBr_3 \xrightarrow{P/Br_2} 3RBr + H_3PO_3$$

$$3ROH + PI_3 \xrightarrow{P/I_2} 3RI + H_3PO_3$$

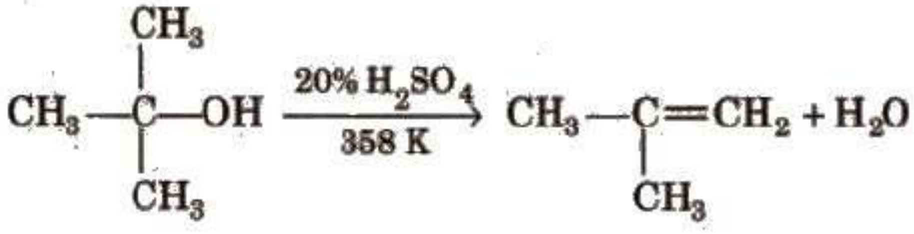
**(c) Reaction with thionyl chloride**

$$ROH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

d) **Dehydration of alcohols** It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group.
Since, the rate determining step is the formation of carbocation, the ease of dehydration is

$$3° > 2° > 1°$$

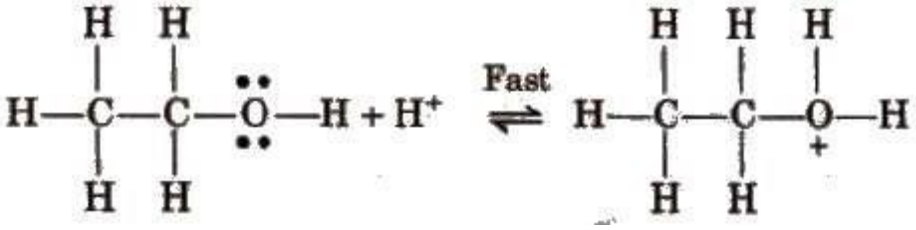
$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$



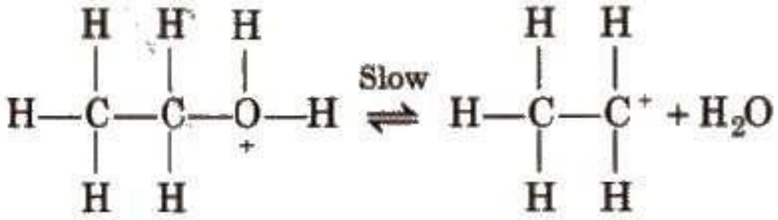
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH \xrightarrow[358\ K]{20\%\ H_2SO_4} CH_3{-}\underset{CH_3}{C}{=}CH_2 + H_2O$$

**Mechanism**

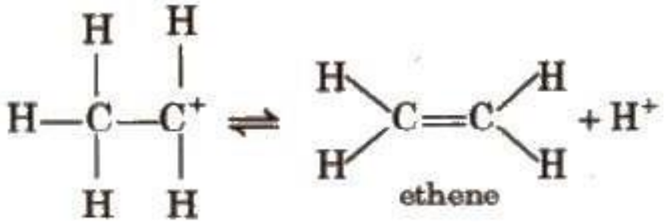
**Step I** Formation of protonated alcohol



**Step II** Formation of carbocation

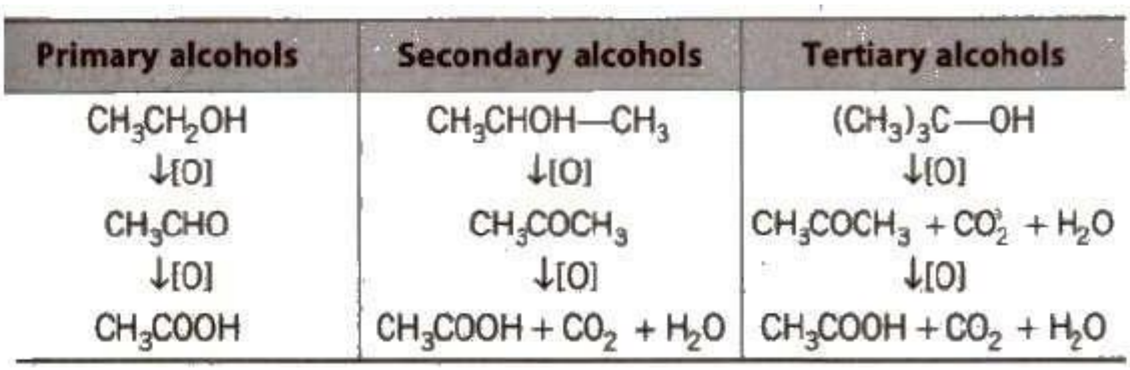


**Step III** Formation of ethene by elimination of a proton


ethene

In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff's rule).

(iii) Oxidation reactions Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$.

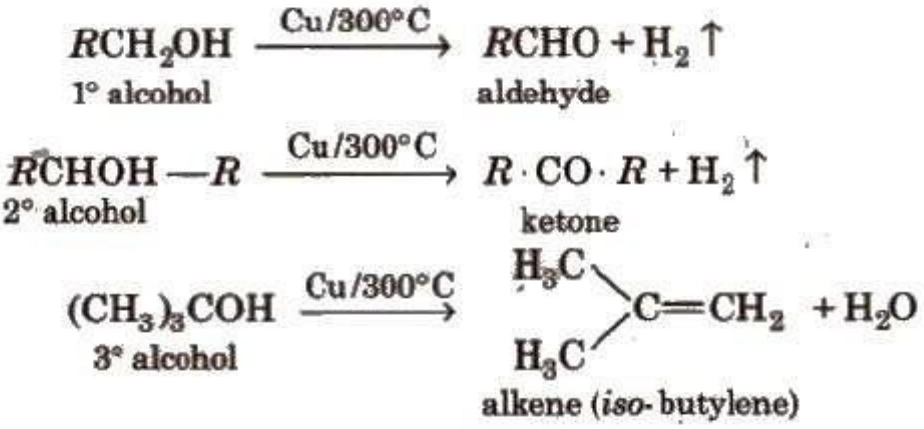


| Primary alcohols | Secondary alcohols | Tertiary alcohols |
|---|---|---|
| $CH_3CH_2OH$ | $CH_3CHOH—CH_3$ | $(CH_3)_3C—OH$ |
| $\downarrow[O]$ | $\downarrow[O]$ | $\downarrow[O]$ |
| $CH_3CHO$ | $CH_3COCH_3$ | $CH_3COCH_3 + CO_2 + H_2O$ |
| $\downarrow[O]$ | $\downarrow[O]$ | $\downarrow[O]$ |
| $CH_3COOH$ | $CH_3COOH + CO_2 + H_2O$ | $CH_3COOH + CO_2 + H_2O$ |

A common reagent that selectively oxidises a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (pCC).

$$CH_3CH{=}CH{-}CH_2OH \xrightarrow{PCC} CH_3CH{=}CH{-}CHO$$

**(e)Dehydrogenation**



$$\underset{1^\circ\ \text{alcohol}}{RCH_2OH} \xrightarrow{Cu/300^\circ C} \underset{\text{aldehyde}}{RCHO} + H_2\uparrow$$

$$\underset{2^\circ\ \text{alcohol}}{RCHOH{-}R} \xrightarrow{Cu/300^\circ C} \underset{\text{ketone}}{R\cdot CO\cdot R} + H_2\uparrow$$

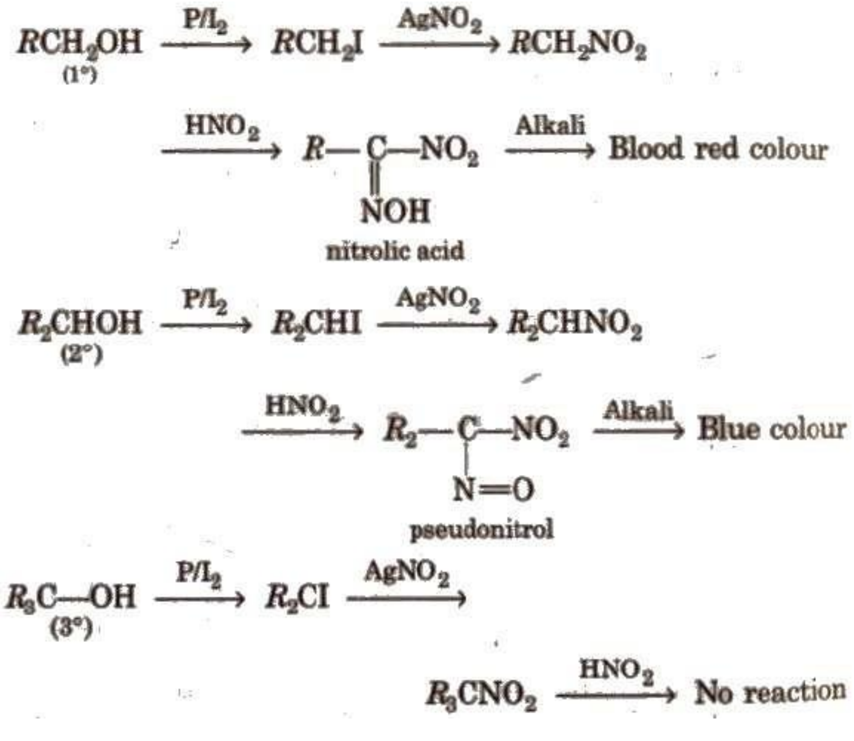
$$\underset{3^\circ\ \text{alcohol}}{(CH_3)_3COH} \xrightarrow{Cu/300^\circ C} \underset{\text{alkene (}iso\text{- butylene)}}{(H_3C)_2C{=}CH_2} + H_2O$$

**Distinction among 1°,2° and 3° Alcohols**

1°, 2° and 3° alcohols are distinguished by Lucas test, oxidation and reduced copper.

**Victor Meyer’s test** is also used to distinguish them.

In this test, primary (1°) alcohols give red colour, secondary (2°) alcohols give blue colour and tertiary (3°) alcohols give no colouration.



$$\underset{(1^\circ)}{RCH_2OH} \xrightarrow{P/I_2} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow{HNO_2} \underset{\text{nitrolic acid}}{R{-}\overset{}{\underset{\|\atop NOH}{C}}{-}NO_2} \xrightarrow{Alkali} \text{Blood red colour}$$

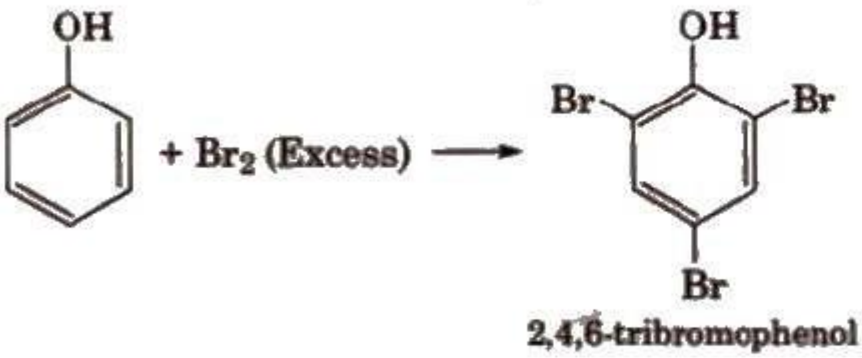
$$\underset{(2^\circ)}{R_2CHOH} \xrightarrow{P/I_2} R_2CHI \xrightarrow{AgNO_2} R_2CHNO_2 \xrightarrow{HNO_2} \underset{\text{pseudonitrol}}{R_2{-}\underset{|\atop N=O}{C}{-}NO_2} \xrightarrow{Alkali} \text{Blue colour}$$

$$\underset{(3^\circ)}{R_3C{-}OH} \xrightarrow{P/I_2} R_3CI \xrightarrow{AgNO_2} R_3CNO_2 \xrightarrow{HNO_2} \text{No reaction}$$

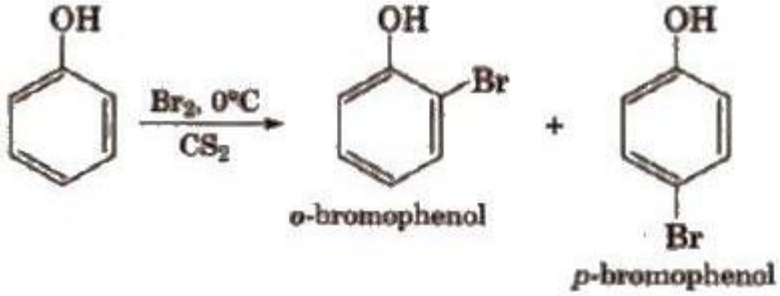
## Reactions of Phenols

(i) **Electrophilic substitution reactions** The -OH group attached to the benzene ring activates it towards electrophilic substitution at ortho and para positions .

### (a) Halogenation

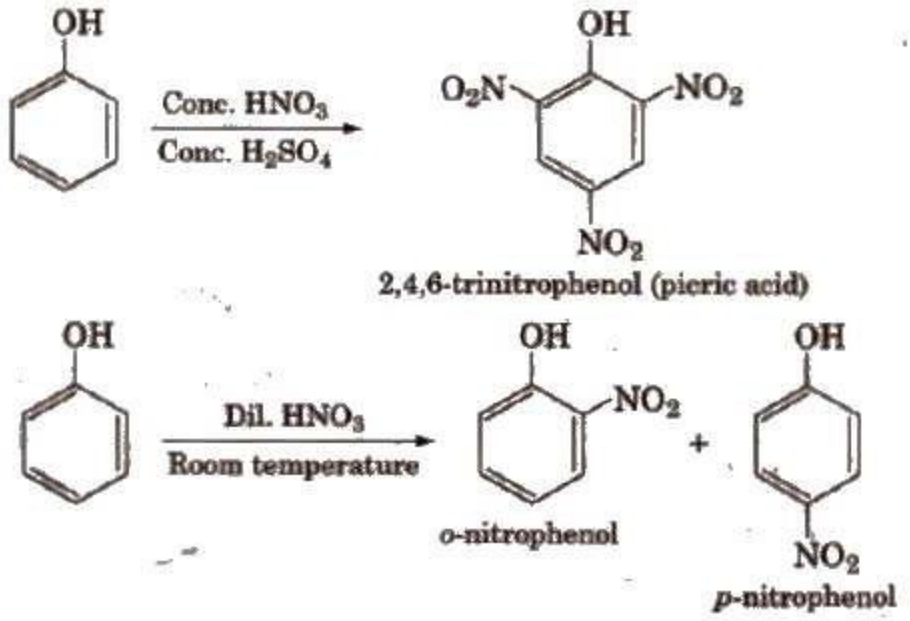


With calculated amount of $Br_2$ in $CS_2$ or $CHCl_3$ it gives ortho and para product.



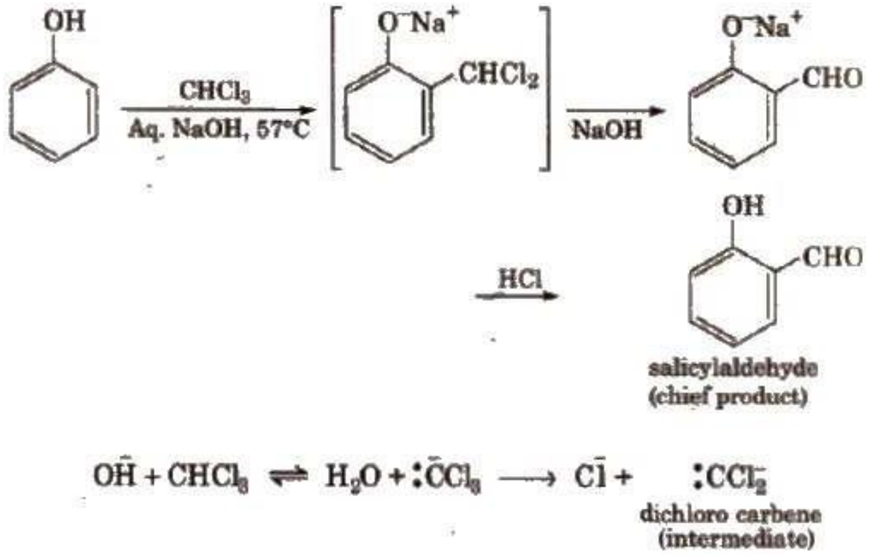
### (a) SuLphonation

**(b)Nitration**



The ortho and para isomers can be separated by steam distillation. This is because o- nitrophenol is steam volatile due to intramolecular hydrogen bonding while p nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

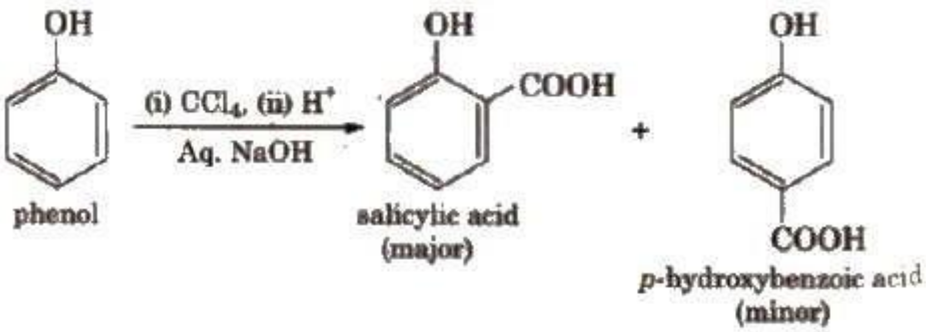
(a) **Reimer-Tiemann reaction**



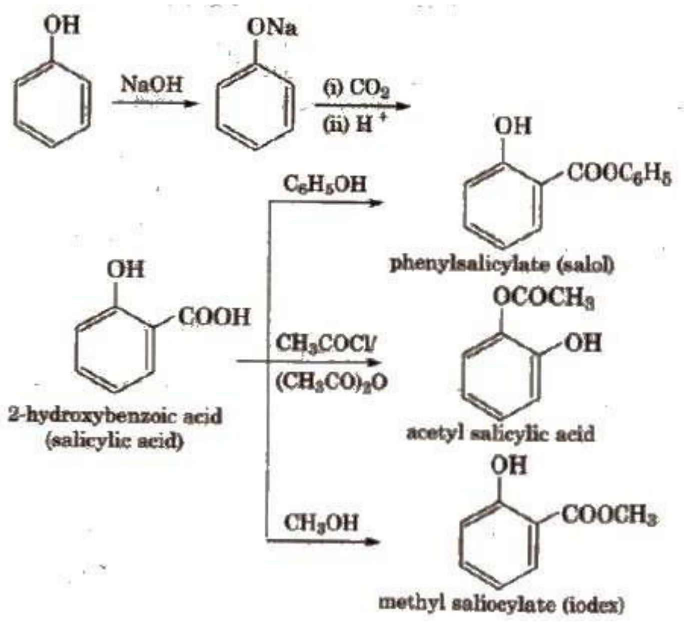
$$\overset{-}{O}H + CHCl_3 \rightleftharpoons H_2O + :\overset{-}{C}Cl_3 \longrightarrow \overset{-}{Cl} + :CCl_2$$

(b) This reaction is an electrophilic substitution reaction and electrophile is dichlorocarbene.

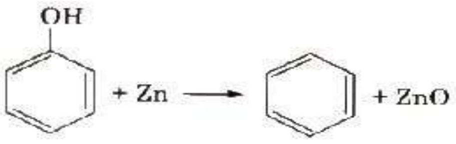
Similarly with carbon tetrachloride and alkali, c- and p-hydroxybenzoic acid are obtained.



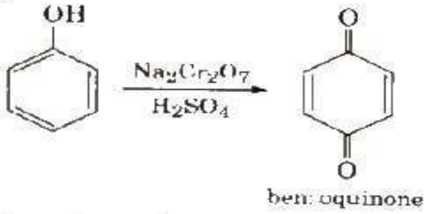
### (ii)**Kolbe's reaction**



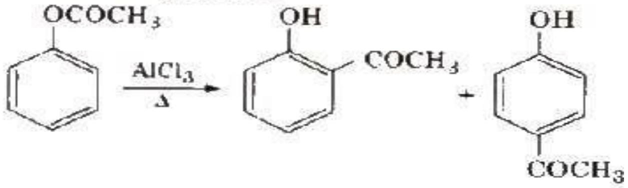
### (iii)Reaction with zinc dust



### (iv) Oxidation



### (v) Fries rearrangement



(a) **Rectified spirit** It contains 95% ethyl alcohol and 45% water. It is an azeotrope (constant boiling mixture) and boils at 74°(.

(b) **Absolute alcohol** Alcohol containing no water, i.e; 100% $C_2H_5OH$ is known as absolute alcohol. It is prepared as follows. 1.Quick lime process 2.Azeotropic method

(c)**Methylated spirit** The rectified spirit rendered poisonous by addition of 4-5% methyl alcohol, traces of pyridine and some copper sulphate and is known as methylated spirit or denatured alcohol.

(d)**Power alcohol** Alcohol mixed with petrol or fuel and used In internal combustion engines Is known as power alcohol.

(e)**Wood spirit** Methyl alcohol ($CH_3OH$) is also called wood spirit. It is obtained by destructive distillation of wood. Pyroligneous add, the product of destructive distillation of wood, contains acetic acid (10%), methyl alcohol (25%) and acetone (05%). Drinking of methanol causes blindness.

(f)**Grain alcohol** Ethyl alcohol $C_2H_5OH$ is also called grain alcohol. It is used In the preparation of various beverages containing different percentages.

## Dihydric Alcohols

These are generally called glycols because of their sweet taste. Ethylene glycol ($CH_2OH – CH_2OH$) is the first and most important member of dihydric alcohol series.

## Methods of Preparation

**(i) From ethylene**

$$CH_2{=}CH_2 + [O] + H_2O \xrightarrow{\text{Baeyer's reagent}} CH_2OH{-}CH_2OH$$

**(1% alkaline $KMnO_4$ is called Baeyer's reagent)**

$$CH_2{=}CH_2 \xrightarrow[Na_2SO_3/H_2O]{OsO_4/\text{pyridine}} CH_2OH{-}CH_2OH$$

**(ii) By reduction of glyoxal**

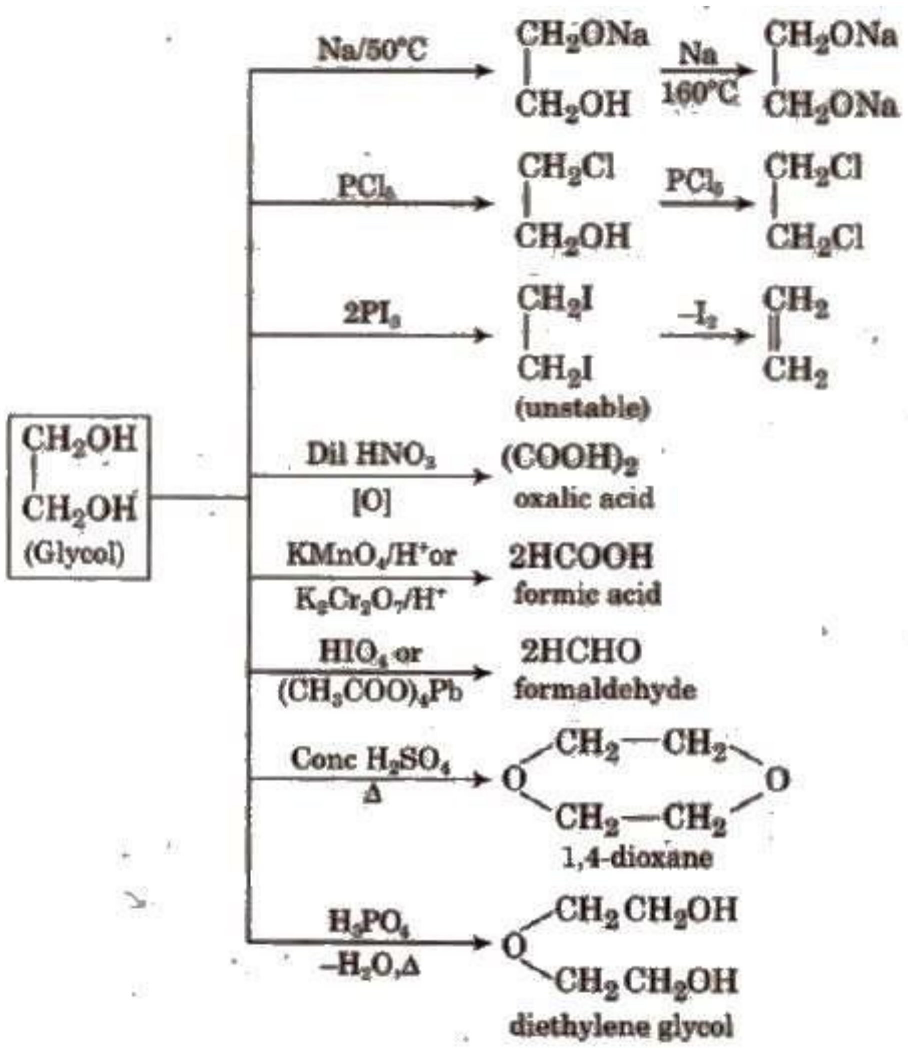
$$\underset{\text{glyoxal}}{\begin{matrix}CHO\\|\\CHO\end{matrix}} + [H] \xrightarrow{LiAlH_4} \underset{\text{ethylene glycol}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}}$$

## Physical Properties

1. It is a colourless, syrupy liquid with sweet taste.
2. Because of its tendency of formation of H-bonds, it is miscible with $H_2O$ and ethanol but not with ether.

**Chemical Properties**

It gives all the general reactions of -OH group.



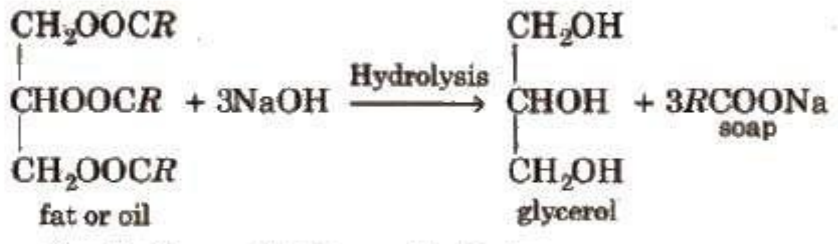
The per-iodic acid cleavage of 1,2-g1ycols is sometimes called Malaprade reaction.

**Trihydric Alcohols**

Glycerol or glycerine, CH$_2$OH – CH(OH)- CH$_2$OH is the first member of this group. Its IUPAC name is propane-l,2,3-triol.

**Method of Preparation**

It is obtained as a by product in saponification reaction.



$$\underset{\text{fat or oil}}{\begin{array}{l}CH_2OOCR\\ |\\ CHOOCR\\ |\\ CH_2OOCR\end{array}} + 3NaOH \xrightarrow{\text{Hydrolysis}} \underset{\text{glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + \underset{\text{soap}}{3RCOONa}$$

(where, $R = C_{17}H_{35}$ or $C_{15}H_{31}$ or $C_{17}H_{33}$)

**Physical Properties**

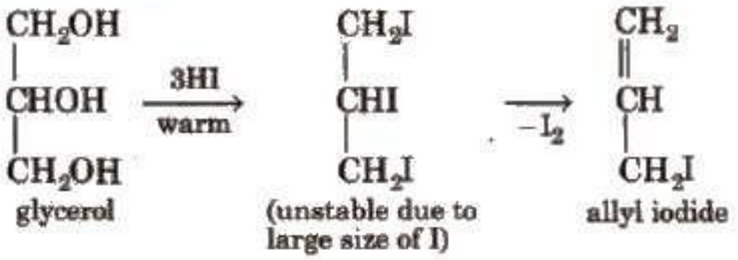
1. It is a colourless, odourless, viscous and hygroscopic liquid.
2. It is sweet in taste and steam volatile.
3. It is soluble in water but insoluble in ether.
4. Due to excessive H-bonding, it is highly viscous and has high boiling point.

**Chemical Properties**

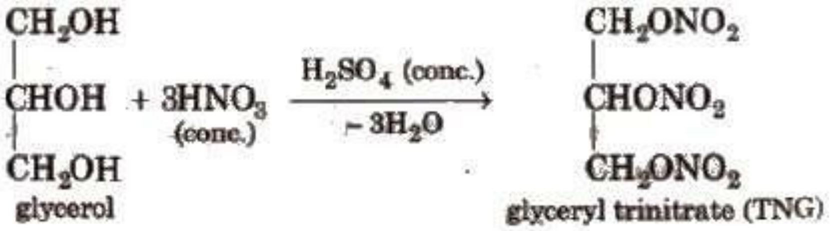
It gives all the general reactions given by -OR group but 2° OR is less reactive as compared to 1° .

Some of its specific reactions are :

**(i) Reaction with HI**



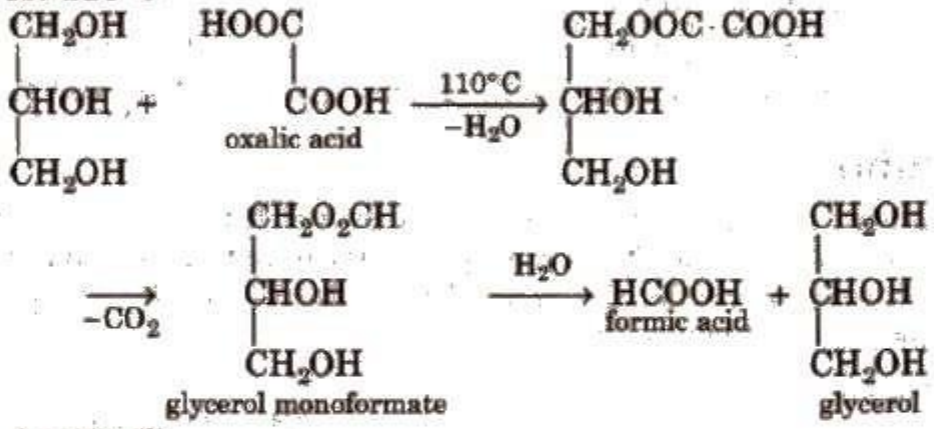
**(ii) Reaction with HNO₃**



Glyceryl trinitrate or tri nitroglycerine, when adsorbed on Kieselguhr is known as dynamite. Mixture of TNG and cellulose trinitrate is called blasting gelatin.

### (iii) Reaction with oxalic acid

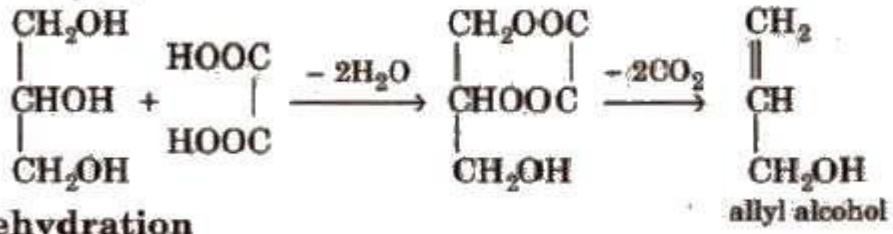
**(a) At 110°C**



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \begin{array}{l}HOOC\\|\\COOH\end{array} \xrightarrow[-H_2O]{110^\circ C} \begin{array}{l}CH_2OOC\cdot COOH\\|\\CHOH\\|\\CH_2OH\end{array}$$

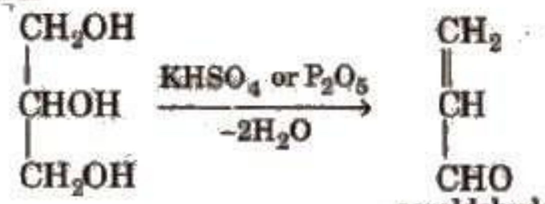
$$\xrightarrow[-CO_2]{} \begin{array}{l}CH_2O_2CH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow{H_2O} HCOOH + \begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}$$

**(b) At 260°C**



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \begin{array}{l}HOOC\\|\\HOOC\end{array} \xrightarrow{-2H_2O} \begin{array}{l}CH_2OOC\\|\qquad\;\;|\\CHOOC\\|\\CH_2OH\end{array} \xrightarrow{-2CO_2} \begin{array}{l}CH_2\\\|\\CH\\|\\CH_2OH\end{array}$$

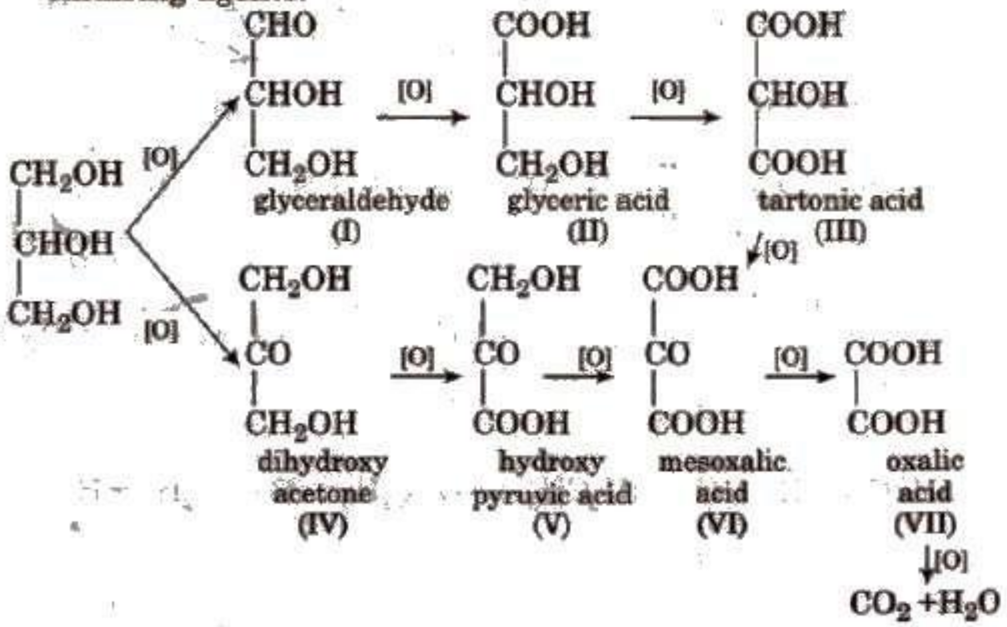
### (iv) Dehydration



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow[-2H_2O]{KHSO_4 \text{ or } P_2O_5} \begin{array}{l}CH_2\\\|\\CH\\|\\CHO\end{array}$$

acraldehyde
or acrolein (bad smelling compound)

**(v) Oxidation** Different products are obtained by different oxidising agents.



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow{[O]} \begin{array}{l}CHO\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow{[O]} \begin{array}{l}COOH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow{[O]} \begin{array}{l}COOH\\|\\CHOH\\|\\COOH\end{array} \xrightarrow{[O]} \begin{array}{l}COOH\\|\\CO\\|\\COOH\end{array}$$

$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow{[O]} \begin{array}{l}CH_2OH\\|\\CO\\|\\CH_2OH\end{array} \xrightarrow{[O]} \begin{array}{l}CH_2OH\\|\\CO\\|\\COOH\end{array} \xrightarrow{[O]} \begin{array}{l}COOH\\|\\CO\\|\\COOH\end{array} \xrightarrow{[O]} \begin{array}{l}COOH\\|\\COOH\end{array} \xrightarrow{[O]} CO_2 + H_2O$$

Conc. $HNO_3$ gives II; dil $HNO_3$ gives II and III; $Bi(NO_3)_3$ or $NaNO_3$ gives VI; Fenton's reagent or NaOBr or $Br_2$ water in $Na_2CO_3$ gives a mixture of I and IV.

Solid $KMnO_4$ oxidises glycerol to VII and $CO_2$ and $H_2O$.

With $HIO_4$ (periodic acid). glycerol gives HCOOH and HCHO.

**Ethers**

Ethers are the organic compounds in which two alkyl or aryl groups are attached to a divalent oxygen. known as ethereal oxygen. These are represented by the general formula R–O-R" where R may be alkyl or aryl groups. e.g.,

$CH_3—O—CH_3$, dimethyl ether

$C_2H_5—O—C_2H_5$ diethyl ether

**Mixed ethers**

$CH_3—O—C_2H_5$, ethyl methyl ether

$CH_3—O—C_3H_7$ methyl *n*-propyl ether

These are the functional isomers of alcohols. These also exhibit chain isomerism and metamerism.

**Nomenclature of Ethers**

In the IUPAC system, ethers are regarded as 'alkoxy alkanes' in which the ethereal oxygen is taken along with smaller alkyl group while the bigger alkyl group is regarded as a part of the alkane.

**Preparation of Ethers  lab method Williamson continuous process**

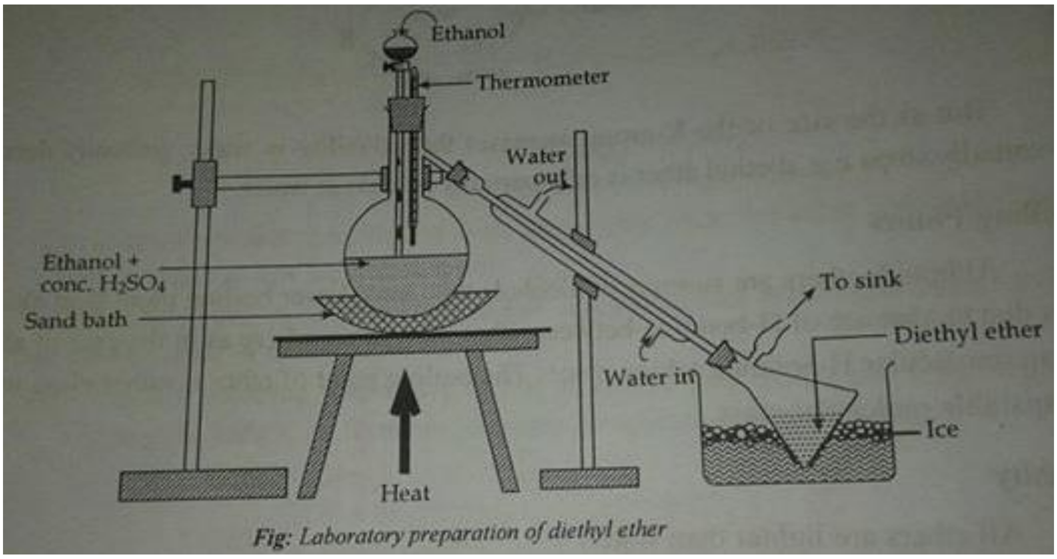


*Fig: Laboratory preparation of diethyl ether*

Principle:-
In the laboratory ethoxyethane is prepared by dehydrating ethanol with c.$H_2SO_4$ in the ratio of 2:1 at 140C temperature.
The reaction completes in two steps:
1)Formation of ethylhydrogen sulphate at 100C

$CH_3CH_2OH$ + conc.$H_2SO_4$ —-> $CH_3CH_2HSO_4$ + $H_2O$

2)Formation of diethylether at 140C

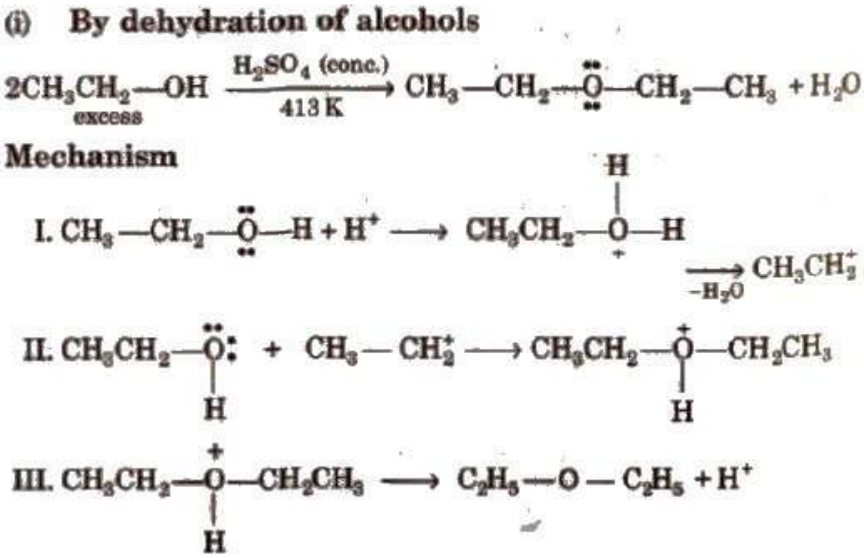
$CH_3CH_2HSO_4 + CH_3CH_2OH$ —-> $CH_3CH_2$-O-$CH_2CH_3$
Equivalet Reaction:-
$2CH_3CH_2OH$ + conc.$H_2SO_4$ —-> $CH_3CH_2$-O-$CH_2CH_3$ + $H_2SO_4.H_2O$

Procedure:-

Mixture of ethanol and conc.$H_2SO_4$ in the ratio of 2:1 is taken in clean Round Bottom Flask (RBF). The flask is fitted with dropping funnel,thermometer and water condensor which is turn is connected to receiver which is immersed in ice cold water.The flask is gently heated on water bath.At 140C,1 volume of ethanol is added at regular interval of time so that ethoxyethane is recieved in receiver continuously.This process of continuous convertion of alcohol into ether is called continuous etherification.Ether thus obtained contains water,alcohol and $SO_2$ as impurities.

Purification:-

The lab preapred ether is impure and may contain $C_2H_5OH$,$SO_2$ and water as impurities.
-Acidic impurities are removed by using dil.NaOH solution.
-The alcohol is removed by using 50% $CaCl_2$ solution.
-To remove soluble salts,the etherial solution is washed with cold water frequently.
-The water is removed by using anh.$CaCl_2$
-Finally,Ether is refined by Redistillation process carried out at about 34C to 36C (Since BPT of diethylether is about 35C)



**(i) By dehydration of alcohols**

$$\underset{\text{excess}}{2CH_3CH_2{-}OH} \xrightarrow[413\,K]{H_2SO_4\,(conc.)} CH_3{-}CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}CH_2{-}CH_3 + H_2O$$

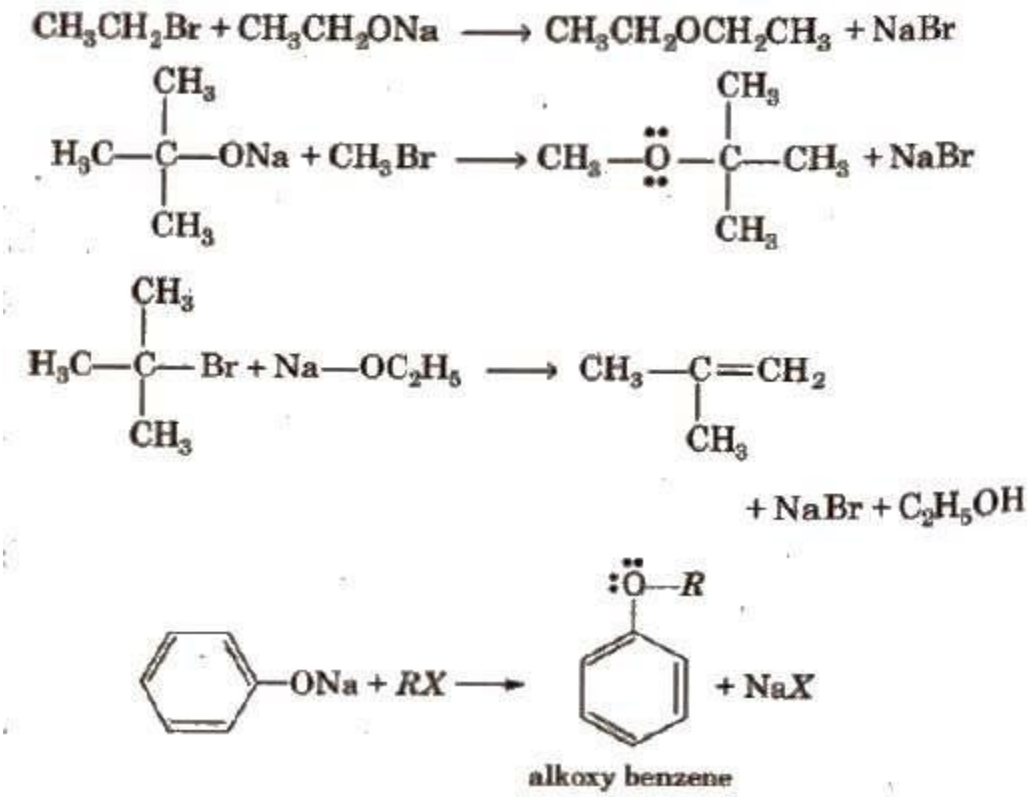
**Mechanism**

$$\text{I. } CH_3{-}CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + H^+ \longrightarrow CH_3CH_2{-}\underset{+}{\overset{\overset{H}{|}}{O}}{-}H \xrightarrow[-H_2O]{} CH_3CH_2^+$$

$$\text{II. } CH_3CH_2{-}\underset{\underset{H}{|}}{\ddot{O}}{:} + CH_3{-}CH_2^+ \longrightarrow CH_3CH_2{-}\underset{\underset{H}{|}}{\overset{+}{O}}{-}CH_2CH_3$$

$$\text{III. } CH_3CH_2{-}\underset{\underset{H}{|}}{\overset{+}{O}}{-}CH_2CH_3 \longrightarrow C_2H_5{-}O{-}C_2H_5 + H^+$$

**(ii)Williamson’s synthesis** Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.



$$CH_3CH_2Br + CH_3CH_2ONa \longrightarrow CH_3CH_2OCH_2CH_3 + NaBr$$

$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-ONa + CH_3Br \longrightarrow CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + NaBr$$

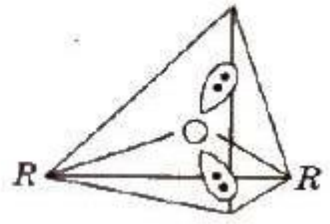
$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br + Na-OC_2H_5 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr + C_2H_5OH$$

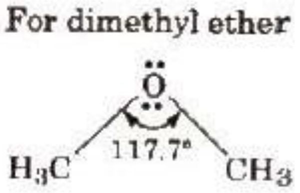
### Physical Properties of Ethers

Ethers are polar but insoluble inH20 and have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

### Structure of Ether

The hybridisation of 0 atom in ethers is $sp^3$ (tetrahedral) and its shape is V-shape.

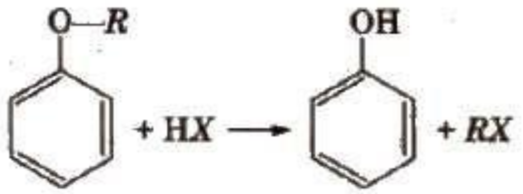




### Chemical Reactions of Ether

#### (i) Reaction with HX

$$R\text{—}O\text{—}R + HX \longrightarrow RX + R\text{—}OH$$



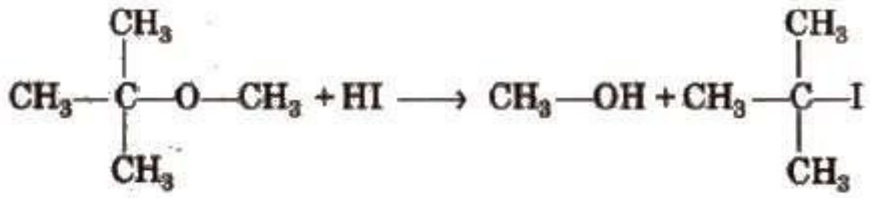
Ethers with two different alkyl groups are also cleaved in the same manner and results in the formation of a primary halide (or smaller and less complex alkyl halide) by S R-O-R’ + $_{N}^{2}$ mechanism.

HX → RX + R’OR

The order of reactivity of hydrogen halides is as follows HI >

HBr > HCl

In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by $S_N{}^1$mechanism.



$$CH_3\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—}O\text{—}CH_3 + HI \longrightarrow CH_3\text{—}OH + CH_3\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—}I$$

#### (ii) Halogenation

$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{Dark}]{Cl_2} \underset{(\alpha\text{-monochloro diethyl ether})}{CH_3CHClOCH_2CH_3}$$

$$C_2H_5OC_2H_5 + \underset{(\text{excess})}{10Cl_2} \xrightarrow[(\text{light})]{h\nu} \underset{(\text{perchlorodiethyl ether})}{C_2Cl_5OC_2Cl_5} + 10HCl$$

#### (iii) Reaction with $PCl_5$

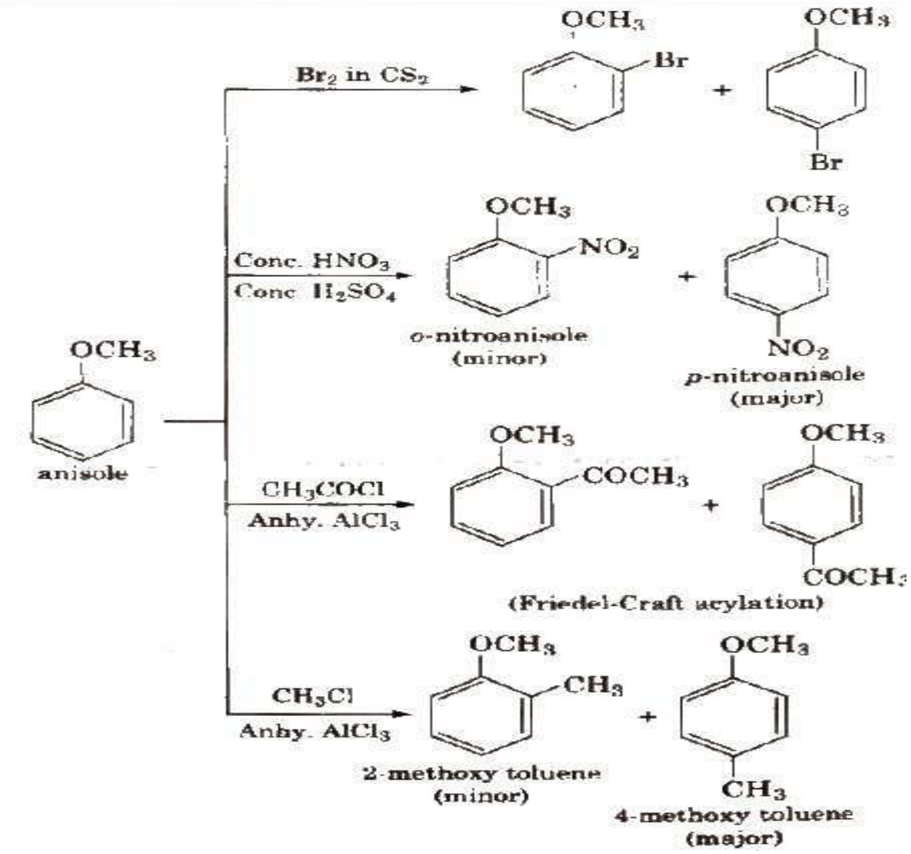
$$R\text{—}O\text{—}R + PCl_5 \xrightarrow{\Delta} 2RCl + POCl_3$$

#### (iv) Reaction with CO

$$ROR + CO \xrightarrow[500\text{ atm}]{BF_3/150°C} RCOOR$$

(v) Electrophilic 8ublititutioD reactions In ethers,-OR is ortho, para directing group and activate. the aromatic ring towards electrophilic substitution reaction.

1. .



Ethyl phenyl ester $C_6H_5OC_2H_5$ is also, known as phenetole.

**Uses of Ethers**

1.Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2.Diethyl Ether is used as an anaesthesia in surgery

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**Uses of Ethers**

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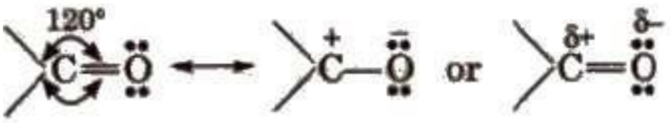
## Chapter -12 Aldehydes, Ketones and Carboxylic Acids

In aldehydes, the carbonyl group ( =C=O) is bonded to carbon and hydrogen, while in the ketones, it is bonded to two carbon atoms

**Nature of Carbonyl Group**

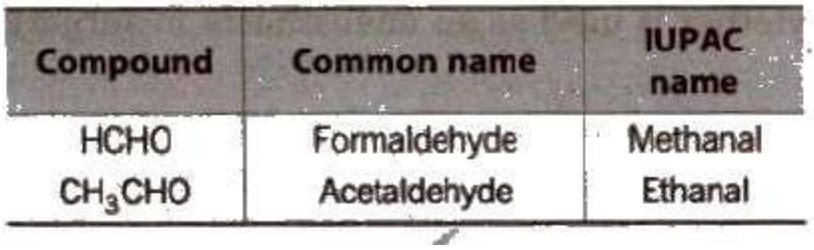
The carbon and oxygen of the carbonyl group are $Sp^2$ hybridised and the carbonyl double bond contains one o-bond and one π-bond.



The electronegativity of oxygen is much higher than that of the carbon, so there electron cloud is shifted towards the oxygen. Therefore, C-O bond is polar in nature.

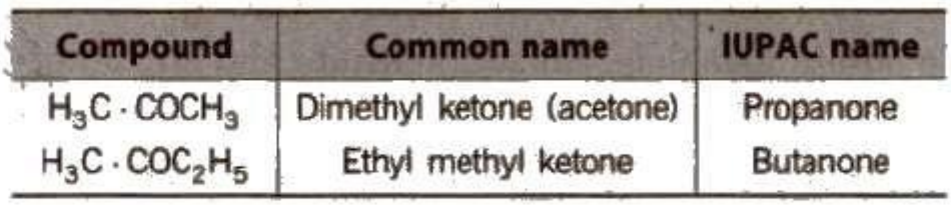
**Nomenclature**

(i) **Nomenclature of aldehydes** In IUPAC system, the suffix “e” of alkane is replaced by the suffIX “al”. e.g.,



| Compound | Common name | IUPAC name |
|---|---|---|
| HCHO | Formaldehyde | Methanal |
| $CH_3CHO$ | Acetaldehyde | Ethanal |

(ii) **Nomenclature of ketones** In IUPAC system, the suffix “e” of alkane is replaced by “one”. e.g.,

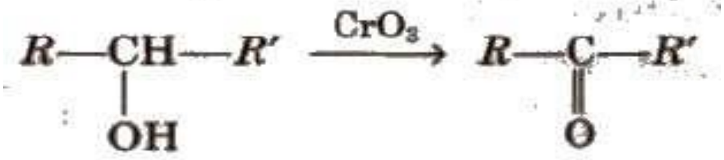


| Compound | Common name | IUPAC name |
|---|---|---|
| $H_3C \cdot COCH_3$ | Dimethyl ketone (acetone) | Propanone |
| $H_3C \cdot COC_2H_5$ | Ethyl methyl ketone | Butanone |

**Preparation of Aldehydes and Ketones**

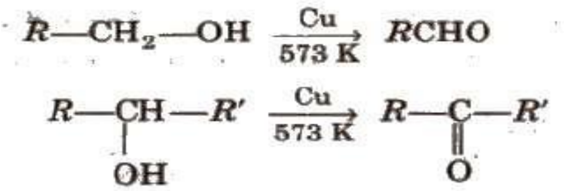
(i) **By oxidation of alcohols** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$



$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{CrO_3} R-\underset{\underset{O}{\|}}{C}-R'$$

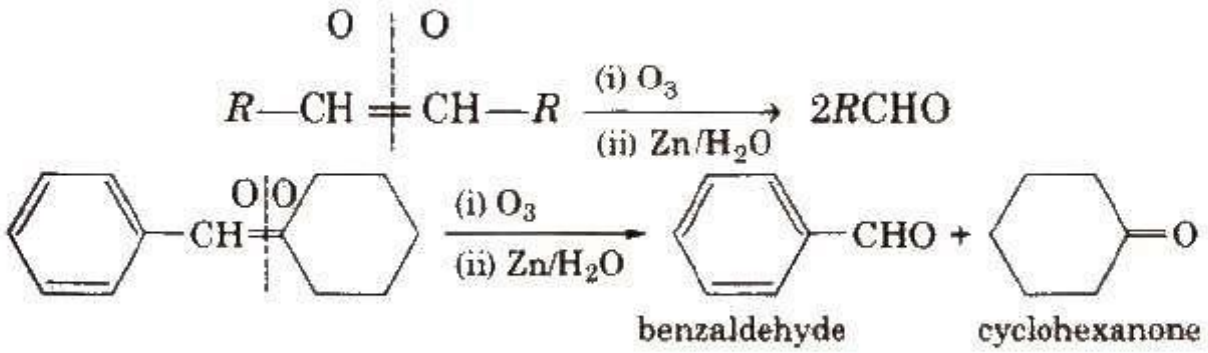
**(ii)By dehydrogenation of alcohols** In this method, alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones.



$$R{-}CH_2{-}OH \xrightarrow[573\,K]{Cu} RCHO$$

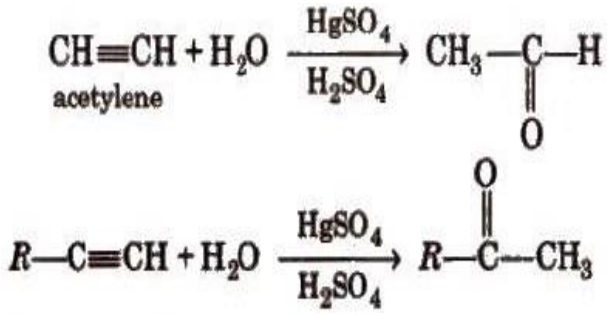
$$R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}R' \xrightarrow[573\,K]{Cu} R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R'$$

**(ii) By ozonolysis of alkenes**



$$R{-}CH{=}CH{-}R \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} 2RCHO$$

(iii) **By hydration of alkynes** Acetylene on hydration gives acetaldehyde and other alkynes on hydration give ketones.



$$\underset{\text{acetylene}}{CH{\equiv}CH} + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}H$$

$$R{-}C{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3$$

(v) **By heating Ca salt of acid**

$$(RCOO)_2Ca \xrightarrow{\Delta} RCOR + CaCO_3$$

To obtain aldehyde, calcium formate and any other Ca salt of acid are heated.

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} RCHO + CaCO_2$$

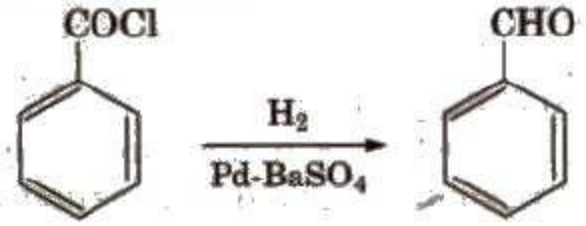
(vi) **By decarboxylation and dehydration of aromatic acids**

$$C_6H_5COOH + HCOOH \xrightarrow[300°C]{MnO} C_6H_5CHO + H_2O + CO_2$$

$$C_6H_5COOH + HOOCH_3 \xrightarrow[100°C]{MnO} C_6H_5COCH_3 + H_2O + CO_2$$

**Preparation of Aldehydes**

(i) **Rosenmund reduction**



benzoyl chloride benzaldehyde

Formaldehyde cannot be prepared by this method as HCOCl is highly unstable.

(ii) **From nitriles**

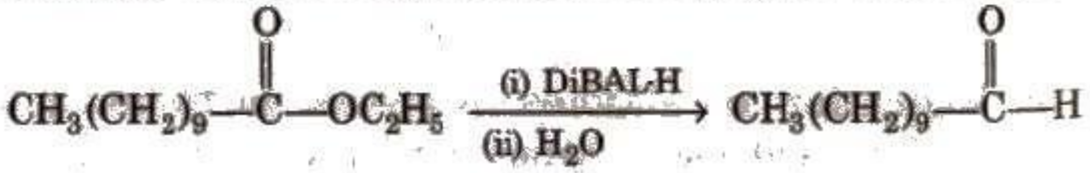
$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

This reaction is called **Stephen reaction**.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, [DiBAL-H] to imines which on hydrolysis give aldehydes.

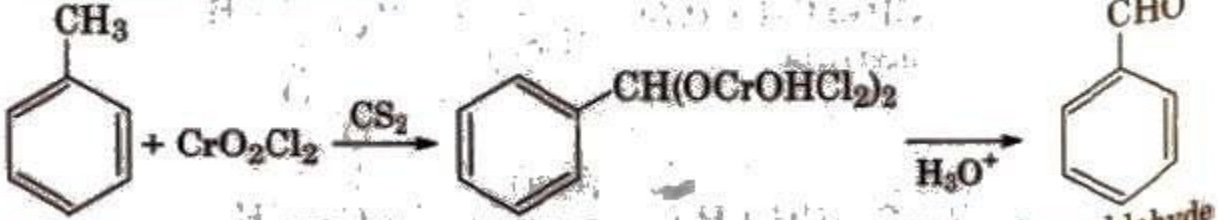
$$RCN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(iBu)_2} RCHO$$

Similarly, esters can also reduced to aldehydes with DiBAL-H.



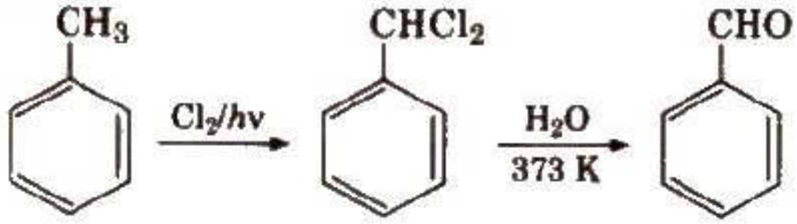
$$CH_3(CH_2)_9-\overset{\overset{\large O}{\|}}{C}-OC_2H_5 \xrightarrow[\text{(ii) } H_2O]{\text{(i) DiBAL-H}} CH_3(CH_2)_9-\overset{\overset{\large O}{\|}}{C}-H$$

(iii) **Etard reaction**

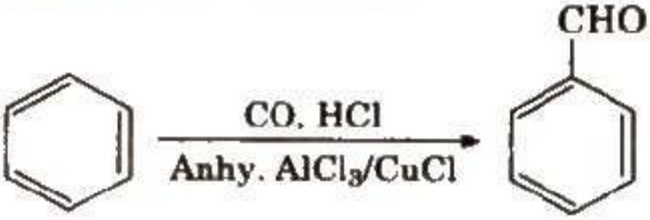


toluene benzaldehyde

### (iv) Side chain halogenatiohn followed by hydrolysis of toluene

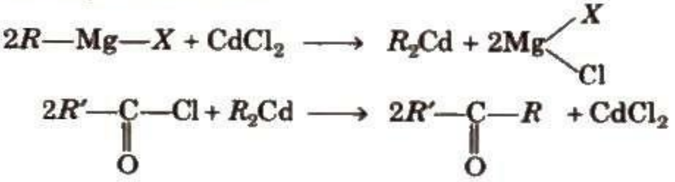


### (v) Gattermann-Koch synthesis



## Preparation of Ketones

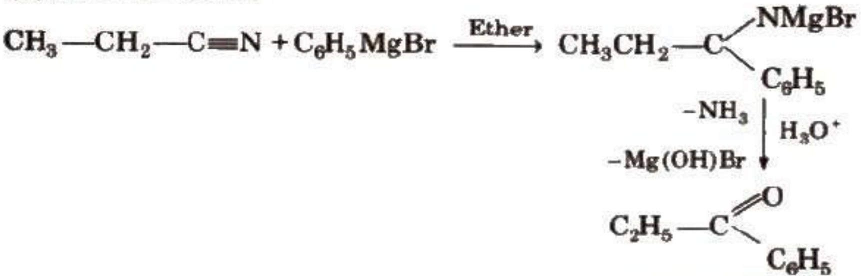
### (i) From acyl chlorides



$$2R{-}Mg{-}X + CdCl_2 \longrightarrow R_2Cd + 2Mg\genfrac{}{}{0pt}{}{X}{Cl}$$

$$2R'{-}\underset{\underset{O}{\|}}{C}{-}Cl + R_2Cd \longrightarrow 2R'{-}\underset{\underset{O}{\|}}{C}{-}R + CdCl_2$$

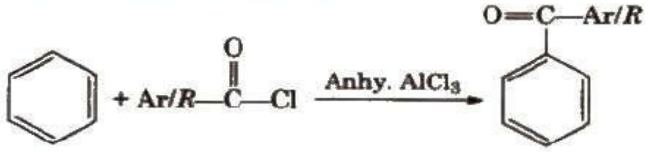
### (ii) From nitriles



$$CH_3{-}CH_2{-}C{\equiv}N + C_6H_5MgBr \xrightarrow{Ether} CH_3CH_2{-}C\genfrac{}{}{0pt}{}{NMgBr}{C_6H_5} \xrightarrow[-Mg(OH)Br]{-NH_3 \quad H_3O^+} C_2H_5{-}C\genfrac{}{}{0pt}{}{=O}{C_6H_5}$$

(1-phenylpropanone)

### (iii) Friedel-Crafts acylation



### (iv) Oppenauer oxidation

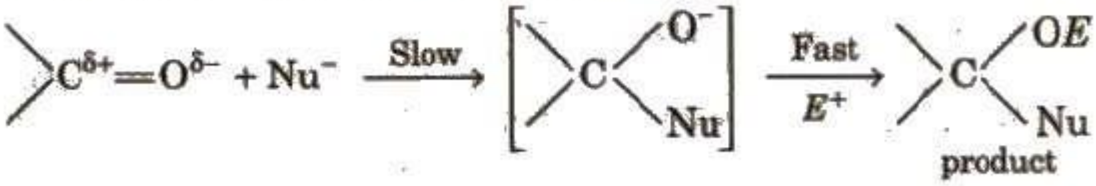
$$\underset{\text{2° alcohol}}{R_2CHOH} + (CH_3)_2C{=}O \xrightarrow{[(CH_3)_3CO]_3Al} \underset{\text{ketone}}{R_2C{=}O} + \underset{\text{iso-propyl alcohol}}{(CH_3)_2CHOH}$$

**Physical Properties of Aldehydes and Ketones**

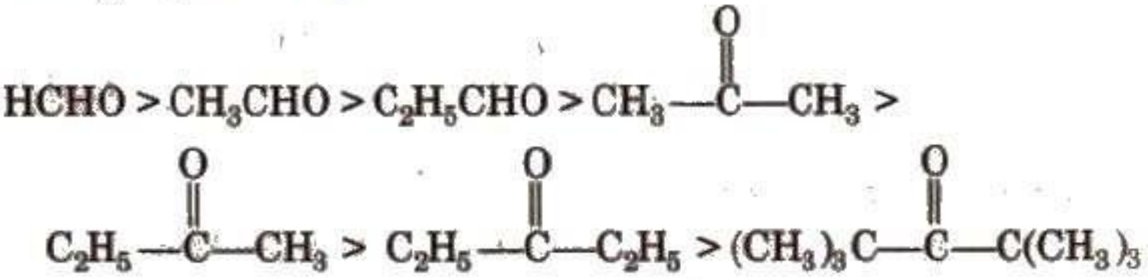
1. Methanal (HCHO) is a gas at room temperature. and its 40% aqueous solution is known as formalin. It is a reducing agent in silvering of mirrors and decolourising vat dyes.
2. Ethanal ($CH_3CHO$) is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.
3. The boiling point of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.
4. Aldehydes and ketones have lower boiling point than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
5. The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.
6. Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.

**Chemical Reactions of Aldehydes and Ketone**

**(i) Nucleophilic addition reactions**



**Reactivity order is**



$$HCHO > CH_3CHO > C_2H_5CHO > CH_3-\overset{\text{O}}{\overset{\|}{C}}-CH_3 >$$

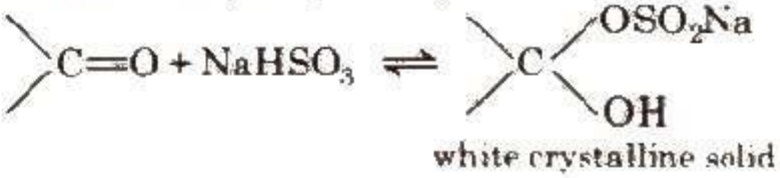
$$C_2H_5-\overset{\text{O}}{\overset{\|}{C}}-CH_3 > C_2H_5-\overset{\text{O}}{\overset{\|}{C}}-C_2H_5 > (CH_3)_3C-\overset{\text{O}}{\overset{\|}{C}}-C(CH_3)_3$$

**It is due to + *I* effect of alkyl groups which decreases the positive charge on carbonyl carbon and steric hinderance (The bulky alkyl group hinder the approach of nucleophile).**

**Addition of hydrogen cyanide**

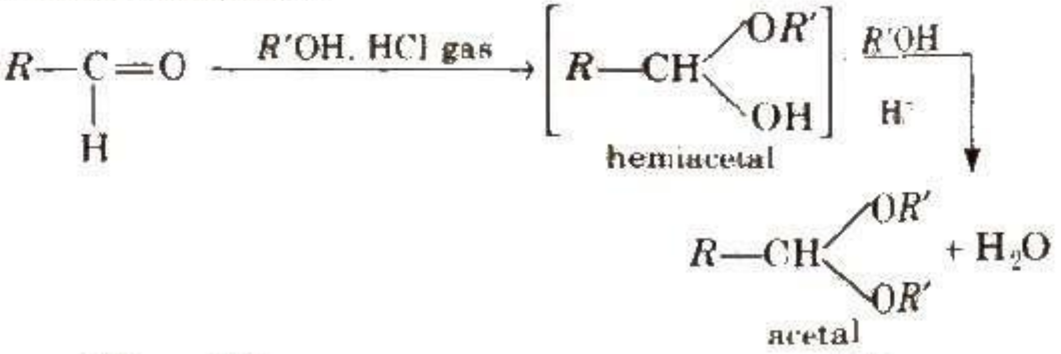
cyanohydrin

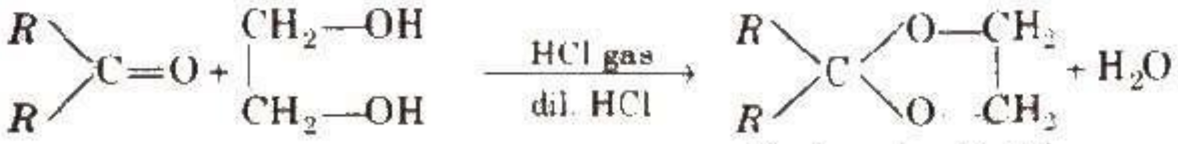
**Addition of sodium hydrogen sulphite**



This reaction is used for the separation and purification of aldehydes and ketones. This is because the addition compound formed, is water soluble and can be converted back to the original carbonyl compound by treating with dilute mineral acid or alkali.

**Addition of lower alcohols**



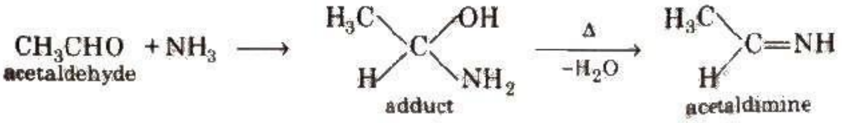


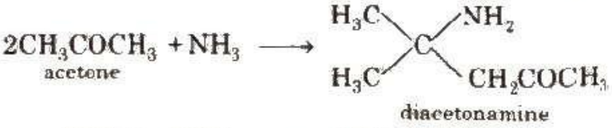
ethylene glycol ketal

(ii) **Addition of ammonia and its derivatives** Reaction with ammonia

$$\underset{\text{formaldehyde}}{6HCHO} + 4NH_3 \longrightarrow \underset{\text{hexamethylene tetramine (urotropine)}}{(CH_2)_6N_4} + 6H_2O$$

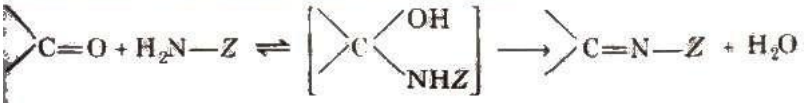
Urotropine on controlled nitration gives the well known explosive RDX (Research and Development explosive).





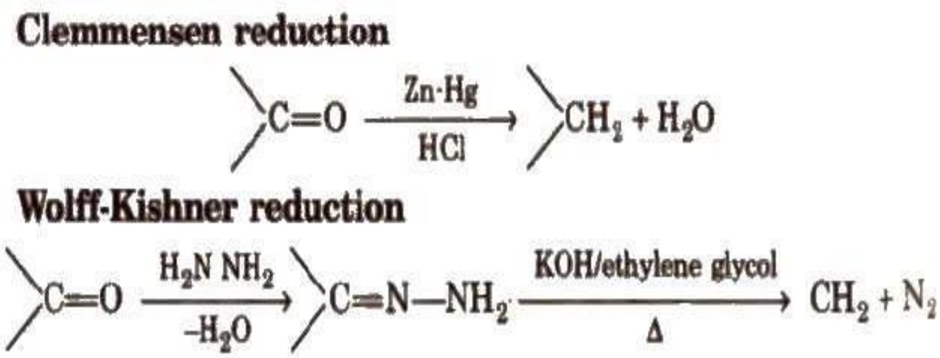
$$RCHO + RHN_2 \longrightarrow \underset{\text{Schiff's base}}{RCH{=}NHR}$$

**Reaction with ammonia derivatives**



where, $Z$ = alkyl, aryl, —OH, —$NH_2$, —$C_6H_5NH$, —$NHCONH_2$ etc.

**Reduction-** Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride [$LiAlH_4$].



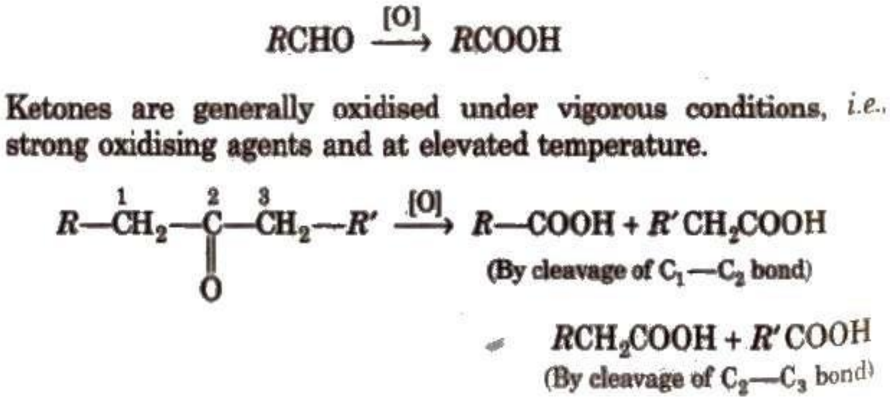
**Clemmensen reduction**

$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$$

**Wolff-Kishner reduction**

$$>C=O \xrightarrow[-H_2O]{H_2N\,NH_2} >C=N-NH_2 \xrightarrow[\Delta]{KOH/ethylene\ glycol} CH_2 + N_2$$

(iii) **Oxidation** Aldehydes get easily oxidised to carboxylic acids by $HNO_3$, $KMnO_4$, $K_2Cr_2O_7$, etc., or even by mild oxidising agent.



$$RCHO \xrightarrow{[O]} RCOOH$$

**Ketones are generally oxidised under vigorous conditions,** *i.e.*, **strong oxidising agents and at elevated temperature.**

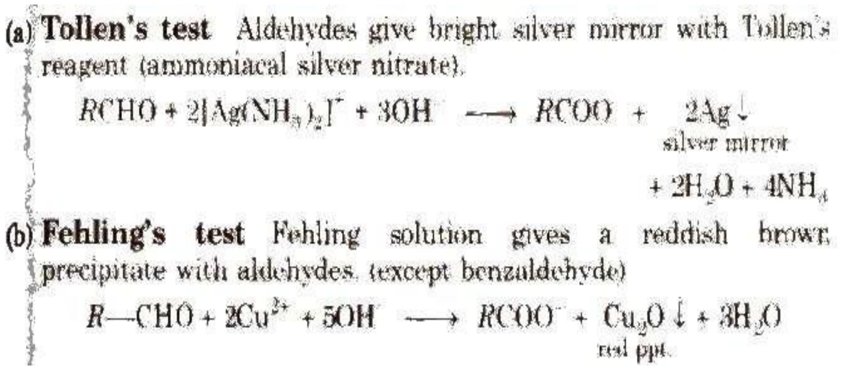
$$R-\overset{1}{C}H_2-\underset{\underset{O}{\|}}{\overset{2}{C}}-\overset{3}{C}H_2-R' \xrightarrow{[O]} R-COOH + R'CH_2COOH$$

(By cleavage of $C_1-C_2$ bond)

$$RCH_2COOH + R'COOH$$

(By cleavage of $C_2-C_3$ bond)

During oxidation of unsymmetrical ketones the point of cleavage is such that keto group stays preferentially with the smaller alkyl group popoff"s rule).



(a) **Tollen's test** Aldehydes give bright silver mirror with Tollen's reagent (ammoniacal silver nitrate).

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + \underset{\text{silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3$$

(b) **Fehling's test** Fehling solution gives a reddish brown precipitate with aldehydes. (except benzaldehyde)

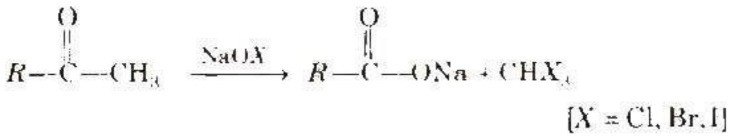
$$R-CHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + \underset{\text{red ppt.}}{Cu_2O\downarrow} + 3H_2O$$

[Fehling solution is a mixture of Fehling solution A and Fehling solution B in 1: 1 ratio. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartrate which is also called, Rochelle salt.]

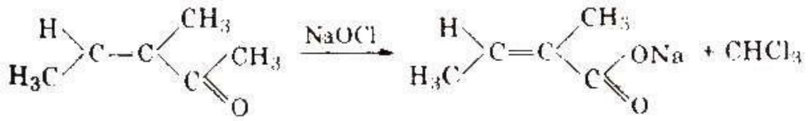
(c)**Benedict solution** With it, aldehydes (except benzaldehyde) also give red ppt. of $CU_2O$.

**(d)Schiff's reagent** It is an aqueous solution of magenta or pink coloured rosaniline hydrochloride which has been decolourised by passing $SO_2$, Aldehydes give pink colour with this reagent but ketones do not.

**Haloform reaction** Aldehydes and ketones having at east one methyl group [3-α hydrogen] linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform.

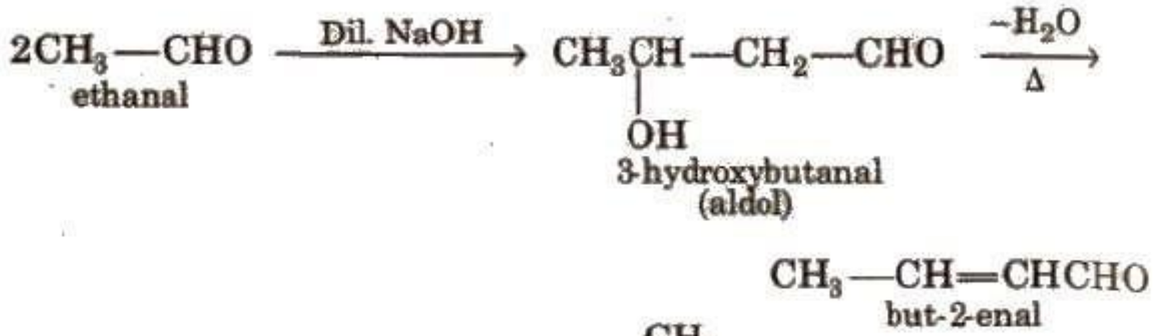


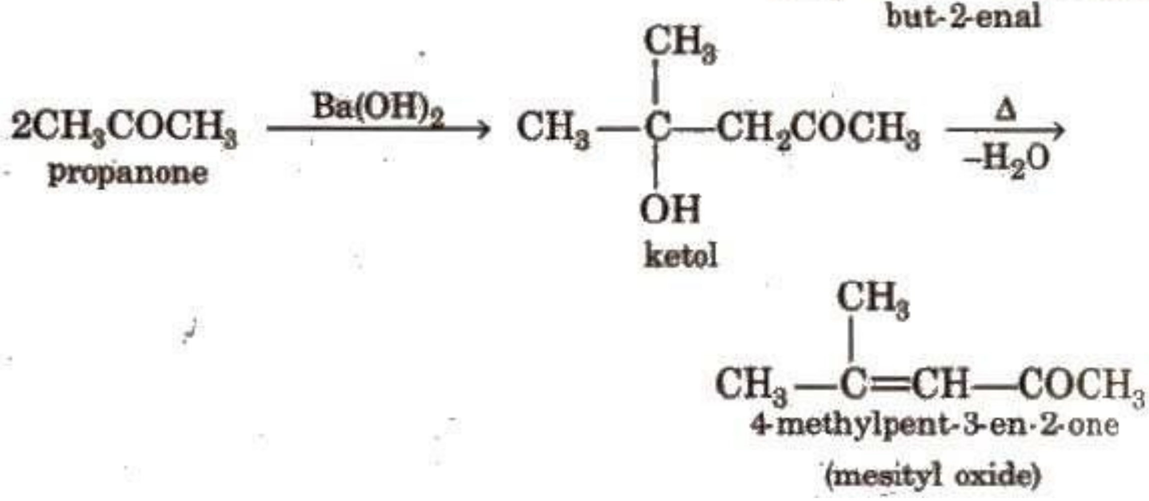
This oxidation does not affect a carbon-carbon double bond, if present in the molecule.



Iodoform reaction with sodium hypoiodite is also used for the detection of $CH_3$ – group or $CH_3CH(OH)$- group by producing yellow solid $CHI_3$.

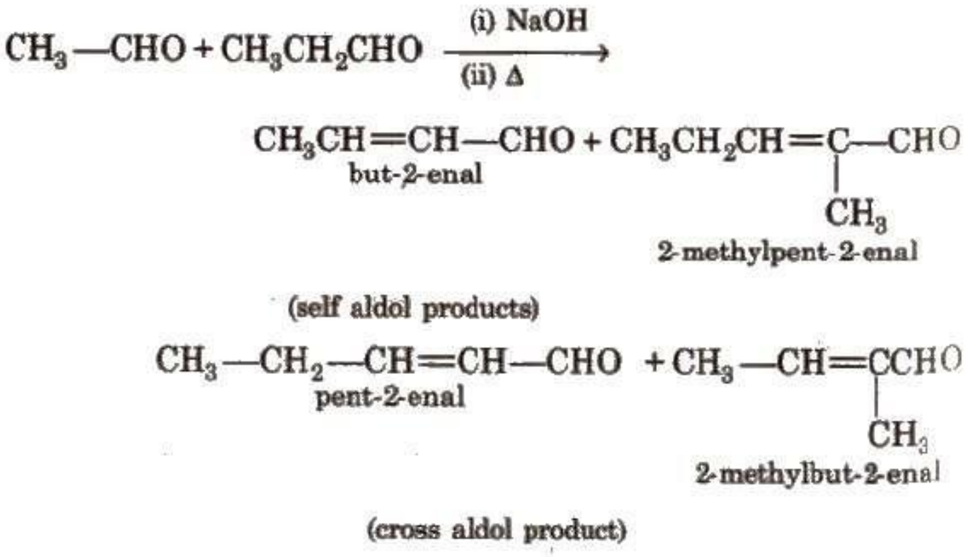
**(ii) Aldol condensation**





This reaction is exhibited by those aldehydes and ketones which have at least one a-hydrogen.

(ii) **Cross aldol condensation** Base catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen-Schmidt condensation or Claisen reaction**.



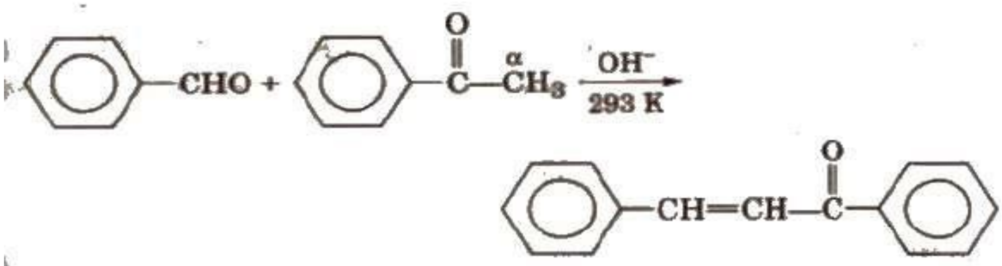
$$CH_3—CHO + CH_3CH_2CHO \xrightarrow[\text{(ii) }\Delta]{\text{(i) NaOH}}$$

$$\underset{\text{but-2-enal}}{CH_3CH=CH—CHO} + \underset{\text{2-methylpent-2-enal}}{CH_3CH_2CH=\underset{\substack{|\\ CH_3}}{C}—CHO}$$

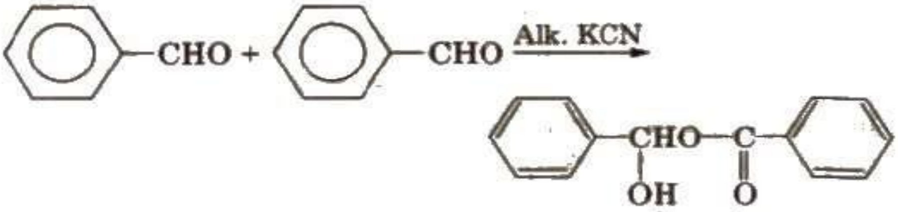
(self aldol products)

$$\underset{\text{pent-2-enal}}{CH_3—CH_2—CH=CH—CHO} + \underset{\text{2-methylbut-2-enal}}{CH_3—CH=\underset{\substack{|\\ CH_3}}{C}CHO}$$

(cross aldol product)



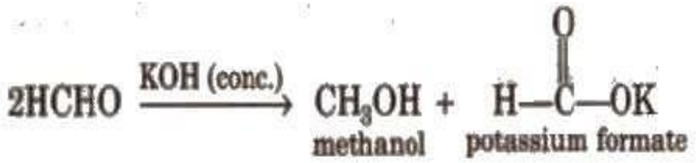
1,3-diphenylprop-2-en-1-one
(benzalacetophenone)
major product

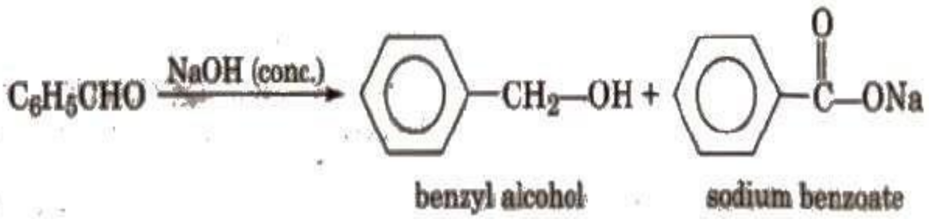


benzoin

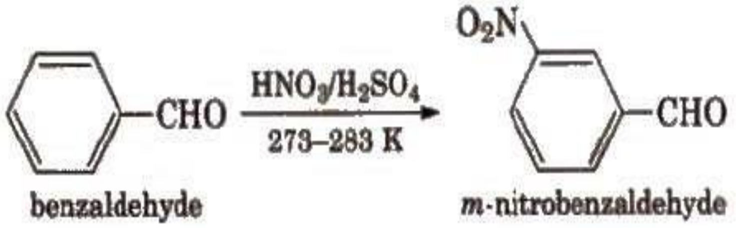
.

(iii) **Cannizzaro reaction** Aldehydes which do not have any α – hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.


$$2HCHO \xrightarrow{KOH\ (conc.)} \underset{\text{methanol}}{CH_3OH} + \underset{\text{potassium formate}}{H-\overset{O}{\overset{\|}{C}}-OK}$$



(iv) **Electrophilic substitution reaction** Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group shows + R effect, therefore acts as a deactivating and meta directing group.



(v) **Baeyer- ViLLiger oxidation** With Caro"s acid ($H_2SO_5$) or per benzoic acid ($C_6H_5CO_3H$) or peracetic acid ($CH_3CO_3H$) aliphatic ketones give ester.

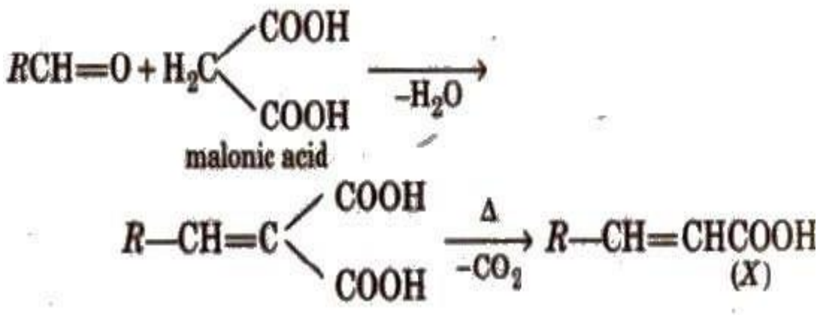
$$R_2CO + \underset{\text{per acid}}{R'CO_3H} \longrightarrow RCOOR + RCOOH$$

(x) **Tischenko's reaction** It is a modified form of Cannizzaro reaction.

$$2CH_3CHO \xrightarrow{(C_2H_5O)_3Al} CH_3COOH + C_2H_5OH$$

$$\longrightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5}$$

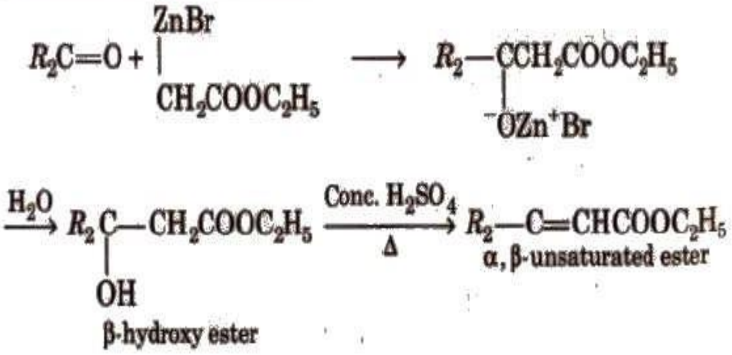
(xi) **Knoevenagel reaction** It involves condensation between active methylene group and ,carbonyl groups in the presence of base.



**(xii) Schmidt reaction**

$$RCHO + \underset{\text{hydrazoic acid}}{N_3H} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{alkyl cyanide}}{R-CN} + \underset{\text{N-alkyl formamide}}{HCONHR} + N_2$$

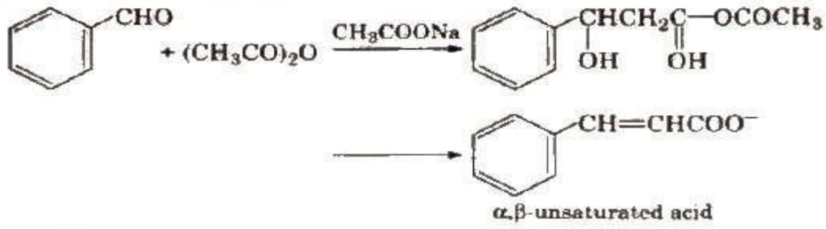
**(xiii) Refomatsky reaction**



$$R_2C{=}O + \underset{CH_2COOC_2H_5}{\overset{ZnBr}{|}} \longrightarrow R_2-\underset{^-OZn^+Br}{C}CH_2COOC_2H_5$$

$$\xrightarrow{H_2O} \underset{\beta\text{-hydroxy ester}}{R_2\underset{OH}{C}-CH_2COOC_2H_5} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\alpha,\beta\text{-unsaturated ester}}{R_2-C{=}CHCOOC_2H_5}$$

**(xiv) Perkin's reaction**



**(xv) Wittig reaction**

$$>C{=}O + PPh_3{=}CH_2 \longrightarrow >C{=}CH_2 + Ph_3P{=}O$$

**(xvi) Polymerisation**

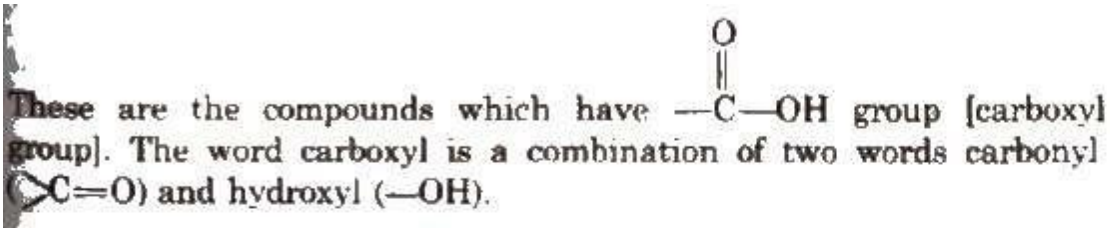
$$nHCHO \longrightarrow \underset{\text{paraformaldehyde}}{(CH_2O)_n}$$

$$3HCHO \longrightarrow \underset{\text{meta formaldehyde or trioxane}}{(HCHO)_3}$$

$$3CH_3CHO \longrightarrow \underset{\text{paraldehyde (hypnotic, sleep producing)}}{(CH_3CHO)_3}$$

$$4CH_3CHO \xrightarrow[\text{Or ionic } H_2SO_4]{\text{DryHCl gas}} \underset{\text{metaldehyde}}{(CH_3CHO)_4}$$

## Carboxylic Acids



These are the compounds which have $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ group [carboxyl group]. The word carboxyl is a combination of two words carbonyl ($>C=O$) and hydroxyl ($-OH$).

### Classification

Depending upon the number of -COOH groups, they are classified as

(i) monocarboxylic acids; containing one -COOH group

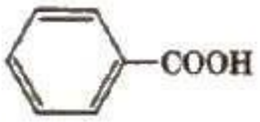
(ii) dicarboxylic acids: containing two -COOH groups.

### Sources of carboxylic acids

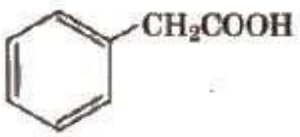
| Formula | Common name | Source |
|---|---|---|
| $HCOOH$ | Formic acid | Red ant (formica) |
| $CH_3COOH$ | Acetic acid | Vinegar (acetum) |
| $C_3H_7COOH$ | Butyric acid | Butter (butyrum) |

### Nomenclature

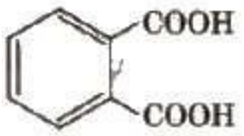
Their IUPAC names have been derived from the corresponding alkanes by replacing the letter „li of the alkane with „oic‟ and adding suffix „acid‟ at the end, Thus, monocarboxylic acids are called alkanoic acids.



Benzene carboxylic acid (Benzoic acid)



2-phenylethanoic acid



Benzene-1, 2-dicarboxylic acid (phthalic acid)

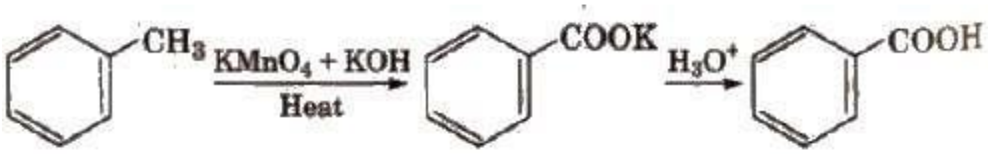
**Methods of Preparation of Monocarboxylic Acids**

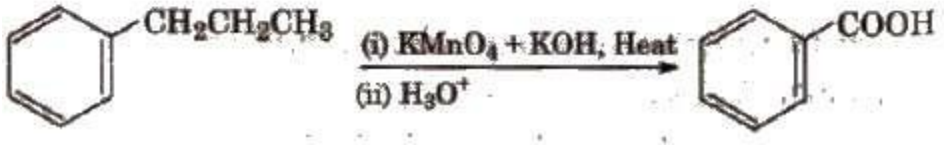
**(i) From primary alcohols and aldehydes**

$$RCH_2OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Alkaline } KMnO_4} R\text{—}COOH$$

$$CH_3(CH_2)_8CH_2OH \xrightarrow{CrO_3 \cdot H_2SO_4} \underset{\text{decanoic acid}}{CH_3(CH_2)_8COOH}$$

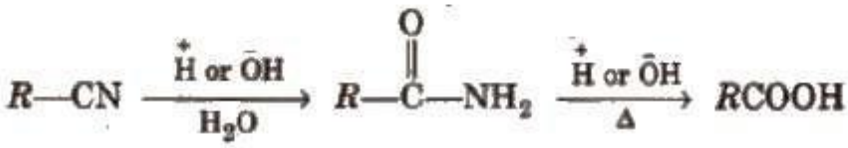
(ii) **From alkyl benzenes** Alkyl benzene when treated with strong oxidising agent like $H_2CrO_4$ (chromic acid), acidic or alkaline $KMnO_4$ gives benzoic acid.





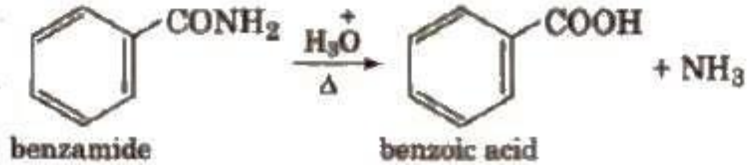
**(iii)From acid derivatives** All acid derivatives like amides ($RCONH_2$), acid halides (RCOCl), esters (RCOOR"), acid anhydrides (RCO-O-COR) on hydrolysis give carboxylic acids. All acid derivatives break from $RCO^+$.

(i) **From nitriles and amides** Nitriles are hydrolysed to amides and then to acids in the presence of $H^+$or $OH^-$ as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

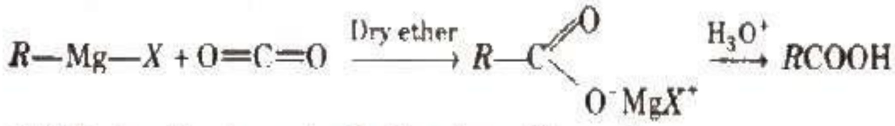


$$R\text{—}CN \xrightarrow[H_2O]{\overset{+}{H} \text{ or } \overset{-}{O}H} R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2 \xrightarrow[\Delta]{\overset{+}{H} \text{ or } \overset{-}{O}H} RCOOH$$

$$\underset{\text{ethanamide}}{CH_3CONH_2} \xrightarrow[\Delta]{H_3\overset{+}{O}} \underset{\text{ethanoic acid}}{CH_3COOH} + NH_3$$

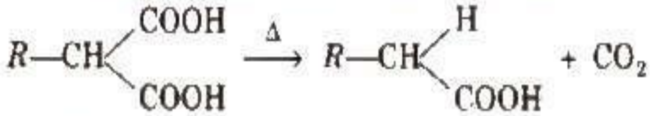


(ii) **From Grignard reagents** Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.



$$R{-}Mg{-}X + O{=}C{=}O \xrightarrow{\text{Dry ether}} R{-}C\begin{smallmatrix}{=}O\\ O^-MgX^+\end{smallmatrix} \xrightarrow{H_3O^+} RCOOH$$

**(vi) By heating geminal dicarboxylic acids**



$$R{-}CH\begin{smallmatrix}COOH\\ COOH\end{smallmatrix} \xrightarrow{\Delta} R{-}CH\begin{smallmatrix}H\\ COOH\end{smallmatrix} + CO_2$$

**(vii) From alkynes**

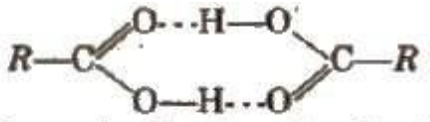
$$R{-}C{\equiv}C{-}R \xrightarrow[KMnO_4/OH^-,\ \Delta]{(i)\ O_3\ (ii).\ H_2O_2\ \text{or}} 2RCOOH$$

**Physical Properties of Carboxylic Acids**

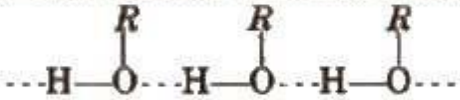
1. Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids.

2. The lower carboxylic acids are freely miscible with water due to the presence of intermolecular hydrogen bonding with $H_2O$ molecules. However, the solubility in water decreases gradually due to increase in the size of alkyl group.

3. Monocarboxylic acids have higher boiling points as compared to the alcohols of comparable molecular masses due to the presence of stronger intermolecular hydrogen bonding as shown below.



hydrogen bonding in carboxylic acids



hydrogen bonding in alcohols

4. Melting points of aliphatic monocarboxylic acids shows alternation or oscillation effect, i.e., the m.p. of an acid with even number of carbon atoms is higher than the next lower and next higher homologue containing odd number of carbon atoms. This is because, in case of acids with even number of carbon atoms, the terminal $-CH_3$ and -COOH groups lie on the opposite sides of the zig-zag chain. As a result, they get closely packed in the crystal lattice.

5. Glacial acetic acid is completely pure acetic acid and represents the solid state of acetic acid. Below 16.6°C temperature pure acetic acid is converted into ice like solid hence it is called glacial acetic acid.

**Chemical Properties of Carboxylic Acids**

Carboxylic acids do not give reactions of carbonyl groups as it enters into resonance with lone pair of O of -OH group.

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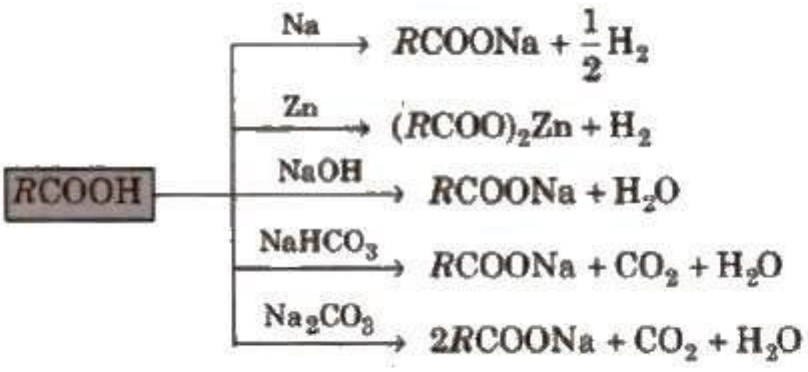
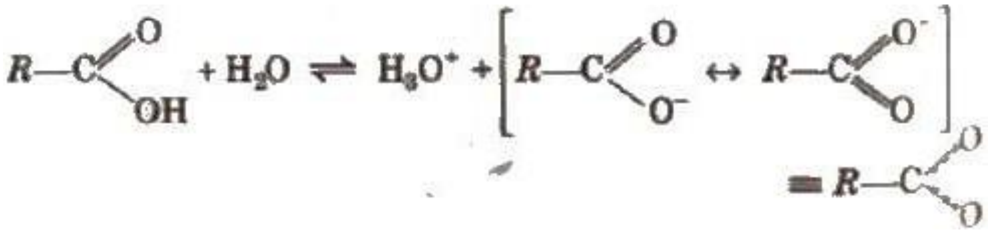
### (i) **Acidity**



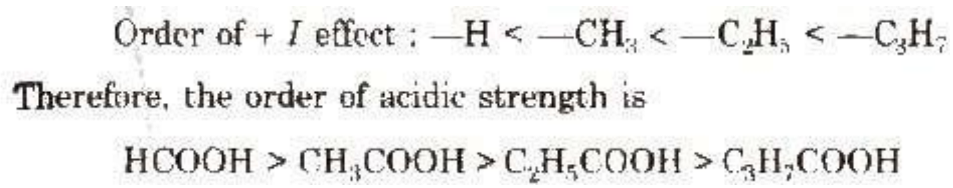
Above reactions are used to detect the presence of carboxyl group in an organic compound. ,

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



The strength of the acid is expressed in terms of the dissociation constant ($K_a$), also called acidity constant. A stronger acid has higher $K_a$ but lesser $pK_a$value ($pK_a$ == -log $K_a$).

The electron releasing substituents (+I effect) decrease the acidic strength of the carboxylic acids by destabilising the carboxylate ion.



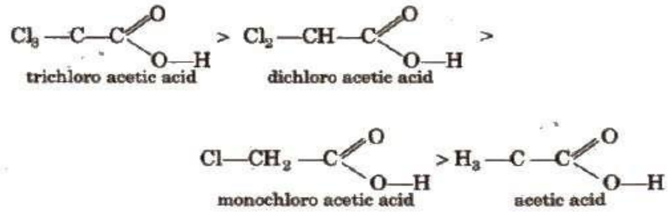
Order of + *I* effect : $—H < —CH_3 < —C_2H_5 < —C_3H_7$

Therefore, the order of acidic strength is

$HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH$

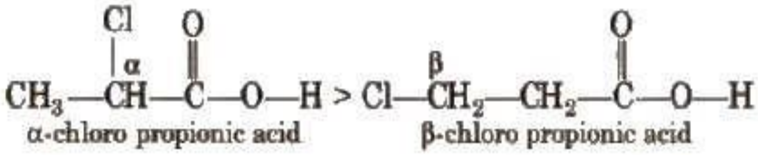
The electron withdrawing substituents (-I effect) such as halogen atoms (X), nitro ($NO_2$) group increase the acidic strength by decreasing the magnitude of the negative charge on the carboxylate anion and thus stabilising it. The release of $H^+$ ion becomes easy.

Acidic strength order



$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

This is because -I effect decreases in the order : F > C1 > Br > I.



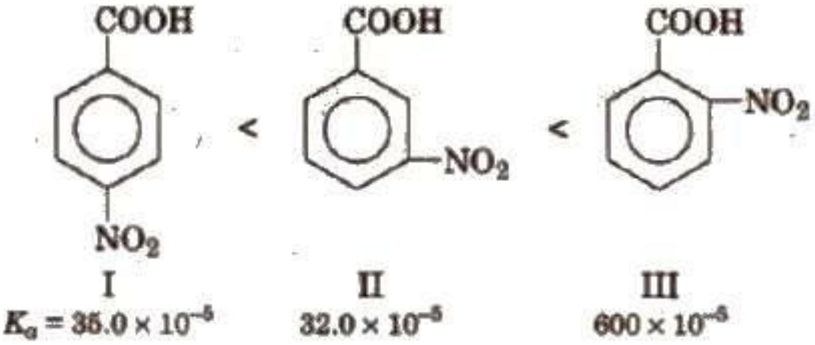
$CH_3-\overset{\overset{Cl}{|}}{C}H-\overset{\overset{O}{\|}}{C}-O-H > Cl-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-H$

This is because – I effect decreases with distance.

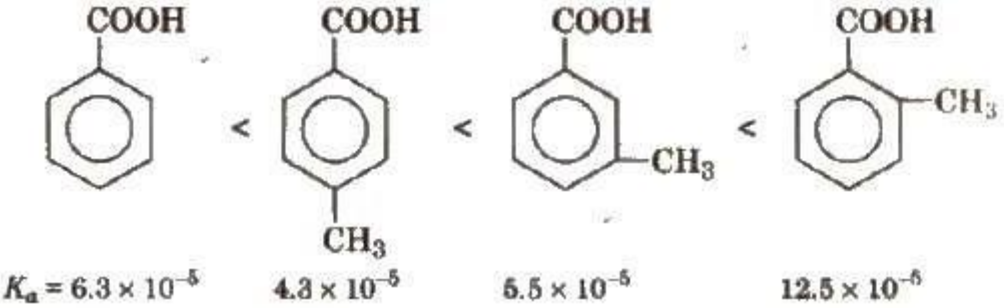
Per acetic acid ($CH_3COOO$-H) is a weaker acid than acetic acid as acetate ion is stabilised by resonance. Acidic strength of aromatic acids The parent member of the family benzoic acid which is a weaker acid ($K_a = 6.3 \times 10^{-5}$) than acid ($K_a = 17.7 \times 10^{-5}$) but stronger than acetic acid.

**Some order of acidity are**

(a)



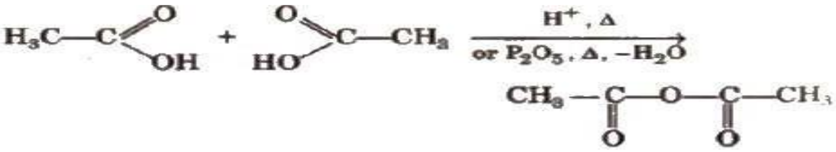
(b) Similarly, $K_a$ values of methyl substituted (toluic acids) at 298 K are as follows:



From the $K_a$ values, it is evident that with the exception of o-isomer, both p and m-toluic acids are weaker acids than benzoic acid whereas the three isomeric nitro benzoic acids are stronger acids than benzoic acid.

### (ii) Reactions involving cleavage of C-O-H bond

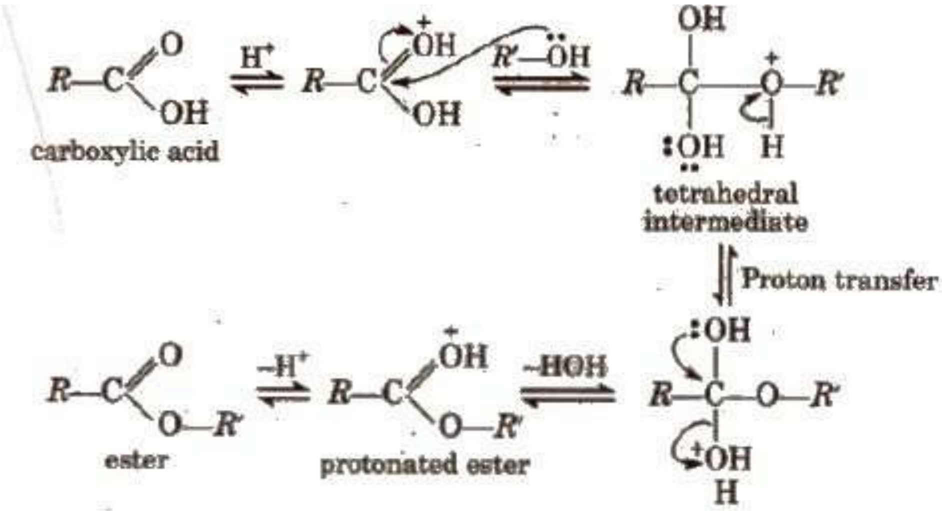
(a) **Formation of anhydride**



**(b) Esterification**

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

**Mechanism**



**(c) Reactions with $PCl_5$, $PCl_3$ and $SOCl_2$**

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$
$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

**(iii)** **Chemical reactions involving – COOH group**

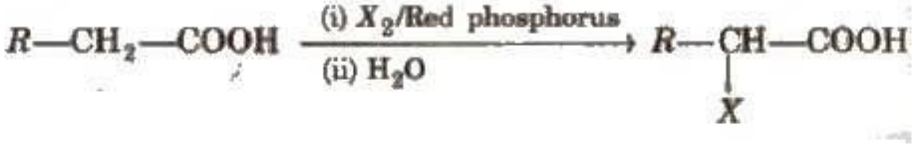
**(a) Reduction**

$$RCOOH \xrightarrow[\text{or } B_2H_6 \text{ (ii) } H_3O^+]{\text{(i) } LiAlH_4\text{/ether}} R{-}CH_2{-}OH$$

**(b) Decarboxylation**

$$RCOONa \xrightarrow[\Delta]{NaOH,\ CaO\ \text{(Ratio 3 : 1)}} R{-}H + Na_2CO_3$$

**(i)Substitution reactions in the hydrocarbon part** α -hydrogen atoms in carboxylic acids are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction.



$$R{-}CH_2{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} R{-}\underset{\substack{|\\ X}}{CH}{-}COOH$$

The reaction is known as Hell-Volhard-Zelinsky reaction.

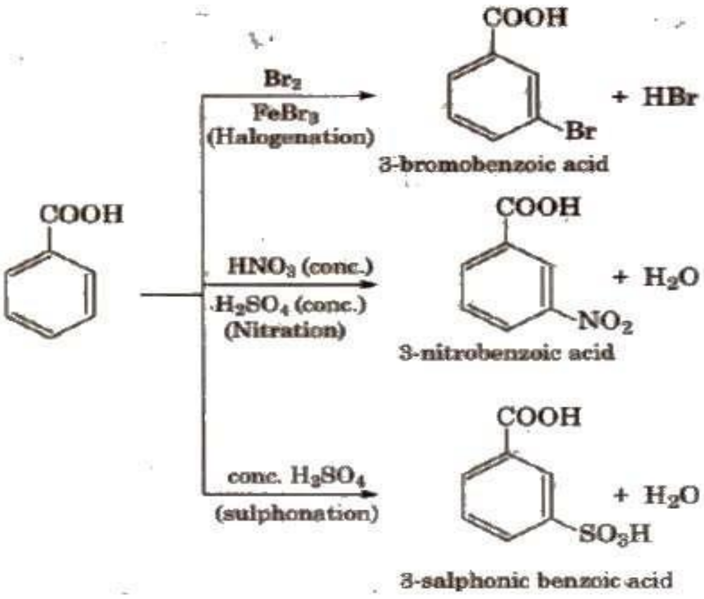
**(ii)Arndt-Eistert reaction** It is method of converting lower carboxylic acids to their higher homologues

$$RCOOH \xrightarrow{PCl_5} RCOCl \xrightarrow{CH_2N_2} \underset{\text{diazo ketone}}{RCOCHN_2} \xrightarrow{HOH} RCH_2COOH$$

(i) **Reducing property-** Among carboxylic acids, formic acid is the only acid that acts as reducing agent. It reduces, acidified $KMnO_4$ to $MnSO_4$, $HgCl_2$ to Hg, Tollen"s reagent to silver mirror and Fehling"s solution to red ppt. and itself gets oxidised to $CO_2$ and $H_2O$.

$HCOOH + HgCl_2 \rightarrow Hg + 2HCl + CO_2$

(ii) **Electrophilic substitution reactions of aromatic acids** -COOH group shows -R effect, therefore, acts as a deactivating and meta-directing group. Carboxylic acids do not undergo Friedel-Craft"s reaction because the carboxylic group IS deactivating and the catalyst $AlCl_3$ (anhy.) gets bonded to the carboxyl group.

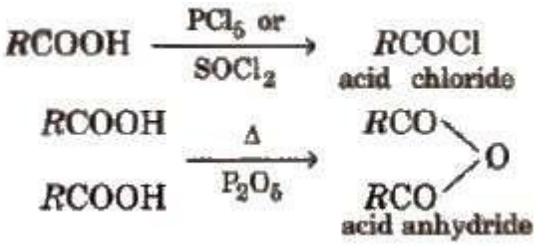


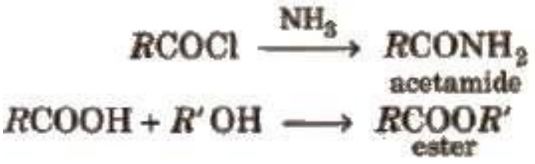
**Uses**

1. Formic acid is used in leather tanning, textile dyeing and finishing.
2. Acetic acid is used in the manufacture of rayon and in plastics, in in rubber and silk industries, in cooking and in vinegar (a 8-10% solution of acetic acid).
3. Benzoic acid and its salts are used as urinary antiseptics.
4. Formic acid can act as a reducing agent.

**Derivatives of Carboxylic acids**

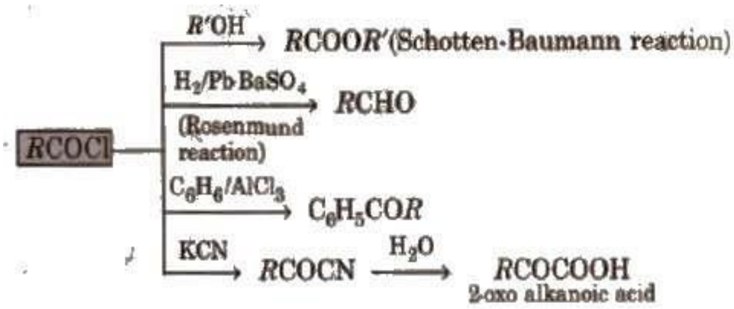
These are obtained when -OH group of carboxylic acids is replaced by Cl, $NH_2$, OR" and OCOR and are called respectively acid chloride, acid amide, ester and acid anhydride



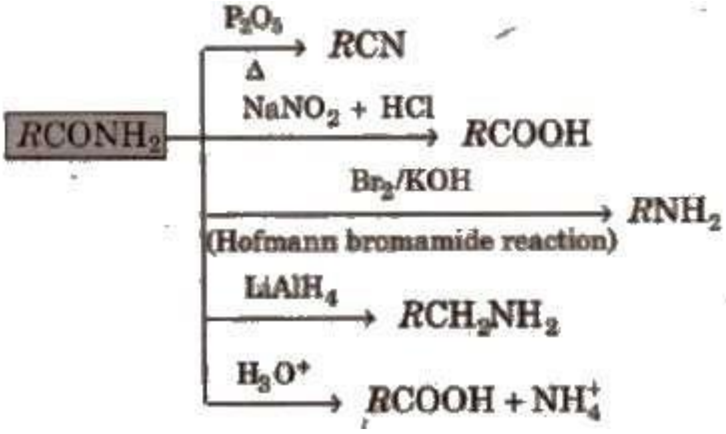


## Properties of Acid Derivatives

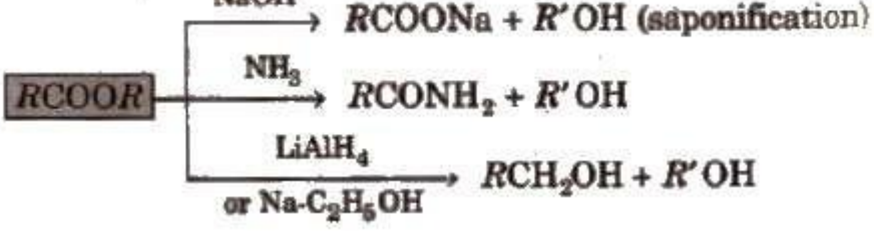
### 1. Chemical reactions of acid halides



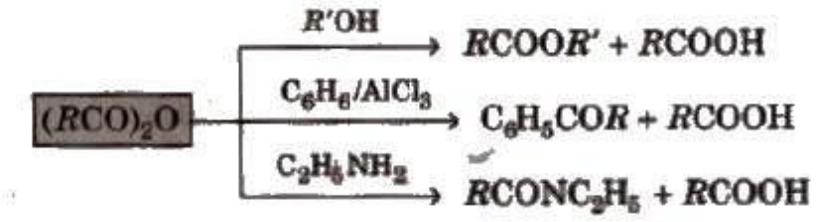
### 2. Chemical reactions of acid amides



### 3. Chemical reactions of ester



### 4. Chemical reactions of anhydrides



## Chapter 14

## Biomolecules

Biomolecules are the organic compounds which form the basis of life, i.e., they build up the living system and responsible for their growth and maintenance.

The sequence that relates biomolecules to living organism is

Biomolecules → Organelles → Cells → Tissues → Organs → Living organism.

### Carbohydrates

Optically active polyhydroxy aldehydes (aldcses) or ketones (ketoses) or compounds which on hydrolysis give these units are known as carbohydrates. They are also called saccharides

(Latin Saccharum = sugar) due to sweet taste of simpler members.

Depending upon their behaviour towards hydrolysis, carbohydrates can be of following three types

### Monosaccharides

These cannot be hydrolysed to simpler molecules and further subdivided into tetroses, pentoses or hexoses depending upon the number of carbon atoms. These are also called homopolysaccharides.

- **Aldotetroses** Erythrose, Threose
- **Aldopentoses** Xylose, Ribose,
- **Aldohexoses** Glucose, Galactose,
- **Ketohexoses** Fructose

All naturally occurring monosaccharides belong to D-series.

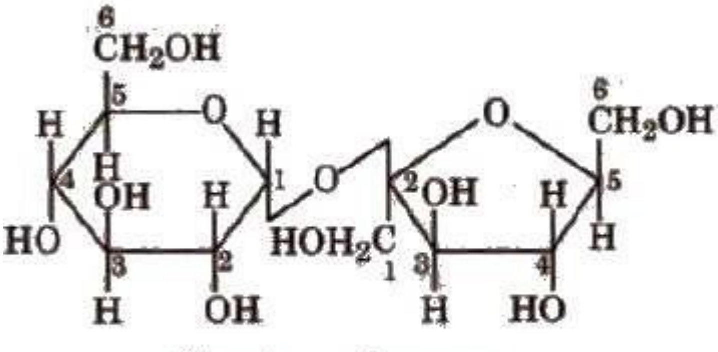
killiani synthesis is used to convert an aldose into next higher aldose.

### Oligosaccharides

(Greek oligos = few). On hydrolysis, they generally give two to nine monosaccharides (same or different) and are further classified as disaccharides, e.g., sucrose, maltose, lactose, trisaccharides and so on. $C_{12}H_{22}O_{11}$ is a disaccharide because it gives two monosaccharides.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The bond formed between two monosaccharides is called a glycosidic bond and normally it is (1, 4) bond.Sucrose is most abundant in plants and known as cane sugar or table sugar or invert sugar as equimolar mixture of glucose and fructose is obtained by hydrolysis of sucrose.



Structure of sucrose

**Trisaccharides Raffinose ($C_{18}H_{32}O_{16}$)**

$$(C_{18}H_{32}O_{16}) + 2H_2O \xrightarrow{H^+} \text{Glucose} + \text{Fructose} + \text{Galactose}$$

**Polysaccharides**

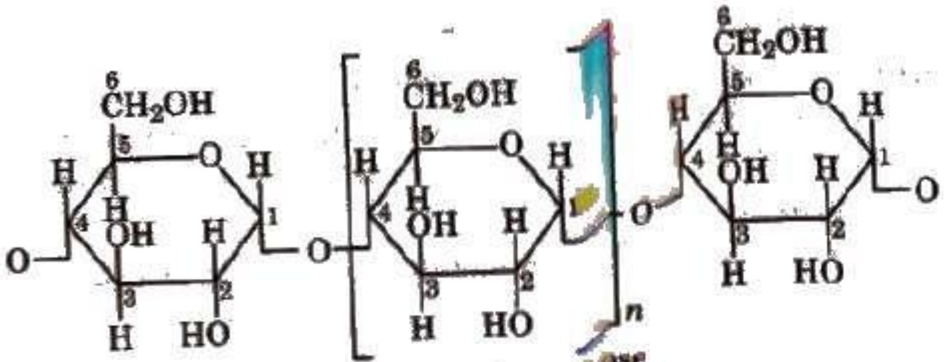
These are polymers of monosaccharides. Examples are starch, cellulose, glycogen, etc.

1. **Starch,** $(C_6H_{10}O_5)_N$

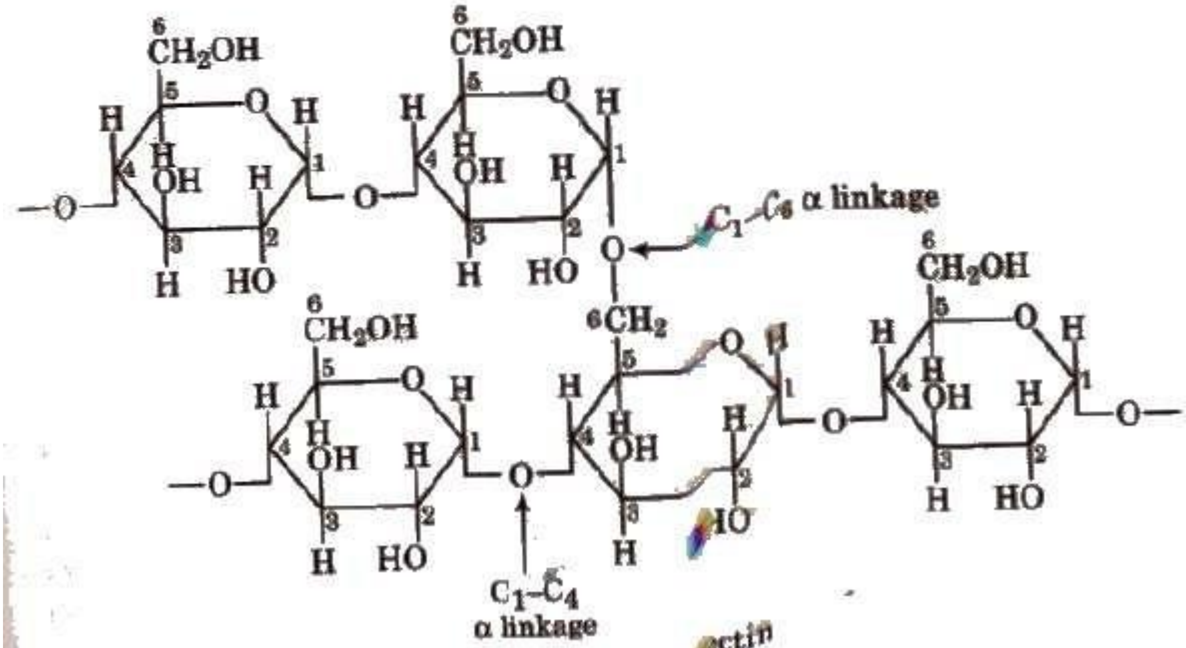
It is a polymer of a-glucose and a major reserve food in plants. It turns blue with iodine. It is a mixture of two components:

1. Amylose (20%), an unbranched water soluble polymer.
2. Amylopectin (80%), a branched water insoluble polymer.

Sources of starch are potatoes, wheat, rice, maize, etc.



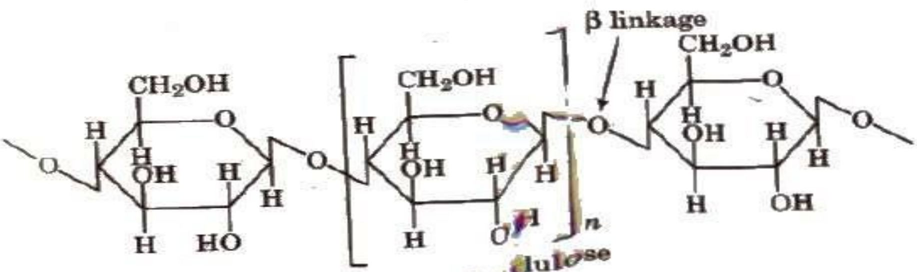
Structure of amylose



Structures of amylopectin

### **2. Cellulose,** $(C_6H_{10}O_5)_n$

It is the most abundant and structural, polysaccharide of plants. It is important food source of some animals It is a polymer of D (+) β-glucose.The chief sources of cellulose are wood (Contains 50% cellulose rest being lignin, resins, etc) and cotton (contains 90% cellulose rest being fats and waxes).



Structure of cellulose

**Several materials are obtained from cellulose:**

1. **Mercerised cotton** Cellulose treated with cone. sodium hydroxide solution acquire silky lustre. It is called mercerissd cotton.
2. **Gun cotton** It is completely nitrated cellulose (cellulose nitrate), highly explosive in nature and is used in the manufacture of smokeless gun powder, called blasting gelatin.
3. **Cellulose acetate** It is used for making acetate rayon and motion picture films.
4. **Cellulosexanthate** It is obtained by treating cellulose with sodium hydroxide and carbon disulphide and is the basic material for VISCOSE rayon.

Oligosaccharides and heteropolysaccharides are also called heteropolysaccharides.

### Reducing and Non-reducing sugars

Based upon reducing and non-reducing properties, carbohydrates are classified as reducing and non-reducing sugars. Carbohydrates reducing Fehling reagent or Tollen‟s reagent are termed as reducing carbohydrates. e.g., All monosaccharides and disaccharides (except sucrose). But carbohydrates which do not reduce such reagents are known as non-reducing carbohydrates. e.g., sucrose and polysaccharides.

### Sugars and Non-sugars

On the basis of their, taste, carbohydrates are classified as sugars and non-sugars. The monosaccharides and oligosaccharides having sweet taste are collectively known as sugars. Polysaccharides which are insoluble in water and not sweet in taste, are non-sugars.

### Glucose

Dextrose, grape sugar, corn sugar, blood sugar ($C_6H_{12}O_6$).

### Manufacture

By hydrolysis of starch with hot dil mineral acids and by hydrolysis of sucrose.

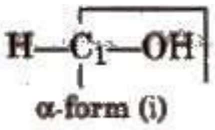
$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[H^+]{} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

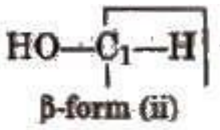
$$\underset{\text{starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393\text{ K; 2-3 bar}]{H^+} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

Extra glucose is stored in liver as glycogen.

**α and β glucose**

In intermolecular hemiacetal formation (cyclic structure), -CHO is converted into -CHOH which can have two configurations as shown below.


α-form (i)

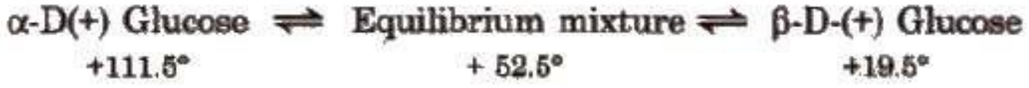

β-form (ii)

Glucose having (i) configuration about $C_1$ is the α-glucose and having (ii) configuration about $C_1$ is β-glucose.

The carbon $C_1$ is known as anomeric carbon and these compounds are called anomers. Both the forms are optically active. ex-D-glucosehas specific rotation +111.5° and β-D-glucose has specific rotation + 19.5°.

**Mutarotation**

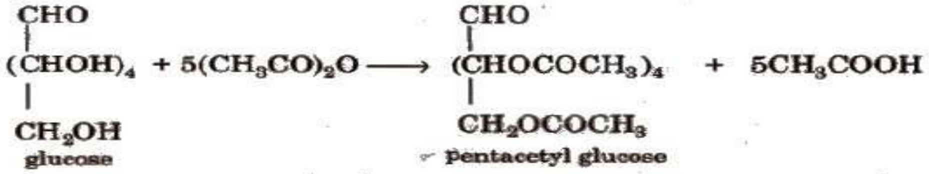
When either of the two forms of glucose is dissolved in water, there is a spontaneous change in specific rotation till the equilibrium value of +52.5°. This is known as mutarotation.


$$\underset{+111.5^\circ}{\alpha\text{-D(+) Glucose}} \rightleftharpoons \underset{+52.5^\circ}{\text{Equilibrium mixture}} \rightleftharpoons \underset{+19.5^\circ}{\beta\text{-D-(+) Glucose}}$$

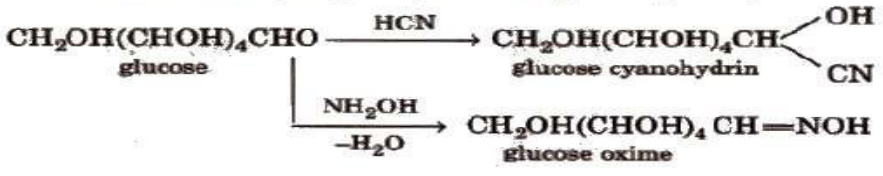
**Properties of glucose**

Glucose has one aldehyde group, one primary hydroxyl (-$CH_2OH$) and four secondary hydroxyl (-CHOH) groups and gives the following reactions:

(i) Glucose on acetylation with acetic anhydride gives a pentaacetate confirming the presence of five hydroxyl groups in glucose.


$$\begin{array}{l} \mathrm{CHO} \\ | \\ \mathrm{(CHOH)_4} \\ | \\ \mathrm{CH_2OH} \\ \text{glucose} \end{array} + 5(\mathrm{CH_3CO})_2\mathrm{O} \longrightarrow \begin{array}{l} \mathrm{CHO} \\ | \\ \mathrm{(CHOCOCH_3)_4} \\ | \\ \mathrm{CH_2OCOCH_3} \\ \text{pentacetyl glucose} \end{array} + 5\mathrm{CH_3COOH}$$

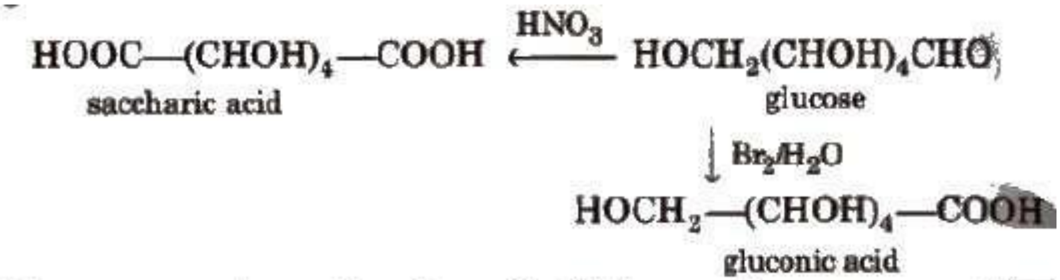
(ii) Glucose reacts with hydroxylamine to give monoxime and adds with a molecule of hydrogen cyanide to give a cyanohydrin.


$$\underset{\text{glucose}}{\mathrm{CH_2OH(CHOH)_4CHO}} \xrightarrow{\mathrm{HCN}} \underset{\text{glucose cyanohydrin}}{\mathrm{CH_2OH(CHOH)_4CH}} \begin{matrix} \mathrm{OH} \\ \mathrm{CN} \end{matrix}$$
$$\xrightarrow[-\mathrm{H_2O}]{\mathrm{NH_2OH}} \underset{\text{glucose oxime}}{\mathrm{CH_2OH(CHOH)_4\,CH{=}NOH}}$$

These reactions confirm the presence of a carbonyl group in glucose.

(iii) Glucose reduces ammoniacal silver nitrate solution (Tollen‟s reagent) to metallic silver and also Fehling‟S solution or Benedict solution to reddish brown cuprous oxide ($Cu_2O$) and itself gets oxidised to gluconic acid. This confirms the presence of an aldehydic group in glucose.

(iv) With mild oxidising agent like bromine water, glucose is oxidised to gluconic acid. Glucose on oxidation with nitric acid gives saccharic acid.



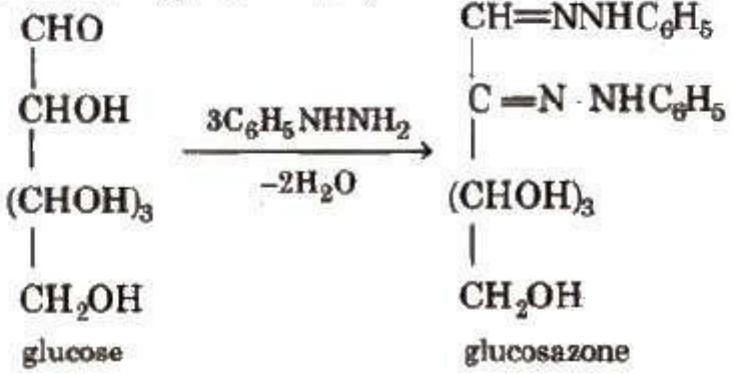
$$\underset{\text{saccharic acid}}{HOOC{-}(CHOH)_4{-}COOH} \xleftarrow{HNO_3} \underset{\text{glucose}}{HOCH_2(CHOH)_4CHO} \xrightarrow{Br_2/H_2O} \underset{\text{gluconic acid}}{HOCH_2{-}(CHOH)_4{-}COOH}$$

(v) Glucose on prolonged heating with HI forms *n*-hexane, suggesting that all the 6 carbon atoms in glucose are linked linearly.

$$HOCH_2{-}(CHOH)_4{-}CHO \xrightarrow{HI,\ \Delta} H_3C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

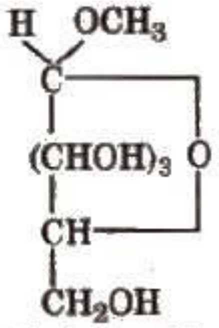
However, with Na/Hg and water, glucose is reduced to sorbitol $HOH_2C(CHOH)_4CH_2OH$.

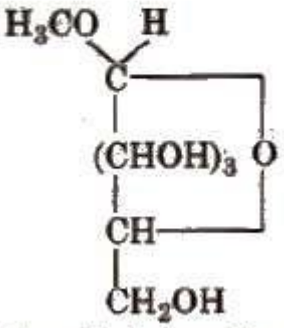
(vi) D-glucose reacts with three molecules of phenyl hydrazine to give osazone (glucosazone).



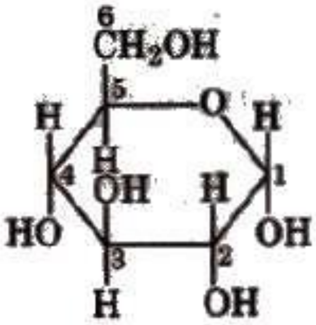
$$\underset{\text{glucose}}{\begin{array}{c} CHO \\ | \\ CHOH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}} \xrightarrow[-2H_2O]{3C_6H_5NHNH_2} \underset{\text{glucosazone}}{\begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}N\cdot NHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}}$$

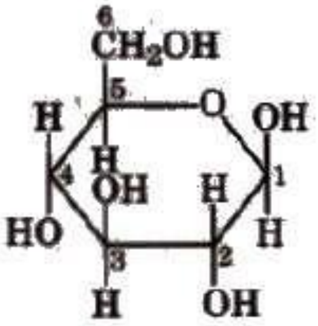
(vii) Glucose on reaction with methyl alcohol in the presence of dry HCl(g) forms α and β- methyl glycosides. The reaction occurs only at the OH of hemiacetylic carbon.


α-methyl glucoside

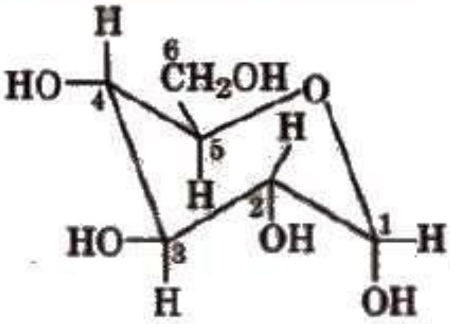

β-methyl glucoside

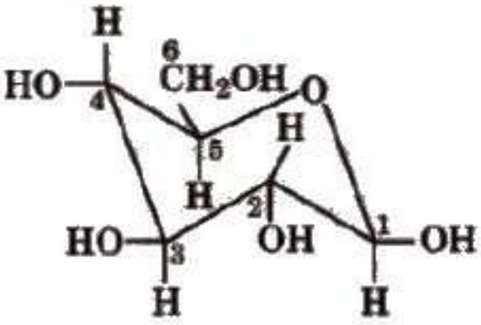
Cyclic structure of glucose Given by Haworth and Hirst.


α-D (+) glucose


β-D (+) glucose

**Glucose is sometimes illustrated as a chair form :**

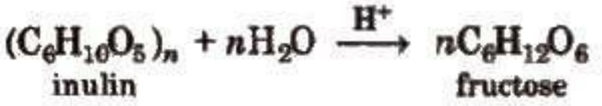

α-anomer


β-anomer

**Fructose Fruit Sugar** ($C_6H_{12}O_6$)

**Manufacture**

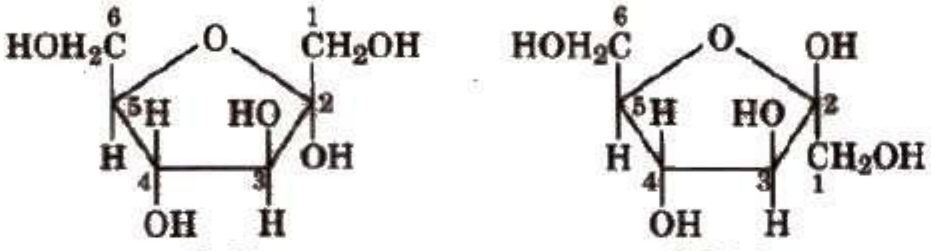
By hydrolysis of inulin.



$$\underset{\text{inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{fructose}}{nC_6H_{12}O_6}$$

## Structure

Fructose has furanose structure, *i.e.*, ring structure consisting of four C atoms and one O atom.

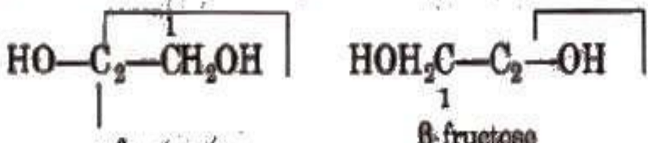


α-D (–) fructofuranose

β-D (–) fructofuranose

**α and β-fructose**

The two forms have different configuration about $C_2$.



α-fructose

β-fructose

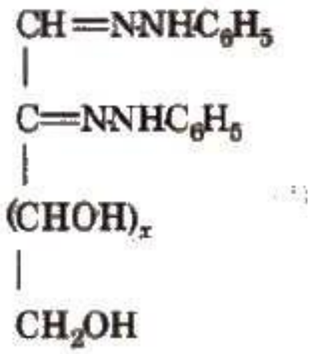
Fructose does not reduce $Br_2$ water.

**Epimers**

Monosaccharides differing in configuration at a carbon other than anomeric carbon are called epimers, e.g., glucose and galactose differ in configuration at $C_4$, hence called epimers.

**Osazones**

Monosaccharides and reducing disaccharides react with excess of phenyl hydrazine to form crystalline substances of the structure.



$$\begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}NNHC_6H_5 \\ | \\ (CHOH)_x \\ | \\ CH_2OH \end{array}$$

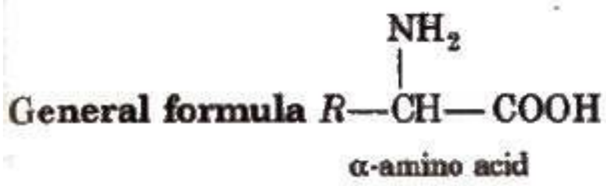
It is known as osazones glucose and fructose give same osazone.

**Molisch Test for Carbohydrates**

In aqueous solution of compound add solution of α-naphthol in alcohol and then cone. $H_2SO_4$ along the walls of the test tube. Purple coloured ring is obtained at the junction.

## Amino Acids

The compounds containing amino group ($-NH_2$) and carboxylic group ($-COOH$) are called amino acids.



**General formula** $R{-}\overset{\overset{NH_2}{|}}{CH}{-}COOH$

α-amino acid

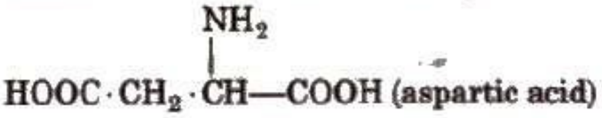
R = H, alkyl or aryl group. Except glycine ($H_2N.CH_2COOH$), others are optically active in nature.

**Classification of Amino Acids**

(a) **α, β, γ-amino acids** Depending upon the position of $-NH_2$ *wrt* $-COOH$ group.

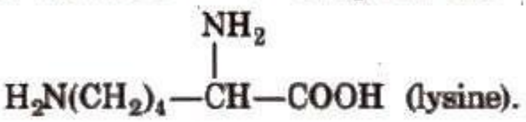
(b) **Neutral** Having one $-NH_2$ and one $-COOH$, *e.g.*, $NH_2 \cdot CH_2 \cdot COOH$ (glycine).

(c) **Acidic** Having one $-NH_2$ and two $-COOH$, *e.g.*,



$HOOC \cdot CH_2 \cdot \overset{\overset{NH_2}{|}}{CH}{-}COOH$ (aspartic acid)

(d) **Basic** Having two or more $-NH_2$ and one $-COOH$, *e.g.*,



$H_2N(CH_2)_4{-}\overset{\overset{NH_2}{|}}{CH}{-}COOH$ (lysine).

**Essential and Non-essential Amino Acids**

Human body can synthesise ten amino acids, called non-essential amino acids. The remaining ten amino acids required for protein synthesis are not synthesised by body and are called essential amino acids. They are;

1. Phenylalanine
2. Histidine
3. Tryptophan
4. Valine
5. Methionine
6. Threonine
7. Arginine
8. Leucine
9. Isoleucine
10. Lysine

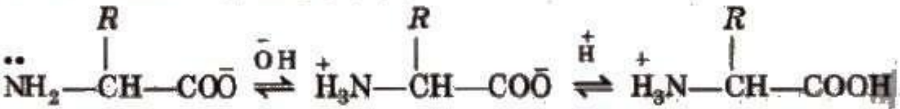
They are known by their common names and abbreviated by first three letters of their common names e.g., glycine as „gly‟ and alanine a as „ala‟.

### Configuration of α-Amino Acids

L-amino acid (NH$_2$ on LHS) D-amino acid (NH$_2$ on RHS)

Naturally occurring α-amino acids are L-amino acids. D-amino acids occur in some antibiotics and bacterial cell walls.

### Structure of Amino Acids

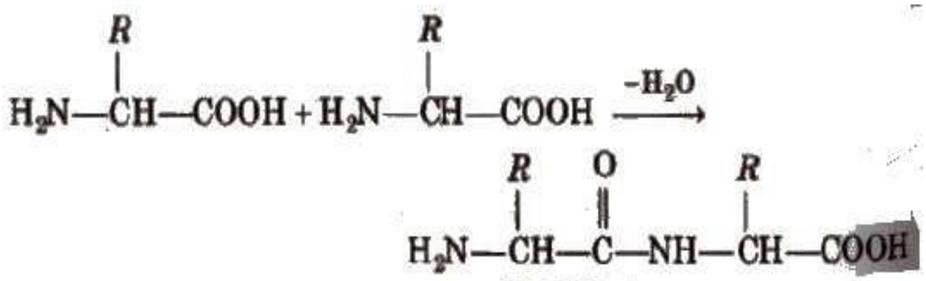


$$\ddot{N}H_2-\overset{R}{\overset{|}{C}H}-CO\bar{O} \underset{}{\overset{\bar{O}H}{\rightleftharpoons}} \overset{+}{H_3N}-\overset{R}{\overset{|}{C}H}-CO\bar{O} \overset{\overset{+}{H}}{\rightleftharpoons} \overset{+}{H_3N}-\overset{R}{\overset{|}{C}H}-COOH$$

as anion (high pH) Zwitter ion, (isoelectric point) as cation (low pH)

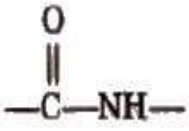
#### Peptides

Peptides are condensation products of two or more amino acids.



$$H_2N-\overset{R}{\overset{|}{C}H}-COOH + H_2N-\overset{R}{\overset{|}{C}H}-COOH \xrightarrow{-H_2O} H_2N-\overset{R}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-NH-\overset{R}{\overset{|}{C}H}-COOH$$

dipeptide



$-\overset{O}{\overset{\|}{C}}-NH-$ is known as peptide linkage and C—N as a peptide bond.

Two molecules of different amino acids can form two dipeptides. Three molecules of different amino acids can give six tripeptides.

Dipeptide has only one peptide bond, tripeptide has two peptide bonds and so on. Thus, a polypeptide made up of n-amino acids has (n – 1) peptide bonds.

### Polypeptides

Condensation Products of many amino acids ( „In P xiucts of many amino acids (≈ 10000) is known as polypeptide and those polypeptides which have molecular mass above than 10000 are called proteins.

### Proteins

They are linear polymers of a-amino acids.

### Structure of Proteins

**(a) Primary structure**

It simply reveals the sequence of amino acids.

**(b) Secondary structure** α-helix structure maintained by hydrogen bonds or β-pleated sheet structure when R is small group.

**(c) Tertiary structure** The folding and superimposition of polypeptide chains forms a compact globular shape, termed as tertiary structure. It is stabilised by covalent, ionic, hydrogen and disulphide bonds.

The precise arrangement constitutes the quaternary structure.

### Classification on the Basis of Hydrolysis Products

**(i) Simple** These yield only a-amino acids upon hydrolysis. e.g.,

albumin.

**(ii) Conjugated proteins** These yield α-amino acids and non-protein part, called prosthetic group.

| Protein | Prosthetic group |
|---|---|
| Nucleoproteins | Nucleic acid |
| Phospho proteins | Phosphoric acid |
| Glycoproteins | Carbohydrates |
| Metalioproteins | Metals |
| Lipoproteins | Lipids |

**(iii) Derived proteins** These are obtained by partial hydrolysis of simple or conjugated proteins.

Proteins → Proteoses → Peptones → Polypeptides

## Classification on the Basis Functions

1. **Structural proteins** Fibrous proteins
2. **Enzymes** Serve as biological catalyst e.g., pepsin, trypsin etc.
3. **Hormones** Insulin
4. **Contractile proteins** Found in muscles, e.g., myosin, actin.
5. **Antibodies Gamma** globulins present in blood.
6. **Blood protein** Albumms, haemoglobin and fibrinogen.

Haemoglobin is a globular protein. Its prosthetic group is heme. It Contains 574 amino acid units distributed in four polypeptide chains.

Two chains containing 141 amino acid residues each are called α-chains and the two chains containing 146 amino acid residues are called β-chains.

Sickle cell anaemia is caused by defective haemoglobin obtained by replacing only one amino acid, i.e., glutamic acid by valine.

## Denaturation of Proteins

The process that changes the three dimensional structure of native proteins is called denaturation of proteins. It can be caused by Change in pH, addition of electrolyte, heating or addition of solvent like water, alcohol or acetone.

## Tests of Proteins

### (i) Biuret Test

Protein solution + NaOH + dil. $CuSO_4$ → pink or violet colour.

### (ii) Millon’s Test

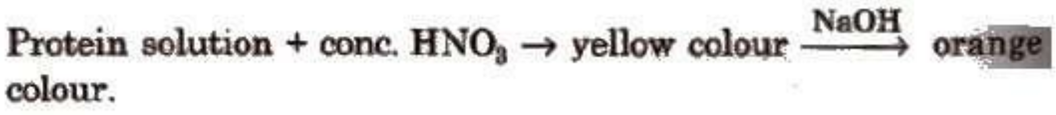
Protein solution + Millon‟s reagent → pink colour

Millon‟s reagent is solution of mercuric nitrate and nitrite in nitric acid containing traces of nitrous acid.

### (iii) Iodine reaction

Protein solution + iodine in potassium iodide solution → yellow colour.

### (iv)Xanthoprotic test



Protein solution + conc. $HNO_3$ → yellow colour $\xrightarrow{NaOH}$ orange colour.

## Enzymes

Enzymes constitute a group of complex proteinoid compounds, produced by living organisms which catalyse the chlemical reaction.

Non-proteinous components enhance the activity of certain enzymes and are known as co- enzymes. These include metal ions like $Mn^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$, $Zn^{2+}$, $Co^{2+}$ etc., heterocyclic ring systems (pyrrole, purine, pyridine, etc.), a sugar residue, phosphoric acid residue of vitamins like thiamine, riboflavin etc.

**Endoenzyme** acts in the same cell in which it is synthesised, while exo-enzyme acts outside the cell in which it is synthesised.

## Nomenclature

They are usually named by adding the suffix „ase‟ to the root name of the substrate e.g., urease, maltase, diastase, invertase, etc.

## Oxidative Enzymes

They catalyse oxidation-reduction reaction and are mostly conjugated proteins.

## Some Common Enzyme

| Name | Substrate | Products |
|---|---|---|
| Urease | Urea | CO<sub>2</sub> + NH<sub>3</sub> |
| Maltase | Maltose | Glucose |
| Invertase | Sucrose | Glucose + fructose |
| Amylase | Starch | Maltose |
| Trypsin | Proteins | Amino acids |
| Ascorbic acid oxidase | Ascorbic acid | Dehydroascorbic acid |

## Characteristic Features of Enzymes

1. **Rate of reaction** They increase the rate of reaction up to $10^6$ to $10^7$ times.
2. **Specific nature** Urease catalyse the hydrolysis of urea and not methyl urea, so these are specific in nature.
3. **Optimum temperature** It is about 20-30°C.
4. **pH of medium** It is about 7 but for pepsin, it is 1.8·2.2 and for trypsin, it is 7.5-8.3.
5. **Concentration** Dilute solutions are more effective.
6. **Amount of enzyme** Very small amount can accelerate the reaction.
7. **Enzyme inhibitors** These compounds inhibit the enzyme action. With the help of such compounds, the reaction can be controlled.

### Mechanism of Enzyme Action

Enzyme + Substrate → [Enzyme substrate] → Product + Enzyme Activated complex

### Applications of Enzymes

(i) **Treatment of diseases** The congenital disease phenyl ketonurie caused by phenylalanine hyroxylase can be cured by diet of low phenylalanine content. Enzyme streptokinase is used for blood clotting to prevent heart disease.

(ii) **In industry** Tanning of leather, fermentation process etc.

### Nucleic Acids

### Important Terms of Nucleic Acids

#### 1. Nucleotides

Nucleotides consist of 5-carbon sugar + nitrogenous base + 1, 3-phosphate groups.

#### 2. Pentose sugar

It is either ribose or deoxy ribose (not having oxygen at $C_2$).

#### 3. Nitrogenous base

Derived from purines having two rings in their structure e.g., Adenine (A) and Guanine (G) and derived from pyrimidines having one ring in their structure e.g.,

Thymine (T), Uracil (U) and Cytosine (C).

Two H-bonds are present between A and T ($A = T$) while three H-bonds are present between C and G ($C \equiv G$).

#### 4. Ribonucleotide

Phosphate unit + Ribose + one base unit from A, G, C, or U.

#### 5. Deoxyribo nucleotide

Phosphate unit + Deoxyribose + one base from A, G, C or T.

#### 6. Nucleoside

Ribose-/deoxyribose + one base unit from A, G, C, Tor U.

## DNA and RNA

Nucleic acid is polynucleotide, present in the living cells or bacterial cells having no nucleus and in viruses having no cells.

**(i) DNA** Deoxy ribonucleic acid.

DNA + $H_2O$ → Phosphoric acid + deoxyribose + A, G, C, T

**(ii) RNA** Ribonucleic acid

RNA + $H_2O$ → Phosphoric acid + Ribose + A, G, C, U

## Structure of DNA

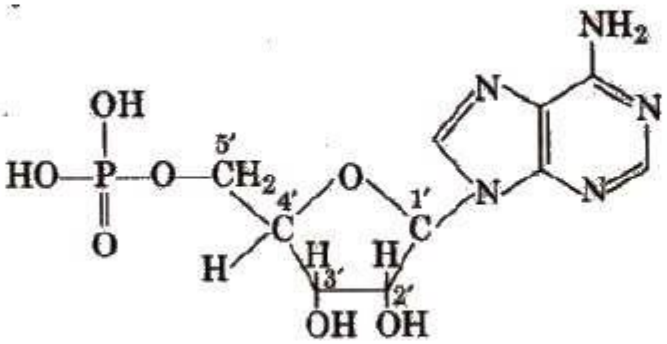
It consists of two polynucleotide chains, each chain form a right handed helical spiral with ten bases in one turn of the spiral. The two chains coil to double helix and run in opposite direction. These are held together by hydrogen bonding.

## Structure of RNA

It is usually a single strand of ribonucleotides and take up right handed helical conformation. Up to 12000 nucleotides constitute an RNA.

It can base pair with complementary strands of DNA or RNA according to standard base pairing rules-G pairs with C, A pairs with U or T. The paired strands in RNA-RNA or RNA- DNA are anti parallel as in DNA.

In both DNA and RNA, heterocyclic base and phosphate ester linkages are at $C_1$ and $C_{5}$„ respectively of the sugar molecule.



## Types of RNA

1. Messanger RNA (m-RNA) It is produced in the nucleus and carries information for the synthesis of proteins.
2. Transfer RNA (Soluble or Adoptive RNA) (s-RNA, t-RNA) It is found in cytoplasm. Its function-is to collect amino acids from cytoplasm for protein synthesis.

**Types of RNA**

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**Functions of Nucleic Acids**

1. Direct the synthesis of proteins.
2. Transfer the genetic information (hereditary characters).

**Replication**

It is a process in which a molecule of DNA can duplicate.

**Template** It means pattern. In the process of replication of DNA, the parent strand serves as template.

**Gene** The portion of DNA carrying information about a specific protein is Called gene.

**Genetic code** The relation between the amino acid and the nucleotide triplet is called genetic code.

**Codons** The nucleotide bases in RNA function in groups of three (triplet) in coding amino acids. These base triplets are called codons.

The world code is used with reference to DNA, codon with reference to m-RNA and anticodon with reference to t-RNA.

**Lipids**

The constituents of animals and plants soluble in organic solvents (ether, chloroform. carbon tetrachloride), but insoluble in water are called lipids. (Greek lipose = fat)

**Types of Lipids**

**(i) Simple lipids**

(a) Fats and oils on hydrolysis give long chain fatty acids + glycerol.

(b) **Waxes** Long chain fatty acids + long chain alcohols.

Vegetable and animal oils and fats have similar chemical structure and are triesters of glycerol, called glycerol.Simple glycerides contain one type of fatty acids. Mixed glycerides contain two or three types of fatty acids.

Common saturated fatty acids $CH_3\text{-}(CH_2)_nCOOH$.

When n = 4 caproic acid; n = 6 caprylic acid; n = 8 capric acid, n = 10 lauric acid n = 12 myristic acid; n = 14 palmitic acid, n = 16 stearic acid.

**Common unsaturated acids**

$C_{17}H_{33}COOH$ oleic acid; $C_{17}H_{33}COOH$ linoleic acid.

**Difference between oils and fats** Oils are liquids at ordinary temprature (below 20° and contain lower fatty acids or unsaturated fatty acids.

Fats are solids or semisolids above 20°C and contain higher saturated fatty acids. Oils and fats act as "energy reservoirs" for the cells.

**(ii) Phospholipids** Phosphate + glycerol + fatty acids + a nitrogen containing base.

**Function of phospholipids are**

1. As emulsifying agents since they carry hydrophilic polar groups and hydrophobic non-polar groups.
2. They absorb fatty acids from the intestine and transport to blood cells.

**(iii)** Glycolipids They contain one or more simple sugars and are important components of cell membranes and chlorplast membranes.

**(iv)** Steroids and Terpenes Menthol, camphor are common plant terpenes. Carotenoids and pigments are also terpenes.

**(a) Essential oils** The volatile, sweet smelling liquids obtained from flowers, leaves, stems, etc. Example of terpenes are esters of lower fatty acid, e.g., clove oil, rose oil, lemon oil.

**(b)** Drying oils The oils which are converted into tough, transparent mass when exposed to air by oxidation polymerisation process are called drying oils. e.g., Linseed oil, perilla, poppy seed oils.Cotton seed oil and til oil are semidrying oils.

**Blood**

An average person has about 6.8 L of blood which is about 6-10% of the body weight. pH of blood is about 7.4.

**Haemoglobin** is globular protein. It is made up of four polypeptide chains which are arranged in tetrahedral manner. Each chain is associated with a non-protein part, called haem.

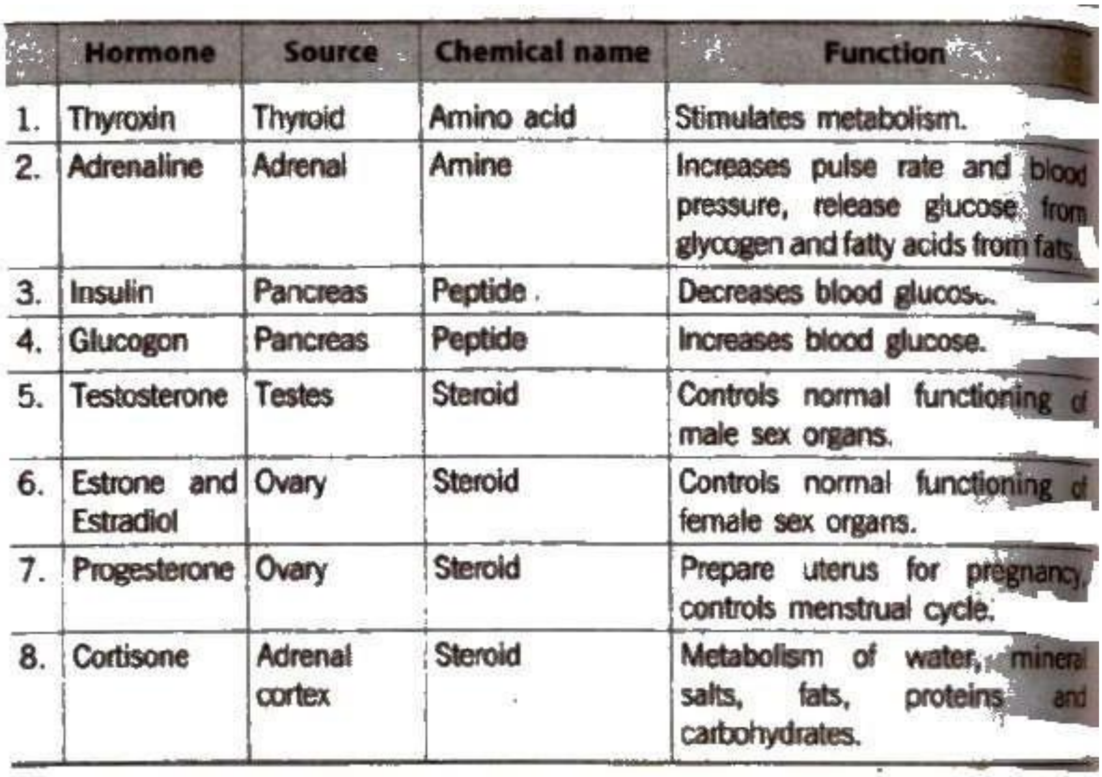
**Haemoglobin**

These axe the chemical substances which are produced by ductless glands in the body.
Hormones acts as chemical messengers.

Some examples of ductless „(endocrine) glands are thyroid, pitutary, adrenal, pancreas, testes and ovaries.

**Hormones** are divided into three types:

1. steroids
2. proteins or polypeptides
3. amines



| | Hormone | Source | Chemical name | Function |
|---|---|---|---|---|
| 1. | Thyroxin | Thyroid | Amino acid | Stimulates metabolism. |
| 2. | Adrenaline | Adrenal | Amine | Increases pulse rate and blood pressure, release glucose from glycogen and fatty acids from fats. |
| 3. | Insulin | Pancreas | Peptide | Decreases blood glucose. |
| 4. | Glucogon | Pancreas | Peptide | Increases blood glucose. |
| 5. | Testosterone | Testes | Steroid | Controls normal functioning of male sex organs. |
| 6. | Estrone and Estradiol | Ovary | Steroid | Controls normal functioning of female sex organs. |
| 7. | Progesterone | Ovary | Steroid | Prepare uterus for pregnancy, controls menstrual cycle. |
| 8. | Cortisone | Adrenal cortex | Steroid | Metabolism of water, mineral salts, fats, proteins and carbohydrates. |

Insulin is a protein hormone which is secreted by β-cells of the pancreas. Insulin was the first polypeptide in which the amino acid sequence was experimentally determined. Its deficiency leads to diabetes mellitus.

## Vitamins

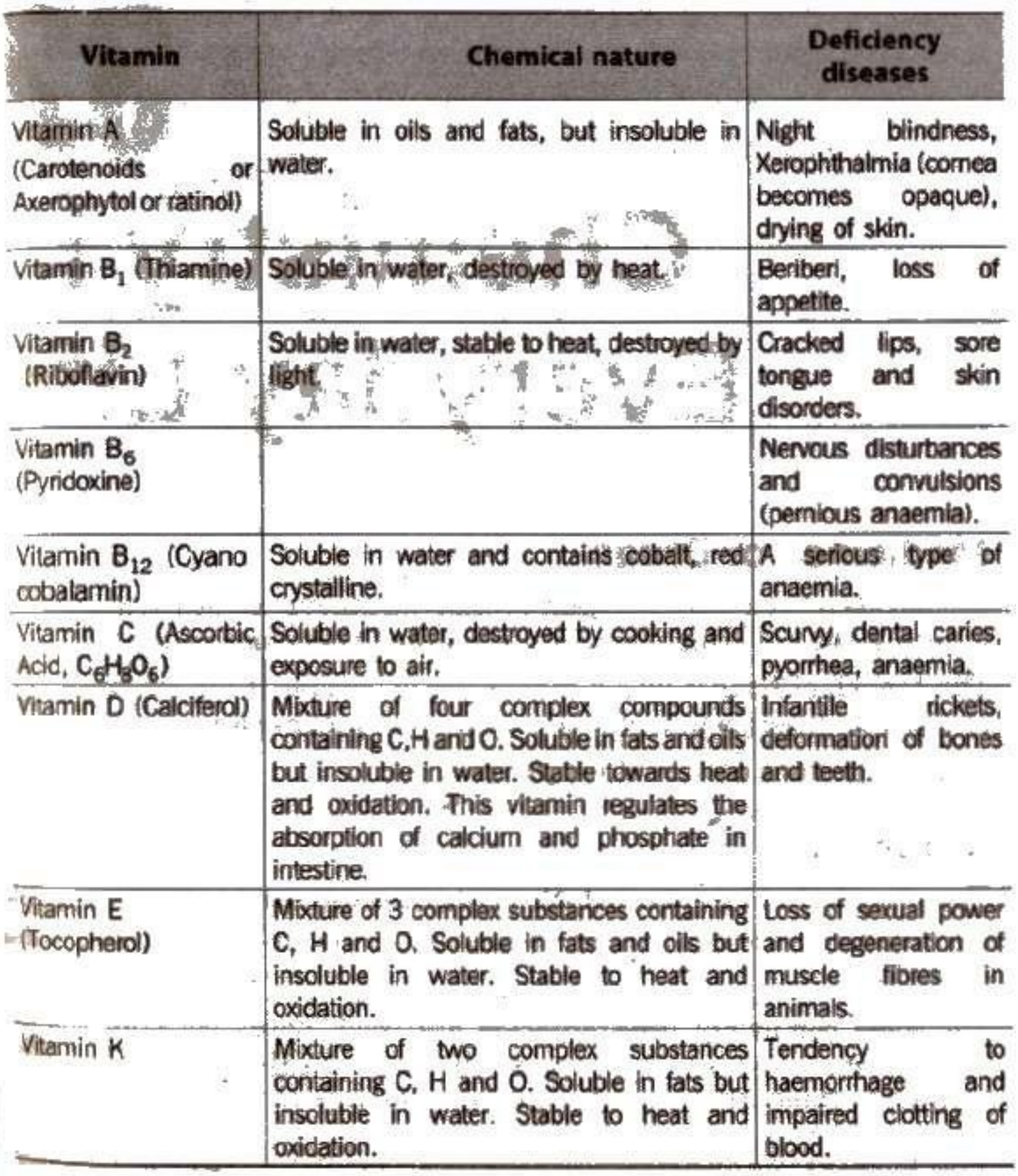
The organic compounds other than carbohydrates, proteins and facts which are required by body to maintain normal health, growth and nutrition are called vitamins.

The vitamins are complex organic molecules. They are represented by letters such as A, B, C, D, E, K.

Vitamins are broadly classified into two types,

1. Water soluble vitamins and
2. oil soluble vitamins.

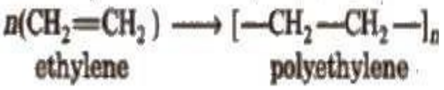
Vitamins A, D, E and K are oil soluble whereas vitamins B and C are water soluble. Vitamin H is neither fat soluble nor water soluble.



| Vitamin | Chemical nature | Deficiency diseases |
|---|---|---|
| Vitamin A (Carotenoids or Axerophytol or ratinol) | Soluble in oils and fats, but insoluble in water. | Night blindness, Xerophthalmia (cornea becomes opaque), drying of skin. |
| Vitamin $B_1$ (Thiamine) | Soluble in water, destroyed by heat. | Beriberi, loss of appetite. |
| Vitamin $B_2$ (Riboflavin) | Soluble in water, stable to heat, destroyed by light. | Cracked lips, sore tongue and skin disorders. |
| Vitamin $B_6$ (Pyridoxine) | | Nervous disturbances and convulsions (pernious anaemia). |
| Vitamin $B_{12}$ (Cyano cobalamin) | Soluble in water and contains cobalt, red crystalline. | A serious type of anaemia. |
| Vitamin C (Ascorbic Acid, $C_6H_8O_6$) | Soluble in water, destroyed by cooking and exposure to air. | Scurvy, dental caries, pyorrhea, anaemia. |
| Vitamin D (Calciferol) | Mixture of four complex compounds containing C,H and O. Soluble in fats and oils but insoluble in water. Stable towards heat and oxidation. This vitamin regulates the absorption of calcium and phosphate in intestine. | Infantile rickets, deformation of bones and teeth. |
| Vitamin E (Tocopherol) | Mixture of 3 complex substances containing C, H and O. Soluble in fats and oils but insoluble in water. Stable to heat and oxidation. | Loss of sexual power and degeneration of muscle fibres in animals. |
| Vitamin K | Mixture of two complex substances containing C, H and O. Soluble in fats but insoluble in water. Stable to heat and oxidation. | Tendency to haemorrhage and impaired clotting of blood. |

## Chapter- 15 Polymers

The word polymer has a Greek origin. which means many units (parts). Polymer is defined as a chemical substance of a high molecular mass formed by the combination of a large number of simple molecules, called monomers. e.g.,



$$\underset{\text{ethylene}}{n(CH_2{=}CH_2)} \longrightarrow \underset{\text{polyethylene}}{[-CH_2-CH_2-]_n}$$

### Polymerisation

The process by which the monomers get combined and transformed into polymers. is known as polymerisation.

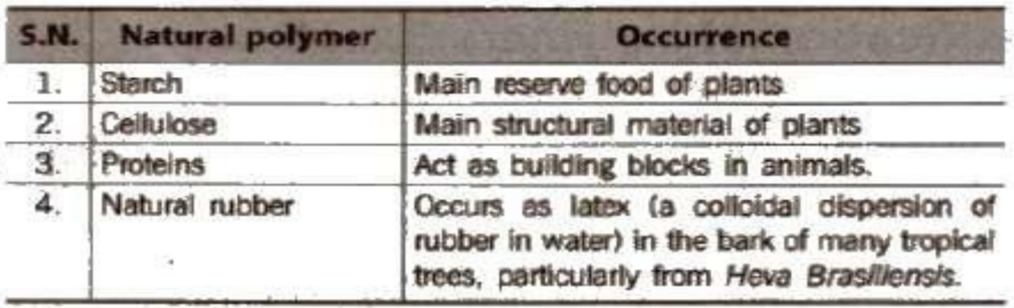
n [Monomer] → Polymer

## Difference between Polymers and Macromolecules

Polymers are also called macromolecules due to their large size but converse is not always true. A macromolecule mayor may not contain monomer units, e.g., chlorophyll ($C_{55}H_{72}O_5N_4Mg$) is a macromolecule but not a polymer since there are no monomer units present so we can conclude that all polymers are macromolecules while all macromolecules may not be polymers in nature.

## Classification of Polymers Based on Source of Origin

(i) Natural polymers Those polymers which occur in nature. i.e., in plants or animals. are called natural polymers.



| S.N. | Natural polymer | Occurrence |
|---|---|---|
| 1. | Starch | Main reserve food of plants |
| 2. | Cellulose | Main structural material of plants |
| 3. | Proteins | Act as building blocks in animals. |
| 4. | Natural rubber | Occurs as latex (a colloidal dispersion of rubber in water) in the bark of many tropical trees, particularly from *Heva Brasiliensis*. |

(ii) **Synthetic polymers** The polymers which are prepared in the laboratory are known as synthetic polymers or man-made polymers, e.g., polythene, synthetic rubber, PVC, nylon-66, teflon, orlon etc.

(iii)**Semisynthetic polymers** Polymers obtained by making some modification in natural polymers by artificial means, are known as semi synthetic polymers, e.g., celluloseacetate (rayon), vulcanised rubber etc.

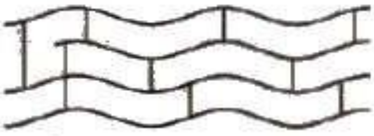
## Classification of Polymers Based on Structure

Linear chain polymer

(i) **Linear polymers** These are the polymers in which the monomer units are linked to one another to form long linear chains. These linear chains are closely packed in space. The close packing results in high densities, tensile strength and high melting and boiling points. e.g., high density polyethene, nylon and polyesters are linear polymers.

Branched chain polymer

(ii) **Branched chain polymers** In such polymers, the monomer units are linked to form long chains with some branched chains of different lengths with source. As a result of branching, these polymers are not closely packed in space. Thus, they have low densities, low tensile strength as well as low melting and boiling points. Some common examples of such polymers are low density polyethene, starch, glycogen etc.



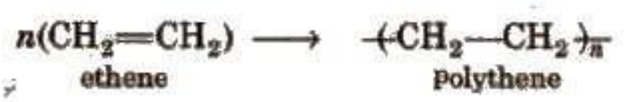
Cross linked polymer

(iii) **Cross-linked polymers or network polymers** In such polymers, the monomer units are linked together to form three dimensional network. These are expected to be quite hard, rigid and brittle. Examples of cross linked polymers are bakelite, glyptal, melamine-formaldehyde polymer etc.

**Classification of Polymers Based on Mode of Polymerisation**

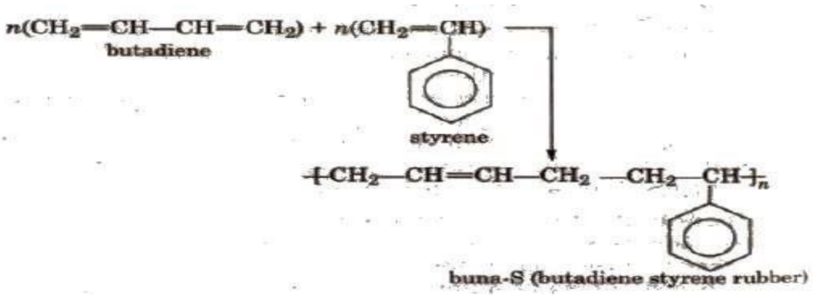
(i) **Addition polymers** The polymers formed by the polymerisation of monomers containing double or triple bonds (unsaturated compounds) are called addition polymers. Addition polymers have the same empirical formula as their monomers. Addition polymers can further be classified on the basis of the types of monomers into the following two classes;

(a) **Homopolymers** The polymers which are obtained by the polymerisation of a single type of monomer are called homopolymers.



$$n(CH_2{=}CH_2) \longrightarrow -\!\!(CH_2{-}CH_2)\!\!-_n$$

**Copolymers** The polymers which are obtained by the polymerisation of two or more monomers are called copolymers.



(ii) **Condensation polymers ;**The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers, e.g., nylon 6,6 is formed by the condensation of hexamethylene diamine with adipic acid.

$$nH_2N(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \longrightarrow \underset{\text{nylon 6,6}}{\left[ NH(CH_2)_6NHCO(CH_2)_4CO \right]_n} + nH_2O$$

**Classification of Polymers Based on Molecular Forces**

1. **Elastomers** These are rubber like solid polymers in which the polymer chains are held together by weakest intermolecular forces, e.g., natural rubber, buna-S, buna-N etc . The weak binding forces permit the polymers to be stretched. A few ‘cross links’ are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber.
2. **Fibres** Fibres belong to a class of polymers which are thread-like and can be woven into fabrics. These are widely used for making clothes, nets, ropes, gauzes, etc. Fibres possess high tensile strength because the chains possess strong intermolecular forces such as hydrogen bonding. The fibres are crystalline in nature and have sharp melting points. A few examples of this class are nylon-66, terylene and polyacrylonitrile.

3. **Thermoplastics** These are linear polymers and have weak van der Waals’ forces acting in the various chains. These forces are intermediate of the forces present in the elastomers and in the fibres. When heated, they melt and form a fluid which sets into a hard mass on cooling. Thus, they can be cast into different shapes by using suitable moulds, e.g., polyethene and polystyrene. (Plasticizers are high boiling esters or haloalkanes. These are added to I plastics to make them soft rubber like. …J
4. **Thermosetting plastics** These are normally semifluid substances with low molecular masses. When heated, they become hard and infusible due to the cross-linking between the polymer chains. As a result, they also become three dimensional in nature. A few common thermosetting polymers are bakelite, melamine-formaldehyde resin and urea formaldehyde resin.

**Molecular Mass of Polymers**

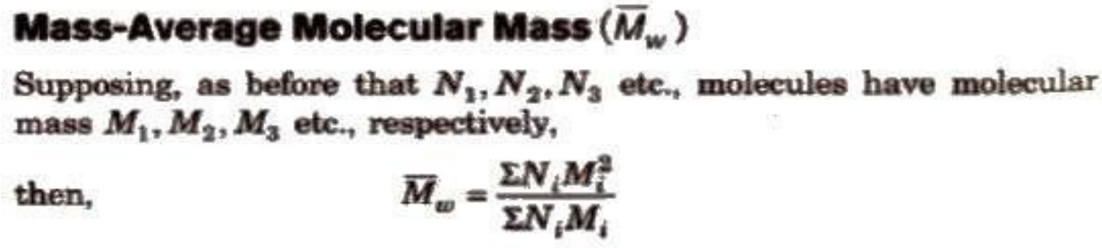
The growth of the polymer chain depends upon the availability of the monomers in the reaction. Thus, the polymer sample contains chain of varying lengths and hence, its molecular mass is always expressed as an average molecular mass.

### Number-Average Molecular Mass $M_n$

If $N_1$ molecules have molecular mass $M_1$ each, $N_2$ molecules have molecular mass $M_2$ each, $N_3$molecules have molecular mass $M_3$ each and so on,

then, $M_n = \Sigma N_i M_i / \Sigma N_i$

It is determined by osmotic pressure method.



### Mass-Average Molecular Mass ($\overline{M}_w$)

Supposing, as before that $N_1, N_2, N_3$ etc., molecules have molecular mass $M_1, M_2, M_3$ etc., respectively,

then, $$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

It is determined by light scattering and ultracentrifugation method.

### PoLydispersity Index

It is the ratio of the mass average molecular mass to the number average molecular mass PDI = $M_w$ /

$M_n$

For natural polymers, PDI is usually equal to one which means that they are monodisperse. In other words, such polymers are more homogeneous. On the contrary, synthetic polymers generally have PDI > 1 which means that they are less homogeneous.

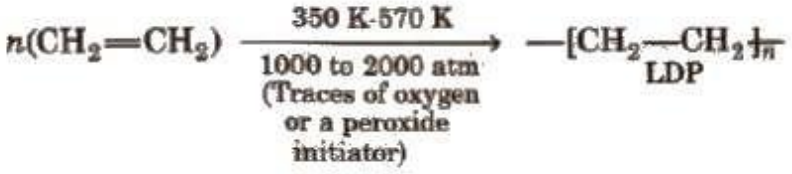
### Polyolefins

These are obtained by the addition polymerisation of ethylene and its derivatives

### 1. Polythene

Polymer of ethylene or ethene.

#### (i) **Low density polythene** (LDP)



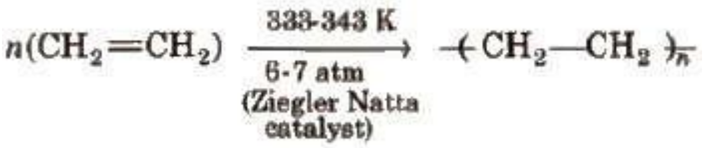
$$n(CH_2{=}CH_2) \xrightarrow[\substack{1000 \text{ to } 2000 \text{ atm} \\ \text{(Traces of oxygen} \\ \text{or a peroxide} \\ \text{initiator)}}]{350 \text{ K-}570 \text{ K}} -\!\!\underset{\text{LDP}}{[CH_2-CH_2]_n}$$

.

It is tough, flexible, transparent, chemically inert as well as poor conductor pf electricity. It has moderate tensile strength but good tearing strength.

It is used in the insulation of electricity carrying wires and manufacture of queeze bottles, toyes and flexible pipes.

(ii) **High density polyethylene** (HOP)



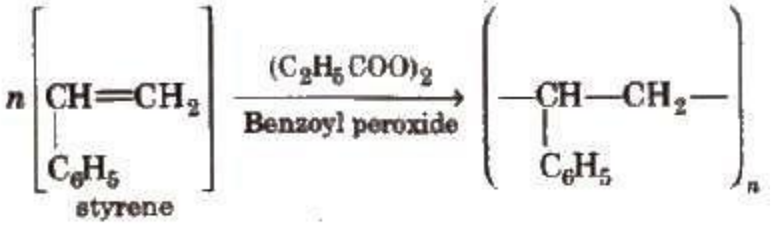
$$n(CH_2{=}CH_2) \xrightarrow[\substack{6\text{-}7\text{ atm}\\ \text{(Ziegler Natta}\\ \text{catalyst)}}]{333\text{-}343\text{ K}} \left( CH_2{-}CH_2 \right)_n$$

It has high density due to close packing. It is also chemically inert and more tougher and harder.

It is used for making containers, house wares, bottles, toyes, electric insulation etc.

**2. Polystyrene** (Styrone)

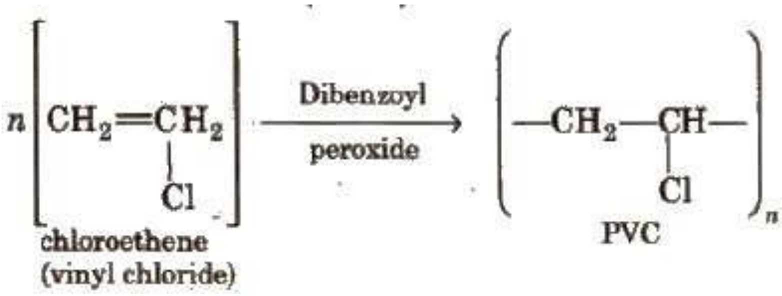
The monomers are styrene molecules. It is thermoplastic. It is used for making toys, radio and TV cabinets



$$n\left[\begin{array}{l} CH{=}CH_2 \\ | \\ C_6H_5 \end{array}\right] \xrightarrow[\text{Benzoyl peroxide}]{(C_6H_5COO)_2} \left(\begin{array}{l} {-}CH{-}CH_2{-} \\ \;| \\ \;C_6H_5 \end{array}\right)_n$$

styrene

**3.** Polyvinylchloride (PVC)



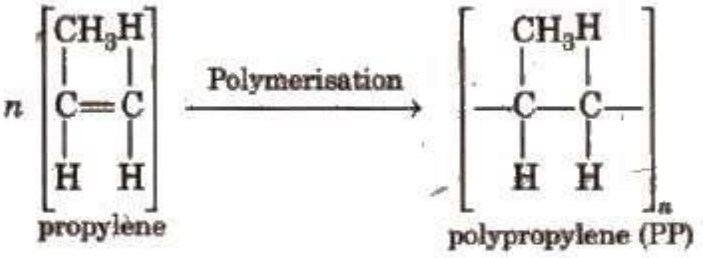
$$n\left[\begin{array}{l} CH_2{=}CH_2 \\ \quad\;\;| \\ \quad\;\;Cl \end{array}\right] \xrightarrow[\text{peroxide}]{\text{Dibenzoyl}} \left(\begin{array}{l} {-}CH_2{-}CH{-} \\ \qquad\;| \\ \qquad\;Cl \end{array}\right)_n$$

chloroethene (vinyl chloride) PVC

It is used for making rain coats, toys, electrical insulation. It is hard and resistant to heat and chemicals.

**4. Polypropylene** (PP)

It is obtained by polymerising propylene in the presence of Ziegler-Natta catalyst.



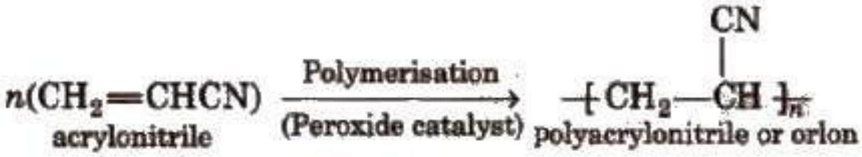
$$n\left[\begin{matrix} CH_3 & H \\ | & | \\ C & = C \\ | & | \\ H & H \end{matrix}\right] \xrightarrow{\text{Polymerisation}} \left[\begin{matrix} & CH_3 & H & \\ & | & | & \\ - & C & - C & - \\ & | & | & \\ & H & H & \end{matrix}\right]_n$$

5. **Polytetrafluoroethene** (Teflon)

$$\underset{\text{tetrafluoroethene}}{n(CF_2{=}CF_2)} \xrightarrow[\text{High pressure}]{\text{Catalyst}} \underset{\text{teflon}}{\left[CF_2-CF_2\right]_n}$$

It is chemically inert and resistant to attack by corrosive reagent. It is used in making oil seals, gaskets and also for non-stick surface coated utensils.

6. **Polyacrylonitrile**



$$\underset{\text{acrylonitrile}}{n(CH_2{=}CHCN)} \xrightarrow[\text{(Peroxide catalyst)}]{\text{Polymerisation}} \underset{\text{polyacrylonitrile or orlon}}{\left[CH_2-\overset{\overset{\displaystyle CN}{|}}{CH}\right]_n}$$

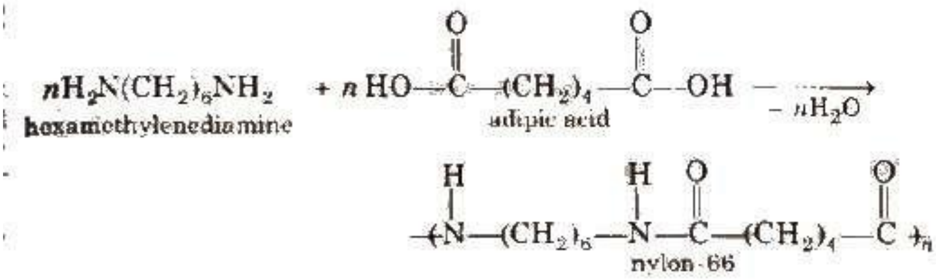
It is used as a substitute for wool in making commercial fibres as orlon or acrilan.

**Polyamides**

The polymers which contain an amide linkage in chain are known as pOlyamide, e.g., nylon-6, 6.

1. **Nylon-66**

It is obtained by the condensation of adipic acid and hexamethylenediamine with the elimination of water molecule



$$\underset{\text{hexamethylenediamine}}{nH_2N(CH_2)_6NH_2} + \underset{\text{adipic acid}}{n\,HO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[-\,nH_2O]{}$$

$$\underset{\text{nylon-66}}{\left[\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}\right]_n}$$

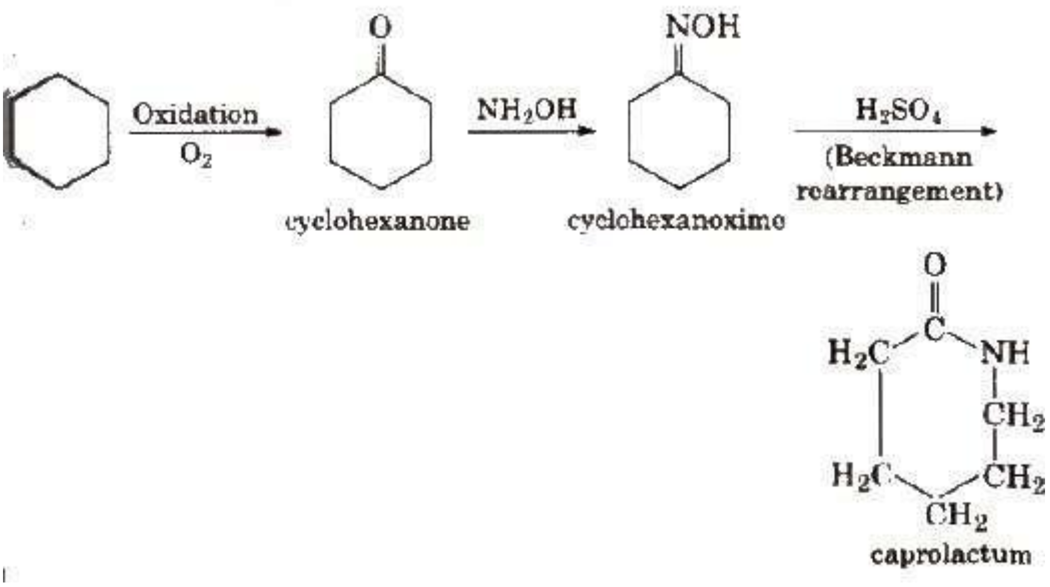
The polyamides are identified by numbers. These numbers refer to the number of carbon atoms in diamine and in the dibasic acid. As in the above case, the carbon atoms are 6 in each case, therefore the product is described as nylon-66.

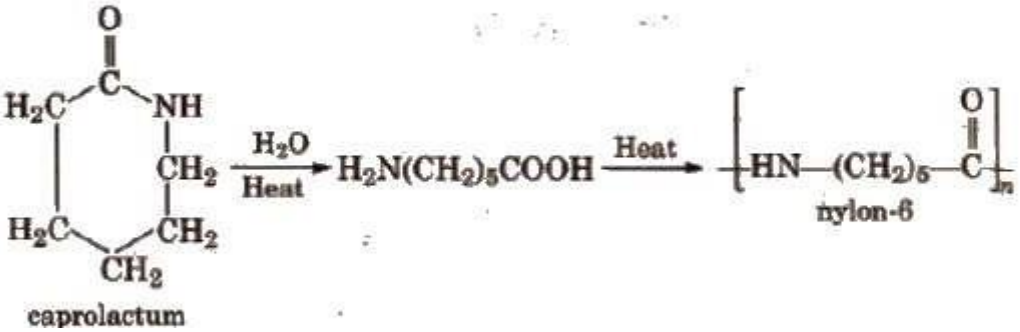
**Properties and uses**

Nylon-66 is a linear polymer and has very high tensile strength. It shows good resistance to abrasion. Nylon-66 is usually fabricated into sheets. It is used in bristles for brushes and in textile

## 2. Nylon-6

Nylon-6 is obtained by heating caprolactam with water at a high temperature.



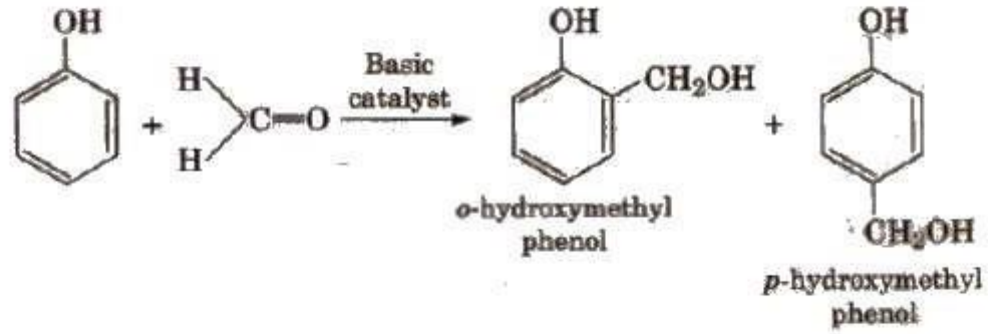


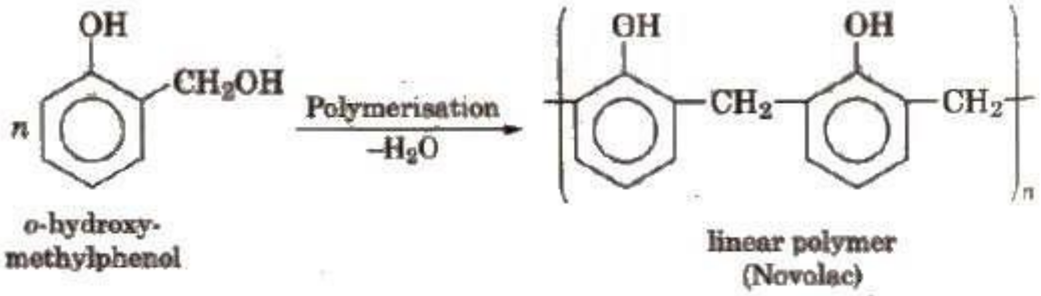
**Resins**

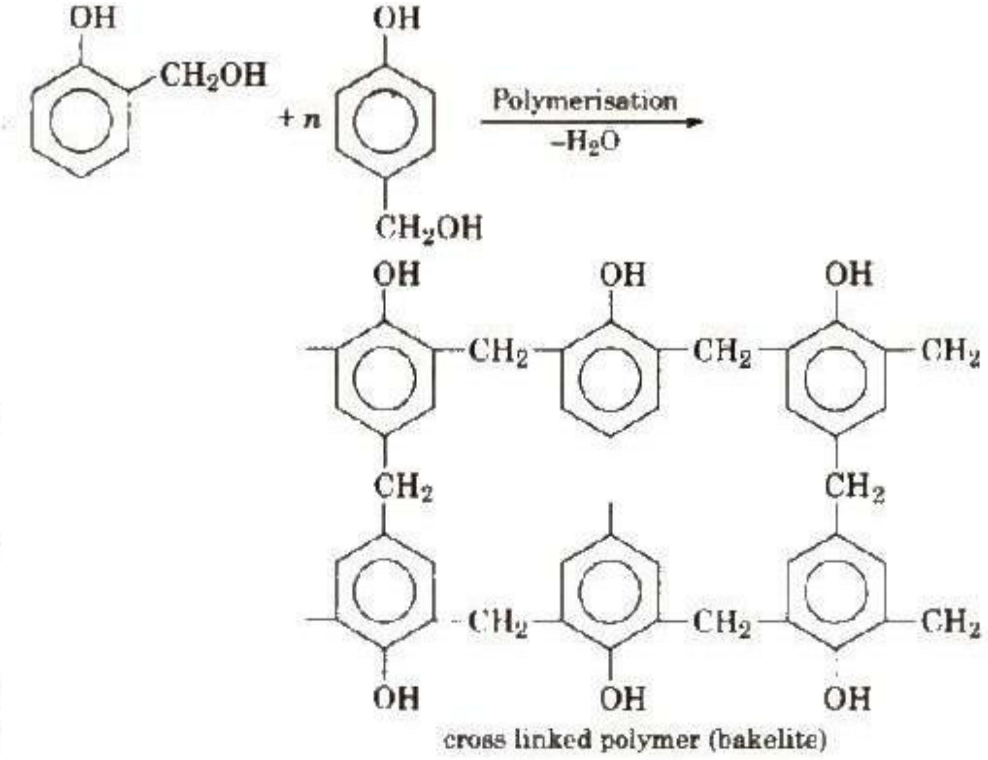
## 1. Phenol-Formaldehyde Polymer

(Bakelite and Related Polymers)

These polymers are obtained by the condensation reaction of phenol with formaldehyde in the presence of either acid or a base catalyst. The reaction involves the formation of methylene bridge at ortho, para or both ortho and para positions. A linear or cross linked material is obtained depending upon the condition of reaction.





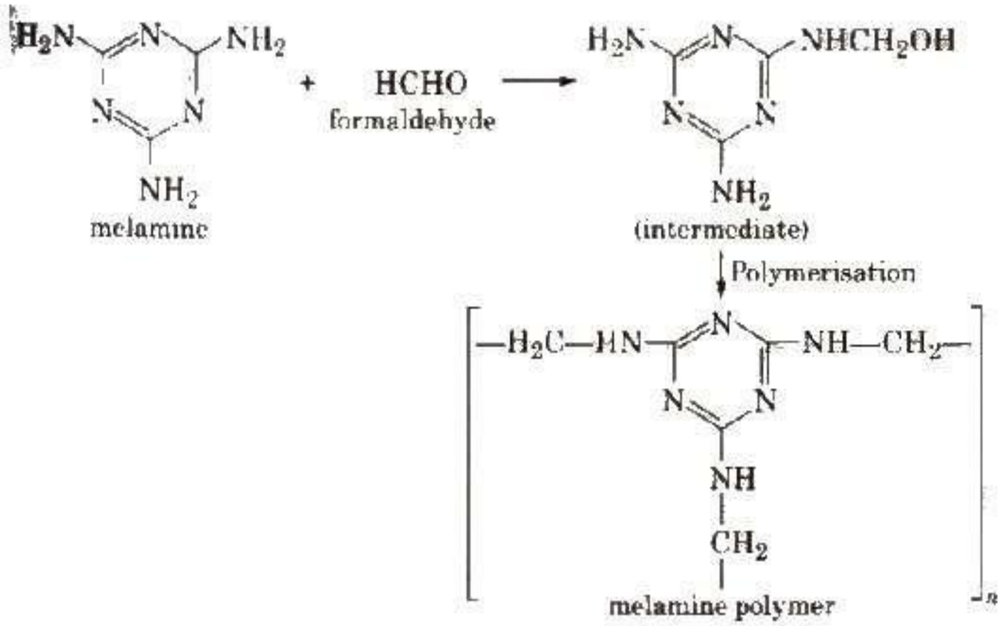


## Uses

Bakelite is used for making combs, photograph records, electrical switches etc. Soft bakelites with low degree of polymerisation are used as binding glue for laminated wooden plants, in varnishes and lacquers.

## 2. Melamine-formaldehyde Resin

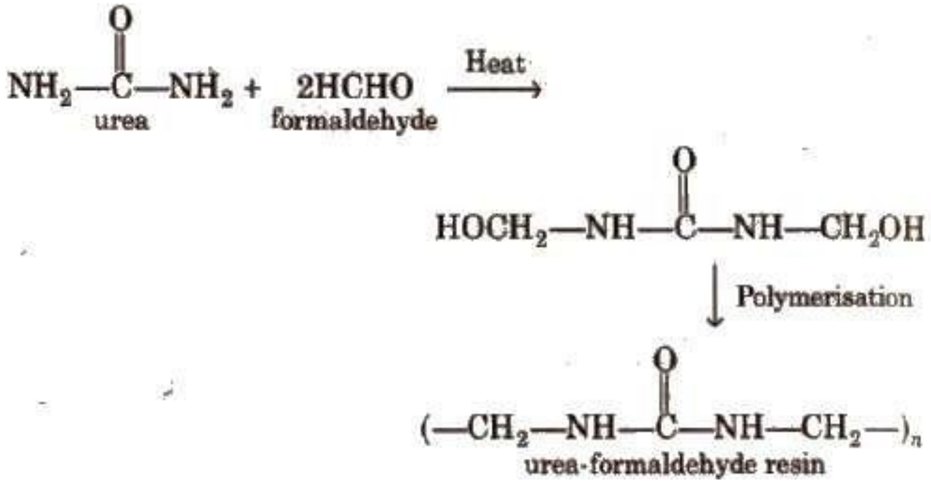
It is a copolymer formed by the polymerisation of melamine (which is a heterocyclic triamine) and formaldehyde as follows :



## Properties and Uses

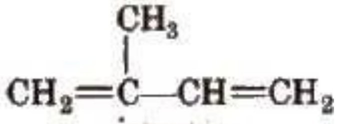
It is very hard and tough. It has assumed great importance these days particularly in making crockery. They do not break even when droped from a height.

## 3. Urea-formaldehyde Resin



## 4. Natural Rubber

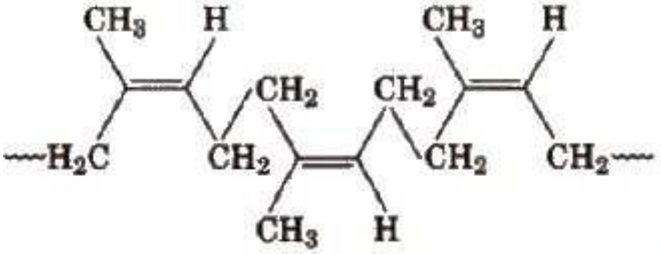
Natural.rubber is a coiled linear 1, 4-polymer of isoprene.



$CH_2=C(CH_3)-CH=CH_2$

isoprene

In the polymer chain of natural rubber, the residual double bonds are located between $C_2$ and $C_3$ of the isoprene unit. All these double bonds have cis configuration, and thus natural rubber is cis-l,4-polyisoprene.



A section of the polymeric chain of natural rubber

In the natural rubber, there is no polar substituent. The only intermolecular forces are van der Waals' type. The cis-configuration gives the polymeric chain of natural rubber a coiled structure. As a result, it can be stretched by the application of a force. When the force is removed, the chain returns back to its original coiled shape.

Natural rubber is soft and sticky. It can be used only in the temperature range 10°C-50°C. At higher temperature, it becomes soft and at low temperature, it becomes brittle. It has higb water absorption capacity. It is attacked by oxidising agents and organic solvents. As such, it cannot be used very extensively for commercial puposes.

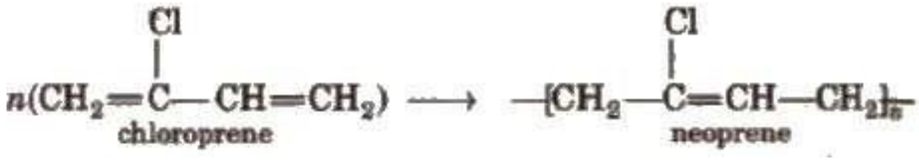
### Vulcanisation of Rubber

The properties of natural rubber can be modified by introducing -S-S- polysulphide crosslinks in its structure. This process of introducing -S-S- crosslnks in the structure of natural rubber by heating with sulphur at 11O°C is called vulcanlsation of rubber.

Vulcanisatlon is carried out by adding sulphur (3-5%) and zinc oxide to the rubber, and then heating the object at about 110°Cfor about 20-30 minutes. Zinc oxide accelerates the rate of vulcanisation. Vulcanisation introduces polysulphide (-S-S-) bonds between the adjacent chains. These crosslinks tend to limit the motion of chains relative to each other.

## 5. Neoprene

Polymer formed by polymerisation of chloroprene is neoprene or synthetic rubber.

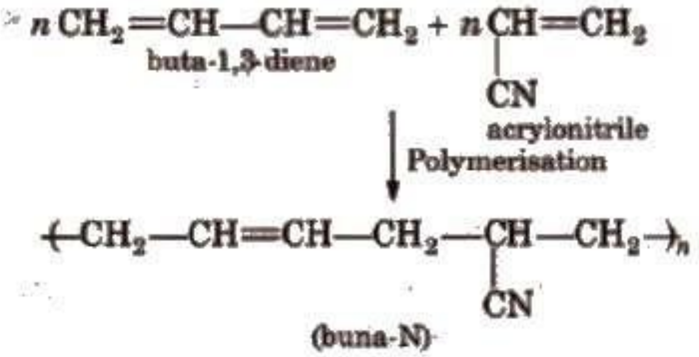


$$\underset{\text{chloroprene}}{n(\mathrm{CH_2{=}\overset{\overset{Cl}{|}}{C}{-}CH{=}CH_2})} \longrightarrow \underset{\text{neoprene}}{\mathrm{-\!\!\left[CH_2{-}\overset{\overset{Cl}{|}}{C}{=}CH{-}CH_2\right]_n\!\!-}}$$

It is used for the manufacturing conveyers belts, gasket and hoses.

### 6. Buna-N

It is a copolymer of buta-l, 3-diene and acrylonitrile. It is formed as follows



$$\underset{\text{buta-1,3-diene}}{n\,\mathrm{CH_2{=}CH{-}CH{=}CH_2}} + \underset{\text{acrylonitrile}}{n\,\mathrm{\underset{\underset{CN}{|}}{C}H{=}CH_2}} \xrightarrow{\text{Polymerisation}} \underset{\text{(buna-N)}}{\mathrm{\left(CH_2{-}CH{=}CH{-}CH_2{-}\underset{\underset{CN}{|}}{C}H{-}CH_2\right)_n}}$$

### Properties and Uses

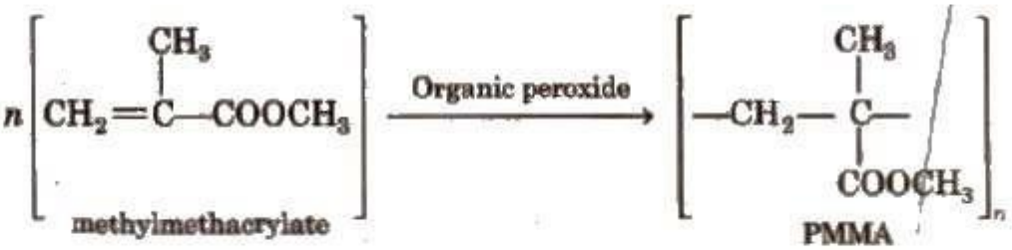
It is insulator in nature and is used for making conveyor belts and printing rollers.

### Polyesters

The polymers which contain an ester linkage are known as polyester, e.g., dacron.

### 1. Polymethylmethacrylate (PMMA)

It is prepared by the polymerisation of methylmethacrylate in the presence of suitable organic peroxide.



$$n\underset{\text{methylmethacrylate}}{\left[\mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}COOCH_3}\right]} \xrightarrow{\text{Organic peroxide}} \underset{\text{PMMA}}{\left[\mathrm{-CH_2{-}\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}}\right]_n}$$

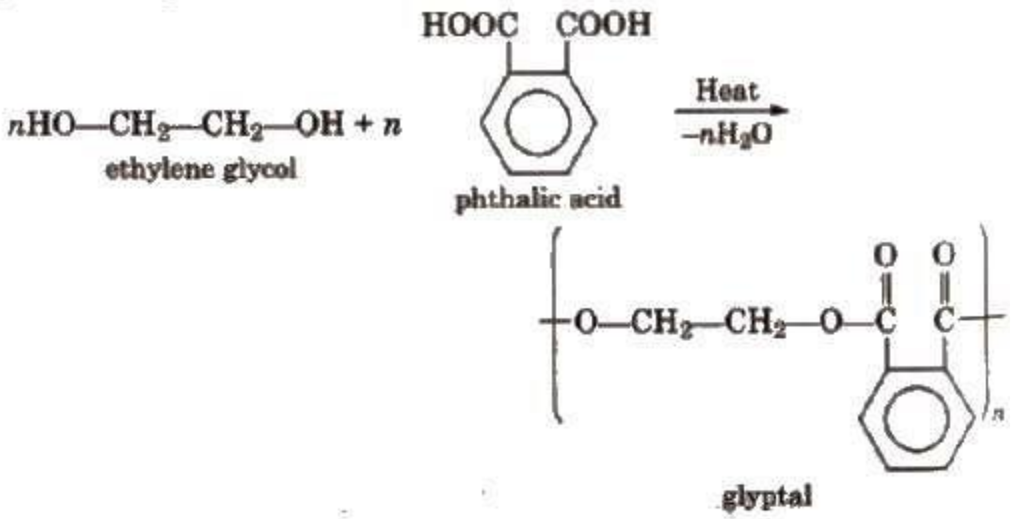
The polymer is known by several commercial names such as lucite, acrylite, plexiglass and perspex.

### Properties and uses

It is a hard and transparent polymer and is quite resistant to the effect of light, heat and ageing. It is used, in the manufacture of unbreakable lights, protective coatings, dentures, and in making windows for aircrafts.

### 2. Glyptal

It is a polyester having crosslinks. It is a thermosetting plastic. It is obtained by condensation of ethylene glycol and phthalic acid or glycerol and phthalic acid.

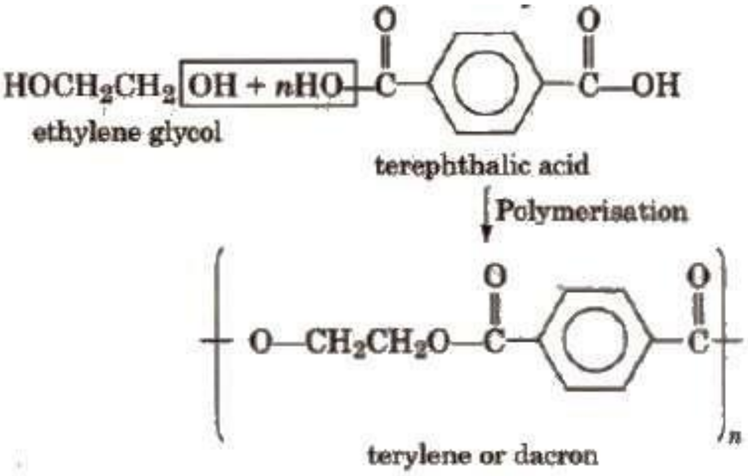


When its solution in a suitable solvent is evaporated, it leaves a tough but non-flexible film. It is, therefore, used in the manufacture of paints and lacquers.

### 3. Terylene (Dacron)

It is a condensation product of ethylene glycol and terephthalic acid.

Polymerisation is carried out at 420 to 460 K in the presence of catalyst mixture of zinc acetate and antimony trioxide.



### Properties and uses

Terylene is highly resistant to the action of chemical and biological agents. Its fibres are quite strong and durable. It can also be blended with wool or cotton to obtain fabrics of desired composition.

Terylene is used in the manufacture of a variety of clothes such as terycot, terywool and terysilk as a result of blending with other yerns. It is also used for preparing magnetic recording tapes, conveyer belts, aprons for industrial workers etc.

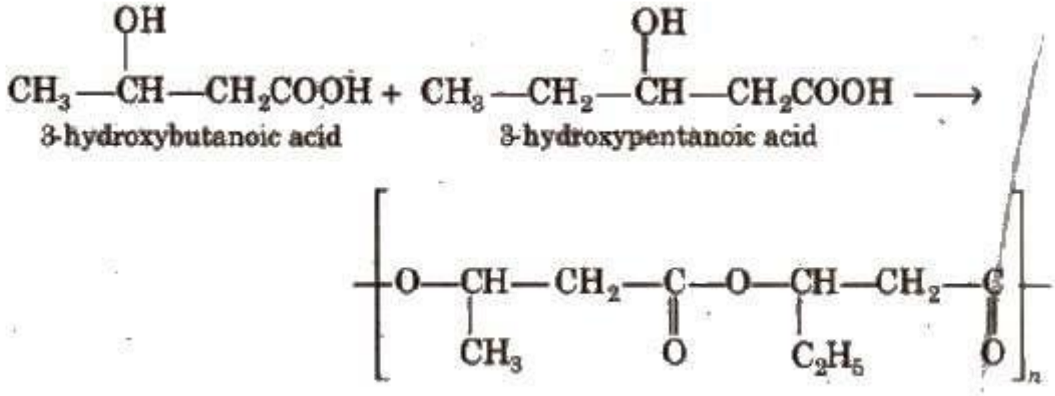
### Biopolymers and Biodegradable Polymers

Synthetic polymers are mostly non-biodegradable i.e., it is very difficult to dispose off the polymeric waste, e.g., polythene bags.

Nature has provided us a variety of polymers which can be produced by the biological systems in plants and animals. These are called biopolymers, e.g., polysaccharides, proteins, nucleic acids, etc. In the biological system, these polymers decompose or hydrolyse in the Presence of different enzymes. This means that they are biodegradable.

Aliphatic polyesters are the common examples of biodegradable Polymers. It is a

copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



$$\underset{\text{3-hydroxybutanoic acid}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2COOH} + \underset{\text{3-hydroxypentanoic acid}}{CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2COOH} \longrightarrow \left[ O-\underset{CH_3}{\underset{|}{C}H}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{C_2H_5}{\underset{|}{C}H}-CH_2-\underset{O}{\underset{\|}{C}} \right]_n$$

### 2. Nylon-2-Nylon-6

It is an alternating polyamide copolymer of glycine ($H_2N-CH_2-COOH$) and amino caproic acid [$H_2N(CH_2)_5COOH$] and is biodegradable.

### Some More Impotant Polymers

1. Saran is a copolymer of vinyl chloride and Isused for wrapping food materials.
2. ASS rubber is a copolymer of acrylonitrile, buta-1, 3-diene and styrene.
3. Bubble gum contains styrene butadiene rubber.

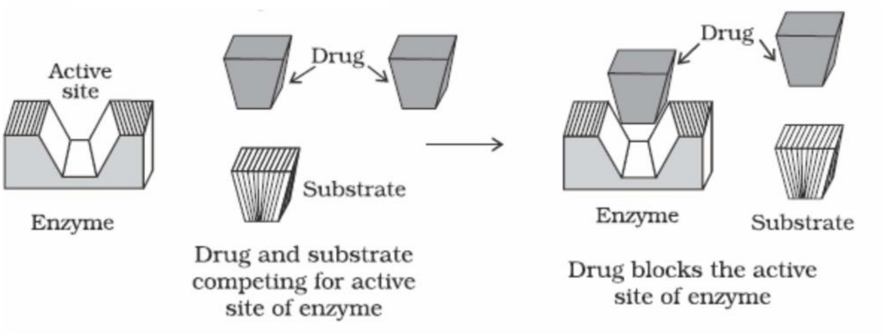
4. Epoxy resins are used In making adhesives such as araldite, etc. These are the copolymer of epichlorohydrin and bisphenol-A.
5. Thikol is another variety of synthetic rubber which is a copolymer of ethylene chloride and sodium tetrasulphide ($Na_2S_4$).
6. Dynells a copolymer of vinyl chloride and acrylonitrile and is used for making human hair wigs.
7. Silk Is a thread like natural polymer which is obtained from cocoons of sllk worms. It is a natural polyamide fibre.
8. Thermocol Is a foamed plastic obtained by blowing air through molter polystyrene or polyurethane.
9. Superglue is a polymer of methyl α-cyanoacrylate and is obtained by anionic polymerisation of monomer.

## Chapter-16 Chemistry in Everyday Life

- **Drugs:**
  Drugs are low molecular mass substances which interact with targets in the body and produce a biological response.
- **Medicines**:
  Medicines are chemicals that are useful in diagnosis, prevention and treatment of diseases
- **Therapeutic effect:**
  Desirable or beneficial effect of a drug like treatment of symptoms and cure of a disease on a living body is known as therapeutic effect
- **Enzymes**
  Proteins which perform the role of biological catalysts in the body are called enzymes
- **Functions of enzymes:**

  (i) The first function of an enzyme is to hold the substrate for a chemical reaction. Active sites of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively.

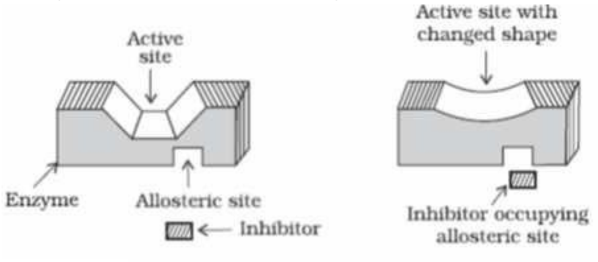
  (ii) The second function of an enzyme is to provide functional groups that will attack the substrate and carry out chemical reaction.
- **Role of drugs:**
  Main role of drugs is to either increase or decrease role of enzyme catalysed reactions. Inhibition of enzymes is a common role of drug action.
- **Enzyme inhibitor:**
  Enzyme inhibitor is drug which inhibits catalytic activity of enzymes or blocks the binding site of the enzyme and eventually prevents the binding of substrate with enzyme.
- Drug can inhibit attachment of substrate on active site of enzymes in following ways:
  (a) Competitive Inhibition: Competitive Inhibitors are the drugs that compete with the natural substrate for their attachment on the active sites of enzymes.



Drug and substrate competing for active site of enzyme

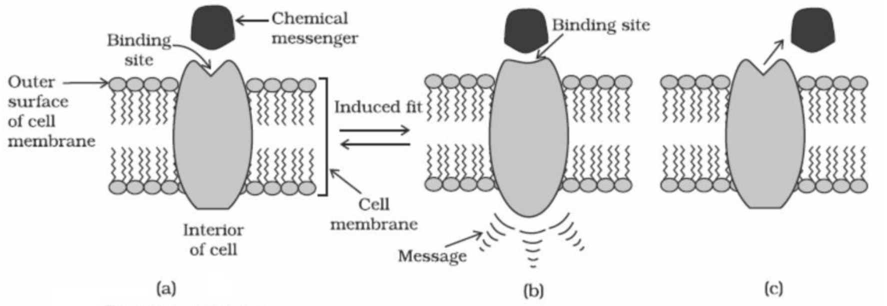
Drug blocks the active site of enzyme

(b) Non-Competitive Inhibition: Some drugs do not bind to the enzyme's active site, instead bind to a different site of enzyme called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate cannot recognise it. If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesizes the new enzyme.



*Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site*

- **Receptors:**
  Proteins which are vital for communication system in the body are called receptors. Receptors show selectivity for one chemical messenger over the other because their binding sites have different shape, structure and amino acid composition.
- **Receptors as Drug Targets:**
  In the body, message between two neurons and that between neurons to muscles is communicated through chemical messengers. They are received at the binding sites of receptor proteins. To accommodate a messenger, shape of the receptor site changes which brings about the transfer of message into the cell. Chemical messenger gives message to the cell without entering the cell.



*Receptor receiving chemical messenger*

*Shape of the receptor changed after attachment of messenger*

*Receptor regains structure after removal of chemical messenger*

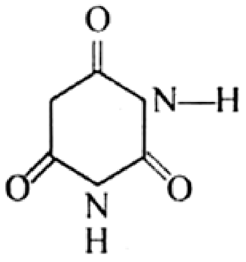
- **Antagonists and Agonists:**
  Drugs that bind to the receptor site and inhibit its natural function are called antagonists. These are useful when blocking of message is required. Drugs that mimic the natural messenger by switching on the receptor are called agonists. These are useful when there is lack of natural chemical messenger.
- **Therapeutic action of different classes of drugs:**

(i) Antacid: Chemical substances which neutralize excess acid in the gastric juices and give relief from acid indigestion, acidity, heart burns and gastric ulcers. Examples: Eno, gelusil, digene etc.

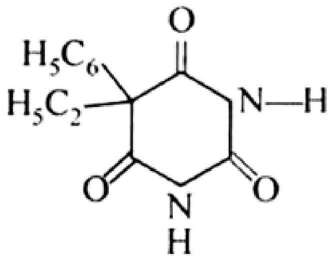
(ii) Antihistamines: Chemical substances which diminish or abolish the effects of histamine released in body and hence prevent allergic reactions. Examples: Brompheniramine (Dimetapp) and terfenadine (Seldane).

(iii) Neurologically Active Drugs: Drugs which have a neurological effect i.e. affects the message transfer mechanism from nerve to receptor.

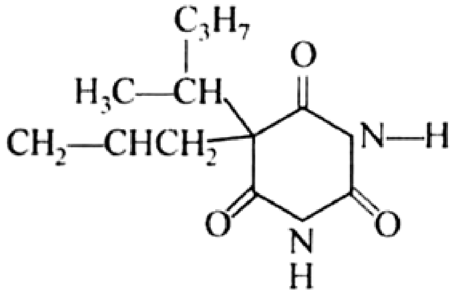
- **Tranquilizers:** Chemical substances used for the treatment of stress and mild or severe mental diseases. Examples: Derivatives of barbituric acids like veronal, amytal, nembutal, luminal, seconal.



Barbituric acid



Luminal



Seconal

- Analgesics: Chemical substances used to relieve pain without causing any disturbances in the nervous system like impairment of consciousness, mental confusion, incoordination or paralysis etc.
- Classification of Analgesics:

a) Non-narcotic analgesics: They are non-addictive drugs. Examples: Aspirin, Ibuprofen, Naproxen, Dichlofenac Sodium.

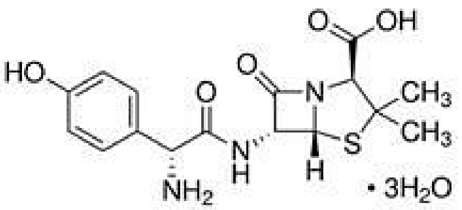
b) Narcotic analgesics: When administered in medicinal doses, these drugs relieve pain and produce sleep. Examples: Morphine and its derivatives

(iv) Antimicrobials:
Drugs that tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively.

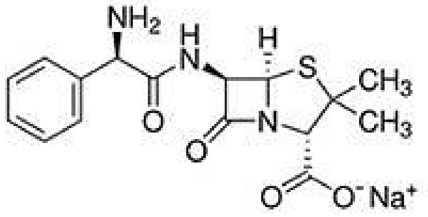
(v) Antifertility Drugs:
Chemical substances used to prevent conception or fertilization are called antifertility drugs. Examples - Norethindrone, ethynylestradiol (novestrol).

- **Types of antimicrobial drugs :**

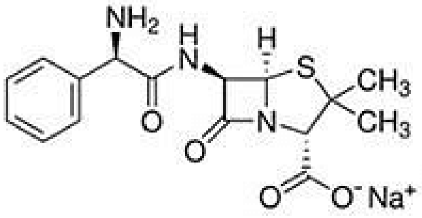
(a) Antibiotics:
Chemical substances produced by microorganisms that kill or prevent the growth of other microbes.



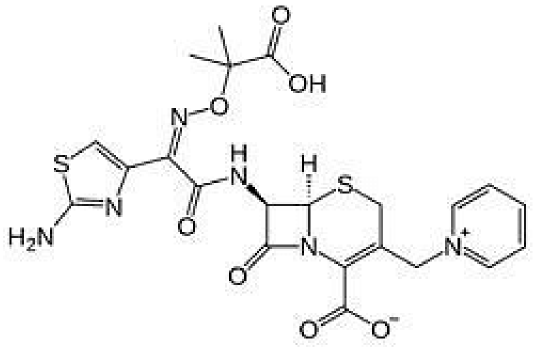
**Amoxicillin**



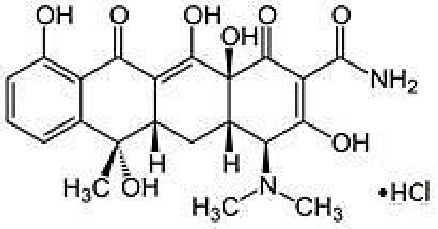
**Ampicillin**



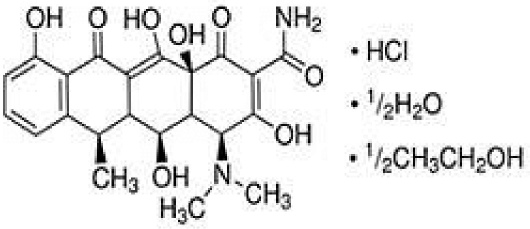
**Penicillin G**



**Ceftazidime**



**Tetracycline**



**Doxycycline**

**Classification of antimicrobial drugs based on the mode of control of microbial diseases:**

a) Bactericidal drugs - Drugs that kills organisms in body. Examples - Penicillin, Aminoglycosides, Ofloxacin.

b) Bacteriostatic drugs - Drugs that inhibits growth of organisms. Examples - Erythromycin, Tetracycline, Chloramphenicol.

**Classification of antimicrobial drugs based on its spectrum of action:**

a) Broad spectrum antibiotics - Antibiotics which kill or inhibit a wide range of Gram- positive and Gram-negative bacteria are called broad spectrum antibiotics. Examples - Ampicillin and Amoxycillin.

b) Narrow spectrum antibiotics - Antibiotics which are effective mainly against Gram- positive or Gram-negative bacteria are called narrow spectrum antibiotics. Examples- Penicillin G.

c) Limited spectrum antibiotics - Antibiotics effective against a single organism or disease

*(b)* Antiseptics*:*

Chemical substances that kill or prevent growth of microorganisms and can be applied on living tissues such as cuts, wounds etc., are called antispetics. Examples - Soframicine, dettol etc.

(c) Disinfectants: Chemical substances that kill microorganisms but cannot be applied on living tissues such as cuts, wounds etc., are called disinfectants. Examples - Chlorine (Cl2), bithional, iodoform etc.

- **Food additives:**

  Food additives are the substances added to food to preserve its flavour orimprove its taste and appearance.
- **Different types of food additives:**

a) Artificial Sweetening Agents: Chemical compounds which gives sweetening effect to the food and enhance its flavour. Examples - Aspartame, Sucrolose and Alitame.

b) Food preservatives: Chemical substances which are added to food material to prevent their spoilage due to microbial growth. Examples - Sugar, Salts, Sodium benzoate

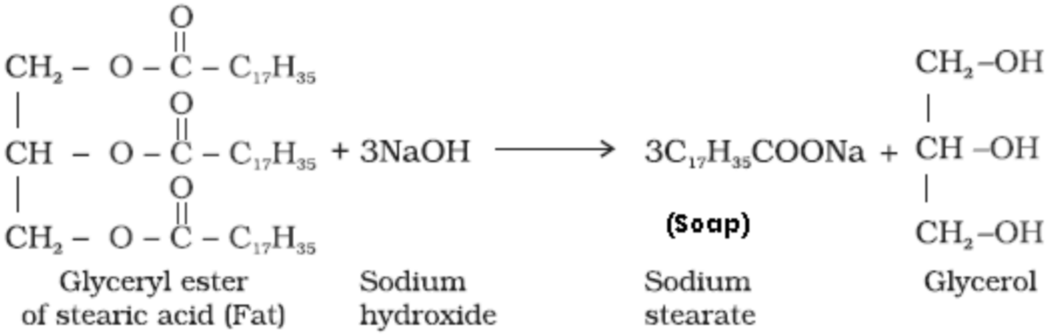
c) Food colours: Substances added to food to increase the acceptability and attractiveness of the food product. Examples - Allura Red AC, Tartrazine

d) Nutritional supplements: Substances added to food to improve the nutritional value. Examples - Vitamins, minerals etc.

e) Fat emulsifiers and stabilizing agents: Substances added to food products to give texture and desired consistency. Examples - Egg yolk (where the main emulsifying chemical is Lecithin)

f) Antioxidants :Substances added to food to prevent oxidation of food materials. Examples - Butylated Hydroxy Toluene (BHT), Butylated Hydroxy Anisole (BHA).

- **Soaps:**
  It is a sodium or potassium salts of long chain fatty acids like stearic, oleic and palmitic acid.



This reaction is known as saponification.

- **Types of soaps:**
  a) Toilet soaps are prepared by using better grades of fats and oils and care is taken to remove excess alkali. Colour and perfumes are added to make these more attractive.
  b) Transparent soaps are made by dissolving the soap in ethanol and then evaporating the excess solvent.
  c) In medicated soaps, substances of medicinal value are added. In some soaps, deodorants are added.
  d) Shaving soaps contain glycerol to prevent rapid drying. A gum called, rosin is added while making them. It forms sodium rosinate which lathers well.
  e) Laundry soaps contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.
  f) Soaps that float in water are made by beating tiny air bubbles before their hardening.
  g) Soap chips are made by running a thin sheet of melted soap onto a cool cylinder and scraping off the soaps in small broken pieces.
  h) Soap granules are dried miniature soap bubbles.
  i) Soap powders and scouring soaps contain some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand, and builders like sodium carbonate and trisodium phosphate.

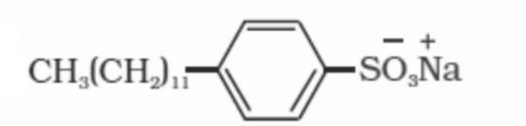
- **Advantages of using soaps:**
  Soap is a good cleansing agent and is 100% biodegradable i.e., micro- organisms present in sewage water can completely oxidize soap. Therefore, soaps do not cause any pollution problems.
- **Disadvantages of using soaps:**
  Soaps cannot be used in hard water because hard water containsmetal ions like $Ca^{2+}$ and $Mg^{2+}$ which react with soap to form white precipitate of calcium and magnesium salts

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + CaCl_2 + 2NaCl \longrightarrow \underset{\text{Insoluble calcium stearate (soap)}}{(C_{17}H_{35}COO)_2\,Ca}$$

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + MgCl_2 + 2NaCl \longrightarrow \underset{\text{Insoluble magnesium stearate (soap)}}{(C_{17}H_{35}COO)_2\,Mg}$$

These precipitates stick to the fibres of the cloth as gummy mass and block the ability of soaps to remove oil and grease from fabrics. Therefore, it interferes with the cleansing ability of the soap and makes the cleansing process difficult.
In acidic medium, the acid present in solution precipitate the insoluble free fatty acids which adhere to the fabrics and hence block the ability of soaps to remove oil and grease from the fabrics. Hence soaps cannot be used in acidic medium

- **Detergents:**
  Detergents are sodium salts of long chain of alkyl benzene sulphonic acids or sodium salts of long chain of alkyl hydrogen sulphates.



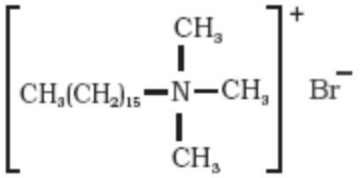
Sodium dodecylbenzenesulphonate

- **Classification of detergents:**

(a) Anionic detergents:
Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogensulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents. Similarly alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali. Anionic detergents are termed so because a large part of molecule is an anion.

They are used in household cleaning like dishwasher liquids, laundry liquid detergents, laundry powdered detergents etc. They are effective in slightly acidic solutions where soaps do not work efficiently.

(b) Cationic detergents: Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cationic parts possess a long hydrocarbon chain and a positive charge on nitrogen atom. Cationic detergents are termed so because a large part of molecule is a cation. Since they possess germicidal properties, they are used as germicides. They has strong germicidal action, but are expensive.


Cetyltrimethyl ammonium bromide

(c) Non- ionic detergents: They do not contain any ion in their constitution. They are like esters of high molecular mass.

Example: Detergent formed by condensation reaction between stearic acid reacts and polyethyleneglycol.

$$CH_3(CH_2)_{16}COOH + HO(CH_2CH_2O)_nCH_2CH_2OH \xrightarrow{-H_2O} CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

Stearic acid Polyethyleneglycol

It is used in Making liquid washing detergents. They have effective H- bonding groups at one end of the alkyl chain which make them freely water soluble.

- **Biodegradable detergents:**

  Detergents having straight hydrocarbon chains that are easily decomposed by microorganisms. Example: Sodium lauryl sulphate

  $$CH_3(CH_2)_{10}CH_2OSO_3^{-}Na^{+}$$

  Sodium laurylsulphate

- **Non-Biodegradable detergents:**

  Detergents having branched hydrocarbon chains that are not easily decomposed by microorganisms