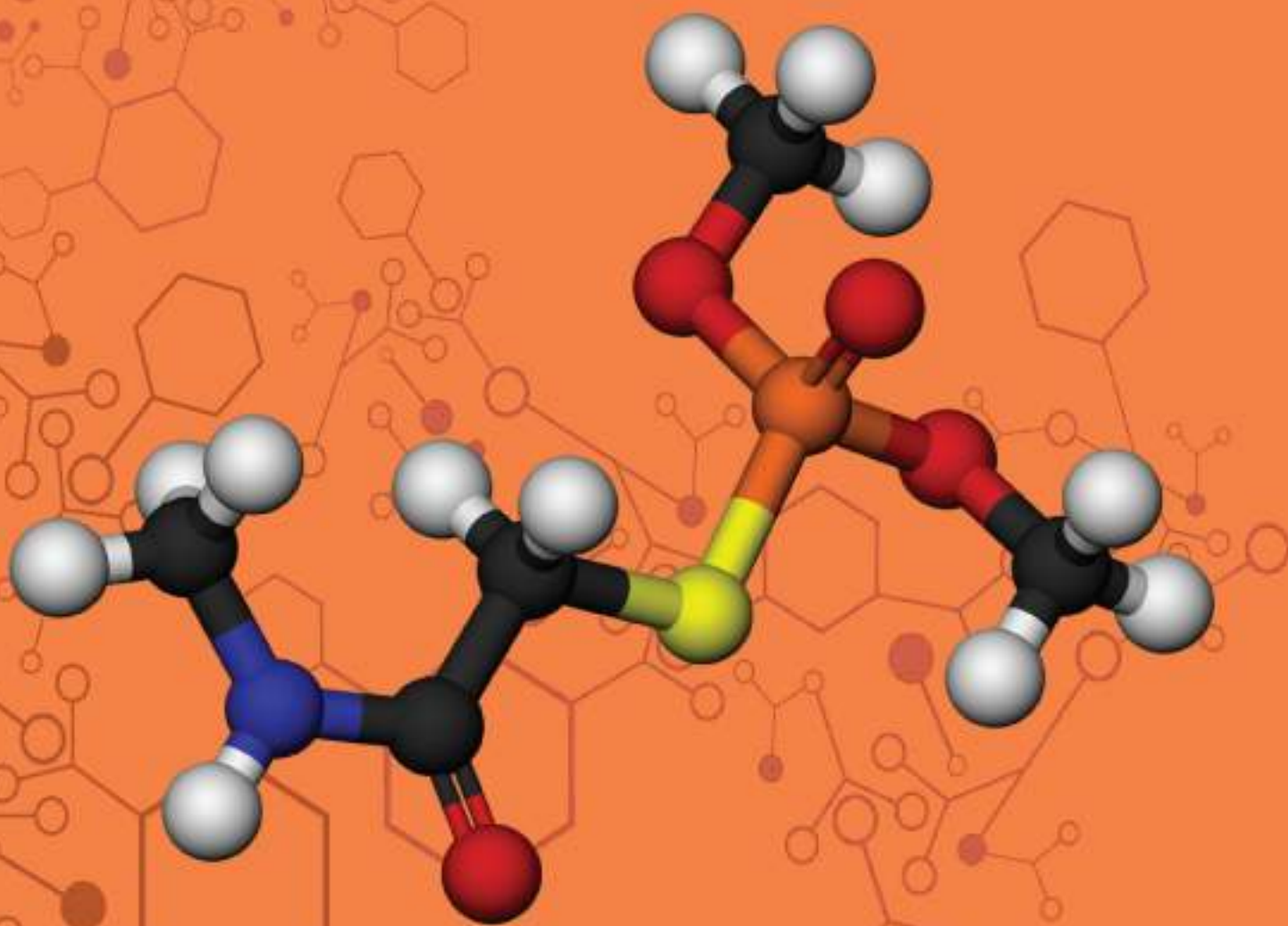


NCERT Synopsis



Contents

The Solid State.....	1
Solutions	22
Electrochemistry	31
Chemical Kinetics	43
Surface Chemistry.....	52
General Principles and Processes of Isolation of Elements	73
The p-Block Elements	85
The d-and f-Block Elements	106
Coordination Compounds	115
Haloalkanes and Haloarenes	126
Alcohols, Phenols and Ethers	142
Aldehydes, Ketones and Carboxylic Acids	158
Amines	169
Biomolecules.....	180
Polymers	194
Chemistry in Everyday Life.....	203

The Solid State

➤ General Characteristics of Solid State

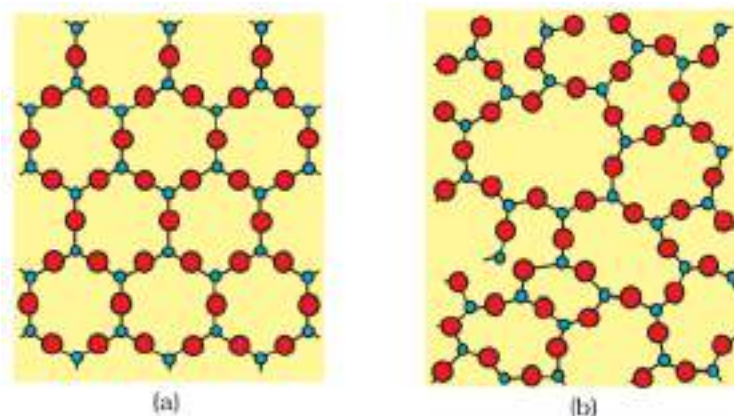
- Have definite mass, volume and shape, incompressible and rigid.
- Intermolecular distances are short.
- Intermolecular forces are strong.
- Constituent particles have fixed positions and can only oscillate about their mean positions.
- They are incompressible and rigid.

➤ Amorphous and Crystalline Solids

- The word amorphous is derived from the Greek word amorphos which means no form.
- Glass, rubber and plastics are typical examples of amorphous solids.
- Amorphous solids soften over a range of temperatures and can be moulded and blown into various shapes. On heating they become crystalline at some temperature.
- Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation.
- Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called pseudo solids or super cooled liquids.
- Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.
- Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.



Two-dimensional structure of (a) quartz and (b) quartz glass

➤ Classification of Crystalline Solids

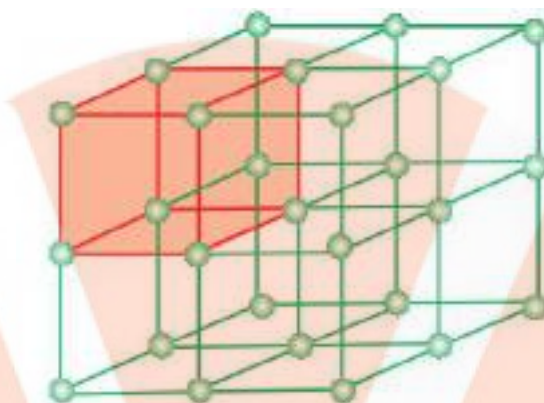
- All the metallic elements like iron, copper and silver; non – metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene form crystalline solids.
- Crystalline solids can be classified on the basis of nature of intermolecular forces operating in them into four categories viz., molecular, ionic, metallic and covalent solids.

Different Types of Solids

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular solids	Molecules	Dispersion or London forces Dipole-dipole interactions Hydrogen bonding	Ar, CCl ₄ H ₂ , I ₂ , CO ₂ HCl, SO ₂ H ₂ O (ice)	Soft	Insulator	Very low
(i) Non polar						
(ii) Polar						
(iii) Hydrogen bonded	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF ₂	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(2) Ionic solids						
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network solids	Atoms	Covalent bonding	SiO ₂ (quartz), SiC, C (diamond), AlN, C ₆₀ (buckminsterfullerene)	Hard	Insulators	Very high
				Soft	Conductor (exception)	

➤ Crystal Lattices and Unit Cells

- A regular three-dimensional arrangement of points in space is called a crystal lattice.
 - There are only 14 possible three-dimensional lattices. These are called Bravais Lattices
- The following are the characteristics of a crystal lattice:
- (a) Each point in a lattice is called a lattice point or lattice site.
 - (b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
 - (c) Lattice points are joined by straight lines to bring out the geometry of the lattice.
- Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.



A portion of a three-dimensional cubic lattice and its unit cell.

- A unit cell is characterised by:
 - (i) Its dimensions along the three edges, a , b and c .
 - (ii) Angles between the edges, α (between b and c) β (between a and c) and γ (between a and b). Thus, a unit cell is characterised by six parameters, a , b , c , α , β and γ .

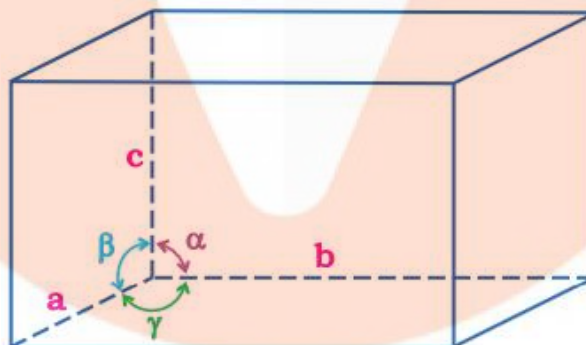


Illustration of parameters of a unit cell

➤ Primitive and Centred Unit Cells

- a. **Primitive Unit Cells** - When constituent particles are present only on the corner positions of a unit cell. In all, there are seven types of primitive unit cells.

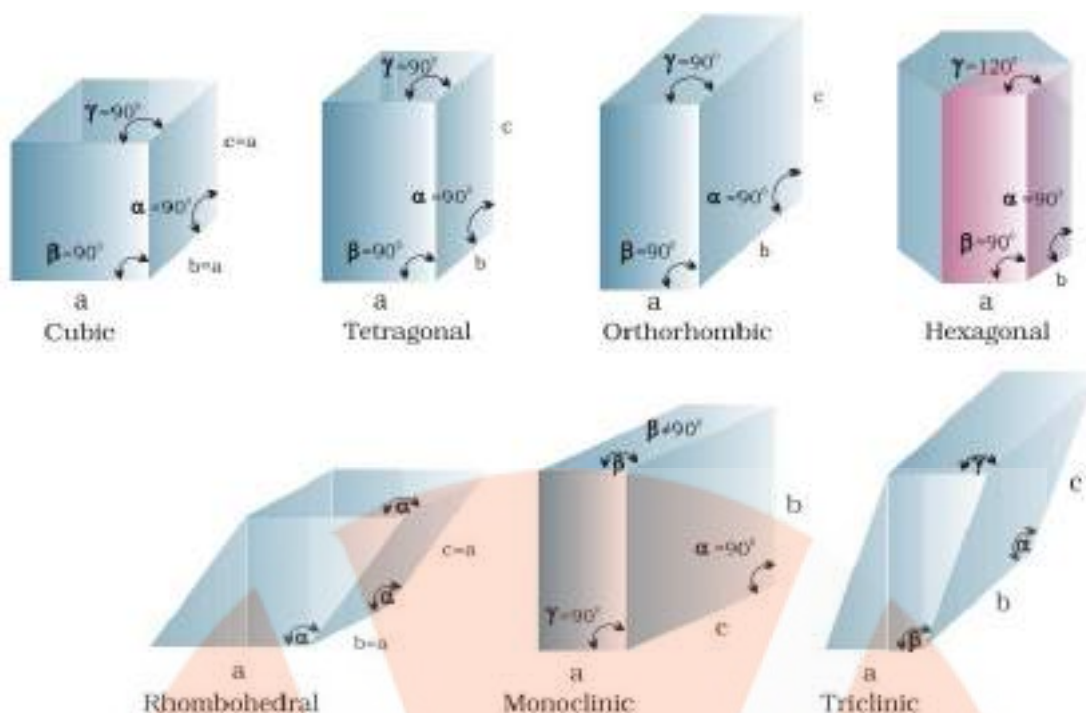


Fig. 1: Seven primitive unit cells in crystals

b. **Centred Unit Cells** - When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners.

Centred unit cells are of three types:

- Body-Centred Unit Cells:** Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.
- Face-Centred Unit Cells:** Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.
- End-Centred Unit Cells:** In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

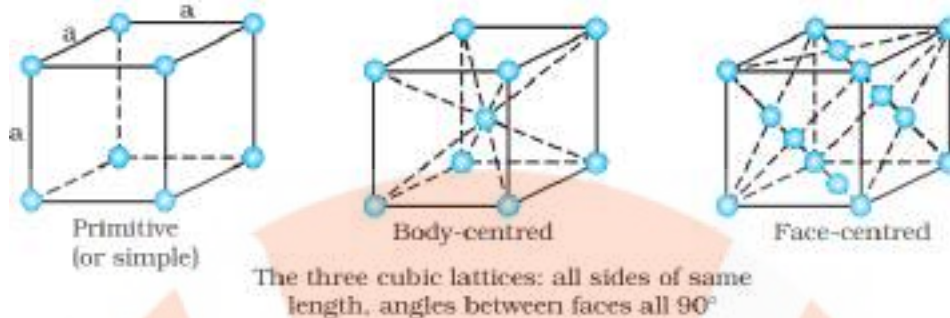
Seven primitive unit cells and their Possible Variations as Centred unit cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2 , TiO_2 , CaSO_4
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Graphite, ZnO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), HgS (cinnabar)

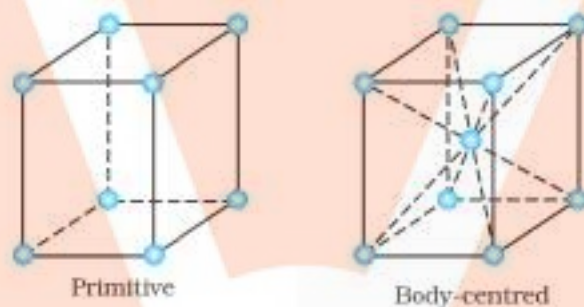
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3

➤ Unit Cells of 14 Types of Bravais Lattices

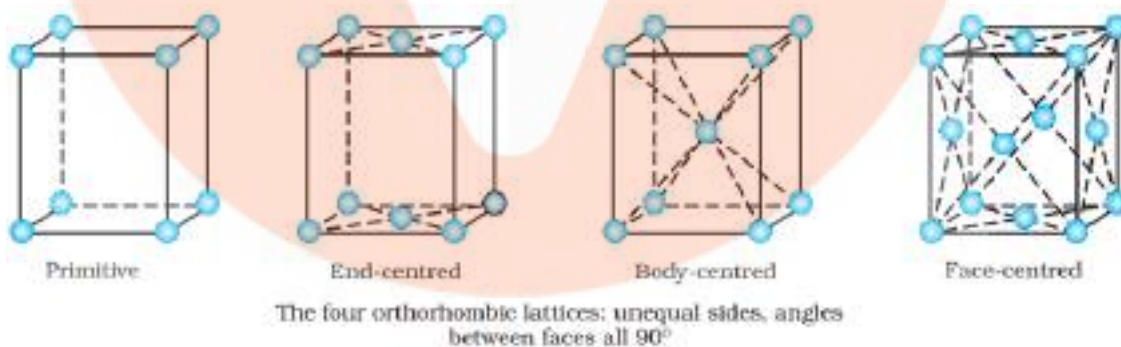
1. Cubic crystal system -



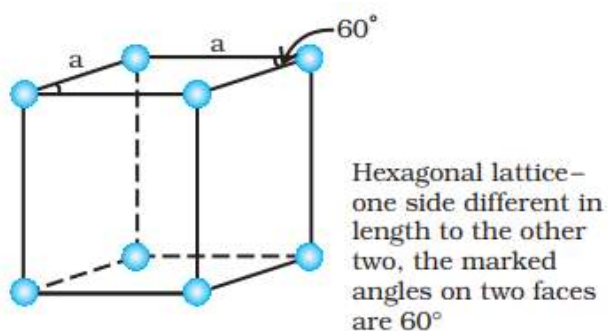
2. Tetragonal crystal system -



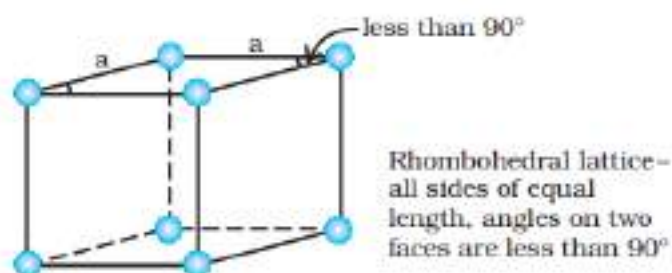
3. Orthorhombic crystal system -



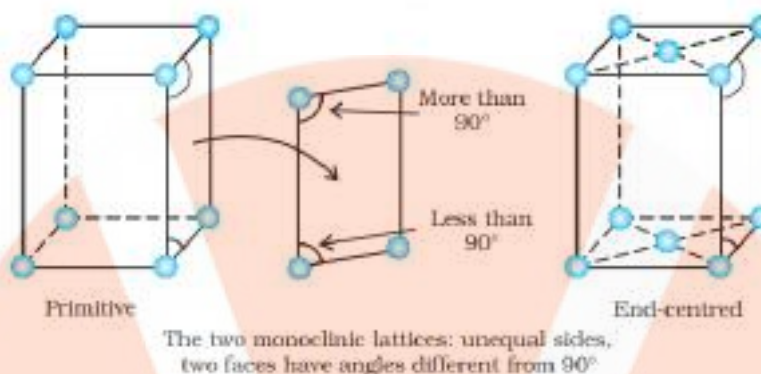
4. Hexagonal crystal system -



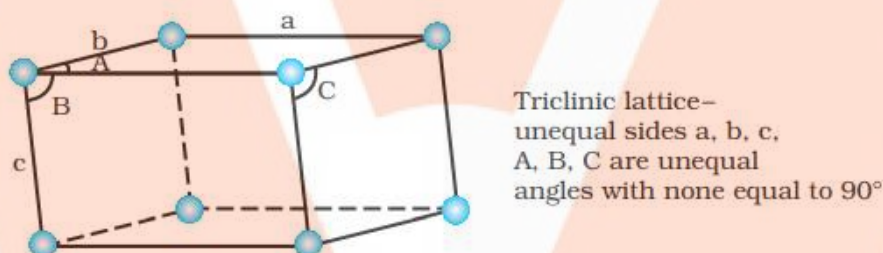
5. Rhombohedral or trigonal crystal system -



6. Monoclinic crystal system -



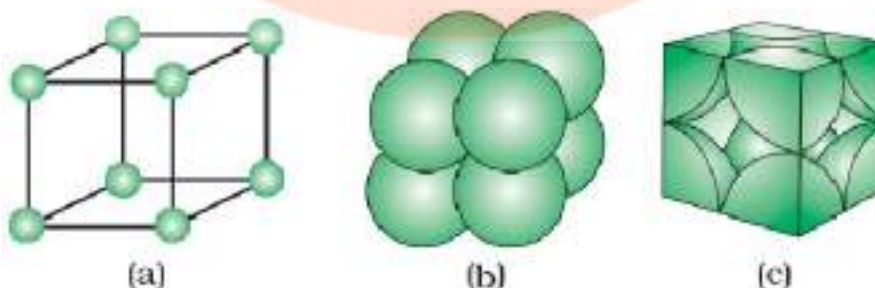
7. Triclinic crystal system -



➤ Number of Atoms in a Unit Cell

❖ Primitive Cubic Unit Cell

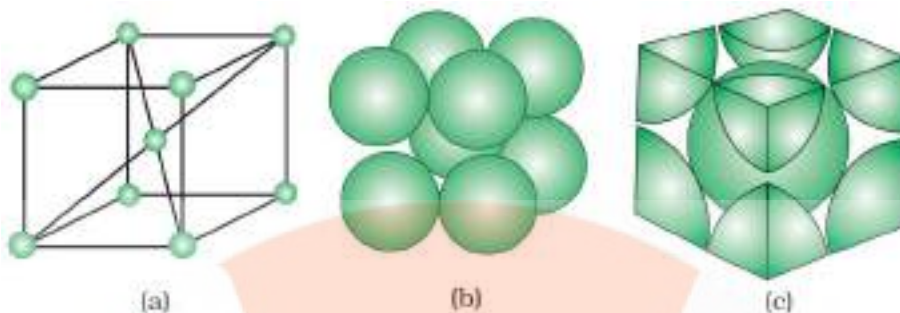
- Primitive cubic unit cell has atoms only at its corner.
- Each atom at a corner is shared between eight adjacent unit cells.
- Everyone shares $\frac{1}{8}$ of its part and there are 8 in total. That's why we can say 1 is the effective number of atoms.



A primitive cubic unit cell (a) open structure (b) space-filling structure
(c) actual portions of atoms belonging to one unit cell.

❖ Body Centred Cubic Unit Cell

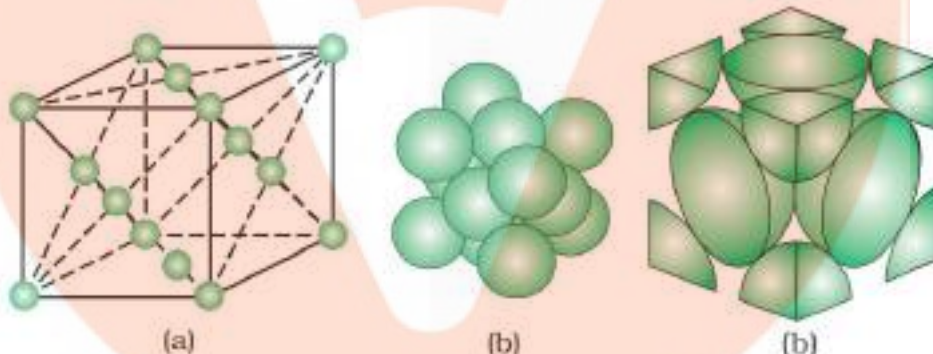
- A body-centred cubic (bcc) unit cell has an atom at each of its corners and also one atom at its body centre.
- $8 \text{ corners} \times \frac{1}{8} \text{ per corner atom} = 1 \text{ atom}$
- $1 \text{ body centre atom} = 1 \times 1 = 1 \text{ atom}$
- Total number of atoms per unit cell = 2 atoms



A body-centred cubic unit cell (a) open structure (b) space filling structure
(c) actual portions of atoms belonging to one unit cell.

❖ Face Centred Cubic Unit Cell

- A face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube.
- $8 \text{ corners} \times \frac{1}{8} \text{ per corner atom} = 1 \text{ atom}$
- $6 \text{ face centres} \times \frac{1}{2} \text{ per face centre atom} = 6 \times 0.5 = 3 \text{ atom}$
- Total number of atoms per unit cell = 4 atoms



A face-centred cubic unit cell (a) open structure (b) space filling structure
(c) actual portions of atoms belonging to one unit cell.

➤ Close Packed Structures

(a) Close Packing in One Dimension

- Each sphere is in contact with two of its neighbours.
- Number of nearest neighbours of a particle is called its coordination number.
- In one dimensional close packed arrangement, the coordination number is 2.



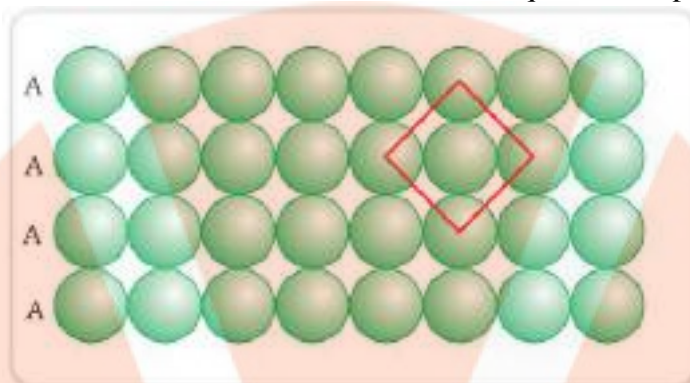
Close packing of spheres in one dimension

(b) Close Packing in Two Dimensions

Structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways -

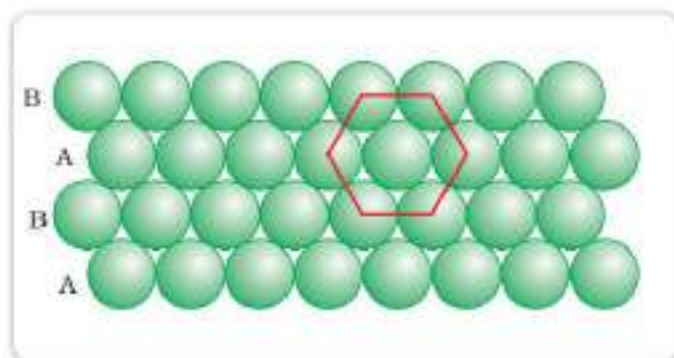
(i) Square close packing in two dimensions (AAAA) -

- Second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row.
- The spheres of the two rows are aligned horizontally as well as vertically.
- If the first row is termed as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type. Similarly, we may place more rows to obtain AAAA type of arrangement.
- Coordination no. 4, named as two-dimensional square close packing.



(ii) Hexagonal close packing of spheres in two dimensions (ABAB) -

- The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row.
- If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type.
- When the third row is placed adjacent to the second in a staggered manner, its spheres are aligned with those of the first layer.
- Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type).
- Hence this arrangement is of ABAB type.
- In this arrangement there is less free space and this packing is more efficient than the square close packing.
- Coordination no 6, named as two-dimensional hexagonal close packing.

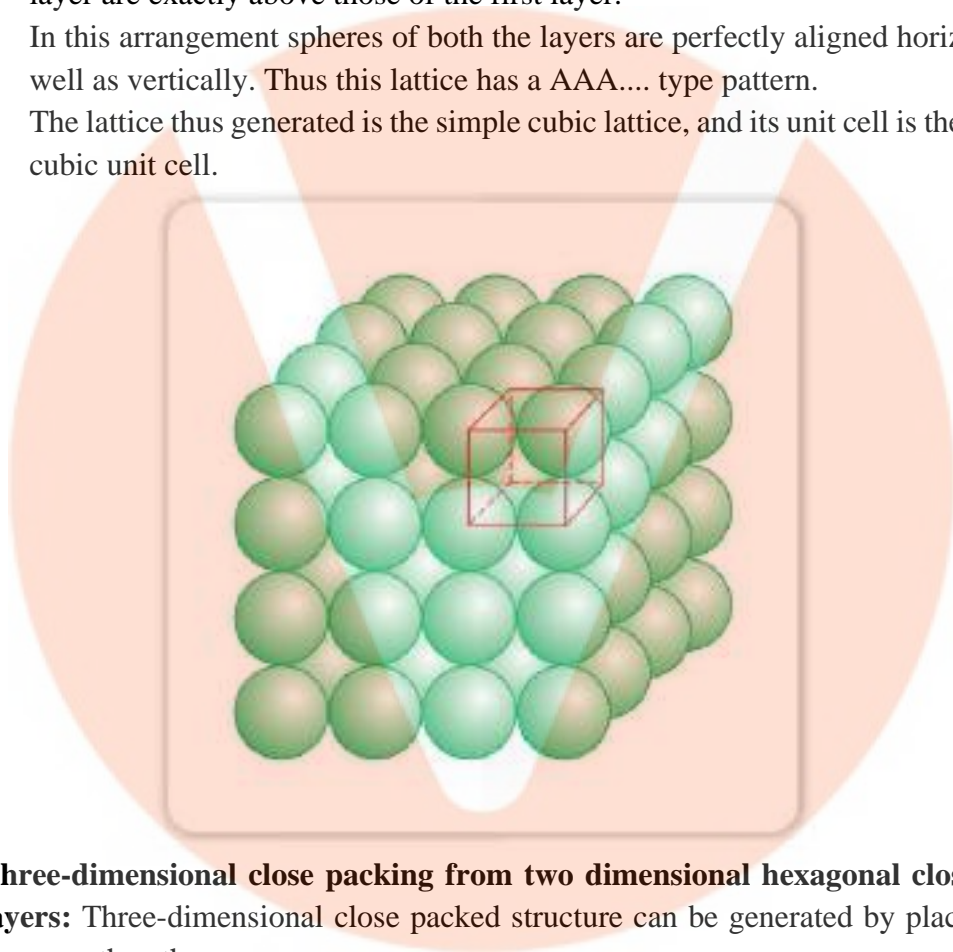


(c) Close Packing in Three Dimensions

- All real structures are three-dimensional structures.
- Can be obtained by stacking two dimensional layers one above the other.

(i) Three-dimensional close packing from two dimensional square close-packed layers (AAA... type)

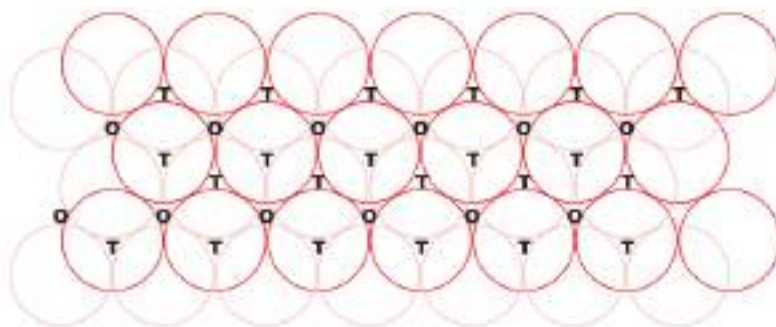
- Three-dimensional close packing from two dimensional square close-packed layers.
- While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other.
- The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer.
- In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically. Thus this lattice has a AAA.... type pattern.
- The lattice thus generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell.



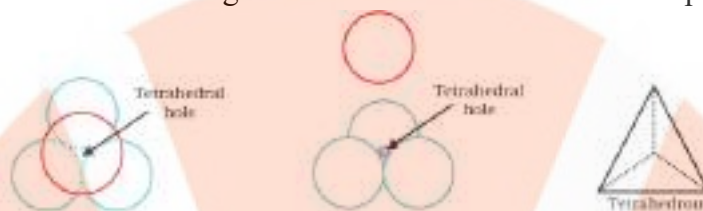
(ii) Three-dimensional close packing from two dimensional hexagonal close packed layers: Three-dimensional close packed structure can be generated by placing layers one over the other.

(a) Placing the second layer over the first layer.

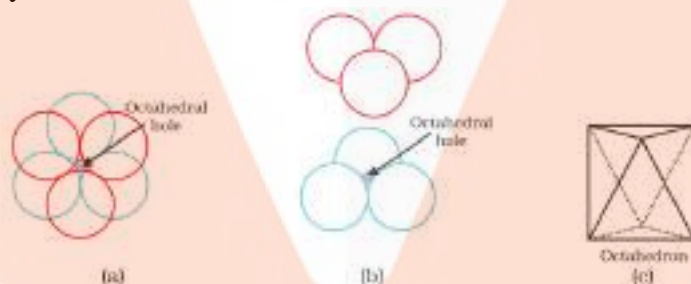
- A two-dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer.
- Since the spheres of the two layers are aligned differently, we call the second layer as B.
- It can be observed from fig. that not all the triangular voids of the first layer are covered by the spheres of the second layer.



- Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called tetrahedral voids because a tetrahedron is formed when the centres of these four spheres are joined. Have been marked as 'T' in Fig. One such void has been shown separately -



- At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap.
- One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O' in above fig. Such voids are surrounded by six spheres and are called octahedral voids. One such void has been shown separately -



- The number of these two types of voids depend upon the number of close packed spheres. Let the number of close packed spheres be N , then:

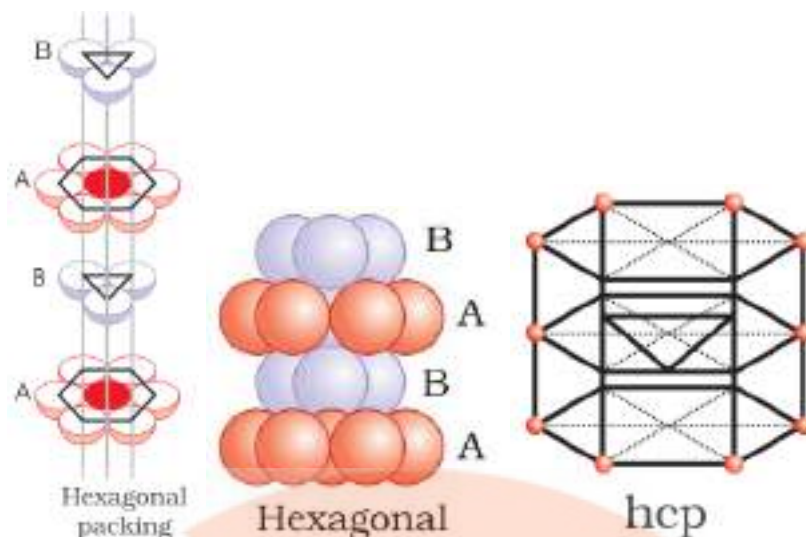
The number of octahedral voids generated = N

The number of tetrahedral voids generated = $2N$

(b) **Placing the third layer over the second layer:** When the third layer is placed over the second, there are two possibilities:

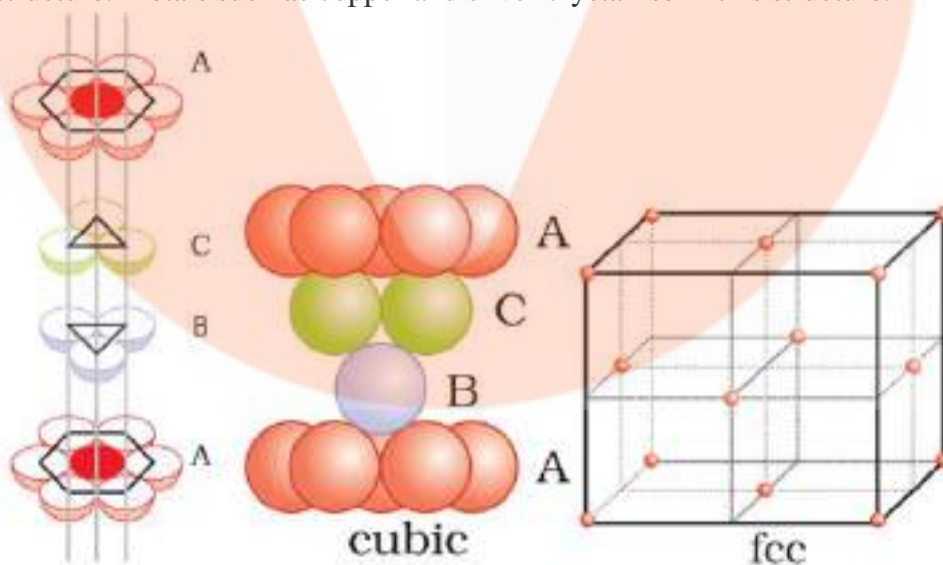
(i) **Covering Tetrahedral Voids:**

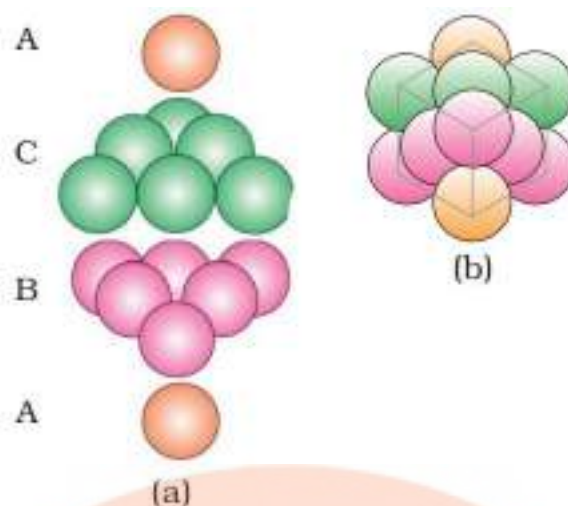
- Tetrahedral voids of the second layer may be covered by the spheres of the third layer. Spheres of the third layer are exactly aligned with those of the first layer.
- Thus, the pattern of spheres is repeated in alternate layers.
- This pattern is often written as ABAB pattern.
- This structure is called hexagonal close packed (hcp) structure.
- This sort of arrangement of atoms is found in many metals like magnesium and zinc.



(ii) Covering Octahedral Voids:

- The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids.
- When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer.
- This arrangement is called 'C' type. Only when the fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs. 1.18 and 1.19.
- This pattern of layers is often written as ABCABC
- This structure is called cubic close packed (ccp) or face-centred cubic (fcc) structure. Metals such as copper and silver crystallise in this structure.





- Both these types of close packing are highly efficient and 74% space in the crystal is filled.
- In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

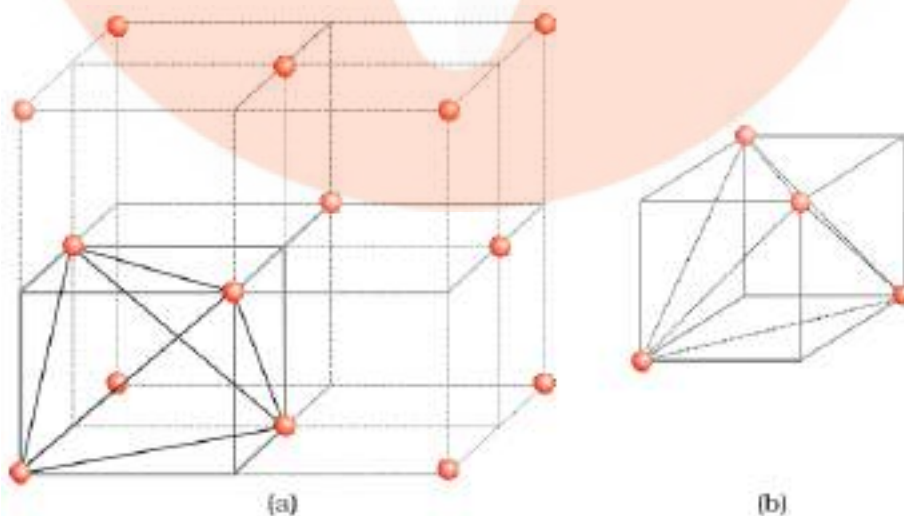
➤ **Formula of a Compound and Number of Voids Filled**

- In ionic solids, the bigger ions (usually anions) form the close packed structure and the smaller ions (usually cations) occupy the voids.
- If the latter ion is small enough then tetrahedral voids are occupied, if bigger, then octahedral voids.
- Not all octahedral or tetrahedral voids are occupied.
- In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound.

➤ **Locating Tetrahedral and Octahedral Voids in ccp arrangement**

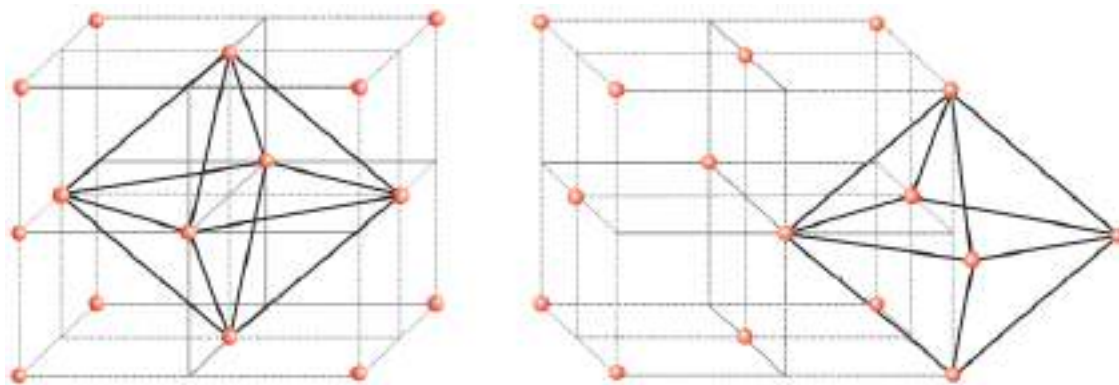
(a) Tetrahedral Voids

- If a cube is divided into 8 equal parts, then each small part will have one tetrahedral void as shown -



(b) Octahedral Voids

- These are present at all edge centres ($\frac{1}{4}^{\text{th}}$ belongs to each unit cell) and at the body center.



➤ Packing Efficiency

Packing efficiency is the percentage of total space filled by the particles.

Structure	Relation between radius and edge length (r & a)	Volume of the atom (v)	Packing fraction	Packing efficiency
Simple cubic	$r = \frac{a}{2}$	$\frac{4}{3} \pi \left(\frac{a}{2}\right)^3$	$\frac{\pi}{6} = 0.52$	52 %
Face-centred cubic	$r = \frac{a}{2\sqrt{2}}$	$\frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}}\right)^3$	$\frac{\sqrt{2}\pi}{6} = 0.74$	74 %
Body-centred cubic	$r = \frac{\sqrt{3}a}{4}$	$\frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4}\right)^3$	$\frac{\sqrt{3}\pi}{8} = 0.68$	68 %

➤ Calculations Involving Unit Cell Dimensions

- In case of cubic crystal:

$$d = \frac{zM}{a^3 N_A}$$

Z = atomic number, M = Molecular Mass, a = edge length. N_A = Avogadro number, d = density

- Edge length of a unit cell of a cubic crystal determined by X-ray diffraction.
- The density of the unit cell is the same as the density of the substance.

➤ Imperfections in Solids

- The defects are basically irregularities in the arrangement of constituent particles.
- Defects are of two types -
 - Point defects - the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance
 - Line defects - the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects.

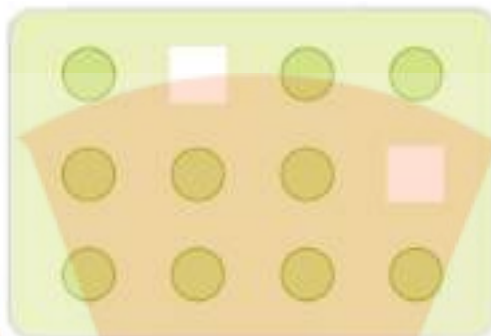
➤ **Types of Point Defects**

(a) Stoichiometric Defects -

- These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects.
- These are of two types, vacancy defects and interstitial defects.

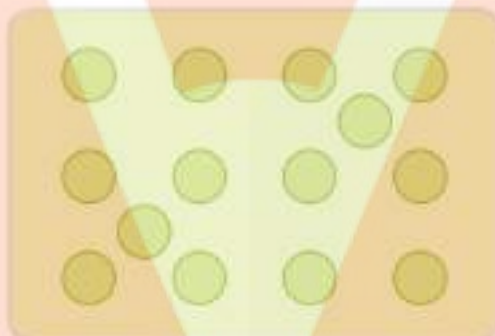
(i) Vacancy Defect:

- Lattice sites are vacant, the crystal is said to have vacancy defects.
- Results in a decrease in density of the substance.
- Can develop when a substance is heated.



(ii) Interstitial Defect -

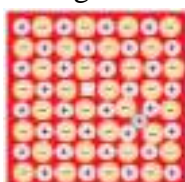
- Constituent particles (atoms or molecules) occupy an interstitial site.
- Increases the density of the substance.



Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. They show Frenkel and Schottky defect instead of simple vacancy and interstitial defects

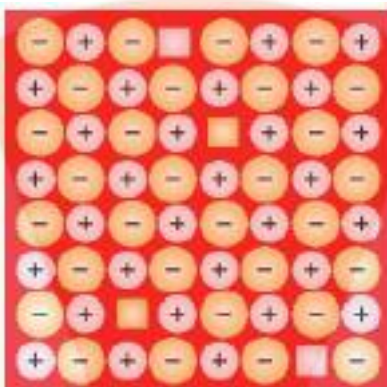
(iii) Frenkel Defect:

- Shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site. It creates a vacancy defect at its original site and an interstitial defect at its new location.
- Also called dislocation defect.
- Does not change the density of the solid.
- Shown by ionic substances in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to the small size of Zn^{2+} and Ag^+ ions.



(iv) Schottky Defect:

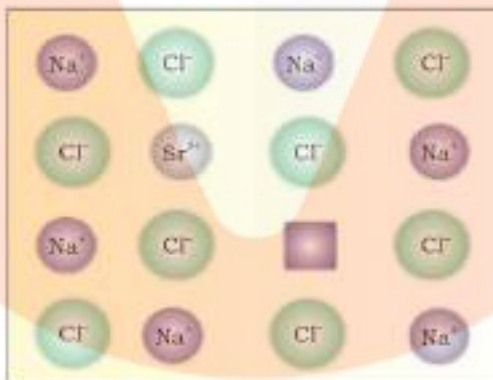
- A vacancy defect in ionic solids.
- In order to maintain electrical neutrality, the number of missing cations and anions are equal.
- Decreases the density of the substance.
- Number of such defects in ionic solids is quite significant.
- In NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions.
- Shown by ionic substances in which the cation and anion are of almost similar sizes. Example: NaCl, KCl, CsCl and AgBr.
- AgBr shows both, Frenkel as well as Schottky defects.



Schottky defects

(b) Impurity Defects

- If molten NaCl containing a little amount of SrCl_2 is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} .



Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}

- Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions.
- Another example is the solid solution of CdCl_2 and AgCl .

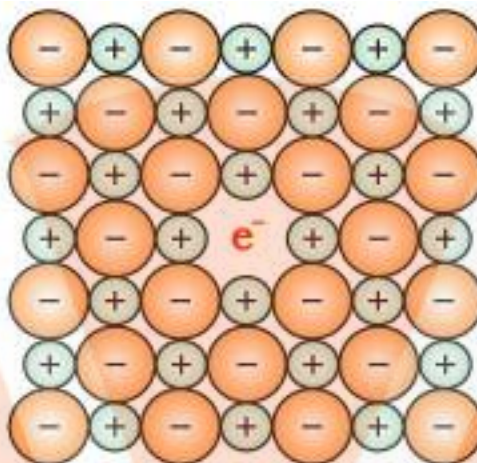
(c) Non-Stoichiometric Defects-

A large number of nonstoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types:

(i) Metal Excess Defect -

(a) Metal excess defect due to anionic vacancies:

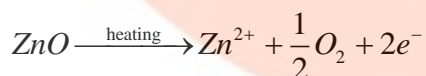
- Alkali halides like NaCl and KCl show this type of defect.
- When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electrons by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites. As a result the crystal now has an excess of sodium.



- The anionic sites occupied by unpaired electrons are called F-centres (from the German word Farbenzenter for colour centre). They impart yellow colour to the crystals of NaCl.
- The colour results from excitation of these electrons when they absorb energy from the visible light falling on the crystals.
- excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac)

(b) Metal excess defect due to the presence of extra cations at interstitial sites:

- Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



- Now there is excess of zinc in the crystal and its formula becomes Zn_{1+x}O .
- The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) Metal Deficiency Defect

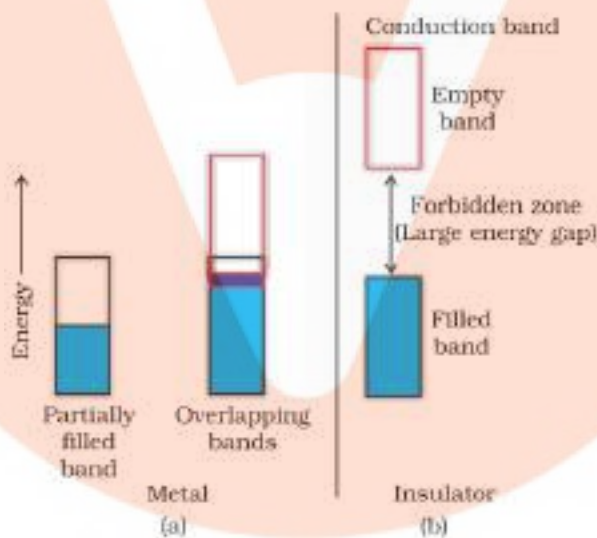
- There are many solids which contain less amount of the metal as compared to the stoichiometric proportion.
- A typical example of this type is FeO which is mostly found with a composition of $\text{Fe}_{0.95}\text{O}$. It may actually range from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$.
- In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of the required number of Fe^{3+} ions.

➤ **Electrical Properties**

- (i) **Conductors** The solids with conductivities ranging between 10^4 to $10^7 \text{ ohm}^{-1}\text{m}^{-1}$ are called conductors. Metals have conductivities in the order of $10^7 \text{ ohm}^{-1}\text{m}^{-1}$ are good conductors.
- (ii) **Insulators**: These are the solids with very low conductivities ranging between 10^{-20} to $10^{-10} \text{ ohm}^{-1}\text{m}^{-1}$.
- (iii) **Semiconductors** : These are the solids with conductivities in the intermediate range from 10^{-6} to $10^4 \text{ ohm}^{-1}\text{m}^{-1}$.

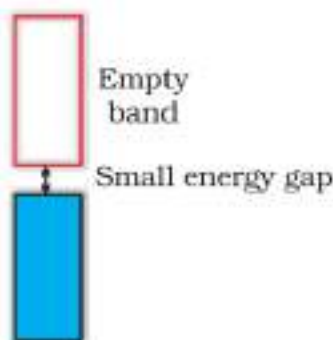
➤ **Conduction of Electricity in Metals**

- Metals conduct electricity in solid as well as molten state.
- Conductivity of metals depends upon the number of valence electrons available per atom.
- The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a band. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity
- If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity and it behaves as an insulator



➤ **Conduction of Electricity in Semiconductors**

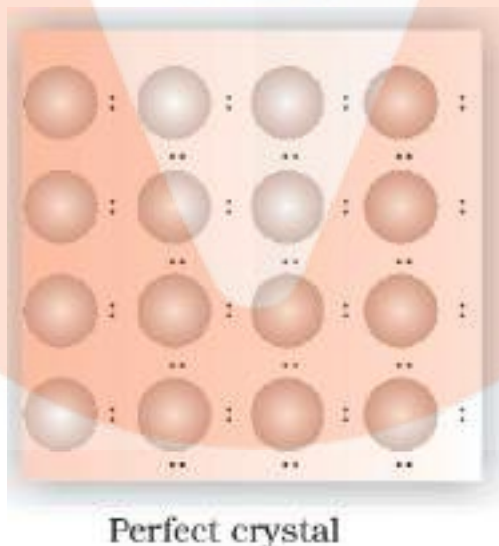
- In the case of semiconductors, the gap between the valence band and conduction band is small. Thus, some electrons may jump to the conduction band and show some conductivity.



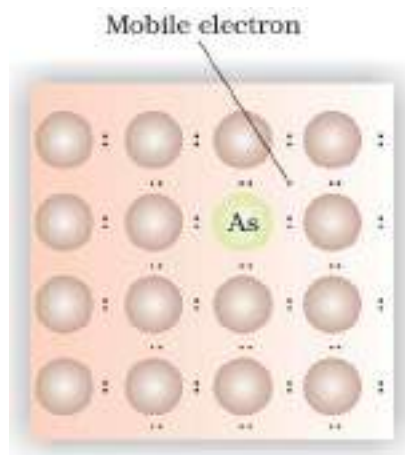
- Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band.
- Substances like silicon and germanium show this type of behaviour and are called intrinsic semiconductors.
- Conductivity of these intrinsic semiconductors is too low to be of practical use.
- Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called doping.
- Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce electronic defects in them.

(a) Electron – rich impurities

- Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours.



- When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal.

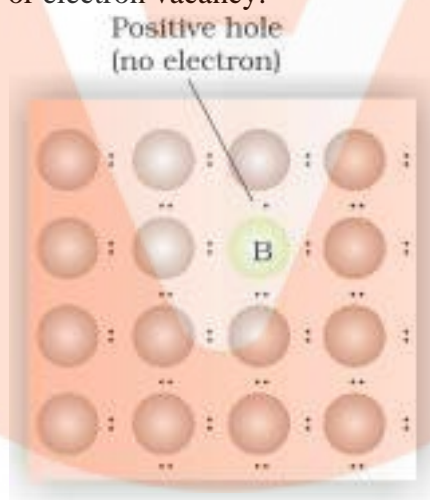


n-type

- Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms.
- The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium).
- Here the increase in conductivity is due to the negatively charged electron. Hence, silicon doped with electron-rich impurity is called n-type semiconductor.

(b) Electron – deficient impurities

- Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. Place where the fourth valence electron is missing is called electron hole or electron vacancy.



p-type

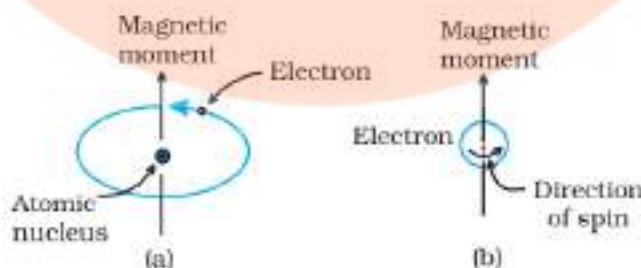
- An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it.
- Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate.
- This type of semiconductors are called p-type semiconductors.

➤ Applications of n-type and p-type semiconductors

- Various combinations of n-type and p-type semiconductors are used for making electronic components.
- Diode is a combination of n-type and p-type semiconductors and is used as a rectifier.
- Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. npn and pnp type of transistors are used to detect or amplify radio or audio signals.
- The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.
- Germanium and silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si.
- Typical compounds of groups 13 – 15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices.
- ZnS, CdS, CdSe and HgTe are examples of groups 12 – 16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.
- It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO₂ and ReO₃ behave like metals. Rhenium oxide, ReO₃ is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO₂, VO₃ and TiO₃ show metallic or insulating properties depending on temperature.

➤ Magnetic Properties

- Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons.
- Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions -
(i) its orbital motion around the nucleus
(ii) its spin around its own axis



- Electrons being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it.
- Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton, μ_B . It is equal to $9.27 \times 10^{-24} \text{ A m}^2$. On the basis of their magnetic properties, substances can be classified into five categories:

(i) Paramagnetism:

- weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field.-
- Paramagnetism is due to the presence of one or more unpaired electrons which are attracted by the magnetic field. O^2 , Cu^{+2} , Fe^{3+} , Cr^{3+} are some examples of such substances.

(ii) Diamagnetism:

- Weakly repelled by a magnetic field. H_2O , $NaCl$ and C_6H_6 are some examples of such substances. They are weakly magnetised in a magnetic field in the opposite direction.
- Shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character

(iii) Ferromagnetism:

- Substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances.
- These substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains.
- Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced.
- This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.



Schematic alignment of magnetic moments in ferromagnetic substance

(iv) Antiferromagnetism:

- Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment



Schematic alignment of magnetic moments in antiferromagnetic substance

(v) Ferrimagnetism:

- Observed when the magnetic moments of the domains in the substance are aligned in parallel and antiparallel directions in unequal numbers.
- Weakly attracted by magnetic fields as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.



Schematic alignment of magnetic moments in ferrimagnetic substance

Solutions

Introduction

- Solutions are homogeneous mixtures of two or more than two components.
- The component that is present in the largest quantity is known as solvent.
- One or more components present in the solution other than solvent are called solutes.
- FACT - 1 part per million (ppm) of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentrations of fluoride ions can be poisonous (for example, sodium fluoride is used in rat poison).

Types of Solutions

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen 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 hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

Expressing Concentration of Solutions

1.

$$\% \text{ by wt.} = \frac{\text{Wt. of the solute (in g)}}{\text{Wt. of the solution (in g)}} \times 100$$

2.

$$\% \text{ by wt./vol} = \frac{\text{Wt. of solute (in g)}}{\text{Vol. of solution (in cc)}} \times 100$$

3.

$$\% \text{ by volume} = \frac{\text{Vol. of solute (in cc)}}{\text{Vol. of solution (in cc)}} \times 100$$

4.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. The concentration of pollutants in water or atmosphere is often expressed in terms of $\mu\text{g mL}^{-1}$ or ppm.

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

5.

In a given solution sum of all the mole fractions is unity, i.e.,

$$X_1 + X_2 + X_3 + \dots = 1$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

6.

$$\text{Molarity (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

7.

Solubility

- Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- It depends upon the nature of solute and solvent as well as temperature and pressure.
- A solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say 'like dissolves like'.
- The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent.
- An unsaturated solution is one in which more solute can be dissolved at the same temperature.

Type of solution	Effect of temperature	Effect of pressure
Solid in Liquid	<ul style="list-style-type: none"> • If $\Delta H > 0$, solubility increases with temperature. • If $\Delta H < 0$, solubility decreases with temperature. 	no significant effect
Gas in a Liquid	Solubility of gases in liquids decreases with rise in temperature	Solubility \propto Pressure (Henry's law)

❖ **Henry's Law:** $p = K_H \cdot X$

- K_H : Henry's law constant.
- Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
- K_H values increase with increase of temperature.

Table 2.2: Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	K_H /kbar	Gas	Temperature/K	K_H /kbar
He	293	144.97	Argon	298	40.3
H ₂	293	69.16	CO ₂	298	1.67
N ₂	293	76.48	Formaldehyde	298	1.83×10^{-4}
N ₂	303	88.84	Methane	298	0.413
O ₂	293	34.86	Vinyl chloride	298	0.611
O ₂	303	46.82			

❖ **Applications of Henry's law:**

- To increase the solubility of CO₂ in soft drinks and soda water.
- To avoid **bends**, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- At high altitudes the partial pressure of oxygen is less which leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers which causes climbers to become weak and unable to think clearly, symptoms of a condition known as **anoxia**.

Vapour Pressure of Liquid Solutions

According to Raoult's law, for solution containing volatile components

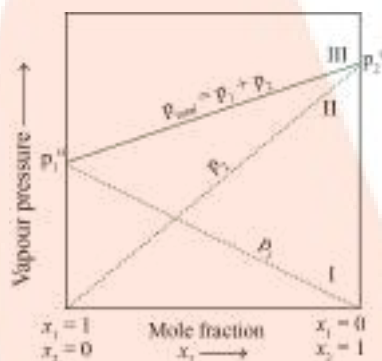
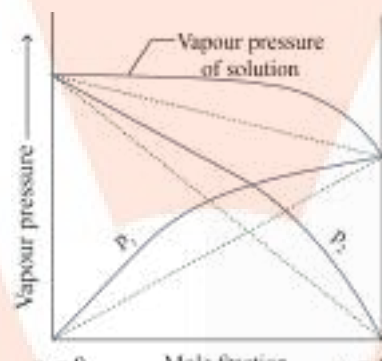
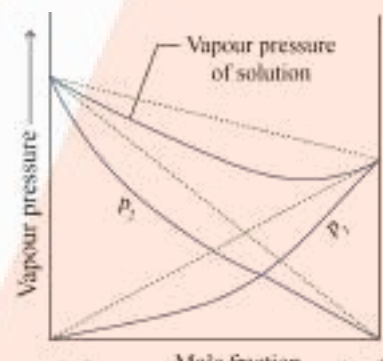
$$\text{A and B, } p_A = x_A p_A^o \text{ and } p_B = x_B p_B^o$$

$$P_{\text{Total}} = p_A + p_B = x_A p_A^o + x_B p_B^o$$

$$= (1 - x_B) p_A^o + x_B p_B^o = (p_B^o - p_A^o) x_B + p_A^o$$

- Raoult law is a special case of Henry's law
- According to Dalton's law of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as: $p_{\text{total}} = p_1 + p_2$

Ideal and Non-ideal Solutions

Ideal Solution	Non-ideal solution	
Follows Raoult's law ($P_T = P_A + P_B$)	Positive Deviation from Raoult's law ($P_T > P_A + P_B$)	Negative Deviation from Raoult's law ($P_T < P_A + P_B$)
$\Delta_{\text{mix}}H = 0, \Delta_{\text{mix}}V = 0$	$\Delta_{\text{mix}}H > 0, \Delta_{\text{mix}}V > 0$	$\Delta_{\text{mix}}H < 0, \Delta_{\text{mix}}V < 0$
Intermolecular attractive forces: A-A and B-B = A-B	Intermolecular attractive forces: A-A and B-B > A-B	Intermolecular attractive forces: A-A and B-B < A-B
Examples: n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene.	Examples: ethanol and acetone, carbon disulphide and acetone, ethanol-water mixture	Example: chloroform and acetone, Nitric acid and water, phenol and aniline.
		
No azeotrope formed.	Form minimum boiling azeotrope at a specific composition. Azeotropic composition for ethanol-water mixture: approximately 95% by volume of ethanol.	Form maximum boiling azeotrope at a specific composition. Azeotropic composition for nitric acid-water mixture: 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

Colligative Properties

- Colligative: from Latin: co means together, ligare means to bind.
- Properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution.

Relative Lowering of Vapour Pressure

- Relative lowering of vapour pressure and is equal to the mole fraction of the solute.

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

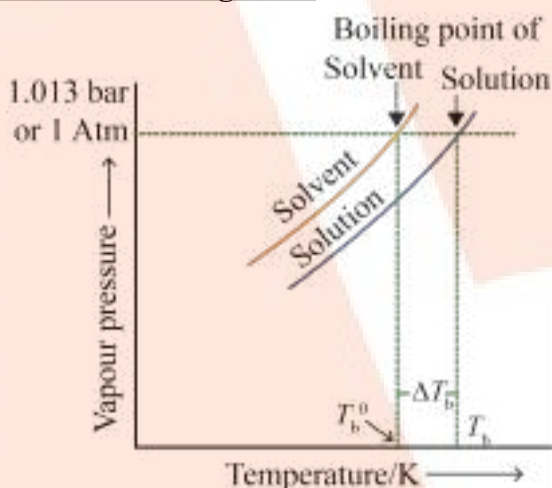
Here n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution.

- For dilute solutions:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute respectively.

Elevation of Boiling Point

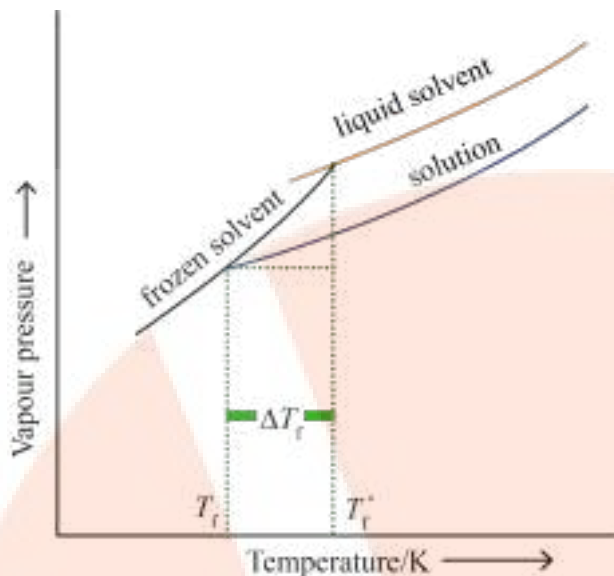


- ❖ $\Delta T_b = K_b m$
 - ΔT_b is known as the elevation of boiling point.
 - K_b is Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant). The unit of K_b is $K \text{ kg mol}^{-1}$.

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{\text{vap}}H}$$

- ❖
 - R = Gas constant, M = Molar mass of solvent
 - T_b = boiling point of pure solvent
 - $\Delta_{\text{vap}}H$ = enthalpy for the vapourisation.

Depression of Freezing Point



$$\Delta T_f = K_f m$$

- ΔT_f is known as the depression of freezing point.
- K_b is Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant. The unit of K_f is $K \text{ kg mol}^{-1}$.

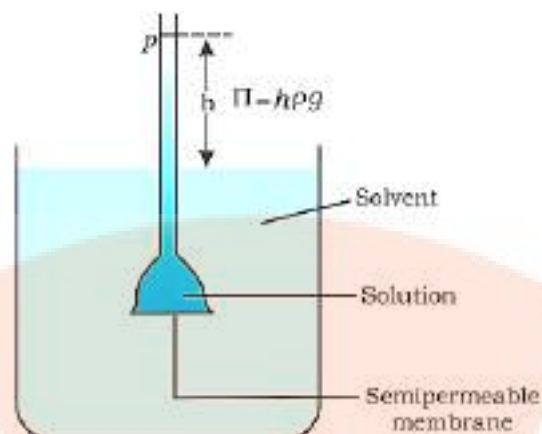
$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{\text{fus}} H}$$

- R = Gas constant, M = Molar mass of solvent
- T_f = freezing point of pure solvent
- $\Delta_{\text{fus}} H$ = enthalpy for the vaporisation

Table 2.3: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

Solvent	b. p./K	$K_b/K \text{ kg mol}^{-1}$	f. p./K	$K_f/K \text{ kg mol}^{-1}$
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.79
Carbon tetrachloride	350.0	5.03	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

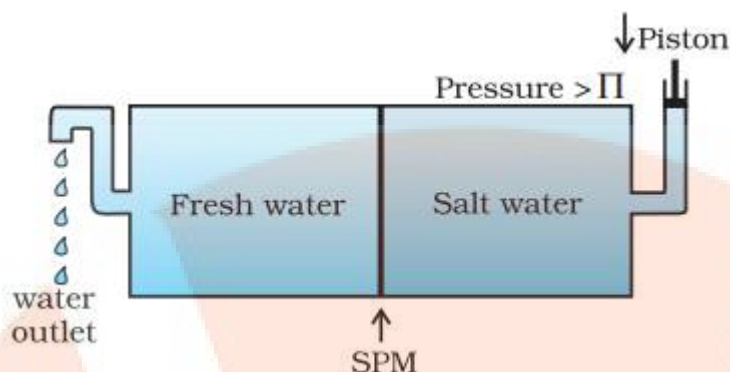
Osmosis and Osmotic Pressure



- ❖ **Semipermeable membrane:** It allows small molecules (solvent generally) to pass through. Example - pig's bladder, parchment, cellophane (synthetic).
- ❖ The process of flow of the solvent from solution of low concentration to a solution of high concentration is called osmosis.
- ❖ The pressure that just stops the flow of solvent is called osmotic pressure of the solution.
- ❖ $\pi = C R T$
 - π = Osmotic pressure, C = Molar concentration, R = Gas constant, T = Absolute temperature.
- ❖ Measurement of osmotic pressure is widely used to determine molar masses of proteins, polymers and other macromolecules. As compared to other colligative properties, its magnitude is large even for very dilute solutions.
- ❖ For two different solutions-
 - if $\pi_A = \pi_B$, solution is isotonic
 - If $\pi_A < \pi_B$, A is hypotonic wrt. B and B is hypertonic wrt. A.
- ❖ Osmosis in daily life -
 - raw mangoes shrivel when pickled in brine (salt water)
 - wilted flowers revive when placed in freshwater
 - blood cells collapse when suspended in saline water
 - When placed in water containing less than 0.9% (mass/ volume) salt, blood cells swell due to flow of water in them by osmosis. The resulting puffiness or swelling is called edema.
 - The preservation of meat by salting and of fruits by adding sugar. A Bacterium on salted meat or candied fruit loses water, shrivels and dies.
 - Water movement from soil into plant roots and subsequently into the upper portion of the plant is partly due to osmosis.

❖ **Reverse Osmosis:**

- Pure solvent flows out of the solution through the semipermeable membrane if a pressure larger than the osmotic pressure is applied to the solution side. This phenomenon is called reverse osmosis.



- Reverse osmosis is used in desalination of seawater. Cellulose acetate is used as SPM which is permeable to water but impermeable to impurities and ions present in seawater.

Abnormal Molar Masses

- ❖ i = van't Hoff factor

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

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

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

- ❖ In the case of association, the value of i is less than unity while for dissociation it is greater than unity.
- ❖ Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^0 - p_1}{p_1^0} = i \cdot \frac{n_2}{n_1}$$

Elevation of Boiling point, $\Delta T_b = i K_b m$

Depression of Freezing point, $\Delta T_f = i K_f m$

Osmotic pressure of solution, $\Pi = i n_2 R T / V$

- ❖ Molecules of ethanoic acid (acetic acid) dimer in benzene due to hydrogen bonding. This normally happens in solvents of low dielectric constant.

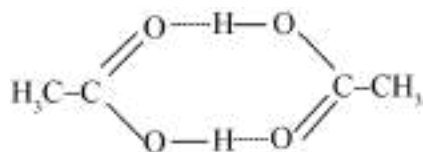


Table 2.4: Values of van't Hoff factor, i , at Various Concentrations for NaCl, KCl, MgSO_4 and K_2SO_4 .

Salt	*Values of i			van't Hoff Factor i for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
MgSO_4	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

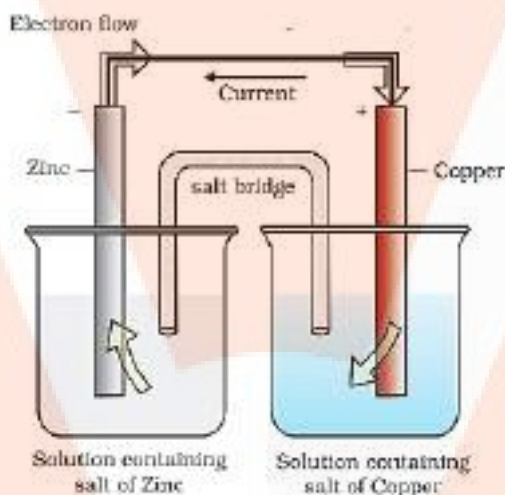
Electrochemistry

Electrochemical Cells

- **Galvanic Cell or voltaic cell:** Electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.
- **Electrolytic cell:** A device for using electrical energy to carry non-spontaneous chemical reactions

Galvanic Cells

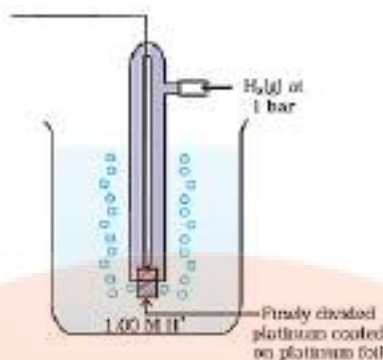
- It is made up of two half cells – oxidation half (anode is a part of this half) and reduction half (cathode is a part of this half)
- Daniel cell is a common example -



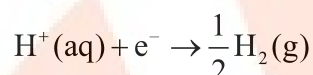
- A potential difference that develops between the electrode and the electrolyte which is called electrode potential.
- When the concentration of all the species involved in a half-cell is unity then the electrode potential is known as standard electrode potential.
- According to IUPAC convention, standard reduction potentials are now called standard electrode potentials.
- The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. We keep the anode on the left and the cathode on the right while representing the galvanic cell.

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

Standard Hydrogen Electrode (SHE)



- Represented by $\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq})$



- It is assigned a zero potential at all temperatures.
- The pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.
- The potential of other half-cells is measured using SHE.
 1. A negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
 2. A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

Electrochemical Series

- Arrangement of different elements in increasing order of SRP is known as electrochemical series or activity series.
- The table below shows reverse electrochemical series:

Reaction (Oxidised form + ne ⁻)	→ Reduced form	E°/V
$\text{F}_2(\text{g}) + 2\text{e}^-$	$\rightarrow 2\text{F}^-$	2.87
$\text{Co}^{3+} + \text{e}^-$	$\rightarrow \text{Co}^{2+}$	1.81
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	$\rightarrow 2\text{H}_2\text{O}$	1.78
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^-$	$\rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{Au}^{3+} + 3\text{e}^-$	$\rightarrow \text{Au(s)}$	1.40
$\text{Cl}_2(\text{g}) + 2\text{e}^-$	$\rightarrow 2\text{Cl}^-$	1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^-$	$\rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$	$\rightarrow 2\text{H}_2\text{O}$	1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^-$	$\rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{Br}_2 + 2\text{e}^-$	$\rightarrow 2\text{Br}^-$	1.09
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^-$	$\rightarrow \text{NO(g)} + 2\text{H}_2\text{O}$	0.97
$2\text{Hg}^{2+} + 2\text{e}^-$	$\rightarrow \text{Hg}_2^{2+}$	0.92
$\text{Ag}^+ + \text{e}^-$	$\rightarrow \text{Ag(s)}$	0.80
$\text{Fe}^{3+} + \text{e}^-$	$\rightarrow \text{Fe}^{2+}$	0.77
$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^-$	$\rightarrow \text{H}_2\text{O}_2$	0.68
$\text{I}_2 + 2\text{e}^-$	$\rightarrow 2\text{I}^-$	0.54
$\text{Cu}^+ + \text{e}^-$	$\rightarrow \text{Cu(s)}$	0.52
$\text{Cu}^{2+} + 2\text{e}^-$	$\rightarrow \text{Cu(s)}$	0.34
$\text{AgCl(s)} + \text{e}^-$	$\rightarrow \text{Ag(s)} + \text{Cl}^-$	0.22
$\text{AgBr(s)} + \text{e}^-$	$\rightarrow \text{Ag(s)} + \text{Br}^-$	0.10
$2\text{H}^+ + 2\text{e}^-$	$\rightarrow \text{H}_2(\text{g})$	0.00

Decrease	$\text{Pb}^{2+} + 2\text{e}^-$	$\rightarrow \text{Pb(s)}$	-0.13	Decrease
	$\text{Sn}^{2+} + 2\text{e}^-$	$\rightarrow \text{Sn(s)}$	-0.14	
	$\text{Ni}^{2+} + 2\text{e}^-$	$\rightarrow \text{Ni(s)}$	-0.25	
	$\text{Fe}^{2+} + 2\text{e}^-$	$\rightarrow \text{Fe(s)}$	-0.44	
	$\text{Cr}^{3+} + 3\text{e}^-$	$\rightarrow \text{Cr(s)}$	-0.74	
	$\text{Zn}^{2+} + 2\text{e}^-$	$\rightarrow \text{Zn(s)}$	-0.76	
	$2\text{H}_2\text{O} + 2\text{e}^-$	$\rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83	
	$\text{Al}^{3+} + 3\text{e}^-$	$\rightarrow \text{Al(s)}$	-1.66	
	$\text{Mg}^{2+} + 2\text{e}^-$	$\rightarrow \text{Mg(s)}$	-2.36	
	$\text{Na}^+ + \text{e}^-$	$\rightarrow \text{Na(s)}$	-2.71	
	$\text{Ca}^{2+} + 2\text{e}^-$	$\rightarrow \text{Ca(s)}$	-2.87	
	$\text{K}^+ + \text{e}^-$	$\rightarrow \text{K(s)}$	-2.93	
	$\text{Li}^+ + \text{e}^-$	$\rightarrow \text{Li(s)}$	-3.05	Increase

Applications:

- Greater the reduction potential of a substance, strong is the oxidising agent.
- In ECS reactivity of metals decreases from top to bottom.
- In ECS reactivity of nonmetals decreases from top to bottom.
- More reactive metals/non-metals displace less reactive metals/non-metals in their solution.
- Metals above H_2 displaces H_2 from acids.

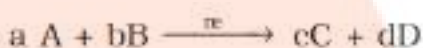
Nernst Equation

- For the electrode reaction: $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightarrow \text{M(s)}$

$$E_{(\text{M}^{n+}/\text{M})} = E_{(\text{M}^{n+}/\text{M})}^{\ominus} - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

R is gas constant, F is Faraday constant (96487 C mol^{-1}), T is temperature in kelvin and $[\text{M}^{n+}]$ is the concentration of the species.

- For a general electrochemical reaction of the type:



$$\begin{aligned} E_{(\text{cell})} &= E_{(\text{cell})}^{\ominus} - \frac{RT}{nF} \ln Q \\ &= E_{(\text{cell})}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \end{aligned}$$

- Equilibrium Constant from Nernst Equation:

$$E_{(\text{cell})}^{\ominus} = \frac{2.303RT}{nF} \log K_c$$

- Electrochemical Cell and Gibbs Energy of the Reaction:

$$\Delta_r G^{\ominus} = -nF E_{(\text{cell})}^{\ominus}$$

$$\Delta_r G^{\ominus} = -RT \ln K$$

- For a given reaction to be spontaneous, E_{cell} must be positive. When the cell reaction attains equilibrium, $E_{\text{cell}} = 0$.

Conductance of Electrolytic Solutions

- The electrical resistance of any object is directly proportional to its length, l , and inversely proportional to its area of cross section, A .

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A}$$

ρ (Greek, rho), is called resistivity (specific resistance). Its SI units are ohm metre (Ω m) and quite often, ohm centimetre (Ω cm) is also used.

- The inverse of resistance, R , is called conductance, G

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1} .

- The inverse of resistivity, called conductivity (specific conductance) is represented by the symbol, κ (Greek, kappa). The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length.
- The SI units of conductivity are S m^{-1} but quite often, κ is expressed in S cm^{-1} .

Conductors, insulators and semiconductors

The values of Conductivity of some Selected Materials at 298.15 K

Material	Conductivity/ S m^{-1}	Material	Conductivity/ S m^{-1}
Conductors		Aqueous Solutions	
Sodium	2.1×10^3	Pure water	3.5×10^{-5}
Copper	5.9×10^3	0.1M HCl	3.91
Silver	6.2×10^3	0.01M KCl	0.14
Gold	4.5×10^3	0.01M NaCl	0.12
Iron	1.0×10^3	0.1M HAc	0.047
Graphite	1.2×10^3	0.01M HAc	0.016
Insulators		Semiconductors	
Glass	1.0×10^{-16}	CuO	1×10^{-7}
Teflon	1.0×10^{-18}	Si	1.5×10^{-2}
		Ge	2.0

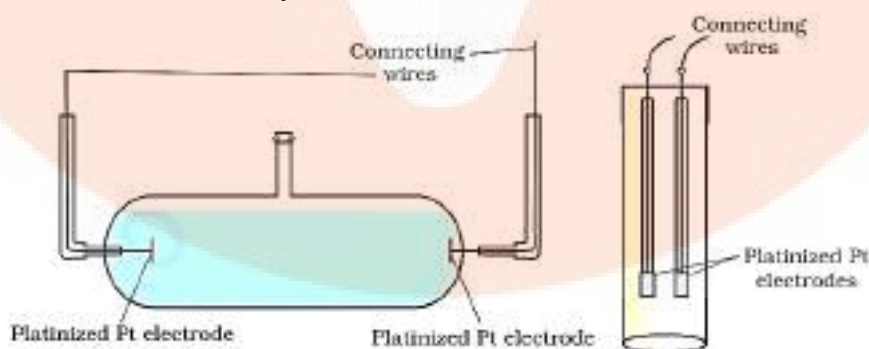
- Metals and their alloys have very large conductivity and are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers are also electronically conducting.
- Substances like glass, ceramics, etc., having very low conductivity are known as insulators.

- Substances like silicon, doped silicon and gallium arsenide having conductivity between conductors and insulators are called semiconductors and are important electronic materials.
- Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.

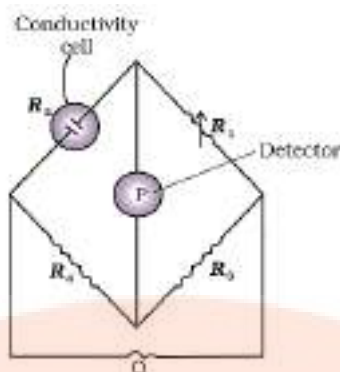
Factors affecting the conductance through metals and ionic solutions

- Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on
 - (i) the nature and structure of the metal
 - (ii) the number of valence electrons per atom
 - (iii) temperature (it decreases with increase of temperature).
- As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged.
- The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:
 - (i) the nature of the electrolyte added
 - (ii) size of the ions produced and their solvation
 - (iii) the nature of the solvent and its viscosity
 - (iv) concentration of the electrolyte
 - (v) temperature (it increases with the increase of temperature).
- Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions

Measurement of the Conductivity of Ionic Solutions



- A conductivity cell (shown above) is connected to an AC source of power with other resistances such that a wheatstone bridge is formed.



$$R_2 = \frac{R_1 R_4}{R_3}$$

Here, Unknown resistance

- The quantity l/A is called cell constant denoted by the symbol, G^* . Using the measured resistance and cell constant, conductivity can be calculated as -

$$k = \frac{\text{cell constant}}{R} = \frac{G^*}{R}$$

Molar conductivity

- Conductivity of a solution containing 1 mole of electrolyte.
 $\Lambda_m = \kappa V$ (volume containing 1 mole of electrolyte)
- Different formulas can be used based on the units of conductivity and concentration:

$$1) \quad \text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

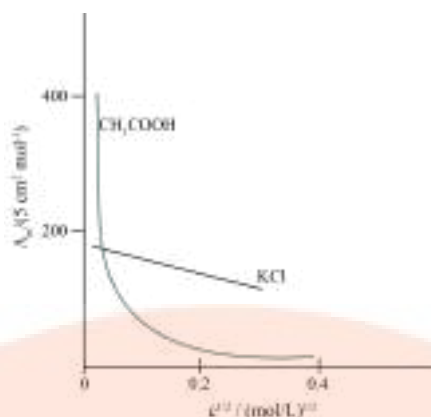
κ is expressed in S m^{-1} and the concentration, c in mol m^{-3} , the units of Λ_m are in $\text{S m}^2 \text{mol}^{-1}$.

$$2) \quad \Lambda_m (\text{S cm}^2 \text{mol}^{-1}) = \frac{\kappa (\text{S cm}^{-1}) \times 1000 (\text{cm}^3 / \text{L})}{\text{molarity (mol / L)}}$$

- $1 \text{ S m}^2 \text{mol}^{-1} = 10^4 \text{ S cm}^2 \text{mol}^{-1}$

Variation of Conductivity and Molar Conductivity with Concentration

- Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes because the number of ions per unit volume that carry the current in a solution decreases on dilution. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.
- $\Lambda_m = \kappa V$ (volume containing 1 mole of electrolyte)
- Molar conductivity increases with decrease in concentration. This is because the total volume, V , of solution containing one mole of electrolyte also increases.
- When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol Λ_m° .



- For weak electrolytes, the molar conductivity increases rapidly with dilution as the number of ions also increases on dilution (Ostwald's law).
- For strong electrolytes, the molar conductivity does not increase at much rate as weak electrolytes. The relationship between molar conductivity and \sqrt{C} for strong electrolytes is given by equation:

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$

The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte, i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. All electrolytes of a particular type have the same value for 'A'.

- NaCl, CaCl₂, MgSO₄ are known as 1-1, 2-1 and 2-2 electrolytes respectively

Kohlrausch law of independent migration of ions

- Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

$$\Lambda_m^\circ (A_a B_b) = a \times \Lambda_m^\circ (A^{b+}) + b \times \Lambda_m^\circ (B^{a-})$$

- For weak electrolytes, Λ_m° cannot be obtained by extrapolation of Λ_m to zero concentration. It is obtained by using Kohlrausch law of independent migration of ions
- For weak electrolytes, the degree of dissociation can be determined using limiting molar conductivity as-

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Using this, dissociation constants can also be calculated, for example for acetic acid,

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ 2} \left(1 - \frac{\Lambda_m}{\Lambda_m^\circ}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^\circ (\Lambda_m^\circ - \Lambda_m)}$$

Electrolytic Cell and Electrolysis

- Many metals like Na, Mg, Al, etc. are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

- Sodium and magnesium metals are produced by the electrolysis of their fused chlorides and aluminium is produced by electrolysis of aluminium oxide in presence of cryolite.

Faraday's Laws of Electrolysis

(i) First Law:

$$\frac{W}{E} = \frac{Q}{F}$$

Weight of substance liberated \propto Quantity of electricity passed.

$W \propto Q$ or $W = ZQ = Z \times I \times t$ (Z = electrochemical equivalent)

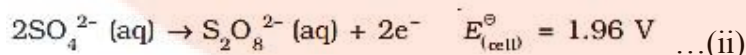
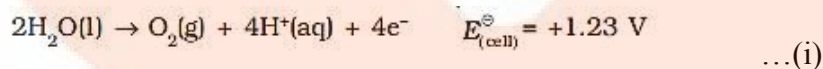
(ii) Second Law:

According to Faraday's second law of electrolysis, for the same quantity of electricity passed through solutions of different electrolytes, (e.g. CuSO_4 and AgNO_3)

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equivalent wt. of Cu}}{\text{Equivalent wt. of Ag}} \quad \boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2}}$$

Deciding the products of electrolysis

- If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons.
- On the other hand, if the electrode is reactive, it participates in the electrode reaction.
- Some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place and extra potential (called overpotential) has to be applied, which makes such process more difficult to occur
- Species having more standard reduction potential are reduced at cathode.
- Species having less standard reduction potential are oxidised at anode.
- Electrolysis of molten NaCl:** Na obtained at cathode, Cl_2 obtained at anode.
- Electrolysis of aqueous NaCl:** H_2 obtained at cathode, Cl_2 obtained at anode (on account of overpotential of oxygen).
- During the **electrolysis of sulphuric acid**, the following processes are possible at the anode:



For dilute sulphuric acid, reaction (i) is preferred but at higher concentrations of H_2SO_4 , reaction (ii) is preferred.

Batteries

- For a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use.

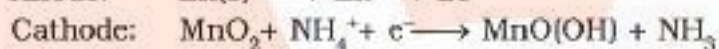
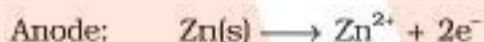
Primary Batteries

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

1. Dry cell (known as Leclanche cell after its discoverer)

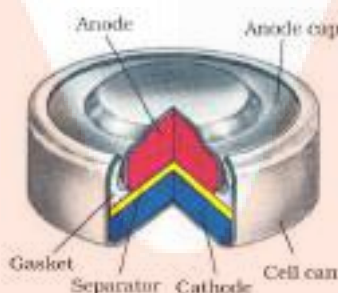


- Used commonly in transistors and clocks.
- The electrode reactions are complex, but they can be written approximately as follows:



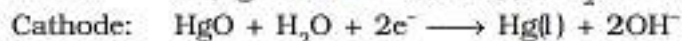
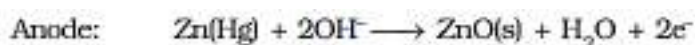
- Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$
- The cell has a potential of nearly 1.5 V.

2. Mercury cell



- Suitable for low current devices like hearing aids, watches, etc.
- Anode - Zinc – mercury amalgam
- Cathode - a paste of HgO and carbon
- Electrolyte - a paste of KOH and ZnO .

- The electrode reactions:



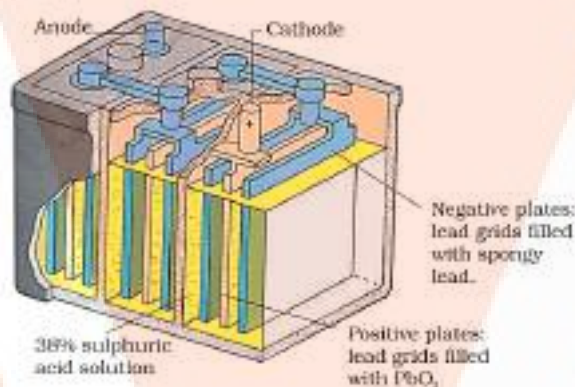
- The overall reaction: $\text{Zn(Hg)} + \text{HgO(s)} \longrightarrow \text{ZnO(s)} + \text{Hg(l)}$

- The cell potential is approximately 1.35 V and remains constant for lifetime as the overall reaction does not involve any ion in solution.

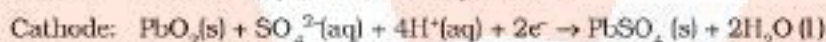
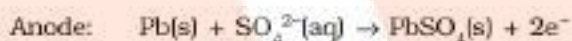
Secondary Batteries

- A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again.
- A good secondary cell can undergo a large number of discharging and charging cycles.

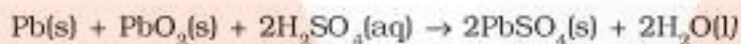
1. Lead storage battery



- The cell reactions when the battery is in use are given below:

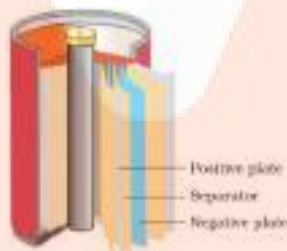


- Overall reaction while discharging:



- On charging the battery the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively.

2. Nickel-cadmium cell



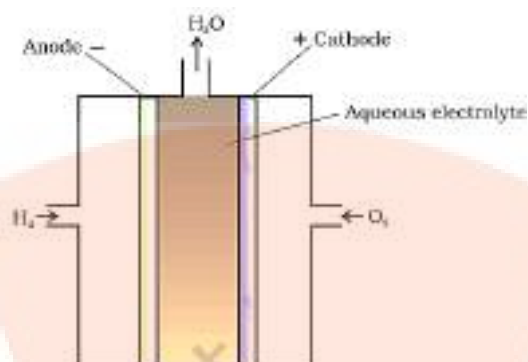
- A jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.
- The overall reaction during discharge is:



Fuel Cells

- Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells.

Hydrogen-oxygen fuel cell



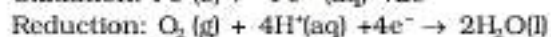
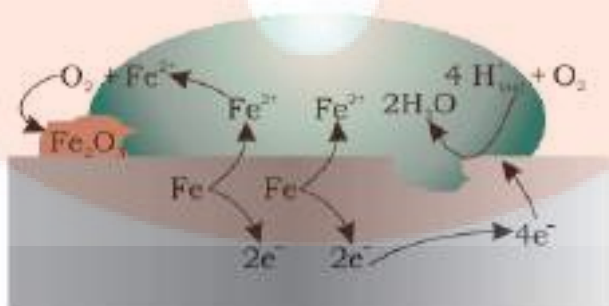
- Hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions.
- The electrode reactions are given below:
Cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$
Anode: $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \longrightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$

Overall reaction:

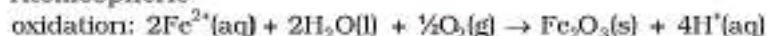


- The cell was used for providing electrical power in the Apollo space programme and the water vapour produced was condensed and used in the drinking water supply.
- Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%.
- Fuel cells are pollution free.

Corrosion



Atmospheric



- The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion.
- In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides.
- Rust is hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)

Method of Prevention of corrosion

- Covering the surface with paint or by some chemicals (e.g. bisphenol).
- Covering the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object.
- Provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

Chemical Kinetics

- Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. The branch of chemistry which deals with the study of reaction rates and their mechanisms is called chemical kinetics. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction.
- The word kinetics is derived from the Greek word 'kinesis' meaning movement.
- Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered.
- The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction.
- Thermodynamic data indicate that diamond shall convert to graphite but in reality, the conversion rate is so slow that the change is not perceptible at all.

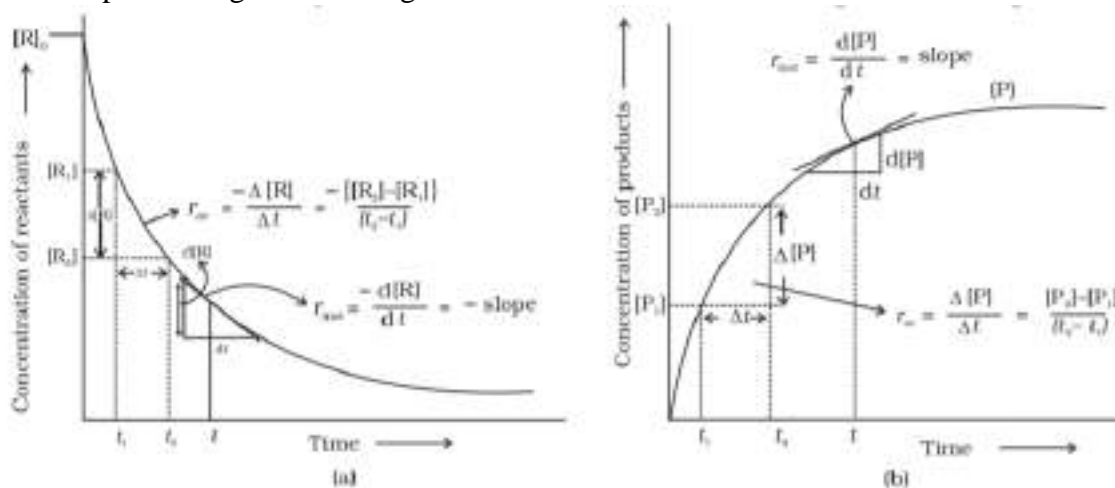
➤ Rate of a Chemical Reaction

- Example of fast reaction - precipitation of silver chloride occurs instantaneously by mixing of aqueous solutions of silver nitrate and sodium chloride.
- Example of a moderate reaction - inversion of cane sugar and hydrolysis of starch.
- Example of a slow reaction - rusting of iron in the presence of air and moisture.
- The speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time.
- To be more specific, it can be expressed in terms of:
 - the rate of decrease in concentration of any one of the reactants.
 - the rate of increase in concentration of any one of the products.
- For a general reaction: $R \rightarrow P$

$$\text{Rate of disappearance of R} = \frac{\text{decrease in concentration of R}}{\text{time taken}} = \frac{-\Delta R}{t}$$

$$\text{Rate of appearance of P} = \frac{\text{increase in concentration of P}}{\text{time taken}} = \frac{\Delta P}{t}$$

These expressions give an average rate of reaction.

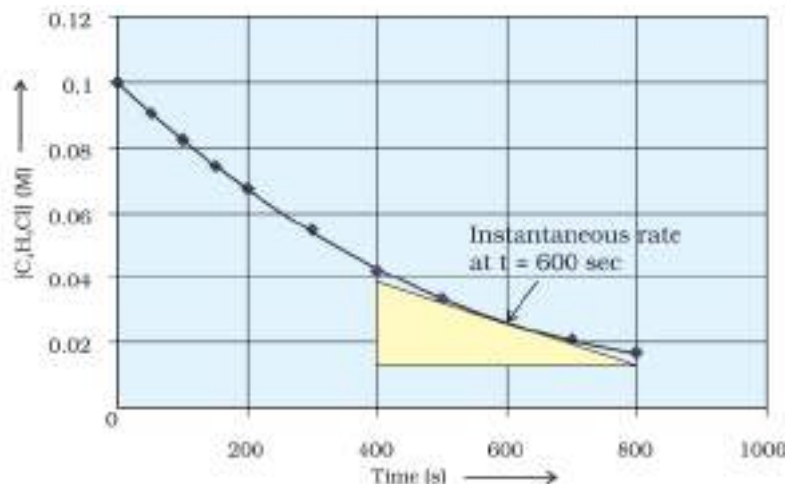


- Units of rate: mol per litre per second or atm per second.

- To express the rate at a particular moment of time we determine the instantaneous rate. mathematically for an infinitesimally small dt instantaneous rate is given by

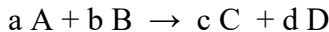
$$r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$

- Instantaneous can be determined graphically by drawing a tangent at time t on either of the curves for concentration of R and P vs time t and calculating its slope.



Instantaneous rate of hydrolysis of butyl chloride(C₄H₉Cl)

- For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometric coefficients.



$$r = -\frac{1}{a} \frac{dA}{dt} = -\frac{1}{b} \frac{dB}{dt} = \frac{1}{c} \frac{dC}{dt} = \frac{1}{d} \frac{dD}{dt}$$

- For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species and hence, rate can also be expressed as rate of change in partial pressure of the reactant or the product.

➤ Factors Influencing Rate of a Reaction

● Dependence of Rate on Concentration

- The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. The representation of rate of reaction in terms of concentration of the reactants is known as rate law. It is also called the rate equation for rate expression.

● Rate Expression and Rate Constant

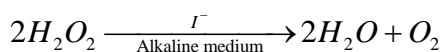
- Consider a general reaction $aA + bB \rightarrow cC + dD$ where a , b , c and d are the stoichiometric coefficients of reactants and products.
- The rate expression for this reaction is $\text{Rate} \propto [A]^x [B]^y$ where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.
- Above equation can also be written as $\text{Rate} = k [A]^x [B]^y$, k is called rate constant.
- Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may

not be the same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

- Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.
- **Order of a Reaction**
 - The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction. Order of a reaction can be 0, 1, 2, 3 and even a fraction.
 - The reactions taking place in one step are called elementary reactions. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions.
 - **Units of rate constant**

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{s} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} s^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{s} \times \frac{1}{(\text{mol L}^{-1})^1} = s^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{s} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$

- **Molecularity of a Reaction**
 - The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
 - Example of unimolecular reaction - $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
 - Example of bimolecular reaction - $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
 - Example of trimolecular reaction - $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
 - The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.
 - Complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.
 - $\text{KClO}_3 + 6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{KCl} + 3\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$ - seems like a tenth order reaction but actually is a second order reaction.
 - The overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step.
 - The decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium takes place in two steps, of which first is slow-
 1. $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$
 2. $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2$
 - The overall reaction and rate law for above reaction is given as-



$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

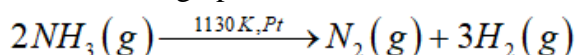
- Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.
- Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reactions molecularity has no meaning.
- For complex reactions, order is given by the slowest step and the molecularity of the slowest step is the same as the order of the overall reaction.

➤ Integrated Rate Laws

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	R→P	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	$[R]$ vs t	$[R]_0/2k$	conc time ⁻¹ or mol L ⁻¹ s ⁻¹
1	R→P	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln([R]_0/[R])$	$\ln[R]$ vs t	$\ln 2/k$	time ⁻¹ or s ⁻¹

● Examples of zero order reactions -

- Some enzyme catalysed reactions
- Reactions which occur on metal surfaces
- The decomposition of gaseous ammonia on a hot platinum surface is a zero-order reaction at high pressure.



In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making the rate of the reaction independent of its concentration.

- The thermal decomposition of HI on the gold surface.

● Examples of first order reactions -

- Hydrogenation of ethene
- All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.
- Decomposition of N₂O₅ and N₂O

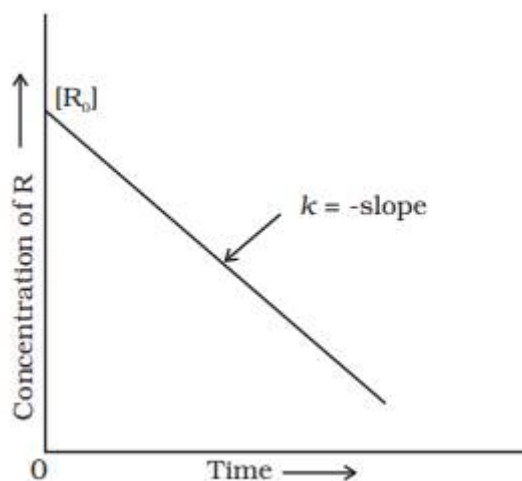
● Half-life of a reaction -

- The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as t_{1/2}.
- t_{1/2} for a zero-order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.
- For a first order reaction, the half-life period is constant, i.e., it is independent of initial concentration of the reacting species.

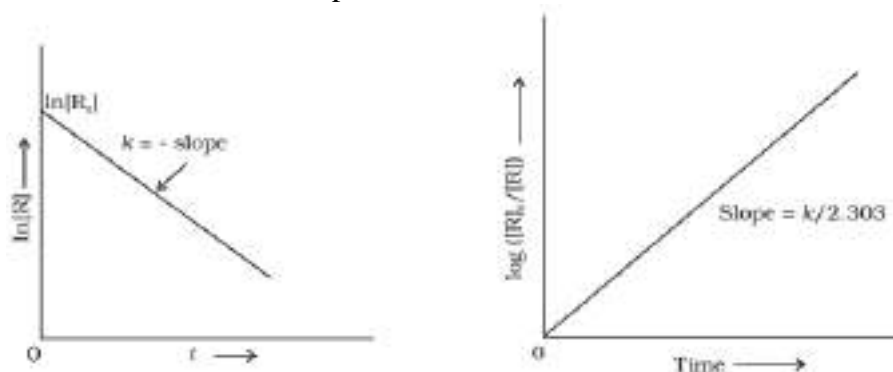
● **Integrated Rate Laws for the Reactions of Zero and First Order –**

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	$R \rightarrow P$	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	$[R]$ vs t	$[R]_0/2k$	conc time^{-1} or $\text{mol L}^{-1}\text{s}^{-1}$
1	$R \rightarrow P$	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln([R]_0/[R])$	$\ln[R]$ vs t	$\ln 2/k$	time^{-1} or s^{-1}

Graph of zero order reaction



Graphs of 1st order reaction



● **Pseudo First Order Reaction**

- The order of a reaction between two substances is sometimes altered when one reactant is present in large excess. The reaction behaves as a first order reaction. Such reactions are called pseudo first order reactions.
- Examples -
 - Hydrolysis of ethyl acetate.
 - Inversion of cane sugar.

➤ **Temperature Dependence of the Rate of a Reaction**

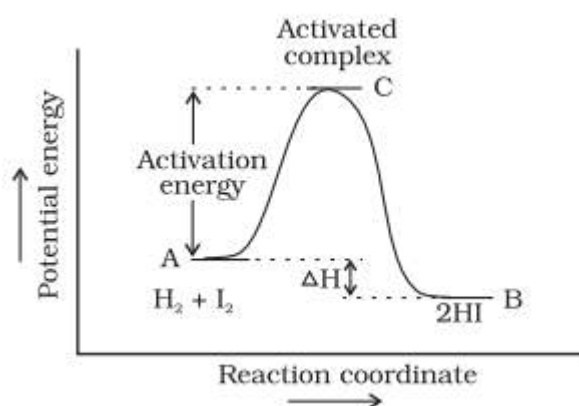
- In a mixture of potassium permanganate (KMnO_4) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), potassium permanganate is decolourised faster at a higher temperature than that at a lower temperature.

- Temperature Coefficient: for a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled.
- Arrhenius' equation was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist Arrhenius provided its physical justification and interpretation.
- Arrhenius equation:

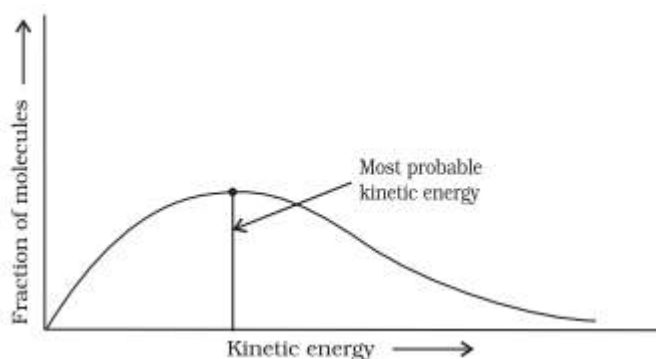
$$k = Ae^{-E_a/RT}$$

where A is the Arrhenius factor or the frequency factor. It is also called a pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and E_a is activation energy measured in joules/mole (J mol^{-1}).

- Activation energy is given by the energy difference between activated complex and the reactant molecules.

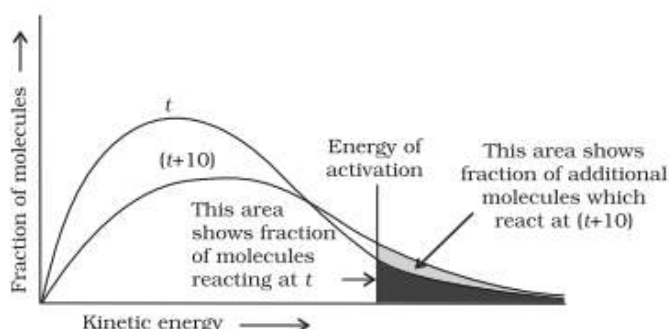


- All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of a large number of molecules. According to them, the distribution of kinetic energy may be described by plotting the fraction of molecules (N_E/N_T) with a given kinetic energy (E) vs kinetic energy. Here, N_E is the number of molecules with energy E and N_T is the total number of molecules.



- The peak of the curve corresponds to the most probable kinetic energy, i.e., kinetic energy of the maximum fraction of molecules. There are a decreasing number of molecules with energies higher or lower than this value.

- When the temperature is raised, the maximum of the curve moves to the higher energy value and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times.



- Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a .
- In the Arrhenius equation, the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a .
- Thus, increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.
- Logarithmic form of Arrhenius equation –

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

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

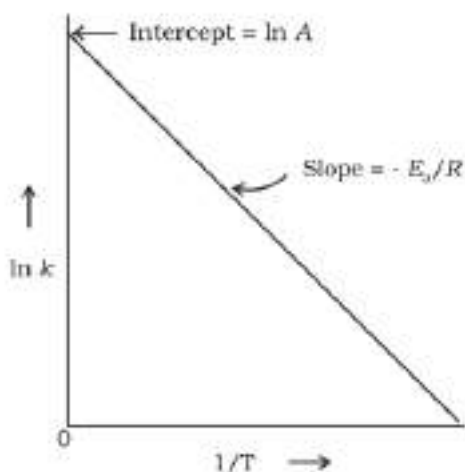
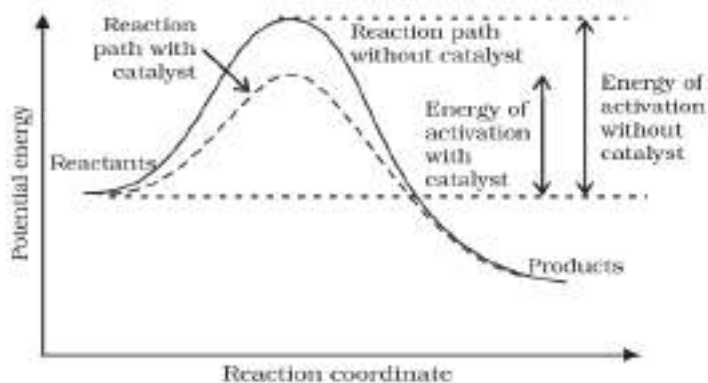


Fig. A plot between $\ln k$ and $1/T$

➤ Effect of Catalyst

- A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.
- Presence of a catalyst lowers the activation energy by providing an alternate path for the reaction.

- The word inhibitor is used when the added substance reduces the rate of reaction.
- **Intermediate complex theory** - A catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.
- It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier



Effect of catalyst on activation energy

- A small amount of the catalyst can catalyse a large amount of reactants
- A catalyst does not alter Gibbs energy, ΔG of a reaction. It catalyses spontaneous reactions but does not catalyse nonspontaneous reactions.
- It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

➤ Collision Theory of Chemical Reactions

- Though Arrhenius' equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916-18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on the kinetic theory of gases.
- The reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).
- For a bimolecular reaction $A \rightarrow B$

$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$
 where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .
- The above equation predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed.
- The reason could be that all collisions do not lead to the formation of products.
- The collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, so as to facilitate breaking of bonds between

reacting species and formation of new bonds to form products are called effective collisions.

- Threshold energy = Activation Energy + energy possessed by reacting species.
- The proper orientation of reactant molecules leads to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

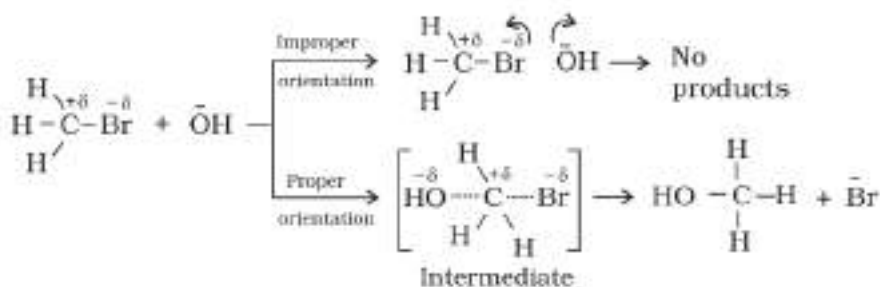


Diagram showing molecules having proper and improper orientation

- To account for effective collisions, another factor P, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

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

- Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.
- Collision theory also has certain drawbacks as it considers atoms/ molecules to be hard spheres and ignores their structural aspect.

Surface Chemistry

- Surface chemistry deals with phenomena that occur at the surfaces or interfaces.
- The interface or surface is represented by separating the bulk phases by a hyphen or a slash.
- For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas.
- Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces.
- Under very high vacuum of the order of 10^{-8} to 10^{-9} pascal, it is now possible to obtain ultra clean surface of the metals. Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen.

➤ Adsorption:

The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption.

- Adsorbate: The substance, which accumulates at the surface.
- Adsorbent: The material on the surface of which the adsorption takes place. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.
- Examples of adsorption –
 1. If a gas like O_2 , H_2 , CO , Cl_2 , NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
 2. In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.
 3. Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
 4. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

Desorption: The process of removing an adsorbed substance from a surface on which it is adsorbed.

❖ Distinction between Adsorption and Absorption

Adsorption	Absorption
<ul style="list-style-type: none"> • The substance is concentrated only at the surface and does not penetrate through the surface. 	<ul style="list-style-type: none"> • The substance is uniformly distributed throughout the bulk of the solid.
<ul style="list-style-type: none"> • When a chalk stick is dipped in ink, the surface retains the colour of the 	<ul style="list-style-type: none"> • When a chalk stick is dipped in ink, the solvent of the ink goes deeper into

ink due to adsorption.	the stick due to absorption.
<ul style="list-style-type: none"> Water vapours are adsorbed by silica gel. 	<ul style="list-style-type: none"> Water vapours are absorbed by anhydrous calcium chloride.

Sorption: Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes.

❖ **Mechanism of Adsorption:** Reason for adsorption: the surface particles are not in the same environment as the particles inside the bulk.

- Inside the adsorbent all the forces acting between the particles are balanced.
- On the surface the particles are not surrounded by the particles of their kind on all sides, and hence they possess unbalanced attractive forces.
- These forces are responsible for attracting the adsorbate particles on its surface.

❖ **Some important points to note about adsorption**

- At a given temperature and pressure, the extent of adsorption increases with the increase of surface area per unit mass of the adsorbent.
- During adsorption, there is a decrease in surface energy which appears as heat. So, ΔH of adsorption is always negative.
- When a gas is adsorbed, the freedom of movement of its molecules becomes restricted. So, ΔS is negative.
- For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative.

❖ **Types of Adsorptions**

- Physisorption:** If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as physical adsorption or physisorption.
- Chemisorption:** When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed chemical adsorption or chemisorption.
- A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dihydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

❖ **Comparison between physisorption and chemisorption**

Physisorption	Chemisorption
1. It arises because of van der Waals' forces.	1. It is caused by chemical bond formation.
2. It is not specific in nature.	2. It is highly specific in nature.
3. It is reversible in nature.	3. It is irreversible.

4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ mol ⁻¹) in this case.	5. Enthalpy of adsorption is high (80-240 kJ mol ⁻¹) in this case.
6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	6. High temperature is favourable for adsorption. It increases with the increase of temperature.
7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
8. It depends on the surface area. It increases with an increase of surface area.	8. It also depends on the surface area. It too increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure.	9. It results into unimolecular layer.

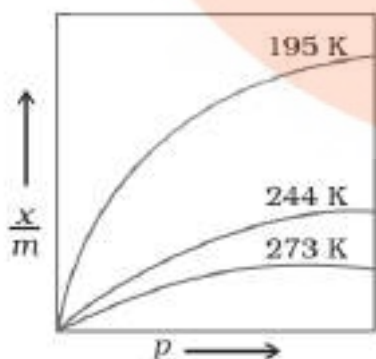
❖ **Adsorption Isotherms:** It is the plot of the amount of gas adsorbed by the adsorbent with pressure at constant temperature.

➤ **Freundlich adsorption isotherm:**

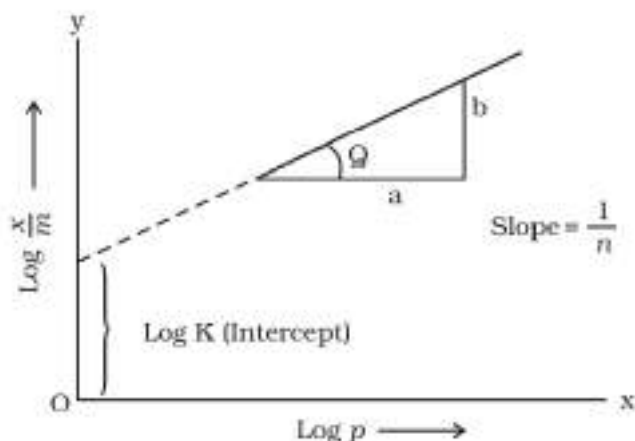
1.

$$\frac{x}{m} = k \cdot p^{1/n} \quad (n > 1)$$

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.



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



Points to remember on Freundlich isotherm equation -

1. The factor $1/n$ can have values between 0 and 1.
2. When $1/n = 0$, $x/m = \text{constant}$, the adsorption is independent of pressure.
3. When $1/n = 1$, $x/m = k p$, i.e. $x/m \propto p$, the adsorption varies directly with pressure.
4. The experimental isotherms always seem to approach saturation at high pressure.
This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

➤ Adsorption from Solution Phase

Examples

- When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution.
- The litmus solution when shaken with charcoal becomes colourless.
- The precipitate of $\text{Mg}(\text{OH})_2$ attains blue colour when precipitated in presence of magneson reagent. The colour is due to adsorption of magneson.

Features-

- The extent of adsorption decreases with an increase in temperature.
 - The extent of adsorption increases with an increase of surface area of the adsorbent.
 - The extent of adsorption depends on the concentration of the solute in solution.
 - The extent of adsorption depends on the nature of the adsorbent and the adsorbate.
- Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure concentration is used:

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

On taking logarithm of the above equation, we have

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

➤ **Applications of Adsorption**

- 1) Production of high vacuum: the remaining traces of air can be adsorbed by charcoal.
- 2) In gas masks: device which consists of activated charcoal or mixture of adsorbents, used for breathing in coal mines to adsorb poisonous gases.
- 3) For Controlling humidity: Silica and aluminium gels are used as adsorbents.
- 4) For the removal of colouring matter from solutions: Animal charcoal is used as adsorbent
- 5) In heterogeneous catalysis: Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
- 6) For separation of inert gases: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
- 7) In curing diseases: Several drugs are used to kill germs by getting adsorbed on them.
- 8) In froth floatation process: Used for concentration of sulphide ores.
- 9) As adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.
- 10) In chromatographic analysis: Chromatographic analysis finds a number of applications in analytical and industrial fields.

➤ **Catalysis**

- Potassium chlorate, when heated strongly decomposes slowly giving dioxygen. The decomposition occurs in the temperature range of 653-873 K.

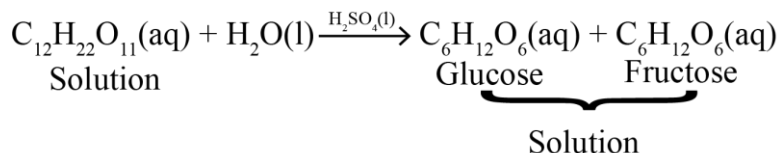
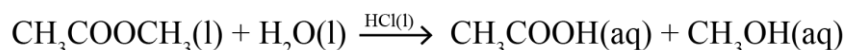
$$2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633 K and also at a much-accelerated rate.
- Berzelius gave the term catalyst.
- **Catalyst and Catalysis:** Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as **catalysts**, and the phenomenon is known as **catalysis**.
- **Promoters and poisons:** Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst. in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

➤ **Catalysis can be broadly divided into two groups:**

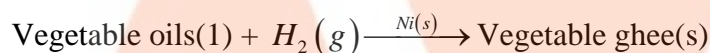
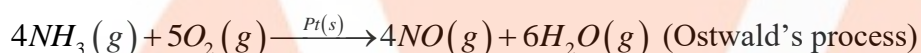
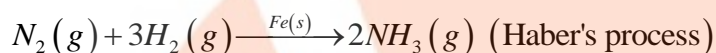
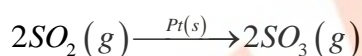
- (i) **Homogeneous catalysis:** When the reactants products and the catalyst are in the same phase (i.e., liquid or gas), the process is said to be homogeneous catalysis.

Examples of homogeneous catalysis:



(ii) Heterogeneous catalysis: The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis.

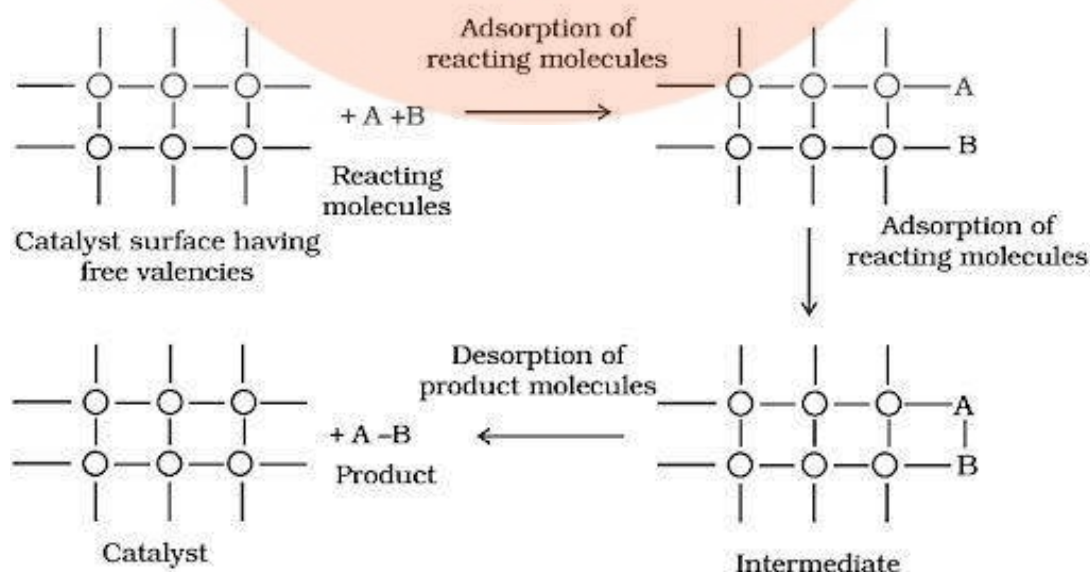
Examples of heterogeneous catalysis:



➤ Adsorption Theory of Heterogeneous Catalysis

This theory explains the mechanism of heterogeneous catalysis. The mechanism involves five steps:

- 1) Diffusion of reactants to the surface of the catalyst
- 2) Adsorption of reactant molecules on the surface of the catalyst.
- 3) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.
- 4) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.
- 5) Diffusion of reaction products away from the catalyst's surface.



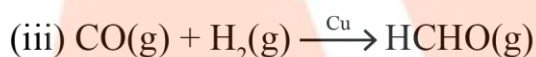
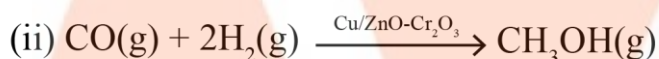
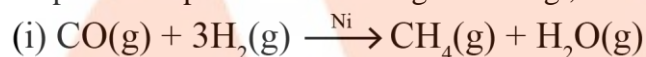
Drawback of this theory is that it does not explain the action of catalytic promoters and catalytic poisons.

➤ **Important features of solid catalysts:**

● **Activity:**

- By activity of a catalyst, we mean its capacity to increase the speed of chemical reaction.
- The activity depends on the strength of chemisorption.
- The adsorption should be reasonably strong but not so strong that the adsorbed molecules become immobile, and no space is available for other reactants to get adsorbed.
- For hydrogenation reaction, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by groups 7-9 elements of the periodic table

- **Selectivity:** By selectivity of a catalyst, we mean its ability to direct the reaction to form particular products excluding others e.g.,



➤ **Shape Selective Catalysis by Zeolites**

- 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.
- Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous aluminosilicates with three-dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework.
- The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites.
- An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

➤ **Enzyme Catalysis**

- Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals.
- They catalyse numerous reactions, especially those connected with natural processes.
- The enzymes are termed as biochemical catalysts and the phenomenon is known as biochemical catalysis.

➤ **Example of few enzyme catalysed reactions are given below:**

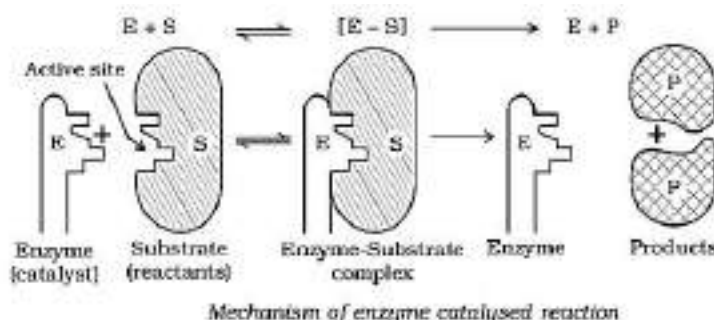
S.No.	Reaction	Enzyme	Source
(i)	Inversion of cane sugar $C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$	Invertase	Yeast
(ii)	Conversion of glucose into ethyl alcohol $C_6H_{12}O_6(aq) \xrightarrow{\text{Zymase}} 2C_2H_5OH(aq) + 2CO_2(g)$	Zymase	Yeast
(iii)	Conversion of starch into maltose $2(C_6H_{10}O_5)_n(aq) + nH_2O(l) \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}(aq)$ <p style="text-align: center;">Maltose</p>	Diastase	Malt
(iv)	Conversion of maltose into glucose $C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6(aq)$ <p style="text-align: center;">Glucose</p>	Maltase	Yeast
(v)	Manufacture of acetic acid from ethyl alcohol $CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$	Mycoderma aceti	Old vinegar
(vi)	Decomposition of urea into NH_3 and CO_2 $NH_2CONH_2(aq) + H_2O(l) \xrightarrow{\text{Urease}} NH_3(g) + CO_2(g)$	Urease	Soyabean
(vii)	Conversion of proteins into peptides in the stomach	Pepsin	Stomach
(viii)	Conversion of proteins into amino acids by hydrolysis in intestine	Trypsin	Intestine
(ix)	Conversion of milk into curd	Lactobacilli	Curd

➤ **Characteristics of enzyme catalysis**

- Efficiency:** One molecule of an enzyme may transform one million molecules of the reactant per minute.
- Specificity:** Each enzyme catalysis only one reaction, so highly specific in nature. The enzyme urease catalyses the hydrolysis of urea only. It does not catalyse hydrolysis of any other amide.
- Optimum temperature and pH:** The optimum temperature range for enzymatic activity is 298-310 K whereas optimum pH range is 5-7.
- Increasing activity in presence of activators and co-enzymes:** The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. **Activators** are generally metal ions such as Na^+ , Mn^{2+} , Co^{2+} , Cu^{2+} , etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Example: Enzyme, Amylase in presence of sodium chloride i.e., Na^+ ions are catalytically very active.
- Influence of inhibitors and poisons:** The activity of enzyme is slowed down in the presence of certain substances called inhibitors or poison. The inhibitors interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes.

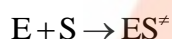
➤ Mechanism of enzyme catalysis

The most accepted mechanism of enzyme- catalysed reaction is known as lock and key mechanism:



The enzyme-catalysed reactions may be considered to proceed in two steps:

Step 1: Binding of enzyme to substrate to form an activated complex. There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $-\text{NH}_2$, $-\text{COOH}$, $-\text{SH}$, $-\text{OH}$, etc. These are the centres on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fit into a lock.



Step 2: Decomposition of the activated complex to form product. Because of the presence of active groups, an activated complex is formed which then decomposes to yield the products.



➤ Catalysts in Industry

Process	Catalyst
1. Haber's process for the manufacture of ammonia $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$	Finely divided iron, molybdenum as promoter: conditions: 200 bar pressure and 723-773 temperature. Now-a-days, a mixture of iron oxide, potassium oxide and alumina are used.
2. Ostwald's process for the manufacture of nitric acid. $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ $4\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \rightarrow 4\text{HNO}_3(\text{aq})$	Platinised asbestos: temperature 573K.
3. Contact process for the manufacture of sulphuric acid. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ $\text{SO}_2(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})$ oleum $\text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{SO}_4(\text{aq})$	Platinised asbestos or vanadium pentoxide (V_2O_5): temperature 673-723K

- **Colloids:** A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

True solution	Colloids	Suspension
Size of solute particles < 1 nm	Size of particle between 1nm to 1000 nm	Size of particle > 1000 nm
Homogeneous	Heterogeneous	Heterogeneous
Particle pass through ordinary filter paper and animal membrane	Particle pass through ordinary filter paper but not through animal membrane	Particle cannot pass through ordinary filter paper and animal membrane
Example - Sugar solution, Salt solution	Example- Fog, mist	Example- Muddy water, Smoke in the air

- **Classification of Colloids**

❖ **Classification Based on Physical State of Dispersed Phase and Dispersion Medium**

Dispersed phase	Dispersion medium	Type or colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gemstones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, butter
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

❖ **Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium**

Lyophilic colloids	Lyophobic colloids
These are easily formed by direct mixing	These are formed by special method
Reversible in nature	Irreversible in nature
Very stable	Unstable, require stabilizers
The particles are heavily hydrated due to	The particles of colloids are not

the attraction for the solvent.	appreciably hydrated
Precipitated by high conc. of electrolyte.	Precipitated by low conc. of electrolyte.
E.g. gum, gelatine, starch, rubber, etc., with a suitable liquid	E.g. Metal solution, gold etc.

❖ Classification Based on Type of Particles of the Dispersed Phase, Multimolecular, Macromolecular and Associated Colloids

- **Multimolecular colloids:** On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (1–1000 nm). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S₈ sulphur molecules.
- **Macromolecular colloids:** Macromolecules in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such systems are called macromolecular colloids. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.
- **Associated colloids (Micelles):** There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids.

❖ Kraft temperature and critical micelle concentration (CMC)

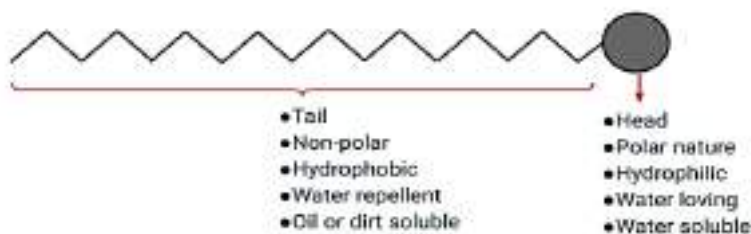
The formation of micelles takes place only above a particular temperature called Kraft temperature (T_k) and above a particular concentration called critical micelle concentration (CMC).

➤ Mechanism of micelle formation

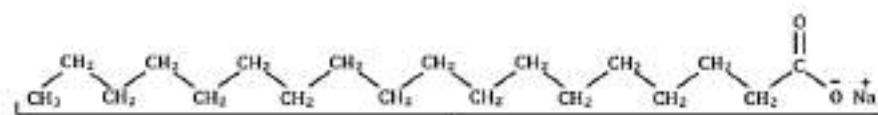
- Mechanism can be explained with the help of soap solution:

Soap (RCOO^-Na^+) is sodium or potassium salt of a higher fatty acids.

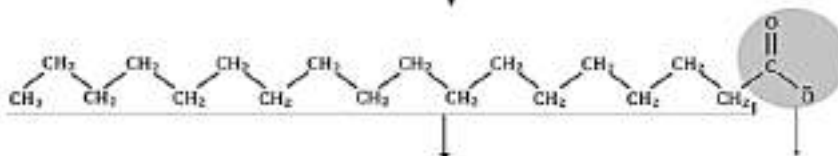
Example of soap :- sodium stearate $\text{CH}_3(\text{CH}_2)_{14}\text{COO}^-\text{Na}^+$



Sodium stearate $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$

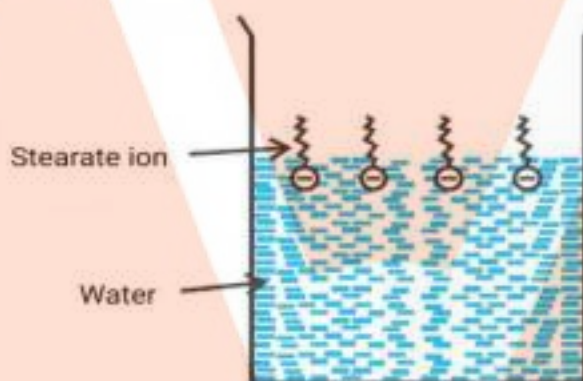


After dissociation in water



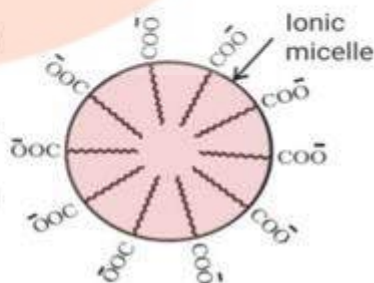
Below CMC

- Polar COO^- groups in water and the hydrocarbon chains R remain at the surface.



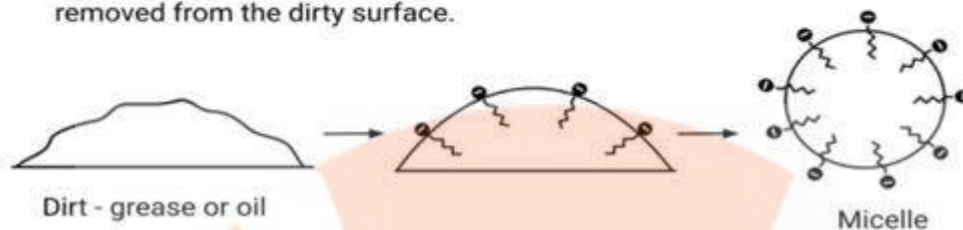
Above CMC

- Aggregate in a spherical form with their hydrocarbon chains pointing towards the centre with COO^- part remaining outward on the surface.
- Aggregation of RCOO^- ions to form an ionic micelle.
- These micelles may contain as many as upto 100 such ions.
- In case of detergents, the polar group is SO_4^{2-} along with the long hydrocarbon chain.
E.g., sodium lauryl sulphate viz. $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$



➤ Cleansing action of soaps

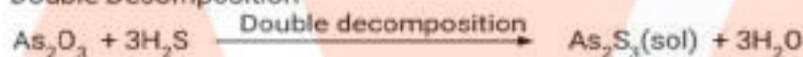
- Cleansing action of soap is due to micelle formation around grease or oil droplet
- Hydrophobic part of the stearate ions is in the oil hydrophilic part projects out of the oil
- Polar groups can interact with water.
- The oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface.



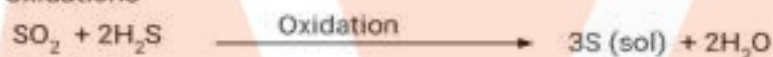
➤ Preparation of Colloids

• Chemical methods

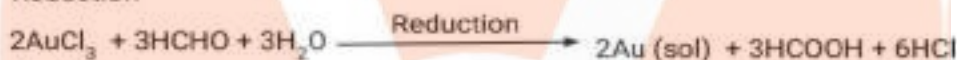
(a) Double Decomposition



(b) Oxidations



(c) Reduction

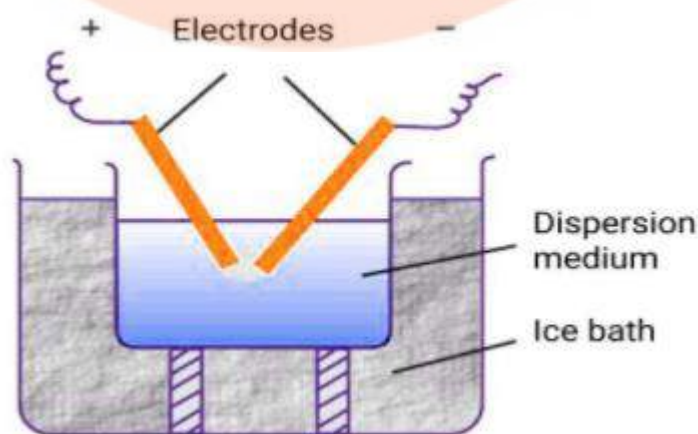


(d) Hydrolysis



• Electrical disintegration or Bredig's Arc method

- This process involves dispersion as well as condensation.
- Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method.
- In this method, an electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.



- **Peptization**

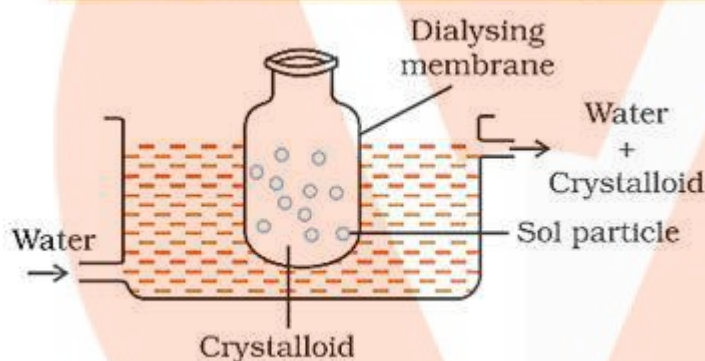
- The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte.
- The electrolyte used for this purpose is called peptizing agent.
- This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

➤ **Purification of Colloidal Solutions**

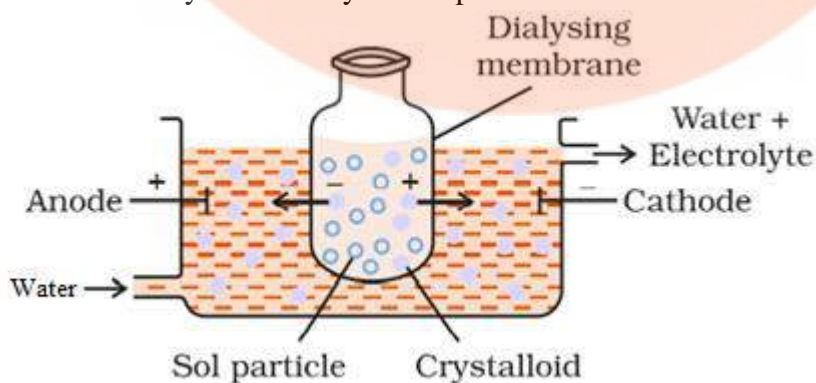
The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution.

- **Dialysis:**

- Process of removing of a dissolved substance from a colloidal solution by means diffusion through suitable membrane.
- The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind
- Apparatus called dialyser.
- Used in purification of blood in the artificial kidney machine



- **Electro-dialysis:** Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis.



● Ultrafiltration:

- Filtration through special type of graded filters called ultra-filters.
- Ultra-filter paper may be prepared by soaking the filter paper in a colloidal solution, hardening by formaldehyde and then finally drying it.
- Colloidion solution is a 4% solution of nitrocellulose in a mixture of alcohol and ether
- Filter paper impregnation with colloidion solution to stop the flow of colloidal particles
- To speed up the process, pressure or suction is applied

➤ Properties of Colloidal Solutions

i) Colligative properties:

- Colloidal sols show the colligative properties (relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure)
- Colligative property which depends upon no. of particles not on nature.
- No. of particles in a colloidal solution is comparatively small as compared to a true solution
- Values of colligative properties are of small order as compared to values shown by true solutions at same concentrations.

ii) Tyndall effect:

- The Tyndall effect is due to the fact that colloidal particles scatter light in all directions in space.
- This scattering of light illuminates the path of the beam in the colloidal dispersion.
- The bright cone of the light is called the Tyndall cone.
- Tyndall effect is observed only when the following two conditions are satisfied:
 - (i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used.
 - (ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.
- Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there.

Ultramicroscope

- Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there.
- Ultramicroscope does not render the actual colloidal particles visible but only observe the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

iii) Colour:

- The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles.
- The wavelength of light further depends on the size and nature of the particles.

- The colour of colloidal solution also changes with the manner in which the observer receives the light.
- For example:
 - a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light.
 - Finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue and finally golden.

iv) Brownian movement:

- When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This motion is known as the Brownian movement.
- This motion was first observed by the British botanist, Robert Brown.
- This motion is independent of the nature of the colloid but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity, faster is the motion.

v) Charge on colloidal particles:

- Colloidal particles always carry an electric charge and may be either positive or negative.

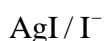
Positively charged sols	Negatively charged sols
Hydrated metallic oxides. e.g., $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{CrO}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, etc.	Metals. e.g.. copper. silver. gold sols.
Basic dye stuffs, e.g., methylene blue sol.	Metallic sulphides, e.g., As_2S_3 , Sb_2S_3 . Cds sols.
Haemoglobin (blood)	Acid dye stuffs, e.g.. eosin. congo red sols.
Oxides, e.g., TiO_2 sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

- The charge on the sol particles can be due to any of the following reasons:
 - due to electron capture by sol particles during electro dispersion of metals
 - due to preferential adsorption of ions from solution
 - due to preferential adsorption of ions from solution
- Development of charge on sol particles by preferential adsorption of ions is described below:
 - The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions.

→ When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place.

→ For example:

- (a) When a highly diluted solution of silver nitrate is added to a highly diluted potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal sol results. However, when KI solution is added to AgNO_3 solution, positively charged sol results due to adsorption of Ag^+ ions from dispersion medium.



Negatively charged

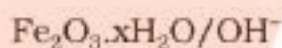


Positively charged

- (b) If FeCl_3 is added to the excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions. However, when ferric chloride is added to NaOH solution a negatively charged sol is obtained with adsorption of OH^- ions.



Positively charged

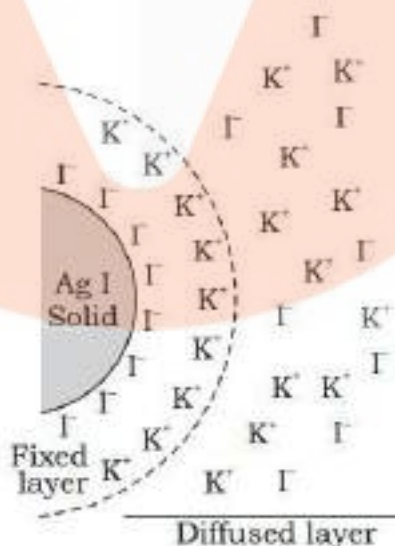


Negatively charged

→ Having acquired a positive or a negative charge by selective adsorption on the surface of a colloidal particle as stated above, this layer attracts counter ions from the medium forming a second layer, as shown below.



- The combination of the two layers of opposite charges around the colloidal particle is called the Helmholtz electrical double layer.
- The first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed diffused layer.



Formation of double layer

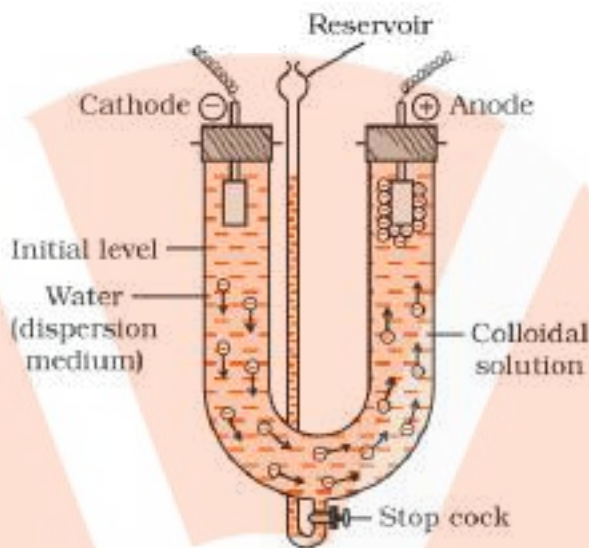
- The charges of opposite signs on the fixed and diffused parts of the double layer result in a difference in potential between these layers in the same manner as potential difference is developed in a capacitor.

→ This potential difference between the fixed layer and the diffused layer of opposite charges is called the **electrokinetic potential or zeta potential**.

The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution

vi) Electrophoresis:

- The movement of colloidal particles under an applied electric potential is called electrophoresis.
- Positively charged particles move towards the cathode
- Negatively charged particles move towards the anode



- When electrophoresis, i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed electroosmosis.

vii) Coagulation or precipitation:

- The process of aggregation of colloidal particles into an insoluble precipitate by the addition of some suitable electrolyte.
- The stability of the lyophobic sols is due to the presence of charge on colloidal particles
- If, somehow, the charge is removed, the particles will come nearer to each other to form aggregates (or coagulate) and settle down under the force of gravity.
- **By electrophoresis:** Colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.
- **By mixing two oppositely sols:** neutralize their charges and get partially or completely precipitated.

Example: Positively charged $\text{Fe}(\text{OH})_3$ and negatively charged As_2S_3 colloidal particle containing sol on mixing get coagulated.

- **By boiling:** Increased collisions between sol particle and the water molecule removed the adsorbed electrolytes.

Example: Sol of sulphur and silver halide

- **By persistent dialysis:** Traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.
- **By addition of electrolyte:** When excess of an electrolyte is added, the colloidal particles are precipitated. A negative ion causes the precipitation charged sol and vice versa.

Hardy-Schulze Rule: The greater the valence of the flocculating ion added, the greater is its power to cause precipitation.

- In the coagulation of a negative sol, the flocculating power is in the order.
 $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^{+}$
- In the coagulation of a positive sol, the flocculating power is in the order.
 $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^{-}$

Coagulation value: The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value.

- The smaller the quantity needed, the higher will be the coagulating power of an ion.

➤ **Coagulation of lyophilic sols**

There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done

- by adding an electrolyte and
- by adding a suitable solvent.

When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

➤ **Protection of colloids**

- Lyophilic sols are more stable than lyophobic sols due to extensively solvated
- Lyophobic sols can easily precipitate by addition of small amount of an electrolyte.
- Lyophobic sol can be prevented from coagulation by addition of some lyophilic colloid by formation of protective layer by lyophilic sols outside lyophobic sols.
- Such lyophilic colloidal are called protective sols

Example: Gelatin, Sodium caseinate, Egg albumin, Gum arabic, Potato starch etc.

➤ **Emulsions**

- These are liquid-liquid colloidal systems.
- If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion.
- There are two types of emulsions:
 - Oil dispersed in water (O/W type): Examples of this type of emulsion are milk and vanishing cream
 - Water dispersed in oil (W/O type): Examples of this type are butter and cream
- Emulsions of oil in water are unstable and sometimes they separate into two layers on standing.

- For stabilisation of an emulsion, a third component called **emulsifying agent** is usually added.
- The emulsifying agent forms an interfacial film between suspended particles and the medium.
- The principal emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc.
- The principal emulsifying agents for W/O, heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.
- Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed, forms a separate layer.
- The droplets in emulsions are often negatively charged and can be precipitated by electrolytes.
- They also show Brownian movement and Tyndall effect.
- Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

➤ Colloids Around Us

- (i) Blue colour of the sky: Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.
- (ii) Fog, mist and rain: When a large mass of air containing dust particles, is cooled below its dew point, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in air in the form of mist or fog. Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositely charged clouds meet. It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.
- (iii) Food articles: Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in one form or the other.
- (iv) Blood: It is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.
- (v) Soils: Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.
- (vi) Formation of delta: River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

➤ Applications of colloids

- (i) Electrical precipitation of smoke: Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates

lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called Cottrell precipitator

- (ii) **Purification of drinking water:** The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.
- (iii) **Medicines:** Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.
- iv) **Tanning:** Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.
- (v) **Cleansing action of soaps and detergents.**
- (vi) **Photographic plates and films:** Photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.
- (vii) **Rubber industry:** Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.
- (viii) **Industrial products:** Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions.

General Principles and Processes of Isolation of Elements

➤ General points:

- **Minerals:** Naturally occurring chemical substances in the earth's crust obtainable by mining.
- **Ores:** Minerals which are viable to be used as a source of the metal.
- **Gangue:** Ores are contaminated with undesired minerals called gangue
- **Metallurgy:** Entire scientific and technological process used for isolation of the metal from its ores.
- **Pyrometallurgy:** Use of high temperatures to extract and purify metals
- Isolation and extraction should be chemically feasible and commercially viable.

➤ Occurrence of metals:

- Abundance in earth crust
 - 2nd most abundant: Fe.
 - ❖ Extracted from oxide ores which do not produce polluting gases (Eg: SO_2 is produced when Fe is extracted from iron pyrites)
 - ❖ Has great importance in biological substances
 - 3rd most abundant: Al.
 - ❖ Extracted from bauxite
 - ❖ Found in mica, clay.
 - ❖ Gemstones contain Al_2O_3 with impurities like Cr(in ruby), Co(in sapphire)).

➤ Metal, its ores and its uses:

Metal	Ore	Uses
Al	Bauxite, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ Cryolite, Na_3AlF_6 Kaolinite $[\text{Al}_2(\text{OH})_4 \cdot \text{Si}_2\text{O}_5]$	1. Al foils - In wrappers for chocolates 2. Al fine dust - In paints, lacquers 3. In extraction of Cr, Mn from their oxides 4. In wires as it is good conductor of electricity 5. Al alloys light in weight and highly useful
Fe	Haematite Fe_2O_3 Magnetite Fe_3O_4 Siderite FeCO_3 Iron pyrites FeS_2	1. Cast iron - Casting stoves, gutter pipes, toys, railway sleepers. 2. Wrought iron - Anchors, wires, bolts, chains, agricultural implements
Cu	Copper pyrites - CuFeS_2 Malachite - $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ Cuprite Cu_2O Copper glance Cu_2S	1. In electric wires, water and steam pipes 2. Alloys - Brass (with Zn), bronze (with tin), coinage alloy (with Ni). They are stronger than metal itself.

		3. In steel manufacturing. 4. Nickel steel - cables, automobiles and aeroplane parts, pendulum, measuring tapes 5. chrome steel - Cutting tools. crushing machines. 6. stainless steel - Cycles, automobiles, utensils, pens.
Zn	1. Zinc blende or Sphalerite, ZnS 2. Calamine, ZnCO_3 3. Zincite, ZnO	1. Galvanising iron 2. In batteries 3. In alloys- brass (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40-50%) 4. Reducing agent - In manufacture of dye-stuffs and paints

➤ **Steps in metallurgical process:**

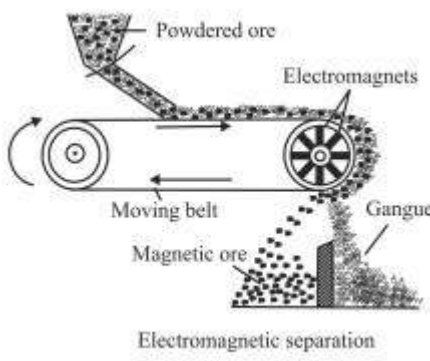
- 1. Crushing:** Ores are graded and crushed to reasonable size.
- 2. Concentration or Dressing or Benefaction of ore:** Removal of unwanted materials (eg: sand, clay) from ore.
- 3. Extraction of crude metal from concentrated ore**
- 4. Refining or purification of the crude metal**

➤ **Concentration of ore:**

Selection of method of concentration depends on the difference in the physical properties between gangue and the metal.

Few important procedures include:

Type	Principle used	Procedure and examples
Hydraulic washing	Difference in the gravities of ore and gangue	Upstream of running water is passed through the powdered ore, washing off the lighter gangue particles.
Magnetic separation	Difference in magnetic properties of the ore and the gangue.	Powdered ore is carried on a conveyor belt which passes over a magnetic roller. Based on the magnetic properties of ore and gangue, one of them gets attracted towards the magnetic roller separating ore from the gangue. Eg: Iron ores

		
Froth floatation	Ore are wetted by oils and gangue particles are wetter by water	<p>Powdered ore is suspended in water and collectors and froth stabilisers are added. Collectors like pine oil, fatty acids, xanthates etc enhance non-wettability and froth stabilisers like Cresols, aniline etc stabilise froth.</p> <p>Minerals become wet by oils and gangue by water. Froth carrying mineral particles is formed due to agitation by a rotation paddle which draws in air. Froth is separated by skimming and dried to recover ore.</p> <p>Eg: Sulphide based ores</p> <p>NOTE: 2 sulphide ores can be separated by adjusting proportion of oil and water or by using depressants. Eg: In ore with ZnS and PbS, depressant NaCN is added which prevents ZnS moving into froth which PbS moves into froth</p>
Leaching	Ore is soluble in the suitable solvent while gangue remains insoluble	<p>Solvent is added externally to leach out the ore as a soluble compound leaving the impurities insoluble. Then the leached out soluble compound is further converted back to the respective ore.</p> <p>Eg:</p> <p>1. Alumina from bauxite: Leachant: NaOH</p> $\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}[\text{Al}(\text{OH})_4](\text{aq}) + 2\text{CO}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s}) + 2\text{NaOH}$ $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s}) \xrightarrow{1470 \text{ K}} \text{Al}_2\text{O}_3(\text{s}) + x\text{H}_2\text{O}(\text{g})$

		<p>NOTE: Bauxite has SiO_2, TiO_2 and iron oxides as impurities. When NaOH is added SiO_2 is also leached out as sodium silicate along with sodium aluminate. But when CO_2 is passed sodium silicate being non reactive to CO_2 remains in water, while sodium aluminate from a precipitate of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$</p> <p>2. Silver and gold from their ores: Leachant: NaCN</p> $4\text{M(s)} + 8\text{CN}^-(\text{aq}) + 2\text{H}_2\text{O(l)} + \text{O}_2(\text{g}) \rightarrow 4[\text{M(CN)}_2]^- + 4\text{OH}^-(\text{aq}) \quad (\text{M} = \text{Ag, Au})$ $2[\text{M(CN)}_2]^- + \text{Zn(s)} \rightarrow [\text{Zn(CN)}_4]^{2-} + 2\text{M(s)}$
--	--	--

➤ **Extraction of crude metal from concentrated ore:**

- Pyrometallurgy: Using thermodynamic principles of reduction of oxides
- Electrometallurgy: Using electrochemical principles
- Hydrometallurgy: Using displacement reaction by dissolving ore in a suitable solution

1. Pyrometallurgy:

Oxides are easy to reduce. Thus in general 2 steps involved in extraction are:

- Conversion to oxides
- Reduction of oxides to respective metals

Conversion to oxides: Via Calcination or roasting

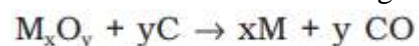
Calcination	Roasting
Heating in absence of air below melting point. Volatile materials evaporate leaving the metal oxide in the furnace	Heating in presence of air below melting point of metal
<p>Eg:</p> $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O(s)} \xrightarrow{\Delta} \text{Fe}_2\text{O}_3(\text{s}) + x\text{H}_2\text{O(g)}$ $\text{ZnCO}_3(\text{s}) \xrightarrow{\Delta} \text{ZnO(s)} + \text{CO}_2(\text{g})$ $\text{CaCO}_3 \cdot \text{MgCO}_3(\text{s}) \xrightarrow{\Delta} \text{CaO(s)} + \text{MgO(s)} + 2\text{CO}_2(\text{g})$	<p>Eg: Sulphide ores</p> $2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2$ $2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2$ $2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$ <p>NOTE: On roasting copper matte ($\text{Cu}_2\text{S} + \text{FeS}$) in a reverberatory furnace lined with silica, FeO and Cu_2O are formed. FeO combines with silica and is removed as iron silicate, also called slag.</p>



NOTE: Flux is the external compound that is added to remove impurities. Flux combines with impurity to form slag which is separated out.

➤ **Reduction of oxides to respective metals:**

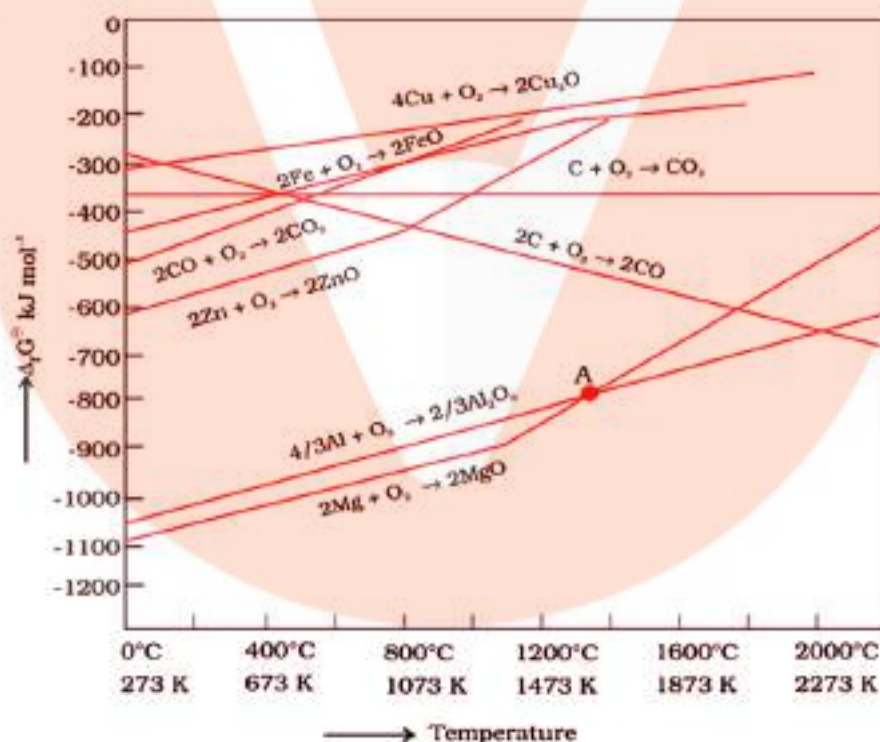
Oxides are heated with strong reducing agents like C, CO etc.



Reduction of metals not only depends on the reducing agent used but also depends on the temperature of reduction. The temperature requirement and the reducing agent to be used can be predicted using gibbs free energy. ΔG for the net reaction should be -ve for the reaction to proceed forward.

➤ **Ellingham diagram:**

- Graphical representation of gibbs free energy. Helps in predicting feasibility of thermal reduction of ore at a specified temperature thereby helps in choosing appropriate reducing agents.



- Interpretation of plot:**

It plots $\Delta_r G$ Vs T for the formation of oxides. Relation between ΔG and T is given below

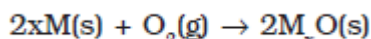
$$\Delta G = \Delta H - T\Delta S$$

Thus, the plot is a straight line.

Slope = $-\Delta S$

Y-intercept = ΔH

Note-1: In general ΔS of the reaction is -ve because the randomness decreases from the reactants to products (Have a look at the reaction below to understand)



Thus, slope of the reaction becomes positive (since $\Delta S = -ve$)

Note-2: ΔH & ΔS values for any chemical reaction remain nearly constant even on varying temperature. Thus, the slope of the plot remains constant with change in temperature.

However, ΔS depends on the physical state of the compound and increases if a compound melts ($s \rightarrow l$) or vapourises ($l \rightarrow g$) due to increase in molecular randomness.

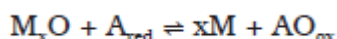
In the plot of ZnO and MgO, the abrupt change in slope i.e abrupt change in ΔS indicates change in phase ($s \rightarrow liq$ or $liq \rightarrow g$). Eg: In the ZnO plot, the change in slope indicates melting.

- **Criteria for selection of reducing agent:**

- The reducing agent and temperature should be chosen in such a way that the combined reaction results in $\Delta G_{\text{reaction}} < 0$. Example calculation is given below:
- In general, ΔG line of reducing agent should be present below the plot of metal oxide for it to reduce the metal oxide.
- Reducing agent selection also depends on the economic viability along with thermodynamic feasibility. Eg: Magnesium can be used to reduce Alumina (Al_2O_3) at $T < 1200^\circ C$ as per the thermodynamic feasibility. But it is still not used because it is uneconomic.
- Constructing similar diagrams for sulphides and halides, helps us understand the reason behind the difficulty in reducing sulphides and halides.

➤ **Limitations of Ellingham Diagram:**

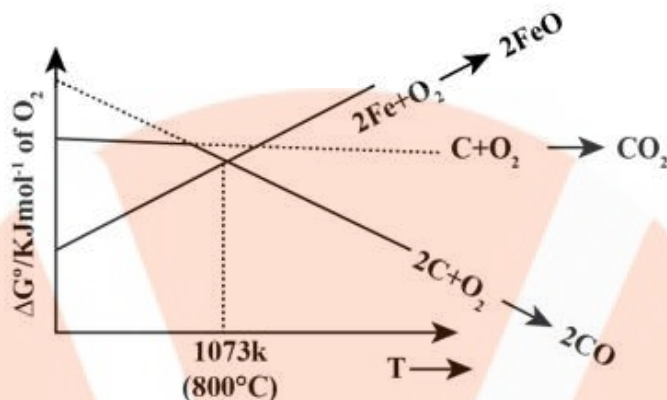
- Talks only about thermodynamics of the reaction but not the kinetics of reaction.
- Assumes reactants and products are in equilibrium because the value of ΔG is interpreted based on equilibrium constant ($\Delta G^\circ = -RT \ln K$).



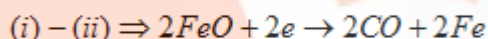
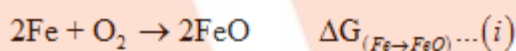
➤ **Extraction of iron from iron oxide ores:**

- **Procedure:** Iron ores are calcinated/roasted (to remove water, decompose carbonates, oxidise sulphides) to form Fe_2O_3 . Fe_2O_3 are mixed with coke and $CaCO_3$ and fed to the **blast furnace** from the top to reduce iron oxides to iron. Also note that the impurities such as S, As, Sb etc are removed via roasting as their oxides.
- **Thermodynamics and reactions in blast furnace:**
 1. **Thermodynamics involved in reduction of iron oxide:**

- ❖ FeO can be reduced using 'C' at a temperature $T > 800^{\circ}\text{C}$ or 1073K. Also note that FeO can also be reduced using CO at specific temperature ranges (For proof use ellingham diagram).
- ❖ Fe_2O_3 can be reduced using 'CO' at much lower temperature ranges in between 500-800K.
- ❖ Example for thermodynamic calculation of reduction of iron oxide: FeO reduction by coke:
- ❖ Consider reduction of FeO using 'C' from ellingham diagram



At $T > 1073 \text{ K}$:



$$\Delta G_{\text{rxn}} = \Delta G_{(\text{C} \rightarrow \text{CO})} - \Delta G_{(\text{Fe} \rightarrow \text{FeO})}$$

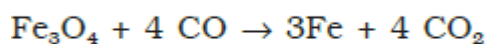
$$\text{when } T > 1073 \text{ K}, \Delta G_{(\text{C} \rightarrow \text{CO})} > \Delta G_{(\text{Fe} \rightarrow \text{FeO})}$$

$$\therefore \Delta G_{\text{rxn}} < 0$$

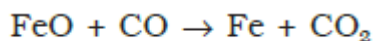
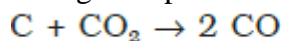
\therefore At $T > 1073 \text{ K}$, reduction of FeO using coke is feasible.

2. Blast furnace construct and reduction reactions:

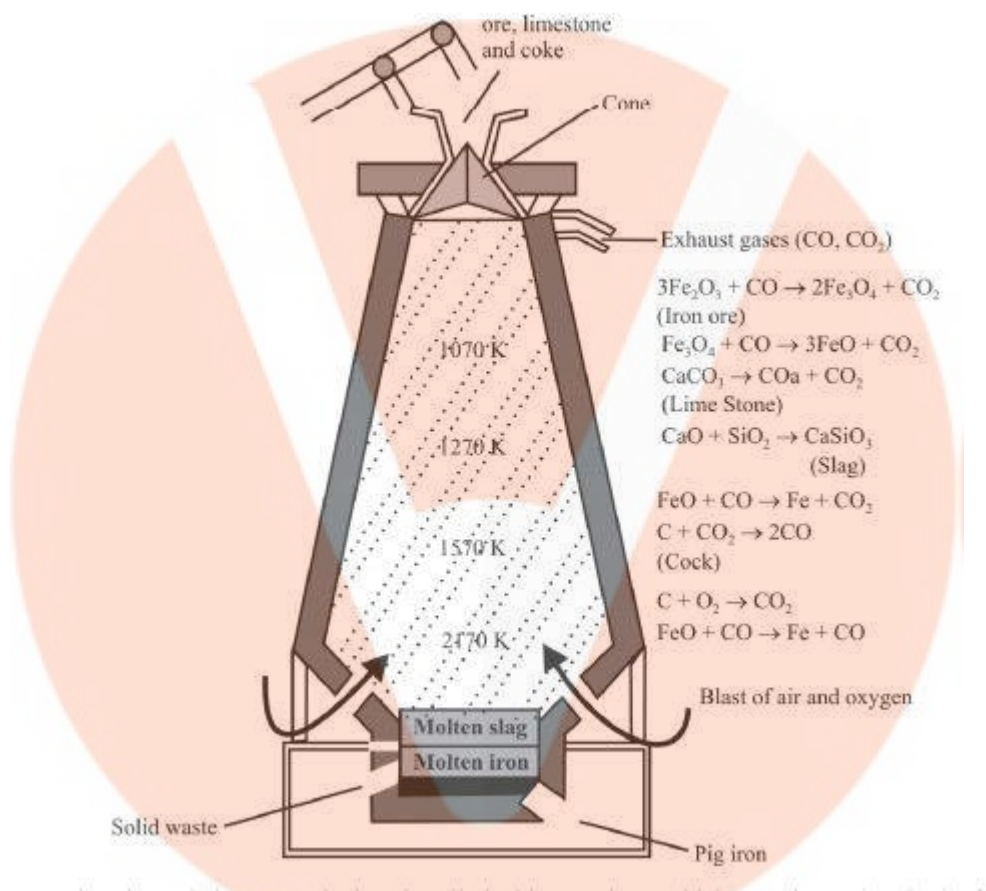
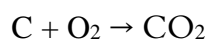
- ❖ In a blast furnace a temperature gradient is present from top to bottom. (Top of the furnace is at low temperature ($\cong 500\text{K}$) and bottom is at high temperature ($\cong 2200\text{K}$)).
- ❖ **Generation of temperature gradient in blast furnace:**
Hot air is blown at the bottom of the furnace and coke added from the top undergoes oxidation due to hot air creating a high temperature zone. As we move up in the furnace the temperature decreases and thereby creates a temperature gradient along the height of the furnace.
- ❖ **Reactions in different temperature zones of the furnace:**
At low temperature zone (500-800K)



At high temperature zone (900-1500K):



At very high temperature zone



❖ **Impurities removal:**

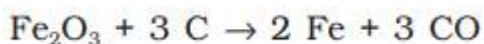
CaCO_3 decomposes at high temperature inside the furnace forming CaO which combines with silica impurities and forms CaSiO_3 which is removed as slag.

● **Types of iron:**

Pig iron: The iron obtained from blast furnace is called pig iron. Consist of 4% carbon and many impurities in smaller amounts (e.g., S, P, Si, Mn).

Cast iron: Melting pig iron with scrap iron and coke using hot air blast. Consist of 3% of carbon and is hard and brittle

Wrought iron: Purest form of commercial iron. By oxidising impurities of cast iron in a reverberatory furnace lined with haematite. Also limestone is added as flux which removes S, Si, P oxides in the form of slag. Metal is then separated from slag



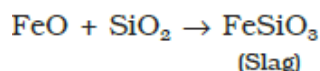
➤ **Extraction of Copper from cuprous oxide:**

● **Thermodynamics involved:**

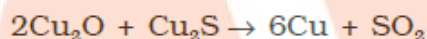
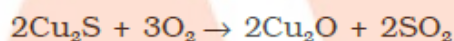
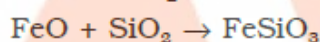
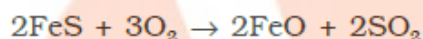
- ❖ From Ellingham diagram Cu_2O line is almost at the top and can be easily reduced by C, CO at low temperatures 500-600K

● **Procedure and reactions involved:**

- ❖ Copper ores usually consist of FeS as major impurity. During roasting of the ore in a reverberatory furnace, the conditions are maintained in such a way that majority FeS is converted into FeO with a minor conversion of Cu_2S to Cu_2O . Now FeO is removed as slag by adding SiO_2 as flux.



- ❖ Thus from reverberatory furnace copper matte is obtained which consist of FeS (minor) and Cu_2S (major)
- ❖ Copper matte is charged into a converter which is lined with silica. Following reactions take place:

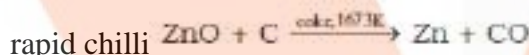


The solidified copper obtained is called blister copper as it has a blistered surface due to SO_2 evolution.

➤ **Extraction of Zn from Zn oxide:**

● **Procedure:**

- ❖ Reduced using coke at higher temperature compared to Cu. ZnO is made into brickettes with coke and clay and reduced. Metal is then distilled and collected by rapid chilli

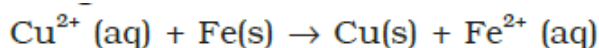


● **Electrometallurgy:**

- ❖ Molten metal salts are reduced to metal via electrolysis. For the reduction to be possible $\Delta G < 0$. It follows the relation:

$$\Delta G^\ominus = -nE^\ominus F$$

For $\Delta G < 0$, $E_{\text{net}}^0 > 0$. Consider the following example



The above reaction has $E_{\text{net}}^0 > 0$, thus Cu^{2+} can be reduced Fe(s).

- ❖ The less reactive metals move into the solution and more reactive metals move into solution.
- ❖ M^{n+} are reduced and deposited at the negative electrode/ cathode.
- ❖ Precautions should be taken so that suitable materials are chosen for electrodes in such a way that they won't react with metal.
- ❖ Flux can be added to make molten mass more conducting.

➤ **Extraction of 'Al' from Al_2O_3 :**

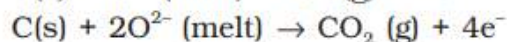
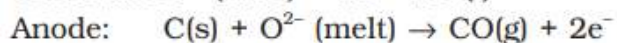
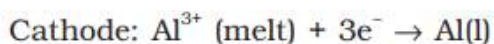
● **Hall-Heroult process:**

Electrolysis of Al_2O_3 to extract 'Al'. Lowering of melting point of Al_2O_3 and increasing conductivity is done by adding Na_3AlF_6 or CaF_2 . Fused material is electrolysed in a steel vessel lined with carbon.

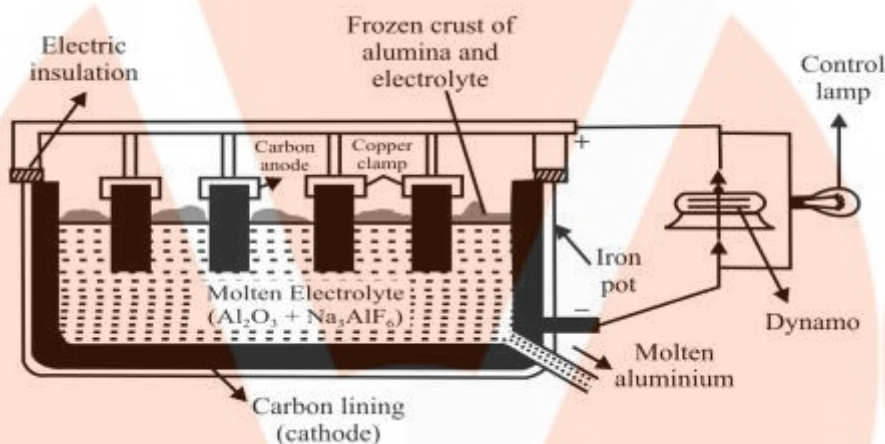
Cathode: Carbon

Anode: Graphite

Reactions

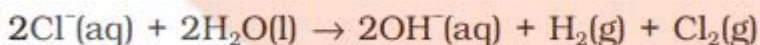


Overall reaction:



➤ **Extraction of Cl_2 from brine solution:**

- In general extractions from ore involves reduction of the ore. But extraction of chlorine involves oxidation (Even leaching of gold involves oxidation of $\text{Au} \rightarrow \text{Au}^+$ and then reduced to Au using Zn). For Chlorine, Brine solution is electrolysed to obtain chlorine gas and NaOH as byproduct.



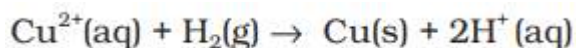
- Mathematically it requires external emf $V > 2.2\text{V}$ because E^0 of the reaction = -2.2V . But usually it requires an excess potential to overcome some other hindering reactions from occurring. Because of this electrolysis of molten NaCl is performed. In that case instead of NaOH, Na metal is obtained along with chlorine gas.

➤ **Hydrometallurgy:**

- The ore is dissolved in a suitable solvent and then ore is converted into metal via displacement reaction.

➤ **Extraction of Cu from low grade ores.**

- By treating it with scrap iron or H_2 .



- Instead of using scrap iron, using scrap Zn will ease out the reduction process because Zn is present above iron in the electrochemical series. But still iron is used because the cost associated with Zn is high.

➤ **Purification of metal/ Refining:**

- Different types include:

(a) Distillation	(b) Liquation
(c) Electrolysis	(d) Zone refining
(e) Vapour phase refining	(e) Chromatographic methods

(a) Distillation:

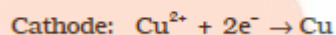
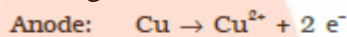
- For low boiling point metals: Zn & Hg.
- The impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation:

- For low melting point metals: Tin
- Flown through a sloping surface and separated from higher Melting point impurities.

(c) Electrolytic refining:

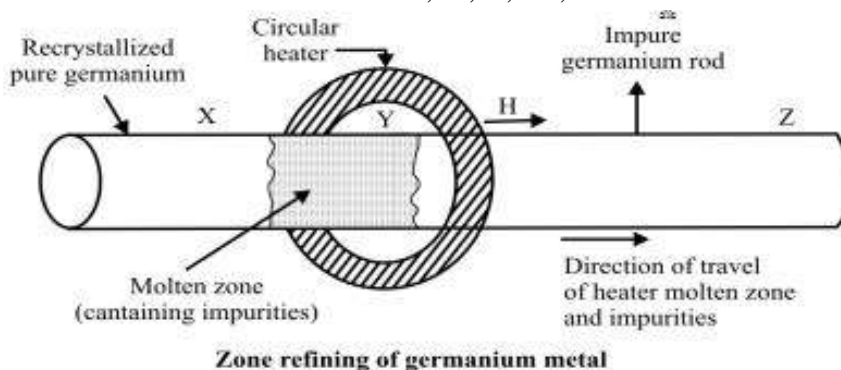
- Cathode: pure metal, Anode: impure metal, electrolytic solution: Soluble salt of same metal
- Example: Zn refining, Cu refining using CuSO_4 as electrolytic solution etc. Cu refining reactions are shown below



- Impurities (Sb, Se, Te, Au, Ag, Pt) deposit as anode mud

(d) Zone refining:

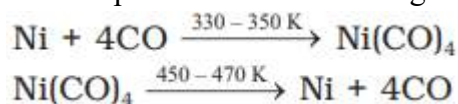
- **Principle:** impurities are more soluble in melt form than in solid state
- Circular mobile heater fixed at one end of the impure metal rod is made to move along the rod. As the heater moves the metal rod melts and pure metal crystallizes out of the melt and impurities pass along with the heater. All the impurities get concentrated at one end of the rod and it is cut off.
- Produces high purity of metals.
- Used for semiconductor materials like Ge, Si, B, Ga, In



(e) **Vapour phase refining:**

- **Principle:** Metal is converted into a volatile compound by adding suitable reagent. The volatile compound is decomposed again to form metal.
- **Requirements:** Metal should form a volatile compound when a suitable reagent is added and volatile compound should be easily decomposable.
- Examples:

❖ Mond's process for 'Ni' refining:



❖ Van arcel method for 'Zr' or 'Ti' refining: For removing impurities oxygen and nitrogen



Note: ZrI_4 being more covalent volatilises and then is heated on a tungsten filament to 1800K to produce pure Zr

(f) **Chromatographic methods:**

- **Principle:** Different components of mixture can be adsorbed by different adsorbents. The impure metal mixture is put in a liquid or gaseous medium and is moved through an adsorbent column. Different components of the mixture are adsorbed at different levels on the column. All the adsorbed components can be removed/ eluted by adding suitable solvents called elutants.
- Column of chromatography consists of 2 phases: mobile phase and stationary phase. Eg: Al_2O_3 column.
- **Mobile phase** - gas or liquid or a supercritical fluid, **Stationary phase:** Immobile phase Eg: Al_2O_3 column in column chromatography. Components of both the phases are chosen such that components of the sample will have different solubilities in both phases.
- Mobile phase along with the metal sample is moved through the stationary phase. Components soluble in stationary phase take longer to cross the travel, whereas component soluble in mobile phase travels faster and moves out of the column first thereby separating both the components.
- Depending upon the two phases and the way the sample is inserted/injected, the chromatographic technique is named. Eg: Gas chromatography, paper chromatography, column chromatography

Eg: Column chromatography: Stationary phase- Al_2O_3 is prepared in a glass tube, Mobile phase- liquid form. Used for purification of elements available in minute quantities and not very different in chemical properties from the element to be purified.

The p-Block Elements

Group 15 & 16

- Diversity in chemistry of p-block elements: due to their ability to react with the elements of s-, d- and f-blocks as well as with their own.
- Group 15: nitrogen, phosphorus, arsenic, antimony, bismuth and moscovium N & P- non-metals, As & Sb- metalloids, Bi & Mc are typical metals. (Metallic character increases down the group).

➤ Occurrence:

- N occurs as NaNO₃ (called Chile saltpetre), potassium nitrate (Indian saltpetre).
- Found in the form of proteins in plants and animals.
- P occurs in minerals of the apatite family, Ca₉(PO₄)₆.CaX₂ (X = F, Cl or OH)
- As, Sb and Bi are found mainly as sulphide minerals.
- Mc has a very short half-life and availability in very little amount.
- Refer to the following table for atomic and physical properties of group 15 elements

Property	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass/g mol ⁻¹	14.01	30.97	74.92	121.75	208.98
Electronic configuration	[He]2s ² 2p ³	[Ne]3s ² 3p ³	[Ar]3d ¹⁰ 4s ² 4p ³	[Kr]4d ¹⁰ 5s ² 5p ³	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
Ionisation enthalpy (ΔH/(kJ mol ⁻¹))	I	1402	1012	947	703
	II	2856	1903	1798	1595
	III	4577	2910	2736	2443
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius/pm ^a	70	110	121	141	148
Ionic radius/pm	171 ^b	212 ^b	222 ^b	76 ^c	103 ^c
Melting point/K	63 [*]	317 ^d	1089 ^e	904	544
Boiling point/K	77.2 [*]	554 ^d	888 ^f	1860	1837
Density/[g cm ⁻³ (298 K)]	0.879 ^h	1.823	5.778 ^h	6.697	9.808

^a E⁴⁺ single bond (E = element); ^b E³⁺; ^c E³⁺; ^d White phosphorus; ^e Grey α-form at 38.6 atm; ^f Sublimation temperature; ^g At 63 K; ^h Grey α-form; ⁱ Molecular N₂.

- All the elements of this group are polyatomic.
- Dinitrogen is a gas while all others are solids.
- Except nitrogen, all the elements show allotropy.
- Oxidation states and trends in chemical reactivity:
- Most common ox states: -3, +3 and +5.
- Bi hardly forms any compound in -3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF₅.
- Besides +5 oxidation state, nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.
- In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution



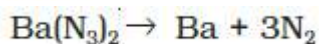
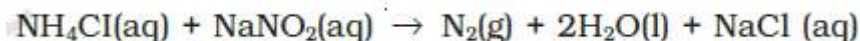
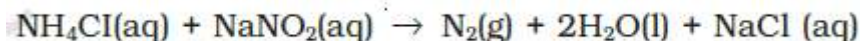
- P also shows +1 and +4 oxidation states in some oxoacids. nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid
- +3 oxidation state in case of As, Sb and Bi does not disproportionate.
- Max covalency of N: 4
- Heavier elements can expand their covalency due to the presence of d orbitals. E.g. PF_6^- .
- Anomalous properties of nitrogen
- small size, high electronegativity, high ionisation enthalpy and non-availability of d orbitals.
- $p\pi - p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).
- P, As and Sb form single bonds as P–P, As–As and Sb–Sb while Bi forms metallic bonds in elemental state.
- N cannot form $d\pi - p\pi$ bond as the heavier elements can e.g., $\text{R}_3\text{P} = \text{O}$ or $\text{R}_3\text{P} = \text{CH}_2$ (R = alkyl group).
- P and As can form $d\pi - d\pi$ bond also with transition metals when their compounds like $\text{P}(\text{C}_2\text{H}_5)_3$ and $\text{As}(\text{C}_6\text{H}_5)_3$ act as ligands.
- Reactivity towards hydrogen: EH_3 where E = N, P, As, Sb or Bi.
- Reducing character of the hydrides increases down the group (BiH_3 is the strongest reducing agent)
- Basicity decreases in the order $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$.

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	–
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) Distance/pm	101.7	141.9	151.9	170.7	–
HEH angle ($^\circ$)	107.8	93.6	91.8	91.3	–
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	–46.1	13.4	66.4	145.1	278
$\Delta_{\text{comb}} H^\circ (\text{E–H}) / \text{kJ mol}^{-1}$	389	322	297	255	–

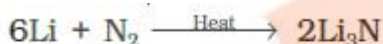
- Reactivity towards oxygen: two types of oxides: E_2O_3 and E_2O_5 .
- the higher oxidation state of the element is more acidic in its oxide form
- N_2O_3 and P_2O_3 are acidic.. As_2O_3 and Sb_2O_3 are amphoteric, Bi_2O_3 - basic
- Reactivity towards halogens: EX_3 and EX_5
- Pentahalides are more covalent than trihalides.
- Trihalides of these elements except those of nitrogen are stable.
- In the case of nitrogen, only NF_3 is known to be stable.
- Trihalides except BiF_3 are predominantly covalent in nature
- Reactivity towards metals: Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).
- Dinitrogen: colourless, odourless, tasteless and non-toxic gas. b.p. 77.2 K

- Preparation:

➤ **Laboratory method:**



- Two stable isotopes: ^{14}N and ^{15}N .
- N_2 is inert at room temperature, however at higher temperatures, it directly combines with some metals to form nitrides



- Haber's Process to form ammonia:

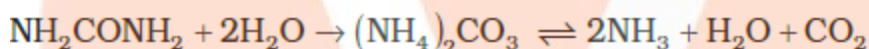


- Dinitrogen combines with dioxygen at around 2000K temp

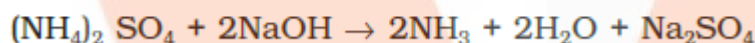
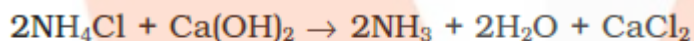


- Ammonia: colourless gas with a pungent odour

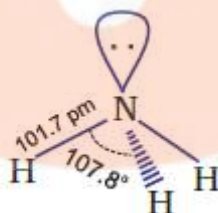
Preparation: from urea



➤ **Small scale production:**



- Large scale production: Haber process
- Shape: trigonal pyramidal



- Highly soluble in water. Its aqueous solution is weakly basic in nature

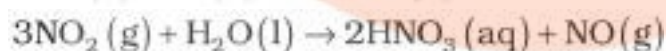
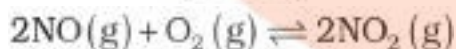
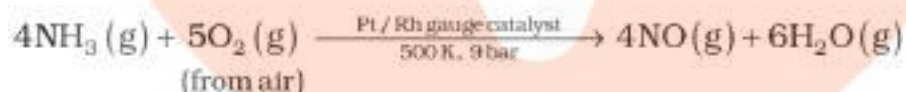
$$\text{NH}_3\text{(g)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^+\text{(aq)} + \text{OH}^-\text{(aq)}$$
- NH_3 forms ammonium salts with acids, e.g., NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, etc. As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.

Structures of Oxides of Nitrogen		
Formula	Resonance Structures	Bond Parameters
N ₂ O	$\ddot{\text{N}}=\ddot{\text{N}}=\ddot{\text{O}} \longleftrightarrow \text{:N}\equiv\text{N}-\ddot{\text{O}}\text{:}$	$\text{N}-\text{N}-\text{O}$ 113 pm 119 pm linear
NO	$\text{:N}=\ddot{\text{O}}\text{:} \longleftrightarrow \text{:}\dot{\text{N}}=\ddot{\text{O}}\text{:}$	$\text{N}-\text{O}$ 115 pm
N ₂ O ₅		 Planar
NO ₂		 Angular
N ₂ O ₄		 Planar
N ₂ O ₃		 Planar

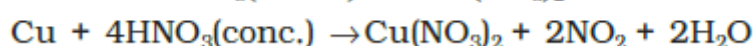
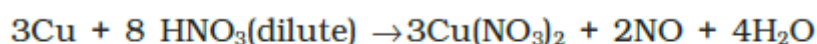
- Nitric oxide: HNO₃ colourless liquid
 $\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$

➤ **Laboratory method:**

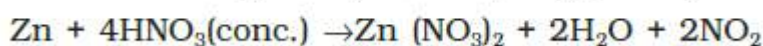
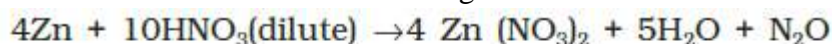
Large scale: Ostwald's process



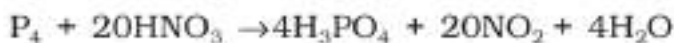
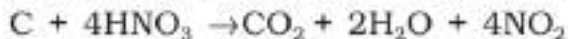
- Conc nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum.
- Products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.



- Zinc reacts with dilute nitric acid to give N₂O and with concentrated acid to give NO₂.

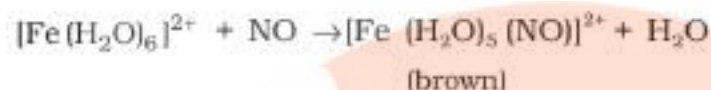
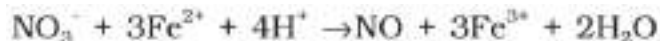


- Concentrated nitric acid also oxidises non-metals and their compounds.

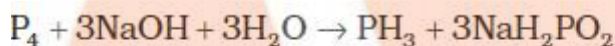


➤ Brown Ring Test:

the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex.

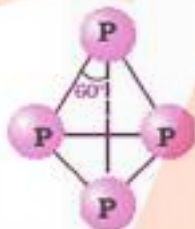


- Phosphorous: Allotropes -white, red and black.
- White phosphorus: poisonous, insoluble in water but soluble in CS_2 . Glows in dark (chemiluminescence).
- It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 .

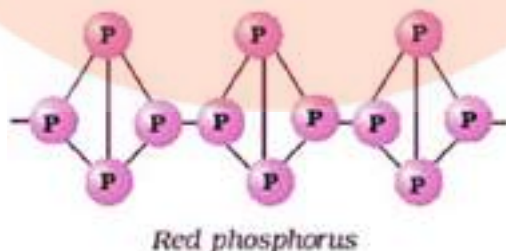


(sodium hypophosphite)

- White P is more reactive than red P because of angular strain in the P_4 molecule (60°). It readily catches fire in air to give dense white fumes of P_4O_{10} .

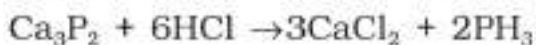
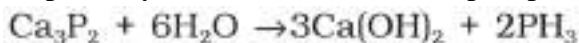


- Red P (iron grey lustre) is obtained by heating white P at 573K in an inert atmosphere for several days.

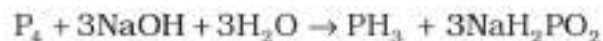


- Red P is odourless, nonpoisonous and insoluble in water as well as in carbon disulphide.
- Red P is much less reactive than white phosphorus.
- It does not glow in the dark
- It is polymeric, consisting of chains of P_4 tetrahedra linked together
- Black phosphorus - α -black and β -black phosphorus.
- α -Black phosphorus is formed when red P is heated in a sealed tube at 803K.

- β -Black phosphorus is prepared by heating white P at 473 K under high pressure
- Phosphine: colourless gas with rotten fish smell and is highly poisonous
- Prepared by the reaction of calcium phosphide with water or dilute HCl.



- In the laboratory: by heating white P with conc NaOH solution in an inert atmosphere of CO_2

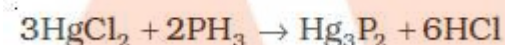


(sodium hypophosphite)

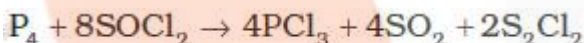
- Pure PH_3 is obtained by adsorbing impure PH_3 in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.



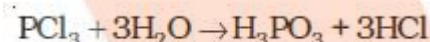
- The solution of PH_3 in water decomposes in presence of light giving red P and H_2 .
- Ph_3RX with CuSO_4 or HgCl_2 solution produce corresponding phosphides



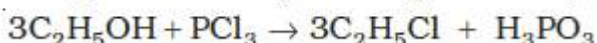
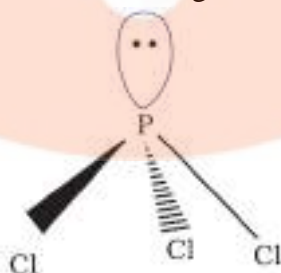
- Phosphorus halide: two types of halides, PX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and PX_5 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$).
- Phosphorus chloride: pyramidal shape and phosphorus is sp^3 hybridised.
- Obtained by passing dry chlorine over heated white phosphorus or by the action of thionyl chloride with white phosphorus.



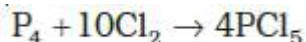
- Colourless oily liquid and hydrolyses in the presence of moisture



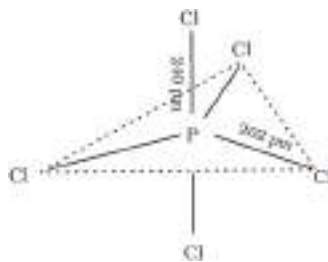
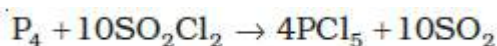
- It reacts with organic compounds containing $-\text{OH}$ group



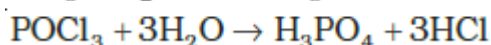
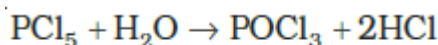
- PCl_5 : trigonal bipyramidal structure
- yellowish white powder, prepared by the reaction of white P with excess of dry chlorine



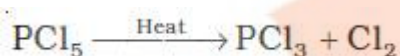
- By the action of SO_2Cl_2 on phosphorus



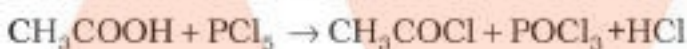
- PCl_5 reacts with moist air to give $POCl_3$ and finally gets converted to phosphoric acid



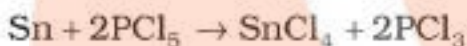
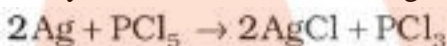
- When heated, it sublimes but decomposes on strong heating.



- Reacts with organic compounds containing $-OH$ group converting them to chloro derivatives.



- Finely divided metals on heating with PCl_5 give corresponding chlorides.



- The three equatorial $P-Cl$ bonds are equivalent, while the two axial bonds are longer than equatorial bonds.

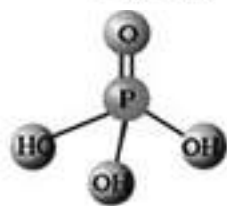
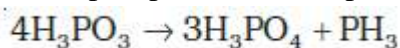
➤ Oxoacids of P:

- Refer the following table for the important oxoacids of phosphorus with their formulas, methods of preparation and the presence of some characteristic bonds in their structures

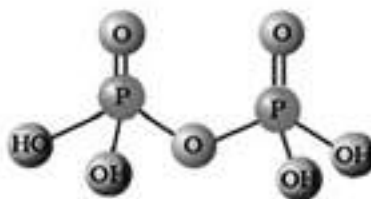
Oxoacids of Phosphorus				
Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One $P-OH$ Two $P-H$ One $P=O$	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two $P-OH$ One $P-H$ One $P=O$	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two $P-OH$ Two $P-H$ Two $P=O$	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four $P-OH$ Two $P=O$ One $P-P$	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three $P-OH$ One $P=O$	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four $P-OH$ Two $P=O$ One $P-O-P$	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	Three $P-OH$ Three $P=O$ Three $P-O-P$	phosphorus acid + $BeCl_2$, heat in a sealed tube

* Exists in polymeric forms only. Characteristic bonds of $H_2P_2O_7$ have been given in the Table.

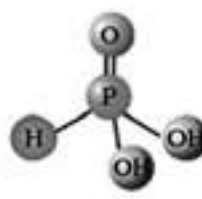
- Orthophosphorous acid (or phosphorous acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.



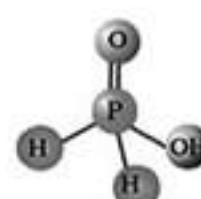
H_3PO_4
Orthophosphoric acid



$\text{H}_4\text{P}_2\text{O}_7$
Pyrophosphoric acid

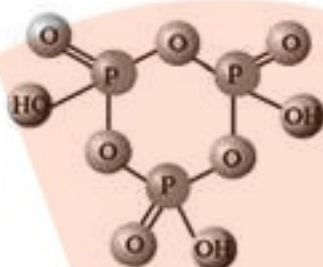


H_3PO_3
Orthophosphorous acid



H_3PO_2
Hypophosphorous acid

Structures of some important oxoacids of phosphorus



Cyclotrimetaphosphoric acid, $(\text{HPO}_3)_3$



Polymetaphosphoric acid, $(\text{HPO}_3)_n$

- Hypophosphorous acid is a good reducing agent as it contains two P–H bonds

$$4\text{AgNO}_3 + 2\text{H}_2\text{O} + \text{H}_3\text{PO}_2 \rightarrow 4\text{Ag} + 4\text{HNO}_3 + \text{H}_3\text{PO}_4$$
- Group 16: chalcogens, general electronic configuration: $ns^2 np^4$
- Oxygen, sulphur, selenium, tellurium, polonium and livermorium
- O & S- non-metals, Se & Te- metalloids, Po- metal and radioactive (Half-life 13.8 days).
- Occurrence: Oxygen forms about 46.6% by mass of earth's crust
- Refer to the following table for atomic and physical properties of group 16 elements

Some Physical Properties of Group 16 Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass/g mol ⁻¹	16.00	32.06	78.96	127.60	210.00
Electronic configuration	$[\text{He}]2s^2 2p^4$	$[\text{Ne}]3s^2 3p^4$	$[\text{Ar}]3d^{10} 4s^2 4p^4$	$[\text{Kr}]4d^{10} 5s^2 5p^4$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^4$
Covalent radius/(pm) ^a	66	104	117	137	146
Ionic radius, E ²⁻ /pm	140	184	198	221	230 ^b
Electron gain enthalpy, /Δ _{eg} H kJ mol ⁻¹	-141	-200	-195	-190	-174
Ionisation enthalpy (Δ _i H), /kJ mol ⁻¹	1314	1000	941	869	813
Electronegativity	3.50	2.58	2.55	2.01	1.76
Density /g cm ⁻³ (298 K)	1.32 ^c	2.06 ^d	4.19 ^e	6.25	–
Melting point/K	55	393 ^d	490	725	520
Boiling point/K	90	718	958	1260	1235
Oxidation states ^a	-2, -1, 1, 2	-2, 2, 4, 6	-2, 2, 4, 6	-2, 2, 4, 6	2, 4

^aSingle bond; ^bApproximate value; ^cAt the melting point; ^dRhombic sulphur; ^eHexagonal grey; ^fMonoclinic form, 673 K.

^{*} Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF₂ and O₂F₂ respectively.

- Sulphur exists primarily as sulphates such as gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, epsom salt $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, baryte BaSO_4 and sulphides such as galena PbS , zinc blende ZnS , copper pyrites CuFeS_2 .
- Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores
- Polonium occurs in nature as a decay product of thorium and uranium minerals.
- Livermorium is a synthetic radioactive element.
- Chemical properties:
- Oxidation state- Oxygen usually shows -2 oxidation state but +2 in OF_2
- Other elements of the group exhibit + 2, + 4, + 6 oxidation states
- Bonding in +4 and +6 oxidation states is primarily covalent.
- Reactivity with hydrogen: H_2E (E = O, S, Se, Te, Po).
- Refer to the following table for some properties of hydrides:

Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p/K	273	188	208	222
b.p/K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle ($^\circ$)	104	92	91	90
$\Delta_f H / \text{kJ mol}^{-1}$	-286	-20	73	100
$\Delta_{\text{diss}} H (\text{H-E}) / \text{kJ mol}^{-1}$	463	347	276	238
Dissociation constant ^a	1.8×10^{-18}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

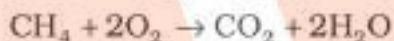
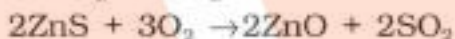
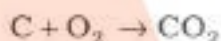
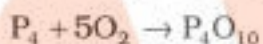
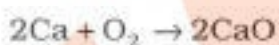
^a Aqueous solution, 298 K

- Acidic character increases from H_2O to H_2Te .
 - Thermal stability of hydrides decreases from H_2O to H_2Po .
 - All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te .
 - Reactivity with oxygen: EO_2 and EO_3 , E = S, Se, Te or Po. Both types are acidic in nature.
 - O_3 and SO_2 are gases while SeO_2 is solid.
 - SO_2 is reducing while TeO_2 is an oxidising agent.
 - Reactivity towards the halogens: EX_6 , EX_4 and EX_2
 - Amongst hexahalides, hexafluorides are the only stable halides.
 - Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons
 - SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid... sp^3d hybridised...TBP geometry.
 - The monohalides exist as dimer in nature, eg. S_2F_2 , S_2Cl_2 , S_2Br_2 , Se_2Cl_2 and Se_2Br_2 . and undergo disproportionation
- $$2\text{Se}_2\text{Cl}_2 \rightarrow \text{SeCl}_4 + 3\text{Se}$$
- Dioxygen: O_2 is a colourless and odourless gas

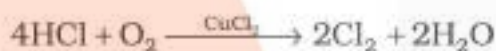
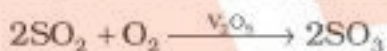
➤ **Laboratory preparation:**



- H_2O_2 is readily decomposed to H_2O and O_2 (Can be catalyzed by finely divided metals and manganese dioxide)
- On large scale it can be prepared from water or air
- Industrially, dioxygen is obtained from air
- Three stable isotopes: ^{16}O , ^{17}O and ^{18}O . O_2 is unique in being paramagnetic
- Oxygen-oxygen double bond strength is high ($493.4 \text{ kJ mol}^{-1}$).
- Some of the reactions of dioxygen with metals, non-metals and other compounds are given below.

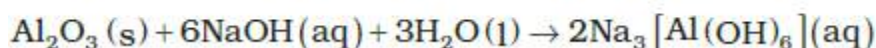
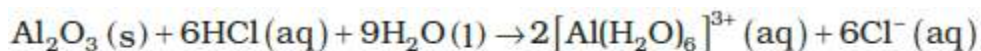


Some compounds are catalytically oxidised. For example,



➤ **Simple oxides:**

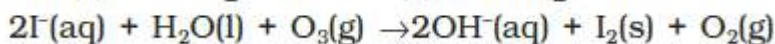
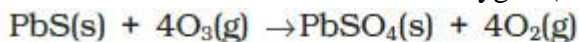
- An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO_2 , Cl_2O_7 , CO_2 , N_2O_5). For example, SO_2 combines with water to give H_2SO_3 , an acid.
- Non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn_2O_7 , CrO_3 , V_2O_5)
(metallic oxides are basic.) The oxides which give a base with water are known as basic oxides (e.g., Na_2O , CaO , BaO). For example, CaO combines with water to give Ca(OH)_2 , a base.
- In general, metallic oxides are basic. Some metallic oxides exhibit a dual behaviour. Eg Al_2O_3 .



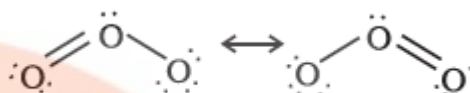
- Examples of neutral oxides are CO , NO and N_2O .
- Ozone: ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.
- Formation of ozone from oxygen is an endothermic process



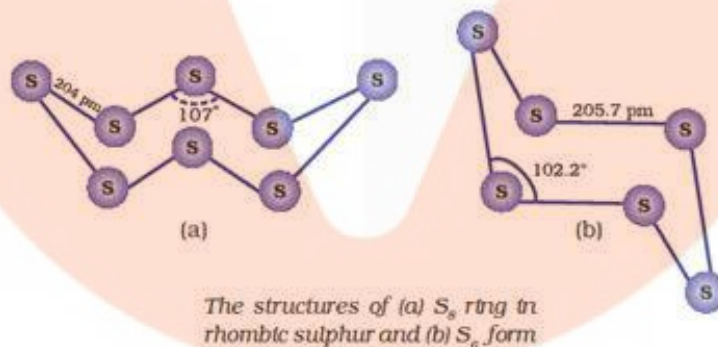
- Pure ozone is a pale blue gas, dark blue liquid and violet-black solid
- Ozone is thermodynamically unstable with respect to oxygen. Due to the ease with which it liberates atoms of nascent oxygen (O), it acts as a powerful oxidising agent.



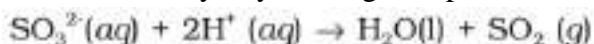
- Quantitative method for estimating O₃ gas: When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate
- Nitrogen monoxide combine very rapidly with ozone to produce NO₂ and O₂
- Oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117 degrees.



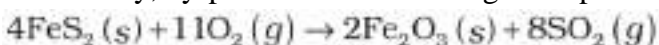
- Sulphur — Allotropic Forms: S₈ - yellow rhombic (α -sulphur) and monoclinic (β -sulphur) forms
- Rhombic sulphur is stable at room temperature and transforms to monoclinic sulphur when heated above 369 K.
- Rhombic sulphur: yellow in colour. Stable above 369 K It is readily soluble in CS₂. Monoclinic sulphur: prepared by melting rhombic sulphur in a dish and cooling.
- At 369 K both the forms are stable. This temperature is called transition temperature.
- At elevated temperatures (~1000 K), S₂ is the dominant species and is paramagnetic like O₂.
- The S₈ ring in both the forms is puckered and has a crown shape.



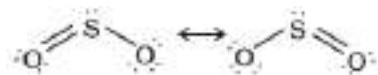
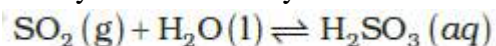
- Sulphur dioxide: SO₂ is angular... colourless gas with pungent smell
- Prepared when sulphur is burnt in air or oxygen
- In the laboratory: by treating a sulphite with dilute sulphuric acid



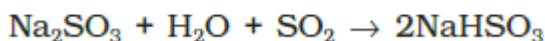
- Industrially, by-product of the roasting of sulphide ores



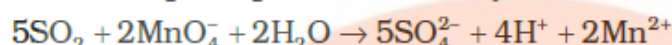
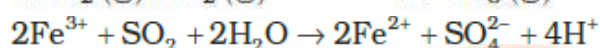
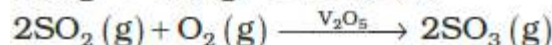
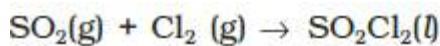
- Sulphur dioxide, when passed through water, forms a solution of sulphurous acid reacts readily with sodium hydroxide solution



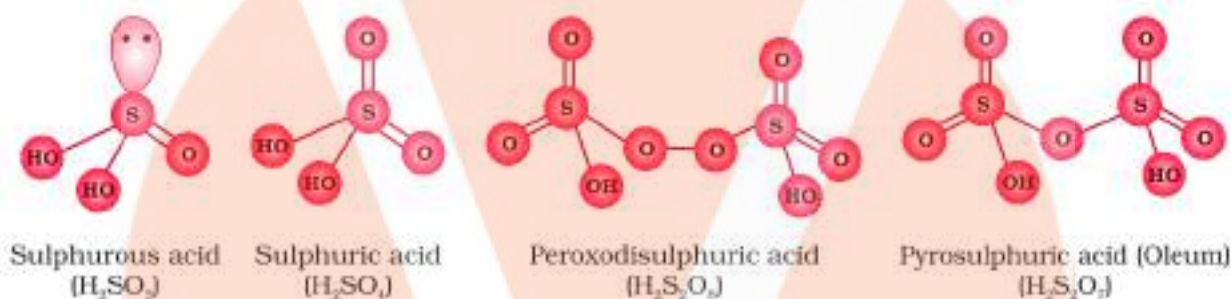
- SO₂ reacts readily with sodium hydroxide solution



- Sulphur dioxide reacts with chlorine to give sulphuryl chloride, SO₂Cl₂.
- It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.
- Moist sulphur dioxide behaves as a reducing agent

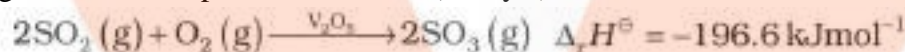


- Oxoacids of Sulphur: H₂SO₃, H₂S₂O₃, H₂S₂O₄, H₂S₂O₅, H₂S_xO₆ (x = 2 to 5), H₂SO₄, H₂S₂O₇, H₂SO₅, H₂S₂O₈

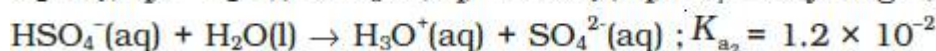


Structures of some important oxoacids of sulphur

- Sulphuric acid: manufactured by the Contact Process
- The key step in the manufacture of H₂SO₄ is the catalytic oxidation of SO₂ with O₂ to give SO₃ in the presence of V₂O₅ (catalyst).



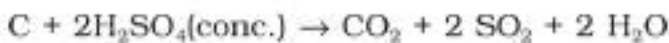
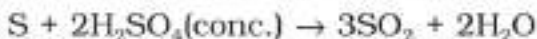
- The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume.
- Low temperature and high pressure are the favourable conditions for maximum yield.
- The sulphuric acid obtained by Contact process is 96-98% pure. Plant operates at a pressure of 2 bar and a temperature of 720 K.
- It's a colourless, dense, oily liquid
- Characteristics: (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent
- In aqueous solution, sulphuric acid ionises in two steps



- H₂SO₄ as a dehydrating agent..charring action on carbohydrates.



- Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2 .



Group 17 & 18

- Group 17: Halogens (salt producers), highly reactive non-metallic elements.
- Members: Fluorine, chlorine, bromine, iodine, astatine and tennessine (At & Ts are radioactive elements)
- Occurrence: F & Cl are fairly abundant.
- F: mainly as insoluble fluorides (fluorspar CaF_2 , cryolite Na_3AlF_6 and fluoroapatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$)
- Cl: deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.
- Refer to the following table for the atomic and physical properties of G-17 elements

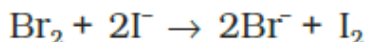
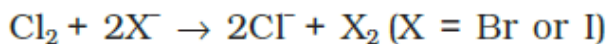
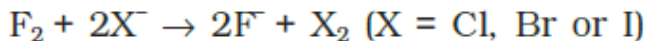
Atomic and Physical Properties of Halogens					
Property	F	Cl	Br	I	At*
Atomic number	9	17	35	53	85
Atomic mass/g mol ⁻¹	19.00	35.45	79.90	126.90	210
Electronic configuration	$[\text{He}]2s^2 2p^5$	$[\text{Ne}]3s^2 3p^5$	$[\text{Ar}]3d^{10} 4s^2 4p^5$	$[\text{Kr}]4d^{10} 5s^2 5p^5$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^5$
Covalent radius/pm	64	99	114	133	-
Ionic radius X ⁻ /pm	133	184	196	220	-
Ionisation enthalpy/kJ mol ⁻¹	1680	1256	1142	1008	-
Electron gain enthalpy/kJ mol ⁻¹	-333	-349	-325	-296	-
Electronegativity ^b	4	3.2	3.0	2.7	2.2
$\Delta_{\text{hyd}}H(\text{X})/\text{kJ mol}^{-1}$	515	381	347	305	-
	F_2	Cl_2	Br_2	I_2	-
Melting point/K	54.4	172.0	265.8	386.6	-
Boiling point/K	84.9	239.0	332.5	458.2	-
Density/g cm ⁻³	1.5 (85) ^c	1.66 (203) ^c	3.19(273) ^c	4.94(293) ^d	-
Distance X - X/pm	143	199	228	266	-
Bond dissociation enthalpy /(kJ mol ⁻¹)	158.8	242.6	192.8	151.1	-
E°/V	2.87	1.36	1.09	0.54	-

* Radioactive; ^b Pauling scale; ^c For the liquid at temperatures (K) given in the parentheses; ^d solid; ^e The half-cell reaction is $\text{X}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{X}(\text{aq})$.

➤ Chemical properties:

- All the halogens exhibit -1 oxidation state
- Cl, Br, and I exhibit +1, +3, +5 and +7 oxidation states
- Higher oxidation states are realised mainly when the halogens are in combination with F and O. e.g., in interhalogens, oxides and oxoacids

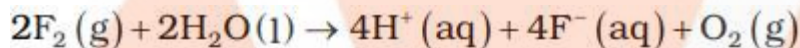
- Halogens react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.
- Ready acceptance of an electron cause halogen to be the strong oxidising agents
- F₂ is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase



➤ **The relative oxidising power of halogens:** evident from their standard electrode potentials their reactions with water

- Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. reaction of iodine with water is nonspontaneous

- I⁻ can be oxidised by oxygen in acidic medium



(where X = Cl or Br)



➤ **Anomalous behaviour of fluorine:**

- Most of the reactions of fluorine are exothermic
- It forms only one oxoacid while other halogens form a number of oxoacids.
- HF is a liquid (b.p. 293 K) due to strong hydrogen bonding
- Halogen (X) reactivity towards hydrogen: All for HX, but affinity for hydrogen decreases from fluorine to iodine
- HX dissolve in water to form hydrohalic acids.
- Acidic strength: HF < HCl < HBr < HI.
- Stability of these halides: H-F > H-Cl > H-Br > H-I.

Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting point/K	190	159	185	222
Boiling point/K	293	189	206	238
Bond length (H - X)/pm	91.7	127.4	141.4	160.9
$\Delta_{\text{ion}} H^\circ / \text{kJ mol}^{-1}$	574	432	363	295
pK_a	3.2	-7.0	-9.5	-10.0

- Reactivity towards oxygen: Halogens form many oxides but most of them are unstable.
- Fluorine forms two oxides OF₂ and O₂F₂. Only OF₂ is thermally stable at 298 K
- Both are strong fluorinating agents. O₂F₂ oxidises plutonium to PuF₆
- Decreasing order of stability of oxides formed by halogens, I > Cl > Br.
- Higher oxides of halogens tend to be more stable than the lower ones.

- Chlorine oxides, Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode.
- ClO_2 is used as a bleaching agent
- Bromine oxides- Br_2O , BrO_2 , BrO_3 are the least stable halogen oxides and are powerful oxidizing agents.
- Iodine oxides- I_2O_4 , I_2O_5 , I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.
- Reactivity towards metals: form metal halides
- The ionic character of the halides decreases in the order $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$
- Halides in higher oxidation state will be more covalent than the one in lower oxidation state. For example, SnCl_4 , PbCl_4 , SbCl_5 and UF_6 are more covalent than SnCl_2 , PbCl_2 , SbCl_3 and UF_4 respectively.
- Reactivity of halogens towards other halogens: interhalogens of the types XX' , XX_3' , XX_5' and XX_7' where X is a larger size halogen and X' is smaller size halogen.
- Chlorine: discovered in 1774 (greenish yellow)
- Preparation: By heating manganese dioxide with concentrated hydrochloric acid.

$$\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$$
- Or a mixture of common salt and concentrated H_2SO_4 is used in place of HCl

$$4\text{NaCl} + \text{MnO}_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{MnCl}_2 + 4\text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$$
- By the action of HCl on potassium permanganate

$$2\text{KMnO}_4 + 16\text{HCl} \rightarrow 2\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} + 5\text{Cl}_2$$

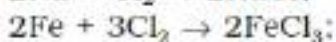
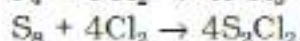
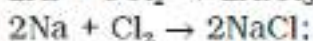
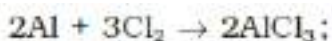
➤ **Manufacture of chlorine:**

- Deacon's process: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of CuCl_2 (catalyst) at 723 K

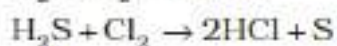
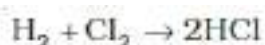
$$4\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}_2} 2\text{Cl}_2 + 2\text{H}_2\text{O}$$

➤ **Electrolytic process:**

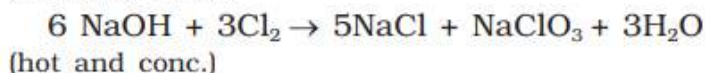
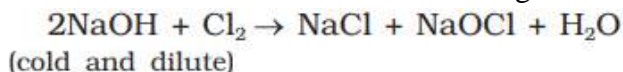
- Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution)
- Properties: It is a greenish yellow gas with pungent and suffocating odour
- 2-5 times heavier than air
- can be liquefied easily into greenish yellow liquid which boils at 239 K.
- It is soluble in water.
- Chlorine reacts with a number of metals and non-metals to form chlorides



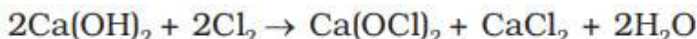
- has great affinity for hydrogen



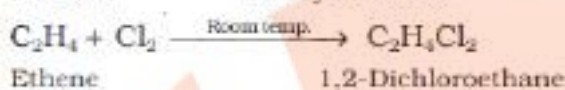
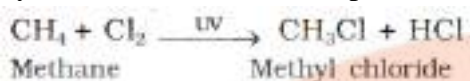
- With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.



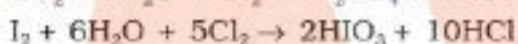
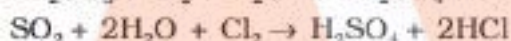
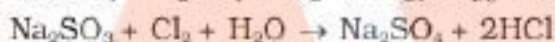
- With dry slaked lime it gives bleaching powder.



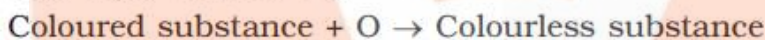
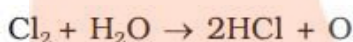
- Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons.



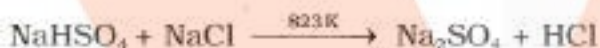
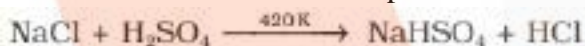
➤ **Chlorine as oxidising agent:**



- Chlorine is a powerful bleaching agent (permanent effect)

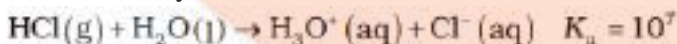


- Hydrogen Chloride: colourless and pungent smelling gas. Prepared by heating sodium chloride with concentrated sulphuric acid



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

- It is extremely soluble in water and ionises as follows:

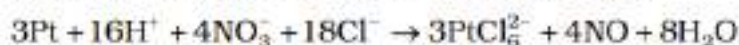
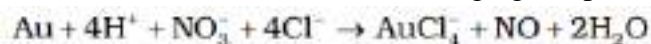


- Aqueous solution is called hydrochloric acid.

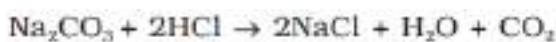
- High value of dissociation constant (K_a) indicates that it is a strong acid in water. It reacts with NH_3 and gives white fumes of NH_4Cl .

- Aqua regia: $3\text{HCl} + \text{HNO}_3$

It is used to dissolve noble metals, e.g., gold, platinum.



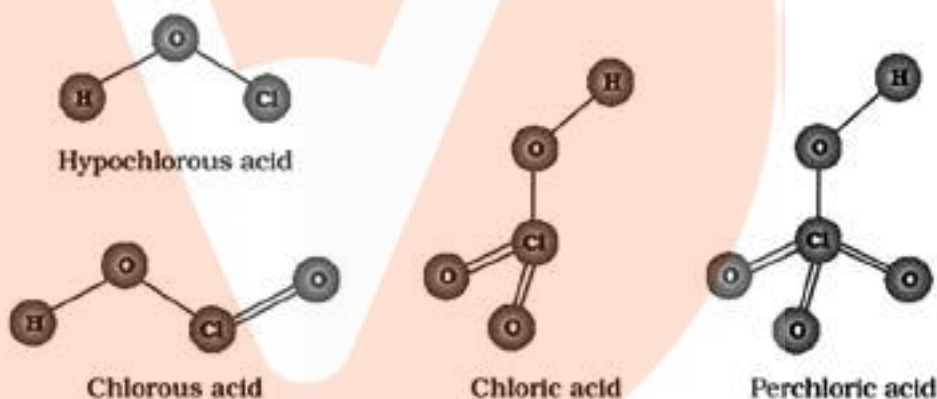
- Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.



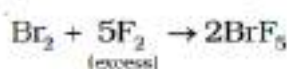
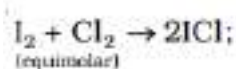
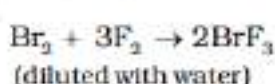
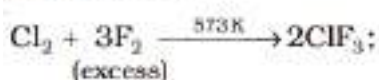
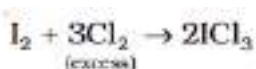
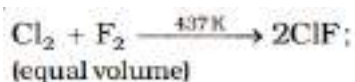
- Uses: (i) in the manufacture of chlorine, NH_4Cl and glucose (from corn starch), (ii) for extracting glue from bones and purifying bone black, (iii) in medicine and as a laboratory reagent.
- Oxoacids of Halogens: F forms only one oxo acid. HOF is known as fluoric (I) acid or hypofluorous acid.
- Several oxo acids of other halogens are possible but only stable in aqueous solutions or in the salt form.

Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	-	HOClO (chlorous acid)	-	-
Halic (V) acid (Halic acid)	-	HOClO ₂ (chloric acid)	HOBrO ₂ (bromic acid)	HOIO ₂ (iodic acid)
Halic (VII) acid (Perhalic acid)	-	HOClO ₃ (perchloric acid)	HOBrO ₃ (perbromic acid)	HOIO ₃ (periodic acid)



- Interhalogen compounds: Of the types XX' , XX_3' , XX_5' and XX_7' where X is a larger size halogen and X' is smaller size halogen.
- Iodine (VII) fluoride has maximum number of atoms as the ratio of radii between I and F should be maximum (IF₇).
- Prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions.



- These are all covalent molecules and are diamagnetic in nature. Only ClF is gas.
- Refer the following table for some properties of interhalogen compounds.

Some Properties of Interhalogen Compounds

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
			Square pyramidal
XX ₇	IF ₇	colourless gas	Pentagonal bipyramidal

^aVery unstable; ^bThe pure solid is known at room temperature; ^cDimerises as Cl-bridged dimer (I₂Cl₂)

- Physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.
- Interhalogen compounds are more reactive than halogens (except fluorine).
- Undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'3), halate (when XX'5) and perhalate (when XX'7) anion derived from the larger halogen.

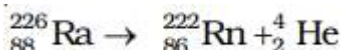


- Interhalogen compounds are very useful fluorinating agents. ClF₃ and BrF₃ are used for the production of UF₆ in the enrichment of ²³⁵U.



- Group 18: noble gases: helium, neon, argon, krypton, xenon, radon and oganesson
- All are gases and chemically unreactive.

- The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of ^{226}Ra .



- Oganesson has been synthetically produced by collision of ^{249}Cf atoms and ^{48}Ca ions



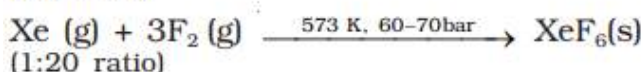
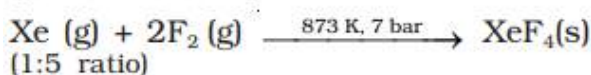
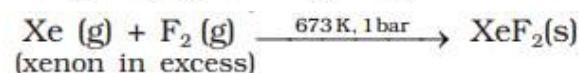
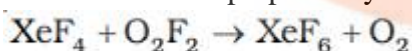
- Refer the following table for Atomic and Physical Properties of Group 18 Elements:

Atomic and Physical Properties of Group 18 Elements

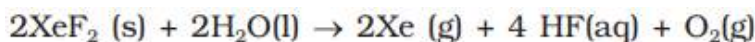
Property	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/ g mol ⁻¹	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	1s ²	[He]2s ² 2p ⁶	[Ne] 3s ² 3p ⁶	[Ar]3d ¹⁰ 4s ² 4p ⁶	[Kr]4d ¹⁰ 5s ² 5p ⁶	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
Atomic radius/pm	120	160	190	200	220	-
Ionisation enthalpy /kJmol ⁻¹	2372	2080	1520	1351	1170	1037
Electron gain enthalpy /kJmol ⁻¹	48	116	96	96	77	68
Density (at STP)/gcm ⁻³	1.8×10 ⁻⁴	9.0×10 ⁻⁴	1.8×10 ⁻³	3.7×10 ⁻³	5.9×10 ⁻³	9.7×10 ⁻³
Melting point/K	-	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10 ⁻⁴	-	1.82×10 ⁻³	0.934	1.14×10 ⁻⁴	8.7×10 ⁻⁶

* radioactive

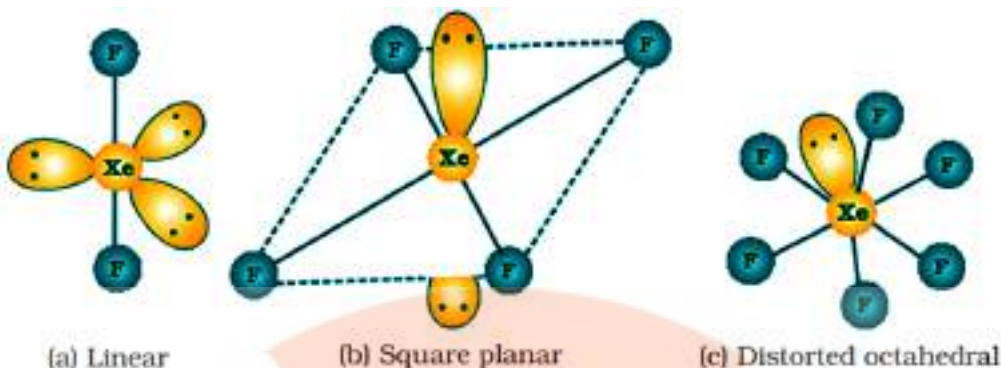
- Monoatomic, colourless, odourless and tasteless.
- Low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces
- Helium has the lowest boiling point (4.2 K) of any known substance.
- The first ionisation enthalpy of molecular oxygen (1175 kJmol⁻¹) was almost identical with that of xenon (1170 kJ mol⁻¹).
- A number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.
- Only the difluoride (KrF₂) has been studied in detail.
- Xenon-fluorine compounds: Xenon forms three binary fluorides, XeF₂, XeF₄ and XeF₆. XeF₆ can also be prepared by the interaction of XeF₄ and O₂F₂ at 143K.



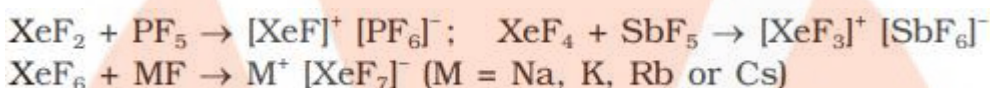
- XeF₂, XeF₄ and XeF₆ are colourless crystalline solids and sublime readily at 298 K.
- They are powerful fluorinating agents.
- Readily hydrolysed even by traces of water. For example, XeF₂ is hydrolysed to give Xe, HF and O₂.



- XeF_2 and XeF_4 have linear and square planar structures respectively.
- XeF_6 has seven electron pairs (6 bonding pairs and one lone pair)- distorted octahedral structure.

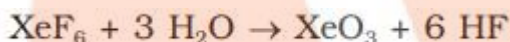


- Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

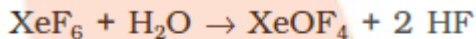


- Xenon-oxygen compounds:

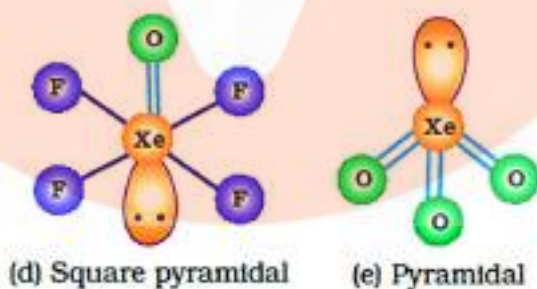
Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3 .



- Partial hydrolysis of XeF_6 gives oxyfluorides, XeOF_4 and XeO_2F_2 .



- XeO_3 is a colourless explosive solid and has a pyramidal molecular structure.
- XeOF_4 is a colourless volatile liquid and has a square pyramidal molecular structure.



The d & f block Elements

d - BLOCK elements

➤ General properties:

- Location: Group 3-12 (Total 10 groups), Period 4- 7 (Total 4 periods)
- Transition elements: Element with incompletely filled d orbitals in its ground state or in any one of its oxidation states.
- Named transition becoz they are flanked in between s and p block
- Zn, Cd, Hg are d-block elements but not transition elements.

3d series	Sc to Zn
4d series	Y to Cd
5d series	La to Hg (Omitting Ce to Lu)
6d series	Ac to - (Incomplete)

- d- orbitals are easily influenced by surrounding atoms and molecules compared to s or p
- Show horizontal similarities in the properties in contrast to s & p block elements

➤ Electronic configuration:

- General electronic configuration: $(n-1)d^{1-10}ns^{1-2}$.
- General electronic configuration has exceptions due to little energy difference between $(n-1)d$ and ns . **Eg:** Cr, Cu
- Outer electronic configuration of d- block elements

1st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

➤ **Physical properties:**

Metallic structures:

- Metallic lustre, ductile, malleable, high thermal and electrical conductivity
- More than one typical metallic structures at normal temperatures except Zn, Cd, Hg, Mn.
- Different lattice structures:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp (ccp, bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

(bcc = body centred cubic; hcp = hexagonal close packed;
ccp = cubic close packed; X = a typical metal structure).

- All elements are hard due to high metallic bonding except Zn, Cd, Hg.

➤ **Enthalpy of atomisation:**

- Higher $\Delta H_a \Rightarrow$ More noble the metal
- More number of unpaired valence $e^- \Rightarrow$ More number of e^- participating in metallic bonding \Rightarrow stronger metallic bonding \Rightarrow High ΔH_a (Except Mn, Tc due to their half filled stability)
- ΔH_a (2nd, 3rd series) $>$ ΔH_a (1st series), due to more frequent metal-metal bonding in 2nd, 3rd series elements.

➤ **Melting and boiling points:**

- High MP & BP, low volatility.
- **MP:**
More unpaired electrons \Rightarrow stronger metallic bonding \Rightarrow higher MP.
MP rises to max at d^5 (except Mn, Tc due to half filled stability and low metallic bonding) and then decreases.
- **BP:**
High $\Delta H_a \Rightarrow$ High BP.

➤ **Atomic and ionic size:**

- Period:
 - ❖ It decreases till Fe, remains constant till Ni, increases till Zn. This is due to interplay between screening effect and nuclear charge.
- Group:
 - ❖ 3d to 4d \Rightarrow increase

- ❖ 4d to 5d => Constant due to filling of 4f electrons => Increase in Z_{eff} => Regular decrease in radii compensates for the increase in size due to new shell addition.
- ❖ Lanthanide contraction: Regular decrease in radii due to increase in Z_{eff} becoz of intervention of 4f electrons.
- ❖ Net result of lanthanide contraction: 4d, 5d series same size (Eg: Zr, Hf) and very similar physical and chemical properties.

➤ **Density ($d = \text{mass/volume}$) :**

- Increases along the period i.e increase in mass dominates over the size (except Zn).

➤ **Ionisation enthalpy:**

- $IE_1 < IE_2 < IE_3$
- The magnitude of increase in 2nd and 3rd IE for the successive elements is much higher.
- **IE_1** : Increases from left to right with irregularities. Low IE of Cr can be attributed to half filled stability and high IE of Zn can be attributed to isonisation from 4s
- Unipositive ions have $d^n s^0$ configuration. By removing $1e^-$, the relative energies change and this leads to transferring of electron from 4s to 3d.
- The energy associated with the transfer of electron is called reorganization energy.

NOTE: Although IE's give some idea about relative stabilities of oxidation states but it is much more complex and cannot be generalised

➤ **Oxidation state (OS):**

- Variable oxidation states.
- Maximum OS shown = sum of d and s electrons (Till Mn)
- OS of 3d series:

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					

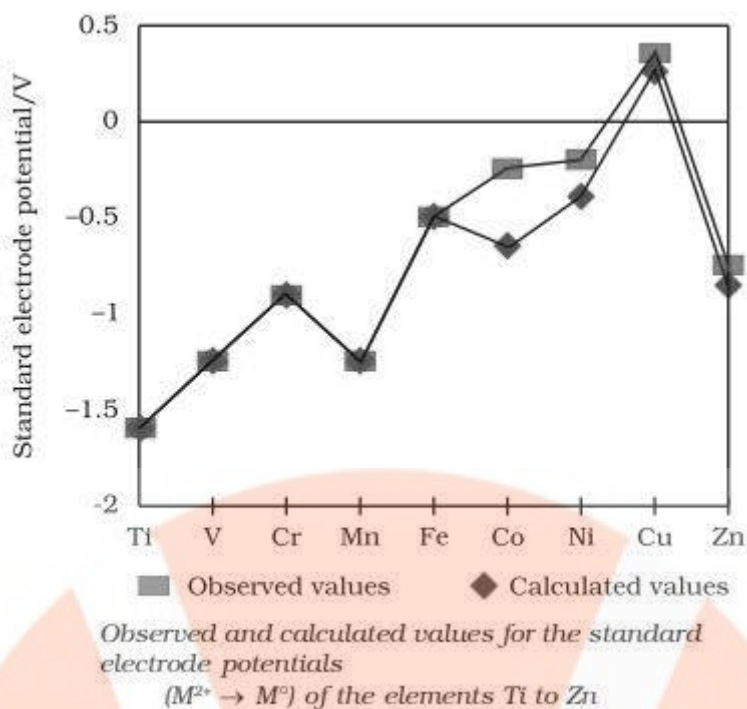
Most common ones are in bold.

- Maximum OS stability decreases from Mn to Zn
- Variability of OS: Transition elements :By 1, Non transition elements :By 2
- Unlike p block elements, in transition elements (group 4 to 10) higher O.S are favoured for heavier elements
- Low OS are found in complexes where ligands have π -acceptor character in addition to the σ -bonding. Eg: $Ni(CO)_4$ and $Fe(CO)_5$, OS of both Ni, Fe are 0

➤ **Standard electrode potential:**

M^{2+}/M :

- Plot:



- Unique behaviour of Copper:
 - Cu^{2+}/Cu has positive E^0 value unlike others.
 - Cu^{2+} cannot liberate H_2 from non oxidising acids such as HCl . It reacts only with oxidising acids like HNO_3 , hot concentrated H_2SO_4 .

M^{3+}/M^{2+} :

- Values (Sc to Zn):

potential E^0/V	M^{3+}/M^{2+}	-	-0.37	-0.20	-0.41	+1.57	+0.77	+1.97	-	-	-
--------------------------	-----------------	---	-------	-------	-------	-------	-------	-------	---	---	---

- low value by Sc is due to Sc^{3+} noble gas configuration.
- Highest values by Zn, Mn due to d_{10} , d_5 stability.
- Comparatively low value of V is due to stability of V^{2+} has half filled t_{2g} level

➤ Stability of higher oxidation states:

Halides:

- Stable halides of 3d series and their oxidation states are given below:

Oxidation Number									
+ 6			CrF_6						
+ 5		VF_5	CrF_5						
+ 4	TiX_4	VX_4	CrX_4	MnF_4					
+ 3	TiX_3	VX_3	CrX_3	MnF_3	FeX_3	CoF_3			
+ 2	TiX_2	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2	ZnX_2
+ 1								CuX	

Key: $\text{X} = \text{F} \rightarrow \text{I}$; $\text{X}^{\text{I}} = \text{F} \rightarrow \text{Br}$; $\text{X}^{\text{II}} = \text{F}, \text{Cl}$; $\text{X}^{\text{III}} = \text{Cl} \rightarrow \text{I}$

- Usually fluorine forms the highest OS due to its high lattice energy to high bond enthalpy.

➤ **Oxides:**

- Stable halides of 3d series and their oxidation states are given below:

Oxidation Number	3	4	5	6	7	8	9	10	11	12
+ 7					Mn ₂ O ₇					
+ 6				CrO ₃						
+ 5			V ₂ O ₅							
+ 4		TiO ₂	V ₂ O ₄	CrO ₂	MnO ₂					
+ 3	Sc ₂ O ₃	Ti ₂ O ₃	V ₂ O ₃	Cr ₂ O ₃	Mn ₂ O ₃	Fe ₂ O ₃				
					Mn ₃ O ₄ ⁺	Fe ₃ O ₄ ⁺	Co ₃ O ₄ ⁺			
+ 2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+ 1									Cu ₂ O	

➤ **Magnetic properties:**

Can be diamagnetic, paramagnetic, ferromagnetic (extreme of paramagnetic. They show magnetic properties even when magnetic field is removed)

Magnetic moment:

$$\mu = \sqrt{n(n+2)}$$

n = number of unpaired electrons

➤ **Coloured compounds:**

Due to excitation of electrons from low energy d orbital to higher they are coloured. 3d⁰, 3d¹⁰ configurations are colourless whereas other ions are coloured

➤ **Complex compounds:**

Forms complexes due to small size, high charge and availability of d orbitals for bond formation.

➤ **Catalytic properties:**

Good adsorption tendency and ability to change oxidation state makes them have catalytic properties. Eg: Ni, Pd, V etc can act as catalysts

➤ **Interstitial compounds:**

Small atoms like H, C, N are trapped inside the crystal lattices making them have high MP, retain metallic conductivity and are chemically inert. They are usually non stoichiometric.

TiC, Mn₄N, Fe₃H, VH_{0.56} and TiH_{1.7},

➤ **Alloy:**

- Homogeneous solid solutions.
- The metal constituents should be of similar radii i.e within 15% of each other
- Eg: Brass (Cu+Zn), bronze (Cu + tin)

➤ **Chemical properties:**

Oxides and oxyanions:

- Highest oxidation in oxides coincides with group number till group 7. Beyond group 7 no higher oxides above Fe_2O_3 are found
Eg: Sc_2O_3 oxidation state = +3
 Mn_2O_7 oxidation state = +7
- As the oxidation state of oxide increases the acidic nature increases.
Example: Acidic nature order: $\text{MnO} < \text{Mn}_3\text{O}_4 < \text{Mn}_2\text{O}_7$, $\text{Cr}_2\text{O}_3 < \text{CrO}_3$, V_2O_3 (Basic) $< \text{V}_2\text{O}_4 < \text{V}_2\text{O}_5$ (amphoteric)
- Acidic oxides give acids in aqueous solution. Eg: Mn_2O_7 gives HMnO_4 and CrO_3 gives H_2CrO_4
- V_2O_5 , CrO_3 have low MP

➤ **Potassium dichromate:**

- Preparation: From chromite (FeCr_2O_4)

$$4 \text{FeCr}_2\text{O}_4 + 8 \text{Na}_2\text{CO}_3 + 7 \text{O}_2 \rightarrow 8 \text{Na}_2\text{CrO}_4 + 2 \text{Fe}_2\text{O}_3 + 8 \text{CO}_2$$

$$2\text{Na}_2\text{CrO}_4 + 2 \text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2 \text{Na}^+ + \text{H}_2\text{O}$$

$$\text{Na}_2\text{Cr}_2\text{O}_7 + 2 \text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2 \text{NaCl}$$
- Chromate and dichromate are interconvertible based on solution pH

$$2 \text{CrO}_4^{2-} + 2 \text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$$

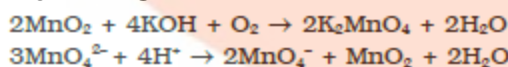
$$\text{Cr}_2\text{O}_7^{2-} + 2 \text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + \text{H}_2\text{O}$$
- Strong oxidising agent and used in volumetric analysis
Ex: In acidic medium it converts to Cr^{3+}

$$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{Fe}^{2+} \rightarrow 2 \text{Cr}^{3+} + 6 \text{Fe}^{3+} + 7 \text{H}_2\text{O}$$
- Chromyl chloride test:
Used to test for Cl^- ions. $\text{K}_2\text{Cr}_2\text{O}_7$ with solid KCl and few drops of H_2SO_4 produces red vapours of chromyl chloride (CrO_2Cl_2)

➤ **Potassium permanganate:**

• **Preparation:**

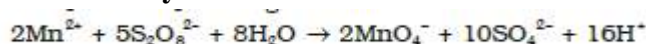
1. From MnO_2



2. Commercial preparation (Electrolytic oxidation)



3. In laboratory:



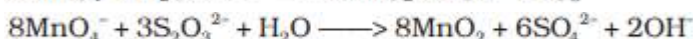
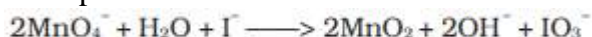
- **Properties:** Intense purple color and temperature dependent paramagnetism
- **Oxidising agent:** pH of the solutions play an important role in influencing the reaction
❖ In acidic medium it converts into Mn^{2+}
Examples:



Note: Titrations with KMnO_4 are not performed in HCl as it would be oxidised to Cl_2 gas

- ❖ In weakly basic medium it converts to MnO_2

Examples:



- ❖ In strong basic medium it form MnO_4^{2-}

f - BLOCK elements

➤ General properties:

- Location: Group 3 (Taken out and placed below), Period 6- 7 (Total 2 periods)
- Inner transition elements:

Lanthanoids (4f series)	La to Lu
Actinoids (5f series)	Ac to Lr

➤ Lanthanides:

Electronic configuration: $4f^{(1-14)} 5d^{(0-1)} 6s^2$

➤ Oxidation state:

- Commonly show +3 oxidation state. Occasionally +2 and +4 are shown.
- Usually +3 and +4 oxidation states tend to be converted to common oxidation state i.e. +3. Thus Eu^{2+} acts as a strong reducing agent and Ce^{4+} act as a good oxidizing agent
- Ce is well known to exhibit +4 state due to noble gas configuration.

➤ Atomic and ionic size:

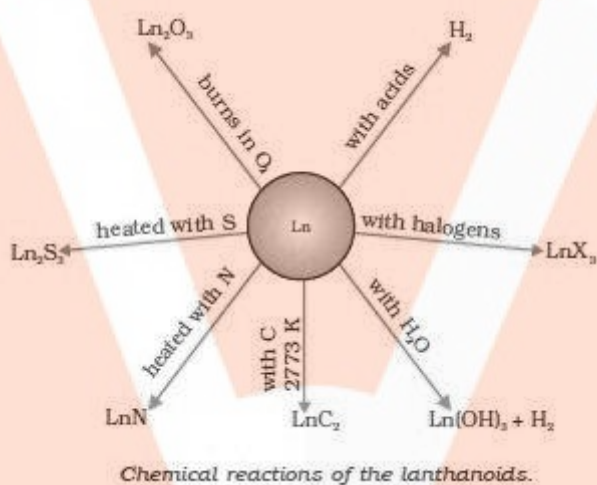
- Overall decrease in size from La to Lu is due to lanthanide contraction
- Trend for atomic radii: Atomic size decreases from La to Lu except Eu which has the highest size in lanthanides.
- Trend for M^{3+} ions: Has a regular trend and the size from La^{3+} to Lu^{3+} decreases gradually.
- Due to lanthanide contraction the size of 4d and 5d series are almost equal and are difficult to separate.

➤ **Properties:**

- Silvery white soft metals and tarnish rapidly in air.
- Good conductors of heat and electricity
- Hardness increases as atomic number increases
- High Melting points. Highest MP is shown by Eu.
- Density and other properties vary smoothly except Eu and Yb
- Colour: M^{3+} ions are coloured due to f-f transition. La^{3+} and Lu^{3+} do not show colour due to f^0 and f^{14} configuration.
- Magnetic property: Their ions are paramagnetic except f^0 (La^{3+} and Ce^{4+}) and f^{14} (Yb^{2+} and Lu^{3+}) types Highest paramagnetism is seen in neodymium.

➤ **Chemical properties:**

- Earlier members of the series behave similar to 'Ca' and later behave more like 'Al'.



- Their oxides being basic form hydroxides when treated with water.

➤ **Uses:**

- In alloy steels for plates and pipes. Eg: Mischmetall has 95% lanthanides and 5% iron and traces of S, C, Ca, Al. Mischmetall with Mg alloy used in bullets and lighter flint.
- Mixed oxides used as catalysts in petroleum cracking.
- Ln based oxides are used in TV screens and fluorescing surfaces

➤ **Actinoides:**

Electronic configuration: $5f^{(1-14)} 6d^{(0-1)} 7s^2$

➤ **Oxidation state:**

- Large number of oxidation states (+3 to +7) are shown unlike lanthanoides because of 5f, 6d, 7s comparable energies.
- Commonly show +3 state except Th which shows +4

➤ **Size:**

- Gradual decrease in the size of atoms or M^{3+} ions is referred to as actinoid contraction. The contraction is greater from element to element than in lanthanides due to poor shielding of 5f electrons.

➤ **Properties:**

- Silvery in appearance.
- The structural variability due to irregularities in metallic radii is greater than lanthanides
- Highly reactive
- Magnetic properties are complex than lanthanides
- IE of actinoides are less than lanthanoids

➤ **Uses:**

- In nuclear reactors, Treatment of cancer etc

➤ **Applications of d and f block elements:**

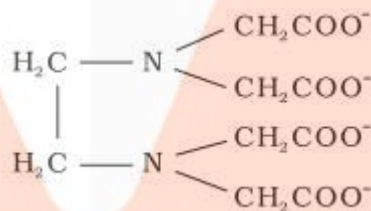
- Iron, steel are important construction materials.
- Nickel, V_2O_5 , Pt, Pd etc have a huge application as catalysts
- Photographic development relies on light sensitive properties of AgBr

Coordination Compounds

- **Double salt:** Dissociate into simple ions completely in water
Eg: Carnallite - $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$,
Mohr's salt - $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
potash alum - $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
- **Coordination complex:** Do Not dissociate completely in water
Eg: $\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$
- **Examples of coordination compounds:** Chlorophyll (Mg), Haemoglobin (Fe)
Vitamin B₁₂ (Co)

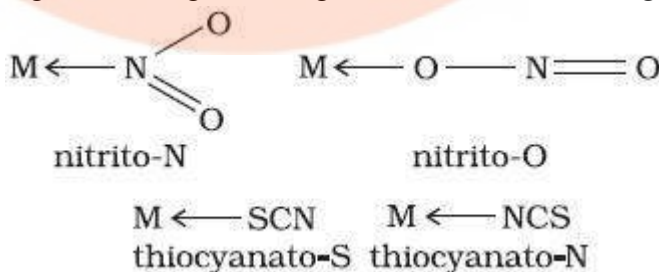
➤ Terminology:

- **Coordination entity:** Central metal atom or ion bonded to a fixed number of ions or molecules.
Ex: $[\text{Ni}(\text{CO})_4]$, $[\text{PtCl}_2(\text{NH}_3)_2]$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$.
- **Central atom/ ion:** The ion/ atom to which one or more molecules form a coordinate bond. In general they are referred to as lewis acids
- **Ligands:** Ions/ molecules bound to central atom via coordinate bond
 - ❖ Classification based on charge: Negative, neutral or positive ligand (rare)
 - ❖ Classification based on number of donor sites:
 - Monodentate/ Unidentate: One donor atom. Eg: Cl^- , H_2O , NH_3 etc
 - Bidentate: Two donor sites. Eg: $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ - Ethane-1,2-diamine, $\text{C}_2\text{O}_4^{2-}$ - Oxalate.
 - Polydentate: Multiple donor sites. Eg: Ethylenediaminetetraacetate ion (EDTA^{4-}) – Hexadentate



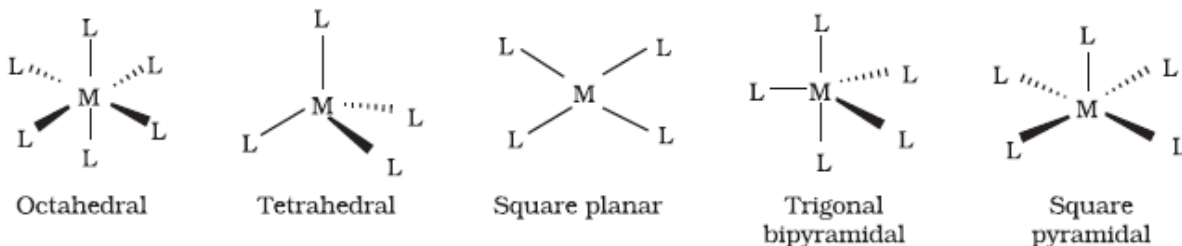
EDTA

- Ambidentate ligand: Can ligate through two different atoms. Eg: NO_2^- , SCN^-



- Eg: $\text{K}_4[\text{Fe}(\text{CN})_6]$: Central atom: Fe^{2+}
Ligands: CN^-
Counter ions: K^+
- **Coordination sphere:** Central atom and the ligands attached to it, enclosed in square brackets. Eg: $\text{K}_4[\text{Fe}(\text{CN})_6]$ - Coordination sphere - $[\text{Fe}(\text{CN})_6]^{4-}$.

- **Coordination polyhedron:** The spatial arrangement of the ligand atoms attached to the central atom. Common polyhedra shapes are:



- **Homoleptic complexes:** One kind of donor. Eg: $[\text{Co}(\text{NH}_3)_6]^{3+}$
- **Heteroleptic complexes:** More than one kind of ligand. Eg: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
- **Oxidation number of central atoms:** Charge the central atom would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. It is the charge on the central atom.
- **Coordination number (CN):** Total number of ligand donor atoms to which metal is directly bonded.
 - CN is determined only by sigma bonds and not by pi bonds
 - Coordination number = Σ number of ligands \times denticity
 - Eg: $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$: CN = 6 ('en' - $\text{C}_2\text{O}_4^{2-}$ is a bidentate ligand).
 - $[\text{PtCl}_6]^{2-}$: CN = 6

➤ **Werner theory:**

- Reactions of a series of cobalt (III) chloride ammonia complexes with AgNO_3 resulted in precipitation of different numbers of moles of AgCl .

Compound	Formula	Colour	Moles of AgCl formed
$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	Yellow	3
$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5]^{2+} 2\text{Cl}^-$	Purple	2
$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4]^+ \text{Cl}^-$	Green	1
$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4]^+ \text{Cl}^-$	Violet	1

- Central metal show 2 types of valences: primary and secondary
- Primary valency: Ionisable ions and satisfied by negative ions
- Secondary valency: non-Ionisable. Satisfied by neutral or negative ions. It is equal to coordination number.
- Ions/groups attached by secondary linkages have a characteristic spatial arrangement corresponding to different coordination numbers called coordination polyhedra
- Most common geometrical shapes are octahedral, tetrahedra, square planar.

$[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, $[\text{CoCl}_2(\text{NH}_3)_4]^+$	Octahedral
--	------------

$[\text{Ni}(\text{CO})_4]$	Tetrahedral
$[\text{PtCl}_4]^{2-}$	Square planar

➤ **Nomenclature of coordination compounds:**

Formulas of Coordination entities:

- Central atom is written first
- Ligands including polydentate are written in alphabetical order. In abbreviated ligands the first letter is used to determine the position.
- The coordination entity is enclosed in square brackets. Ligands when polyatomic are enclosed in parentheses.
- No space between ligands and metal.
- When written without a counter-ion, then the charge is represented as the right superscript with the number before the sign. Eg: $[\text{Co}(\text{CN})_6]^{3-}$
- Charge on cations is balanced by charge of the anions

➤ **Naming of coordination compounds:**

- Cation is named first (both positive and negative coordination entities)
- Ligands are named in alphabetical order before the name of the central atom/ion.
- Anionic ligands: end with -o. Neutral and cationic ligands - same names. Except H_2O - aqua, NH_3 - ammine, CO - carbonyl, NO - nitrosyl.
- Prefix mono, di, tri etc used to indicate the number of ligands. When the names of ligands have numerical prefixes, use bis, tris, tetrakis.
- Oxidation state is indicated by roman numerals in parentheses.
- Neutral or cationic complex: Metal named same as element. Eg: Co - Cobalt
Anionic complex: Metal ends with suffix -ate. Eg: Co - Cobaltate.
In a few metals latin names are used- Eg: Fe - Ferrate.

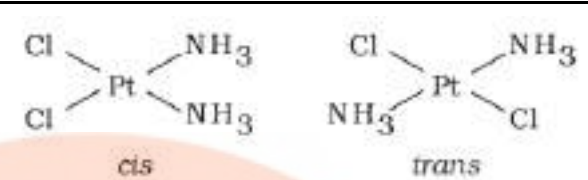
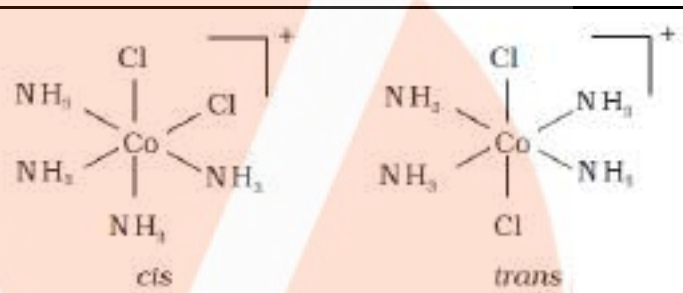
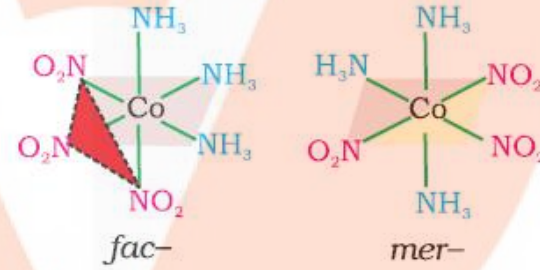
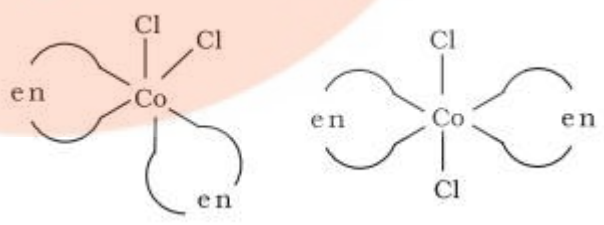
Examples:

$[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$	triamminetriaquachromium(III) chloride
$[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]_2(\text{SO}_4)_3$	tris(ethane-1,2-diamine) cobalt (III) sulphate
$[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$	diamminesilver(I) dicyanidoargentate(I)
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$	Tetraammineaquachloridocobalt(III) chloride
$\text{K}_2[\text{Zn}(\text{OH})_4]$	Potassium tetrahydroxidozincate(II)
$\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatoaluminate(III)
$[\text{CoCl}_2(\text{en})_2]^+$	Dichloridobis(ethane-1,2-diamine) cobalt (III)
$[\text{Ni}(\text{CO})_4]$	Tetracarbonylnickel(0)

Isomerism: Two or more compounds having the same chemical formula but different arrangement of atoms.

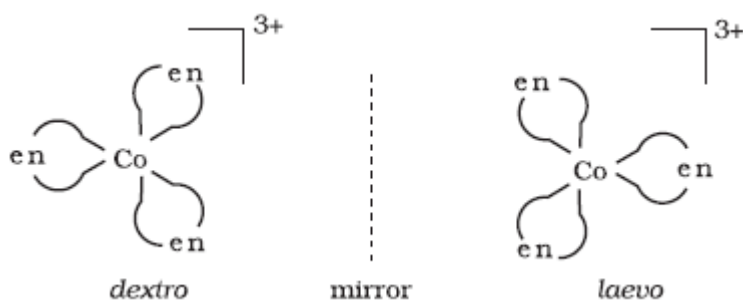
Stereoisomerism: Same chemical formula but different spatial arrangement.

(a) Geometrical isomerism: (imp cases)

Type	Number of GI	Example
[Ma ₂ b ₂]	2 (cis, trans)	 <p style="text-align: center;"><i>cis</i> <i>trans</i></p>
[Mabcd]	3	
[Ma ₂ b ₄]	2 (cis, trans)	 <p style="text-align: center;"><i>cis</i> <i>trans</i></p>
[Ma ₃ b ₃]	2 (facial and meridional)	 <p style="text-align: center;"><i>fac-</i> <i>mer-</i></p>
[Ma ₂ (AA) ₂] (AA): bidentate	2 (cis, trans)	

(b) Optical isomerism:

- Enantiomers: Non superimposable mirror images. These molecules or ions are called chiral.
- Compounds are optically active if there is no element of symmetry present in it.
- Two forms: dextro (d), laevo (l)



- Observed in octahedral and tetrahedral complexes only not in square planar complexes
- Examples: $[\text{Ma}_2(\text{AA})_2]$ (Eg: $[\text{CrCl}_2(\text{ox})_2]^{3-}$, $[\text{PtCl}_2(\text{en})_2]^{2+}$) Cis isomer shows optical isomerism but not trans isomer.

➤ Structural isomerism

(a) Linkage isomerism: Due to ambidentate ligands. Eg: $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)] \text{Cl}_2$. If NO_2 is bound via oxygen then it is red form and when bound via nitrogen it is yellow form.

(b) Coordination isomerism: Due to interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Eg: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

(c) Ionisation isomerism: Counter ions and ligands interchange themselves.

$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)] \text{Br}$, $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$.

(d) Solvate isomerism: Differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

Eg: $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$ (violet), $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$ (grey-green)

➤ Bonding in Coordination compounds:

VBT (Valence bond theory):

- Central atom/ ion uses its (n-1) d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

- Geometry can be predicted using magnetic behaviour. Few ligands like NH_3 , CN^- are observed to cause pairing while others like F^- , Cl^- doesn't cause pairing.

$[\text{Co}(\text{NH}_3)_6]^{3+}$	<ol style="list-style-type: none"> 1. Diamagnetic 2. Electrons are paired. 3. Hybridisation: d^2sp^3, shape: Octahedral 4. Inner orbital complex or low spin or spin paired complex.
-----------------------------------	---

	<p>Orbitals of Co^{3+} ion</p> <p>$d^2 sp^3$ hybridised orbitals of Co^{3+}</p> <p>$[\text{Co}(\text{NH}_3)_6]^{3+}$ (inner orbital or low spin complex)</p> <p>Six pairs of electrons from six NH_3 molecules</p>
$[\text{CoF}_6]^{3-}$	<ol style="list-style-type: none"> 1. Paramagnetic 2. Electrons aren't paired. 3. Hybridisation: $sp^3 d^2$, shape: Octahedral 4. Outer orbital or high spin or spin free complex. <p>Orbitals of Co^{3+} ion</p> <p>$sp^3 d^2$ hybridised orbitals of Co^{3+}</p> <p>$[\text{CoF}_6]^{3-}$ (outer orbital or high spin complex)</p> <p>Six pairs of electrons from six F^- ions</p>
$[\text{NiCl}_4]^{2-}$	<ol style="list-style-type: none"> 1. Paramagnetic 2. Electrons aren't paired 3. Hybridisation: sp^3, shape: Tetrahedral 4. Outer orbital or high spin or spin free complex. <p>Orbitals of Ni^{2+} ion</p> <p>sp^3 hybridised orbitals of Ni^{2+}</p> <p>$[\text{NiCl}_4]^{2-}$ (high spin complex)</p> <p>Four pairs of electrons from 4 Cl^-</p>
$[\text{Ni}(\text{CN})_4]^{2-}$	<ol style="list-style-type: none"> 1. Diamagnetic 2. Electrons are paired 3. Hybridisation: dsp^2, shape: Square planar 4. Inner orbital complex or low spin or spin paired complex.

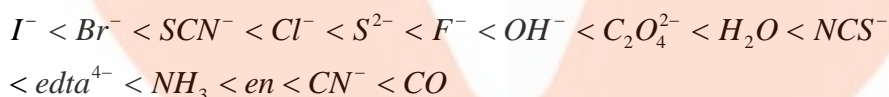
	<p>Orbitals of Ni^{2+} ion</p> <p>$3d$</p> <p>$4s$</p> <p>$4p$</p> <p>dsp^3 hybridised orbitals of Ni^{2+}</p> <p>$3d$</p> <p>dsp^3 hybrid</p> <p>$4p$</p> <p>$[\text{Ni}(\text{CN})_4]^{2-}$ (low spin complex)</p> <p>$3d$</p> <p>Four pairs of electrons from 4 CN^- groups</p> <p>$4p$</p>
$[\text{Ni}(\text{CO})_4]$	<ol style="list-style-type: none"> 1. Diamagnetic 2. Electrons are paired 3. Hybridisation: sp^3 (Because Ni oxidation state is 0)

➤ **Limitations of valence bond theory:**

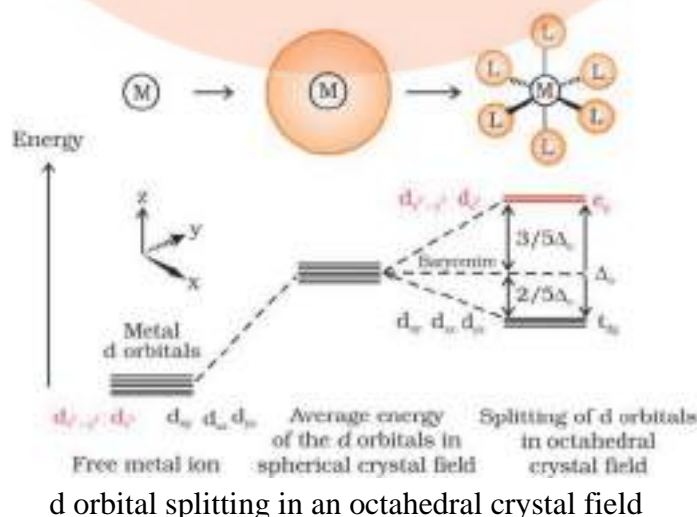
- No quantitative interpretation of magnetic data.
- No explanation on the colour of coordination compounds.
- No quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- Does not explain about weak and strong ligands (ie which ligands cause pairing and which does not).

➤ **Crystal field theory (CFT):**

- Electrostatic model. Consider metal- ligand bonds to be ionic. Ligands are treated as point charges in case of anions and dipole in case of neutral molecules.
- The degeneracy of d orbitals would be lost as the ligands asymmetrically approach the central atoms and it results in splitting of d orbitals.
- Strong ligands mean they cause large splitting and weak ligands cause smaller splitting. Spectrochemical series (experimentally determined based on absorption of light by complexes) in the increasing order of field strength.



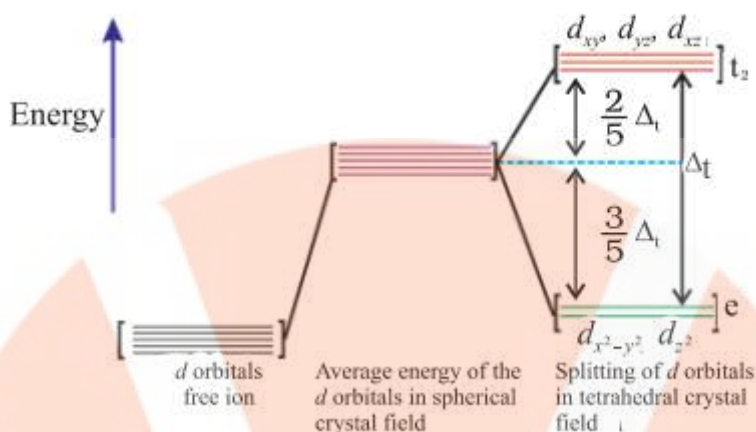
❖ **Crystal field splitting in octahedral species:**



- Say P is the pairing energy and Δ_o is the octahedral splitting energy
 - If $\Delta_o < P$: 4th electron enters e_g instead of causing pairing in t_{2g} . Such ligands are called weak field ligands and form high spin complexes
 - If $\Delta_o > P$: 4th electron enters t_{2g} causing pairing. Such ligands are called strong field ligands and form low spin complexes.

❖ **CFT in tetrahedral complexes:**

- Energy of $d_{x^2-y^2}$ and d_{z^2} would be less in comparison with other d orbitals



- In general, $\Delta_t < P$ always. Thus, there is no pairing.
- **Important relation:** $\Delta_t = (4/9) \Delta_o$.

➤ **Magnetic moments:**

$$\mu = \sqrt{n(n+2)}$$

For octahedral complexes the data is given below:

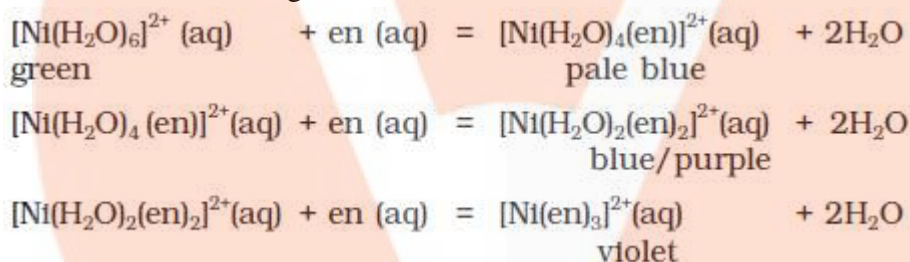
d electrons	Availability of d electrons	Magnetic behaviour
d^1, d^2, d^3	2 vacant d orbitals available strong or weak field: d^2sp^3	Magnetic behaviour is the same as free ion.
d^4, d^5, d^6	2 vacant d orbital are available only when there is pairing of electrons <ul style="list-style-type: none"> • Strong field: d^2sp^3 • Weak field: sp^3d^2 	Magnetic behaviour depends on ligands attached. Eg: $[\text{Mn}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$: d^2sp^3 $[\text{MnCl}_6]^{3-}$, $[\text{FeF}_6]^{3-}$, $[\text{CoF}_6]^{3-}$: sp^3d^2
d^8, d^9, d^{10}	On pairing also vacant orbitals are unavailable <ul style="list-style-type: none"> • strong or weak field: sp^3d^2 	

➤ **Colour in coordination complexes:**

- Transition metal complexes show a wide range of colours. The colour of the complex is complementary to the colour absorbed. Eg: If green light is absorbed then it appears red.

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet Not in visible region	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green	Violet

- Colour is shown due to d-d transition i.e excitation and deexcitation of electrons amongst splitted d orbitals. Eg: $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$: Electron jumps from $(t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1)$.
- In the absence of ligands, no d orbital splitting and thus colourless.
Eg: $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating renders it colourless.
Anhydrous CuSO_4 is white, but $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour.
- Influence of ligands on the colour is shown below:
Stronger the ligand, the splitting of the d orbitals will be high, thus more energy absorbed and wavelength absorbed becomes less.



NOTE: en (ethylene diamine) is a stronger ligand compared to water, thus as the number of 'en' ligands increases, the wavelength decreases.

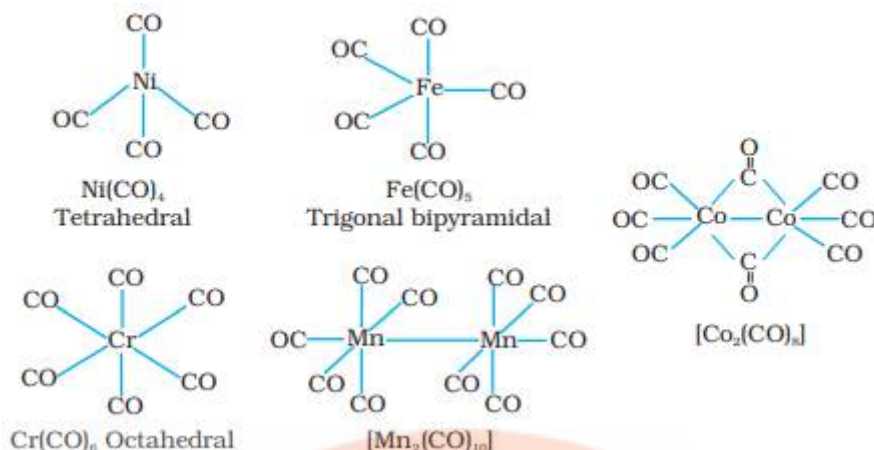
- Colour of gemstones:** Ruby: Al_2O_3 containing 0.5-1% Cr^{3+} ions.
Emerald: $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ containing Cr^{3+} ions in the octahedral sites.

➤ **Limitations of CFT:**

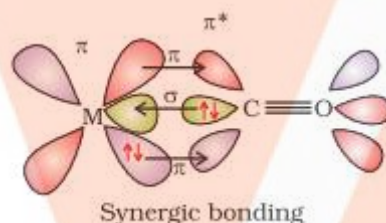
- Assuming that ligands are point charges implies that anionic ligands should exert greatest splitting effect but they are observed to be at the low end of the spectrochemical series.
- Does not take into account the covalent character of the bond between ligand and the central atom

➤ **Bonding in metal carbonyls:**

- Have well defined structures - $[\text{Ni}(\text{CO})_4]$: Tetrahedral
 $[\text{Fe}(\text{CO})_5]$: Trigonal bipyramidal
 $[\text{Cr}(\text{CO})_6]$: Octahedral
 $[\text{Mn}_2(\text{CO})_{10}]$: Made of two square pyramidal $\text{Mn}(\text{CO})_5$ units joined by Mn - Mn bond
 $\text{Co}_2(\text{CO})_8$: Made by Co-Co bridged by two CO groups

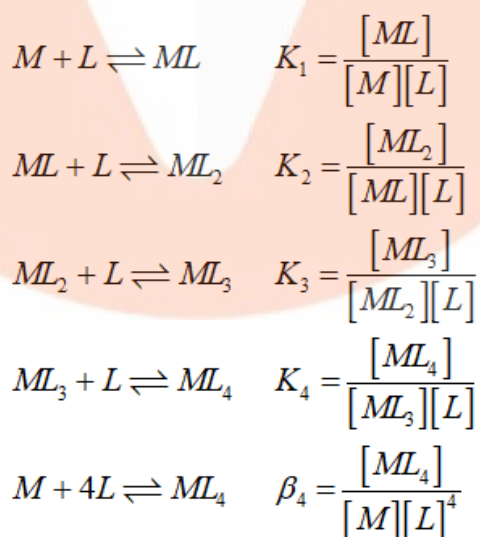


- Metal carbonyls possess both σ and π character. CO donates lone pairs to metal forming a σ bond. Metal atom donates a pair of electrons from filled d orbital into vacant antibonding π^* orbital of carbon monoxide. This creates a synergic effect which strengthens the bond between CO and metal.



➤ Stability of Coordination compounds:

- Stability of complex refers to the degree of association between the two species involved in the state of equilibrium. Equilibrium constant quantitatively expresses the stability.



- K_1, K_2 , etc., are referred to as stepwise stability constants. Thus, overall constant is β_4 .

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$$
- A pattern found for most formation constants is that the successive stability constants decrease.

- The instability constant or the dissociation constant is reciprocal of the formation constant.

➤ **Applications of coordination compounds:**

- **For quantitative and qualitative chemical analysis**

Metal ions form coloured complexes with ligands and form the basis for their detection. Eg: EDTA, DMG (dimethylglyoxime), α -nitroso- β -naphthol, cupron, etc.

- **Hardness of water:** By titration with $\text{Na}_2(\text{EDTA})$. The metal ions causing hardness, that is Ca^{2+} and Mg^{2+} , form stable complexes with EDTA.
- **Metal extraction and purification:** Extraction of metals, such as silver and gold, is carried out by forming their water soluble cyanide complexes with the ore (Eg: $[\text{Au}(\text{CN})_2]^-$). Pure gold can then be obtained from the solution by addition of zinc. Similarly, metals can be purified by formation and then decomposition of their coordination compounds. For example, impure Ni is purified by first converting it to nickel carbonyl ($[\text{Ni}(\text{CO})_4]$) and then decomposing to form pure Ni.

- **Catalysis:** Used as catalysts

Zeigler-Natta catalyst	TiCl_4 and trialkyl aluminium	Polyethylene
Wilkinson catalyst	$\text{RhCl}(\text{PPh}_3)_3$	Hydrogenation of alkenes
Rhodium complexes	$[\text{Rh}(\text{CO})_2\text{I}_2]$ $[\text{Rh}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$ $[\text{Rh}(\text{Cl})(\text{CO})_2]_2$	Monsanto acetic acid process

- **Electroplating:**
 - a. Silver plating, $\text{K}[\text{Ag}(\text{CN})_2]$ is used as an electrolyte
 - b. Gold plating, $\text{K}[\text{Au}(\text{CN})_2]$ is used as an electrolyte
 - c. Copper plating, $\text{K}_3[\text{Cu}(\text{CN})_4]$ is used as an electrolyte
- **Biological importance:**
 - a. Chlorophyll : Mg^{2+} complex (green pigment)
 - b. Haemoglobin: Fe^{2+} complex (red pigment)
 - c. Vitamin B12: Co^{3+} complex .
- **Medicinal uses:**
 - a. Treating metal poisoning: Complexing or chelating agents are used. The coordination complex is formed between toxic metal in excess metal and the complexing agent.
 1. EDTA is used in lead poisoning. EDTA, when injected intravenously into the bloodstream, traps lead forming a compound that is flushed out of the body with the urine.
 2. Other heavy metal (Hs, As, Al, Cr, Co, Mn, Ni, Se, Zn, Sn, Tl) poisonings that can be treated similarly with chelation therapy
 3. For Cu and Fe - chelating ligands D-penicillamine and desferrioxamine B are used respectively.
 4. New potent drugs are being created using various derivatives of metallocene.
 5. Pt complex - $[\text{PtCl}_2(\text{NH}_3)_2]$ called cisplatin is used in treatment of cancer.

Haloalkanes and Haloarenes

Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group

Classification

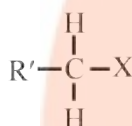
- **On the Basis of Number of Halogen Atoms**
mono, di, or polyhalogen (tri-,tetra-, etc.) compounds



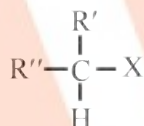
- **Compounds Containing sp^3 C—X Bond (X= F, Cl, Br, I)**

(a) Alkyl halides or haloalkanes (R—X)

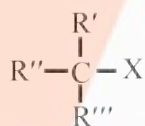
primary, secondary or tertiary



Primary (1°)



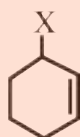
Secondary (2°)



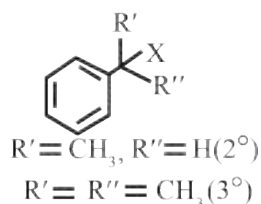
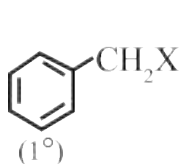
Tertiary (3°)

(b) Allylic halides

The Halogen atom is bonded to an sp^3 - hybridised carbon atom adjacent to carbon-carbon double bond ($C=C$) i.e. to an allylic carbon.



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

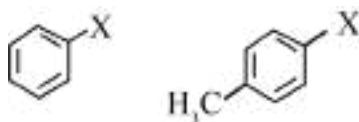


- **Compounds Containing sp^2 C—X Bond**

(a) Vinylic halides : halogen atom is bonded to an sp^2 -hybridised carbon atom



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



Nomenclature:

- The common name of haloalkanes is alkyl halides.
- Haloarenes are the common as well as IUPAC names of aryl halides.

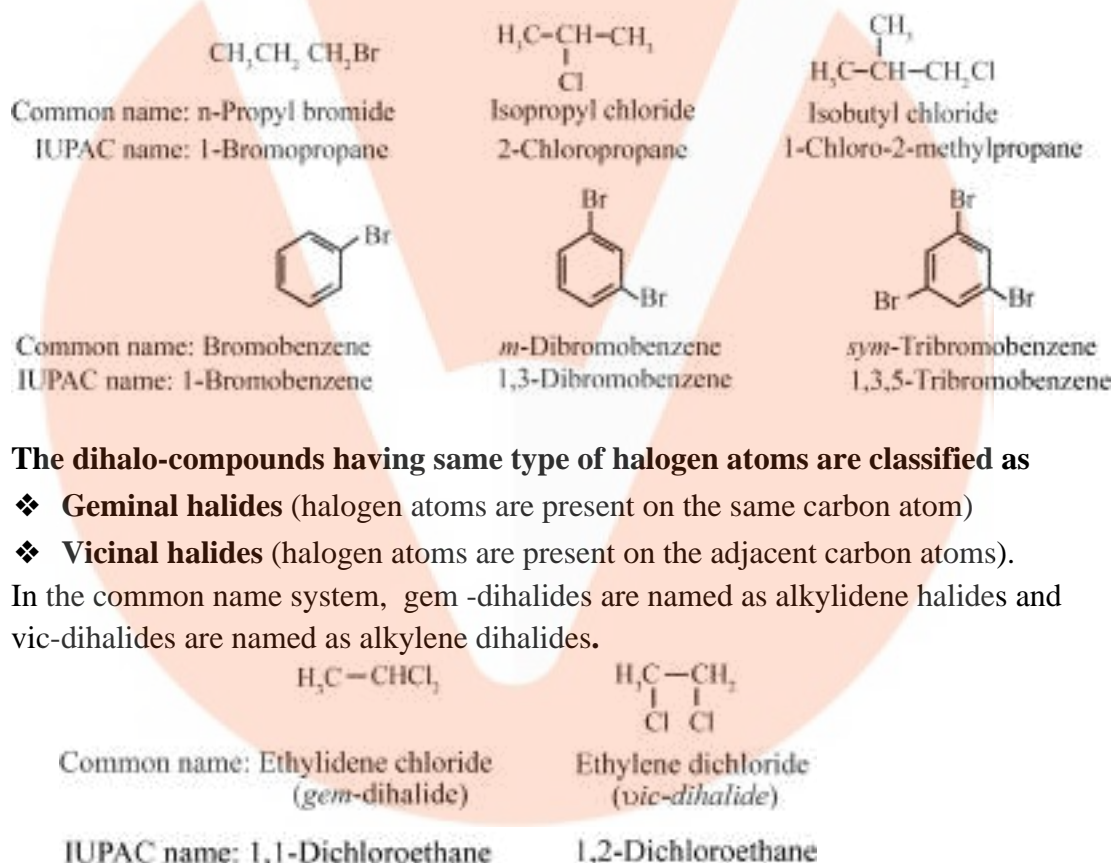
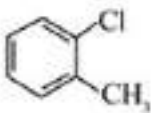
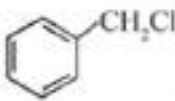
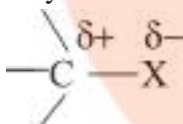


Table : Common and IUPAC names of some Halides

Structure	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	sec-Butyl chloride	2-Chlorobutane
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(\text{CH}_3)_3\text{CBr}$	tert-Butyl bromide	2-Bromo-2-methylpropane
$\text{CH}_2 = \text{CHCl}$	Vinyl chloride	Chloroethene
$\text{CH}_2 = \text{CHCH}_2\text{Br}$	Allyl bromide	3-Bromopropene
	<i>o</i> -Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
CHCl_3	Chloroform	Trichloromethane
CHBr_3	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	n-Propyl fluoride	1 - Fluoropropane

Nature of C-X Bond

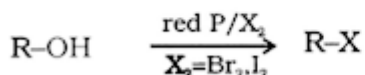
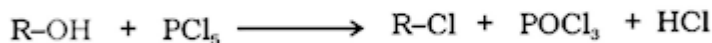
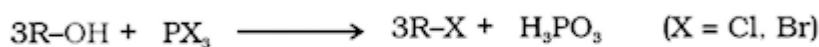
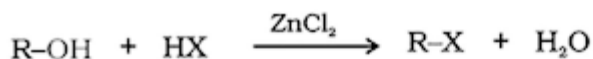
- Halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised



Methods of Preparation

➤ From Alcohols

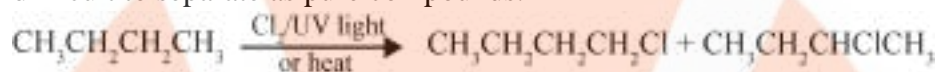
- Thionyl chloride is preferred because the other two products are escapable gases. Hence the reaction gives pure alkyl halides.
- The order of reactivity of alcohols with a given haloacid is $3^\circ > 2^\circ > 1^\circ$



➤ **From Hydrocarbons:**

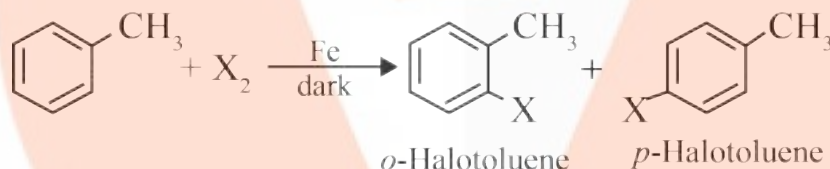
(a) **By free radical halogenation**

- Gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to separate as pure compounds.



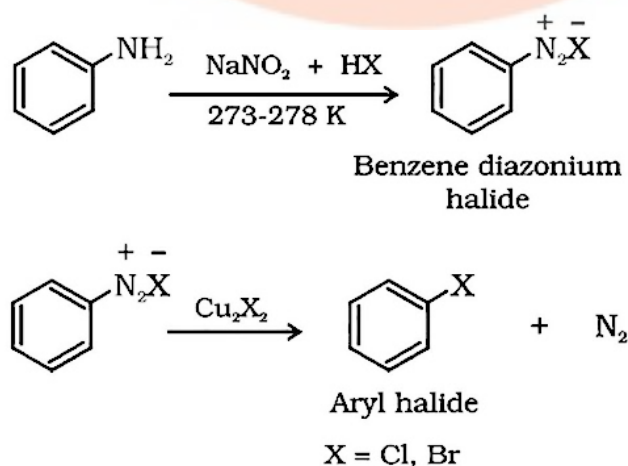
(b) **By electrophilic substitution**

- Aryl chlorides and bromides can be easily prepared.
- Reactions with iodine are reversible in nature and require an oxidising agent ($\text{HNO}_3, \text{HIO}_4$) to oxidise the HI formed during iodination.
- Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

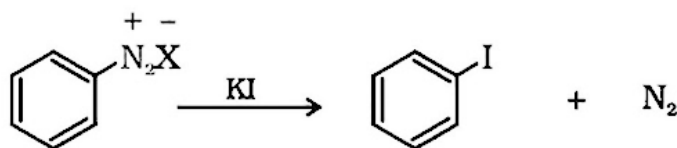


(c) **Sandmeyer's reaction**

- Primary aromatic amine, dissolved in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed.
- diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by $-\text{Cl}$ or $-\text{Br}$



- Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide

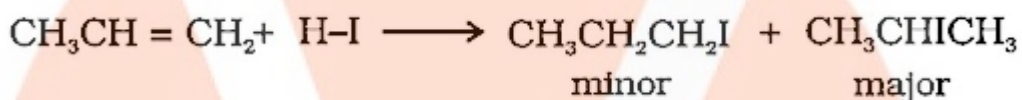


(d) From alkenes

(i) Addition of hydrogen halides:

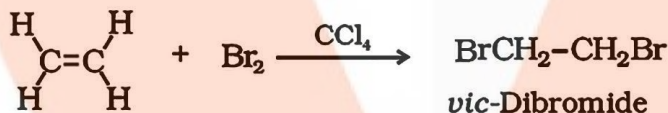


- Propene yields two products, only one predominates as per Markovnikov's rule.



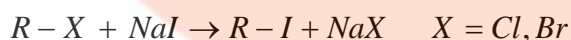
(ii) Addition of halogens:

- Addition of bromine in CCl_4 to an alkene resulting in discharge of reddish brown colour of bromine constitutes an important method for the detection of double bond in a molecule
- The addition results in the synthesis of vic-dibromides, which are colourless



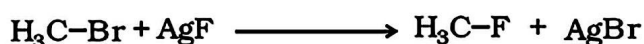
➤ **Halogen Exchange**

- Finkelstein reaction**



- Swarts reaction.**

Alkyl fluoride is easily prepared by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF , Hg_2F_2 , CoF_2 or SbF_3 .



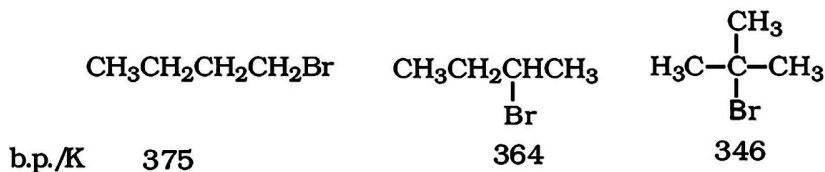
Physical Properties

- Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light.

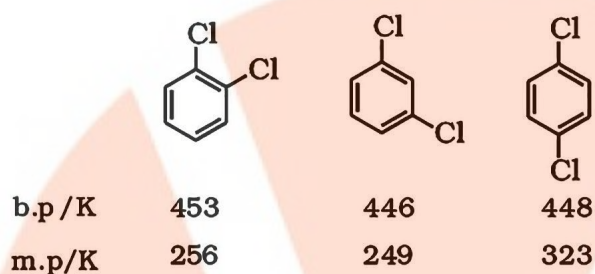
➤ **Melting and boiling points:**

- For same alkyl group, the boiling points of alkyl halides decrease in the order:
 $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$.

- This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.
- The boiling points of isomeric haloalkanes decrease with increase in branching



- Boiling points of isomeric dihalobenzenes are very nearly the same.
- The para-isomers are high melting as compared to their ortho- and meta-isomers. It is due to symmetry of para-isomers fits in crystal lattice better as compared to ortho- and meta-isomers



➤ **Density:**

- Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water.
- The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms

➤ **Solubility:**

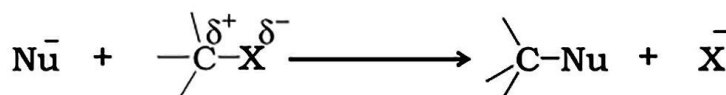
- The haloalkanes are only very slightly soluble in water.
- Haloalkanes tend to dissolve in organic solvents, because of the new intermolecular attractions between haloalkanes and solvent molecules.

Chemical Reactions:

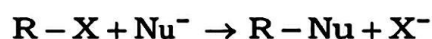
➤ **Reactions of Haloalkanes**

1. **Nucleophilic substitution:**

- Substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.



Nucleophilic Substitution of Alkyl Halides



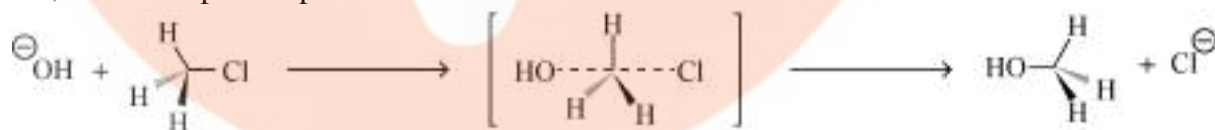
Reagent	Nucleophile (Nu ⁻)	Substitution product R-Nu	Class of main product
NaOH (KOH)	HO ⁻	ROH	Alcohol
H ₂ O	H ₂ O	ROH	Alcohol
NaOR'	R'O ⁻	ROR'	Ether
NaI	I ⁻	R—I	Alkyl iodide
NH ₃	NH ₃	RNH ₂	Primary amine
R'NH ₂	R'NH ₂	RNHR'	Sec. amine
R'R''NH	R'R''H	RNR'R''	Tert. amine
KCN	$\text{C}\equiv\text{N:}$	RCN	Nitrile (cyanide)
AgCN	Ag-CN	RNC (isocyanide)	Isonitrile
KNO ₂	O=N—O ⁻	R—O—N=O	Alkyl nitrite
AgNO ₂	Ag— $\ddot{\text{O}}$ —N=O	R—NO ₂	Nitroalkane
R'COOAg	R'COO ⁻	R'COOR	Ester
LiAlH ₄	H ⁻	RH	Hydrocarbon
R ⁺ M'	R ⁺	RR ⁺	Alkane

- Groups like cyanides and nitrites possess two nucleophilic centres and are called **ambident nucleophiles**.

Mechanism

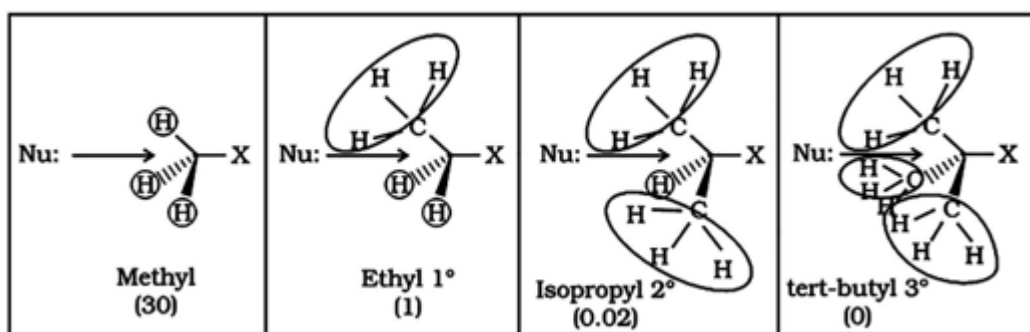
(a) Substitution nucleophilic bimolecular (S_N2)

- The reaction between CH₃Cl and hydroxide ion follows a **second order kinetics**, i.e., the rate depends upon the concentration of both the reactants.



- The incoming nucleophile causes the carbon-halide bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a **single step and no intermediate is formed**.
- The configuration of carbon atom under attack inverts in much the same way as an umbrella is turned inside out. This process is called as **inversion of configuration**.
- Carbon atoms in the transition state are simultaneously bonded to five atoms and therefore it is unstable.
- Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus the order of reactivity followed is:

Primary halide > Secondary halide > Tertiary halide



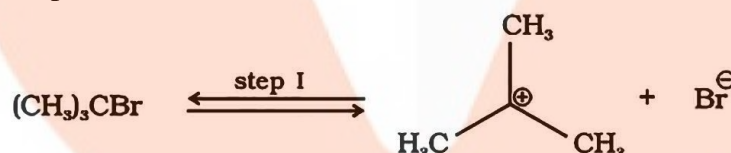
Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

(b) Substitution nucleophilic bimolecular (S_N1)

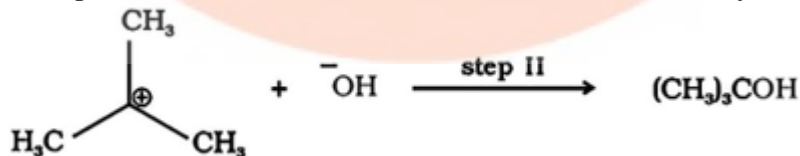
- S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.).
- The reaction between tert-butylbromide and hydroxide ion yields tert-butyl alcohol and follows the **first order kinetics**, i.e., the rate of reaction depends upon the concentration of only one reactant, which is tert-butyl bromide.



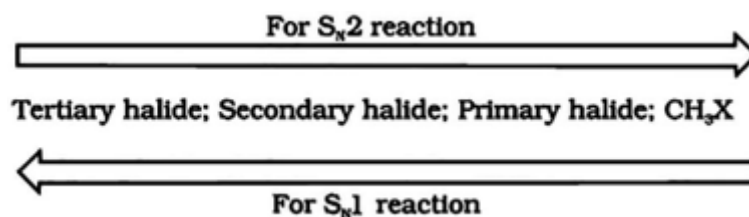
- It occurs in two steps.
 - ❖ **In step I**, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion.
 - ❖ Step I is the slowest and reversible



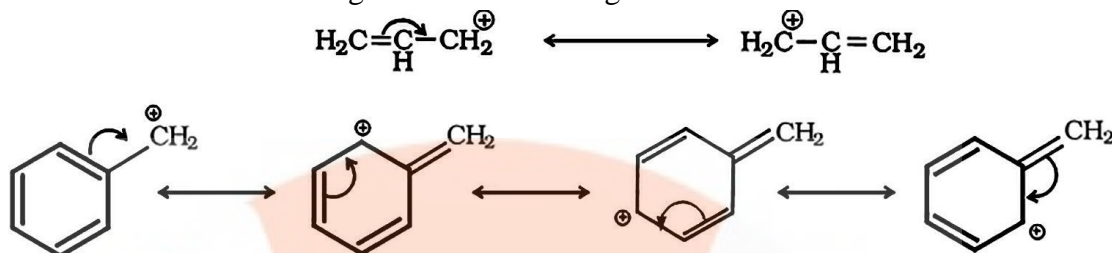
- ❖ In step II, The carbocation thus formed is then attacked by nucleophiles.



- 3° alkyl halides undergo S_N1 reaction** very fast because of the high stability of 3° carbocations.
- order of reactivity of alkyl halides towards S_N1 and S_N2 reactions as follows:



- Allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance



- For given alkyl group, the reactivity of the halide, R-X , follows the same order in both the mechanisms



(c) Stereochemical aspects of nucleophilic substitution reactions

(i) Plane polarised light and optical activity :

- Compounds which rotate the plane polarised light are called **optically active compounds**.
- The angle by which the plane polarised light is rotated is measured by an instrument called **polarimeter**.
- If the compound rotates the plane polarised light to the right, i.e., clockwise direction, it is called **dextrorotatory or the d-form** and is indicated by placing a positive (+) sign before degree of rotation.
- If the light is rotated towards left, the compound is said to be **laevo-rotatory or the l-form** and a negative (-) sign is placed before the degree of rotation.
- Such (+) and (-) isomers of a compound are called **optical isomers** and the phenomenon is termed as **optical isomerism**

(ii) Molecular asymmetry, chirality and enantiomers :

- If all the four substituents attached to tetrahedral carbon are different, such a carbon is called **asymmetric carbon or stereocenter**.
- The asymmetry of the molecule is responsible for the **optical activity**
- The objects which are non-superimposable on their mirror image (like a pair of hands) are said to be **chiral** and this property is known as **chirality**. While the objects, which are superimposable on their mirror images are called **achiral**.
- The stereoisomers related to each other as non-superimposable mirror images are called **enantiomers**

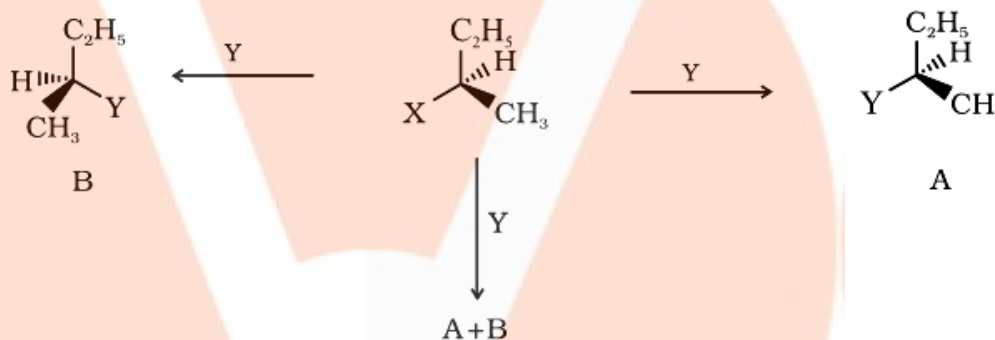
- Enantiomers possess identical physical properties namely, melting point, boiling point, solubility, refractive index, etc. They only differ with respect to the rotation of plane polarised light.
- A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as **racemic mixture or racemic modification**.
- A racemic mixture is represented by prefixing dl or (\pm) before the name, for example (\pm) butan-2-ol.
- The process of conversion of enantiomer into a racemic mixture is known as **racemisation**.

(iii) **Retention:**

- If the product will have the same general configuration of groups around the stereocenter as that of reactant.

(iv) **Inversion, retention and racemisation:**

- There are three outcomes for a reaction at an asymmetric carbon atom.

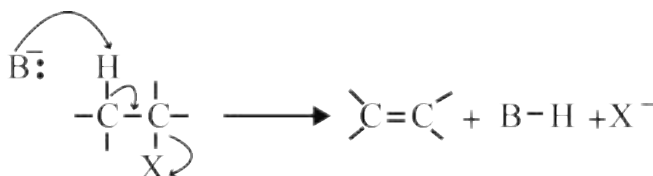


- If (A) is the only compound obtained, the process is called **retention** of configuration.
- If (B) is the only compound obtained, the process is called **inversion** of configuration.
- If a 50:50 mixture of the above two is obtained then the process is called **racemisation** and the product is optically inactive

A S_N2 reaction proceeds with complete stereochemical inversion while S_N1 reaction proceeds with racemisation.

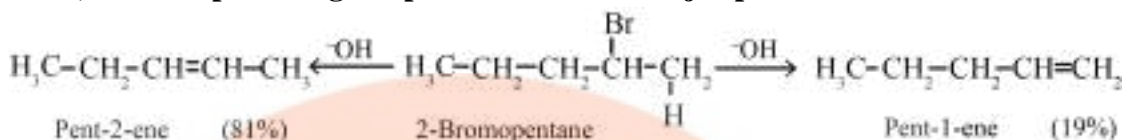
2. **Elimination reactions:**

- When a haloalkane is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β -carbon and a halogen atom from the α -carbon atom. As a result, an alkene is formed.
- Since β -hydrogen atom is involved in elimination, it is often called **β -elimination**.



B = Base : X = Leaving group

- **Saytzeff rule** : “ in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms
- **Thus, 2-bromopentane gives pent-2-ene as the major product**

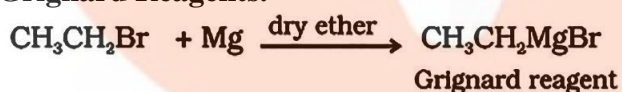


Elimination versus substitution

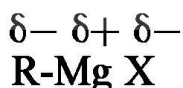
- A bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and vice versa.
- Primary alkyl halide will prefer a $\text{S}_{\text{N}}2$ reaction,
- Secondary halide- $\text{S}_{\text{N}}2$ or elimination depending upon the strength of base/nucleophile.
- Tertiary halide- $\text{S}_{\text{N}}1$ or elimination depending upon the stability of carbocation or the more substituted alkene

3. Reaction with metals:

- Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as **organo-metallic compounds**
- An important class of organo-metallic compounds is RMgX , referred to as **Grignard Reagents**.



- In the Grignard reagent, the carbon-magnesium bond is **covalent** but highly polar



- Grignard reagents are highly reactive and react with any source of proton (Even water, alcohols, amines) to give hydrocarbons.



- It is therefore necessary to avoid even traces of moisture from a Grignard reagent

➤ Wurtz reaction

- Alkyl halides react with sodium in dry ether to give hydrocarbons



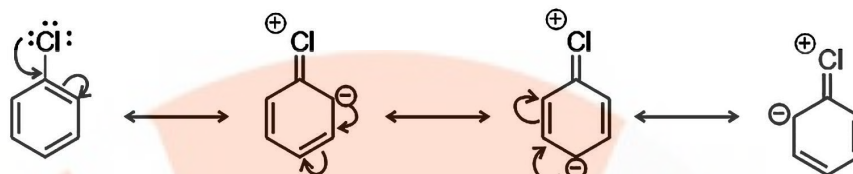
Reactions of Haloarenes

➤ Nucleophilic substitution

- Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

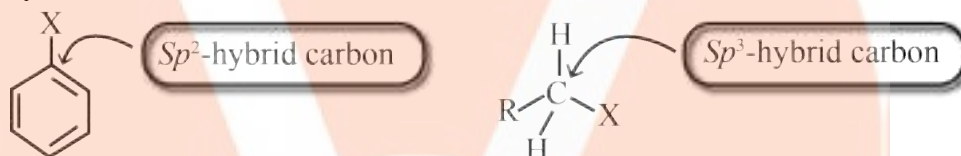
(i) Resonance effect :

- In haloarenes, **C—Cl bond acquires a partial double bond character** due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane



(ii) Difference in hybridisation of carbon atom in C—X bond:

- Haloarene, The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 -hybridised carbon in haloalkane with less s-character



(iii) Instability of phenyl cation:

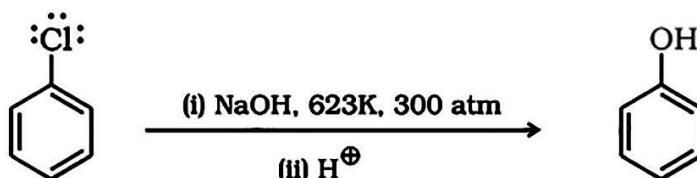
- In case of haloarene, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

(iv) Because of the possible repulsion:

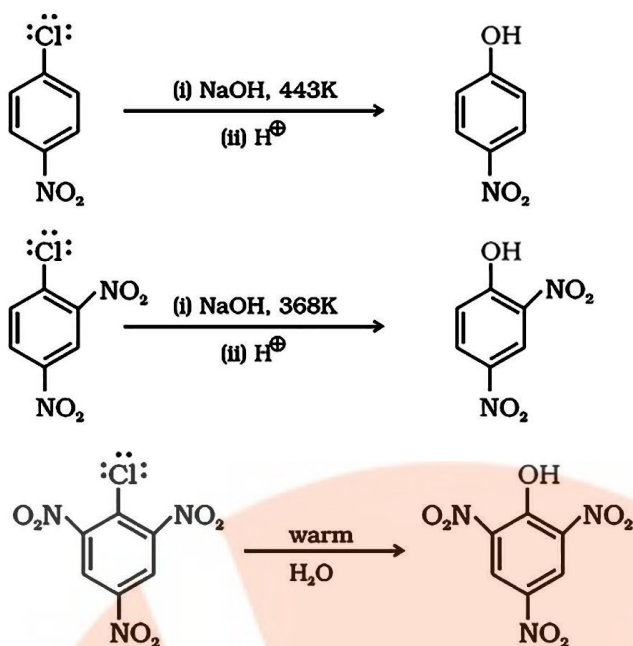
- It is less likely for the electron rich nucleophile to approach electron rich arenes.

➤ Replacement by hydroxyl group

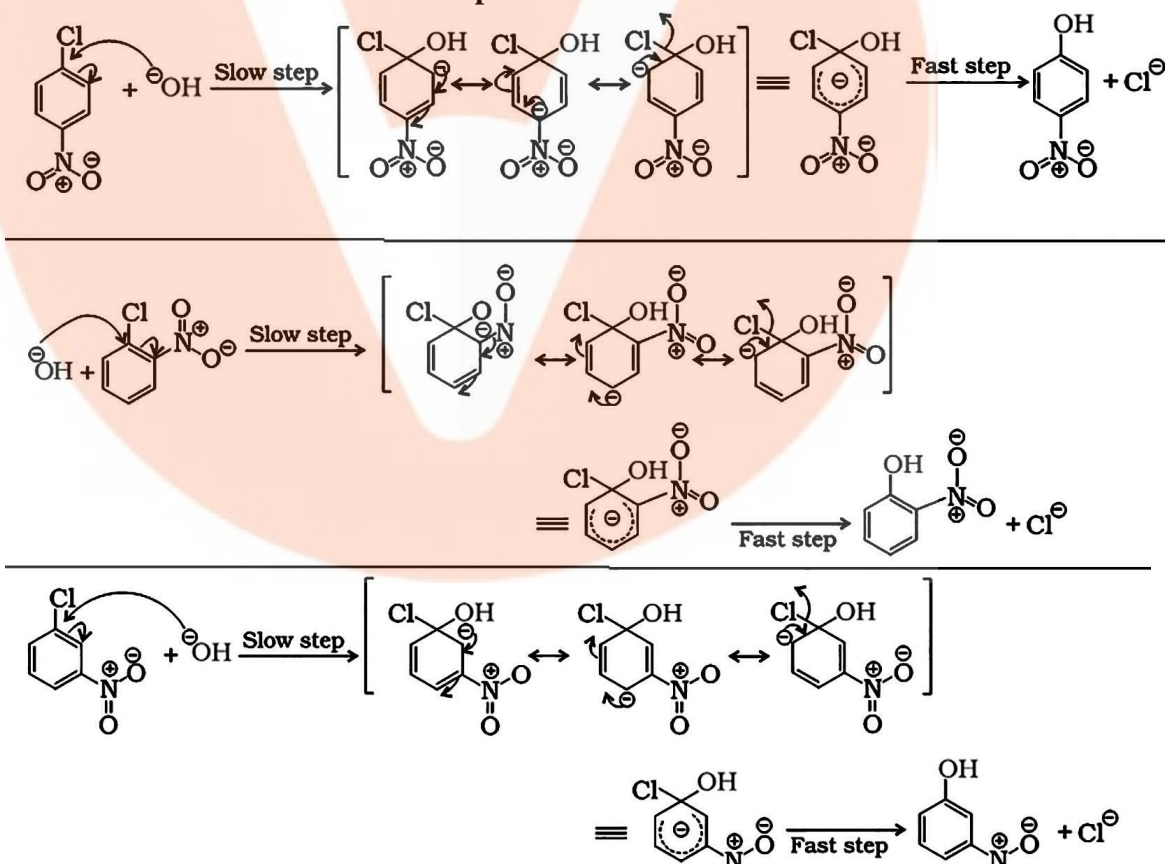
- Chlorobenzene can be converted into phenol



- The presence of an electron withdrawing group ($-NO_2$) at ortho- and para-positions increases the reactivity of haloarenes

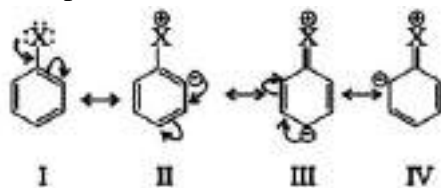


- No effect on reactivity of haloarenes is observed by the presence of electron withdrawing groups at meta-position.
- Mechanism of the reaction is as depicted:

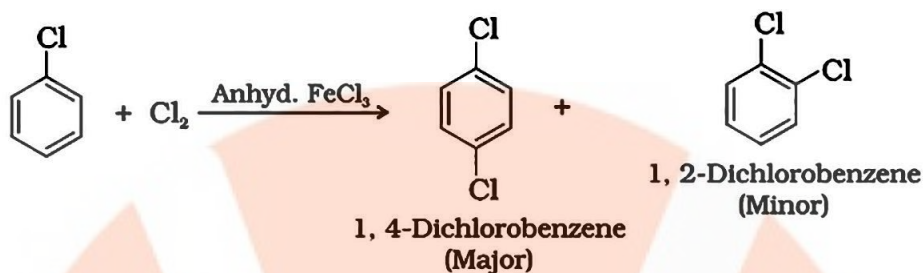


➤ Electrophilic substitution reactions

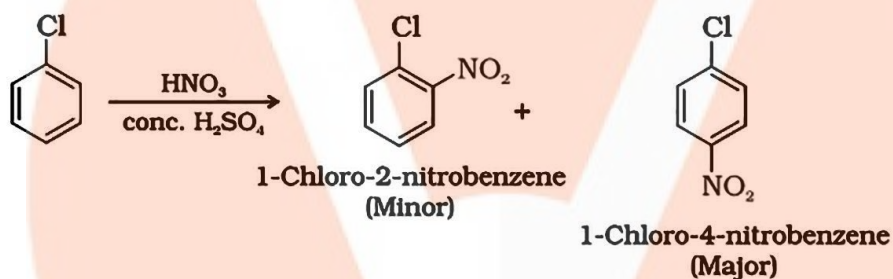
- Halogen atoms besides being slightly deactivating are o, p -directing; due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions.



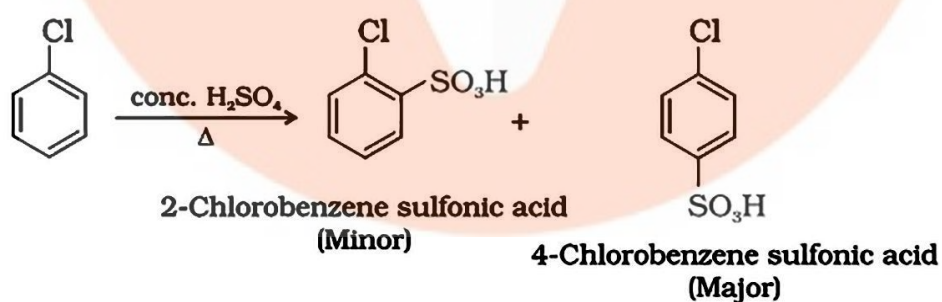
(i) Halogenation



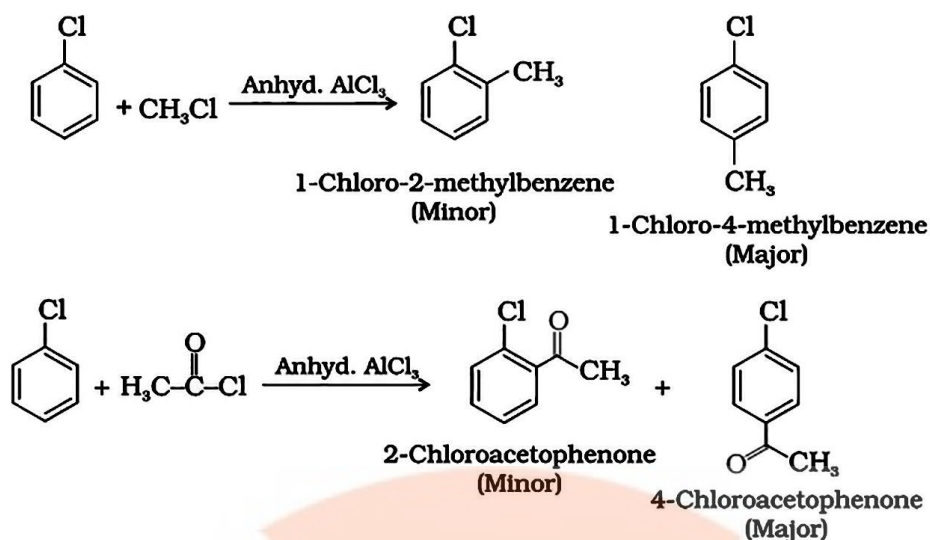
(ii) Nitration



(iii) Sulphonation



(iv) Friedel-Crafts reaction



➤ Reaction with metals

(i) Wurtz-Fittig reaction

A mixture of an alkyl halide and aryl halide gives an alkyl arene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.



(ii) Fittig reaction

When two aryl groups are joined together. It is called the Fittig reaction.



Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds.

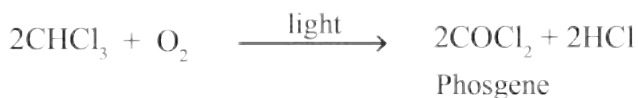
- **Dichloro-methane (Methylene chloride)**

- ❖ Widely used as a solvent as a paint remover, as a propellant in aerosols.

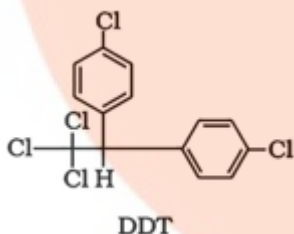
- **Trichloro-methane (Chloroform)**

- ❖ The major use of chloroform today is in the production of the freon refrigerant R-22.

- ❖ Slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene.



- ❖ It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.
- **Triiodo-methane (Iodoform)**
 - ❖ It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to the iodoform itself.
- **Tetrachloro-methane (Carbontetrachloride)**
 - ❖ It is also used as feedstock in the synthesis of chlorofluorocarbons.
 - ❖ When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer.
- **Freons**
 - ❖ The chlorofluorocarbon compounds of methane and ethane are collectively known as freons.
 - ❖ It is manufactured from tetrachloromethane by Swarts reaction.
 - ❖ These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.
 - ❖ In the stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.
- **p,p' -Dichloro-diphenyl-trichloro-ethane(DDT)**
 - ❖ DDT, the first chlorinated organic insecticides.
 - ❖ DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues.

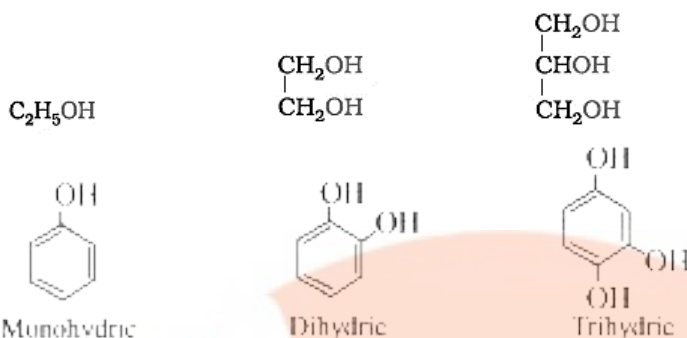


Alcohols, Phenols and Ethers

➤ Classification

● On the Basis of Number of Hydroxyl group

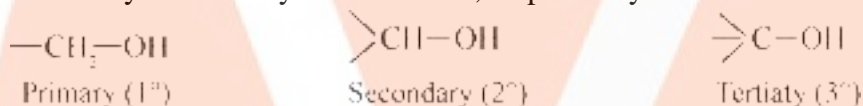
Mono, di, or Polyhydric (tri-, tetra-, etc.) compounds



● According to the hybridisation of the carbon atom to which the hydroxyl group is attached

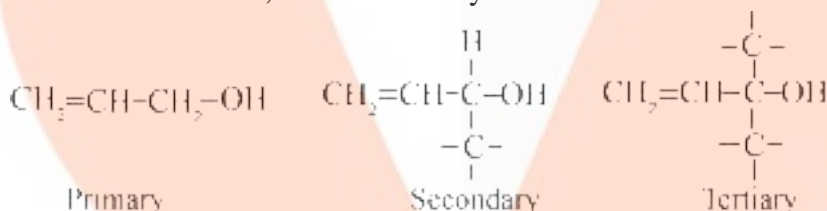
Compounds Containing $\text{sp}^3 \text{C}-\text{OH}$ Bond

(a) Primary, secondary or tertiary alcohols: The $-\text{OH}$ group is attached to primary, secondary and tertiary carbon atoms, respectively.

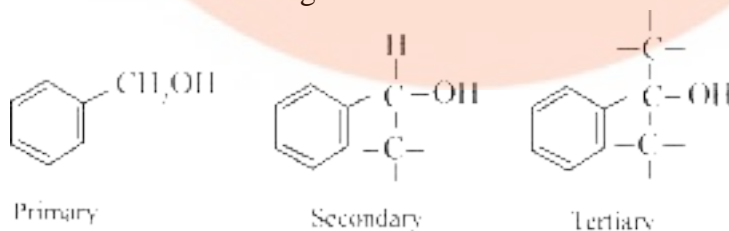


(b) Allylic Alcohols

The $-\text{OH}$ group is attached to an sp^3 -hybridised carbon atom next to the carbon-carbon double bond, that is to an allylic carbon.



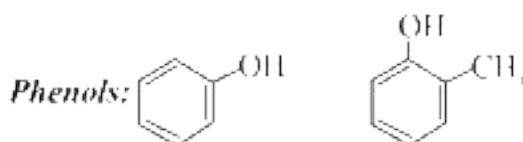
(c) **Benzylic Alcohols:** The $-\text{OH}$ group is bonded to an sp^3 -hybridised carbon atom next to an aromatic ring.



● Compounds Containing $\text{sp}^2 \text{C}-\text{OH}$ Bond

(a) **Vinylic Alcohols:** Bonded to an sp^2 -hybridised carbon atom of carbon-carbon double bond. $\text{CH}_2 = \text{CH} - \text{OH}$

(b) **Aryl Alcohols:** Bonded to an sp^2 -hybridised carbon atom of an aromatic ring.



➤ **Ethers: classification**

- **Simple or symmetrical:** If the alkyl or aryl groups attached to the oxygen atom are the same. $C_2H_5OC_2H_5$.
- **Mixed or unsymmetrical:** If the alkyl or aryl groups attached to the oxygen atom are different.
 $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$

➤ **Nomenclature:**

a) Alcohols:

Common name: The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it.

For example, CH_3OH is methyl alcohol.

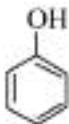
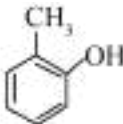

IUPAC naming:

The name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting 'e' of alkane with the suffix 'ol'.

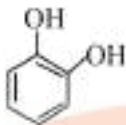
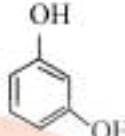

Compound	Common name	IUPAC name
CH_3-OH	Methyl alcohol	Methanol
$CH_3-CH_2-CH_2-OH$	<i>n</i> -Propyl alcohol	Propan-1-ol
$CH_3-\underset{\substack{ \\ OH}}{CH}-CH_3$	Isopropyl alcohol	Propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	<i>n</i> -Butyl alcohol	Butan-1-ol
$CH_3-\underset{\substack{ \\ OH}}{CH}-CH_2-CH_3$	<i>sec</i> -Butyl alcohol	Butan-2-ol
$CH_3-\underset{\substack{ \\ OH}}{OH}-CH_2-CH_3$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} CH_3 \\ \\ CH_3-C-OH \\ \\ CH_3 \end{array}$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{c} CH_2-CH-CH_2 \\ \quad \quad \\ OH \quad OH \quad OH \end{array}$	Glycerol	Propane - 1, 2, 3-triol

b) Phenols:

The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name.

				
Common name	Phenol	<i>o</i> -Cresol	<i>m</i> -Cresol	<i>p</i> -Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- and 1, 4-benzenediol.

			
Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

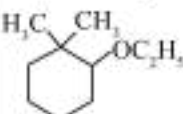
c) Ethers:

Common name: Ethers are derived from the names of alkyl/ aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end.

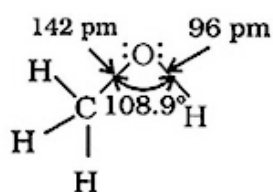
For example, $\text{CH}_3\text{OC}_2\text{H}_5$ is ethylmethyl ether.

IUPAC name: Ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an $-\text{OR}$ or $-\text{OAr}$ group, where R and Ar represent alkyl and aryl groups, respectively.

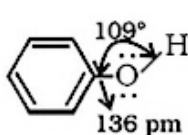
For example, $\text{CH}_3\text{OC}_2\text{H}_5$ is named as 1-methoxy ethane.

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6-\text{CH}_3$	Heptylphenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Phenylisopentyl ether	3-Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

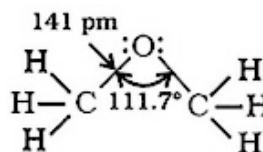
➤ Structures of Functional Groups



Methanol



Phenol



Methoxymethane

The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (i) partial double bond character on account of the conjugation of an unshared electron pair of oxygen with the aromatic ring and (ii) sp^2 hybridised state of carbon to which oxygen is attached.

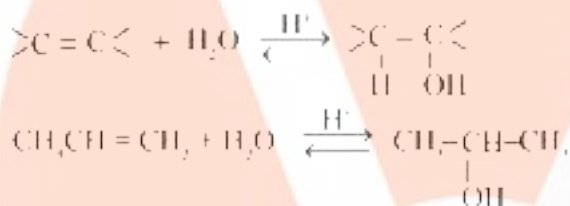
➤ Alcohols and Phenols

Preparation of Alcohols:

❖ 1. From Alkene:

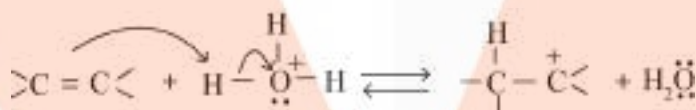
(i) By acid catalysed hydration:

→ In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule

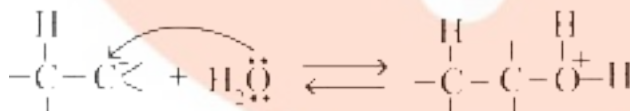


▪ Mechanism:

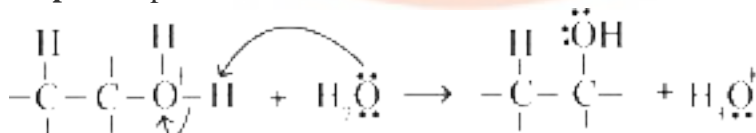
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+



Step 2: Nucleophilic attack of water on carbocation.



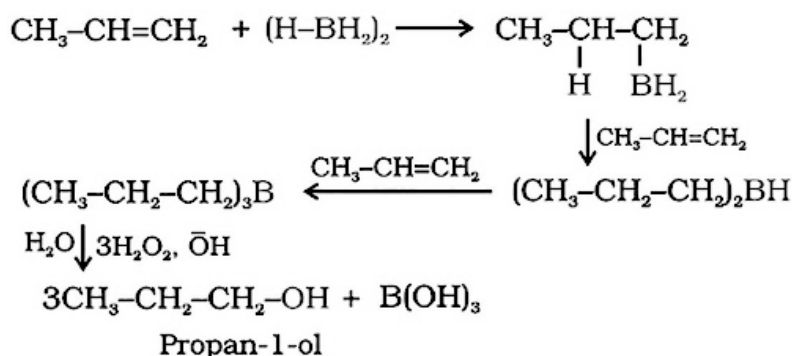
Step 3: Deprotonation to form an alcohol.



(ii) By hydroboration-oxidation:

Diborane (BH_3)₂ reacts with alkenes to give trialkyl boranes as addition product. Which is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

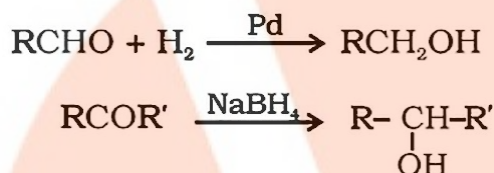
The addition of borane takes place in a way opposite to Markovnikov's rule.



2. From carbonyl compounds:

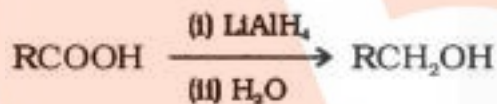
(i) By reduction of aldehydes and ketones:

- Aldehydes yield primary alcohols whereas ketones give secondary alcohols.
- Reducing agents used are by catalytic hydrogenation and by hydride transfer reducing agents like LiAlH_4 and NaBH_4 .

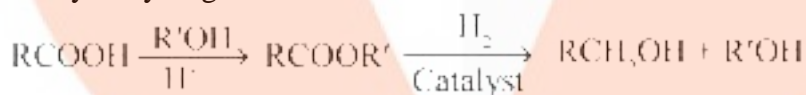


(ii) By reduction of carboxylic acids and esters:

- Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride, a strong reducing agent.

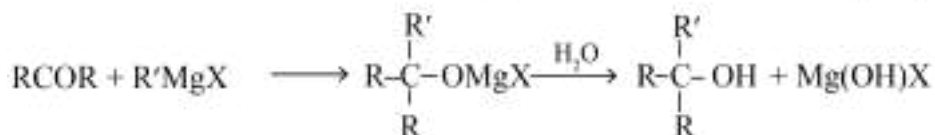
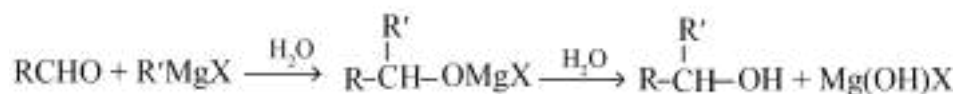
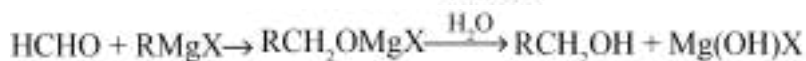
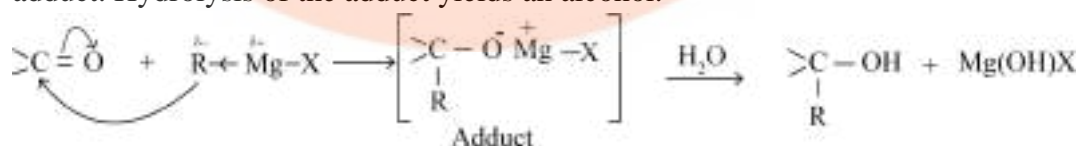


- Commercially, alcohols are prepared by converting acid to the esters followed by catalytic hydrogenation.



3. From Grignard reagents

- Nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



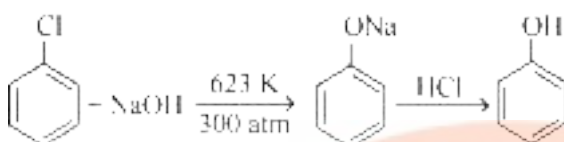
The reaction of Grignard reagents with methanal produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols.

➤ Preparation of Phenols

Phenol, also known as carbolic acid,

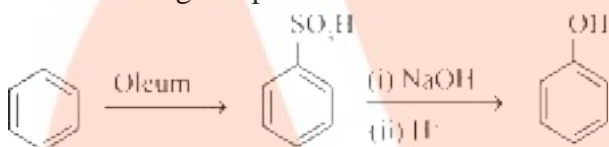
1. From haloarenes

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.



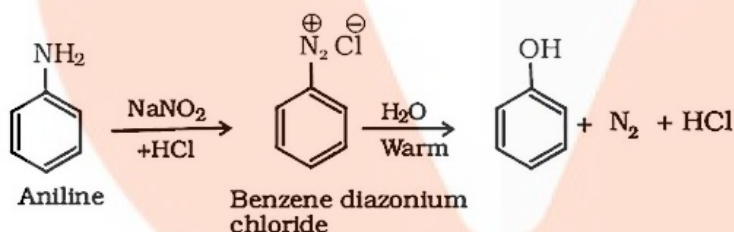
2. From benzene sulphonic acid

Benzene first gives benzene sulphonic acid with oleum. Benzene sulphonic acid converted to sodium phenoxide on heating with molten sodium hydroxide, which on acidification gives phenol.



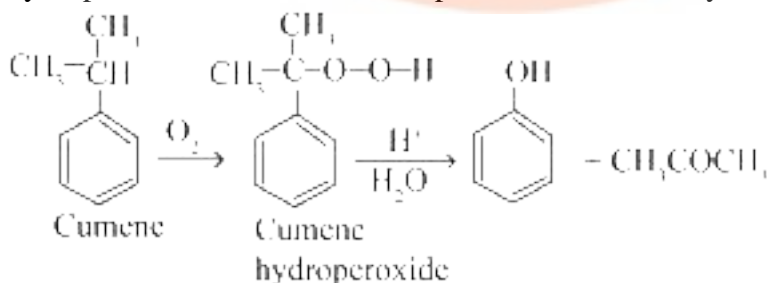
3. From diazonium salts

Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.



4. From cumene

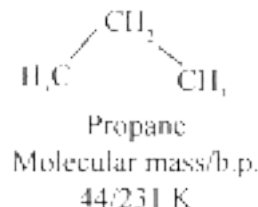
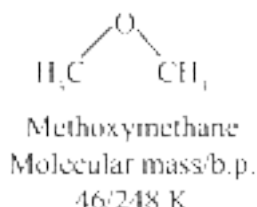
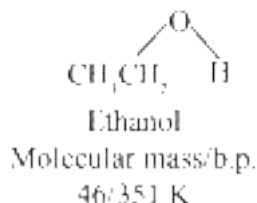
Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid.



➤ Physical Properties

● Boiling Points

- ❖ In alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces).
- ❖ In alcohols, decrease with increase of branching in the carbon chain.



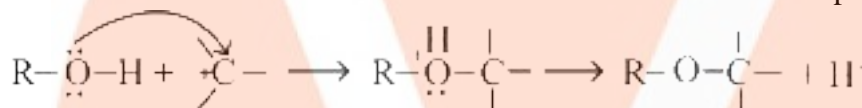
- ❖ Boiling points of alcohols and phenols are higher in comparison to other classes of compounds mainly due to the presence of intermolecular hydrogen bonding.

● Solubility

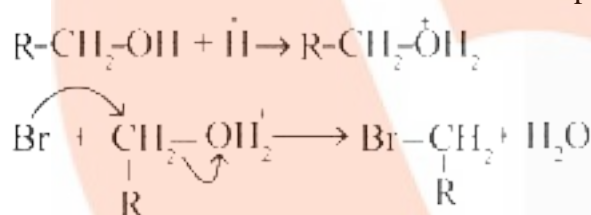
- ❖ Solubility is due to their ability to form hydrogen bonds with water molecules
- ❖ The solubility decreases with increase in size of alkyl/aryl (hydro-phobic) groups.

➤ Chemical Reactions

- The bond between O-H is broken when alcohols react as nucleophiles.



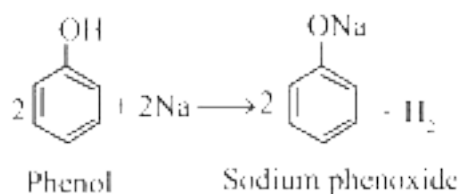
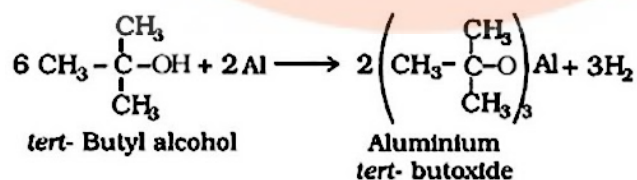
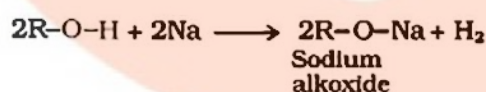
- The bond between C-O is broken when the protonated alcohol reacts as electrophiles.



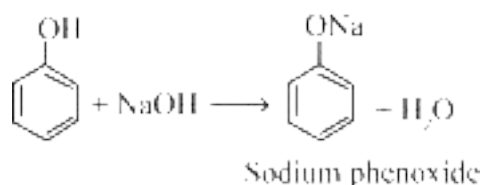
(a) Reactions involving cleavage of O-H bond

1. Acidity of alcohols and phenols

(i) Reaction with metals:



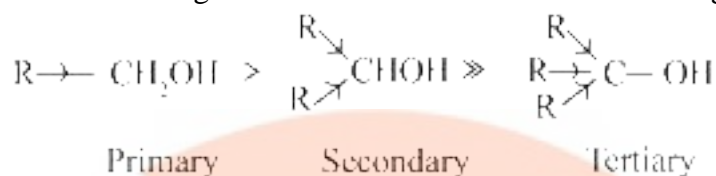
phenols react with aqueous sodium hydroxide to form sodium phenoxides



alcohols and phenols are Brönsted acids i.e., they can donate a proton to a stronger base

(ii) Acidity of alcohols:

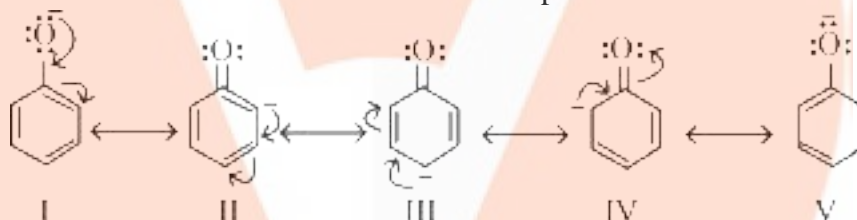
- The acid strength of alcohols decreases in the following order



- Electron-releasing group ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$) increases electron density on oxygen tending to decrease the polarity of O-H bond
- Alcohols are weaker acids than water.

(iii) Acidity of phenols:

- Phenols are stronger acids than alcohols and water.
- In alkoxide ion, the negative charge is **localised** on oxygen while in phenoxide ion, the charge is **delocalised**. Which makes phenoxide ion more stable and favours the ionisation of phenol.

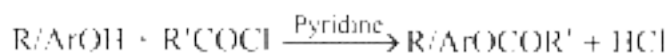
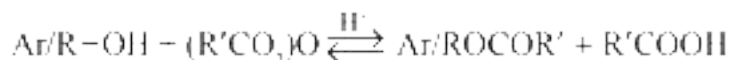
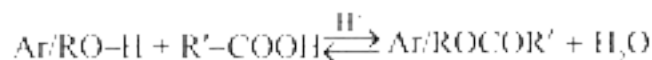


- In substituted phenols electron withdrawing groups at ortho and para positions such as nitro group, enhances the acidic strength.
- In substituted phenols electron releasing groups, such as alkyl groups, decrease in acid strength.

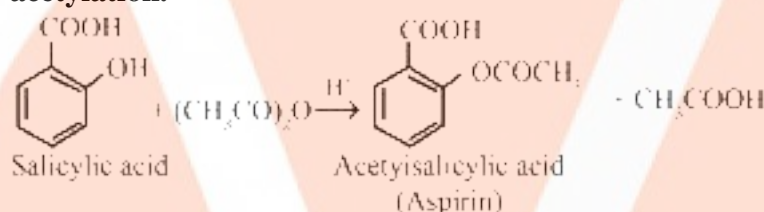
Compound	Formula	pK_a
<i>o</i> - Nitrophenol	<i>o</i> -O ₂ N-C ₆ H ₄ -OH	7.2
<i>m</i> - Nitrophenol	<i>m</i> -O ₂ N-C ₆ H ₄ -OH	8.3
<i>p</i> - Nitrophenol	<i>p</i> -O ₂ N-C ₆ H ₄ -OH	7.1
Phenol	C ₆ H ₅ -OH	10.0
<i>o</i> - Cresol	<i>o</i> -CH ₃ -C ₆ H ₄ -OH	10.2
<i>m</i> - Cresol	<i>m</i> -CH ₃ -C ₆ H ₄ -OH	10.1
<i>p</i> - Cresol	<i>p</i> -CH ₃ -C ₆ H ₄ -OH	10.2
Ethanol	C ₂ H ₅ OH	15.9

2. Esterification

- Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.



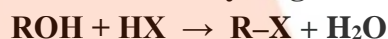
- Reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl.
- The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed.
- The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as **acetylation**.



(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

The reactions involving cleavage of C–O bonds take place only in alcohols. Phenols show this type of reaction only with zinc.

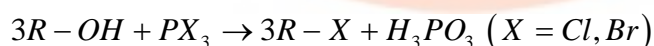
1. Reaction with hydrogen halides



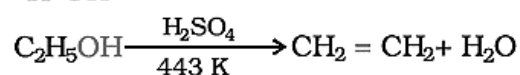
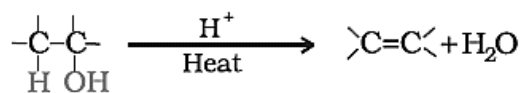
Lucas test: Lucas reagent (conc. HCl and ZnCl_2)

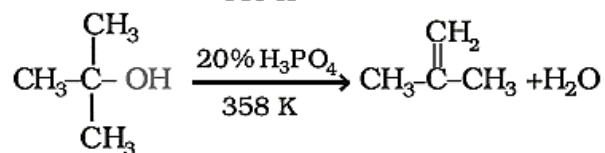
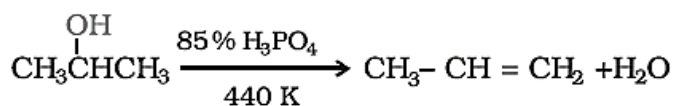
- Alcohols are soluble in Lucas reagent (conc. HCl and ZnCl_2) while their halides are immiscible and produce turbidity in solution.
- Tertiary alcohols, turbidity is produced immediately.
- Primary alcohols do not produce turbidity at room temperature.

2. Reaction with phosphorus trihalides: Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide.



3. Dehydration

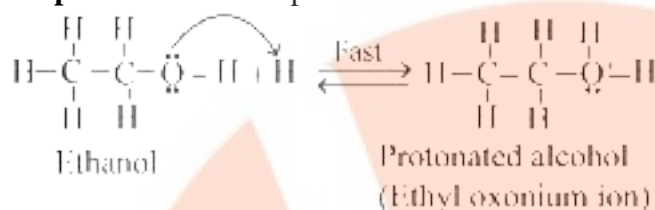




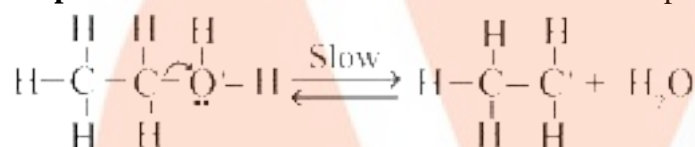
- dehydration of alcohols follows the order:
Tertiary > Secondary > Primary

➤ Mechanism

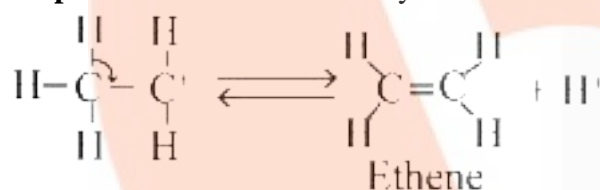
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation is the slowest step and rate determining step

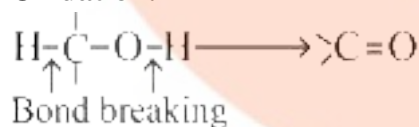


Step 3: Formation of ethene by elimination of a proton.



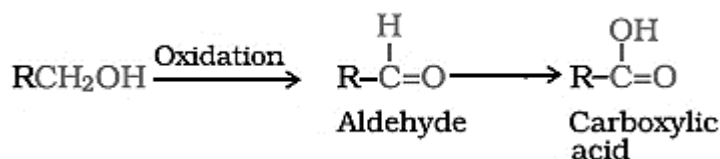
To drive the equilibrium to the right, ethene is removed as it is formed.

❖ Oxidation:

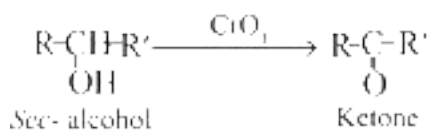
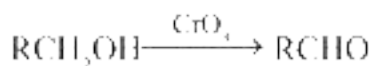


These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule.

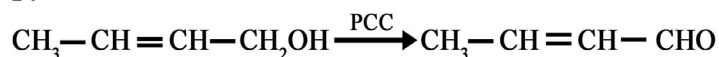
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly.



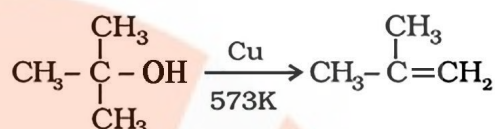
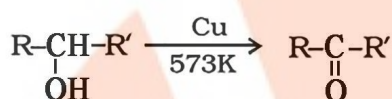
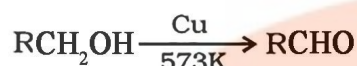
CrO₃ in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.



- A better reagent for oxidation of primary alcohols to aldehydes in good yield is **pyridinium chlorochromate (PCC)**



- When the vapours of a primary or a secondary alcohol are passed over heated copper

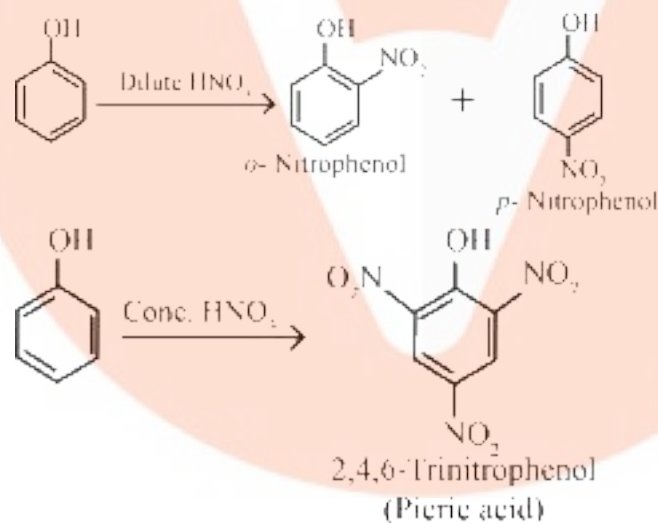


(c) Reactions of phenols

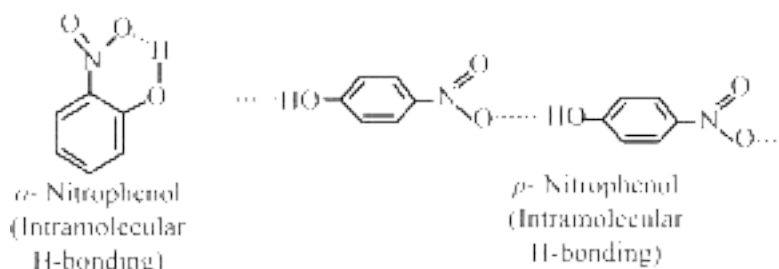
1. Electrophilic aromatic substitution:

The -OH activates ring towards electrophilic substitution at ortho and para positions

(i) Nitration

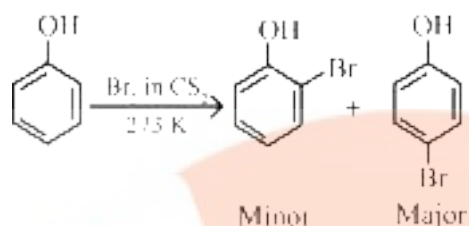


- The ortho and para isomers can be separated by steam distillation.
- *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

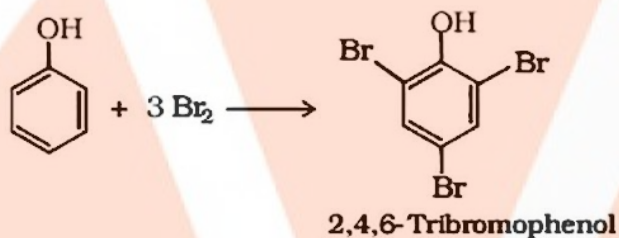


(ii) Halogenation:

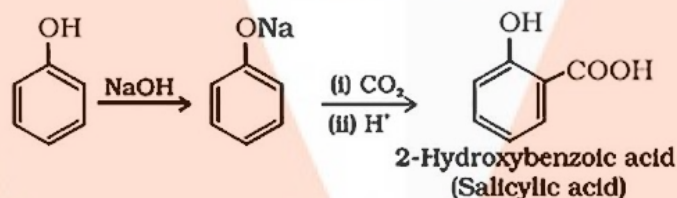
(a)



(b) with bromine water, 2,4,6-tribromophenol is formed as white precipitate



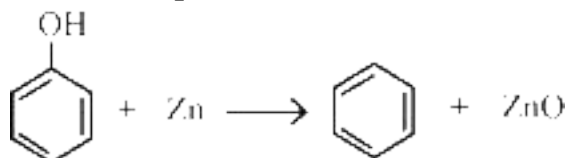
2. Kolbe's reaction



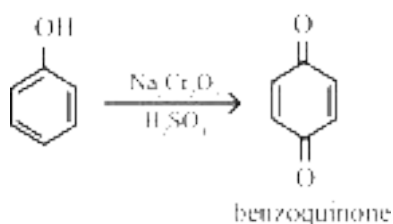
3. Reimer-Tiemann reaction



4. Reaction of phenol with zinc dust



5. Oxidation:

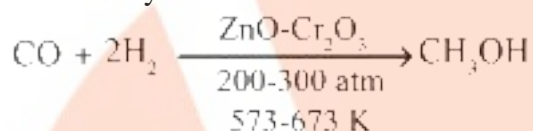


In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing **quinones**.

➤ Some Commercially Important Alcohols

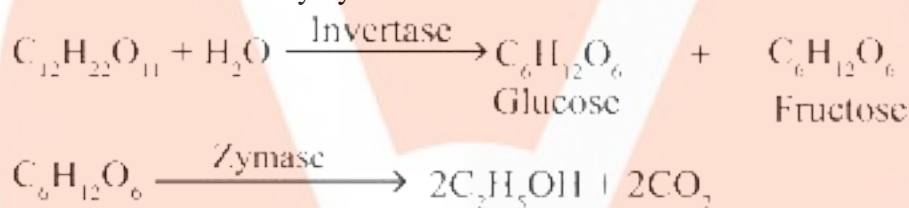
1. Methanol

- Also known as 'wood spirit'.
- It is highly poisonous in nature.
- Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.



2. Ethanol

- Obtained commercially by fermentation.

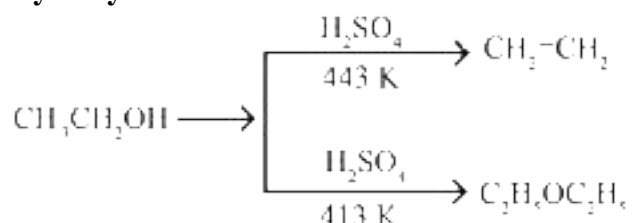


- Fermentation takes place in anaerobic conditions i.e. in absence of air, because the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.
- The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

➤ Ethers

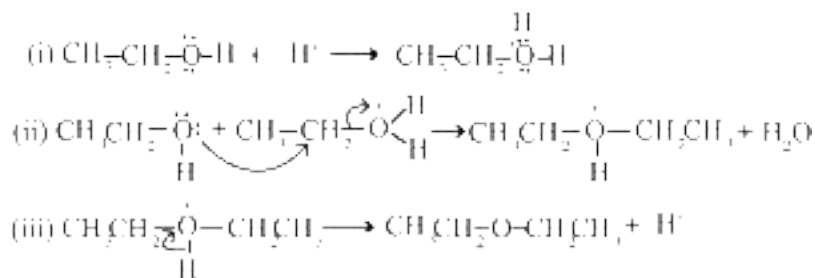
• Preparation of Ethers

1. By dehydration of alcohols

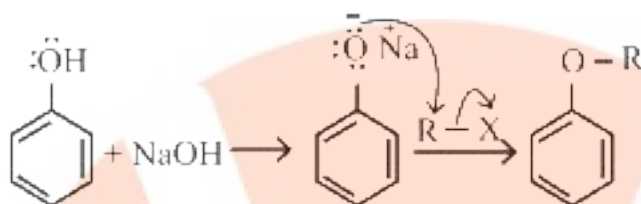
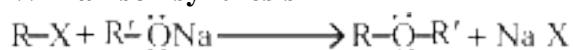


- The formation of ether is a nucleophilic bimolecular reaction ($\text{S}_{\text{N}}2$)
- The method is suitable for the preparation of ethers having primary alkyl groups only.
- In dehydration of secondary and tertiary alcohols alkenes are easily formed.

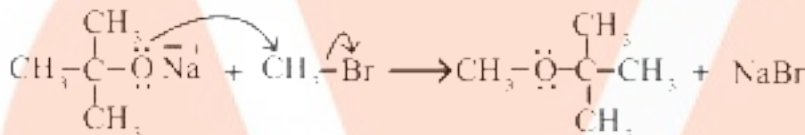
● **Mechanism**



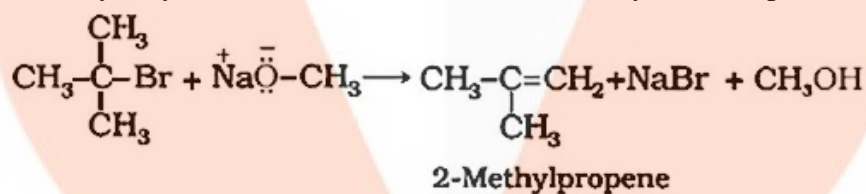
2. Williamson synthesis



- The reaction involves $\text{S}_{\text{N}}2$ attack of an alkoxide ion on primary alkyl halide.

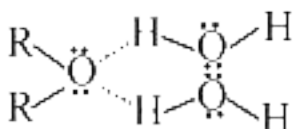


- Better results are obtained if the alkyl halide is primary.
- In case of secondary and tertiary alkyl halides, elimination competes over substitution.
- If tertiary alkyl halide is used, an alkene is the only reaction product.



➤ **Physical Properties**

- The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.
- miscibility of ethers with water resembles those of alcohols of the same molecular mass



➤ **Chemical Reactions**

1. Cleavage of C-O bond in ethers

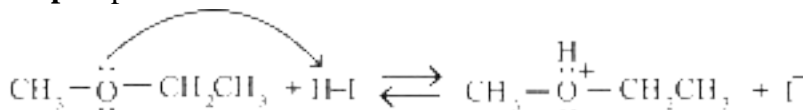
- The cleavage of C-O bond in ethers takes place under drastic conditions with excess of hydrogen halides



The order of reactivity of hydrogen halides is as follows: $\text{HI} > \text{HBr} > \text{HCl}$.

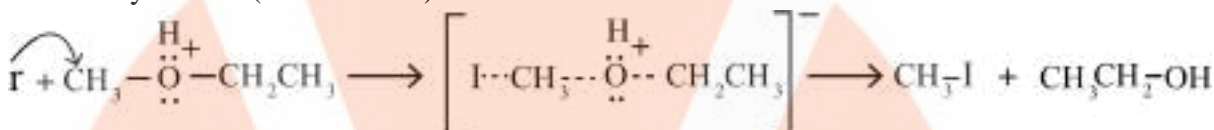
Mechanism:

Step 1: protonation of ether molecule



The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

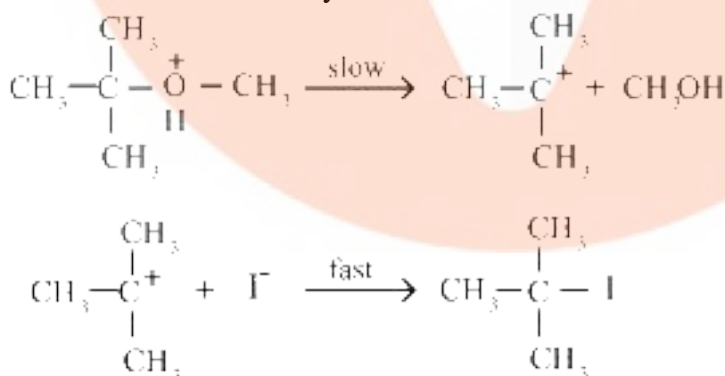
Step 2: primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N^2 reaction).



Step 3: When HI is in excess and at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.



- Reaction follows S_N^1 mechanism when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.

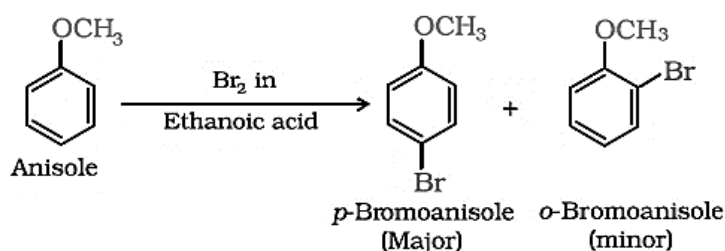


- In Anisole, I^- ion breaks $\text{O}-\text{CH}_3$ bond to form CH_3I .
- $\text{O}-\text{CH}_3$ is weaker than the bond $\text{O}-\text{C}_6\text{H}_5$ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character.

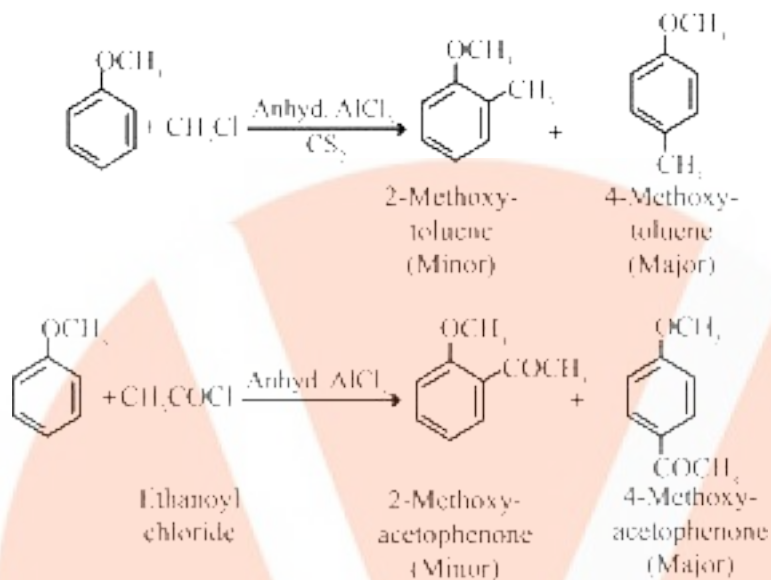
2. Electrophilic substitution

The alkoxy group ($-\text{OR}$) is ortho, para directing

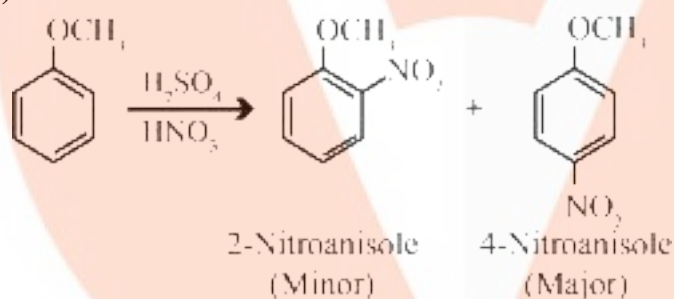
(i) **Halogenation:** Para isomer is obtained in 90% yield.



(ii) Friedel-Crafts reaction:



(iii) Nitration:

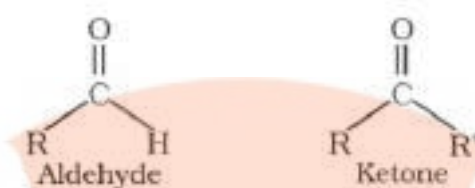


Aldehydes and Ketones

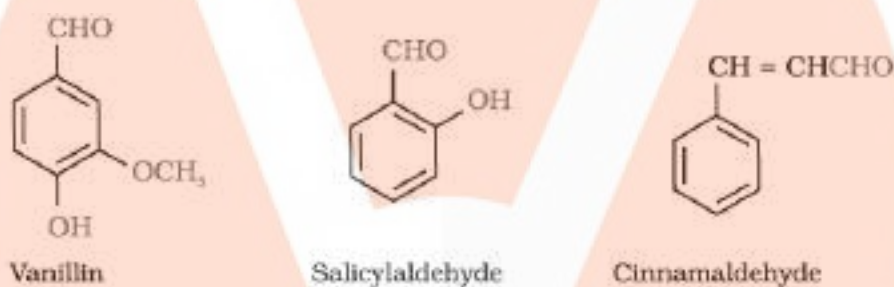
Introduction:

Organic compounds containing carbon-oxygen double bonds ($>C=O$) are called carbonyl groups.

In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms.



They add fragrance and flavour to nature, for example, vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.



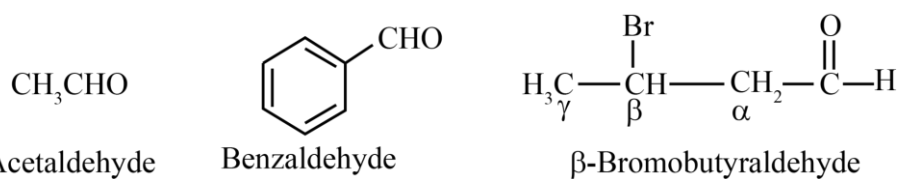
They are used in many food products and pharmaceuticals to add flavours. Some of these families are manufactured for use as solvents (i.e., acetone) and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics.

➤ Nomenclature and Structure of Carbonyl Group

Aldehydes and ketones

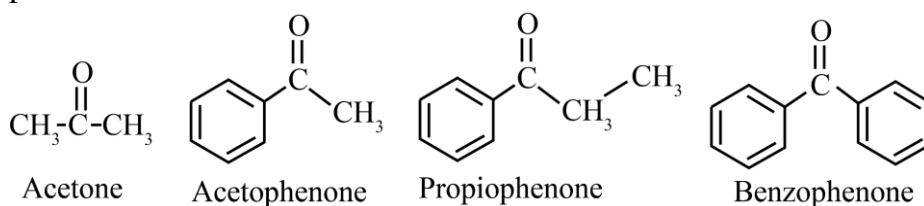
(a) Common names

- The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending $-ic$ of acid with aldehyde
- The location of the substituent indicated by Greek letters α , β , γ , δ , etc.
- The α -carbon being the one directly linked to the aldehyde group.



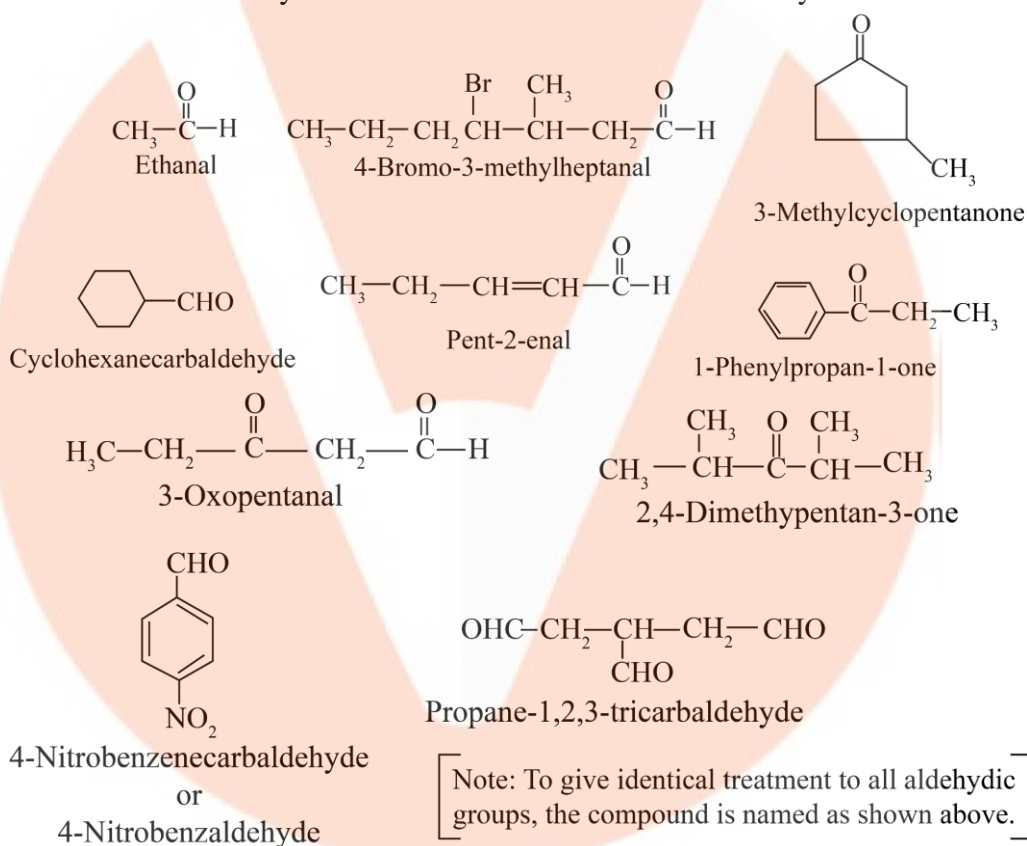
Some ketones have historical common names, the simplest dimethyl ketone is called acetone.

Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone.



(b) IUPAC names:

- The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –e with –al and –one respectively.
- Common name benzaldehyde is also accepted by IUPAC.
- Other aromatic aldehydes are named as substituted benzaldehydes.

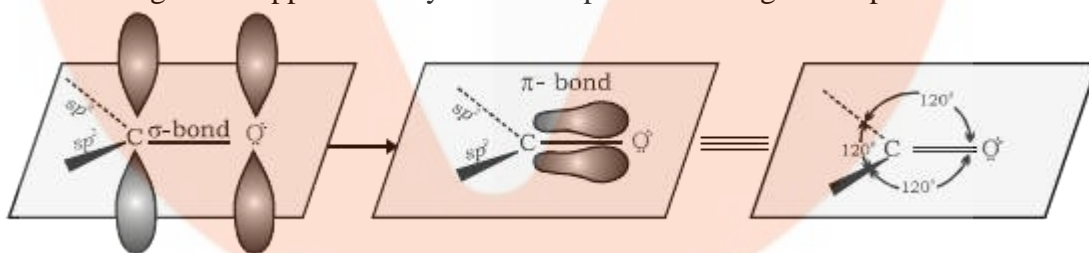


[Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.]

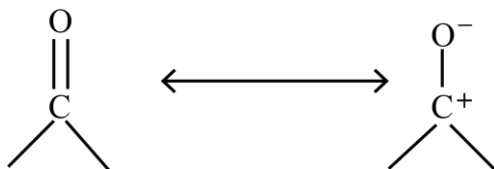
Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
(CH ₃) ₂ CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexane	3-Methylcyclohexanecarbaldehyde
CH ₃ CH(OCH ₃)CHO	α-Methoxypropionaldehyde	2-Methoxypropanal
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Valeraldehyde	Pentanal
CH ₂ =CHCHO	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
	<i>m</i> -Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
CH ₃ COCH ₂ CH ₂ CH ₃	Methyl <i>n</i> -propyl ketone	Pentan-2-one
(CH ₃) ₂ CHCOCH(CH ₃) ₂	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
(CH ₃) ₂ C=CHCOCH ₃	Mesityl oxide	4-Methylpent-3-en-2-one

➤ Structure of the Carbonyl Group

- The carbonyl carbon atom is sp²-hybridised and forms three sigma (σ) bonds
- The bond angles are approximately 120° as expected of a trigonal coplanar structure

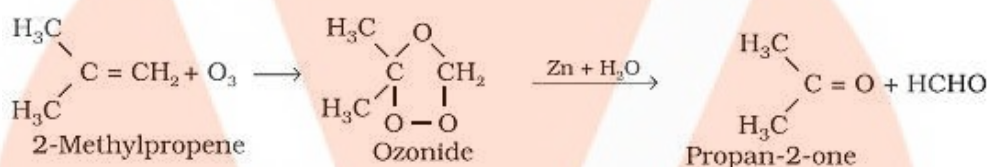
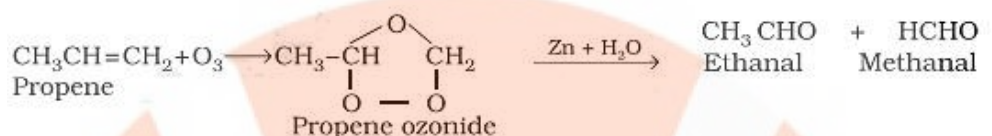


- The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre.
- Carbonyl compounds have substantial dipole moments and are more polar than ethers.

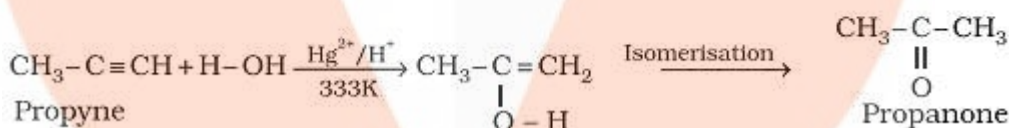
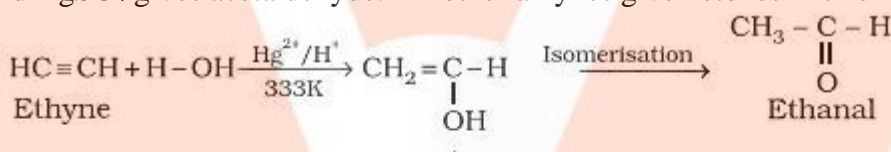


➤ **Preparation of Aldehydes and Ketones**

1. **By oxidation of alcohols:** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.
2. **By dehydrogenation of alcohols:**
 - This method is suitable for volatile alcohols and is of industrial application.
 - Alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively.
3. **From hydrocarbons:**
 - **By ozonolysis of alkenes:** ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene.

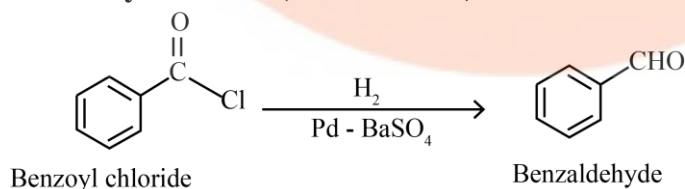


- **By hydration of alkynes:** Addition of water to ethyne in the presence of H_2SO_4 and HgSO_4 gives acetaldehyde. All other alkynes give ketones in this reaction.



➤ **Preparation of Aldehydes**

1. **From acyl chloride (acid chloride): Rosenmund reduction.**

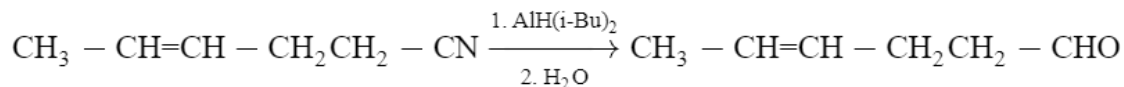
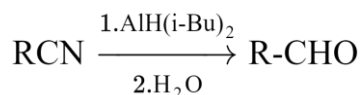


2. **From nitriles and esters:**

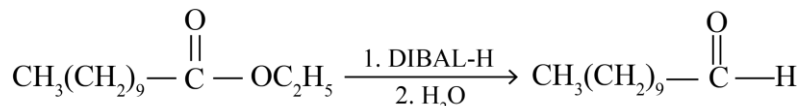
- **Stephen reaction:** Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.



- Nitriles are selectively reduced by, (DIBAL-H) to imines followed by hydrolysis to aldehydes.



- Esters are also reduced to aldehydes with DIBAL-H

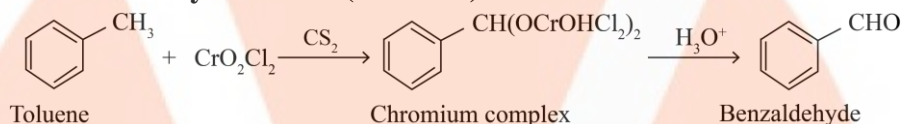


3. From hydrocarbons

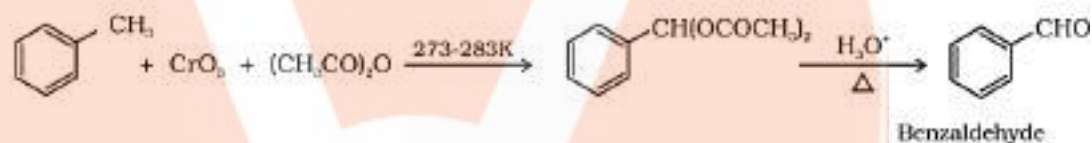
I. By oxidation of methylbenzene

- ❖ Strong oxidising agents oxidise toluene and its derivatives to benzoic acids.
- ❖ To stop the oxidation at the aldehyde stage suitable reagents are used that convert the methyl group to an intermediate that is difficult to oxidise further.

a) Use of chromyl chloride (CrO_2Cl_2): Etard reaction

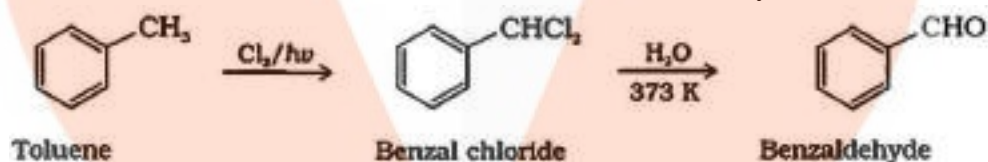


b) Use of chromic oxide (CrO_3)

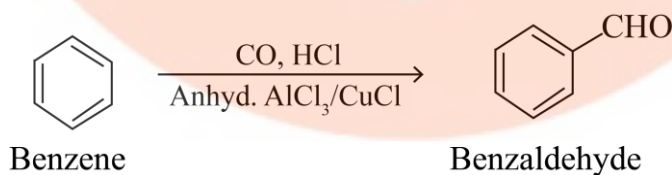


II. By side chain chlorination followed by hydrolysis

This is a commercial method of manufacture of benzaldehyde

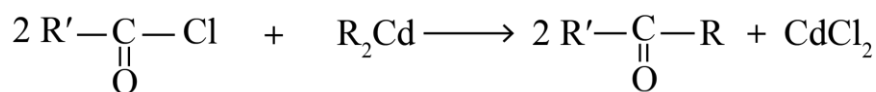
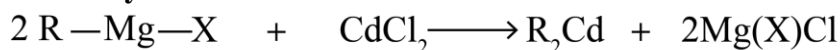


III. By Gatterman – Koch reaction

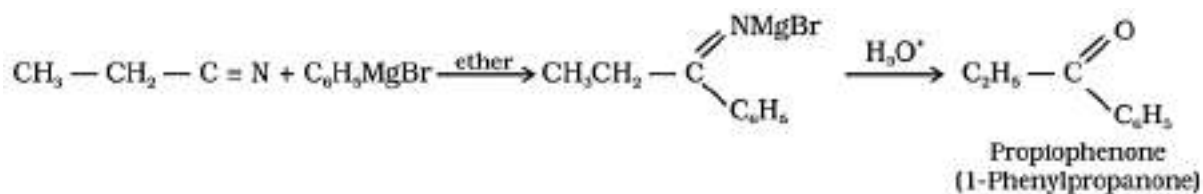


➤ Preparation of Ketones

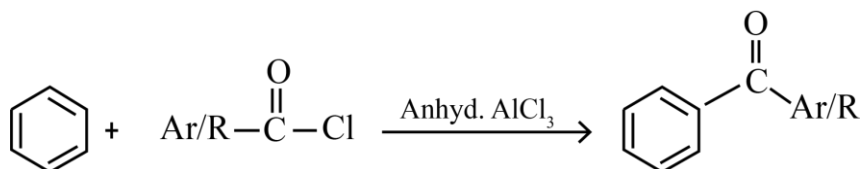
1. From acyl chlorides:



2. From nitriles:



3. From benzene or substituted benzenes: Friedel-Crafts acylation reaction:



➤ Physical Properties

- Methanal is a gas at room temperature. Ethanal is a volatile liquid.
- Boiling points of aldehydes and ketones are higher than hydrocarbons and ethers & lower than those of alcohols of similar molecular masses.
- Methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bonds with water.



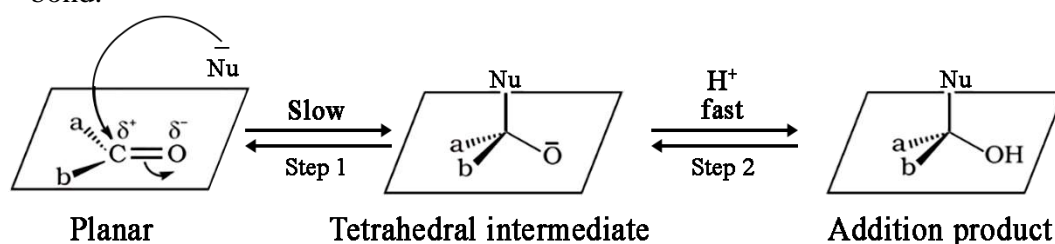
- All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform.
- The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant.

➤ Chemical Reactions

1. Nucleophilic addition reactions

(i) Mechanism of nucleophilic addition reaction.

- A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group.
- The hybridisation of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced.
- This intermediate captures a proton from the reaction medium to give the electrically neutral product.
- The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.

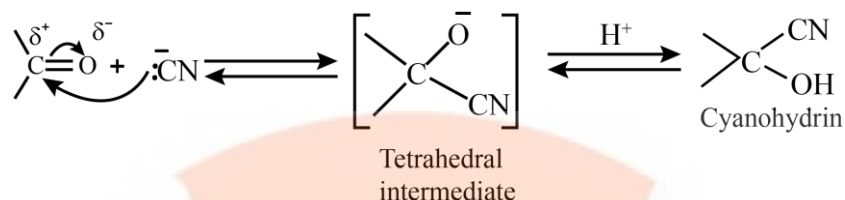
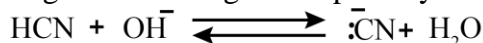


(ii) **Reactivity**

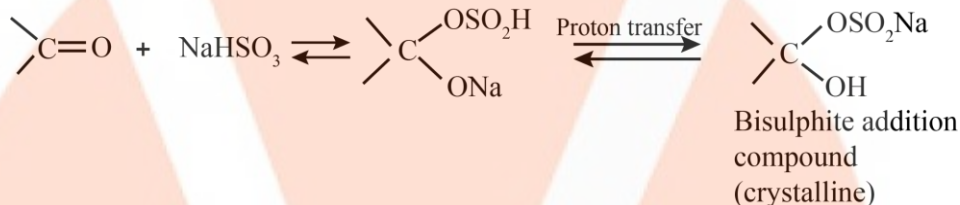
- Aldehydes are generally **more reactive** than **ketones** in nucleophilic addition reactions due to steric and electronic reasons.

(iii) **Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:**

(a) **Addition of hydrogen cyanide (HCN):** This reaction is catalysed by a base to generate strong nucleophile cyanide ion (CN^-).

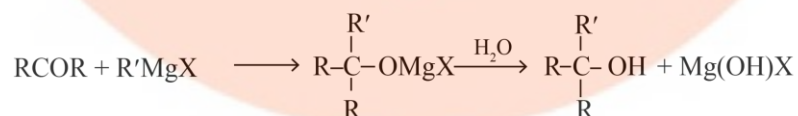
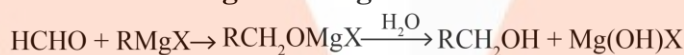


(b) **Addition of sodium hydrogensulphite:**

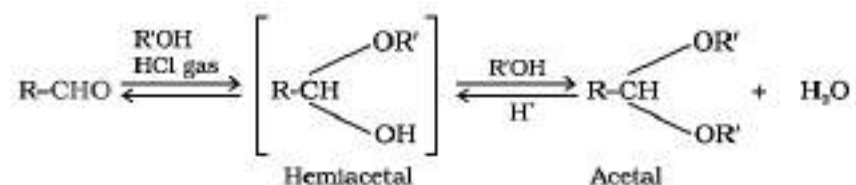


- The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons.
- The hydrogen sulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali.
- These are useful for separation and purification of aldehydes.

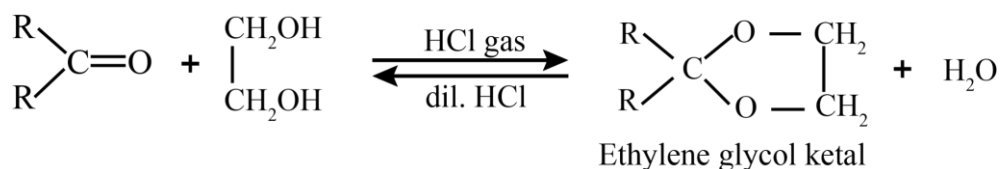
(c) **Addition of Grignard reagents:**



(d) **Addition of alcohols:**



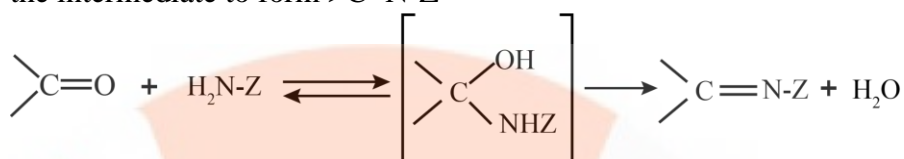
Ketones react with ethylene glycol to form cyclic products known as ethylene glycol ketals

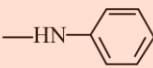
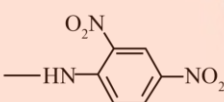


- Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

(e) Addition of ammonia and its derivatives :

- The reaction is reversible and catalysed by acid.
- The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>\text{C}=\text{N}-\text{Z}$



Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\begin{array}{c} \diagup \\ \text{C}=\text{NH} \\ \diagdown \end{array}$	Imine
-R	Amine	$\begin{array}{c} \diagup \\ \text{C}=\text{NR} \\ \diagdown \end{array}$	Substituted imine (Suhiff's base)
-OH	Hydroxylamine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{OH} \\ \diagdown \end{array}$	Oxime
-NH ₂	Hydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}_2 \\ \diagdown \end{array}$	Hydrazone
-HN- 	Phenylhydrazine	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_5 \\ \diagdown \end{array}$	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine,	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \diagdown \end{array}$	2,4 Dinitrophenylhydrazine
-NH-C(=O)-NH ₂	Semicarbazide	$\begin{array}{c} \diagup \\ \text{C}=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2 \\ \diagdown \end{array}$	Semicarbazone

2. Reduction:

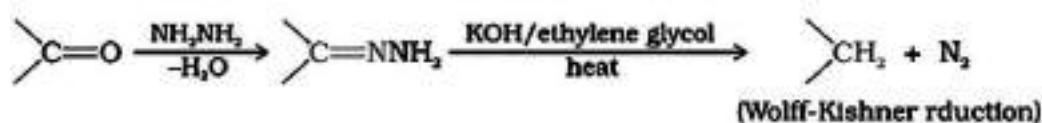
(i) **Reduction to alcohols:** Reduced to primary and secondary alcohols respectively by NaBH_4 or LiAlH_4 as well as by catalytic hydrogenation.

(ii) **Reduction to hydrocarbons:**

❖ **Clemmensen Reduction**

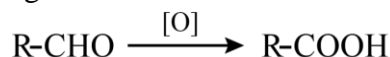


❖ **Wolff-Kishner reduction:**



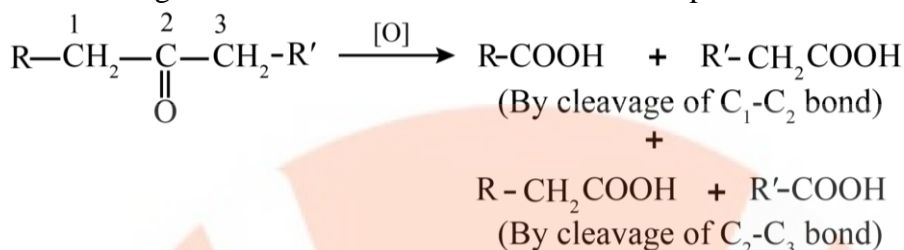
3. Oxidation:

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents.



Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures.

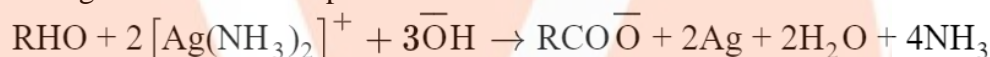
Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



The mild oxidising agents given below are used to **distinguish aldehydes from ketones**.

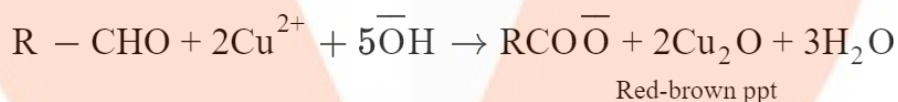
(i) Tollens' test:

- Ammoniacal silver nitrate solution (**Tollens' reagent**)
- A bright silver mirror is produced due to the formation of silver metal.



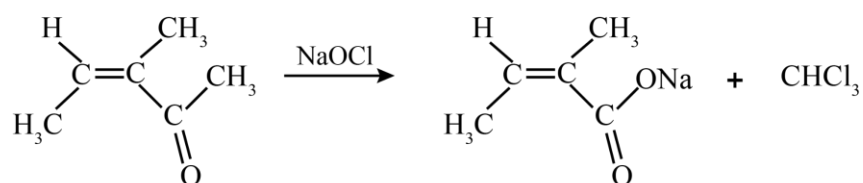
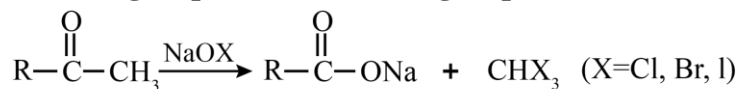
(ii) Fehling's test

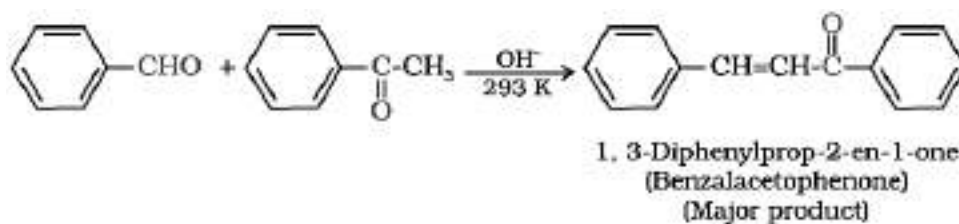
- Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartrate (**Rochelle salt**).
- **Aromatic aldehydes** do not respond to this test.



(iii) Oxidation of methyl ketones by haloform reaction:

- Aldehydes & ketones having at least one methyl group linked to the carbonyl carbon atom are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound.
- This oxidation does not affect a carbon-carbon double bond.
- **Iodoform reaction** with sodium hypoiodite is also used for detection of **CH₃CO group** or **CH₃CH(OH) group**.

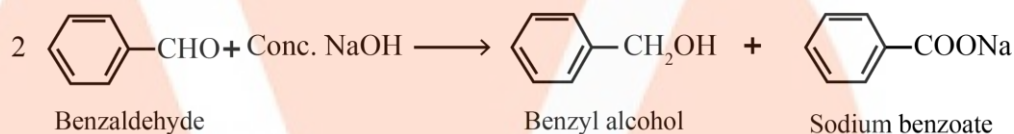
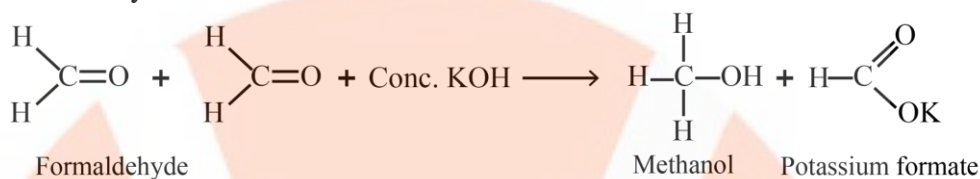




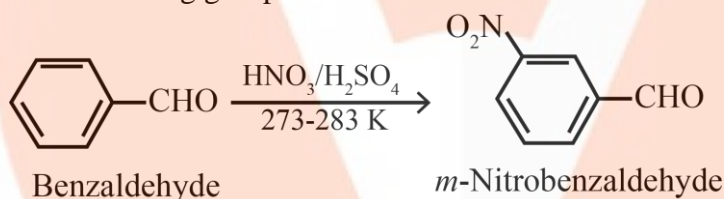
5. Other reactions:

(i) Cannizzaro reaction:

- Aldehydes which do not have an α -hydrogen atom, undergo self-oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.
- One molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



(ii) Electrophilic substitution reaction: Carbonyl group acts as a deactivating and meta-directing group.



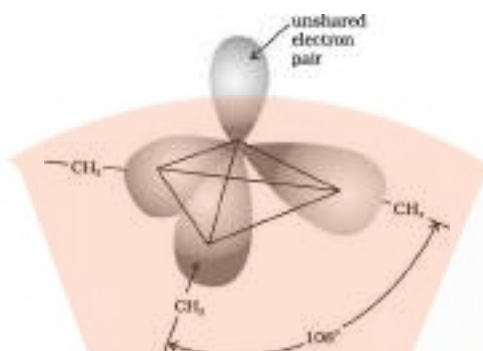
(iii) Uses of Aldehydes and Ketones

- Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite.
- Benzaldehyde is used in perfumery and in dye industries.
- Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

Amines

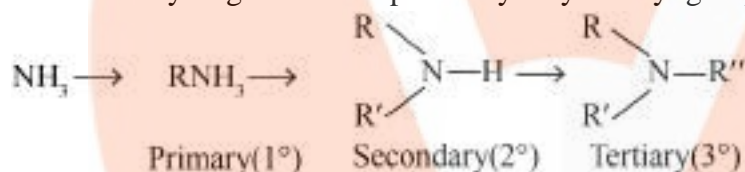
Amines can be considered as derivatives of ammonia.

- **Structure of Amines:** The geometry of amines is pyramidal and sp^3 hybridization. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of an unshared pair of electrons, the angle C–N–E, (where E is C or H) is less than 109.5° ; for instance, it is 108° in case of trimethylamine.




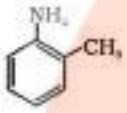
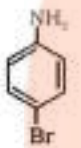
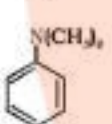
➤ **Classification:**

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecules.



➤ **Nomenclature:**

In common name system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g., methylamine) **IUPAC system**, amines are named as alkanamines.

Amine	Common name	IUPAC name
$\text{CH}_3\text{--CH}_2\text{--NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--NH}_2$	<i>n</i> -Propylamine	Propan-1-amine
$\begin{array}{c} \text{CH}_3\text{--CH--CH}_3 \\ \\ \text{NH}_2 \end{array}$	Isopropylamine	Propan-2-amine
$\begin{array}{c} \text{CH}_3\text{--N--CH}_2\text{--CH}_3 \\ \\ \text{H} \end{array}$	Ethylmethanamine	N-Methylethanamine
$\begin{array}{c} \text{CH}_3\text{--N--CH}_3 \\ \\ \text{CH}_3 \end{array}$	Trimethylamine	N,N-Dimethylmethanamine
$\begin{array}{c} \text{C}_2\text{H}_5\text{--N--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3 \\ \\ \text{C}_2\text{H}_5 \end{array}$	N,N-Diethylbutylamine	N,N-Diethylbutan-1-amine
$\text{NH}_2\text{--CH}_2\text{--CH=CH}_2$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2\text{--(CH}_2\text{)}_6\text{--NH}_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	<i>o</i> -Toluidine	2-Aminotoluene
	<i>p</i> -Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylaniline	N,N-Dimethylbenzenamine

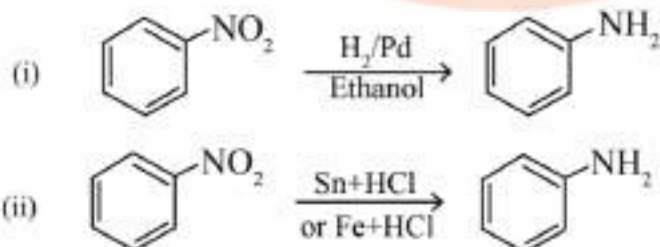
$\text{C}_6\text{H}_5\text{NH}_2$ in the common system, it is known as aniline.

It is also an accepted IUPAC name. While naming arylamines according to the IUPAC system, the suffix 'e' of arene is replaced by 'amine'.

Thus, in the IUPAC system, $\text{C}_6\text{H}_5\text{NH}_2$ is named as benzenamine.

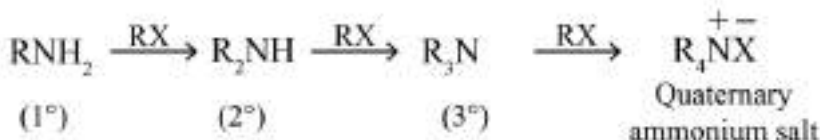
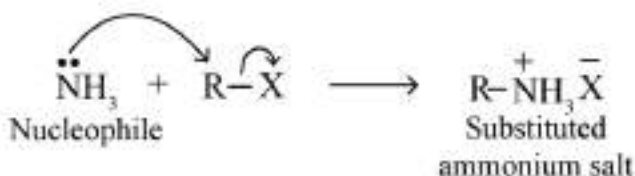
➤ Preparation of Amines

1. Reduction of nitro compounds:



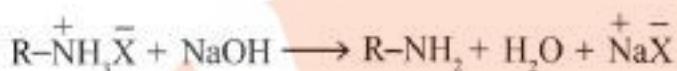
Reduction with iron scrap and hydrochloric acid is preferred because FeCl_2 formed gets hydrolysed to release hydrochloric acid during the reaction.

2. Ammonolysis of alkyl halides: Process of cleavage of the C–X bond by ammonia molecule is known as ammonolysis.



Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

The free amine can be obtained from the ammonium salt by treatment with a strong base

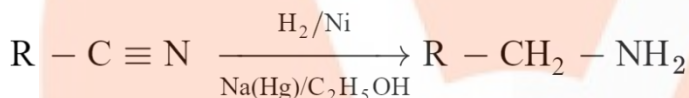


The order of reactivity of halides with amines is $\text{RI} > \text{RBr} > \text{RCl}$.

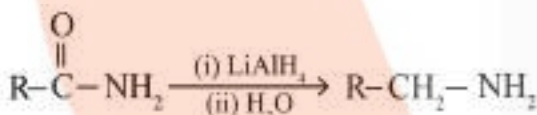
3. Reduction of nitriles:

Reduction with lithium aluminium hydride (LiAlH_4) or catalytic hydrogenation produces primary amines.

This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.

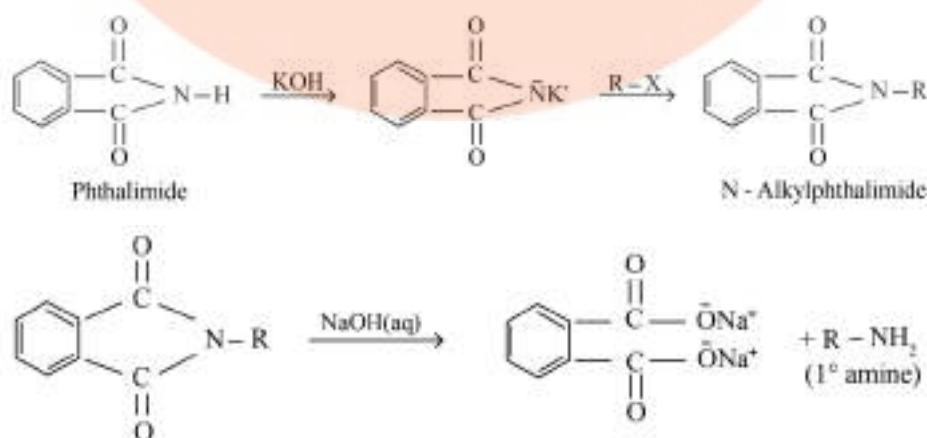


4. Reduction of amides



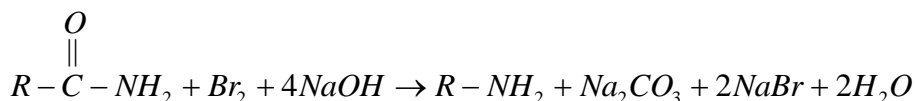
5. Gabriel phthalimide synthesis

- Used for the preparation of primary amines.
- Aromatic primary amines cannot be prepared by this method.



6. Hoffmann bromamide degradation reaction:

- Preparation of primary amines
- The amine so formed contains one carbon less than that present in the amide.

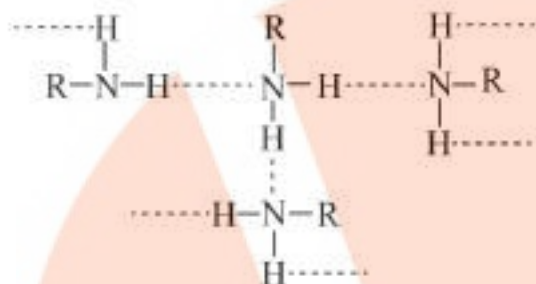


➤ Physical Properties

- Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.
- Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules.
- Amines are soluble in organic solvents like alcohol, ether and benzene
- The order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

- Intermolecular hydrogen bonding in primary amines



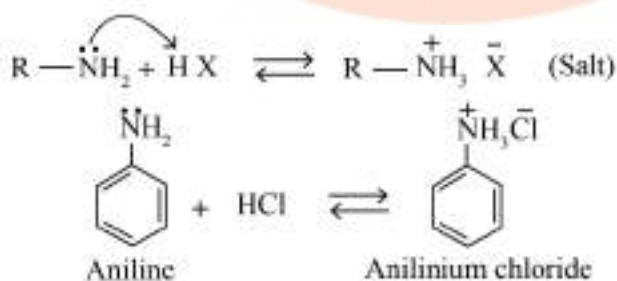
- Comparison of Boiling Points of Amines, Alcohols and Alkanes of Similar Molecular Masses

Sl. No.	Compound	Molar mass	b.p./K
1.	n-C ₄ H ₉ NH ₂	73	350.8
2.	(C ₂ H ₅) ₂ NH	73	329.3
3.	C ₂ H ₅ N(CH ₃) ₂	73	310.5
4.	C ₂ H ₅ CH(CH ₃) ₂	72	300.8
5.	n-C ₄ H ₉ OH	74	390.3

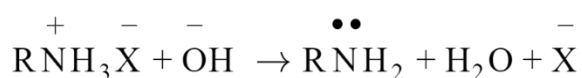
- **Chemical Reactions:** Amines behave as nucleophiles due to the presence of an unshared electron pair.

1. Basic character of amines

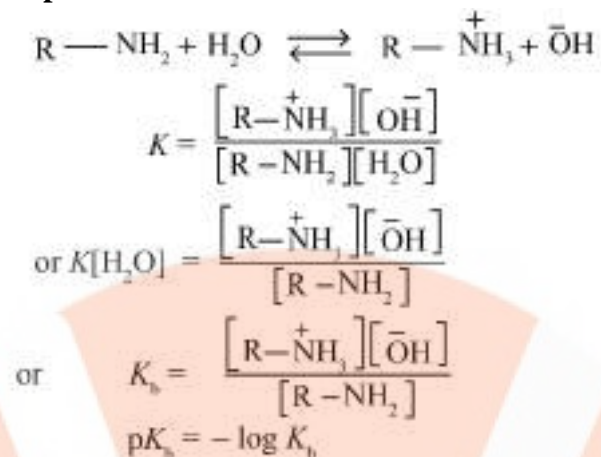
- Amines, being basic in nature, react with acids to form salts.



- Amine salts on treatment with a base like NaOH, regenerate the parent amine.



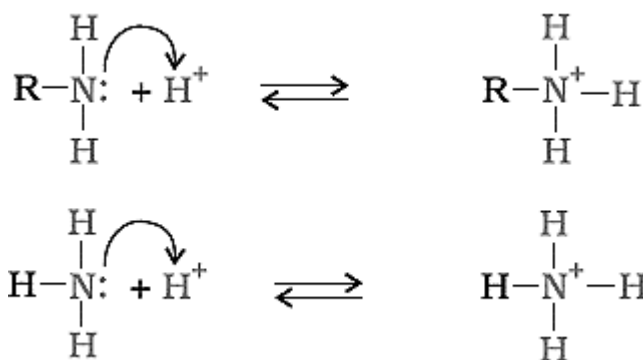
- Amine salts are soluble in water but insoluble in organic solvents like ether. This reaction is the basis for the separation of amines from the non-basic organic compounds insoluble in water.
- Amines behave as **Lewis base**.
- ❖ **K_b values as explained below**



- Larger the value of K_b or smaller the value of pK_b , stronger is the base.
- ❖ **Table: K_b Values of Amines in Aqueous Phase**

Name of amine	pK_b
Methanamine	3.38
<i>N</i> -Methylmethanamine	3.27
<i>N,N</i> -Dimethylmethanamine	4.22
Ethanamine	3.29
<i>N</i> -Ethylethanamine	3.00
<i>N,N</i> -Diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
<i>N</i> -Methylaniline	9.30
<i>N,N</i> -Dimethylaniline	8.92

- **Structure-basicity relationship of amines:** Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, the more basic is the amine.
 - a) **Alkyl amines versus ammonia:**
 - ❖ Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups

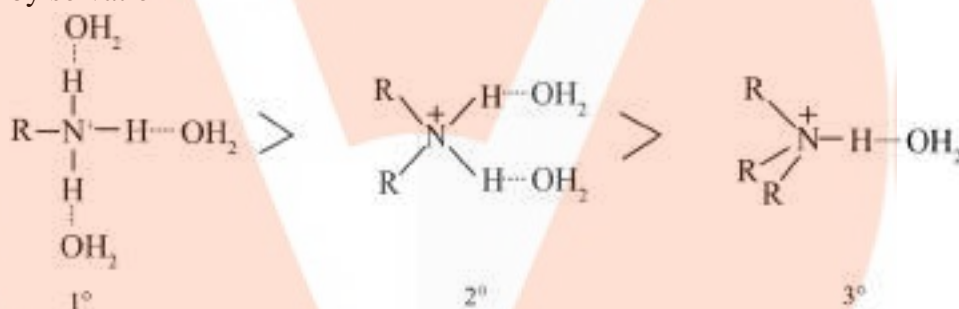


- **Gaseous phase**

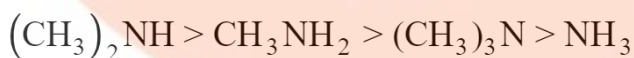
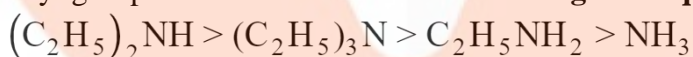
- ❖ The order of basicity of amines: **tertiary amine > secondary amine > primary amine > NH_3**

- **Aqueous phase**

- ❖ Substituted ammonium cations get stabilised not only by +I effect of the alkyl group but also by solvation with water molecules.
- ❖ The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion.
- ❖ Decreasing order of extent of H-bonding in water and order of stability of ions by solvation

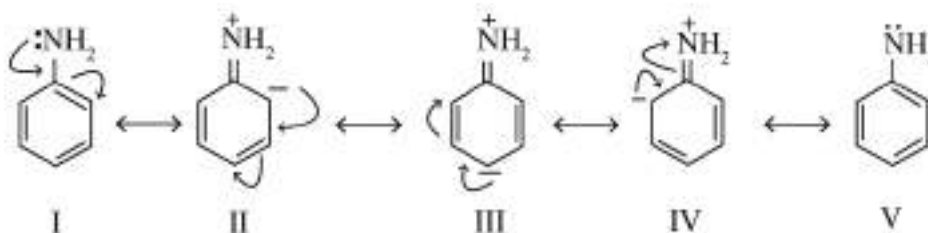


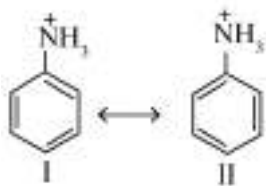
- ❖ Considering the Inductive effect, solvation effect and steric hindrance of the alkyl group decides the order of **basic strength in aqueous solution**.



b) Arylamines versus ammonia

- ❖ In arylamines unshared electron pair on nitrogen atoms is in conjugation with the benzene ring and thus making it less available for protonation.
- ❖ Hence, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia



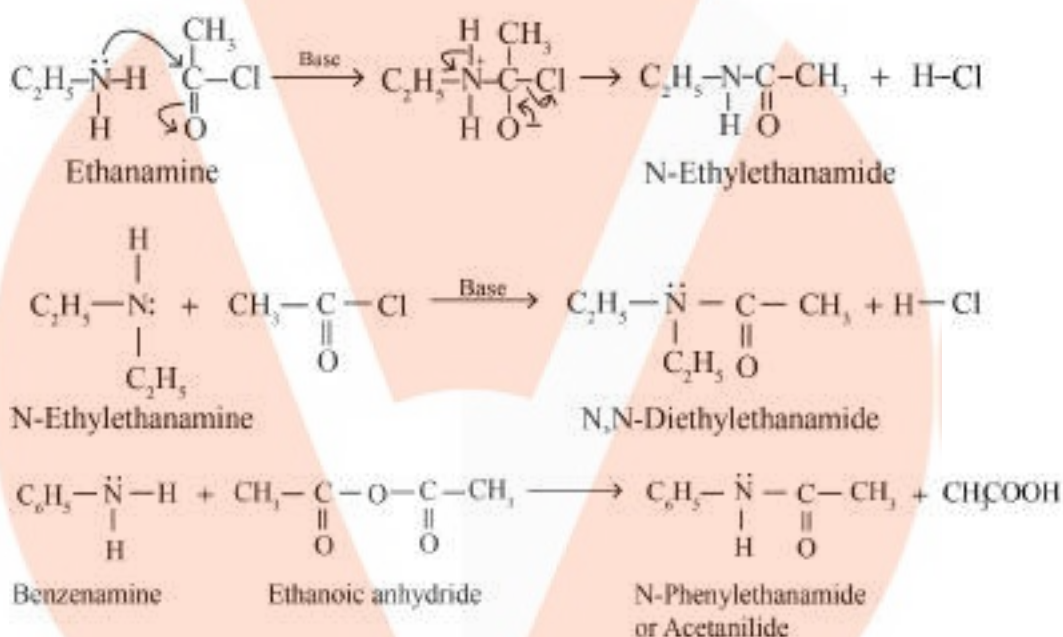


- ❖ In case of substituted aniline, electron releasing groups like $-\text{OCH}_3$, $-\text{CH}_3$ increase basic strength whereas electron withdrawing groups like $-\text{NO}_2$, $-\text{SO}_3$, $-\text{COOH}$, $-\text{X}$ decrease it.

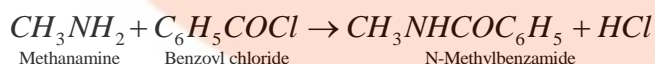
2. **Alkylation:** Amines undergo alkylation on reaction with alkyl halides.

3. **Acylation:**

- Carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.

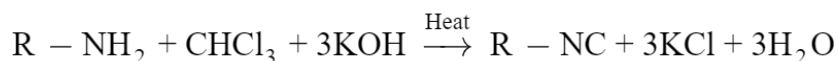


- Amines react with benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$). & the reaction known as benzoylation



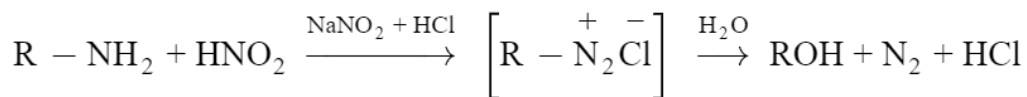
4. **Carbylamine reaction**

- Known as carbylamine reaction or isocyanide test and is used as a test for **Aliphatic and aromatic primary amines**.
- In this reaction isocyanides or carbylamines which are foul smelling substances.
- Secondary and tertiary amines do not show this reaction.

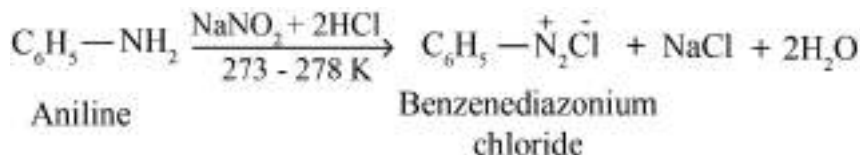


5. **Reaction with nitrous acid:**

- a) **Primary aliphatic amines** react to form aliphatic diazonium salts which, being **unstable**, liberate nitrogen gas quantitatively and alcohols.



b) **Aromatic amines** react at low temperatures (273-278 K) to form **diazonium salts**.

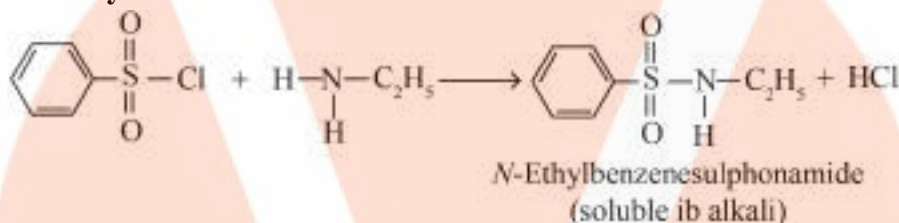


Secondary and tertiary amines react with nitrous acid in a different manner.

6. Reaction with arylsulphonyl chloride:

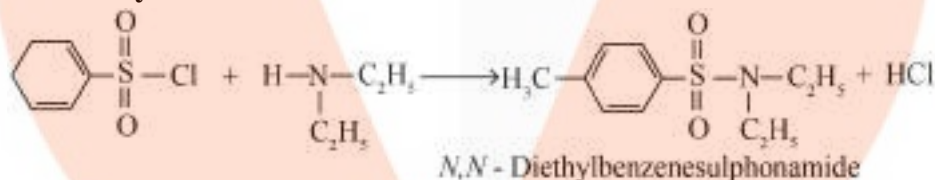
- Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), **Hinsberg's reagent**
- Used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.
- These days benzenesulphonyl chloride is replaced by p-toluenesulphonyl chloride

a) **Primary amine:**



The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of a strong electron withdrawing sulphonyl group. Hence, it is **soluble in alkali**.

b) **Secondary amine:**



No hydrogen atom attached to nitrogen atom and hence **insoluble in alkali**.

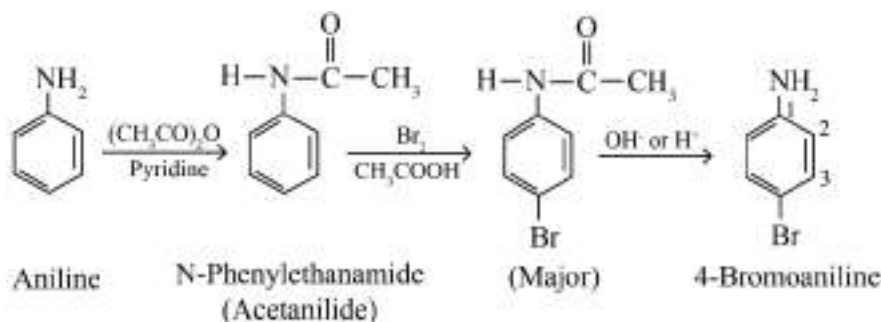
c) **Tertiary amines** do not react with benzenesulphonyl chloride.

7. Electrophilic substitution: $-NH_2$ group is ortho and para directing and a powerful activating group.

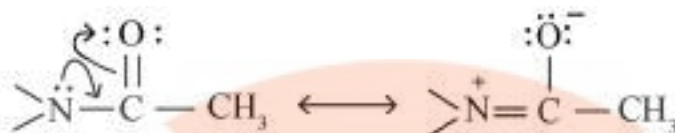
a) **Bromination:** With bromine water give a white precipitate of 2,4,6-tribromoaniline.



- Monosubstituted aniline derivatives are formed by protecting the $-NH_2$ group by acetylation with acetic anhydride, followed by hydrolysis.



- The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

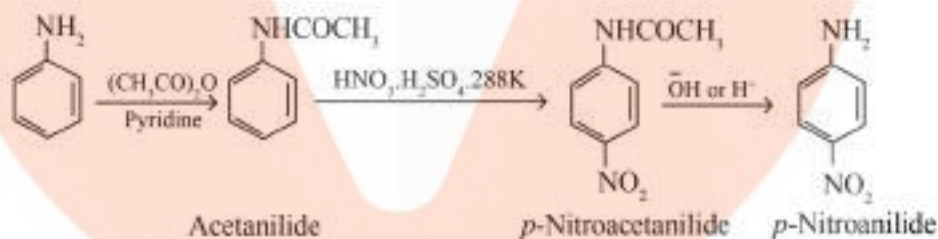


b) Nitration:

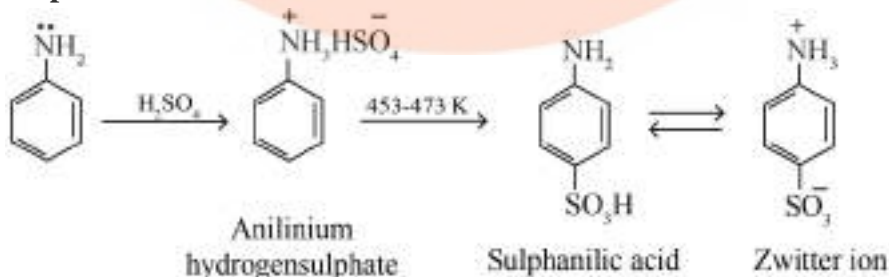
- Strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing.



- By protecting the $-\text{NH}_2$ group by acetylation, p-nitro derivatives obtained as the major product.



c) Sulphonation:



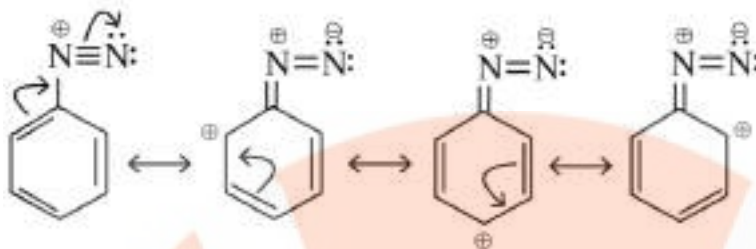
Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride.

➤ Diazonium Salts

● General formula RN_2^+X^-

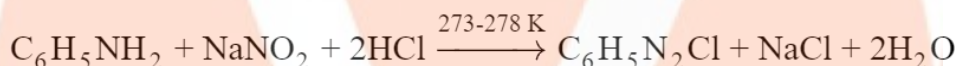
N_2^+ group is called the diazonium **group**. R is aryl group and X^- ion may be Cl^- , Br^- , HSO_4^- , BF_4^- .

- Primary aliphatic amines form highly unstable alkyldiazonium salts. Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures.
- The stability of arenediazonium ion is explained on the basis of resonance.



❖ Method of Preparation of Diazonium Salts

- The conversion of primary aromatic amines into diazonium salts is known as **diazotization**.
- Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.



❖ Physical Properties

- Readily soluble in water and is stable in cold but reacts with water when warmed.
- It decomposes easily in the dry state.
- Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

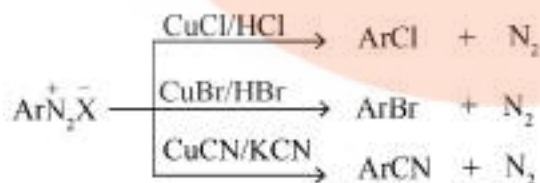
❖ Chemical Reactions:

a) Reactions involving displacement of nitrogen

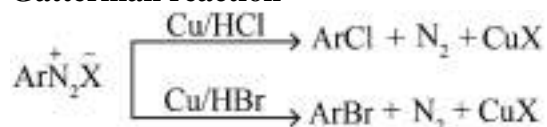
Diazonium group being a very good leaving group, is substituted by other groups

1. Replacement by halide or cyanide ion:

Sandmeyer reaction

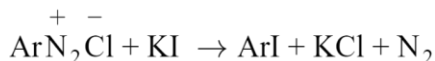


Gatterman reaction

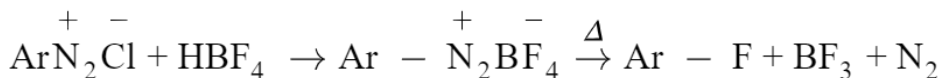


2. Replacement by iodide

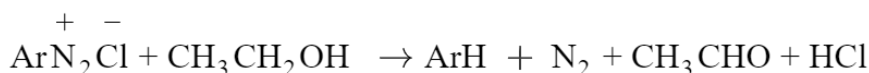
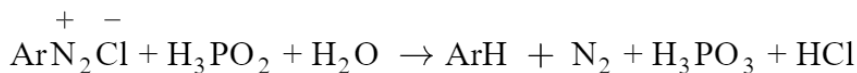
Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed



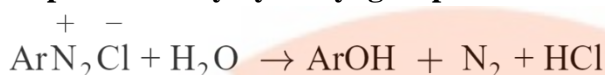
3. **Replacement by fluoride ion:**



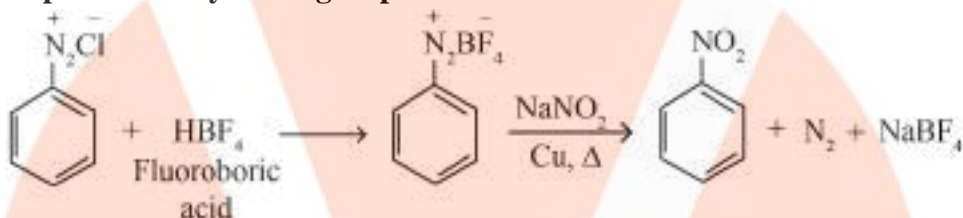
4. **Replacement by H:**



5. **Replacement by hydroxyl group:**



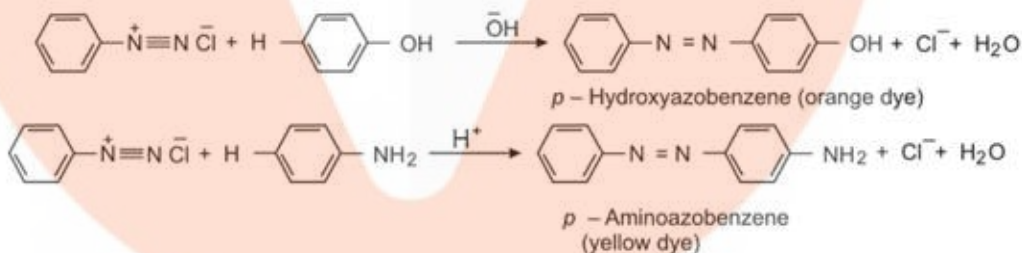
6. **Replacement by $-\text{NO}_2$ group:**



b) **Reactions involving retention of the diazo group.**

❖ **Coupling reactions**

- Reaction having both the aromatic rings joined through the $-\text{N}=\text{N}-$ bond is known as **coupling reaction**
- The azo products obtained with an extended conjugate system are often coloured and are used as dyes.



❖ **Importance of Diazonium Salts in Synthesis of Aromatic Compounds**

The replacement of diazo group by other groups is helpful in preparing those substituted aromatic compounds which cannot be prepared by direct substitution like Aryl fluorides and iodides & cyanobenzene.

Biomolecules

➤ Carbohydrates

- Optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.
- **General formula:** $C_x(H_2O)_y$
- Hydrates of Carbon. Eg: $C_6H_{12}O_6$ fits in $C_6(H_2O)_6$
- Not all molecules fitting to the formula are carbohydrates Eg: CH_3COOH is not a carbohydrate.
- Examples: Sugar, glucose, starch etc

➤ Classification of carbohydrates

Based on reducing nature:

- Reducing sugar: Reduce Fehling's solution and Tollens' reagent.
- Nonreducing sugar: Do not reduce Fehling's solution and Tollens' reagent

➤ Based on sweetness:

- Sugars: Carbohydrates which are sweet to taste. Eg: Sucrose
- Non sugars: Carbohydrates which are not sweet to taste. Eg: Starch

➤ Based on behaviour on hydrolysis:

• Monosaccharides:

- ❖ Simplest form and cannot be further hydrolysed. Eg: Glucose, fructose, ribose etc.
- ❖ Aldose: Has aldehyde group, Ketose: Has ketone group
- ❖ Naming of compounds:

Carbon Atoms	General Term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

• Oligosaccharides:

- ❖ Yield two to ten monosaccharide units on hydrolysis.
- ❖ Disaccharides, trisaccharides, tetrasaccharides produce 2, 3, 4 units on hydrolysis.
- ❖ Eg: Sucrose (disaccharide) on hydrolysis produces glucose and fructose, Maltose produces 2 glucose molecules.

• Polysaccharides:

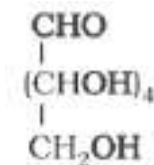
- ❖ Yield a large number of monosaccharide units on hydrolysis.
- ❖ Eg: Starch, cellulose, glycogen, etc.

➤ **Monosaccharides**

1. Glucose

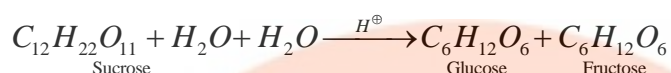
- Aldohexose. Formula: $C_6H_{12}O_6$.

- **Structure:**

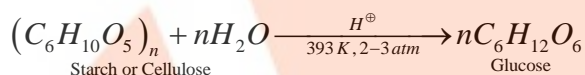


- **Preparation:**

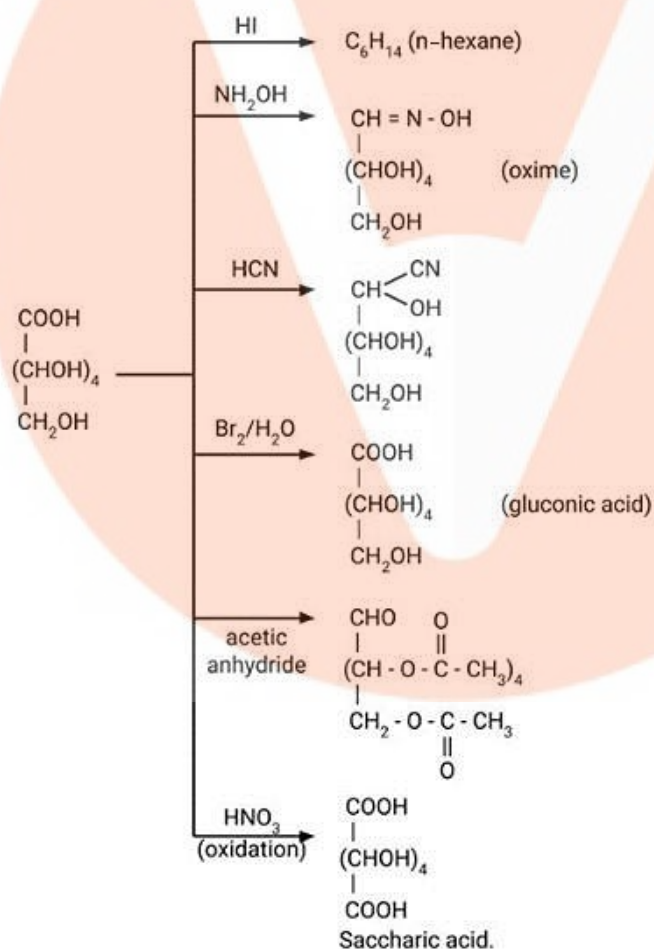
- ❖ From sucrose:



- ❖ From starch:

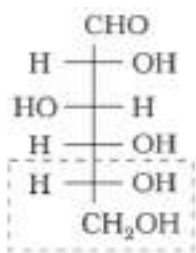


- **Chemical reactions:**



- **Configuration of glucose**

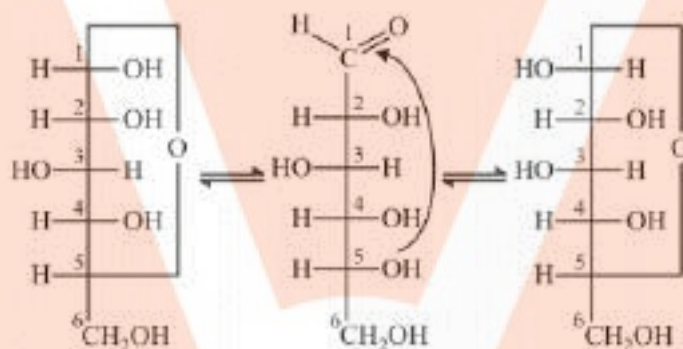
NOTE: D and d are both different. D represents the configuration i.e. -OH on the right. +/d represents that the molecule is dextrorotatory



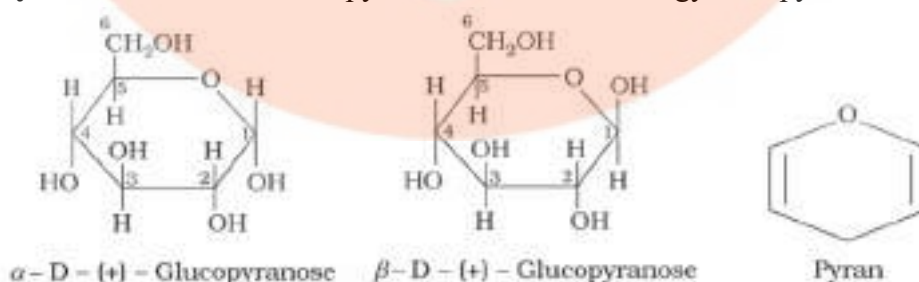
D-(+) - Glucose

- **Cyclic structures of glucose**

- ❖ **2 crystalline forms of glucose:** α and β form which differ only in the configuration of the hydroxyl group at C1, called anomeric carbon.
- ❖ α -form (m.p. 419 K): By crystallisation of conc. glucose at 303 K.
- ❖ β -form (m.p. 423 K): By crystallisation of hot and saturated glucose at 371 K.
- ❖ Glucose forms a six-membered hemiacetal ring in which $-\text{OH}$ at C-5 is involved in ring formation.

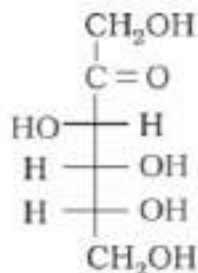


- ❖ α , β forms exist in equilibrium with the open chain form whose specific rotation is $+52.5^\circ$.
- ❖ Due to absence of free $-\text{CHO}$ in cyclic form:
 - Doesn't give Schiff's test (with NaHSO_3 it does not form hydrogensulphite).
 - Pentaacetate of glucose does not react with hydroxylamine
- ❖ **Cyclic structures:** Called 'pyranose' due to its analogy with pyran



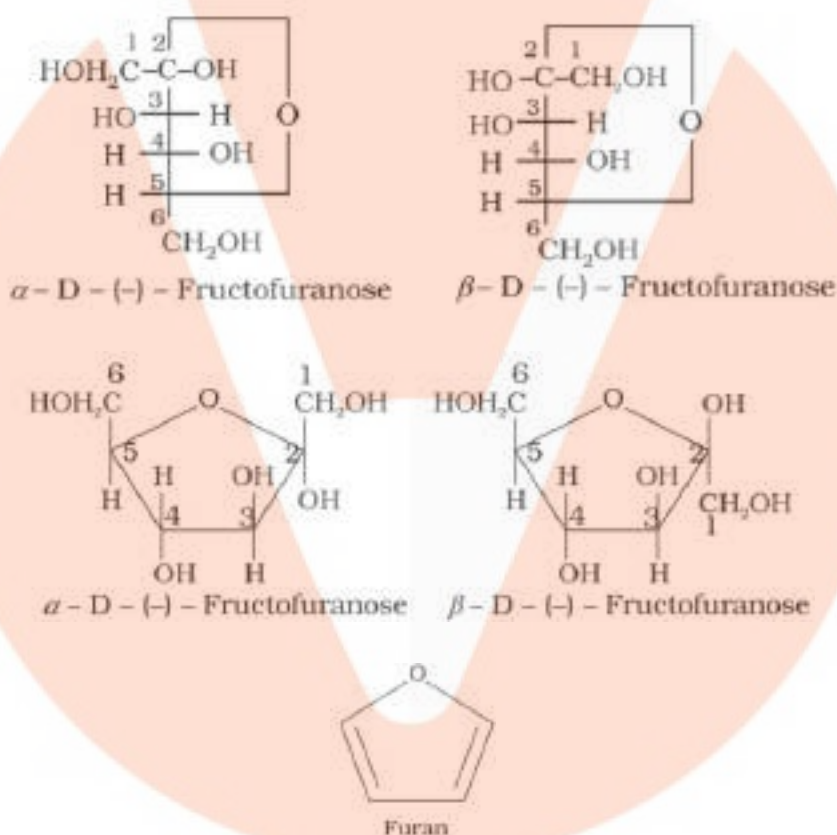
2. Fructose

- Ketohexose (keto group on carbon-2). Formula: $C_6H_{12}O_6$.
- **Structure:**



D - (-) - Fructose

- **Cyclic form of fructose:** Called furanose due to its analogy with furan



Note: Both glucose and fructose give tollen's test and fehling's test.

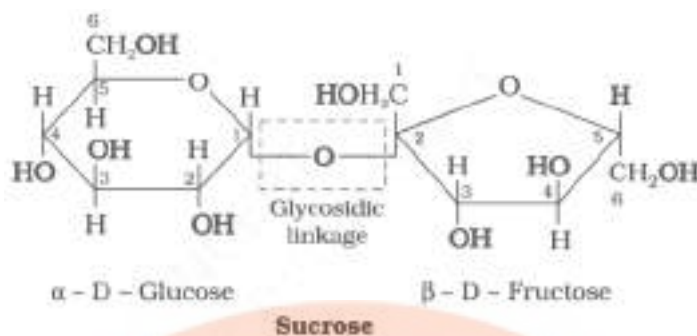
➤ Disaccharides:

- Two monosaccharides join together by an oxide linkage called glycosidic linkage, formed by the loss of a water molecule
- If the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are free then reducing sugars else they would be non-reducing.

1. Sucrose:

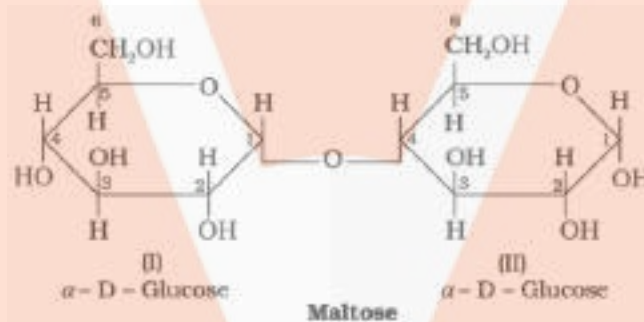
- Monosaccharides: α -D-glucose & β -D-fructose
- Glycosidic linkage: C1 of α -D-glucose and C2 of β -D-fructose
- Reducing nature: Non reducing

- Is dextrorotatory, but on hydrolysis gives a laevorotatory mixture. Also called invert sugar due to this reason
- Structure:



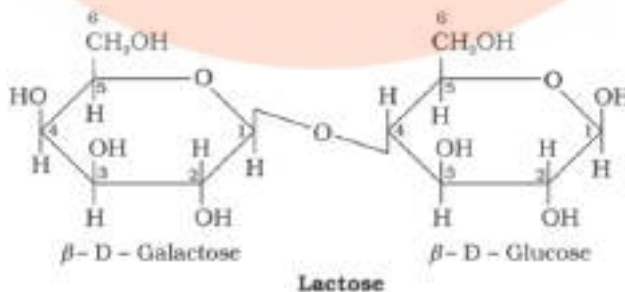
2. Maltose:

- Monosaccharides: 2 α -D-glucose
- Glycosidic linkage: C1 of glucose (I) and C4 of glucose (II)
- Reducing nature: Reducing (Free aldehyde at C1 of glucose (II))
- Structure:



3. Lactose (Milk sugar):

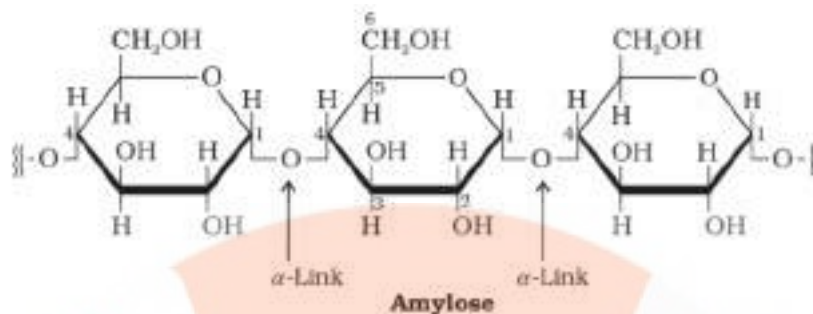
- Monosaccharides: β -D-galactose and β -D-glucose.
- Glycosidic linkage: C1 of galactose and C4 of glucose (II)
- Reducing nature: Reducing (Free aldehyde at C1 of glucose)
- Structure:



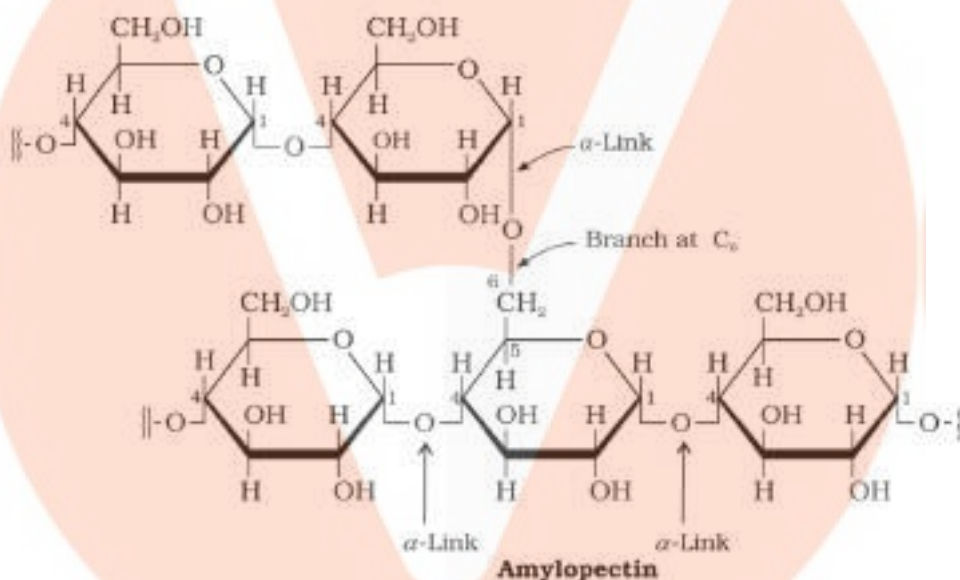
➤ Polysaccharides

1. Starch:

- Monosaccharides: α -glucose
- 2 components: Amylose and Amylopectin
- Amylose (15 -20 %): Water soluble, long unbranched chain with C1– C4 glycosidic linkage of α -D-(+)-glucose units.

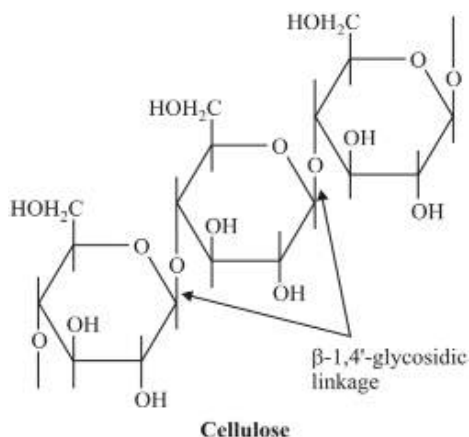


- Amylopectin (80- 85%): Water insoluble, long branched chain formed by C1–C4 glycosidic linkage and branching is formed by C1–C6 glycosidic linkage.



2. Cellulose:

- Predominant constituent of cell wall of plant cells.
- Monosaccharide: β -D-glucose units by glycosidic linkage between C1 & C4 of glucose units.



3. Glycogen:

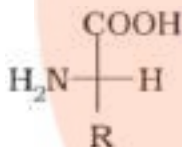
- Carbohydrates are stored in the animal body as glycogen.
- Called animal starch as it is similar to amylopectin but more highly branched.
- Present in liver, muscles, brain, in yeast and fungi.
- Glycogen is broken into glucose when the body needs glucose.

➤ Proteins:

- Polymers of α -amino acids connected by peptide linkage
- Majorly found in milk, cheese, pulses, peanuts, fish, meat, etc.

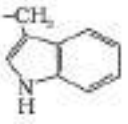
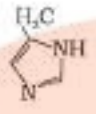
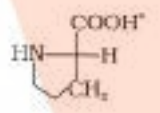
➤ Amino acids:

- Contain amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups.
- Based on relative position of $-\text{NH}_2$ and $-\text{COOH}$ they are classified as α , β , γ , δ etc
- General structure: α -amino acid



- Colourless, crystalline solids, Water-soluble, high melting solids
- Behave like salts due to presence of both acidic and basic groups.
- Total 22 amino acids are naturally represented and the list is given below

Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine (N)	H	Gly	G
2. Alanine (N)	$-\text{CH}_3$	Ala	A
3. Valine* (N)	$(\text{H}_3\text{C})_2\text{CH}-$	Val	V
4. Leucine* (N)	$(\text{H}_3\text{C})_2\text{CH}-\text{CH}_2-$	Leu	L
5. Isoleucine* (N)	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\text{CH}- \\ \\ \text{CH}_3 \end{array}$	Ile	I
6. Arginine* (B)	$\begin{array}{c} \text{HN}=\text{C}-\text{NH}-(\text{CH}_2)_3- \\ \\ \text{NH}_2 \end{array}$	Arg	R
7. Lysine* (B)	$\text{H}_2\text{N}-(\text{CH}_2)_4-$	Lys	K
8. Glutamic acid (A)	$\text{HOOC}-\text{CH}_2-\text{CH}_2-$	Glu	E
9. Aspartic acid (A)	$\text{HOOC}-\text{CH}_2-$	Asp	D
10. Glutamine (N)	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2- \end{array}$	Gln	Q

11. Asparagine(A)	$\text{H}_2\text{N}-\text{C}(\text{O})-\text{CH}_2-$	Asn	N
12. Threonine*(N)	$\text{H}_3\text{C}-\text{CHOH}-$	Thr	T
13. Serine(N)	$\text{HO}-\text{CH}_2-$	Ser	S
14. Cysteine(N)	$\text{HS}-\text{CH}_2-$	Cys	C
15. Methionine*(N)	$\text{H}_3\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-$	Met	M
16. Phenylalanine*(N)	$\text{C}_6\text{H}_5-\text{CH}_2-$	Phe	F
17. Tyrosine(N)	$(p)\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-$	Tyr	Y
18. Tryptophan*(N)		Trp	W
19. Histidine*(B)		His	H
20. Proline(N)		Pro	P

N – Neutral

A – Acidic

B – Basic

• Classification of amino acids:

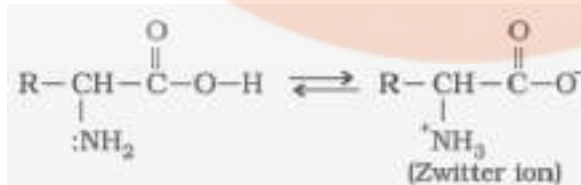
- ❖ **Essential amino acids:** Cannot be synthesized by body and need to be obtained from diet.

Nonessential amino acids: Synthesized by body

- ❖ **Acidic, Basic and Neutral amino acids** based on their overall charge present on them

• Zwitterion:

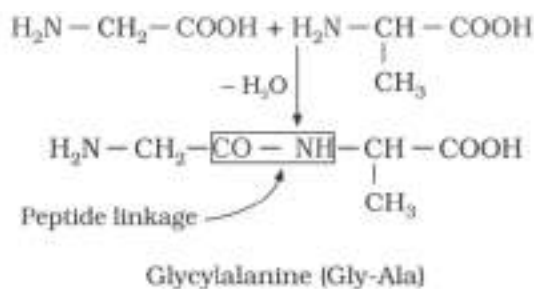
- ❖ In aqueous solution the $-\text{COOH}$ group loses proton and $-\text{NH}_2$ accepts proton.
- ❖ Neutral but has both negative and positive charges i.e. dipolar ion.
- ❖ Amphoteric and reacts with both acid and base



- **Optical activity:** Except glycine, all are optically active
- **D and L configuration:** 'L' represents $-\text{NH}_2$ on left and 'D' represents $-\text{NH}_2$ on right. Naturally occurring amino acids usually have L configuration.

➤ Structure of proteins:

- Amino acids join together by amide linkage also called as peptide linkage



- All the amino acids join together to form polypeptides. Long polypeptide chains of Mol.mass > 10,000u is called a protein
- **Classification of proteins:** Based on molecular shapes into 2 types

Fibrous proteins	Globular proteins
Polypeptide chains run parallel and are held together by hydrogen and disulphide bonds forming fibrous structures.	Polypeptides coil around to give a spherical shape
Insoluble in water	Soluble in water
Eg: keratin (In hair, wool, silk) and myosin (in muscles)	Eg: Insulin, albumin

- Structure of protein is divided into 4 levels: Primary, secondary, tertiary and quaternary
(1) Primary structure: Specific sequence of amino acids in a polypeptide chain is said to be the primary structure of protein. Any change in it will create a different protein.

(2) Secondary structure: It refers to the shape in which a long polypeptide chain can exist. Due to H-bonding, the polypeptide chain can fold into two shapes: α -helix and β -pleated sheet structure.

α -helix: Polypeptide chain is twisted into a right-handed screw (helix) due to H-bonding between the $-\text{NH}$ group of each amino acid with $-\text{C}=\text{O}$ of the adjacent amino acid.

β -pleated sheet: Polypeptide chains are stretched out and then laid side by side, which are held together by intermolecular hydrogen bonds.

(3) Tertiary structure: 2° structure on further folding gives tertiary structure. Folding gives rise to 2 shapes - fibrous and globular. Forces present here are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction

(4) Quaternary structure: Two or more polypeptide chains referred to as subunits are spatially arranged with respect to each other to form quaternary structure.

➤ **Denaturation of proteins:**

- Each protein has its own unique 3D structure called native protein.
- **Denaturation:** If this native protein is subjected to change in pH or temperature or any physical change then the hydrogen bonds are disturbed causing the protein to unfold and it loses its biological activity. 2° , 3° structures are destroyed but 1° remains intact

Eg: The coagulation of egg white on boiling, curdling of milk due to the formation of lactic acid by the bacteria present in milk.

➤ **Enzymes:**

- Biocatalysts which catalyse various biochemical reactions like digestion of food etc
- Usually, enzymes are globular proteins
- Named after the compound or class of compounds upon which they work. Eg: Maltase enzyme catalyses hydrolysis of maltose.
- Named after reactions also. Eg: Enzyme's catalysis oxidation of one substrate and reduction of other are called oxidoreductase enzymes.
- **Mechanism of action:** They bind to the specific substrate similar to lock and key and convert it into product. They reduce the magnitude of activation energy.

➤ **Vitamins:**

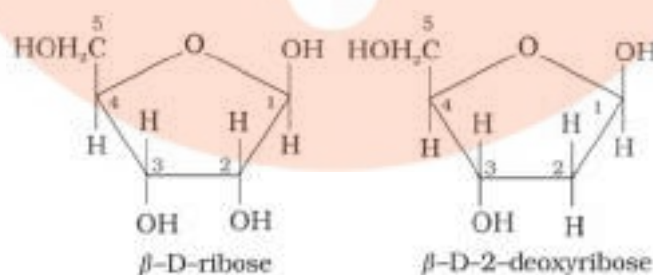
- "Vitamin" = vital + amine (Earlier identified compounds had amino groups).
- Organic compounds required in small amounts in diet to perform specific biological functions for normal maintenance of optimum growth.
- Deficiency causes specific diseases => essential food factors for the human body.
- Generally synthesized by plants. In humans, bacteria present in gut synthesizes few vitamins
- Different vitamins include: A, B, C, D, K. Vitamin B has subgroups B₁, B₂, B₆, B₁₂, etc.
- Classification: Based on water soluble or fat soluble
 - ❖ Fat soluble vitamins: Vitamin A, D, E, K are fat soluble. They are stored in liver and adipose tissue.
 - ❖ Water soluble vitamins: Group B and C vitamins are water soluble. Must to be supplied in diet and are not stored in body but are excreted in urine (except B₁₂)

Important vitamins			
	Vitamin	Sources	Deficiency diseases
(i)	Vitamin-A (Retinol or eye vitamin)	Milk, cod liver oil, butter, carrots, green leaves, tomatoes, eggs, etc.	Night blindness, xerophthalmia (i.e. hardening of cornea of eye) and xerosis.
(ii)	Vitamin – B Thiamine or Aneurin	Pulses, nuts, green vegetables, and polished rice. Yeast and egg yolk.	Beriberi (a disease of the nervous system) and loss of appetite.
(iii)	Vitamin – B ₂ or Riboflavin or Lactoflavin	Milk, meat, green vegetables and yeast,	Inflammation of tongue or dark red tongue (glossitis), and cheilosis (cracking or fissuring the lips and corners of the mouth)
(IV)	Vitamin – B ₆ or Pyridoxine or Adermine	Rice, bran, yeast, meat, fish, egg, yolk, maize, spinach and lettuce.	Specific dermatitis called acrodynia, pellagra (shrivelled

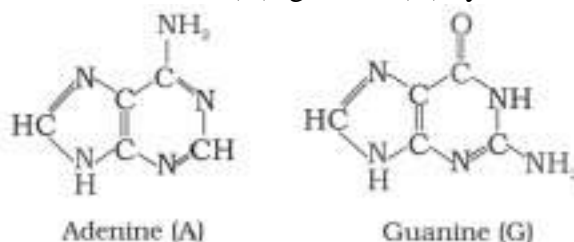
			skin) anaemia and convulsions.
(V)	Vitamin – B ₁₂ or Cyanocobalamin	Milk, liver, kidney, and eggs.	Inflammation of tongue, mouth etc. and pernicious anaemia.
(VI)	Vitamin – C or L-Ascorbic	Citrous fruits, amla, (oranges, lemons), sprouted pulses, germinated.	Scurvy and brittleness of bones, swelling and bleeding of gums and loosening of teeth.
(VII)	Vitamin D or Ergocalciferol (or antirachitic vitamin of sunshine vitamin)	Fish liver oil, cod liver oil, milk and eggs.	Rickets (softening and bending of bones) in children, controls Ca and P metabolism.
(VIII)	Vitamin-E or tocopherols (α , β and γ) or Antisterility	Eggs, milk, fish wheat germ, oil, cotton seed oil etc.	Sterility (loss of sexual power and reproduction)
(IX)	Vitamin – H (Biotin)	Yeast, liver, Kidney and milk.	Dermatitis, loss of hair and paralysis.
(X)	Vitamin-K or phylloquinone or Antihemorrhagic vitamin	Cabbage, alfalfa, spinach and carrot tops,	Haemorrhage and lengthens time of blood clotting.

➤ Nucleic Acids:

- Long chain polymers of nucleotides also called as polynucleotides
- Hereditary components present in the cell, called chromosomes, are made of nucleic acids.
- 2 types: Deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA)
- Hydrolysis of DNA or RNA yields pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases).
- DNA: Made of β -D-2-deoxyribose units, RNA: Made of β -D-ribose units.

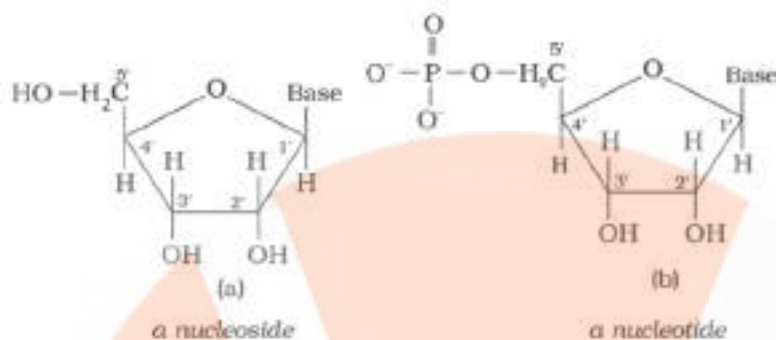


- DNA contains four bases: adenine (A), guanine (G), cytosine (C) and thymine (T)
RNA contains four bases: adenine (A), guanine (G), cytosine (C) and uracil (U).



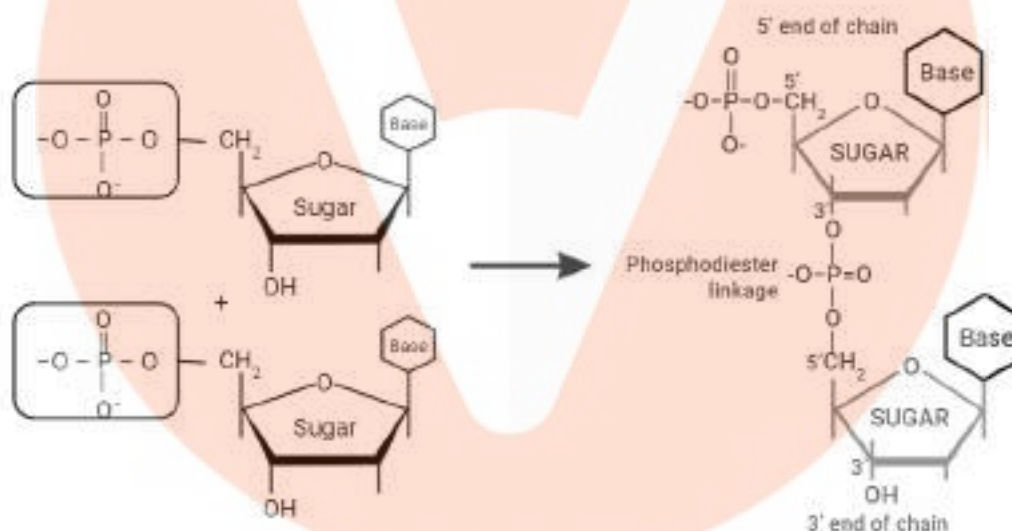


- **Structure of a nucleotide:**



- **Structure of a nucleic acid:**

Nucleotides join together by phosphodiester linkage between 5' and 3' atoms of the pentose sugar to form nucleic acid chains.



➤ **Structure of DNA:**

- Double stranded, helix structure (Proposed by Watson and crick)
- 2 nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases.
- Both strands are complementary. Adenine (A) forms hydrogen bonds with Thymine (T) and Cytosine (C) forms hydrogen bonds with Guanine (G)



➤ **Structure of RNA:**

- Single stranded.
- 3 types: messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA). All are used for different functions within cell

➤ **Biological function of RNA and DNA:**

- Reserve of genetic information and basis of heredity.
- DNA maintains the identity of different species over millions of years
- DNA is capable of self duplication and identical DNA is transferred to daughter cells.
- RNA is used to synthesize proteins in the cell but the message for synthesis is present in DNA

➤ **DNA fingerprinting:**

- Sequence of bases on DNA is unique for a person and the information regarding this is called DNA fingerprinting.
- Used in forensics for identification of criminals, determination of paternity of an individual, identification of dead bodies in any accident by comparing with parental DNA and to identify racial groups to rewrite biological evolution

➤ **HORMONES:**

- Intracellular messengers
- Produced by endocrine glands and poured directly into bloodstream
- They can be
 - ❖ Steroids - Eg: Estrogens and androgens
 - ❖ Polypeptides - Eg: Insulin and endorphins
 - ❖ Amino Acid derivatives - Eg: epinephrine and norepinephrine

➤ **Biological activities of few hormones:**

- **Insulin** is released when the blood glucose levels are high and it reduces the levels. **Glucagon** tends to increase blood glucose level. Both of them regulate the amount of glucose in blood.
- **Growth and sex hormones:** Important for growth and development
- **Epinephrine and norepinephrine:** Mediate responses to external stimuli.
- **Thyroxine:** An iodinated derivative of amino acid tyrosine, is important in maintenance of bones, brain development etc. Low levels cause hypothyroidism. characterised by lethargicness and obesity. High levels cause hyperthyroidism.

Note: Low level iodine diet leads to hypothyroidism and enlargement of thyroid gland. Patients with such medical conditions are advised to take iodised salt.

- **Adrenal cortex hormones (Steroid hormone):**

- ❖ Glucocorticoids: Control the carbohydrate metabolism, modulate inflammatory reactions, and are involved in reactions to stress.
- ❖ Mineralocorticoids: Control the level of excretion of water and salt by the kidney
- ❖ Addison's disease: Due to improper functioning of adrenal cortex. Causes hypoglycemia, weakness and increased susceptibility to stress. Should be treated with glucocorticoids and mineralocorticoids.

- **Hormones by gonads (Steroid hormone):**

- ❖ For the development of secondary sex characters.
- ❖ Testosterone: Main male sex hormone and is responsible for development of secondary male characteristics (deep voice, facial hair etc)
- ❖ Estradiol: Main female sex hormone and is responsible for development of secondary female characteristics and in the control of menstrual cycle.
- ❖ Progesterone: responsible for preparing the uterus for implantation of fertilised egg.

Polymers

The term polymer is defined as very large molecules having high molecular mass. Referred to as macromolecules, which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerisation.

➤ Classification of polymer

Classification based on source

1. Natural Polymer- Found in plants and animals. e.g., proteins, cellulose, starch, some resins.
2. Semi-synthetic polymers- Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate
3. Man Made / Synthetic polymers - used in daily life as well as in industry. Examples - plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S)

➤ Classification based on structure of the polymers

1. Linear polymers- Consist of long and straight chains. e.g. - high density polythene, polyvinyl chloride, etc. These are represented as:



2. Branched chain polymers- Contain linear chains having some branches, e.g., low density polythene. These are depicted as follows



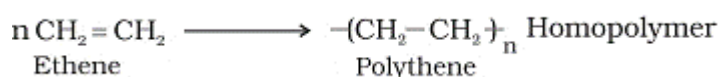
3. Cross linked or Network polymers- Formed from bi-functional and trifunctional monomers and contain strong covalent bonds between various linear polymer chains, e.g. bakelite, melamine, etc. These polymers are depicted as follows:



➤ Classification Based on Mode of Polymerisation

1. Addition polymers -

- ❖ Formed by the repeated addition of monomer molecules possessing double or triple bonds, e.g., polythene from ethene and polypropene from propene.
- ❖ Homopolymers - Formed by polymerisation of a single monomeric species. e.g., polythene.

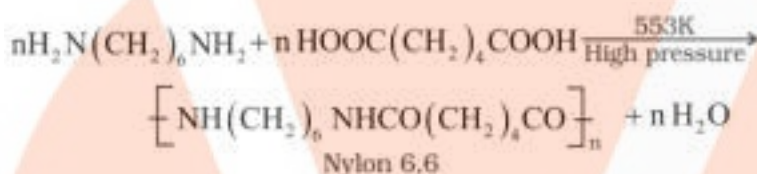


- ❖ Copolymers - Formed using two different monomers are termed as, e.g., Buna-S, Buna-N



2. Condensation polymers -

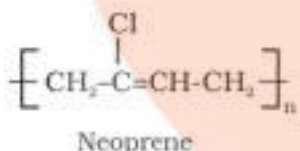
- ❖ Formed by repeated condensation reactions between two different bi-functional or tri-functional monomeric units.
- ❖ In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. E.g. terylene (dacron), nylon 6, 6, nylon 6, etc. For example, nylon 6, 6 is formed by the condensation of hexamethylenediamine with adipic acid.



➤ Classification Based on Molecular Forces

Polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer.

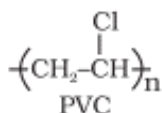
1. Elastomers - Rubber like solids with elastic properties. Held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. Examples are buna-S, buna-N, neoprene, etc.



2. Fibres - Thread forming solids which possess high tensile strength and high modulus. These strong forces like H Bonding lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.



3. Thermoplastic polymers - Linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. e.g. polythene, polystyrene, polyvinyls, etc.



4. Thermosetting polymers - Cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. cannot be reused. e.g bakelite, urea-formaldehyde resins, etc.



➤ Classification Based on Growth Polymerisation

Addition and condensation polymers are also known as chain growth polymers and step growth polymers depending on the type of polymerisation mechanism they undergo during their formation.

➤ Types of Polymerisation Reactions

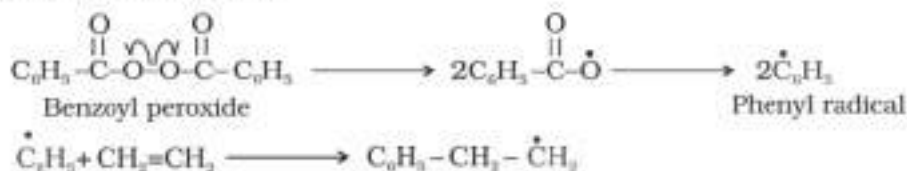
Addition Polymerisation or Chain Growth Polymerisation -

The monomers used to add together on a large scale to form a polymer are unsaturated compounds, e.g., alkenes, alkadienes and their derivatives. This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species.

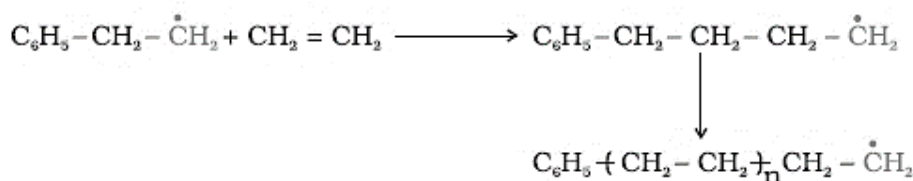
➤ Free radical mechanism

- Polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, the polymerisation of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator.
- The process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical. This step is called chain initiation step. As this radical reacts with another molecule of ethene, another bigger sized radical is formed.
- The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is termed as chain propagation step.
- Ultimately, at some stage the product radical thus formed reacts with another radical to form the polymerised product. This step is called the chain terminating step. The sequence of steps may be depicted as follows:

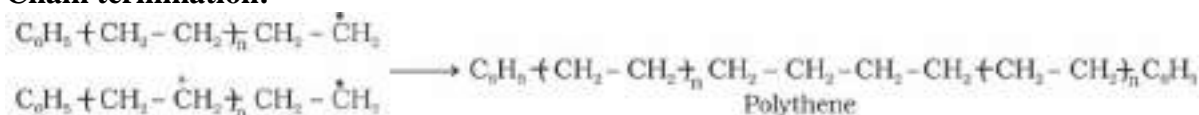
Chain initiation steps



Chain propagating step



Chain termination:



➤ Preparation of some important addition polymers

a) Polythene

i) Low density polythene:

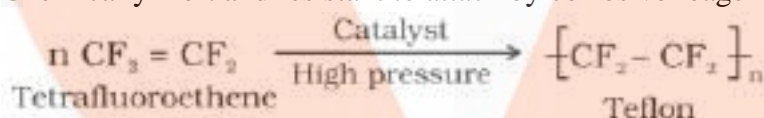
- Obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst).
- Low density polythene (LDP) obtained through the free radical addition and H-atom abstraction has a highly branched structure.
- Chemically inert and tough but flexible and a poor conductor of electricity.

ii) High density polythene:

- Formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethyl aluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres.
- Consists of linear molecules and has a high density due to close packing.
- Chemically inert and more tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

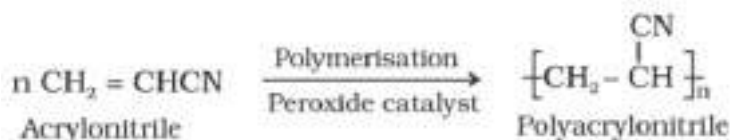
b) Polytetrafluoroethene (Teflon)

- Manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures.
- Chemically inert and resistant to attack by corrosive reagents.



c) Polyacrylonitrile

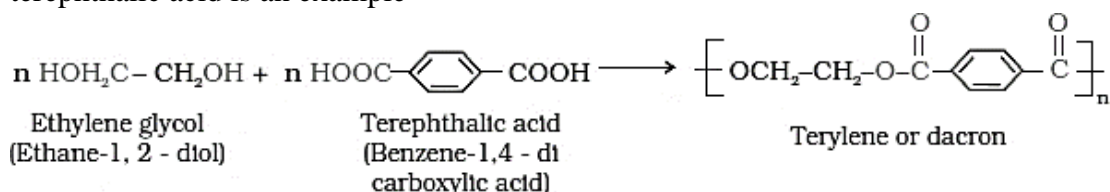
- The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation.
- Used as a substitute for wool in making commercial fibres as orlon or acrilan.



➤ Condensation Polymerisation or Step Growth polymerisation

- Involves a repetitive condensation reaction between two bi-functional monomers.
- Reactions may result in the loss of some simple molecules such as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.
- Product of each step is again bi-functional species and the sequence of condensation goes on.

- Since each step produces a distinct functionalized species and is independent of each other, this process is also called **step growth polymerisation**.
- The formation of terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example

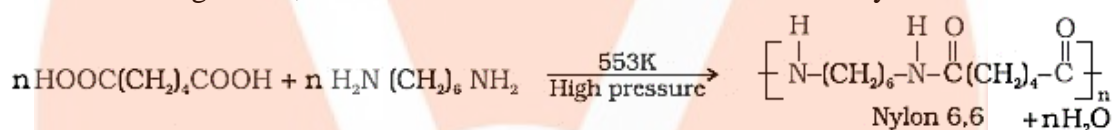


➤ Polyamides

- Polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons.
- Method of preparation consists of the condensation polymerisation of diamines with dicarboxylic acids and also of amino acids and their lactams.

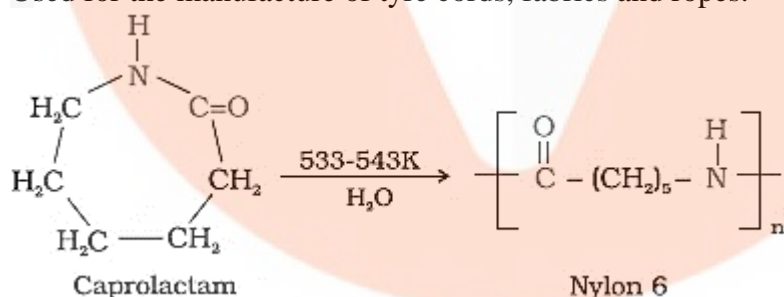
❖ Nylon 6,6:

- Prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.
- Used in making sheets, bristles for brushes and in the textile industry.



❖ Nylon 6:

- Obtained by heating caprolactam with water at a high temperature.
- Used for the manufacture of tyre cords, fabrics and ropes.



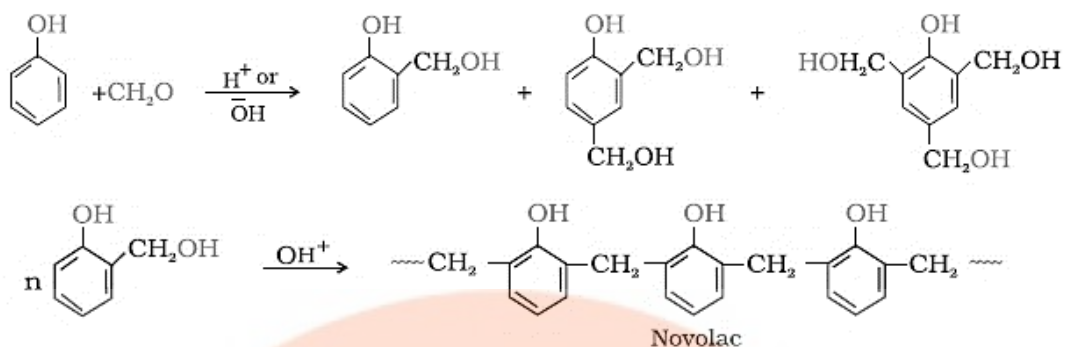
➤ Polyesters

- Polycondensation products of dicarboxylic acids and diols. e.g. Dacron or terylene is Manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate antimony trioxide catalyst.

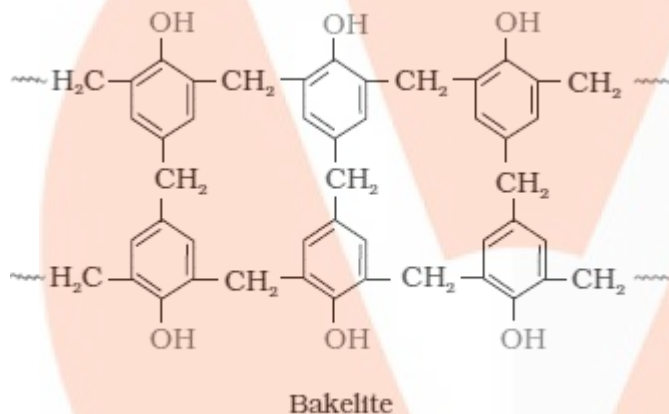
❖ Phenol - formaldehyde polymer (Bakelite and related polymers)

- Oldest synthetic polymers.
- Obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst.

- Reaction starts with the initial formation of o-and/or p-hydroxymethyl phenol derivatives, which further react with phenol to form compounds having rings joined to each other through $-\text{CH}_2$ groups. The initial product could be a linear product – Novolac which is used in paints

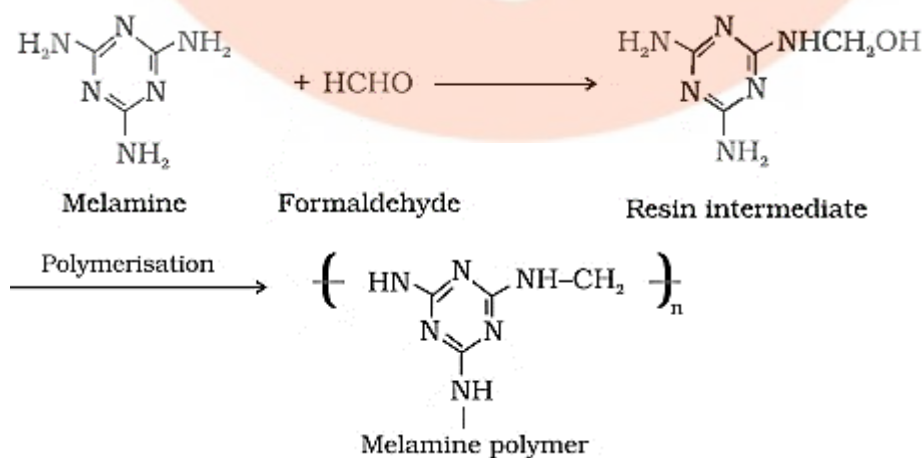


- Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called bakelite.
- Used for making combs, phonograph records, electrical switches and handles of various utensils.



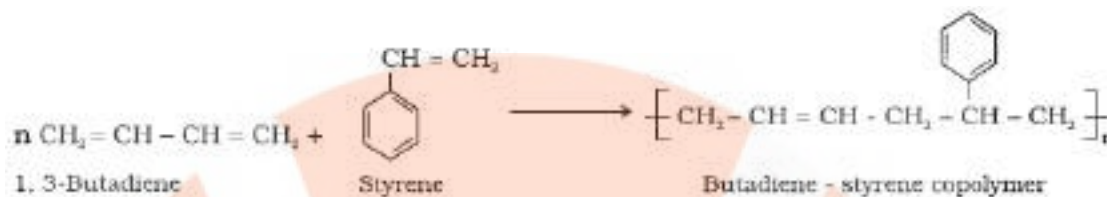
❖ Melamine

- Formed by the condensation polymerisation of melamine and formaldehyde.
- Used in the manufacture of unbreakable crockery.



➤ Copolymerization

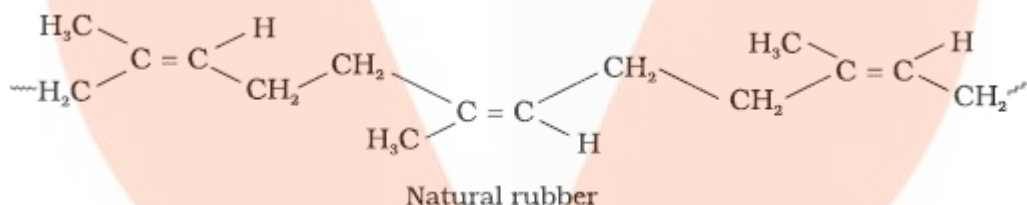
- Polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer.
- Can be made not only by chain growth polymerisation but by step growth polymerisation also. It contains multiple units of each monomer used in the same polymeric chain.
- Example - a mixture of 1, 3 – butadiene and styrene can form a copolymer.
- Used for the manufacture of auto tyres, floor tiles, footwear components, cable insulation, etc.



➤ Rubber

❖ Natural rubber

- Natural polymer and possesses elastic properties. Also termed as elastomer.
- Manufactured from rubber latex which is a colloidal dispersion of rubber in water.
- Obtained from the bark of rubber tree and is found in India, Srilanka, Indonesia, Malaysia.
- Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis - 1, 4 - polyisoprene.

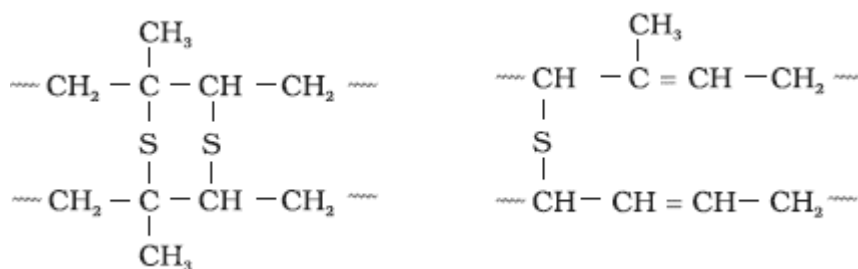


- cis-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

❖ Vulcanisation of rubber:

- Natural rubber becomes soft at high temperature ($>335\text{ K}$) and brittle at low temperatures ($<283\text{ K}$) and shows high water absorption capacity. It is soluble in non-polar solvents and is non-resistant to attack by oxidising agents. To improve upon these physical properties, a process of vulcanisation is carried out.
- Process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K . On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened. In the manufacture of tyre rubber, 5% of sulphur is used as a crosslinking agent.

❖ **Vulcanised structures -:**

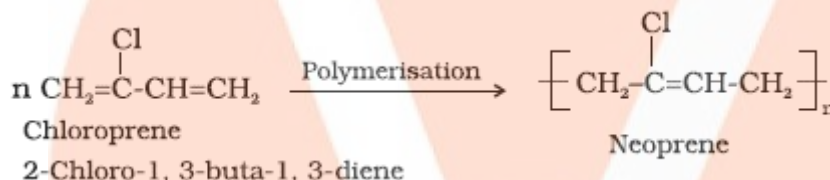


❖ **Synthetic rubbers**

- Any vulcanised rubber-like polymer, which is capable of getting stretched to twice its length.
- Returns to its original shape and size as soon as the external stretching force is released.
- Thus, synthetic rubbers are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

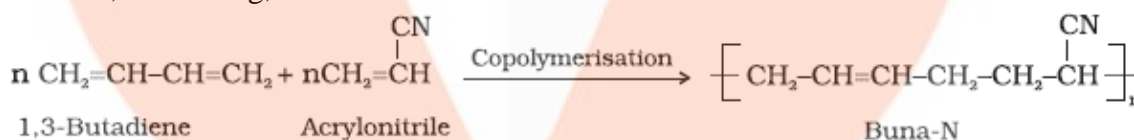
➤ **Preparation of Synthetic Rubbers**

- i) Neoprene - formed by the free radical polymerisation of chloroprene.



- ii) Buna - N

- Obtained by the copolymerisation of 1, 3 - butadiene and acrylonitrile
- Resistant to the action of petrol, lubricating oil and organic solvents. It is used in making oil seals, tank lining, etc.



➤ **Molecular Mass of Polymers**

Polymer properties are closely related to their molecular mass, size and structure. The growth of the polymer chain during their synthesis is dependent upon the availability of the monomers in the reaction mixture. Thus, the polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average. The molecular mass of polymers can be determined by chemical and physical methods.

➤ **Biodegradable Polymers**

Contains functional groups similar to the functional groups present in biopolymers. Aliphatic polyesters are one of the important classes of biodegradable polymers. examples

-

1. Poly β -hydroxybutyrate - co- β -hydroxy valerate (PHBV)

- Obtained by the copolymerisation of 3-hydroxybutanoic acid and 3 - hydroxypentanoic acid.
- Used in speciality packaging, orthopaedic devices and in controlled release of drugs.
- Undergoes bacterial degradation in the environment

➤ **Nylon 2–nylon 6**

- An alternating polyamide copolymer of glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) and amino caproic acid [$\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$] and is biodegradable.

➤ **Polymers of Commercial Importance**

Some Other Commercially Important Polymers

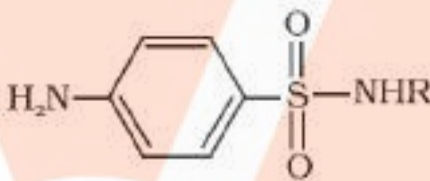
Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left(\text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left(\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left(\text{CH}_2 - \underset{\text{Cl}}{\text{CH}} \right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\left(\text{NH} - \text{CO} - \text{NH} - \text{CH}_2 \right)_n$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left(\text{OCH}_2 - \text{CH}_2\text{OOC} - \text{C}_6\text{H}_4 - \text{CO} \right)_n$	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	$\left(\text{C}_6\text{H}_4(\text{OH}) - \text{CH}_2 - \text{C}_6\text{H}_4(\text{OH}) - \text{CH}_2 \right)_n$	For making combs, electrical switches, handles of utensils and computer discs.

Chemistry in Everyday Life

➤ Chemistry in drugs:

- **Drug:** Low molecular weight chemicals used for diagnosis, prevention, treatment and cure.
- Drugs interact with macromolecular targets to produce biological response
- **Medicine:** Drugs used for therapeutic purposes. If chemicals are used for therapeutic purposes, it is called chemotherapy
- If higher doses are taken than prescribed, they are dangerous.

➤ Classification of drugs:

Based on pharmacological effect	Eg: Analgesics - Painkillers, Antiseptic - Kill or arrest growth of microbes.
Based on drug action on particular biochemical process	Eg: Antihistamines -Inhibit histamine which causes inflammation in body
Based on chemical structure	Eg: sulphonamides  Note: Similar structures features → similar pharmacological activity.
Based on molecular targets	Drug targets can be Carbohydrates, proteins, nucleic acids or lipids

Note: Drugs with common structural features may have same mechanism of action on targets

➤ Drug target interaction:

- Two types of protein targets
 1. Enzymes: Biological catalysts
 2. Receptors: Communication system of cells

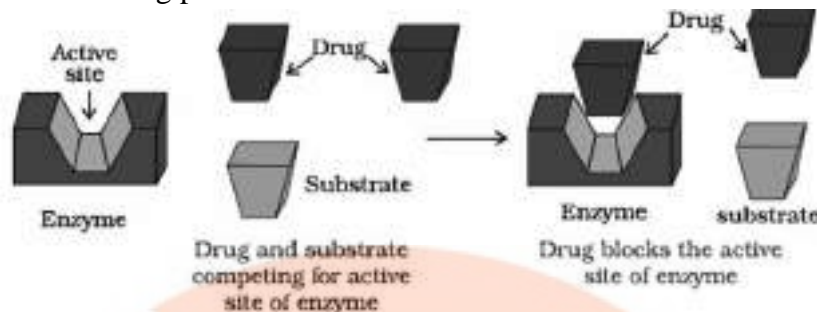
1. Enzymes as drug targets:

● Enzymatic action:

- ❖ Enzymes consist of active sites at which the substrate binds and forms enzyme substrate complexes.
- ❖ Substrate binds due to interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole interaction
- ❖ It provides functional groups which attack substrates and convert them to products.
- ❖ $E + S \rightleftharpoons ES \text{ complex} \rightarrow E + \text{products}$.

- **Drug, enzyme interaction:**

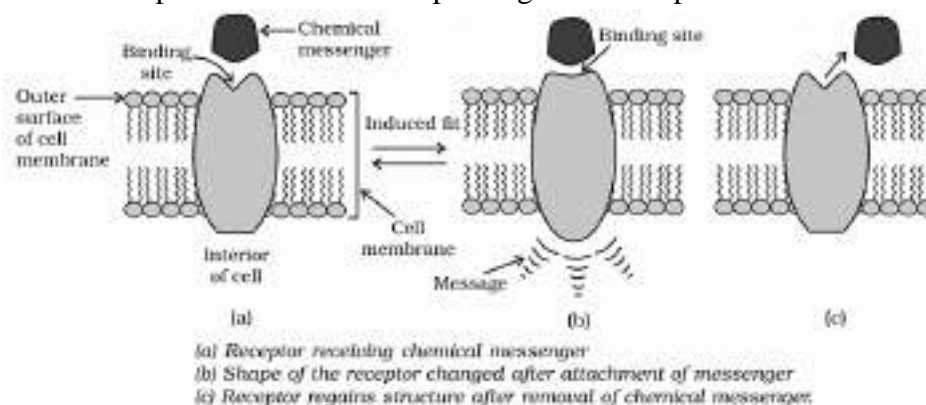
- ❖ Drugs act by inhibiting the enzymes, thereby preventing product formation.
- ❖ Inhibition can be of two types:
 - **Competitive inhibition:** Drug binds at the active site instead of substrate and thus inhibiting product formation



- **Non-competitive inhibition:** Drug binds to enzymes at a region called allosteric site. This changes the structure of the active site and thereby prevents binding of substrate.
- ❖ If the bond b/w drug and enzyme is a strong covalent bond then it cannot be broken easily and thus the enzyme-drug complex would finally be degraded by the body.

2. Receptors as drug targets:

- Receptors are the proteins embedded in the cell membranes and are important communication systems.
- Similar to enzymes, they also have active sites which are projected on the outer region of the cell.
- In body messages from neurons to muscles are transferred by chemicals called chemical messengers.
- Receptors bind only to specific messenger molecules because their binding sites have different shape, structure and amino acid composition.
- ❖ **Action of receptors:**
 - Receptor binds specifically to chemical messengers.
 - Due to binding of messenger molecules, the shape of the receptor changes which result in transfer of message into cells.
 - Due to change in the shape of the receptor, chemical messengers detach from the receptor and then the receptor regains its shape.



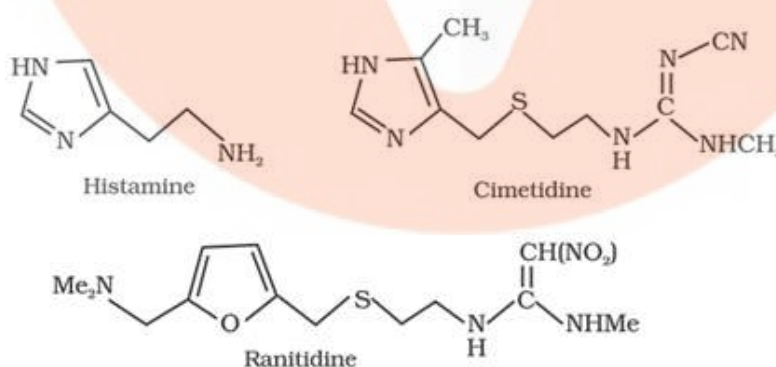
❖ **Based on drug's interaction with receptor:**

- Agonist: Mimics the action of a natural messenger. Used when there is deficiency of natural messengers
- Antagonist: Opposes the action of a natural messenger, blocking the transmission of messages into cells.

➤ **Therapeutic action of different class of drugs:**

1. Antacids:

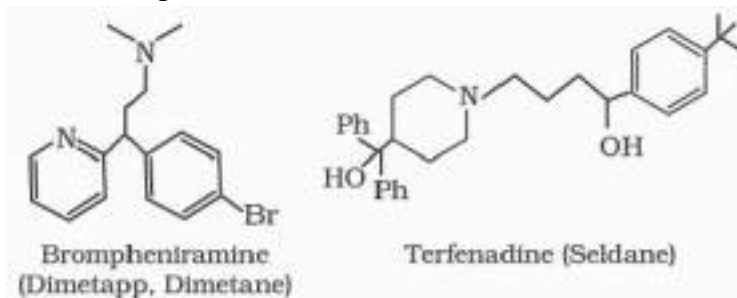
- Used when the stomach overproduces acid causing irritation and pain which may lead to ulcers in extreme conditions
- **Chronology:**
- ❖ Till 1970:
 - Treatment: Antacids such as sodium hydrogencarbonate or a mixture of aluminium and magnesium hydroxide used.
 - Disadvantages: All control only symptoms but not the cause. Excess of sodium hydrogencarbonate causes an alkaline stomach, triggering production of excess acid. Metal hydroxides are better as they do not increase pH above neutrality. Also in advanced stages of ulcers, surgical removal of the affected part is the only treatment.
- ❖ After 1970:
 - Treatment: Cimetidine (Tagamet) drug
 - Drug action: Histamine is a chemical which stimulates secretion of pepsin and HCl in the stomach. By targeting histamine i.e preventing histamine to bind to its receptors, acid production would be reduced.
- ❖ Currently:
 - Treatment: Ranitidine (Zantac) drug
- Structures of examples:



2. Antihistamines:

- Histamine: Potent vasodilator, contracts smooth muscles in bronchi, gut and relaxes other muscles such as walls of blood vessels. Also responsible for nasal congestion during common cold and allergic response to pollen
- Antihistamine drugs: Brompheniramine (Dimetapp) and terfenadine (Seldane). They compete with histamine and bind to its receptor sites inhibiting its action.

- Note: Antacids and antiallergic drugs both target histamine molecules, but work on different receptors
- Structures of examples:

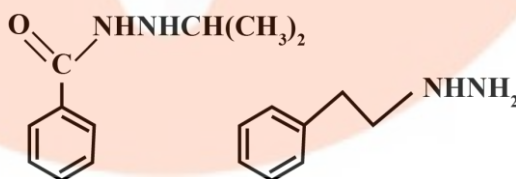


3. Neurologically active drugs:

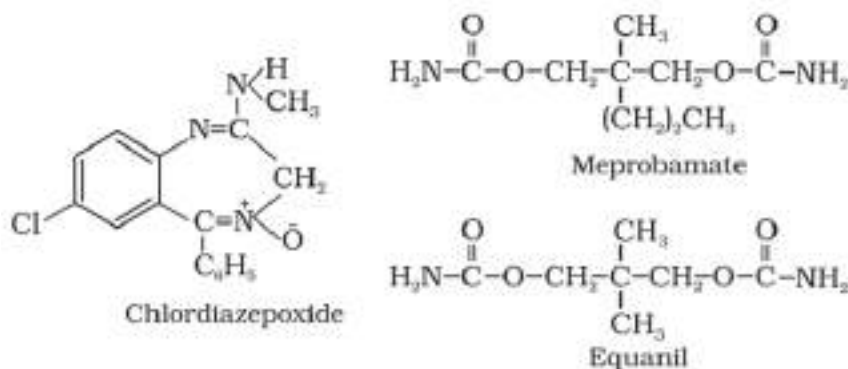
Function by affecting the message transfer mechanism from nerve to receptor.

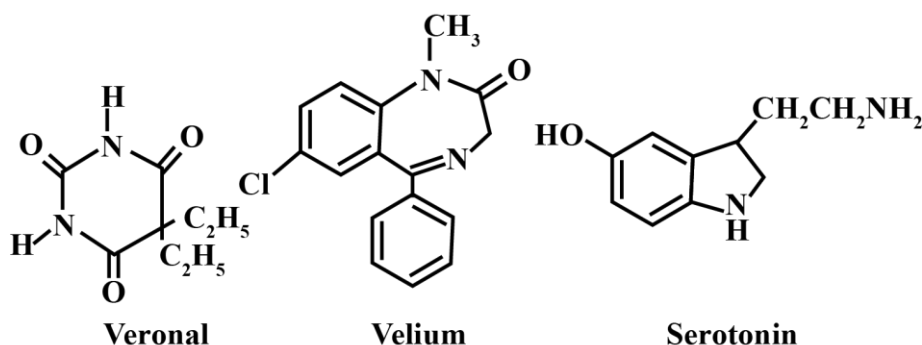
I. Tranquilisers:

- Treatment of stress and mild or severe mental disorders.
- Essential component of sleeping pills.
- Antidepressant drugs:
 - ❖ Noradrenaline, a neurotransmitter, is responsible for mood changes. If levels are very low, it causes depression. In such cases antidepressants are given which inhibit enzymes which degrade noradrenaline thereby increasing the span of noradrenaline. Eg: Iproniazid and phenelzine are antidepressants.
- Other examples of tranquilisers:
 - ❖ Chlordiazepoxide and meprobamate - For relieving tension
 - ❖ Equanil - depression and hypertension
 - ❖ Derivatives of barbituric acid such as Veronal, amytal, nembutal, luminal and seconal - Hypnotic i.e. sleep producing agents.
 - ❖ Valium
 - ❖ Serotonin
- Structures of examples:



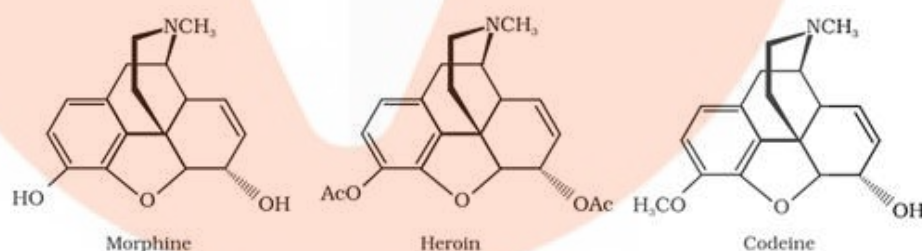
Iproniazid Phenelzine (Nardil)





II. Analgesics:

- Reduces pain without impairment of consciousness, mental confusion, incoordination or paralysis or other disturbances of the nervous system.
- Two types:
 - Non-narcotic (non-addictive):
 - Eg: Paracetamol and Aspirin
 - Aspirin - Painkiller, relieves skeletal pain such as due to arthritis, antipyretic (reduces fever), prevention of heart attacks as it prevents platelet coagulation. Aspirin acts by inhibiting prostaglandins which cause inflammation and pain in tissue.
 - Narcotic (Addictive):
 - Used for relief of postoperative pain, cardiac pain and pains of terminal cancer and during childbirth
 - Administered in medicinal doses relieves pain and produces sleep. In large amounts causes coma, convulsions, stupor and ultimately death.
 - Eg: Opiates (Obtained from opium poppy) such as morphine, heroin, codeine etc.
 - Structure of examples:



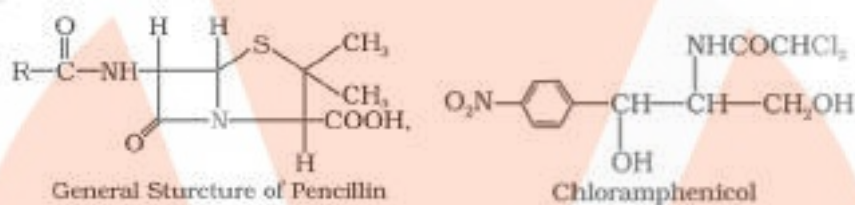
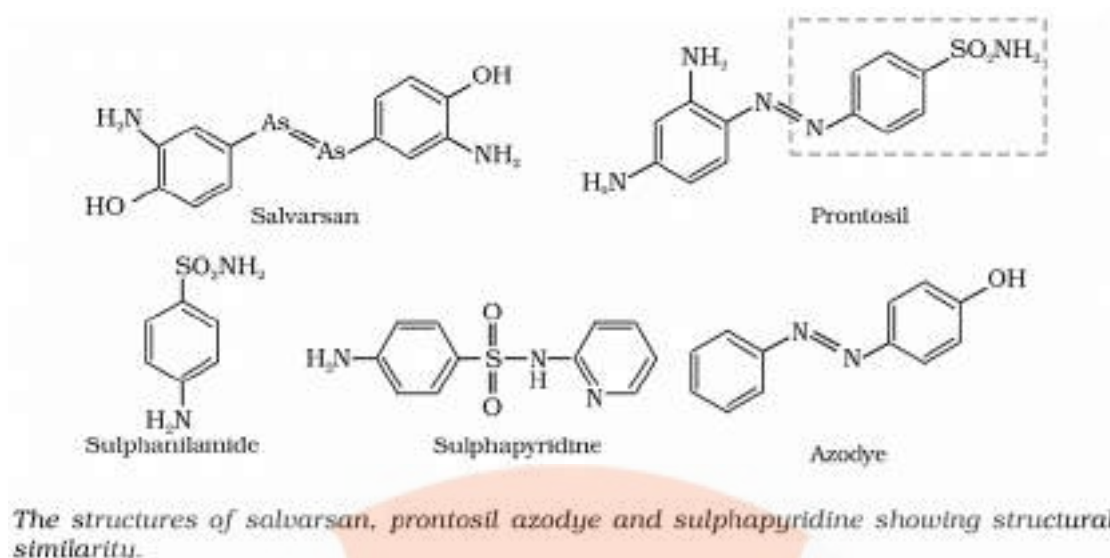
4. Antimicrobials:

- Destroys or inhibits pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal drugs), viruses (antiviral drugs), or other parasites (antiparasitic drugs).
- Different types include antibiotics, antiseptics, disinfectants.

1. Antibiotics:

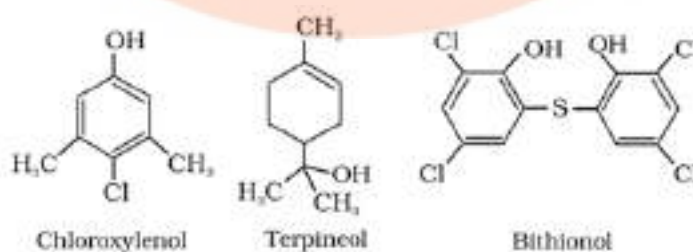
- Past definition: Chemical substances produced by microorganisms that inhibit the growth or even destroy microorganisms.

- Current definition: Substance produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys microorganisms by intervening in their metabolic processes.
- Examples:
 - ❖ Arsphenamine (salvarsan): Arsenic based compound used for treatment of syphilis. Its toxicity is much higher on spirochete (causes syphilis) than humans
 - ❖ Azo Dyes: Have structural similarities with salvarsan. (-As=As- in salvarsan is similar to -N=N- in azo dyes).
 - ❖ Prontosil (Resembles salvarsan): In the body it is converted into sulphanilamide (actual active compound).
 - ❖ Sulphapyridine: Analogue of sulphonamide
 - ❖ Penicillin - Alexander Fleming isolated it from Penicillium fungus which has antibacterial properties.
- Two types:
 - ❖ Bactericidal: Kills microbes. Eg: Penicillin, Aminoglycosides, Ofloxacin
 - ❖ Bacteriostatic: Inhibits microbes. Eg: Erythromycin, Tetracycline, Chloramphenicol.
- Classification based on spectrum of action:
 - ❖ Broad range spectrum:
 - Kill or inhibit a wide range of gram negative and gram-positive bacteria.
 - Eg: Ampicillin and Amoxicillin (synthetically modified penicillins)
 - ❖ Narrow range spectrum:
 - Kill or inhibit a narrow range of gram negative or gram-positive bacteria.
 - Examples:
- Penicillin. (Manufactured by Hindustan antibiotics, Pimpri in India)
Note: It's important to test for sensitivity (allergy) to penicillin before administering.
- Chloramphenicol: Rapidly absorbed from the gastrointestinal tract and hence can be given orally in case of typhoid, dysentery, acute fever, certain form of urinary infections, meningitis and pneumonia.
- Vancomycin and ofloxacin
 - ❖ Limited spectrum:
 - Effective against a single organism or disease.
 - Example: dysidazine - Toxic to few strains of cancer
- Structures of examples:



2. Antiseptics:

- Applied to living tissues like wounds, cuts, ulcers or diseased skin surfaces.
- Should Not be ingested like antibiotics
- Examples:
 - ❖ Dettol: Mixture of chloroxylenol and terpineol
 - ❖ Bithionol or biothional: Added to soaps.
 - ❖ Iodine: 2-3% mixture is called tincture of iodine. Used to sterilize skin before surgical procedures.
 - ❖ Iodoform: For wounds.
 - ❖ Boric acid: Weak antiseptic for eyes.
 - ❖ Others include furacine, soframycin etc
- Structures of examples:

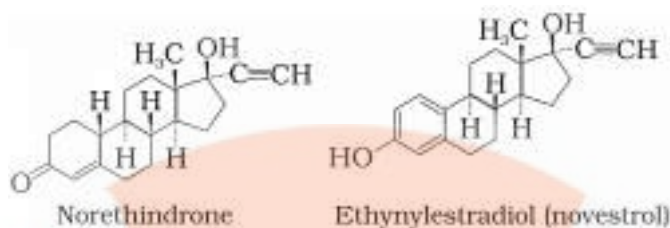


3. Disinfectants:

- Applied to inanimate objects like floors, drainage systems, instruments etc.
- Examples: Chlorine (0.2-04 ppm), SO₂ in very low concentration
- Note: Phenol - 0.2% act as antiseptic, 1% act as disinfectant.

5. Antifertility drugs:

- For population control and family planning
- Birth control pills contain a mixture of synthetic estrogen and progesterone derivatives. Eg: Norethindrone (synthetic progesterone), Ethynylestradiol /novestrol (estrogen derivative used with progesterone derivative).
- progesterone suppresses ovulation. Synthetic progesterone derivatives are more potent than progesterone
- Structures of examples:



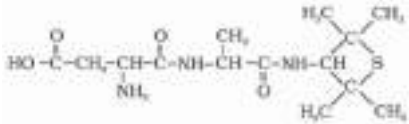
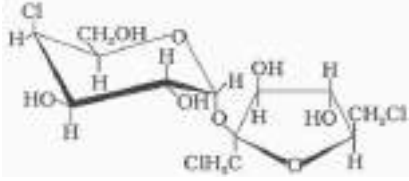
➤ Chemistry in food:

- **Added for:** Preservation, enhancing appeal, adding nutritional value.
- **Main Categories:**
 - (i) Food colours
 - (ii) Flavours and sweeteners
 - (iii) Fat emulsifiers and stabilising agents
 - (iv) Flour improvers - antistaling agents and bleaches
 - (v) Antioxidants
 - (vi) Preservatives
 - (vii) Nutritional supplements such as minerals, vitamins and amino acids.

➤ Artificial sweetening agents:

- Importance: Natural sweeteners are high in calories so artificial sweeteners are used as substituents.
- Few examples:

Compound	Sweetness	Points	Structure
saccharin	550	Use: For diabetic persons Points: <ol style="list-style-type: none"> 1. Also called Ortho-sulphobenzimide 2. Excreted from the body in urine unchanged. 3. Harmless and inert. 	
Aspartame	100	Use: In cold foods and soft drinks as it is unstable at high temperatures. Points: <ol style="list-style-type: none"> 1. Methyl ester of dipeptide 	

		formed from aspartic acid and phenylalanine	
Alitame	2000	Points: 1. High potency sweetener 2. Stable than aspartame but tough to control sweetness.	
Sucralose	600	Points: 1. Trichloro derivative of sucrose 2. Appearance and taste as sugar 3. No calories 4. Stable at cooking temperature	

➤ **Food preservatives:**

- Prevent spoilage of food due to microbial growth.
- Common eg: table salt, sugar, vegetable oils, sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$), salts of sorbic acid & propanoic acid.

➤ **Chemistry in Cleansing agents:**

- Substances to remove stains, dirt etc.
- Two types of detergents used as cleansing agents: (1) Soaps, (2) Synthetic detergents
- Helps in removal of fats which bind other materials to the fabric or skin

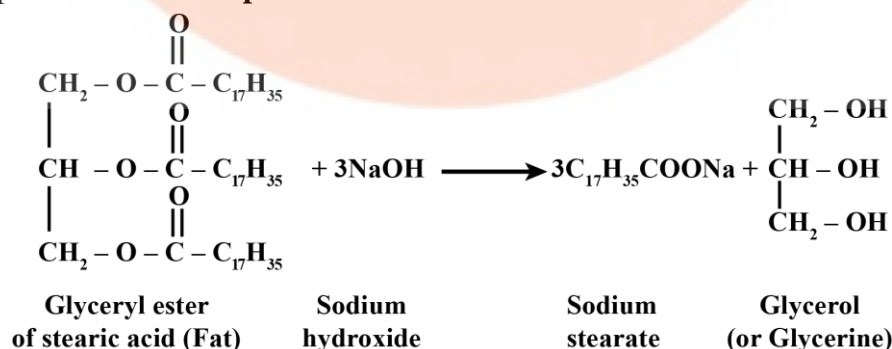
Soaps

- Sodium or potassium salts of long chain fatty acids are soluble in water and are used for cleaning purpose

Eg: stearic, oleic and palmitic acids

• **Preparation:**

1. Heating fat (i.e. Glyceryl ester of fatty acid) with NaOH form sodium salt and the process is called **saponification**.



2. Esters of fatty acids are hydrolysed and the soap obtained remains in colloidal form. It is precipitated from the solution by adding NaCl. The solution left after removing the soap contains glycerol, which can be recovered by fractional distillation.
3. To prepare potassium salt use KOH instead of NaOH.

- Potassium soaps are softer to skin than sodium soaps.

- **Types of soaps:**

Different types of soaps can be made by using different raw materials

- **Toilet soap:** Better grade of fats and oils used. Excess alkali is removed. Colour and perfumes are added for aesthetic purpose
- **Soaps floating in water:** Made by beating tiny air bubbles before their hardening
- **Transparent soaps:** Made by dissolving the soap in ethanol and then evaporating the excess solvent.
- **Medicated soaps:** By adding medicinal substances.
- **Shaving soaps:** Contain glycerol for rapid drying. Rosin gum is added to form rosinate which lathers well.
- **Laundry soaps:** Contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.
- **Soap chips:** Made by running a thin sheet of melted soap onto a cool cylinder and scraping off the soaps in small broken pieces.
- **Soap granules:** Dried miniature soap bubbles.
- **Soap powder and scouring soap:** Contains some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand, and builders like sodium carbonate and trisodium phosphate. Builders make the soaps act more rapidly.
- **Soaps in Hard water:**
 - Hard water has Ca, Mg salts. These react with sodium salt in soap and form Ca and Mg soaps. The insoluble Ca, Mg soaps separate out as scum and are useless with no cleansing activity.



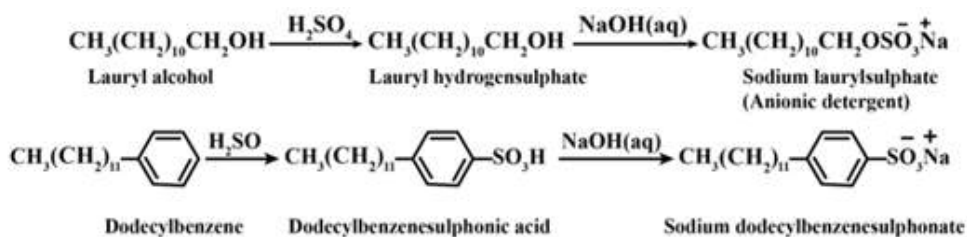
- Precipitates of these soaps adhere onto the fibre of the cloth as gummy mass.
- Hair becomes dull, dyes do not absorb evenly on cloth due to this sticky precipitate.

➤ **Synthetic detergents:**

- Have all properties of soap but do not contain any soap.
- Can give foam with hard water unlike soaps. Some of them give foam even with ice cold water also.
- Classification: Anionic, cationic, non ionic

(1) Anionic detergents:

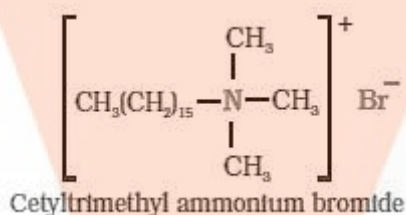
- Sodium salts of sulphonated long chain alcohols or hydrocarbons.
- Anionic part is involved in cleansing activity.
- Eg: Sodium salts of alkylbenzenesulfonates
- Preparation: Treating long chain alcohols with conc. H_2SO_4 and neutralised with alkali to form anionic detergents. Similarly alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali.



- Used in household work and in toothpaste

(2) Cationic detergents:

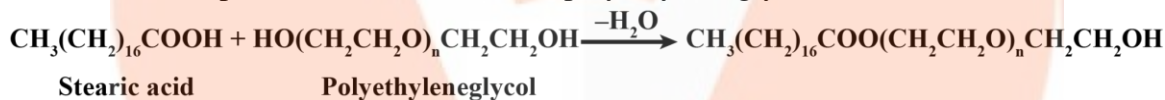
- Quaternary ammonium salts of amines with acetates, chlorides or bromides as anions.
- Eg: Cetyltrimethylammonium bromide



- Used in hair conditioners. Have germicidal properties and are expensive.

(3) Non ionic detergents:

- No ions
- Preparation: Stearic acid with polyethylene glycol.



- Cleansing action is the same as soap, removes grease and oil by micelle formation.
- Used in liquid dish washing.

● Problems with detergents:

- Water pollutant: Cannot be degraded by bacteria due to highly branched hydrocarbons and are accumulated. They persist even after sewage treatment and reach rivers, ponds etc causing foaming and thereby polluting water bodies. These days branching is controlled and kept to a minimum. Unbranched chains are biodegradable.