SOLID STATE

⇒ In solid state, the constituent particles are closely packed and the intermolecular forces of attraction are very strong, In solid state, the constituent particles are only able to vibrate about their mean positions.

⇒ Characteristics of the solid are :

(i) Definite shape and definite volume

(ii) High rigidity and high density

(iii) Low compressibility

(iv) Only vibrational motion of the constituent particles.

⇒ Types there are two types of solids.

(i) Crystaline solid, characterized by

- (i) sharp edges, fat faces
- (ii) sharp melting point
- (iii) presence of long range order (baisc unit repeats itself infinitely)
- (iv) anisotropic in nature
- (v) definite geometrical shape
- (vi) consist of very large number of units called crystals.

(2) Amorphous solids

- (i) The arrangement of building constituents is not regular but haphazard
- (ii) Melting points are not sharp
- (iii) Isotropic in nature
- (iv) called supercooled liquids.

Space lattice and unit cell

A regular repeating arrangement of points in space is called space lattice. It is an array of points showing how molecules or atoms or ion are arranged in different sites in three dimensional space.

A unit cell is the smallest, but complete unit in space lattice which when repeated in three dimensional space generates the crystal. A unit cell possesses all the structural properties of the given crystal.

Types of unit cells

(1) Primitive : atoms are present only at the corners, not at anyother position.

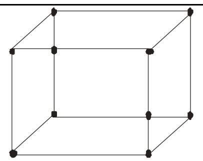
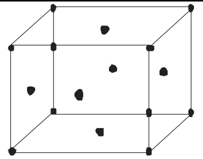
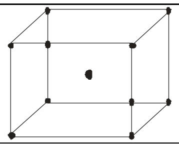
(2) Non-primitive or centered : atoms are present at other positions (centre of face, edge, body) in addition to atoms at the corners.

Three are seven primitive unit cells called seven crystal systems :

All crystals do not have simple lattices. There can be 14 different ways in which similar points can be arranged a three dimensional space. These are called 14 Bravais lattices.

System	Axes	Angles	Examples
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^0$	NaCl, CsCl, ZnS diamond, alums, CaF_2
Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90^0$	TiO_2 (rutile), Sn (White) $ZrSiO_4$
Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90^0$	$CdSO_4$, $HgBr_2$, $BaSO_4$, KNO_3, S(rhombic)
Rhombohedral or Trigonal	a = b = c	$\alpha = \beta = \gamma \neq 90^0$	$CaCO_3$ (calcite), $NaNO_3$, Quartz
Hexagonal	a = b ≠ c	$\alpha = \beta = 90^0$ $\gamma \neq 90^0$	SiO_2, graphite, PbI_2, Mg, ZnO
Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq 90^0$ $\neq 90^0$	$NaHSO_3$, $CuSO_4$, $5H_2O$, $K_2Cr_2O_7$

Types :

Type	Structure	No. of atoms per unit cell	Atomic radius
Simple cubic		$\frac{1}{8}\times 8=1$	$r=\frac{a}{2}$ -
Face centered cubic (fcc)		$\frac{1}{8}\times 8+\frac{1}{2}\times 6=4$ (Corners)(Face)	$r=\frac{\sqrt{2}}{4}a$
Body centered cubic (bcc)		$\frac{1}{8}\times 8+1=2$ (Corners)	$r=\frac{\sqrt{3}}{4}a$

⇒ The structure of solid is determined by X-ray diffraction method. Diffraction is the bending of light and the patterns produced when a light falls on a solid are called diffraction patterns.

⇒ Bragg's Law : When X-rays falls on a crystal face, they penetrate into the crystal and strike the atoms in different planes. X-rays are deflected from each of these planes. Bragg gave the relationship between the wavelength of the X-rays and the distance between the plaes as

$$2d\sin\theta = n\lambda$$

where d = interplanar distance

λ = wavelength of the X-rays

θ = reflection angle or glancing angle

n =1, 2.... positive integer, relfects the order of reflection.

Types of ionic crystals :

⇒ Coordination number is the number of nearest neighbours. It is also defined as the number of oppositely charged ions surroundings the central ion.

Types of ionic crystals :

(1) Rock salt type lattice (NaCl type) [AB type]

The cation A^+ are present at the centre of each edge and at the centre of the cube. Anion B^- present at the corners as well as at the centre of each face.

Coordination number of each ion is 6. The number of formula units per unit cell is 4. The distance between the cation and anion is $r_A + r_B = \frac{a}{2}$ where a = cell edge.

Example : KCl, KNO_3, $LiAlH_4$, KCN

(2) Cesium chloride type lattice (CsCl) : The cation A^+ are present at the centre of the cube, and the anion B^- are present at the corner. The coordination number of each ion is 8. (8 : 8 coordination lattice). The number of formula units equal to 1. The distance between the cation and anion is $r_A + r_B = \frac{\sqrt{3}}{2}a$

Example : CsBr, TiCl, TiBr.

(3) The sphalerite structure (ZnS) : Zn^{2+} ions are present at one fourth of the distance along each body diagonal and sulphide ions are present at the lattice points (at the corners and at the centre of each face). The coordination number of each ion is 4. The number of formula units equal to 4. Example : CuCl, CuBr

(4) Fluorite type AB_2 (CaF_2) : This isa 8 : 4 coordinatio lattice. The cation A^{2+} are at the fcc lattice points and the B^- occupy all the eight tetrahedral voids. There are 4 formula units per unit cell. Example SrF_2, BaF_2, PbF_2 and $BaCl_2$.

(5) Antifluorite Type (A_2B) : This is a 4 : 8 coordination lattice. There are 4 formula units per unit cell. The cation and anion position as obtained in the fluorite structure gets reversed. Example : Na_2O, Li_2O, K_2O, Rb_2O, Rb_2S.

Density Calculation :

The density of solid is defined as $d = \frac{zM}{a^3 N_A}$

z = number of atoms or formula units per unit cell

M = mole mass of formula mass

N_A = Avogadro's number

a = cell edge

The density of solid generally we express in g per cm^3.

⇒ Packing in solids means close-packed arrangement of atoms and the atom is conidered as a hard sphere. Crystal can be generated by stacking one layer over another. The external shape of the crystal is related to the shape of the unit cell. There are four types of packing :

(1) square based packing (also called simple cubic) : The atoms are arranged in such a way that the centres of all the particles in any row are in a straight line. The coordination number within the layer is four.

(2) Body-centered cubic (bcc) : In this packing, the spheres of the second layers are placed between the vacant space of the first layer. The coordination number is 8.

(3) Hexagonal close packing (hcp) and cubic close packing (ccp) :

(i) In both, the coordination number within a layer is six, but in three dimension, the coordination number is 12.

(ii) In hcp, the packing pattern is ABABAB ...... every third layer has same arrangement of atoms as the first.

(iii) In ccp, the packing pattern is ABC, ABCABC ......

(iv) In both hcp and ccp, the packing fraction is 0.74.

(v) Examples of hcp are Mg, Zn and ccp are Cu, Ag, Au.

Packing Fraction :

(i) Simple cubic (square based packing) : No. of atoms per unit cell = 1

$$V_{\text{one atom}} = \frac{4}{3}\pi r^3$$

In simple cubic, the atoms are in touch with each other along the cell edge, therefore, a = 2r and

$$V_{\text{unit cell}} = a^3 = 8r^3 \quad .$$

Hence, packing fraction. $\phi = \frac{1 \times \frac{4}{3}\pi r^3}{8r^3} = \frac{\pi}{6} = 0.52$

(ii) Body centered cubic packing : Atoms are in touch with each other along the body diagonal, therefore,

$$4r = \sqrt{3}\,a \text{ and } a^3 = \frac{64}{3\sqrt{3}} r^3$$

Packing fraction $\phi = \frac{2 \times \frac{4}{3}\pi r^3}{\frac{64}{3\sqrt{3}} r^3} = 0.68$

(iii) Cubic close packing (fcc) :

$$\phi = \frac{4\times\frac{4}{3}\pi r^3}{a^3} \text{ but } a = \frac{4}{\sqrt{2}}r \text{ (atoms are in touch along the face diagonal).}$$

$$\therefore a^3 = \frac{64}{2\sqrt{2}}r^3 \quad \text{and} \quad \phi = \frac{4\times\frac{4}{3}\pi r^3}{\frac{64}{2\sqrt{2}}r^3} \quad \phi = 0.74$$

VOIDS :

⇒ The unoccupied space in the lattice is called void or hole or interstices. In a cubic close packed structure, there are two types of voids.

(1) Octahedral void, the coordination number of an atom occupying the void is 6.

(2) Tetrahedral void, the coordination number is 4. Tetrahedal void is smaller in size than octanedral void in cubic close packed structure.

The number of octahedral voids = 2 × number of atoms in a ccp structure.

RADIUS RATIO

⇒ For ionic solids, the ratio of the radius of the cation to that of anion is called the radius ratio. The radius ratio for a given coordination number is fixed. radius ratio = $\frac{r_+}{r_-}$

Radius ratio	Coordination number	Types of lattice	No. of formula units per unit cell	Example
0.155 to 0.225	3	Planar triangle	-	BO_3^{3-}, solid SO_3
0.225 to 0.414	4	ZnS type	4	ZnS, CuCl
0.414 to 0.732	6	NaCl type	4	MaO, NaBr
0.732 to 1.00	8	CsCl type bcc	2 atoms in bcc and 1 formula unit in CsCl	CsCl, CsBr

⇒ In a ccp structure, the octahedral voids can be located at the centre of each edge and at the body center. Thus, the number of octahedral voids.

$$= 1 + \frac{1}{4}\times 12 = 4$$

⇒ Tetrahedral voids are located at the body diagonal. Each body diagonal has two tetrahedral void.

∴ the number of tetrahedral voids = 8

CRYSTAL DEFECTS :

⇒ Any deviation from an ordered arrangement in a crystal is called imperfection or defect. Defect due to missing atoms or ion is called point defect. The point defect propagating along a line is called line defect and propagating along a plane is called plane defect.

A. Point defects are of two types :

(1) Stoichiometric defect in which the cation to anion ratio is 1 : 1 and

(2) Non-stoichiometric defect in which the cation to anion ratio is not equal to 1 : 1.

⇒ There are two types of stoichiometric defect.

(1) Schottky defect :

- one pair of ions (one cation and one anion) missing from the lattice position.
- The lattice remains electrically neutral.
- The density of the solid decreases.
- The defect of found only in those solids with high coordination number and high ionic character.
- Examples : NaCl, KNO_3, KCl

(2) Frenkel defect :

- In this one of the ion (preferably cation) occupies the interstitial sites leaving lattice site vacant.
- The density of the solid remains same.
- The defect is observed in ionic crystals in which anion is much larger in size than the cation, e.g. AgBr, ZnS.

⇒ Silver halides (AgBr) are the solids which shows both Schottky and the Frenkel defect.

The defects in which there is a change in overall chemical combinations are called Non-stoichiometric defects.

B. Non-stoichiometric defects.

Non-stoichiometric defects are of two types

(1) Metal excess

(2) Metal deficiency

⇒ Metal excess defects : It can be of two types

(1) A negative anion is missing from the lattice site which is occupied by an extra electron to make the lattice electrical neutral. The lattice position occupied by electron is called F-centre. The solids with F-centre are paramagnetic and coloured. Example : Alkali metal / alkali metal halide.

(2) An extra cation is present in the interstitial position and to maintain electrical neutrality, we also add one electron tot he interstitial position. such crystals are coloured and semiconductor. Example ZnO is a white solid (stoichiometric) at low temperature but yellow (non-stoichiometric) at high temperature.

● Metal deficiency defect : In this one of the cation is missing from the lattice site and the extra negative charge can be neutralized by developing an extra positive charge on the nearby cation. These crystals show semiconduction. Example : NiO, FeO. The defects which arises due to the presence of impurities in the crystal are called impurity defects.

Class 12 Chemistry
Solutions

Concentration Terms

1. Molarity (M) = moles of solute / volume of solution (in L)
2. Molality (m) = moles of solute / mass of solvent (in kg)
3. Mole Fraction (X) = moles of component / total moles of solution
4. Normality (N) = equivalents of solute / volume of solution (in L)

Raoult's Law

For a solution of two volatile liquids, A and B:

Partial pressure of A, PA = P°A * XA

Partial pressure of B, PB = P°B * XB

Where P°A and P°B are vapor pressures of pure components A and B, respectively, and XA and XB are their mole fractions.

Colligative Properties

1. Relative Lowering of Vapor Pressure: (P°A - PA) / P°A = XB
2. Elevation of Boiling Point (Delta Tb): Delta Tb = Kb * m
3. Depression of Freezing Point (Delta Tf): Delta Tf = Kf * m
4. Osmotic Pressure (Pi): Pi = MRT

   where Pi is the osmotic pressure, M is molarity, R is the gas constant, and T is temperature in Kelvin.

Van't Hoff Factor (i)

i = (observed colligative property) / (calculated colligative property assuming no dissociation or association)

For ionizing solutes: i > 1, indicating dissociation.

For associating solutes: i < 1, indicating association.

Modified Colligative Property Formulas with Van't Hoff Factor

1. Delta Tb = i * Kb * m
2. Delta Tf = i * Kf * m
3. Pi = i * MRT

ELECTROCHEMISTRY

Electrochemistry is that branch of chemistry which deals with the relationship between electrical energy and chemical energy changes taking place in a redox reaction.

(1) Resistance:It measures the obstruction to the flow of current.

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

Where ρ is the constant of proportionality and is called specific resistance or resistivity. The resistance depends upon the nature of the material.Units: The unit of resistance is ohm $((\Omega)$.

(2) Resistivity or specific resistance:

$\because R = \rho \frac{l}{a}$; Now, if $l = 1$ cm, a = 1 cm^2 then $R = \rho$

Thus, resistivity is numerically equal to the resistance of a conductor of 1 cm length and having area of cross-section equal to 1 cm^2.

Units: The unit of resistivity is $\rho = R \frac{a}{l} = \text{Ohm} \frac{\text{cm}^2}{\text{cm}} = \text{Ohm.cm}$ (c.g.s unit). Its SI Unit is Ohm metre.

(3) Conductance: It measures the ease with which current flows through a conductor. It is an additive property. It is expressed as C. It is reciprocal of the resistance, i.e.

$$C = \frac{1}{R}$$

Units: The c.g.s. unit of conductance is (ohm^{-1}) or mho.

According to SI system, the units of electrical conductance is Siemens, S (i.e. $1S = \Omega^{-1}$).

(4) Conductivity(κ) : The inverse of resistivity is called conductivity (or specific conductance). It is represented by the symbol κ. It may be defined as, the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section.

Thus, $\kappa = \frac{1}{\rho}$

Units: The units of conductivity is $\kappa = \frac{1}{\text{Ohm.cm}} = \text{Ohm}^{-1}\text{cm}^{-1}$ or $\Omega^{-1}\text{cm}^{-1}$

Its SI unit is Sm^{-1}.

(5) Molar conductivity or molar conductance: Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

$$\Lambda = \frac{\kappa \times 1000}{M}$$

The c.g.s. unit of molar conductance is ohm^{-1} cm^2 mol^{-1}

The SI unit of molar conductance is Sm^2 mol^{-1}.

(6) Equivalent conductivity: It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_{eq} and

$\Lambda_{eq} = \kappa \times \frac{1000}{N}$, where, N = Normality of solution.

The units of equivalent conductance (a) Ohm^{-1} cm^2 (gm equiv)$^{-1}$ (in c.g.s. system) (b) Sm^2 equiv^{-1} (in S.I. system)

(7) Experimental measurement of conductance

(i) The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance.

(ii) Calculation of conductivity: We have seen that conductivity (κ) is reciprocal of resistivity (ρ), i.e.

$$\therefore\ \kappa = \frac{1}{R}\left(\frac{l}{a}\right) \text{ or } \kappa = C\left(\frac{l}{a}\right) \quad \text{Conductivity = Conductance} \times \text{Cell constant}$$

$\Rightarrow$ Cell consant = l/a, unit of cell constant (a) cm^{-1} (c.g.s unit) (b) m^{-1} (S.I. unit)

Factors affecting the electrolytic conductance

(1) Nature of electrolyte

(2) Concentration of the solution: The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase indilution.

(3) Temperature: The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increase.

Kohlrausch's Law

Kohlrausch's law states that "Equivalent conductivity of any electrolyte at infinite dilution is the sum of the equivalent conductivities of the cations and the anions" i.e. $\wedge_m^0$ for $A_xB_y = x \times \lambda^0_{A^{y+}} + y\lambda^0_{B^{x-}}$

Application of Kohlrausch's law: Some typical applications of the Kohlrausch's law are described below,

(i) In the determination of Λ_M^∞ for weak electrolyte:

(ii) In the determination of the degree of ionisation of an weak electrolyte

(iii) In the determination of the ionisation constant of a weak electrolyte

(iv) In the determination of the solubility of a sparingly soluble salt

Transport number or Transference number

Definition : "The fraction of the total current carried by on ion is known as transport number, transference number or Hittorf number may be denoted by sets symbols like t_+ and t_- or t_c and t_a or n_c and n_a".

From this definition

$$t_a = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}} \text{ and } t_c = \frac{\text{Current carried by an cation}}{\text{Total current passed through the solution}}$$

evidently, $t_a + t_c = 1$

Determination of transport number: Transport number can be determined by Hittorf's method, moving boundary method, emf method and from ionic mobility.

(a) Primary cells are those which cannot be recharged e.g. dry cell and mercury cell.

(b) Secondary cells are those which can be recharged e.g. lead storage battery and Ni-Cd cell.

(c) Fuel cells are those in which energy produced from the combustion of fuels can be converted into electrical energy e.g. H_2–O_2 fuel cell.

Main features of different cells.

	Nature of cell/Battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite	MnO_2 + C (touching cathode) NH_4Cl + $ZnCl_2$ touching anode
(ii)	Mercury cell	Zinc	Grpahite	HgO + KOH (moist)
(iii)	Lead storage battery	Lead	Lead dioxde	H_2SO_4 (38%)
(iv)	Ni-Cd cell	Cadmium	Nickel dioxide	KOH (sol.)

Conductors and Insulators

Those which allow the passage of current are known as conductors. The others which do not allow electric current to pass through are insulators.

Types of conductors

Difference between Electronic/Metallic conductors and Electrolyte conductors

	Electronic conductors		Electrolytic Conductors
(i)	Flow of electricity is due to flow of electrons	(i)	Flow of electricity is due to flow of ions.
(ii)	Flow takes place without decomposition of the substance.	(ii)	Flow is accompanied by decomposition of the substance
(iii)	Conduction decreases with temperature because kernels start vibrating which interfere in the flow of electrons.	(iii)	Conduction increases with temperature because dissociation increases.

Electrolyte: An electrolyte is defined as the substance that, in solution or in the molten state, conducts electric current and is simultaneously decomposed by it.

Electrode: An electronic conductor in contact with an electrolytic conductor is known as an electrode or a half cell.

Electrode potential: The potential difference set up across the surface of separation of an electronic and electrolytic conductor in contact with each other is known as electrode potential or half cell e.m.f.

Cell: An assembly of two half cells.

ELECTROLYSIS

The phenomenon in which passage of current through an electrolyte (molten or solution) brings in chemical changes involving electronation (reduction) as well as oxidation (de-electronation) of ions is known as electrolysis.

1. The cations migrate towards cathode, where they gain electrons and show reduction.

   At cathode: $M^{n+} + ne \longrightarrow M$ (reduction)

2. The anions migrate towards anode, where they lose electrons and show oxidation

   At anode: $A^{n-} \longrightarrow A + ne$ (oxidation)

The Products formed During Electrolysis Depends Upon

1. Nature of electrodes (attackable or non-attackable electrodes)
2. Nature of electrolyte (Motlen or aqueous solution)
3. Charge density flown during the process
4. Concentration of solution used

e.g.

Electrolyte	Electrode	Cathodic Reaction	Anodic Reaction
NaCl (fused)	Pt	$Na^+ + e \longrightarrow Na$	$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$
NaCl (aq, very dilute)	Pt	$H^+ + e \longrightarrow \frac{1}{2}H_2$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
NaCl (aq.)	Hg	$Na^+ + e \longrightarrow Na$	$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$
HCl (aq.)	Pt	$H^+ + e \longrightarrow \frac{1}{2}H_2$	$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

$NaNO_3$ (aq) or Na_2SO_4 (aq)	Pt	$2H^+ + 2e \longrightarrow H_2$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
$CuSO_4$ (aq)	Pt	$Cu^{2+} + 2e \longrightarrow Cu$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
$AgNO_3$(aq)	Pt	$Ag^+ + e \longrightarrow Ag$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
H_2SO_4 (at normal current density)	Pt	$2H^+ + 2e \longrightarrow H_2$	$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$
H_2SO_4 (at high current density)	Pt	$2H^+ + 2e \longrightarrow H_2$	$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$

Note: 1. The phenomenon of electrolysis occurs only at the electrodes. Oxidation occurs at anode, reduction occurs at cathode.

2. In case of two or more similar ions to be discharged, the more is discharge potential of an ion, lesser is its tendency to get itself discharged at the electrodes.

3. The discharge of ions at the different electrodes takes place only during the passage of charge.

FARADAY'S LAWS OF ELECTROLYSIS

1st Law: The amount (W) of substance deposited on electrode is directly proportional the charge passed into the fused state or in aqueous solution of electrolyte.

i.e. $W \propto Q \ (Q\,Q = it)$

$W \propto it$

$\therefore \quad W = z \cdot i \cdot t$ ...(i)

$\frac{W_1}{W_2} = \frac{z_1 i_1 t_1}{z_2 i_2 t_2}$, when $i_1 t_1 = i_2 t_2$ then $\frac{W_1}{W_2} = \frac{z_1}{z_2}$

i.e $w \propto z$ at constant Q.

IInd Law : By passing the same charge into different electrolytes, the amount of substances deposited on electrode are directly proportional to their no of equivalent .

i.e $w \propto E$ when Q is constant

or $\frac{w_1}{w_2} = \frac{E_1}{E_2}$ when Q is constant.

Note : (i) By passing 1 coulomb of charge, Z gm of substance is deposited on electrode.

(ii) By passing 1 F of charge, E gram of substance is deposited on electrode.

(iii) $W_{gm} = ZCt = \frac{E}{F} \times C \times t = \frac{A}{V} \times \frac{C_{amp} \times t_{sec}}{F}$

APPLICATIONS OF ELECTROLYSIS

1. In extracton of metals
2. Preparation of Chemicals
3. Preparation of Organic Compounds
4. Corrosion and its Prevention
5. In purification of metals

Types of Cells

	Electrolytic Cells	Electrochemical Cells
1.	Passage of current brings in chemical changes	A chemical change brings in passage of current.
2.	Electrical energy is converted into chemical energy	Chemical energy is converted into electrical energy.

ELECTROCHEMICAL CELLS

Sl. No.	Chemical Cells	Concentration Cells
1.	A net chemical change inside the cell occurs, e.g., Daniel Cell $Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$ Anode: $Zn \longrightarrow Zn^{2+} + 2e$ Cathode: $Cu^{2+} + 2e \longrightarrow Cu$	No net chemical change occurs. e.g., $M \mid M^+_{C_1} \parallel M^+_{C_2} \mid M$ $M \longrightarrow M^+_{C_1} + e$ $M^+_{C_2} + e \longrightarrow M$
	Redox change, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$	Net change, $M^+_{C_2} \longrightarrow M^+_{C_1}$ where C_1 and C_2 are conc. of the electrolyte of the same metal whose two electrodes are used. The cell will work only when $C_2 > C_1$
2.	A decrease in free energy during the redox change brings in an equivalent amount of electrical work done.	A decrease in free energy during the transfer of concentration from C_2 to C_1 brings in an equivalent amount of electrical work done.
3.	The electrode having high standard oxidation potential works as anode, i.e., negative electrode.	The electrode having more dilute solution surrounding, works as anode.

Chemical Cells: These are also known as redox cells or galvanic cells or voltaic cells. The simplest example of this category is Daniel cell. The cell is represented as,

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

Characteristics of Daniel Cell

i) Oxidation and reduction occur simultaneously.

ii) oxidation occurs at one electrode (i.e, anode) whereas reduction occurs at other electrode (i.e., cathode)

iii) The number of electrons released at anode = No. of electrons consumed at cathode.

iv) The electrons released at anode flow through external wire towards cathode where they are used up.

Nernst Equation for Electrode Potential

Nernst gave an expression to express electrode potential for a change.

Metal: $\underset{\text{Reduced State (R.S.)}}{M} \rightleftharpoons \underset{\text{Oxidised state(O.S.)}}{M^{n+}} + ne$

$$E_{OP} = E^0_{OP} - \frac{RT}{nF}\ln\frac{a_{O.S.}}{a_{RS.}} = E^0_{OP} - \frac{0.0591}{n}\log\frac{a_{O.S.}}{a_{RS.}} (\text{at } 25^0C)$$

Non-metal: $\underset{\text{O.S.}}{A} + ne \rightleftharpoons \underset{\text{R.S.}}{A^{n-}}$

$$E_{RP} = E^0_{RP} - \frac{RT}{nF}\ln\frac{a_{R.S.}}{a_{OS.}} = E^0_{RP} - \frac{0.0591}{n}\log\frac{a_{RS.}}{a_{OS.}} (\text{at } 25^0C)$$

Factors influencing electrode potential

1. Nature of electrode (i.e., $E^{0)}$
2. Concentration of ion in solution, i.e., [O.S.] and [R.S.]
3. Temperature: The temperature dependence of electrode potential has been discussed in application (iii) of Nernst equation under heading heat of reaction.

Some applications of Nernst equation

(i) In computation of the e.m.f. of cell

$$E^0_{cell} = E^0_{OP} + E^0_{RP}$$

$$E_{cell} = E_{OP} + E_{RP}$$

(ii) e.m.f. of Cell and equilibrium constant:

$$\Delta G = \Delta G^0 + RT\ \ln Q$$

At equilibrium $\Delta G = 0$

$$\therefore \Delta G^0 = -RT\ K_{eq} = -2.303\ RT \log K_{eq}$$

$$\therefore \qquad E^0 = \frac{2.303}{nF} RT \log K_{eq} \quad = \frac{0.0591}{n} \log K_{eq} \text{ at } 25°C$$

(iii) Heat of reaction for cell reaction:

$$\Delta H = nF\left[T\left(\frac{\delta E}{\delta T}\right)_P - E\right]$$

where $\left(\frac{\delta E}{\delta T}\right)_P$ is called as temperature coefficient of e.m.f., i.e., rate of change of e.m.f. (E) with temperature at constant pressure.

(iv) To decide spontaneity of cell reaction:

(v) To evaluate solubility product

(vi) To evaluate pH of solution.

Reversible and Irreversible Cells

In order to find out if a given cell is reversible or not, it is connected to an external source of E.M.F. and if,

1. the e.m.f. of test cell is slightly greater than the e.m.f. of external cell, the current flows from the test cell to external cell and cell reacton takes place.
2. the e.m.f. of test cell is slightly lesser than the external e.m.f. the current flows from external cell to test cell and reaction is reversed.
3. the e.m.f. of test cell is equal to external e.m.f., then no current is given out by the cell and no chemical reaction takes place in the cell.

Electrochemical Series

1. An electrochemical series is one in which elements are placed in order of their decreasing tendency to lose electrons or decreasing tendency to get oxidised, measured interms of E^0_{OP} (decreasing trend) or increasing tendency to gain electrons or increasing tendency to get reduced, measured in terms of E^0_{RP} (increasing trend).

2. More or +ve is E^0_{OP}, more is the tendency to get oxidised
3. Stronger is oxidant, weaker is its conjugate reductant in a redox pair and vice versa.
4. The reducing power of metals decreases down the series.
5. The oxidsing power of metal ions increases down the series.
6. The activity of metals decreases down the series
7. The metal placed above in series replaces the other from its electrolyte solution placed below in series.

   $Zn \longrightarrow Zn^{2+} + 2e$ More E^0_{OP}

   $Fe^{2+} + 2e \longrightarrow Fe$ Less E^0_{OP}

   $Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$

8. The metals placed above H in series produce H_2(g) on reaction with dilute acids.

   $Zn \longrightarrow Zn^{2+} + 2e$ More E^0_{OP}

   $2H^+ + 2e \longrightarrow H_2$ Less E^0_{OP}

   $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

9. The reducing power of halide ion decreases down the series HI > HBr > HCl > HF

   or $I^- > Br^- > Cl^- > F^-$ (Q E^0_{OP} decreases)

10. The oxidising power of halogens increases down the series.

    $I_2 < Br_2 < Cl_2 < F_2$ (Q E^0_{OP} decreases)

IMPORTANT INFORMATIONS

1. Reactions occurring in lead storage battery (a) Reactions occurring during discharge.

   At anode : $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

   At cathode : $PbO_2 + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

   The complete reaction may be written as

   $$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

   As H_2SO_4 is consumed, the consumed, the voltage of the battery drops.

   (b) Reactions occurring during charging are the reverse of the above reactions.

2. Corrosion is the process of change of metal surface into oxides, sulphides, carbonates etc. due to attack of atmospheric gases.

3. Factors which enhance corrosion are
   - (i) Presence of impurities in the metal (pure metal do not corrode)
   - (ii) Presence of moisture (e.g. in rainy season)
   - (iii) Presence of electrolytes (.e.g saline water)

4. Corrsion can be prevented by the following methods :
   - (i) Barrier protection by oil/grease layer, paints or electroplating
   - (ii) Sacrificial protection by coating the metal with more electropositive metal (e.g. Zn called galvanisation).
   - (iii) Electrical protection by connecting the iron pipe to a more electropositive metal with a wire.

5. Effect of concentration and temperature on Transport number. With increase in concentration, transport number decreases. Further, for 1 : 1 electrolyte. if transport number of an ion is greater than 0.5 it decreases

with increase of temperature but if it is less than 0.5, it increases with increase in temperature till it approaches a value of 0.5.

- Loss of electron is oxidation whereas gain of electron is reduction.
- Increase in oxidation no. is said to be oxidation whereas decrease in oxidation number is said to be reduction
- Oxidised substance is said to be reducing agent whereas reduced substance is said to be oxidising agent.
- Equivalent mas of oxidising agent $= \dfrac{\text{Formula mass of O.A.}}{\begin{array}{c}\text{No. of electrons gained}\\ \text{by one molecule of O.A.}\end{array}} = \dfrac{\text{Formula mass of O.A.}}{\begin{array}{c}\text{Decrease in oxidation no. of active}\\ \text{element / s present in one molecule of O.A.}\end{array}}$
- Equivalent mass of Reducing agent $= \dfrac{\text{Formula mass of R.A.}}{\begin{array}{c}\text{No. of electrons lost}\\ \text{by one molecule of R.A.}\end{array}} = \dfrac{\text{Formula mass of R.A.}}{\begin{array}{c}\text{Decrease in oxidation no. of active}\\ \text{element / s present in one molecule of R.A.}\end{array}}$
- Types of redox reaction
  - (a) Inter molecular redox reaction $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
  - (b) Intra molecular redox reaction $2KClO_3 \rightarrow 2KCl + 3O_2$
  - (c) Disproportion reaction $2Cu^{+} \rightarrow Cu^{2+} + Cu$

CHEMICAL KINETICS

CHEMICAL KINETICS

The branch of physical chemistry which deals with the rates of chemical reaction, the mechanism by which the chemical reactions take place and the effects of various factors (such as concentration, temperature, pressure, catalyst etc) on reaction rates is called chemical kinetics.

Types of Chemical reactions (On the basis of their rates)

1. Very fast or instantaneous reactions: These reactions occur at a very fast rate. Generally these reactions involve ionic species and known as ionic reaction.

   e.g. $AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3$

2. Moderate reaction : These reactions proceed with a measurable rates at normal temperature and it is these reactions that are studied in chemical kinetics. Mostly these reactions are molecular in nature. e.g. (a) Hydrolysis of ester (b) Decomposition of N_2O_5
3. Very slow reactions: These reactions are extremely slow.

   e.g. Rusting of iron : $Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3.\,xH_2O}$

Rate of a reaction : It is defined as the change in concentration of reactant or product per unit time.

$$\frac{\Delta x}{\Delta t} \text{ or } \frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1}\right)$$

⇒ The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate and

$$\text{Instantaneous rate} = (\text{Average rate})_{\Delta t \to 0}$$

$$\Rightarrow A + B \to C + D,\ r = \frac{-d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$$

and for the reaction aA + bB = cC + dD

$$r = \frac{1}{a}\left\{-\frac{d[A]}{dt}\right\} = \frac{1}{b}\left\{-\frac{d[B]}{dt}\right\} = \frac{1}{c}\left\{+\frac{d[C]}{dt}\right\} = \frac{1}{d}\left\{+\frac{d[D]}{dt}\right\}$$

⇒ The rate of reaction is always positive.

⇒ Unit for rate of reaction $= \frac{\text{Unit of conc.}}{\text{Unit of time}} = \text{mole } L^{-1}\text{time}^{-1}$.

For gaseous reaction, the unit is atm time^{-1}

Factors affecting rate of a reaction

The rate of a chemical reaction depends on the following factors

1. Nature of reactants

(i) Physical state of reactants:
(ii) Physical size of the reactants:
(iii) Chemical nature of the reactants.

2. Temperature:

The rate of chemical reaction generally increases on increasing the temperature. The rate of a reaction becomes almost doubled or tripled for every 10°C rise in temperature.

Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differed by 10° (generally 25°C and 35°C).

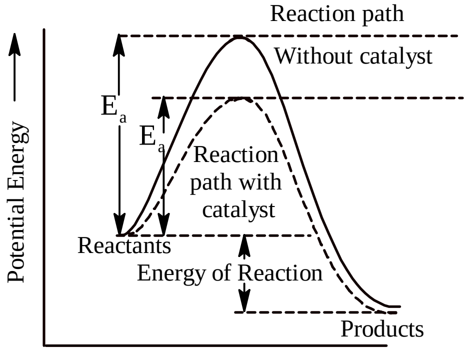
$$\text{Temperature coefficient} = \frac{K\ \text{at}(t+10^{\circ}C)}{K\ \text{at}\ t^{\circ}C} = \frac{k_{35^{\circ}C}}{k_{25^{\circ}C}}$$

3. Concentration of reactants :

The rate of a chemical reaction depends upon the concentration of the reactants.

4. Presence of catalyst :

Rate of reaction depends on presence of catalyst. Positive catalyst decreases the value of Ea and increases the value of K (rate constant) and hence increases the rate of reaction.



A catalyst changes the reaction path

5. Effect of sunlight (For photochemical reaction):

Rate equation

It is mathematical equation which corelates rate of reaction with concentration (activity) of reactants.

For $aA + bB \rightarrow \text{Product}$,

$r = K a_A^m a_B^n$, where $m \le a$ & $n \le b$

Rate constant :

It is equal to rate of reaction when concentration fo each reactant is unity. It is a constant for a particular reaction at a given temperature and also known as specific rate cosntant or specific reaction rate (because rate constant is equal to rate of reaction under specific condition when concentration of each reactant is unity).

Consider a general reaction

$$aA + bB \longrightarrow \text{products}$$

$$\frac{dx}{dt} = k[A]^m[B]^n \quad \text{where } m \le a \ \& \ n \le b$$

when $C_A = C_B = 1$

then $\frac{dx}{dt} = k$

Unit of rate constant

Unit of rate constant depends on order of reaction.

$\therefore$ Unit of K is Litre^{n-1} mol^{1-n} time^{-1} where n = order of reaction

Molecularity	Order of Reaction
1. It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction	1. It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction.
2. It is always a whole number	2. It may be a whole number, zero, fractional, positive or negative
3. .It is theoritical concept	3. .It is experimentally determined.
4. It is meaningful only for simple reaction or individual steps of a complex reaction. It is meaningless for overall complex reaction	4. It is meant for the reaction and not for its individual steps.

Table: Rate constant and other parameters of different order reactions

Order	Rate constant constant	Unit of rate constant	Effect on rate by changing conc. to m times	Half-life period ($t_{1/2}$)
0	$k_0 = \frac{x}{t}$	conc. time^{-1} (mol L^{-1}s^{-1})	No change	$\frac{a}{2k_0}$
1	$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$, $C = C_0 e^{-k_1 t}$ $N = N_0 e^{-k_1 t}$, $k_1 = \frac{2.303}{(t_2 - t_1)}\log_{10}\left(\frac{a-x_1}{a-x_2}\right)$	time^{-1}(s^{-1})	m times	$\frac{0.693}{k_1}$
2.	$k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{x}{ta(a-x)}$ (for the case when each reactant has equal concentration) $k_2 = \frac{2.303}{t(a-b)}\log_{10}\left[\frac{b(a-x)}{a(b-x)}\right]$ (for the case when both reactants have different concentration)	conc^{-1} time^{-1} (mol L^{-1})$^{-1}$ s^{-1}, L mol^{-1} s^{-1}	m^2 times	$\frac{1}{k_2 a}$
3.	$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$	conc^{-2} time^{-1} (mol L^{-1})$^{-2}$ s^{-1}, L^2 mol^{-2} s^{-1}	m^3 times	$\frac{3}{2k_3 a^2}$

n $n \geq 2$	$k_n = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{(a)^{n-1}}\right]$;	$\text{conc}^{(1-n)}\text{time}^{-1}$ $(\text{mol L}^{-1})^{(1-n)}\text{s}^{-1}$,	m^n times $L^{(n-1)}\text{mol}^{(1-n)}\text{s}^{-1}$	$\frac{2^{n-1}-1}{(n-1)k_n(a)^{n-1}}$ $n \geq 2$

For a reaction of general type: nA $\longrightarrow$ products, to be of:

Zero order:

$$k_0 = \frac{x}{nt} \text{ and } t_{1/2} = \frac{a}{2nk_0}$$

First Order

$$k_1 = \frac{2.303}{nt}\log\frac{a}{(a-x)} \text{ and } t_{1/2} = \frac{0.6932}{nk_1}$$

Second order

$$k_2 = \frac{1}{nt}\left\{\frac{x}{a(a-x)}\right\} \text{ and } t_{1/2} = \frac{1}{nak_2}$$

Third order

$$k_3 = \frac{1}{2nt}\left\{\frac{x(2a-x)}{a^2(a-x)^2}\right\} \text{ and } t_{1/2} = \frac{3}{2nk}$$

Relation between '$t_{1/2}$' and initial concentration 'a' for nth order reaction

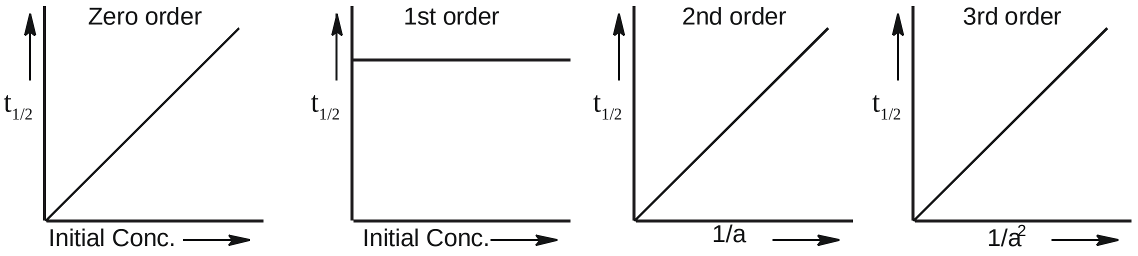
$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}};\ (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}};\ \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)\,[\log_{10}a_2 - \log_{10}a_1]$$

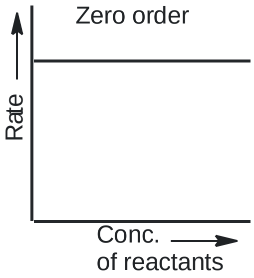
$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10}a_2 - \log_{10}a_1)}$$

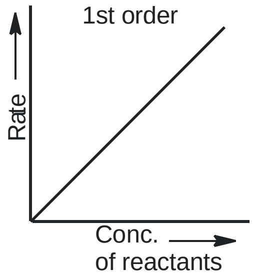
Important Graphs

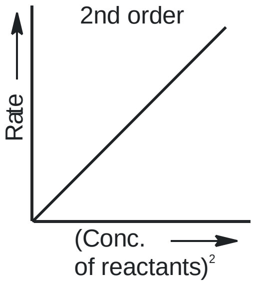
(a) Plots of half-lives Vs initial concentrations (a)

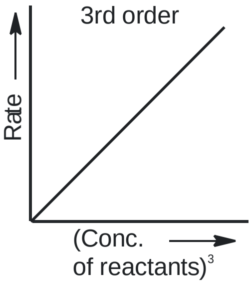


(b) Plots of rate Vs concentrations [Rate = k(conc.)^n]

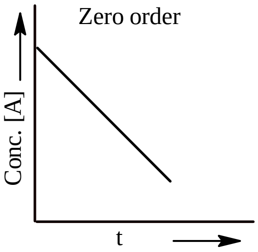


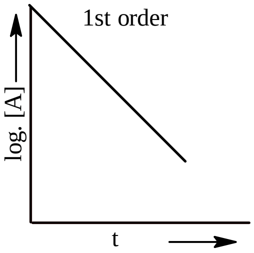


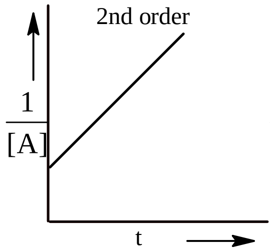


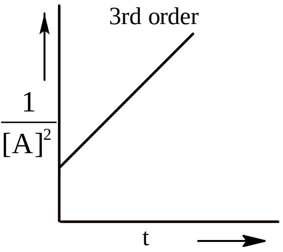


(c) Plots from integrated rate equations









⇒ Activation energy

The minimum amount of energy which must be absorbed by the reactants to undergo chemical reactions is called activation energy (E_a).

Activation energy = Threshold energy – Average kinetic energy of reacting molecules.

$$E_a = E_{(\text{Threshold energy})} - E_{(\text{Reactants})}$$

Arrhenius equation

Arrhenius proposed a quantitative relationship between rate contatnt and temperature as,

$$K = Ae^{-E_a/RT} \qquad \dots \text{(i)}$$

This equation is called Arrhenius equation.

In which A is known as frequency factor or Arrhenius constant. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and R is the gas constant

Both A and E_a are collectively known as Arrhenius parameters.

Taking logarithm equation (i) may be written as,

$$\ln K = \ln A - Ea/RT$$

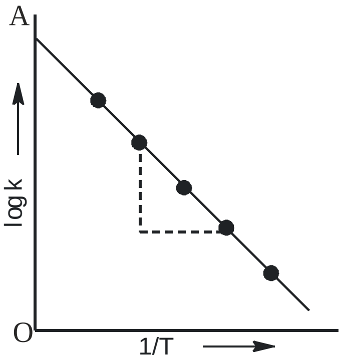
$$\log K = \log A - \frac{E_a}{2.303RT}$$

$$\log K = \left(-\frac{Ea}{2.303R}\right) \times \frac{1}{T} + \log A \qquad \text{(ii)}$$

$$(y \quad = \quad mx + c)$$

(As the value of activation energy (E_a) increases, the value of k decreases and therefore, the reaction rate decreases.)

When log K is plotted against 1/T, we get a straight line.



Intercept = OA = log A

Slope = $\tan\theta = \frac{-Ea}{2.303R}$

From equation (ii)

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right](\text{where } T_2 > T_1) \qquad \ldots \text{(iii)}$$

where k_1 and k_2 are rate constant at temperatures T_1 and T_2

Photochemical reaction

The chemical reactions, which are initiated as a result of absorption of light, are known as photochemical reactions.

Characteristics of photochemical reactions

(i) Each molecule taking part in a photo chemical process absorbs only one photon of radiant energy thereby increasing its energy level by hv or $\frac{hc}{\lambda}$

(ii) Photochemical reactions do not occur in dark.

(iii) Each photochemical reaction requires a definite amount of energy which is characteristic of a particular wavelength of photon.

(iv) The rate of photochemical reactions depend upon the intensity of radiation’s absorbed.

(v) The ΔG values for light initiated reactions may or may not be negative.

Quantum yield (or quantum efficiency):

The quantum efficency or quantum yield (ϕ) of a photochemical reaction is expressed as,

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photon absorbed}}$$

SURFACE CHEMISTRY

SURFACE CHEMISTRY

Indroduction:

The branch of chemistry which deals with the nature of surfaces and changes occurring on the surfaces is called surface chemistry.

Adsorption

The phenomenon of higher concentration of molecular species (gases or liquids) on the surface of a solid than in the bulk is called adsorption

Desorption

The process of removal of an adsorbed substance from the surface on which it is adsorbed is called desorption.

Sorption

When both absorption and adsorption occur together and are not distinguisable, the substance gets uniformly distributed into the bulk of the solid but at the same time, its concentration is higher at the surface than in the bulk, the phenomenon is called sorption.

Example : Dyes get adsorbed as well as absorbed in the cotton fibres i.e. sorption takes place.

Positive adsorption:

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

Negative adsorption:

When the concentration of the adsorbate is less on the surface relative to its concentration in the bulk, it is called negative adsorption.

Factors affecting adsorption of gases by Solids

Almost all solids adsorb gases to some extent. The extent of adsorption of a gas on a solid surface depends on the following factors:

1. Nature of the gas (or adsorbate): Under given conditions of temperature and pressure, the easily liquefiable gases such as CO_2, HCl, NH_3, Cl_2 etc. are adsorbed more than the permanent gases such as H_2, N_2 and O_2.
2. Nature of adsorbent : The extent of adsorption of a gas depends upon the nature of adsorbent.
3. Specific area of the adsorbent : The specific area of the adsorbent is the surface area available for adsorption per gram of the adsorbent. The larger the surface area of the solid, the greater would be its adsorbing capcity.
4. Effect of pressure : The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas.
5. Effect of temperature : Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic and therefore, extent of adsorption decreases with increasing temperature at constant pressure.

Physical Adsorption : When the particles of the adsorbate are held to the surface of the adsorbent by the physical forces such as Van der Waal's forces, the adsorption is called physical adsorption or physisorption. The attractive forces are weak and therefore, these can be easily overcome either by increasing the temperature or by decreasing the pressure. In other words, physical adsorption can be easily reversed.

Chemical adsorption : When the molecules of the adsorbate are held to the surface of the adsorbent by the chemical forces, the adsorption is called chemical adsorption or chemisorption.

Adsorption Isotherms :

The variation of the amount of the gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve. This curve is termed as adsorption isotherm at the particular temperature.

Freundlich's adsorption isotherm:

Freundlich in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the equation

$$\boxed{\frac{x}{m} = kp^{\frac{1}{n}}} \quad \dots (1)$$

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

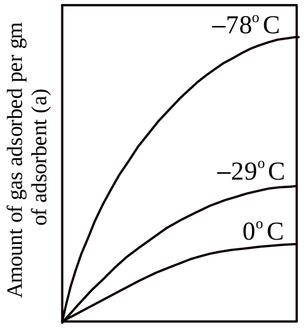


Fig (a) Adsorption isotherm

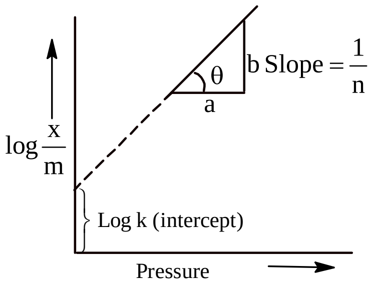


Fig (b) Freundlich isotherm

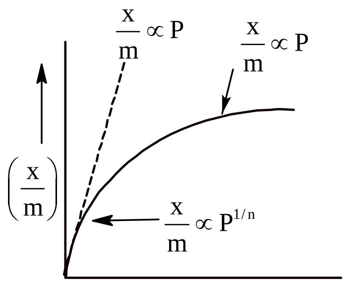


Fig. (c) Pressure (P)

Taking logarithm of equation .... (i)

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

$$\boxed{\log\frac{x}{m} = \frac{1}{n}\log P + \log k} \quad \dots (ii)$$

⇒ The slope of the straight line gives the value of 1/n.

⇒ The intercept on the y-axis gives the value of log k.

In his derivation, Langmuir considered adsorption to consist of the following two opposing processes:

(i) Adsoprtion of the gas molecules on the surface of the solid.

(ii) Desorption of the adsorbed molecules from the surface of the solid.

Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation.

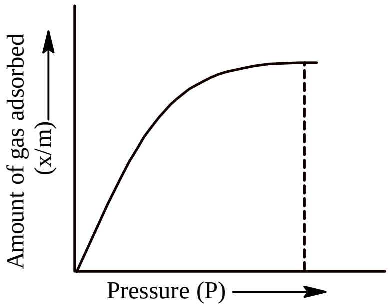
$$\boxed{\frac{x}{m} = \frac{ap}{1+bp}} \quad \dots (i)$$

where a and b are two Langmuir parameters.

Case I: i.e., at very high pressure:

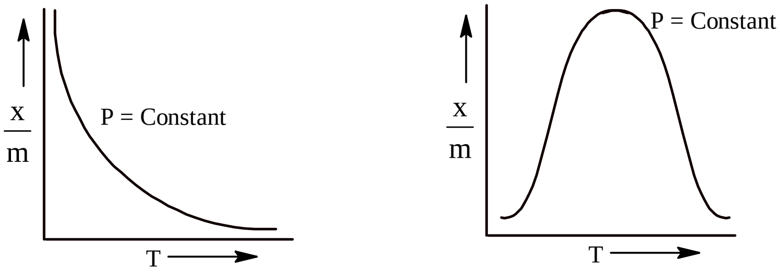
$$\boxed{\frac{x}{m} = \frac{a}{b}} \quad \dots (ii)$$

Case II: i.e., at very low pressure:



Adsorption Isobars

A graph drawn between degree of adsorption (x/m) and temperature ‘T’ at a constant pressure of adsorbate gas is known as adsorption isobar.



(Physi-sorption isobars) (Chemi-sorption isobars)

Adsorption isobars of physical and chemical adsorption shows an important difference and this difference is helpful in distinguishing these two adsorptions.

CATALYSIS

Substance which alter the velocity of a reaction, without undergoing any change in mass and composition, are termed as catalysts and the phenomenon is known as catalysis.

Classification of Catalysis

Catalysis can be broadly classified into two main groups as:

(i) Homogeneous catalysis and

(ii) Heterogeneous catalysis

Homogeneous catalysis : When the catalyst is in the same phase as the reactants and products, then the catalyst is said to be homogeneous catalyst and such catalytic reaction is said to be homogeneous catalysis.

$$C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(l) + C_6H_{12}O_6(l)$$

Heterogeneous catalysis : When the catalyst is in the different phase as the reactants and products, then the catalyst is said to be heterogeneous catalyst and such catalytic reaction is said to be Heterogeneous catalysis

Examples: $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

Positive catalysis : When the rate of reaction is accelerated by a foreign substance, it is said to be a positive catalyst and the phenomenon is positive catalysis.

e.g., Oxidation of sulphur dioxide in presence of nitric oxide.

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

Negative catalysis : The substance which when added to the reaction mixture, retards the reaction rate is termed negative catalyst and the phenomenon is known as negative catalysis.

The oxidation of chloroform by air is retarded if some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{\text{Alchol(l)}} 2COCl_2(g) + 2HCl(g)$$

ENZYME CATALYSIS

The enzymes are also termed as bio-chemical catalysts and the phenomenon is known as bio-chmeical catalysis. Enzymes are highly specific in nature.

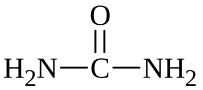
e.g., (i) Normal conversion of glucose into ethanol by zymase (enzyme) present in yeast.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

(ii) Oxidation of alcohol to acetic acid by mycoderma aceti.

$$C_2H_5OH + O_2 \xrightarrow[\text{aceti}]{\text{Mycoderma}} CH_3COOH + H_2O$$

(iii) Hydrolysis of urea (NH_2CONH_2) by urease (enzyme) present in soyabean.



$$\underset{\text{Urea}}{H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

On the basis of particle size of the substance, solutions are divided into three classes as:

1. True solution
2. Suspension
3. Colloidal solution

True solution is a homogeneous solution in which molecules or ions are uniformly dispersed in the solvent (dispersion phase). A suspension is heterogeneous solution in which particle of the solute do not dissolve completely. A colloidal solution is a heterogeneous solution in which particle size is bigger than that of true solution but smaller than that of suspension.

Classification of Colloids

On the basis of nature of interaction between dispersed phase and dispersion medium, colloids may be of two types, viz. lyophilic and lyophobic. If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

1. Lyophilic colloids : The colloidal solution in which the particle of the dispersed phase have a great affinity (or love) for the disperion medium are called lyophilic colloids.
2. Lyophobic colloids : The colloidal solution in which there is no affinity (or love rather they have hatred tendency) between particles of the dispersed phase and dispersion medium are called lyophobic colloids.

PREPARATION OF COLLOIDAL SOLUTIONS

1. By dispersion : By breaking up suspension particles into colloidal size, the goal is achieved.

(a) By Grinding : Freshly precipitated mass + medium $\xrightarrow[\text{ingrinder}]{\text{Grind}}$ sols

(b) Peptization : The phenomenon of converting freshly prepared precipitate into colloidal sol by the action of solute or solvent is known as peptization. The solute or solvent used are known as peptizing agent.

Freshly precipitated $Fe(OH)_3$ is passed in colloidal sol by the action of $FeCl_{3(aq).}$

Bredig's arc method:

Two metal electrodes are immersed in a liquid medium. Both of them are connected to a high tension battery by which an electric arc is produced between the electrodes. High temperature of the arc vaporizes some of the metal which condenses on cooling to form sols. The heat generated during process is removed by putting system under ice cold water. The method in general used for preparation of metal sols in water.

2. By condensation : By aggregating true solution particles into colloidal size. The goal is achieved by
   - A. Physical method:
     1. By exchange of solvent : Sulphur, phenolphthalein, indigo … sols are prepared by adding their solutions in suitable solvent drop by drop in water. Liquid indigo marketing is based on this aspect.
     2. By excessive cooling : Water + chloroform mixture on sudden cooling leads to formation of ice in chloroform sol.
   - B. Chemical Methods:
     1. Double decomposition : On passing H_2S through cold and dilute solution of some metal salts e.g. As and Cd (Yellow) sols are formed. $As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$
     2. Hydrolysis : Addition of $FeCl_3$ drop by drop to boiling water forms red coloured, positively charged $Fe(OH)_3$ sol. $FeCl_3 + 3H_2O \xrightarrow[\text{Water}]{\text{Boiling}} \underset{\text{sol}}{Fe(OH)_3} + 3HCl$
     3. Oxidation : During II group analysis by passing H_2S in cold solution having an oxidizing agent, reduction of H_2S leads to the formation of white, grey turbidity of sulphur sol instead of precipitate of 2nd group radicals. $2H_2S + SO_2 \longrightarrow 2H_2O + \underset{\text{(Sol.)}}{3S}$
     4. Reduction : Metal salts in water on reduction with non electrolytic reducing agents such as HCHO, HCOOH, $SnCl_2$, NH_2NH_2 leads to metalsols.

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{\text{(Sol.)}}{2Au} + 3SnCl_4$$

PURIFICATION OF SOLS

Sols so obtained are contained with two types of impurities and need purification.

(a) Insoluble impurities : These are removed by simple filtration of impure sols. Impurities are retained on filter paper and sols are filtered.

(b) Soluble impurities : Special methods are required to separate these impurities.

1. Dialysis: The separation of soluble impurities from sols on the basis of their different rates of diffusion through parchment membrane is known as dialysis. This principle is based upon the fact that colloidal particles cannot pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.

Electrodialsysis: The ordinary process of dialysis is slow. To increase the process of purification, the dialysis is carried out by applying electric field. This process is called electro dialysis.

2. Ultra filtration: It is the process of removing the impurities from the colloidal solution by passing it through graded filter papers called ultra-filter papers.
3. Ultra-centrifugation : In this method, the colloidal sol is taken in a tube which is placed in an ultra centrifuge. On rotation of the tube at high speeds, the colloidal particles settle down at the bottom of the tube and the impurities remain down in the solution called centrifugate.

PROPERTY OF COLLOIDS

1. Colligative properties:

   Like true solutions, colloidal solutions also exhibit colligative properties such as osmotic pressure, elevation in b.pt, depression in freezing point, lowering in vapour pressure.

2. Optical Properties :

   When a strong beam of light is passed through a true solution placed in a beaker, in a dark room,the parth of the light does not become visible. However, if the light is passed through a sol, placed in the same room, the path of the light becomes visible when viewed from a direction at right angle to that of the incident beam.

3. Electrical Properties:

(i) Sol particles carry +ve or –ve charge.

(ii) Metal sols are –ve; blood is –ve sol, smoke is –vely charged.

(iii) Origin of charge : The origin of charge on sol particle have been explained in terms of following concepts.

(1) Frictional electricity: Due to friction between dispersed phase & dispersion medium.

(2) Due to electron capture by sol particles.

4. Electrophoresis or Cataphoresis

The presence of the charge on the sol particles and its nature whether positive or negative can be determined with the help of phenomenon known as electrophoresis. In this phenomenon, the colloidal particles move towards positive or negative electrodes depending upon their chage under the influence of electrical field.

The phenomenon of movement of colloidal particles under an applied electric field is called electrophoresis.

5. Coagulation

A small amount of an electrolyte is necessary for the stability of the colloidal sol. The ions of the electrolytes are adsorbed on the sol particles and impart them some charge; positive or negative. The charged colloidal particles repel one another and are prevented from coming close together to unite into bigger particles. However, in the presence of a large excess of the electrolyte, the charge on the particles of the dispersed phase is neutralized and as a result, they come closer, grow in size and ultimately form precipitates. This is called precipitation or coagulation. Thus, The phenomenon of the precipitation of a colloidal solution by the addition of the excess of an electrolyte is called coagulation or flocculation.

Hardy Schulze Rule:

Thus, according to Hardy Schulze rule :

(i) The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.

(ii) Coagulating power of an electrolyte is directly proportional to the valence of the active ions (ions causing coagulation). For example, to coagulate negative sol of As_2S_3, the coagulating power of different cations has been found to decrease in the order as:

$$As^{3+} > Mg^{2+} > Na^{+}$$

Similarly to coagulate a positive sol such as $Fe(OH)_3$, the coagulating power of different anions has been found to decrease in the order:

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$$

The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as flocculation value. It is usually expressed as millimoles per litre.

POINTS TO REMEMBER:

Coagulation value: $KNO_3 > Ba(NO_3)_2 > Al(NO_3)_3 > Th(NO_3)_4$
Coagulation power: $K^+ < Ba^{2+} < Al^{3+} < Th^{4+}$

Protection

(i) Lyophobic sols are relatively less stable than lyophilic sols, however their stability may be increased on addition of lyophilic sols. This phenomenon of stabilizing lyophobic sols by the addition of lyophilic colloids is known as protection. The lyophilic colloids which are used for this purpose are known as protective colloids.

(ii) The protective character of various lyophilic substances has been expressed in terms of gold number.

(iii) Gold number of a lyophilic colloid is defined as the minimum amount of lyophilic colloid in milligrams which prevents the coagulation of 10 ml gold sol against 1 ml of 10% NaCl solution.

Emulsions

If a mixture of two immiscible or partially miscible liquid is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion.

Classification of colloids based on type of particles of dispersed phase

Depending upon the type of the particles of the dispersed phase, the colloids are classified as:

(i) Multimolecular colloids (ii) Macromolecular colloids (iii) Associated colloids.

Mechanism of Micelle Formation

Micelles are generally formed by the aggregation of several ions or molecules with lyophobic as well as lyophilic parts. For example, sodium stearate ($C_{17}H_{35}COONa$) is a typical example of such type of molecule. The micelle many cotain as many as 100 molecules or more. When sodium stearate is dissolved in water, it gives Na^+ and $C_{17}H_{35}COO^-$ ions.

$$\underset{\text{Sod. sterate}}{C_{17}H_{35}COONa} \rightleftharpoons \underset{\text{Stearate ion}}{C_{17}H_{35}COO^-} + Na^+$$

The stearate ions associate to form ionic micelles of colloidal size (in fig). It has long hydrocarbon part of $C_{17}H_{35}$ radical which is lyophobic end and COO^- part which is lyophilic. In the figure, the chain corresponds to stearate ion, $C_{17}H_{35}COO^-$. When the concentration of the solution is below its critical micelle concentration (10^{-3} mol L^{-1}), it behaves as normal electrolyte. But above this concentration, it is aggregated to behave as micelles.

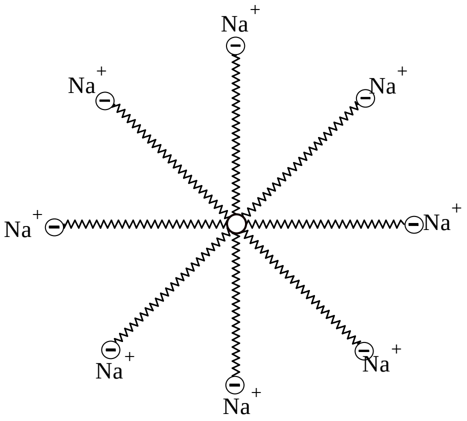


Fig. Aggregation of several ions to form ionic micelle

Emulsion

The colloids in which both the dispersed phase and dispersion medium are liquid.

Types of Emulsion:

(i) Oil in water emulsion: Oil is dispersed as dispersion medium e.g. milk

(ii) Water in oil emulsion: Water acts as disperesed phase and oil acts as dispersion medium e.g. cold cream, butter

Emulfication

The process of making an emulsion is known as emulsification. Soap and detergens are most frequently used as emulsifier.

Principles and Processes of Extraction of Elements

METALLURGY :

The branch of chemistry which deals with the methods of extraction of metals from their ores and alloy formation, is called metallurgy.

Modes of Occurrence of Elements

Element may occur either in the native (or free) state or int he combined state. This is mainly due to the reason that different elements possess different chemical reactivities.

(i) Native State : Element which are not attacked by moisture,oxygen and carbon dioxide of the air occur in the native state. For example, gold, platinum, noble gases etc.

(ii) Combined state : Elements which are readily attacked by moisture, oxygen and carbon dioxide of the air occur in the combined state in form of their compounds called minerals. In the combined state non-metals are found in the reduced from while metals are found in the oxidised from such as elements are generally present as oxides, Carbonates, sulphides, silicates etc. as shown is table.

Ore Type	Examples
Native	Cu, Ag, Au, Hg, As, Bi, Sb, Pd, Pt, S, noble gases
Oxides	Al2O_3. H_2O (diaspore) Al_2O_3. 2H_2O (bauxite), MnO_2 (pyrolusite),
Carbonates	$CaCO_3$ (calcite), $CaCO_3$. $MgCO_3$ (dolomite), $FeCO_3$(siderite).
Sulphides	Ag_2S (silver glance or argentite), Cu_2S (copper glance or chalacocite), copper pyrites ($CuFeS_2$), PbS (lead glance), ZnS (zinc blende).
Halides	AgCl (silver glance)
Sulphates	$BaSO_4$, $CaSO_4.2H_2O$

Composition of earth's crust :

Earth's crust is the main source of elements. Oxygen is the most abundant non-metal and aluminium is the most abundant metal in the earth's crust.

Minerals :

The various compounds of metals which occur in the earth's crust and are obtained by mining, are called minerals. A mineral may be a single compound or a mixture.

Ore :

The mineral from which a metal can be profitably and easily extracted is called an ore.

All ores are minerals but all the minerals are not ores.

Gangue or Matrix :

The undesirable impurities (clay, sand, pebbles, etc.) present in an ore are called gangue or matrix.

Flux : Flux is an external material that is added during smelting to convert infusible impurities into an easily fusible material known as slag.

$$\text{Flux + Infusible gangue} \rightarrow \text{Slag.}$$

Acidic flux : It is used to remove basic impurities. The cheapest acidic flux is SiO_2 (silica).

Acidic flux + basic gangue → slag.

Basic flux : It is used for removing acidic impurities. Examples are CaO, MgO, etc.

Basic flux + acidic gangue → slag.

Slag : It is the product of the reaction between flux and infusible impurities. Slag possesses following properties.

(a) Molten slag is not miscible with molten metal.

(b) Melting poing of slag is lower than that of the metal.

(c) Density of molten slag is lower than that of molten metal and hence molten slag floats over molten metal.

Refractory material is that substance which can withstand a very high temperature without getting decomposed or becoming soft. The refractory material may be acidic (Silica, Quartz, sandstone etc.), basic (lime, dolomite, magnesite) and neutral (Graphite, Chromite, bone ash etc.)

EXTRACTION OF METALS :

The extraction of a metal from its ore is completed in the following four steps.

A. Concentration of the ore

B. Calcination and Roasting

C. Reduction to the metal

D. Refining of the metal

A. Concentration, Beneficiation or ore dressing :

The removal of impurities from the ore is called its concentration. It is carried out in one or more of the following ways :

(i) Gravity separation or Levigation : This method of concentration of the ore is based on the difference in the specific gravities of the ore and the gangue particles. Powdered ore is agitated with a running stream of water. The lighter gangue particles are taken away by water while heavier ore particles settle down.

(ii) Froth Floatation method : This method is mainly employed for the concentration of sulphide ores. The method is based on the different wetting characteristics of the gangue and the sulphide ore with water and oil. The gangue is preferrentially wetted by water and the ore by oil.

The crushed ore along with water (slurry) is taken in a floatation cell. Various substances (additives) are added depending on the nature of the ore and a current of air is blown in. The substances added are usually of three types :

(a) Frothers : They generate a stable froth which rises to the top of the tank. The best example of frother is pine oil. Other oils such as eucalyptus oil, creosote oil, etc. may also be used.

Froth is a colloidal system of gas in liquid. It has very good adsorption capacity.

(b) Collectors : Ethyl xanthate and Potassium Ethyl Xanthate are used as collectors. These attach themselves by polar groups to the grains of the ores which then become water repellant and pass on into the froth.

(c) Activators or depressants : These reagents activate or depress the floatation properly and help in the separation of different sulphide ores present in a mixture. An example of a depressant is NaCN and alkali. An activator is $CuSO_4$.

(iii) Magnetic separation :

(iv) Chemical separation : Some of the ores are concentrated by means of chemical treatment. For example, bauxite ($Al_2O_3.2H_2O$) associated with the oxides of iron, titanium, and silicon, is purified by this method.

Leaching : It involues the treatment of the ore with a suitable reagent which dissolves the ore while impurities are left insoluble. It is used for concentration of Au and Ag ores by dissolving them as their cyanide complexes. Also is Boeyer’s process for concenteration of Bauxite containing Fe_2O_3 as impurity, Al_2O_3 is leached out with NaOH sol in the form of sodium meta aluminate.

B. Calcination :

It is the heat treatment given to oxide, hydroxide or carbonate ores. The concentrated ore is heated in a reverberatory furnace, below its melting point, in the limited supply of air without addition of any external substance.

$$\underset{\text{Calamine}}{ZnCO_3} \xrightarrow[\Delta]{\text{Calcination}} ZnO + CO_2$$

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \xrightarrow[\Delta]{} 2CuO + CO_2 + H_2O$$

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2$$

Advantages of Calcination :

- (i) Moisture is removed
- (ii) Organic matter is destroyed
- (iii) The hydroxide and the carbonate ores are converted into their oxides
- (iv) The mass becomes porous and easily workable.

Roasting : The removal of excess sulphur contained in sulphide ores by heating in an excess of air is called roasting.

Advantages of Roasting :

(i) Excess of sulphur is removed as volatile oxide.

$$S + \underset{(\text{air})}{O_2} \to SO_2 \uparrow$$

(ii) Impurities of arsenic and antimony are removed as their volatile oxides.

$$4As + \underset{(\text{air})}{3O_2} \xrightarrow{\Delta} 2As_2O_3 \uparrow$$

$$4Sb + 3O_2 \xrightarrow{\Delta} 2Sb_2O_3 \uparrow$$

(iii) The metal sulphide is converted into metal oxide.

Roasting of Galena ; zinc blende, etc.

$$\underset{\text{Galena}}{2PbS} + \underset{(\text{air})}{3O_2} \xrightarrow{\text{Roasting}} 2PbO + 2SO_2 \uparrow$$

$$\underset{\text{Zinc}}{2ZnS} + \underset{\text{blende}}{3O_2} \xrightarrow{\text{Roasting}} 2ZnO + 2SO_2 \uparrow$$

Roasting of copper pyrites :

$$2CuFeS_2 + \underset{(\text{air})}{O_2} \xrightarrow{\text{Roasting}} Cu_2S + 2FeS + SO_2 \uparrow$$

$$2Cu_2S + \underset{(\text{air})}{3O_2} \to 2Cu_2O + 2SO_2 \uparrow$$

$$2FeS + \underset{(\text{air})}{3O_2} \to 2FeO + 2SO_2 \uparrow$$

C. Reduction to the Metal :

The compound of the metal obtained after calcination and roasting of the ore is reduced to get the metal. Depending upon the nature of the metal, the following methods of reduction are used :

(i) Cathodic or Electrolytic reduction : This method is mainly used in the extraction of highly electropositive metals. For example, alkali metals (IA), alkaline earth metals (IIA), lanthanides, and aluminium.

Except aluminium, all the other metals are prepared by the electrolysis of their fused salts (particularly the chlorides).

(ii) Chemical reduction (Smelting) : In this method, chemical substances such as active metals, carbon (coke), etc., are used as reducing agent to prepare less active metals such as chromium, manganese, nickel, tin, etc.

Smelting : The process which involves melting in the extraction of metal from its ore, is called smelting.

(a) Active metals as reducing agents :

Na, Mg, Al, Ca, etc., metals are used as reducing agents in the preparation of less active metals :

For example : Titanium and Zirconium are obtained as follows :

$$\underset{\text{Rutile}}{TiO_2} + 2C + 2Cl_2 \xrightarrow{\Delta} TiCl_4 + 2CO\uparrow$$

$$TiCl_4 + 4Na \xrightarrow[\text{Kroll's process}]{\Delta,\text{Ar}} Ti + 4NaCl$$

Goldschmidt thermite process : In this process, metallic aluminium is used as a reducing agent. Chromium and manganese are obtained by the reduction of their oxides by aluminium.

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 3Cr + \text{heat}$$

$$3MnO_2 + 4Al \xrightarrow{\Delta} 2Al_2O_3 + 3Mn + \text{heat}$$

(b) Carbon as reducing agent : Carbon, often in the form of coke, is used as a reducing agent for metal oxides.

$$\text{Metal oxide} + \underset{\text{coke}}{C} + \text{flux} \xrightarrow{\text{smelting}} \text{Metal} + CO\uparrow + \text{slag}$$

Carbon reduction for tin : Calcined cassiterite is mixed with carbon (anthracite coal) and lime (CaO) and heated to melt.

$$SnO_2 + 2C + \underset{\text{basic flux}}{CaO} \xrightarrow{\text{Smelting}} Sn + 2CO + \text{slag}$$

$$\underset{\substack{\text{Basic}\\ \text{flux}}}{CaO} + \underset{\substack{\text{Acidic}\\ \text{Impurity}}}{SiO_2} \rightarrow \underset{\substack{\text{Calcium}\\ \text{silicate slag}}}{CaSiO_3}$$

Carbon reduction for Zn :

$$\underset{\text{Zinc blende}}{2ZnS} + \underset{(\text{air})}{3O_2} \xrightarrow[\text{Reverberatory furnace}]{\text{Roasting in}} \underset{\text{Zinc oxide}}{2ZnO} + 2SO_2\uparrow$$

$$\underset{\text{Roasted ore}}{ZnO} + \underset{\text{Coke}}{C} \xrightarrow[\text{strongly}]{\text{heated}} Zn + CO\uparrow$$

(c) Carbon monoxide as reducing agent

$$3Fe_2O_3 + CO \xrightarrow{500^\circ C} 2Fe_3O_4 + CO_2\uparrow$$

$$Fe_3O_4 + CO \xrightarrow{600^\circ C} 3FeO + CO_2\uparrow$$

$$FeO + CO \xrightarrow[\text{Spongy iron}]{700^\circ C} Fe + CO_2\uparrow$$

D. Refining of Metals :

Metal obtained by the reduction of its compound still contains some objectionable substance and has to be refined. Depending upon the nature of the metal and impurities, the following methods are used for purification of metals :

(i) Liquation : This method is used for the refining of metals having low melting point and are associated with high melting impurities. Examples, Pb, Sn, Sb and Bi. The impure metal is heated on the sloping hearth of a furnace. The pure metal flows down leaving behind the non-fusible material on the hearth.

* The infusible matter during liquation is called dross.

(ii) Zone refining : Metals of very high purity are obtained by zone refining. This refining method is based on the fact that impurities tend to remain dissolved in molten metal. Ge, Si and Ga, used as semiconductor are refined in this manner.

(iii) Oxidation processes : These processes are used for refining of metals associated with impurities having high affinity for oxygen than the metal itself. Cupellation and bassemerization are important oxidation processes employed for refining different metals.

* Cupellation is used for the purification of silver associated with lead as impurity.

(iv) Vapour phase refining : In this method, metal is removed as a volatile compound from impure metal sample. This volatile compound is decomposed on heating to give pure metal. For example,

(a) Mond's process : This method is used for the purification of nickel.

Ni forms a volatile carbonyl compound at 25°—50°C which decomposes at about 180°C.

$$\mathrm{Ni}(s) + 4\mathrm{CO}(g) \xrightarrow{25^\circ\mathrm{C}—50^\circ\mathrm{C}} \underset{\substack{\text{Nickel tetra}\\ \text{carbonyl, volatile}\\ \text{compound}}}{\mathrm{Ni}(\mathrm{CO})_4(l)}$$

$$\mathrm{Ni}(\mathrm{CO})_4(g) \xrightarrow{180^\circ\mathrm{C}} \underset{\text{pure}}{\mathrm{Ni}(s)} + 4\mathrm{CO}(g)$$

(b) Van-Arkel process : Ti, Zr, Hf, Si, U are refined by this process. For example, impure Zr is heated with a limited amount of I_2 in an evacuated glass apparatus at 523 K. The vapours of ZrI_4 formed are allowed to diffuse on a tungston filament heated at about 1800K. The gas zirconium tetraiodide is decomposed on coming in contact with hot filament and pure metal is deposited on it.

$$\underset{\text{Impure}}{\mathrm{Zr}(s)} + 2\mathrm{I}_2(g) \rightarrow \mathrm{ZrI}_4(g)$$

$$\mathrm{ZrI}_4(g) \xrightarrow[\mathrm{W-filament}]{\approx 1800\,\mathrm{K}} \underset{\text{pure}}{\mathrm{Zr}(s)} + 2\mathrm{I}_2$$

(v) Electro-refining of metals : Metals such as Cu, Ag, Zn, Sn, Pb, Al, Ni, Cr, are refined by this method. The impure metal is made the anode of an electrolytic cell, while catho9de is a thin plate or pure metal. Electrolyte is the solution of a soluble salt of the metal. On passing the electric current, pure metal from the anode dissolves and gets deposited at the cathode. The soluble impurities go into the solution while insoluble impurities settle down below the anode as anode mud or sludge.

e.g.

(a) Electro refining of Copper

Anode : Blister copper (98% purity).

Cathode : Pure copper.

Electrolyte : An aqueous solution of $CuSO_4$ (15%) + (5%) dil. H_2SO_4.

(vi) Cupellation : The impurity of Pb present in Ag is removed by cupellation. The cupel is a boat shaped dish made up of bone ash or cement. The crude metal is taken in the cupel and blast of hot air is blown over it. The impurities escape is the form of volatile oxides leaving behind the pure metal, e.g., Pb impurity is converted into litharge (PbO) which being volatile escapes leaving behind pure silver.

Class-12 Chemistry
The P-Block Elements

- **The p-Block elements:**
  Elements belonging to groups 13 to 18 of the periodic table are called p-block elements.
- **General electronic configuration of p-block elements:**
  The p-block elements are characterized by the ns^2np^{1-6} valence shell electronic configuration.
- **Representative elements:**
  Elements belonging to the s and p-blocks in the periodic table are called the representative elements or main group elements.
- **Inert pair effect:**
  The tendency of ns2 electron pair to participate in bond formation decreases with the increase in atomic size. Within a group the higher oxidation state becomes less stable with respect to the lower oxidation state as the atomic number increases. This trend is called 'inert pair effect'. In other words, the energy required to unpair the electrons is more than energy released in the formation of two additional bonds.

GROUP 15 ELEMENTS

- **Nitrogen family:**
  The elements of group 15 – nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) belong to configuration is ns^2np^3.
- **Atomic and ionic radii:**
  a) Covalent and ionic radii increase down the group.
  b) There is appreciable increase in covalent radii from N to P.
  c) There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.
- **Ionisation energy:**
  a) It goes on decreasing down the group due to increase in atomic size.
  b) Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements.
  c) Group 15 elements have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half-filled p-orbitals.
- **Allotropy:**
  All elements of Group 15 except nitrogen show allotropy.
- **Catenation:**
  a) Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent.
  b) The tendency to show catenation decreases down the group.
- **Oxidation states:**
  a) The common oxidation states are +3, +5 and –3.

b) The tendency to show –3 oxidation state decreases down the group because of decrease in electronegativity by the increase in atomic size.

c) The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect.

d) Nitrogen shows oxidation states from –3 to +5.

e) Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionation.

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

- **Reactivity towards hydrogen:**
  - a) All group 15 elements from trihydrides, MH_3.
  - b) It belongs to sp^{3h}ybridisation.
  - c) The stability of hydrides decreases down the group due to decrease in bond dissociation energy down the group.

  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
- **Boiling point:**

  $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$
  - a) Boiling point increases with increase in size due to increase in van der Waals forces.
  - b) Boiling point of NH_3 is more because of hydrogen bonding.
- **Bond angle:**

  NH_3 (107.8°) > PH_3 (99.5°) > AsH_3 (91.8°) ≈ SbH_3 (91.3°) > BiH_3 (90°)
  - a) Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs. Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.
  - d) Basicity decreases as $NH_3 > PH_3 > AsH_3 > SbH_3 < BiH_3$. This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3. It will decrease down the group as the electronegativity decreases down the group. The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.
- **Reactivity towards oxygen:**
  - a) All group 15 elements from trioxides (M_2O_3) and pentoxides (M_2O_5).
  - b) Acidic character of oxides decreases and basicity increases down the group. This is because the size of nitrogen is very small.
  - c) It has a strong positive field in a very small area. Therefore, it attracts the electrons of water O-H bond to itself and release H+ ions easily.
  - d) As we move down the group, the atomic size increases and so, the acidic character of oxide decreases and basicity increases down the group.
- **Reactivity towards halogen:**

  Group 15 elements form trihalides and pentahalides.

  a) Trihalides

These are covalent compounds and become ionic down the group with sp^3 hybridisation, pyramidal shape.

b) Pentahalides

  i) They are lewis acids because of the presence of vacant d – orbitals.

  ii) They possess sp^3d hybridisation and hence possess trigonal birpyamidal shape.

$$PCl_5 + Cl^- \rightarrow [PCl_6]^-$$

  iii) PCl_5 is ionic in solid state and exist as $[PCl_4]^+[PCl_6]^-$.

  iv) In PCl_5, there are three equatorial bonds and two axial bonds. The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.

  v) Nitrogen does not form pentahalides due to absence of *d*- orbitals.

- **Reactivity towards metals:**

  All elements react with metals to form binary compounds in –3 oxidation state.

- **Anomalous behaviour of nitrogen:**

  The behaviour of nitrogen differs from rest of the elements.

  Reasons:

  i. It has a small size.

  ii. It does not have d – orbitals

  iii. It has high electronegativity

  iv. It has high ionization enthalpy

- **Dinitrogen:**

  a) **Preparation:**

$$NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{Heat} N_2(g) + 2H_2O(l) + NaCl(aq)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \xrightarrow{Heat} Ba + 3N_2$$

  b) **Physical Properties:**

  i) It is a colourless, odourless, tasteless and non – toxic gas.

  ii) It is chemically un-reactive at ordinary temperature due to triple bond in N ≡ N which has high bond dissociation energy.

- **Ammonia:**

  a) Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex.

  b) It has 3 bond pairs and 1 lone pair.

  c) N is sp^3 hybridised.

  d) Preparation:

  Haber's process:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta_f H^0 = -46.1 kJ\ mol^{-1}$$

  Pressure 200x10 Pa Temperature 773 K Catalyst is FeO with small amounts of K_2O and Al_2O_3

- **Nitric Acid:**

  Ostwald Process:

  The NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4. Nitric acid is strong oxidizing agent in the concentrated as well as in the dilute state.

$$4NH_3 + 5O_2 \xrightarrow{Pt/Rh \text{ gauge 500k, 9 bar}} 4NO + 6H_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

- **Phosphorus:**
  a) It shows the property of catenation to maximum extent due to most stable P – P bond.
  b) It has many allotropes, the important ones are:
     i. White phosphorus
     ii. Red phosphorus
     iii. Black phosphorus
- **White phosphorus:**
  a) Discrete tetrahedral P_4 molecules
  b) Very reactive
  c) Glows in dark
  d) Translucent waxy solid
  e) Soluble in CS_2 but insoluble in water
  f) It has low ignition temperature, therefore, kept under water
- **Red phosphorus**
  a) Polymeric structure consisting of chains of P_4 units linked together
  b) Less reactive than white phosphorus
  c) Does not glow in dark
  d) Has an iron grey lustre
  e) Insoluble in water as well as CS_2
- **Black phosphorus**
  a) Exists in two forms - α black phosphorus and β black phosphorus
  b) Very less reactive
  c) Has an opaque monoclinic or rhombohedral crystals

$$\text{White phosphorus} \xrightarrow{\text{573k in an inert atmosphere for several days}} \text{Red phosphorus}$$

$$\text{White phosphorus} \xrightarrow{\text{High pressure,473K}} \text{Black phosphorus}$$

$$\text{Red phosphorus} \xrightarrow{\text{In a sealed tube,803K}} \text{Black phosphorus}$$

- **Phosphine**
  a) It is highly poisonous, colourless gas and has a smell of rotten fish.
  b) Preparation

$$\underset{\substack{\text{Calcium}\\ \text{Phosphide}}}{Ca_3P_2} + \underset{\text{Water}}{6H_2O} \rightarrow \underset{\substack{\text{Calcium}\\ \text{Hydroxide}}}{3Ca(OH)_2} + \underset{\text{Phosphine}}{2PH_3}$$

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + \underset{\text{Phosphine}}{2PH_3}$$

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\substack{\text{Sodium}\\ \text{Hypophosphite}}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$$

- **Chlorides of Phosphorous:**

a) Phosphorus Trichloride

i) It is a colourless oily liquid.

ii) Preparation

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

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

iii) With water,

It gets hydrolysed in the presence of moisture.

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

iv) Pyramidal shape, sp3 hybridisation

v) With acetic acid

$$3CH_3COOH + PCl_3 \rightarrow CH_3COCl + H_3PO_3$$

vi) With alcohol

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

b) Phosphorus pentachloride

i) Yellowish white powder.

ii) Trigonal bipyramidal shape, sp^3d hybridisation .

iii) Preparation

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

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

iv) With water

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

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

v) With acetic acid

$$3CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

vi) With alcohol

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

vii) With metals

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

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

GROUP 16 ELEMENTS

- **Oxidation states:**
  a) They show -2, +2, +4, +6 oxidation states.
  b) Oxygen does not show +6 oxidation state due to absence of d – orbitals.
  c) Po does not show +6 oxidation state due to inert pair effect.
  d) The stability of -2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity.
  e) Oxygen shows -2 oxidation state in general except in OF_2 and O_2F_2
  f) Thus, the stability of +6 oxidation state decreases and +4 oxidation state increases due to inert pair effect.
- **Ionisation enthalpy:**
  a) Ionisation enthalpy of elements of group 16 is lower than group 15 due to half-filled p-orbitals in group 15 which is more stable.
  b) However, ionization enthalpy decreases down the group.
- **Electron gain enthalpy:**
  a) Oxygen has less negative electron gain enthalpy than S because of small size of O.
  b) From S to Po electron gain enthalpy becomes less negative to Po because of increase in atomic size.
- **Melting and boiling point:**
  a) It increases with increase in atomic number.
  b) Oxygen has much lower melting and boiling points than sulphur because oxygen is diatomic (O_2) and sulphur is octatomic (S_8).
- **Reactivity with hydrogen:**
  a) All group 16 elements form hydrides.
  b) They possess bent shape.
  c) Bond angle: H_2O [373K] > H_2S [213K] < H_2Se [232K] < H_2Te [269K]
- Acidic nature:

  $H_2O < H_2S < H_2Se < H_2Te$

  This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.
- Thermal stability:

  $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

  This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.
- Reducing character:

  $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

  This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.
- **Reactivity with oxygen:** EO_2 and EO_3

a) Reducing character of dioxides decreases down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.
b) Acidity also decreases down the group.
c) SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

- **Reactivity with halogens:** EX_2, EX_4 and EX_6
  a) The stability of halides decreases in the order F- > Cl- > Br- > I-.
  b) This is because E-X bond length increases with increase in size.
  c) Among hexa halides, fluorides are the most stable because of steric reasons.
  d) Dihalides are sp^3 hybridised and so, are tetrahedral in shape.
  e) Hexafluorides are only stable halides which are gaseous and have sp^3d^2 hybridisation and octahedral structure.
  f) H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.
- **Oxygen:**
  a) Preparation:

$$2KClO_3 \xrightarrow{Heat/MnO_2} 2KCl + 3O_2$$
$$2H_2O_2(aq) \xrightarrow{Finely\text{ divided metals}} 2H_2O(l) + O_2(g)$$
$$2Ag_2O(s) \xrightarrow{Heat} 4Ag(s) + O_2(g)$$
$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$
$$2\underset{\text{Re}d\text{ lead}}{Pb_3O_4}(s) \xrightarrow{\Delta} 6PbO(s) + O_2(g)$$
$$2PbO_2(s) \xrightarrow{\Delta} 2PbO(s) + O_2(g)$$

- **Oxides:**
  The compounds of oxygen and other elements are called oxides.
- **Types of oxides:**
  a) Acidic oxides: Non- metallic oxides are usually acidic in nature.
  $$SO_2 + H_2O \rightarrow H_2SO_3(Sulphurous\text{ acid})$$
  b) Basic oxides: Metallic oxides are mostly basic in nature. Basic oxides dissolve in water forming bases e.g.,
  $$Na_2O + H_2O \rightarrow 2NaOH$$
  $$K_2O + H_2O \rightarrow 2KOH$$
  $$CaO + H_2O \rightarrow Ca(OH)_2$$
  c) Amphoteric oxides: They show characteristics of both acidic as well as basic oxides.
  $$Al_2O_3 + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O$$
  $$Al_2O_3 + 6NaOH(aq) + 3H_2O(l) \rightarrow 2Na_3[Al(OH)_6](aq)$$
  d) Neutral oxides: These oxides are neither acidic nor basic. Example: Co, NO and N2O

- **Ozone:**
  a) Preparation:
  It is prepared by passing silent electric discharge through pure and dry oxygen 10 – 15 % oxygen is converted to ozone.
  $$3O_2(g) \rightarrow 2O_3(g); \Delta H = +142kJ\ \text{mol}^{-1}$$
  b) Structure of Ozone:
  Ozone has angular structure. Both O = O bonds are of equal bond length due to resonance.
- **Sulphur:**
  a) Sulphur exhibits allotropy:
    i. Yellow Rhombic (α - sulphur)
    ii. Monoclinic (β - sulphur)
  b) $\alpha - sulphur \xrightarrow{369K} \beta - sulphur$
  c) At 369 K both forms are stable. It is called transition temperature.
  d) Both of them have S_8 molecules.
  e) The ring is puckered and has a crown shape.
  f) Another allotrope of sulphur – cyclo S_6 ring adopts a chair form.
  g) S_2 is formed at high temperature (~ 1000 K).
  h) It is paramagnetic because of 2 unpaired electrons present in anti bonding π^* orbitals like O_2.
- **Sulphuric acid:**
  a) Preparation:
  By contact process
  $$\frac{1}{8}S_8 + O_2 \rightarrow SO_2$$
  $$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5/2bar\ \ 720\text{k}} 2SO_3(g)$$
  $$\Delta H^{\theta} = -196.6kJ\ \text{mol}^{-1}$$
  b) Exothermic reaction and therefore low temperature and high pressure are favourable.
  $$SO_3(g) + H_2SO_4 \rightarrow H_2S_2O_7(oleum)$$
  $$H_2S_2O_7 + H_2O \rightarrow \underset{(96-98\%)}{2H_2SO_4}$$
  c) It is dibasic acid or diprotic acid.
  d) It is a strong dehydrating agent.
  e) It is a moderately strong oxidizing agent.

GROUP 17 ELEMENTS

- **Atomic and ionic radii:**
  Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.

- **Ionisation enthalpy:**
  They have very high ionization enthalpy because of small size as compared to other groups.
- **Electron gain enthalpy:**
  a) Halogens have maximum negative electron gain enthalpy because these elements have only one electron less than stable noble gas configuration.
  b) Electron gain enthalpy becomes less negative down the group because atomic size increases down the group.
- **Electronegativity:**
  a) These elements are highly electronegative and electronegativity decreases down the group.
  b) They have high effective nuclear charge.
- **Bond dissociation enthalpy:**
  a) Bond dissociation enthalpy follows the order: $Cl_2 > Br_2 > F_2 > I_2$
  b) This is because as the size increases bond length increases.
  c) Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2.
- **Colour:**
  All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher energy levels.
- **Oxidising power:**
  a) All halogens are strong oxidising agents because they have a strong tendency to accept electrons.
  b) Order of oxidizing power is: $F_2 > Cl_2 > Br_2 > I_2$
- **Reactivity with Hydrogen:**
  a) Acidic strength: HF < HCl < HBr < HI
  b) Stability: HF > HCl > HBr > HI. This is because of decrease in bond dissociation enthalpy.
  c) Boiling point: HCl < HBr < HI < HF. HF has strong intermolecular H bonding. As the size increases van der Waals forces increases and hence boiling point increases.
  d) % Ionic character: HF > HCl > HBr > HI Dipole moment: HF > HCl > HBr > HI. Electronegativity decreases down the group.
  e) Reducing power: HF < HCl < HBr < HI
- **Reactivity with metals:**
  a) Halogens react with metals to form halides.
  b) Ionic character: MF > MCl > MBr > MI. The halides in higher oxidation state will be more covalent than the one in the lower oxidation state.
- **Interhalogen compounds:**
  Reactivity of halogens towards other halogens:
  a) Binary compounds of two different halogen atoms of general formula X $X_n^{'}$ are called interhalogen compounds where n = 1, 3, 5, or 7. All these are covalent compounds.

b) Interhalogen compounds are more reactive than halogens because X-X’ is a more polar bond than X-X bond.

c) All are diamagnetic.

d) Their melting point is little higher than halogens.

e) XX’ (CIF, BrF, BrCl, ICl, IBr, IF) (Linear shape) XX’$_3$ (CIF$_3$, BrF$_3$, IF$_3$, ICl$_3$) (Bent T-shape) XX’$_5$ – CIF$_5$, BrF$_5$, IF$_5$, (square pyramidal shape) XX’$_7$ – IF$_7$ (Pentagonal bipyramidal shape)

- **Oxoacids of halogens:**
  a) Fluorine forms only one oxoacid HOF (Fluoric (I) acid or hypofluorous acid) due to high electronegativity.

  b) Acid strength: $HOCl < HClO_2 < HClO_3 < HClO_4$

  c) Reason:

$$HClO_4 \rightarrow H^+ + ClO_4^- Most \text{ Stable}$$

d) Acid strength: HOF > HOCl > HOBr > HOI. This is because Fluorine is most electronegative.

GROUP 18 ELEMENTS:

- **Ionisation enthalpy:**
  a) They have very high ionization enthalpy because of completely filled orbitals.

  b) Ionisation enthalpy decreases down the group because of increase in size.
- **Atomic radii:**
  Increases down the group because the number of shells increases down the group.
- **Electron gain enthalpy:** They have large electron gain enthalpy because of stable electronic configuration.
- **Melting and boiling point:**
  It has low melting and boiling point due to the presence of only weak dispersion forces.
- **Shapes:**
  XeF_2 is linear, XeF_4 is square planar and XeF_6 is distorted octahedral. KrF_2 is known but no true compound of He Ne and Ar are known.
- **Compounds of Xe and F:**

$$Xe + F_2 \xrightarrow{673k,1bar} XeF_2$$

$$Xe + 2F_2 \xrightarrow{873k/7bar} XeF_4$$

$$Xe + 3F_2 \xrightarrow{573k/60-70bar} XeF_6$$

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

XeF_2, XeF_4 and XeF_6 are powerful fluorinating agents.

- **Compounds of Xe and O:**

$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

d & f-Block Elements

d-Block elements :

The elemnts in which the last electron (or differentiating electron) enters (n - 1) d-subshell are known as d-Block elements. Their outer two shell are incompletely filled with electrons. Their general outer electronic configuration is (n - 1) d^{1-10} ns^{1-2}. In the long form of periodic table, d-Block elements are placed between s-and p-Block elements in the middle of the periodic table.

Technically, transition elements may be defined "as elements which have incompletely filled d-orbitals in atomic form or in some of their common oxidation states.

- Some of the typical properties of transition elements like paramagnetic or ferromagnetic behaviour, formation of coloured salts, high melting and boiling points (due to strong metallic bonds) are due to incompletely filled d-orbitals.

There are four series of transition elements in the periodic table :

(i) First transition series :
    or 3d-series : $_{21}$Sc..........................$_{30}$Zn
(ii) Second transition series :
    or 4d-series : $_{39}$Y............................$_{48}$Cd
(iii) Third transition series :
    or 5d-series : $_{57}$La, $_{72}$Hf...........................$_{80}$Hg
(iv) Fourth transition series : (Incomplete filled series)
    or 6d-series : $_{80}$Ac, $_{104}$Z..........................$_{112}$Z

- Group 12 elements Zinc (Z = 30), Cadmium (Z = 48) and Mercury (Z = 80) are not regarded as transition elements because their (n – 1) d sub-shell are fully filled with electrons, i.e., they have (n – 1) d^{10} configuration in elemental as well as in ionic forms. Their d-electrons do not take part in bond formation. Hence, many of the properties of transition elements are not shown by these elements. Even then they are included in the series of transition elements because their last electron enters the (n – 1) d-sub-shell.
- Copper ($3d^{10}$ $4s^1$), Silver ($4d^{10}$ $5s^1$) and Gold ($5d^{10}$ $6s^1$) are transition elements although their (n-1) d-sub-shell are completely filled with electrons. It is due to the fact that their (n – 1) d-electrons participate in bond formation Cu^{2+} (d^9), Ag^{2+} (d^9) and Au^{3+} (d^8). They show all the characteristics of transition elements.
- Group 3 elements (Sc, Y and La) form only tripositive ions with noble gas configuration. Their properties are quite different than that of other transition elements, e.g., their compounds are colourless and diamagnetic. These do not show variable oxidation states. But these elements have incompletely filled d-subshell in their elemental form, these are considered as transition elements.
- Group 3 (Sc, Y and La) and group 12 (Zn, Cd and Hg) are sometimes referred to as 'non-typical' transition elements.
- All transition elements are d-block elements but all d-block elements are not transition elements

General Characteristics

- Transiton elements resemble in their physical and chemical properties as they have similar ns^2 configuration in their outermost energy shell. They are hard metals, have high tensile strength, ductility, malleability and are good conductors of heat and electricity. They have high M.P. and B.P. and form alloys with other metals. Their reactivity decreases with the increase in their atomic number.
  - Metallic character : All the transition elements are metals - They exhibit all the three types of structure hcp, bcc and ccp.
  - Metallic bonding is due to $ns^1 or\, ns^2$ and unpaired electrons of $(n–1)d^x$.

- Cr, Mo and W have max. number of unpaired (n–1)d electrons and they are hard where as Zn, Cd and Hg are soft as they do not have any unpaired electrons.
- Atomic radii - Smaller than s-block and larger than p-block elements of corresponding period. The atomic radii of the elemenets of a given series are decrease with increase in atomic no. but this decrease becomes smaller after mid way. This is due to screening effect and nuclear charge effect which oppose eachother.
- The value of atomic radii at the end of each series ae bit higher. This is due to electron-electron repulsions among (n–1)d electrons. These repulsions become predominant at the end of each series and thus size increases.
- In the vertical column atomic radii increase down the group from 1st transition series to the second transition series but the similarity in the atomic radii of the elements of 2nd and 3rd transiton series is due to lanthanoid contraction.

Se_{21}	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn_{30}
1.44 A	1.32	1.22	1.18	1.17	1.17	1.16	1.15	1.17	1.25
Y_{39}	Zr	Pb	Mo	Tc	Ru	Rh	Pd	Ag	Cd_{48}
1.62 Å	1.45	1.34	1.30	-	1.25	1.25	1.28	1.34	1.48
La	H^{+}	Ta	W	Re	Os	Ir	Pt	Au	Hg
1.68Å	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.49

Ionic Radii : Ionic radii follow the same trend as the atomic radii. In the same oxidation state the ionic radii generally decreases as the atomic number increases in a particular series.

Ion	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Ionic radii	0.95	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.69

- Ionic radii decreases with increase in charge on the ion.

$${}^{r}Fe^{3+} < {}^{r}Fe^{2+}, {}^{r}Ni^{3+} < {}^{r}Ni^{2+}, {}^{r}Mn^{3+} < {}^{r}Mn^{2+}$$

Density : Except last two elements density increases from left to right in the series due to increases in atomic mass and decrease in atomic radii

- $\rho_{Ir} = 22.61\, gr/cc$ and $\rho_{0s} = 22.57\, gr/c.c.$, ρ_{Sc} is lowest (3.1 gm/cc) an transition elements.
- except Sc, Ti and Y all transiton elements have densities greater than 5gm/c.c.

M.P. and B.P. - have high M.P. and B.P. due to strong metallic bonding

- In each series, the melting point and B.P. of these metals rise to a maximum value and then decrease with increase in atomic number.
- Mn and Tc have abnormally low melting points.
- Tungesten (W) has the highest M.P. amongst transition elements.
- Zn, Cd and Hg have low M.P. as they do not contain unpaired electrons.
- Ionisation enthalpies - Lie in between s and p-block elements
- Transiton elements do not form ionic compounds so readily as s and p-block elements do. Generally in oxidation state, compounds are ionic whereas in higher oxidation state compounds are covalent.
- Ionisation potential values increase in a period from left to right the increase however is not regular.
- $I.E_2$ For Cu and Cr are sufficiently higher than those of neighbouring elements.

This is due to completely filled and half filled configuration of 3d-subsehll.

- In vertical columns i.e. In groups, Ionisation potential decreases from first member to 2nd member in most of the cases as expected however, the third member has the higher value than 2nd member. This is due to lanthanoid contraction.

Variable oxidation states :

The characteristic property of transitional elements is to show several oxidation states. This is because both (n – 1) d and ns electrons can take part in bond formation due to small energy difference between them.

- The maximum variation in oxidation state is observed when the electronic configuration is (n–1) d^5ns^2.
- The highest oxidation states are found in the compounds with fluorine and oxygen since they are highly electronegative elements. The highest oxidation state shown by the transition metal is eight, e.g., OsO_4.
- The relative stability of different oxidation states w.r.t. oxidation can be determined with the help of standard electrode potential data. For example, E^o values for couples $Cr^{+3}/Cr^{+2} = -0.41$ V and $Mn^{+3}/Mn^{+2} = +1.51$ V. These values suggest that Cr^{+2} get easily oxidised to Cr^{+3} while Mn^{+3} gets easily reduced to more stable Mn^{+2} in aqueous solutions. Similarly, Fe^{+2} is unstable in aerated water and gets oxidised to Fe^{+3}.
- The common oxidation state of elements of 3d-series is +2 (Scandium is an exception) but Cr^{+2} (Chromous ion) is unstable in water with respect to oxidation.
- In the +2 and +3 oxidation states, bonds formed are electrovalent. As the oxidation state of the transitional element increases, the covalent nature of the bond also increases. For example, in MnO_4^- ion, all the Mn—O bonds are covalent.
- Within a group, the maximum oxidation state increases with atomic numbers. For example, iron shows the common oxidation state of +2 and +3 in its compounds but ruthenium and osmium in the same group give compounds in +4, +6 and +8 oxidation states.
- Transitional metals also form compounds in low oxidation states like zero and +1. For example, in metal carbonyls $M(CO)_n$, the metal M is in zero oxidation state, e.g., $Ni(CO)_4$, $Fe(CO)_5$, etc.

Oxidation states :

Colour :-

Most of the compounds of transition metals are coloured in solid state or in solution states. This is due to the presence of incompletely filled d-orbitals.

- Colour is due to d- d transiton.
- Sc^{3+}, Ti^{4+}, V^{5+} are colourless as they have 3d° configuration.
- Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg^{2+} are colourless because they have completely filled d-orbitals.
- Colours of $Cr_2O_7^{2-}$, CrO_4^{2-}, MnO_4^-, MnO_4^{2-} are due to charge transfer.
- Compounds of s and p-block elements are generally colourless as high energy is requried for promotion of eleectrons which is not available in visible region. The required energy is available in u-v region.
- Magnetic properties - Majority of substances show paramagnetic nature.

  Transition Metal compounds are paramagnetic due to presence of unpaired electron in (n–1) d subshell.

  Transition metal compounds are diamagnetic due to absence of unpaired electron in (n–1) d-subshell.
- Magnetic Moment : (μ) is given as

$$\mu = \sqrt{n(n+2)}\ \text{B.M.} \qquad 1\ \text{B.M} = \frac{eh}{4\pi mc}$$

Complex formation :-

Transition metals form a large no. of complexes due to (a) small size (b) high charge and (c) presence of vacant d-orbitals in their outermost cells.

Alloy formation :- transiton metals form large number of alloys since they are similar insize.

Alloys containing Hg are called amalgams. Elements of (VIII) group do not form amalgam.

Catalytic property :- d-block elements and their compounds act as catalyst in various reaction due to utilisation of (n–1) orbtials or formation of interstitial compound.

Inner-transiton elements

- Element having Z = 58 to Z = 71 are lanthanides or Lonthanoes or lanthanoids i.e. Lanthanides are Ce_{58} to Lu_{71}.
- Th_{90} to Lw_{103} are Actinides or actinones or actinoids.
- Lanthanides mostly form ionic compounds in +3 oxidation state.

Atomic and Ionic size

The ionic radii of lanthanoids show a progressive decrease with increasing atomic number. The decrease in size of Ln^{3+} is known as Lantanoid contraction.

- Due to Lanthaide contraction, the elements of 4d and 5d transtion series resemble each other much more closely than do the elements of 3d and 4d series.
- Oxidation states - The common oxidation states of al the lanthanides is +3.

Other oxidation states are +2 and +4 in particular.

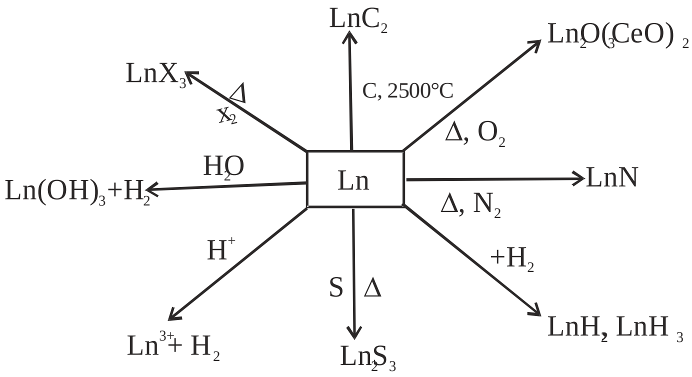
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
+3	+3	+3	+2	+3	+2	+2	+3	+3	+3	+3	+3	+2	+2	+3
	+4	+4	+3			+3	+4					+3	+3	
			+4		+3			+4	+4					

- Colours of ions - Ions of lanthanides are coloured in the solid state as well as in aqueous solution (except – La^{3+}, Ce^{3+}, Gd^{3+}, Yb^{3+} and Lu^{3+})

Colour of these ions are due to f-f-transition.

- Magnetic properties - Ions having $4f^0$ (La^{3+}, Ce^{4+}) and $4f^{14}$ (Yb^{2+} and Lu^{3+}) are diamagnetic and having other configuration are paramagnetic.

Chemical reactivity :



ACTIONOIDS

- have three shell (n–2), (n–1) and n shell incompletely filled and differentiating electron enters into 5f-orbital.
- G.E.C. $[Rn]5f^{1-14}\ 6d^{0-1}\ 7s^2$.
- The variation in the electronic configuration of the actionoids like those of lanthanoids is due to extra stabilities of f^0,f^7 and f^{14} electronic configuration of the 5f orbitals.
- All actionoids are radioactive and are $\alpha-$ray emitters.
- Atomic and Ionic Size :- The ionic radii for the M^{3+} and M^{4+} ions contract slightly with increasing atomic number. The decrase in size of An^{3+} is known as actinoide contraction.
- Oxidation states :- The actinide in general show +3 oxidation stole. There is also a greater range of oxidation states due to comparable energies of 5f, 6d and 7s.
- The actinoids resemble the lanthanoids in having more compounds in +3 state than in +4 state but they tend ot hydrolyse.

- U^{3+} in aqueous solution evolves H_2 on standing.
  Aq. solution of Np^{3+} and Pu^{3+} are stbale but are easily oxidised to Np^{4+} and Pu^{4+}.
- U^{4+} and Np^{4+} are stable to water but are slowly oxidised by air to UO_2^{2+} and NpO_2^{2+}
- Pu^{4+} disproportionates to Pu^{3+} and Pu_2^{2+} when solutin is strongly acidic.
- LiO_2^+ disproportionates to Li^{4+} and LiO_2^{2+}.
- Ionisation energy of the early actinoids are smaller than those of early lanthanoids.

IMPORTANT COMPOUNDS

1. Copper sulphate (Blue vitriol), $CuSO_4.5H_2O$ -

(i) Preparation - By dissolving CuO or $CuCO_3$ or malachite in dil. H_2SO_4 and evaporating the solution to crystalization point.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + H_2O + CO_2$$

(ii) Properties -

(a) Blue crystalline solid, soluble in water.

(b) Action of heat :

$$\begin{tikzcd}
SO_3 + CuO & CuSO_4.5H_2O \arrow[r, "373\text{ K}"] & CuSO_4.H_2O \arrow[d, "423\text{ K}"] \\
 & & CuSO_4 \arrow[ull, "773\text{ K}"']
\end{tikzcd}$$

$CuSO_4$ White (anhydrous salt)

(iii) Uses -

(a) Used in copper refining, electroplating, dying, calico printing and Fehling's solution.

(b) Also used in the preparation of Bordeaux mixture (a mixture of $CuSO_4$ solution + lime), used as a fungicide for fruit trees, grapes, and vine plants.

(a) Action of NH_4OH :
With ammonia solution; it forms the soluble blue complex. First it forms a precipitate of $Cu(OH)_2$ which dissolves in excess of ammonia solution.

$$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 \text{ ppt} \downarrow + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow \underset{\text{Tetrammine cupric sulphate}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

$[Cu(NH_3)_4]\ SO_4$ is known as Schwizer's reagent

(b) Action of alkalies :
Alkalies form a pale blue precipitate of copper hydroxide.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 \downarrow + Na_2SO_4$$

(c) Action of potassium iodide :

First of all cupric iodide is formed which decomposes to give white cuprous iodide and iodine.

$$[CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(d) Action of potassium cyanide :

First of all cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cupro cyanide $K_3[Cu(CN)_4]$.

$$2CuSO_4 + 10KCN \longrightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2$$

(e) Action of potassium ferrocyanide :

Reddish brown precipitate of cupric ferrocyanide is formed. (test of Cu^{2+} ion)

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$$

(f) Addition of electropositive metals :

$$CuSO_4(aq) + Fe \longrightarrow Cu + FeSO_4$$

$$CuSO_4(aq) + Zn \longrightarrow Cu + ZnSO_4$$

(g) Action of H_2S :

When H_2S is passed into copper sulphate solution, a black precipitate of copper sulphide is formed.

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$$

The black precipitate dissolves in conc. HNO_3

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

(h) Action of potassium sulphocyanide :

Cupric sulphocyanide is formed.

$$2CuSO_4 + 2KCNS + SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2 + K_2SO_4 + 2H_2SO_4$$

(i) Double sulphates :

Copper sulphate forms double salts with alkali sulphate K_2SO_4. $CuSO_4$. $6H_2O$ and with ammonium sulphate as $(NH_4)_2SO_4CuSO_4.6H_2O$.

(j) Action of sodium thiosulphate :

Sodium thiosulphate reacts with copper sulphate to form cupric thiosulphate which is reduced by sodium thiosulphate. The cuprous compound thus formed dissolves in excess of sodium thiosulphate to form a sodium cuprothiosulphate

$$CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow \underset{\text{Sodium cuprothiosulphate}}{Na_4[Cu_6(S_2O_3)_5]}$$

2. Mercurous Chloride (Hg_2Cl_2 - Calomel) :

Methods of preparation : (i) Hg_2Cl_2 (calomel) is formed as white precipitate when soluble chloride (say NaCl) is added to soluble mercurous salt (say $Hg_2(NO_3)_2$:

$$Hg(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 \downarrow + 2NaNO_3$$

(ii) Hg_2Cl_2 is also formed when aq $HgCl_2$ and aq. $SnCl_2$ are mixed in 1 : 1 molar ratio or $HgCl_2$ is reduced by Hg.

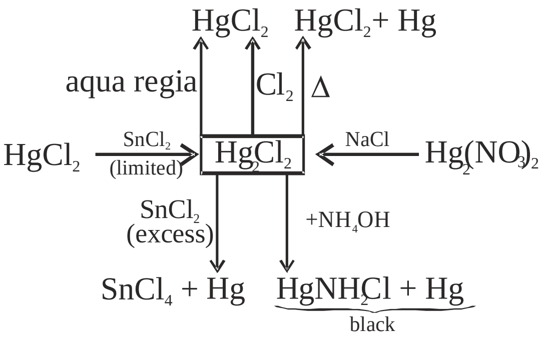
$$2\ HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

Excess of $SnCl_2$ would reduce Hg_2Cl_2 to Hg :

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

(iii) $$HgCl_2 + Hg \xrightarrow[\text{in iron tank}]{\Delta} Hg_2Cl_2$$

Properties of Hg_2Cl_2 : It is an amosphous, tasteless, odourless, non-poisonous, white power which is sparingly soluble in water.



- Mercurous ion is diamagnetic; this indicates that there is no unpaired electron, hence mercurous ion is not Hg^+ but Hg_2^{2+}:

3. Mercuric Chloride ($HgCl_2$ - Corrosive Sublimate)

Preparation :

(i) It is prepared by heating a mixture of mercuric sulphate with common salt, in presence of a little manganese dioxide (was to prevent the formation of any mercurous chloride). Mercuric chloride sublimes off and condenses on the cooler parts of the vessel.

$$HgSO_4 + 2NaCl \longrightarrow HgCl_2 + Na_2SO_4$$

(ii) By heating the Hg in a current of chlorine.

$$Hg + Cl_2 \longrightarrow HgCl_2$$

(iii) It can be prepared by dissolving mercuric oxide in hydrochloric acid.

$$HgO + 2HCl \longrightarrow HgCl_2 + H_2O$$

(iv) It can also be prepared by dissolving Hg or Hg_2Cl_2 in aqua-regia.

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

$$Hg_2Cl_2 + 2Cl \longrightarrow 2HgCl_2$$

Properties :

(i) It is a white crystalline compound having highly poisonous nature. It is less soluble in cold water but more soluble in hot water. It behaves like a covalent compound as it is soluble in organic solvents and very slightly ionised in water.

(ii) It is reduced by stannous chloride first into mercurous chloride (white) and then into mercury (black)

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2} + SnCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{Black}}{2Hg} + SnCl_2$$

(iii) Potassium iodide forms a scarlet precipitate of mercuric iodide when added to $HgCl_2$ solution.

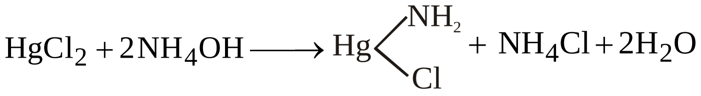
$$HgCl_2 + 2NaOH \longrightarrow HgO + 2NaCl + H_2O$$

$$HgCl_2 + 2KI \longrightarrow 2KCl + HgI_2$$

$$HgI_2 + 2KI \longrightarrow K_2HgI_4$$

The precipitate of mercuric iodide dissolves in excess of potassium iodide forming a complex, K_2HgI_4. The alkaline solution of K_2HgI_4 is known as Nessler's reagent. This reagent is used for testing ammonia.

(iv) When aqueous ammonia is added to the solution of mercuric chloride, a white precipitate of mercuric amino chloride is formed.



$$HgCl_2 + 2NH_4OH \longrightarrow Hg\begin{matrix} \diagup NH_2 \\ \diagdown Cl \end{matrix} + NH_4Cl + 2H_2O$$

(v) Mercuric chloride absorbs gaseous ammonia and forms an addition compound.

$$HgCl_2 + 2NH_3 \longrightarrow HgCl_2.2NH_3$$

(vi) When H_2S is passed into its solution, it forms a black precipitate of mercuric sulphide.

$$HgCl_2 + H_2S \longrightarrow \underset{\text{black}}{HgS} \downarrow + 2HCl$$

(vii) When heated with sodium carbonate or sodium hydroxide in solution, a yellow precipitate of mercuric oxide is formed.

$$HgCl_2 + Na_2CO_3 \longrightarrow HgO + 2NaCl + CO_2$$

4. Potassium dichromate :

A. Preparation. It is obtained from chromite ($FeO.Cr_2O_3$) by the following steps :-

(a) Fusion of ore with caustic soda -

$$4(FeOCr_2O_3) + 16NaOH + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

(b) Acidification of extract

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(c) Conversion into Pot. dichromate -

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2\ NaCl$$

B. Properties.-

(a) Pot. dichromate exists as orange crystals which are soluble in water.

(b) On strong heating $K_2Cr_2O_7$ decomposes to evolve oxygen -

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2Cr_2O_4 + 2Cr_2O_3 + 3O_2$$

(c) When alkali is added, orange red solution of dichromate changes into yellow solution of chromate. The dichromate and chromate ions exist in equilibrium as under :

$$2CrO_4^{2-} \underset{alkali}{\overset{Acid}{\rightleftharpoons}} Cr_2O_7^{2-} + H_2O$$

(d) (i) Cold, conc. H_2SO_4 converts dichromate into red crystals of chromic anhydride

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3 + 2KHSO_4 + H_2O$$

(ii) With hot conc. H_2SO_4, oxygen gas is evolved.

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

(iii) It acts as a strong oxidising agent and oxidises I^- to I_2, Fe^{2+} to Fe^{3+}, H_2S to S, NO_2^- to NO_3^-, SO_3^{2-} to SO_4^{2-}, Sn^{2+} to Sn^{4+}, Cl^- to Cl_2, alcohols to aldehydes and finally acids.

(f) It gives chromyl chloride when heated with concentration H_2SO_4 and a chloride.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

In acidic medium with H_2O_2 it gives deep blue colour due to the formation of CrO_5. This compound finally decomposes to Cr^{3+}.

(c) Uses - Potassium dichromate is used

(a) for cleaning glassware by making chromic acid
(b) in chrome tanning in leather industry
(c) as a laboratory reagent
(d) as a strong oxidising agent
(e) for the preparation of large number of important compounds like chrome alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, Chrome yellow ($PbCrO_4$) and Chrome red ($PbCrO_4.PbO$) etc.

(d) Structure - Chromate ion is tetrahedral in geometry while dichromate ion is formed by the linking of two chromate ions through one O-atom.

5. Potassium permanganate :

A. Preparation - It is prepared from pyrolusite (MnO_2) by the following stages :

(a) Conversion of pyrolusite to potassium manganate by the action of KOH in the presence of oxygen.

$$2KMnO_4 + 4KOH + O_2 \xrightarrow{Heat} K_2MnO_4 + 2H_2O$$

(b) Conversion of potassium manganate to potassium permanganate by passing ozone or chlorine or carbon dioxide or by electrolysis.

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

(ii) Properties -

(a) Pot. permanganate exists in the form of dark purple coloured prism like crystals. These crystals become dull in air due to the reduction on surface.

(b) This is soluble in water but solubility is much more in hot water.

(c) Action of heat

$$2KMnO_4 \xrightarrow{\text{Heat}} K_2MnO_4 + MnO_2 + O_2$$

(d) Action of conc. H_2SO_4

With cold H_2SO_4, it makes Mn_2O_7 which on heating changes into MnO_2

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$$

When heated with conc. H_2SO_4, oxygen gas is evolved.

$$4KMnO_4 + 6H_2SO_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$$

It acts as a strong oxidising agent in all the three media acidic, alkaline and neutral. The reactions in different media are :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \text{ (In acidic medium)}$$

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O] \text{ (In alkaline medium)}$$

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O] \text{ (In neutral medium)}$$

In acidic medium $KMnO_4$ oxidises I^- to I_2, SO_3^{2-} to SO_4^{2-}, $C_2O_4^{2-}$ to CO_2, Fe^{2+} to Fe^{3+}, alcohols to aldehydes and finally acids. In alkaline medium it oxidises I^- to IO_3^-, toluene to benzoic acid.

(iii) Structure - Permanganate ion is tetrahedral in geometry due to sp^3 hybridised manganese.

(iv) Uses - Potassium permanganate is used :

(a) As an oxidising agent in different media (acidic, alkaline as well as neutral).

(b) As water purifier particularly for tank water and stinking wells.

(c) As a laboratory reagent for various types of redox titrations and testing various anions.

IRON

Symbol : Fe, At. Number : 26 At. mass : 55.847, Elect. conf. : $[Ar]3d^6 4s^2$, Oxid. states : +2, +3, Position in the periodic table : Belongs to group 8, period 4

1. Occurrence :

Iron is the fourth most abundant element and second most abundant metal (next to aluminium) occurring in the Earth's crust. Iron is rarely found in native state. In the combined form, it is generally found as oxides and carbonates as -

(i) Haematite (red haematite), Fe_2O_3

(ii) Limonite (Brown haematite), $Fe_2O_3.3H_2O$

(iii) Magnetite, Fe_3O_4

(iv) Siderite, $FeCO_3$

(v) Iron pyrites, FeS_2

(vi) Copper pyrites, $CuFeS_2$

2. Extraction :

The following steps are involved in the extraction of cast iron from haematite ore :

(i) Concentration : The ore is crushed and concentrated by levigation in a steam of water and by electromagnetic separation.

(ii) Roasting : The concentrated ore is roasted in air to remove moisture, volatile impurities such as S, As etc. and to convert any lower oxide like FeO or Fe_3O_4 to more porous Fe_2O_3 which can be easily reduced.

$$Fe_2O_3 \cdot 3H_2O \longrightarrow Fe_2O_3 + 3H_2O$$

$$2FeCO_3 \longrightarrow 2FeO + 2CO_2$$

$$S + O_2 \longrightarrow SO_2$$

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

(iii) Smelting (Reduction) : The roasted ore is mixed with coke (reducing agent) and limestone (flux).In the ratio of 8 : 4 : 1 and introduced into a blast furnace for smelting. The following reaction take place in the blast furnace in different zone as

(a) Combustion zone lowest part of the furnace above earth)

$$\underset{\text{Coke}}{C} + \underset{\text{Hot air}}{O_2} \longrightarrow CO_2 + \text{Heat}$$

$$CO_2(g) + \underset{\text{Coke}}{C} \longrightarrow 2CO(g)$$

Reduction Zone : (Uppermost part of the furnace) :

$$3Fe_2O_3 + CO \xrightarrow{300^\circ - 400^\circ} 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \xrightarrow{500 - 600^\circ} 3FeO + CO_2$$

$$FeO + CO \xrightarrow{700 - 600^\circ} \underset{\text{spongy iron}}{Fe} + CO_2$$

(c) Slag formation : Central Zone

$$CaCO_3 \xrightarrow{1073\text{ K}} CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow \underset{(\text{slag})}{CaSiO_3}$$

(d) Zone of fusion :

The molten slag is lighter than molten iron and thus floats on the molten iron. The molten iron tapped off from the blast furnace is called pig iron the pig iron is remelted and cast into moulds. This is known as cast iron.

3. Various forms of Iron :

(i) Cast Iron : It is the most impure form of iron and contains 2.5% to 5% carbon as the main impurity with traces of sulphur, phsophorus and manganese. It is hard and brittle.

(a) White Cast Iron : In white cast iron carbon is present form of cementite (Fe_3C). It is obtained when molten pig iron is cooled once.

(b) Grey Cast iron : In the grey cast iron carbon is present in the form of graphite. It It is obtained when molten pig iron is cooled slowly and slowly.

(ii) Wrought Iron or Malleable Iron : It is is the purest form of iron and contains minimum amount of carbon (0.1 to 0.25%). It is soft ductile and malleable.

(iii) Steel : The percentage of carbon contained in steel is (0.25 to 2%) intermediate between that in wrought iron and cast iron. It is the most important form of iron and have extensive applications.

4. Manufacture of Steel :

Steel is manufactured from cast iron by various processes viz:

(i) Bessemer's process
(ii) L.D. (Linz Donawitz) process
(iii) Open Hearth process or Siemins - Martin process
(iv) Electric Furnace process
(v) Duplex process etc.

Note : Spiegeleisen (an alloy of Fe, Mn and C) is added during manufacture of steel. Mn and C serve as deoxidiser and reduce FeO (if any) and the rest dissolves in molten steel. Mn makes steel harder and increases its tensile strength.

5. Heat Treatment of Steel :

The properties of steel such as hardness, toughness and tensile strength can be controlled to a great extent by proper heat treatment. Various methods of heat treatment are :

(i) Annealing : It is the process of heating steel to bright redness and then cooling it slowly. By annealing, steel becomes soft and pilable.

(ii) Hardening : It is the process of heating steel to bright redness and then cooling suddenly by plunging in oil or water (quenching). The resultant steel is hard and brittle.

(iii) Tempering : It is the process of heating the hardened steel to a temperature much below redness and then cooling it slowly. The resultant steel retains its hardness but brittleness disappears.

(iv) Case hardening : It is a process of giving a thin coating of hardened steel to a mild steel by heating it in contact with charcoal followed by quenching it in oil. Thus, due to hardened surface layer it can bear wears and tears. The inside, being still mild steel, can withstand shock. Locomotive axles are made of case hardened mild steel.

(v) Nitriding : It is a process of heating steel in an atmosphere of dry ammonia at 500^0C to 600^0C to 4 days. This process imparts a hard coating of iron nitride on the surface of steel.

Types of Steel :- The properties of steel depends upon its carbon content. With the increase in carbon content, the hardness of steel increases while its ductileness decreases. Based upon the percentage of carbon, steel may be classified as under :-

(i) Soft Steel - Contains less percentage of carbon (0.25%)
(ii) Mild Steel - Contains medium percentage of carbon (0.25 – 0.25%)
(iii) Hard Steel - Contains high percentage of carbon (0.5 – 1.5%)
(iv) Alloy Steels or Special Steels - Very useful and valuable properties may be imparted to steel by alloying it with other metals e.g. Ni, Co, Cr, W, V etc. All these alloy of steels are called alloy steels.

COPPER

Symbol : Cu, At. No.: 29, At. mass : 63.546, Elect. conf.: [Ar]$3d^{10}4s^1$, Oxid. states : +1, +2; Position in the periodic table : Belongs to group 11, period 4

1. Occurrence :

Copper occurs in native as well as in combined state. In combined state it is found as -

(i) Copper pyrites (Charcopyrites), $CuFeS_2$
(ii) Copper glance (Charcocite), Cu_2S

(iii) Malachite, $CuCO_3Cu(OH)_2$
(iv) Azurite, $2CuCO_3.Cu(OH)_2$
(v) Cuprite or ruby copper, Cu_2O etc.

2. Extraction :

Copper is generally extracted from copper pyrites. There are two processes for the extraction of copper based on concentration of copper in the ore (i) Pyrometallurgical (smelting) process employed in case of Cu rich ore, (ii) Hydrometallurgical process employed in case of Cu Poorer ore.

Pyrometallurgical Process :

It involves the following steps :

(i) Concentration : The powdered ore is concentrated by froth floatation process.

(ii) Roasting : The concentrated ore is heated strongly in the presence of air in reverberatory furnace.

$$S + O_2 \longrightarrow SO_2$$

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

$$4Sb + 3O_2 \longrightarrow 2Sb_2O_3$$

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

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

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

(iii) Smelting : The roasted ore is mixed with sand (flux) and coke (fuel) and heated strongly in a blast furnace. The smelted ore contains mainly Cu_2S and a little FeS and FeO. It is called as matte.

$$FeS + Cu_2O \longrightarrow FeO + Cu_2S$$

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

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

(iv) Bessemerisation : Molten matter is heated with a little sand in a Bessemer converter. The ferrous sulphide (FeS) undergoes oxidation first and is removed as a slag, then part of the cuprous sulphide (Cu_2S) is converted into cuprous oxide which react with unchanged sulphide to give the molten metal called as blister copper (contains 98% Cu and 2% impurities of Fe, S, Ag, Au etc).

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

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

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

$$Cu_2S + 2Cu_2O \longrightarrow \underset{\text{blister copper}}{6Cu} + SO_2$$

(v) Refining : The blister copper is refined either by fire refining (poiling) or by electrolysis.

(a) Refining (Poiling) : Blister copper is melted on the hearth of a furnace and stirred with logs of green wood. The hydrocarbons liberated by the decomposition of wood reduce any Cu_2O to copper.
Note : Poling of copper is a reduction process.

(b) Electrolytic refining : A cell is constructed using following components :

Electrolyte : $CuSO_4$ + dil.H_2SO_4
Anode : Block of impure copper
Cathode : Thin strip of pure copper

On passing current, pure Cu (99.99% Pure) gets transferred from anode to cathode which gradually grows in size. The impurities settle down below the anode as anodic mud. (Anode mud contains Ag, Au and Pt)

SILVER

Symbol : Ag, At. No. : 47, At. mass No. : 107.8682, Elect. conf. $[Kr]4d^{10}5s^1$,
Oxid. state : +1, Position in the periodic table : Belongs to group 11, period 5

1. Occurrence :

It is found both in free and combined state as -

(i) Horn silver (Chlorargyrite), $AgCl$
(ii) Argentite (Silver glance), Ag_2S
(iii) Pyrargyrite, (Ruby silver) $3Ag_2S.Sb_2S_3$
(iv) Silver copper glance, $(Cu, Ag)_2S$

2. Extraction :

The principal methods used for the extraction of silver are :

(i) Extraction from silver ores (Mac Arthur-Forest Cyanide Process) :

This is the most modern and widely used method for the extraction of Ag from argentite, Ag_2S. It involves the following steps :

(a) Concentration : The ore is crushed and concentrated by forth floatation process.

(b) Cyanidation : The concentrated ore is treated with a dilue solution (0.5%) on NaCN in the presence of air. The silver ions are changed into sodium argentocyanide, $Na[Ag(CN)_2]$.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

The air also oxidises Na_2S to free sulphur and thus enables the forward reaction to proceed for completion.

$$Na_2S + H_2O + ½O_2 \longrightarrow 2NaOH + S\downarrow$$

(c) Recovery of silver : The silver complex thus obtained is treated with zinc dust to precipitate out Ag.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

(d) Refining : Impure silver is refined electrolytically. (Anode : Block of impure Ag. Cathode: Thin strip of pure Ag. Electrolyte : $AgNO_3$ + dil. HNO_3). On passing electric current pure Ag is transferred from anode to cathode.

(ii) Extraction of Ag from Argentiferous lead (separation of Ag from lead containing silver) - Mainly three methods are used. These are :

(a) Cupellation process
(b) Pattinson's process
(c) Parke's process

(iii) Extraction of Ag from coins ornaments (Alloy of Ag and Cu) : The coins or ornaments are dissolved in HNO_3. The solution is boiled to remove HNO_3 and then treated with HCl. AgCl is precipitated out while Cu remains in solution. AgCl is filtered and reduced to Ag.

Extraction of silver from coins :

A silver coin is an alloy of silver and copper. The alloy is heated with dilute HNO_3. It is dissolved forming silver and copper nitrates.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2(aq) + 2NO + 4H_2O$$

$$3Ag + 4\underset{\text{dil.}}{\overset{\text{dil.}}{HNO_3}} \rightarrow 3AgNO_3(aq) + NO + 2H_2O$$

The solution so obtained is treated with HCl when a white ppt. of AgCl is formed. It is separated by filtration. AgCl is converted into metallic silver by

(a) Strongly heating it with Na_2CO_3 :

$$4AgCl(s) + 2Na_2CO_3 \xrightarrow{\text{Strong heating}} 4Ag + 4NaCl + 2CO_2 + O_2$$

(b) Dissolving AgCl in KCN and adding zinc :

$$AgCl + 2KCN(aq) \rightarrow K\left[Ag(CN)_2\right](aq) + KCl$$

$$2K\left[Ag(CN)_2\right] + Zn \rightarrow K_2\left[Zn(CN)_4\right] + 2Ag \downarrow$$

MERCURY

Symbol : Hg, At. No. : 80, At. mass : 200.59, Elect. conf.: [Xe] $5d^{10}6s^2$, Oxid. states : +1, +2, Position in the periodic table : Belongs to group 12, period 6

1. Occurrence :

It is rarely found in native state. The chief source of Hg is Cinnabar, HgS ore.

Recovery of mercury :

Ore is powdered and concentrated by froth floatation process. Then it is roasted at 570K to 580 K in excess of air to form HgO which then decomposes to Hg vapours and O_2. Hg vapours are condensed and refined.

$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$$

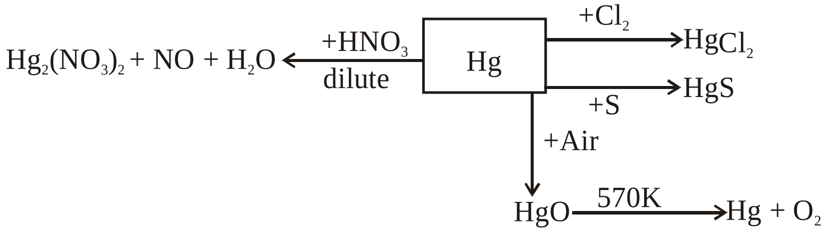
$$2HgO \rightarrow 2Hg \uparrow + O_2 \uparrow$$

Refining of mercury :

Impure mercury is filtered through thick canvass or chamios leather. Then it is dropped into 5% HNO_3 to remove metallic impurities like Fe, Cu, Zn, Pb etc.(as their soluble nitrates) This mercury is further refined by distillation under reduced pressure.

4. Properties of Hg :

At room temperature, it is a lustrous, silvery white heavy liquid (density 13.6 g cm^{-3}). It freezes at 234.13 K and boils at 630 K. Its vapours are monoatomic and poisonous.



5. Amalgams :

Almost all metals (except Fe and Pt) are known to dissolve in mercury. The alloys of Hg with metal(s) are known as amalgams.

Note :

(i) Due to insolubility of Fe in Hg, mercury is transported in iron containers.

(ii) Dental alloy : An amalgam of Ag, Sn, Zn and Hg is used for filling of teeth.

(iii) Mercury tree : When a little mercury is poured into a $AgNO_3$ solution, a tree like growth of silver amalgam is produced, known as mercury tree.

(iv) Ammonium amalgam (Mercury butter) : When Na-Hg amalgam is kept in conc. solution of NH_4Cl, mercury undergoes swelling upto the extent of nearly three times of its original volume and forms a butter like mass of soluble mercury which is known as ammonium amalgam or mercury butter.

5. Uses of Mercury :
   - (i) It is used in scientific equipment such as thermometers, barometers and high vacuum pumps.
   - (ii) It is also used in mercury vapour lamps and rectifiers.
   - (iii) Certain compounds of Hg like Mercurochrome etc., are extensively used as antiseptic and germicide.
   - (iv) Amalgamated zinc plates are used in galvenic batteries.
   - (v) Sodium amalgam is used as a reducing agent.

ZINC

Symbol : Zn, At. number : 30, At. mass : 65.37, Elect. conf. : $[Ar]3d^{10}4s^2$,
Oxid. state : +2, Position in the periodic table : Belongs to group 12, period 4.

1. Occurrence : Zinc is usually found in the combined state as :
   - (i) Zinc blende (Sphalerite), ZnS
   - (ii) Calamine (Smith stone or zinc spar), $ZnCO_3$
   - (iii) Zincite (Red zinc), ZnO
   - (iv) Silicious zinc, $Zn_2SiO_4.H_2O$
   - (v) Franklinite, $ZnO.Fe_2O_3$
2. Extraction :

Zinc is mainly extracted from zinc blende and calamine. It extraction of zinc from zinc blends occurs in the following steps :

(i) Concentration of ore :

The powdered ore is concentrated by froth floatation process.

(ii) Roasting :

The concentrated ore is strongly heated in the presence of excess of air. By roasting, ZnS is changed into zinc oxide and SO_2.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$$

$$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$$

(iii) Reduction :

The roasted ore is heated with coke at 1473 K so that oxide is converted into metal.

$$ZnO + C \xrightarrow{1400^0 C - 1500^0 C} Zn + CO$$

(iv) Purification :

Impure zinc, known as spelter is purified by electrolysis. Electrolysis is carried out in a cell having acidified $ZnSO_4$ and dilute H_2SO_4 as electrolyte. The anode is of impure zinc while cathode is pure zinc plate.

3. Properties of Zinc :

It is bluish white, lustrous metal (m.p. 692 K, b.p. 1180 K, density 7.14 g cm^{-3}). It is brittle at ordinary temperature, malleable and ductile at 410-430 K and again become brittle at 493 K. This is due to its different allotropic forms. It is a good conductor of electricity.

4. Uses of Zinc :

It is extensively used for galvanizing iron to prevent it from rusting. It is used as a reducing agent in dry cells, extraction of Au and silver. Various alloys of zinc like German silver (Cu, Zn and Ni), Brass (Cu and Zn), gun metal (Sn, Zn and Cu) are commercially important.

CO-ORDINATION CHEMISTRY

CO–ORDINATION CHEMISTRY

The branch of inorganic chemistry that deals with the study of coordination compounds.

Addition or molecular compounds

When solution of two or more simple stable salts are mixed together in simple molecular proportion and the solution thus obtained is allowed to evaporate, crystals of a new compound are formed. This new compound is called addition or molecular compound.

Simple compounds — Addition compounds

$$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.\ MgCl_2.\ 6H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \xrightarrow{\text{Camollite}} K_2SO_4.Al_2(SO_4)_3.24H_2O$$

TYPE OF ADDITION COMPOUNDS :

Addition compounds are of two types

1. Double salts. These are the addition compounds which are stable in the solid state but give their constituent ions when dissolved in water or in any other ionic solvent. In these compounds the individual properties of the constituent ions are not lost. e.g. $KCl.\ MgCl_2.\ 6H_2O$
2. Coordination (or complex) compounds. These are the addition compounds which donot give all their constituent ions when dissolved in water. In these compounds the individual properties of some constituent ions are lost.

$$K_3[Fe(CN)_6] \rightleftharpoons \underset{\text{simple cation}}{3K^+} + \underset{\text{complex anion}}{\left[Fe(CN)_6\right]^{3-}}$$

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons \underset{\text{complex cation}}{[Co(NH_3)_6]^{3+}} + \underset{\text{simple anion}}{3Cl^-}$$

Difference between double salt and a coordination compound

Double salt

1. Double salts exist only in solid state and dissociate into ions in aqueous solution or in any other solvent.
2. They lose their identity in solution.
3. The properties of the double salt are essentially the same as those of constituent compounds.
4. In a double salt, metal ions exhibit their normal valency.

COORINATION COMPOUND

1. Coordination compounds exist in the solid state.
2. When dissolved in water or any other solvent they do not completely lose their identity in solution.
3. The properties of coordination compound are different from the constituents.
4. In coordination compound, metal ion is surrounded by a number of oppositely charged ions or neutral molecules.

Postulates of Werner's Coordination Theory

1. In co–ordination compounds, metal atoms exhibit two types of valencies namely, the primary valency and the secondary valency.

   The primary valency is ionizable whereas the secondary valency is non–ionizable. In modern terminology, the primary valency corresponds to oxidation state and the secondary valency corresponds to coordination number.
2. Every metal atom has a fixed number of secondary valencies i.e. it has a fixed coordination number.
3. The metal atom tends to satisfy both its primary as well as secondary valencies. Primary valencies are satisfied by negative ions whereas secondary valencies are satisfied either by negative ions or by neutral molecules. In certain cases, a negative ion may satisfy both types of valencies.
4. The secondary valencies are always directed towards the fixed positions in space and this leads to definite geometry of the coordination compound. In other words, second valencies have characteristic spatial arrangements corresponding to different coordination numbers. In the modern terminology, such spactial arrangements are called coordination polyhedra.

   The secondary valencies, thus, determine the stereochemistry of the complex. On the other hand, the primary valency is non–directional.

Important terms in co–ordination chemistry

Central Metal atom or ion : A complex ion contains a metal atom or ion known as the central metal atom or ion. It is sometimes also called a nuclear atom.

Coordination sphere: The central metal atom or ion and the ligands that are directly attached to it are enclosed in a square bracket. This has been called coordination sphere or first sphere of attraction. It behaves as a single unit.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$

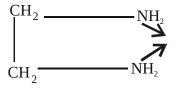
The charge on the complex ion is the algebraic sum of the charges carried by central metal ion and the legends attached to it.

1. Ligands: The neutral molecules anions or cations which are directly linked with the central metal atom or ion in a complex ion are called ligands. The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage.

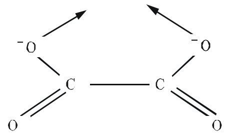
   Types of Ligands : On the basis of denticity ligands are classified as :

   (i) Mono or unidentate ligands: They supply only one electron pair to central metal atom or ion. F^-, Cl^-, Br, H_2O NH_3, CN^- NO_2^-, OH^-, CO, etc., are monodentate ligands.

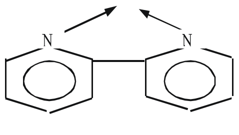
   (ii) Bidentate Ligands : Bidentate Ligands form two co-ordinate bonds with central metal atom/ ion



Ethylenediamine (en)

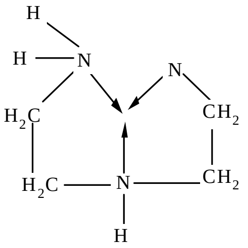


Oxalate (ox)

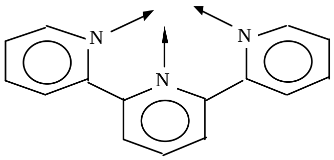


2,2 ′- Dipyridyl (Dipy)

   (iii) Tridentate ligands: Tridentate Ligands from three coordinate bonds with centralmetal atom/ion

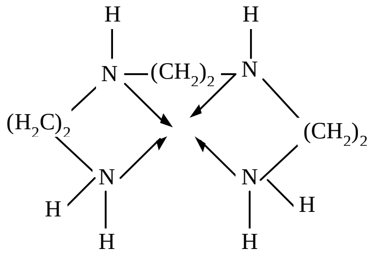


Diethylene triamine (dien)



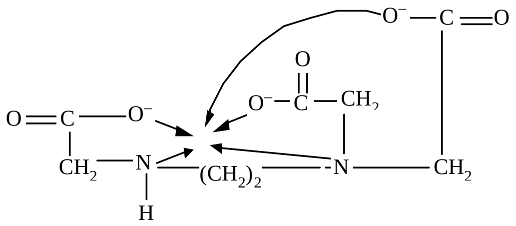
2, 2′, 2″ - Terpyridine (terpy)

(iv) Tetradentate ligands: Tetradentate Ligands from four coordinate bonds with centralmetal atom/ion



Triethylene tetramine
(trien)

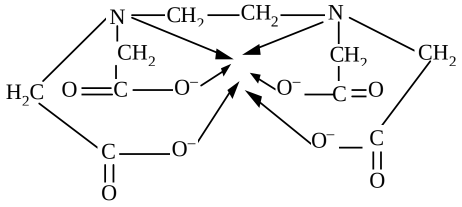
(iv) Pentadentate ligads: Pentadentate Ligands from five coordinate bonds with centralmetal atom/ion



Ethylenediamine triacetate ion

$(EDTA)^{3-}$

(v) Hexadentate ligands: Hexadentate Ligands from six coordinate bonds with centralmetal atom/ion



Ethylenediamine tetracetate ion $(EDTA)^{4-}$

Note: (i) The ligands that form two or more coordinate bonds with centalmetal atom/ion are called polydentate or multidentate ligands.

(ii) A multidentate ligands is known as a chelating ligands if on coordination it results in formation of a closed or cyclic ring. The complexes thus formed are called chelates. The chelates are comparatively more stable than ordinary complexes.

(iii) Polydentate ligands have flexdentate character. It is not jnecessary that all the donor atoms presetn in the polydentate ligands should form coordinate bonds with central metal atom or ion.

(iv) There are certain ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands.

$M \longleftarrow CN$ Cyano

$M \longleftarrow NC$ Isocyano

$M \longleftarrow SCN$ Thiocyanide

$M \longleftarrow NCS$ Isothiocyanide

Chelating Ligands and Chelates

A chelating ligand is a bidendate or polydentate ligand which is attached to the same central metal atom by two or more of its donor atoms resulting in the formation of a complex having a strain free ring structure. The complex having a the ring structure is called chelate or chelated complex. The chelate is also called by various other names like cyclic complex, ring–type complex etc. The formation of a chelate is called chelation or cyclisation.

Factors affecting the stability of chelates

Following are important factors which influence the stability of chelates.

1. Size of the chelate ring. Chelates having six membered rings including the metal atomare more stable than those having five–membered rings which in turn are more stable than the chelates with four membered rings and so on.
2. Number of chelate rings. Greater in the number of chelate rings, greater is the stability of the chelate.
3. Resonance effects. Resonance enhances the stability of the chelate.
4. Chelate effect. The chelated complexes are known to be more stable than the non–chelated complexes. This effect is known as chelate effect.

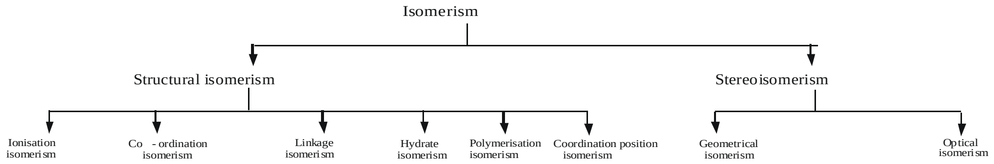
Coordination number: The number of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion.

$$\underbrace{\left[\mathrm{Cu(NH_3)_4}\right]}_{\text{Co-Ordination sphere}}\ \underbrace{\mathrm{SO_4}}_{\text{Ionisation sphere}}$$

$$\begin{aligned}\text{Central Metal ion} &= \mathrm{Cu^{2+}}\\ \text{Ligand} &= \mathrm{NH_3}\\ \text{Co-ordination Number} &= 6\end{aligned}$$

ISOMERISM IN CO–ORDINATION COMPOUNDS

Compounds having the same molecular formula but different structures or spatial arrangements are called isomers and the phenomenon is referred as isomerism.



STRUCTURAL ISOMERISM

The isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called structural isomers and such phenomenon is said to be structural isomerism.

1. Ionisation isomerism: The compounds which have same molecular formula but give different ions in solution are called ionisaion isomers.

   e.g. (i) $[Co(NH_3)_4Cl_2]\ NO_2$ & $[Co(NH_3)_4\ Cl(NO_2)]Cl$

   (ii) $[Co(NH_3)_5\ (NO_3)\ ]\ SO_4$ & $[Co(NH_3)_5\ (SO_4)]NO_3$

2. Coordination isomerism: The type of isomerism occurs in compounds containing both cationic and anionic entities as a complex ion. Coordination isomers differ in the distribution of ligands in the coordination entity of cationic and anionic parts. The examples are

   (i) $[Co(NH_3)_6]\ [Cr(NH)_6]$ and $[Cr(NH_3)_6]\ [Co(CN)_6]$

   (ii) $[Cu(NH_3)_4]\ [PtCl_4]$ and $[Pt(NH_3)_4]\ [CuCl_4]$

3. Linkage Isomerism : The compounds which have the same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers.

e.g. $\left[CO\left(NH_3\right)_5 NO_2\right]Cl_2$ and $\left[CO\left(NH_3\right)_5 (ONO)\right]Cl_2$

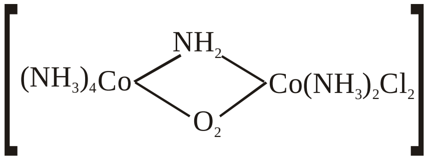
4. Hydrate Isomerism : The compounds which have the same molecular formula but differ in the number of water molecules present as ligands or as molecules of hydration are called hydrate isomers.

The following two isomers are hydrate isomers.

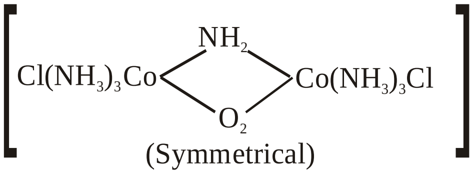
$[Co(en)_2 (H_2O) Cl]Cl_2$ and $[Co(en)_2 Cl_2]Cl.H_2O$
$[Co(NH_3)_4 (H_2O)Cl]Cl_2$ and $[Co(NH_3)_4 Cl_2]Cl.H_2O$
$[Cr(py)_2(H_2O)_2 Cl_2]Cl$ and $[Cr(py)_2H_2O.Cl_3].H_2O$

5. Coordination position isomerism

This type of isomerism is shown by those complex compounds which contain bridging ligands and arises when the non–bridging ligands are differently placed round the central metal atom. Thus (I) and (II) are coordination position isomers to each other, since NH_3 molecules and Cl^- ions (non–bridging ligands) are differently placed round the two Co^{3+} ions.



(Unsymmetrical)



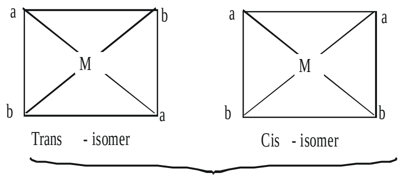
(Symmetrical)

Stereo Isomerism or space Isomerism

Compounds having same molecular formula, same structural formula but different stereo forms are said to be stereoisomers and such phenomenon is said to be stereo isomerism.

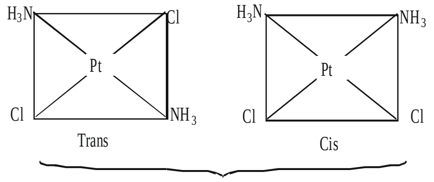
(A) Geometrical Isomerism: This is type of isomerism arises due to ligands occupying different position around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another. This type of isomerism is also known as cis–trans isomerism.

(i) Complexes with general formula, Ma_2b_2 (where both 'a' and 'b' are monodentate) can have cis– and trans–isomers.



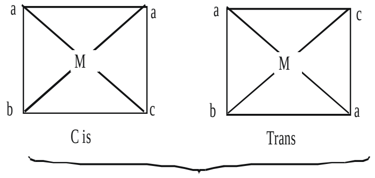
Trans - isomer Cis - isomer

$[Ma_2b_2]$



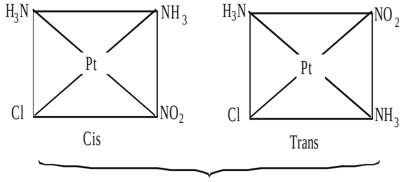
Trans Cis

(ii) Complexes with general formula Ma_2bc can have cis and trans–isomers.



Cis Trans

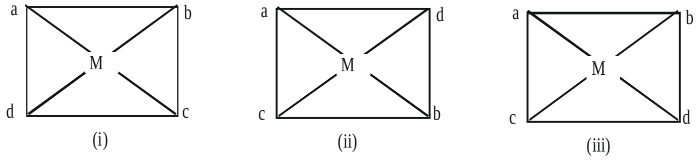
$[Ma_2bc]$



Cis Trans

$[Pt(NH_3)_2 ClNO_2]$

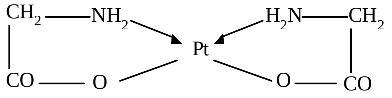
(iii) Complexes with general formula, Mabcd, can have three isomers.



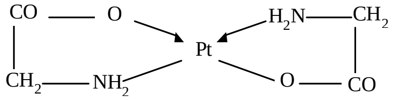
(i) (ii) (iii)

Example: $[Pt(NH_3)(NH_2OH)(NO_2)(py)]NO_2$

(iv) Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism. For example, platinum glycinato complex, $[Pt(Gly)_2]$, exhibit geometrical isomerism.

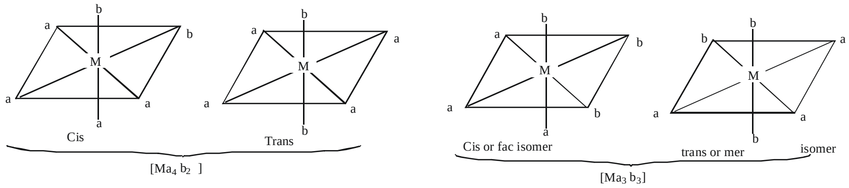


Cis-isomer



Trans-isomer

Octahedral complexes of the type Ma_4b_2, Ma_4bc and $Ma_3 b_3$ exhibit geometrical isomerism. In Ma_3b_3, if groups occupy one of the octahedral faces, it is facial facisomer while if the position of trio of donor atoms are around the maridian of octahedral, it is called meridional or mer–isomer.



Example: $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_3Cl_3]$

Note:

1. Octahedral complexes of general formula, Mabcdef, can have fifteen geometrical isomers.
2. Geometrical isomerism is not observed in complexes of coordination number 2 and 3.
3. Geometrical isomerism is not observed in complexes of coordination number 4 of tetrahedral geometry.
4. The complexes of general formulae, Ma_3b or Mab_3, or Ma_4 of square planar geometry do not show geometrical isomerism.
5. The complexes of general formula, Ma_6 and Ma_5b, of octahedral geometry do not show geometrical isomerism.

(B) Optical Isomerism: A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same molecular formula, same structural formula but differ in their abilities to rotate directions of the plane of polarised light are said to exhibit optical isomerism and molecules are optical isomers. The optical isomers are pair of molecules which are non–superimposable mirror images of each other. The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure. The isomer which rotates the plane of polarised light to right direction is termed dextro (d–form) while the isomer which rotates the plane of polarised light to left direction is termed laevo (l–form). The two optically active isomers are collectively called enantiomers. Enantimers are mirror image to each other and their physical properties are different.

Optically isomers rarelyoccur in square planar complexes on account of the presence of axis of symmetry.

Optically isomerism is very common in octahedral complexes. Octahedral complexes of general formulae.

$\left[Ma_2b_2c_2\right]^{n\pm}, \left[Mabcdef\right], \left[M(AA)_3\right]^{n\pm}, \left[M(AA)_2a_2\right]^{n\pm}$, (where AA = symmetrical bidentate ligands)

$[M(AA)_2ab]^{n\pm}$ and $[M(AA)_3]^{n\pm}$ (where AB unsymmetrical ligands) show optical isomerism.

Trans forms of $[M(AA)_2a_2]^{n\pm}$ does not show optical isomerism.

Valence Bond Theory (VBT)

This theory was developed by Pauling. It describes the binding in terms of hybridized orbitals of the central metal atom or ion. The theory mainly deals with the geometry and magnetic properties of complexes. This theory is based on the following assumptions.

1. The central metal atom or ion in the complex makes available an adequate number of empty orbitals for the formation of coordinate bonds with suitable ligands. the number of empty orbitals made available for the purpose is equal to the coordination number of the central ion.
2. The appropriate atomic orbitals (s, p and d) of the metal hybridise to give an equal number of new orbitals of equivalent energy, called hybrid orbitals. The hybrid orbitals are directed towards the ligand positions according to the geometry of the complex.
3. The d orbitals involed in the hybridisation may be inner, viz., $(n-1)d$ orbitals or the outer, viz., nd orbitals. For example, octahedral hybridisation may be either $(n-1)d^2sp^3$ or $nsnp^3nd^2$. The complexes thus formed are referred to as low spin and high spin complexes, respectively.
4. Each ligand has at least one orbital containing a lone pair of electrons.
5. The empty hybrid orbitals of metal atom or ion overlap with the fully filled orbitals of the ligand, forming the ligand–metal coordinate bond. The number of such bonds varies with the number of empty orbitals made available by the central ion.

LIMITATIONS OF VALENCE BOND THEORY

(i) It involves a number of assumptions.

(ii) It gives only the qualitative explanations for complexes.

(iii) It does not explain the detailed magnetic properties of the complexes.

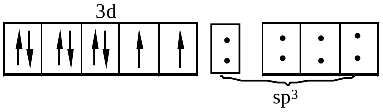
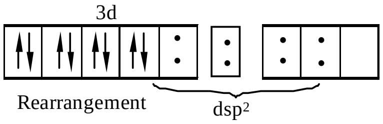
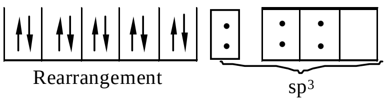
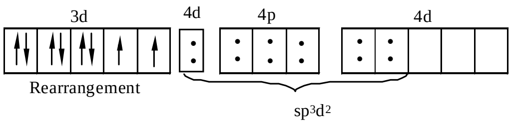
(iv) This theory does not explain the spectral properties of the coordination compounds.

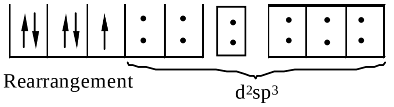
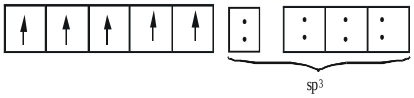
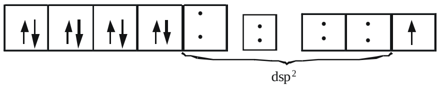
(v) It does not explain the thermodynamic and kinetic stabilities of different coordination compounds.

(vi) It does not make exact predictions regarding the tetrahedral or square planar structures of 4–coordinate complexes.

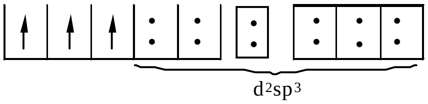
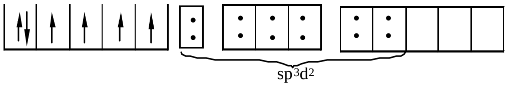
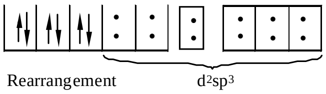
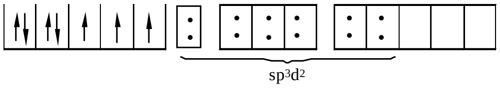
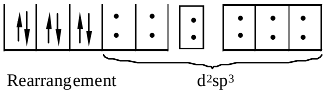
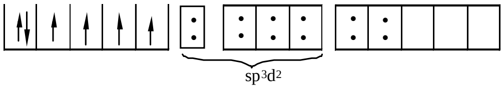
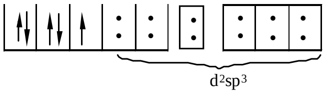
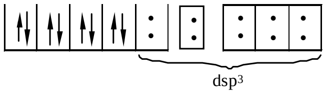
(vii) It does not distinguish between weak and strong ligands.

Geometry and magnetic nature of some of the complexes

Complex	Configuration(2)	Oxidation (3) state of metal	Type of (4) hybridization	Geometry (5) shape	No. of unpaired electrons	Magnetic (7) nature
$[NiCl_4]^{2-}$		+2	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2+}$		+2	dsp^2	Square planar	0	Diamagnetic
$Ni(CO)_4$		0	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(NH_3)_6]^{2+}$		+2	sp^3d^2(outer)	Octahedral	2	Paramagnetic

$[Mn(CN)_6]^{4+}$		+2	d^2sp^3(Inner)	Octahedral	1	Paramagnetic
$[MnCl_4]^{2-}$		+2	sp^3	Tetrahedral	5	Paramagnetic
$[Cu(NH_3)_4]^{2+}$		+2	dsp^2	square planar	1	Paramagnetic

One electron is shifted from 3d– to 4p–orbital

$[Cr(NH_3)_6]^{3+}$		+3	d^2sp^3(Inner)	Octahedral	3	Paramagnetic
$[CoF_6]^{3-}$		+3	sp^3d^2(Outer)	Octahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$		+3	d^2sp^3(inner)	Octahedral	0	Diamagnetic
$[Co(H_2O)_6]^{2+}$		+2	sp^3d^2(outer)	Octahedral	3	Paramagnetic
$[Fe(CN)_6]^{4-}$		+2	d^2sp^3	Octahedral	0	Diamagnetic
$[Fe(H_2O)_6]^{2+}$		+2	sp^3d^2(outer)	Octahedral	4	Paramagnetic
$[Fe(CN)_6]^{3-}$		+3	d^2sp^3(Inner)	Octahedral	1	Paramagnetic
$Fe(CO)_5$		0	dsp^3(Inner)	Trigonal bipyramidal	0	Diamagnetic

Crystal Field Theory :

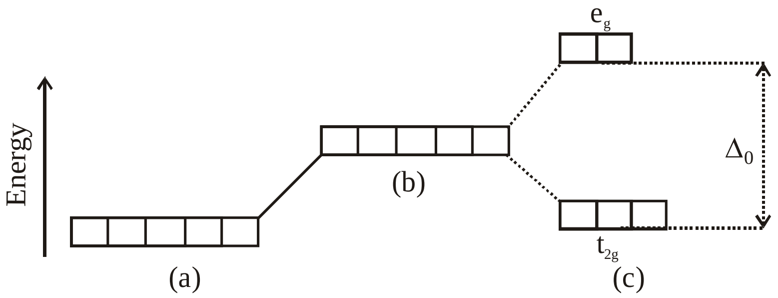
(i) The central metal cation is surrounded by ligands which contains one or more ion pairs of electrons.

(ii) The ionic ligands e.g. F^-, Cl^-, CN^- etc.) are regarded as negative point charges (also called point charges) and the neutrla ligand (e.g. H_2O, NH_3, etc) are regarded point dipoles or simply dipoles i.e. according to this theory neutral ligands are dipolar point dipoles or simply dipoles, i.e. according to this theory neutral ligands are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation.

(iii) The CFT does not provide for electrons to enter the metal orbitals.Thus the metal ion and the ligands do not mix their orbitals or share electrons, i.e it does not consider any orbital overlap.

(iv) According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic.

Splitting of d–orbital in Different Field :

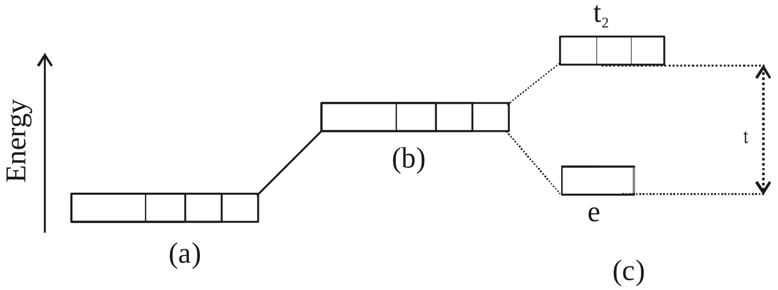


(Crystal field splitting of d-ortbials in an octahedral field)

(a) Five degenerate d-orbitals of free metal cation

(b) Hypothetical degenerate d-orbitals at higher energy level under spherically symmetrical ligand field

(c) Splitting of di-orbitals under the influence of ligands



(Crystal field splitting of d-ortbials in tetrahedral field)

(a) Five degenerate d-orbitals of free metal cation

(b) Hypothetical degenerate d-orbitals at higher energy level under spherically symmetrical ligand field

(c) Splitting of di-orbitals under the influence of ligands

Factors affecting stability of Complexes :

(i) Charge on the central metal atom or ion - Higher the charge greater is the stabiliity e.g. Pt^{4+} complexes are more stable than those of Pt^{2+} complex.

(ii) Position of metal in d-block - A metal belonging to 4-d series makes more stable complexes than thoseof metal of 3d-series. Similarly 5d-series metal make most stable complexes.

(iii) Basic nature of ligands - Higher the base strength of a ligand more stable complex it can make. The order of ligand strengths is called spectrochemical series.

(iv) Presence of chelate rings – Ring complexes formed by bidentate or polydentate ligands are generally more stable.

Prep^n of Co–ordination Compounds:

Coordination compounds are generally prepared by the application of the following methods

(i) Ligand substitution reaction : A reaction involving the replacement of the ligands attached to the central metal ion in the complex by other ligands is called a ligand substition reaction.

$$\underset{\text{Light blue}}{\left[Cu(H_2O)_4\right]^{2+}}(aq) + 4NH_{(aq)} \rightarrow \underset{\text{Deep blue}}{\left[Cu(NH_3)_4\right]^{2+}}(aq) + 4H_2O(l)$$

(ii) Direct mixing of reagnet :

$$PtCl_2 + 2H_2N - \underset{(en)}{C}H_2 - CH_2 - NH_2 \rightarrow \underset{(\text{Dichloro bis ethylene diamine platium II})}{[Pt(en)_2Cl_2]}$$

Organometallic Compounds

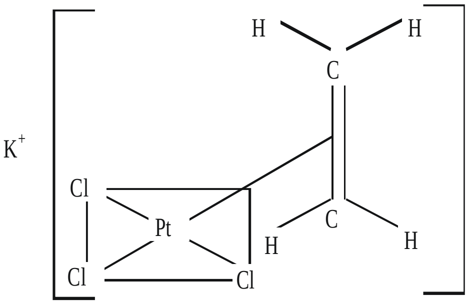
These are the compounds in which a metal atom or a metalloid (Ge, Sb) or anon-metal atom like B, Si, P, etc. (less elecronegative than C) is directly linked to a carbon atom of a hydrocarbon radical or molecule. Organometallic compounds contain at least one.

(1) Metal - Carbon bond, (2) Metalloid - Carbon bond, (3) Non metal – Carbon bond

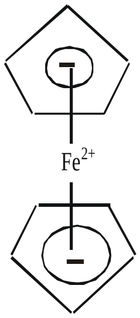
Organometallic compounds may be classified in three classes:

1. Sigma (σ) bonded complexes,
2. Pi (π) bonded complexes,
3. Complexes containing both σ – and π –bonding characteristics.

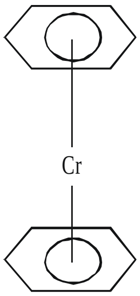
1. Sigma bonded complexes: In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond.
   - (i) Grignard reagents, R – Mg – X where R is an alkyl or aryl group and X is a halogen.
   - (ii) Zinc compounds of the formula R_2Zn such as $(C_2H_5)_2Zn$. This was first isolated by Frankland in 1849. Other similar compounds are $(CH_3)_4Sn$, $(C_2H_5)_4$ Pb, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$. $Pb(CH_3)_4$, etc.
2. π –bonded organometallic compounds : These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the π –electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium.



Zeise's salts
$K[PtCl_3(\eta^2\text{-}C_2H_4)]$

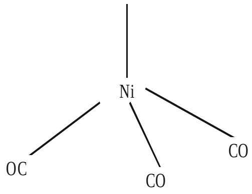


Ferrocene
$Fe(\eta^5\text{-}C_5H_5)_2$

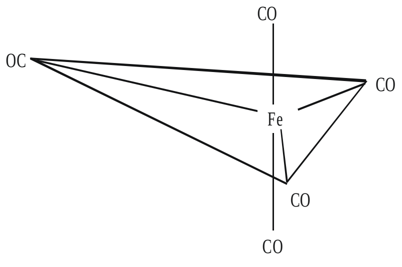


Dibenzene choromium
$Cr(\eta^6\text{–}C_6H_6)_2$

3. σ – and π – bonded organometallic compounds: Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. These compounds possess both s–and p–bonding. The oxidation state of metal atoms in these compounds is zero.



tetracabony nickel (0)
$Ni(CO)_4$



pentacarbonyl ion (0)
$Fe(CO)_5$

Qualitative Analysis

Qualitative Inorganic Analysis

Qualitative inorganic analysis involves the detection of cations (basic radicals) and anions (acid radicals) present in an inorganic compound or a mixture of inorganic comopounds. For a systematic study, qualitative analysis may be studied in the following parts :

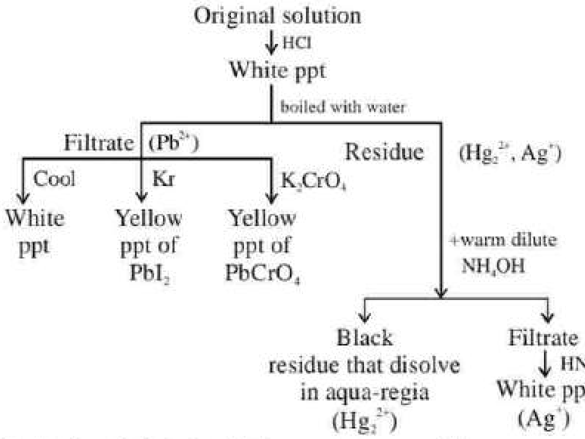
(A) Dry tests for inorganic compounds
(B) Confirmatory tests for basic radicals
(C) Confirmatory tests for acid radicals

Calssification of Basic Radicals

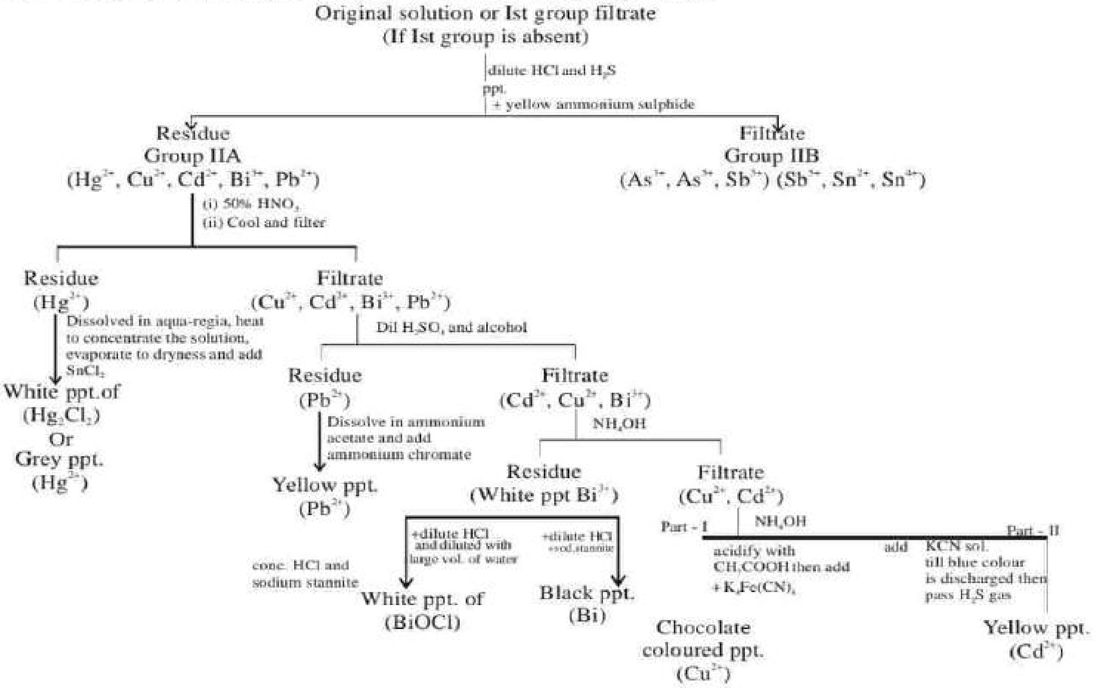
The qualitative analysis of basic radicals is based on the concept of solubility product, solubility and common ions. These concpets play very important role even in the classification of radicals in six groups and their group reagents.The common occuring cations have been divided into six groups.

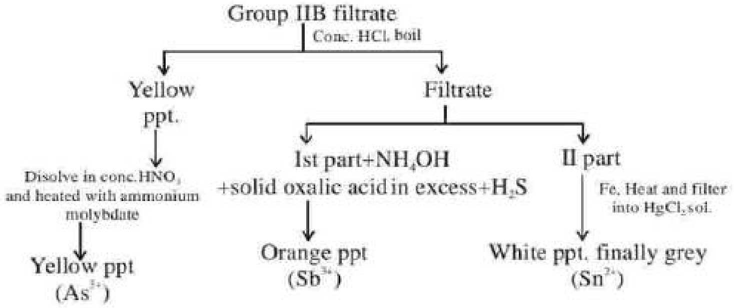
Group	Group reagent	Basic radical	Composition and colour of the ppt.
I.	Dil. HCl	Ag^+ Pb^{2+} Hg_2^{2+}	$AgCl$......White $PbCl_2$......White Hg_2Cl_2......White
II.A	H_2S in the presence of dil. HCl	Hg^{2+} Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+}	HgS......Black PbS......Black Bi_2S_3......Black CuS......Black CdS......Yellow
II.B	H_2S in the presence of dil. HCl	As^{3+} Sn^{4+} Sb^{3+} Sn^{2+}	As_2S_3......Yellow SnS_2......Yellow Sb_2S_3......Orange SnS......Brown
III.	NH_4OH in the presence of excess of NH_4Cl	Fe^{3+} Cr^{3+} Al^{3+}	$Fe(OH)_3$......Reddish brown $Cr(OH)_3$......Dirty green $Al(OH)_3$......White gelatinous ppt.
IV.	H_2S in presence of NH_4OH	Co^{2+} Ni^{2+} Zn^{2+} Mn^{2+}	CoS......Black NiS......Black ZnS......Bluis white MnS...Buff (flesh) coloured
V.	$(NH_4)_2CO_3$ in the presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	$BaCO_3$......White $SrCO_3$......White $CaCO_3$......White
VI.	No specific group reagent	Mg^{2+} Na+ K+	$Mg(NH_4)PO_4$......White
Zero	NaOH	NH_4^+	NH_3 gas is evolved

1. Ist Group Basic Radicals : (Ag^+, Pb^{2+}, Hg_2^{2+})

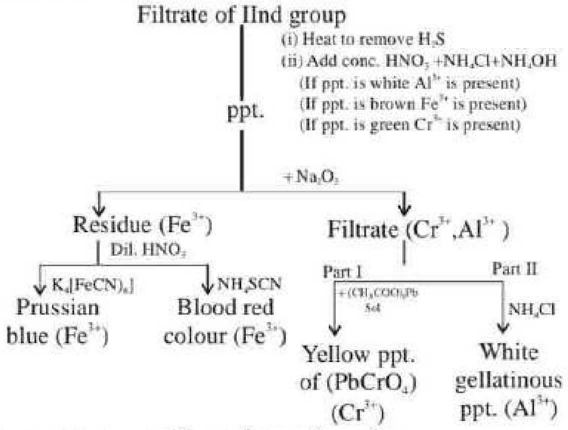


2. IInd Group Basic Radicals : Original solution or Ist group filtrate

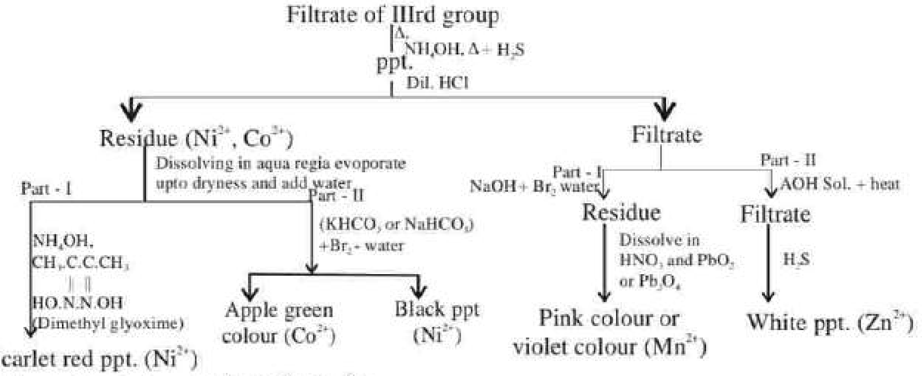




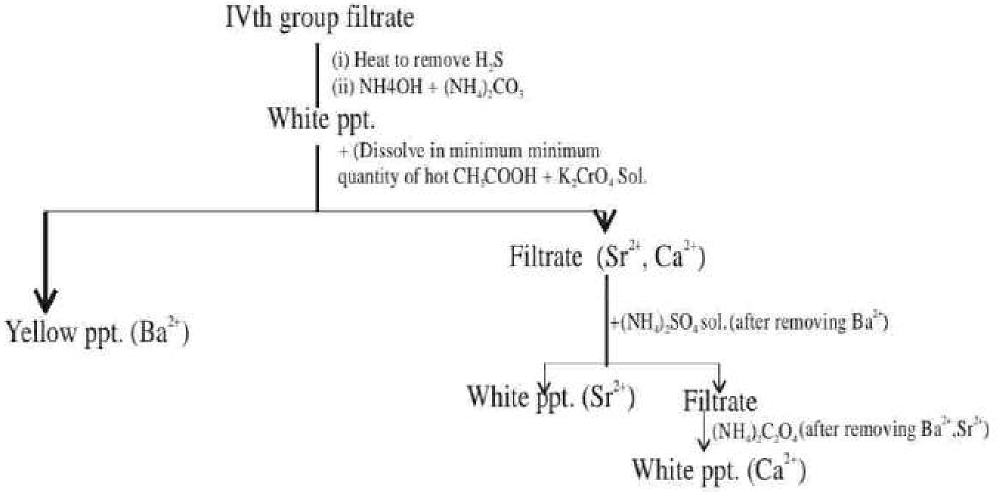
IIIrd Group Basic Radicals :



4. IV Group Baisc Radicals : (Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}) :



5. Vth Group Basic Radicals : (Ba^{2+}, Sr^{2+}, Ca^{2+})



6. VI Group Basic Radical

Filtrate of Vth group

↓ Heat and add $(NH_4)_2C_2O_4$. If any ppt. is obtained. Now add NH_4OH and Na_2HPO_4 skretch with glass rod.

White crystalline ppt.

7. Zero Group Basic Radical : It contains $NH_4^{\oplus}$ ion.

   (a) The salt is heated with NaOH, ammonia is evolved. The ammonia gives white fumes with HCl.

   (b) NH_4^+ gives brown ppt. with Nessler's reagent.

Reactions :

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

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$NH_4Cl + 2K_2HgI_4 + 3KOH \longrightarrow NH_2HgOHgI + 7KI + 2H_2O$$

Reaction involve :

Pb^{2+}

$$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4} + 2KCl$$

$$PbCrO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$

Ag^+

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Diaminesilver(I)chloride}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl} + 2NH_4NO_3$$

Hg_2^{2+}

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg + Hg(NH_2)Cl}_{\text{Black}} + NH_4Cl + 2H_2O$$

Hg^{2+}

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$$

$$2Hg(NH_2)Cl + 6Cl \longrightarrow 2HgCl_2 + 4HCl + N_2$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

$$3HCl + HNO_3 \longrightarrow 2H_2O + NOCl + 2Cl$$

$$3HgS + 2NOCl + 4Cl \longrightarrow 3HgCl_2 + 2NO + 3S$$

Pb^{2+}

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow Pb(CH_3COO)_{2+}(NH_4)_2SO_4^{-})$$

$$Pb(CH_3COO)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2CH_3COOK$$

Bi^{3+}

$$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$$

$$BiCl_3 + H_2O \longrightarrow \underset{\text{White ppt.}}{BiOCl} + 3HCl$$

$$BiCl_3 + 3NaOH \longrightarrow Bi(OH)_3 + 3NaCl$$

$$2Bi(OH)_2 + 3\underset{\text{Sod.stannite}}{Na_2SnO_2} \longrightarrow \underset{\text{Black}}{2Bi(OH)_3} + 3H_2O$$

Cu^{2+}

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

$$[Cu(NH_3)_4]SO_4 + 4CH_3COOH \longrightarrow CuSO_4 + 4CH_3COONH_4$$

$$2CuSO_4 + K_4[Fe(CN)_6 \longrightarrow \underset{\text{(Coper ferrocyanide choclate brown)}}{Cu_2[Fe(CN)_6]\downarrow + 2K_2SO_4}$$

Cd^{2+}

$$[Cd(NH_4)_4]SO_4 + 4KCN \longrightarrow K_2[Cd(CN)_4] + K_2SO_4 + 4NH_3$$

$$K_2[Cd(CN)_4] + H_2S \longrightarrow \underset{\text{Yellow ppt.}}{CdS} + 2KCN + 2HCN$$

As^{3+}

$$As_2S_6 + 10HNO_3 \longrightarrow \underset{\text{Aresenic acid (Soluble)}}{2H_3AsO_4} + 10NO_2 + 5S + 2H_2O$$

$$H_3AsO_4 + 12(NH_4)_2MoO_4 \longrightarrow \underset{\text{Yellow ppt. of ammonium arsenomolydate}}{(NH_4)_3AsO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Ie^{3+}

$$Fe(OH)_3 + 3HCl \longrightarrow \underset{\text{Soluble}}{FeCl_3} + 3H_2O$$

$$FeCl_3 + 3NH_4CNS \longrightarrow \underset{\text{Blood red}}{Fe(CNS)} + 3NH_4Cl$$

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Ferri ferrocyanide (Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

Cr^{3+}

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4} + 2CH_3COONa$$

Al^{3+}

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow \underset{\text{White ppt.}}{Al(OH)_3 + NH_4} + NaCl$$

Zn^{2+}

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2} + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{(Soluble)}}{Na_2ZnO_2} + 2H_2O$$

$$Na_2ZnO_2 + H_2S \longrightarrow \underset{\text{White ppt.}}{ZnS} + 2NaOH$$

Mn^{2+}

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 + 2NaCl$$

$$Mn(OH)_2 + O \longrightarrow MnO_2 + H_2O$$

$$2MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$$

$$2Mn(NO_3)_2 + 5Pb_3O_4 + 26HNO_3 \longrightarrow \underset{\substack{\text{Permanganic}\\ \text{acid (pink)}}}{2HMnO_4} + 15Pb(NO_3)_2 + 12H_2O$$

Ni^{2+}

$$CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4Co(CO_3)_3 + 3H_2O + 3CO_2$$

$$Br_2 + H_2O \longrightarrow 2HBr + O$$

$$2Na_4Co(CO_3)_3 + H_2O + O \longrightarrow \underset{\substack{\text{Sod. cobalti carbonate}\\ \text{(Green colouration)}}}{2Na_3Co(CO_3)_3} + 2NaOH$$

$$NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2$$

$$2NiCO_3 + O \longrightarrow \underset{\text{(Black)}}{Ni_2O_3} + 2CO_2$$

Ba^{2+} (barium)

$$Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2CH_3COOK$$

Sr^{2+} (strontium)

$$Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow \underset{\text{White ppt.}}{SrSO_4} + 2CH_3COONH_4$$

Ca^{2+} (calcium)

$$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White ppt.}}{CaC_2O_4} + 2CH_3COONH_4$$

DRY TEST

Dry tests are of great importance as these tests give clear indications of the presence of certain radicals. The following tests are performed in dry state:

(i) Flame test
(ii) Borax bead test
(iii) Micro-cosmic salt bead test
(iv) Charcoal cavity test
(v) Cobalt nitrate charcoal test

Flame Test

Alkali and Alkaline earth Metals Salts give characteristic colour when introduced in Bunsen flame. The colour produced by them are given below.

Li	Grimson red	Ca	Brick red
Na	Golden yellow	Sr	Crimson
K	Violet	Ba	Apple green

Note :

Flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radicals form alloy with platinum and hence, the wire is spoiled.

Borax bead test

On heating borax the colourless glassy bead formed consists of sodium metaborate and boric anhydride.

$$Na_2B_4O_7K.10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 \xrightarrow{\text{Heat}} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy bead}}$$

On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidising flame.

$$CuSO_4 \longrightarrow CuO + SO_3$$

$$CuO + B_2O_3 \longrightarrow \underset{\substack{\text{Copper metaborate} \\ \text{(Blue)}}}{Cu(BO_2)_2}$$

Metal	Colour of the bead in			
	Oxidising-flame		Reducing-flame	
	Hot	Cold	Hot	Cold
Copper	Green	Blue	Colourless	Brown-red
Iron	Brown-yellow	Pale-yellow	Bottle green	Bottle green
Chromium	Green	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet	Amethyst red	Grey	Grey
Nickel	Violet	Brown	Grey	Grey

Microcosmic salt bead test

This test is similar to borax bead test. When microcosmic salt is heated, a colourless transparent bead of sodium metaphosphate is formed.

$$\mathrm{Na(NH_4)HPO_4} \longrightarrow \underset{\substack{\text{Sodium}\\ \text{metaphosphate}}}{\mathrm{NaPO_3}} + \mathrm{NH_3} + \mathrm{H_2O}$$

Sodium metaphosphate combines with metallic oxides to form orthophosphates which are usually coloured. The shade of the colour gives a clue regarding the presence of metal.

Metal	Colour of the bead in			
	Oxidising-flame		Reducing-flame	
	Hot	Cold	Hot	Cold
Copper	Green	Blue	Colourless	Red
Iron	Yellow or reddish-brown	Yellow	Yellow	Colourless
Chromium	Green	Green	Green	Green
Manganese	Violet	Violet	Colourless	Colourless
Cobalt	Blue	Blue	Blue	Blue
Nickel	Brown	Brown		Grey

Test for acid radicals : Add dil. HCl or H_2SO_4 to a small amount of substanceand warm gently, observe.

Carbonate or CO_3^{2-} :

(i) Brisk effervescences of colourless gas CO_2; may be carbonate.

$$\mathrm{CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2\uparrow}$$

(ii) The gas turns lime water milky

$$\mathrm{CO_2 + Ca(OH)_2 \longrightarrow \underset{Milky}{CaCO_3}\downarrow + H_2O}$$

(iii) Excess of passage of gas through lime water is milkyness disappears

$$\mathrm{CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2(Soluble)}$$

Sulphite or SO_3^{2-} :

(i) Colourless gas with suffocating odour of burning sulphur; may be sulphite.

$$\mathrm{CaSO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + SO_2\uparrow}$$

(ii) The gas turns orange colour of acidic $K_2Cr_2O_7$ to green

$$\mathrm{\underset{Orange}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{Green}{Cr_2(SO_4)_3} + H_2O}$$

Note : CO_2 does not turns orange colour of acidic $K_2Cr_2O_7$ to green

Sulphide (S^{2-}) :

(i) The sulphide salts from H_2S which smells like rotten eggs.

$$\mathrm{Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S\uparrow}$$

(ii) On exposure to this gas, the lead acetate paper turns black due to the formationof lead sulphide.

$$Pb(CH_3COO)_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COOH$$

(iii) The sulphides also turn sodium nitroprusside solution violet (use sodium carbonate extract for this rest).

$$Na_2S + Na_2[FeNO(CN)_5] \longrightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COOH$$

Note : Sulphide of lead, calcium, nickel, cobalt antimony and stannic are not decomposed with dil. H_2SO_4. Conc. HCl should be used for their test. However, brisk evolution of H2S takes place even by use of dil. H2SO4 if a pinch of zinc dust is added.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

$$HgS + 2H \longrightarrow Hg + H_2S$$

Acetate (CH_3COO^-)

(i) Acetates decompose to give acetic acid vapours having characteristic smell of vinegar.

$$2CH_3COONa + H_2SO_4 \longrightarrow 2CH_3COOH + Na_2SO_4$$

(ii) All acetates are soluble in water and their aqueous solution on addition to neutral $FeCl_3$ solution develops a blood red colour due to the formation of ferric acetate.

$$FeCl_3 + 3CH_3COONa \longrightarrow \underset{\text{Blood red colour}}{(CH_3COO)_3Fe} + 3NaCl$$

Note :

1. The ferric chloride solution supplied in the laboratory is always acidic due to hydrolysis. It is made neutrla by the addition of dil. solution of NH_4OH drop by drop with constant stirring till the precipitate formed does not dissolve. The filtrate is called neutral ferric chloride solution.
2. Before testing acetate inthe aqueous solution by $FeCl_3$, it must be made sure that the solution does not contain,

   (i) CO_3^{2-} (ii) SO_3^{2-} (iii) PO_4^{3-} (v) I^-

   since these also combine will Fe^{+3}. Therefore the test of acetate should be performed by neutral ferric chloride solution only after the removal of these ions by $AgNO_3$ solution.

Chloride (Cl^-)

(i) Colourless pungent fumes of hydrogen chloride are evolved.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$

(ii) The gas evolved forms white fumes of ammonium chloride with NH_4OH.

$$NH_4OH + HCl \longrightarrow \underset{\text{White fumes}}{NH_4Cl} + H_2O$$

(iii) The gas evolved or solution of chloride salt forms a curdy precipitate of silver chloride with silver nitrate solution.

$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$$

(iv) Yellowish-green chlorine gas with suffocating odour is evolved on addition of MnO_2 to the above reaction mixture.

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

Note : The curdy precipitate of AgCl dissolves in ammonium hydroxide forming a complex salt.

$$AgNO_3 + 2NH_4OH \longrightarrow AgCl(NH_3)_2Cl + 2H_2O$$

(v) Chromyl chlorde test : When solid chloride is heated with conc. H_2SO_4 in presence of $K_2Cr_2O_7$, deep red vapours of chromyl chloride are evolved.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$CrO_3 + 2HCl \longrightarrow \underset{\text{Chromyl chloride}}{CrO_2Cl_2} + H_2O$$

These vapours on passing through NaOH solution, form the yellow solution due to the formation of sodium chromate.

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{Yellow colour}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

The yellow solution neutralized with acetic acid gives a yellow solution due to the formation of sodium chromate.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4} + 2CH_3COONa$$

Note :

1. This test is not given by the chloride of mercury, tin, silver lead and antimony.
2. The chromyl chloride test is a always to be performed in a dry test tube otherwise the chromyl chloride vapours will be hydrolysed in the test tube.

$$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$$

3. Bromides and iiodies do not give this test.

2. Bromide (Br^-)

(i) Reddish-brown fumes of bromine are formed.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + 2H_2O + SO_2$$

(ii) More reddish-brown fumes of bromine are evolved when MnO_2 is added

$$2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2$$

(iii) The aqueous solution of bromide or sodium carbonate extract gives pale yellow precipitate of silver bromide which partly dissolves in excess of NH_4OH forming a soluble complex.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow ppt.}}{AgBr\downarrow} + NaNO_3$$

$$AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2Br + 2H_2O$$

3. Iodide (I^-)

(i) Violet vapours of iodine are evolved.

$$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

(ii) Violet vapours with starch produce blue colour.

$$I_2 + \text{Starch} \longrightarrow \text{Blue colour}$$

(iii) More violet vapours are evolved when MnO_2 is added.

$$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$$

4. Nitrate (NO_3^-)

(i) Light brown fumes of nitrogen dioxide are evolved.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$2HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$$

(ii) These fumes intensify when copper turnings are added.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iii) Brown ring test : An aqueous solution of salt containing nitrate is mixed with freshly solution of salt solution and conc. H_2SO_4 is poured in test tube from sides, a brown ring is formed an account of the formation of a complex at the junction of two liquids.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

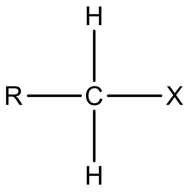
$$\underset{\text{Ferrous sulphate}}{[Fe(H_2O)_6]SO_4.H_2O} + NO \longrightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + 2H_2O$$

Class -12 Chemistry

Haloalkanes and Haloarenes

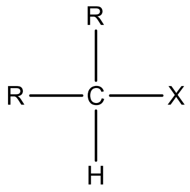
1. Introduction

The alkyl halides or halogenated alkanes are a group of compounds derived from alkanes that contain one or more halogens. They are commonly used as flame retardants, fire extinguishing agents, refrigerants, propellants, solvents, and drugs. Haloalkanes are roughly classified into three types based on the type of carbon atom to which the halogen atom is connected.



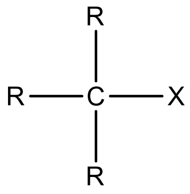
$$\begin{array}{c} H \\ | \\ R-C-X \\ | \\ H \end{array}$$

1° Primary



$$\begin{array}{c} R \\ | \\ R-C-X \\ | \\ H \end{array}$$

2° Secondary



$$\begin{array}{c} R \\ | \\ R-C-X \\ | \\ R \end{array}$$

3° Tertiary

X may be F, Cl, Br or I.

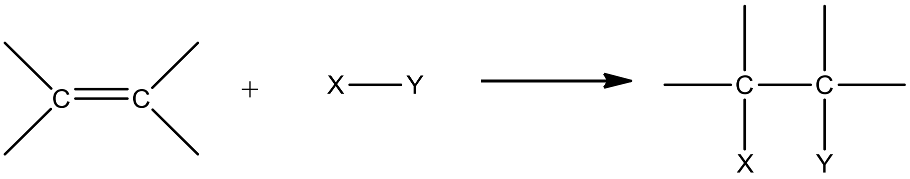
2. Reactions in organic chemistry

2.1 Depending on the reaction conditions and the attack reagents, various types of reactions can occur in organic compounds. There are 3 types of reactions in organic chemistry:

2.2 Addition Reaction

A new compound is formed by the reaction of two or more compounds. It is generally the attack of a reagent on a **π** bond.

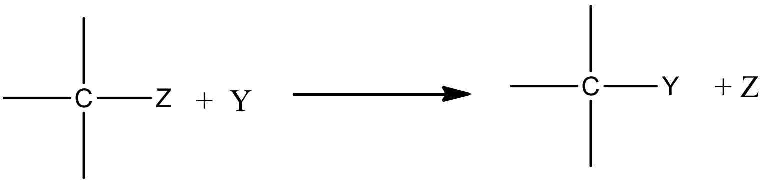
Example-1



2.3 Substitution Reaction

When a functional group attacks and replaces other functional group in a compound, the type of reaction is known as substitution reaction. The group which is replaced is called as the leaving group.

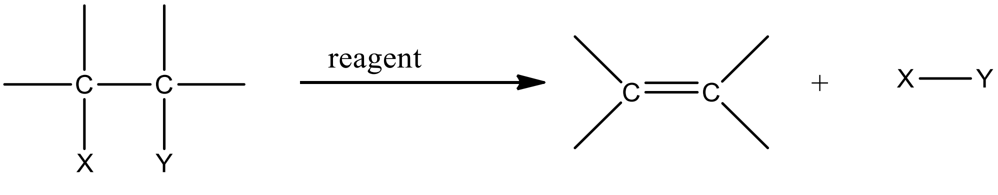
Example-2



2.4 Elimination Reaction

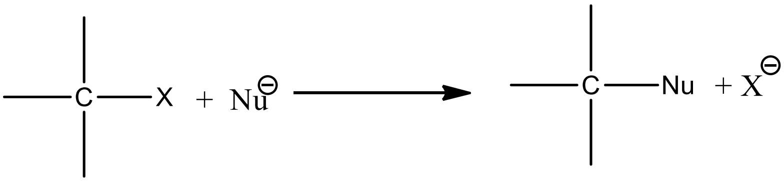
The reagent removes the groups (For example Hydrogen, Vicinal halides) present in ∝-β position to form an unsaturated compound.

Example-3



3. Nucleophilic substitutions reactions

Example-4

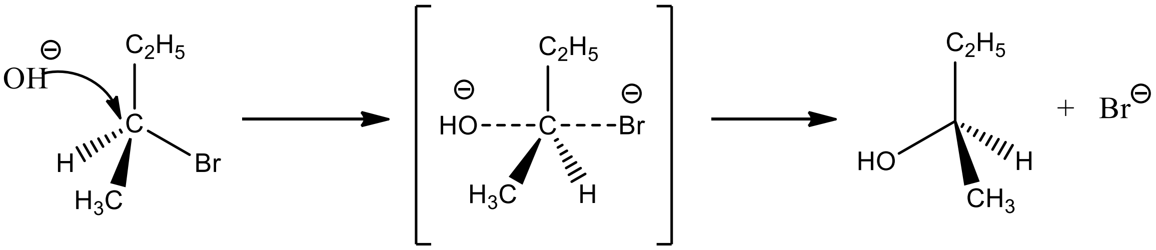


The replacement of halogen atom (leaving group) by the attacking nucleophile is called nucleophilic substitution reaction at sp^3 carbon. This reaction proceeds through two mechanism i.e. **S_N2** and **S_N1.**

3.1 Substitution Nucleophilic Bimolecular - S_{N^2}

Example-5

Key Features of S_{N^2} Mechanism



Transition state

Note:

1. Single step reaction.
2. Rate=k [RX] [Nu]
3. No intermediate is formed. Reaction proceeds through one sp^3d transition state where one bond breaks and one is formed simultaneously.
4. Rearrangement is not observed.
5. Inversion of configuration is observed
6. Order of reactivity of alkyl halides:

$CH_3X > 1^\circ > 2^\circ > 3^\circ$

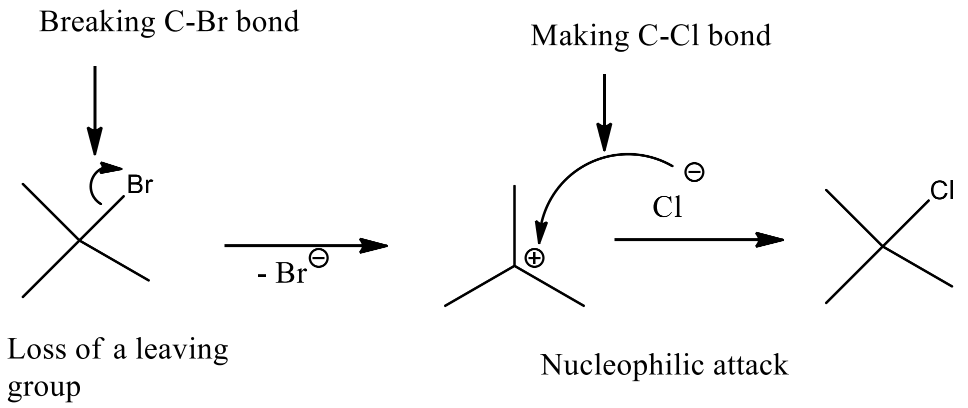
As the size increases steric hindrance increases, so there is difficulty in formation of transition state.

7. Favored by aprotic solvents.

3.2 Substitution Nucleophilic Unimolecular- S_{N^1}

Example -6

The S_N1 is a stepwise mechanism



Key features of S_{N^1} mechanism

1. It is a two-step reaction. First step involves formation of carbocation as well as its rearrangement such that carbocation is at most stable position, then nucleophile attacks the carbocation to form the final product which is the second step.

2. $\text{Rate} = k\,[\,RX\,]$

3. Intermediate is formed which is carbocation.

4. Rearrangement is commonly observed.

5. Racemic mixture is obtained.

6. Order of reactivity of alkyl halides:

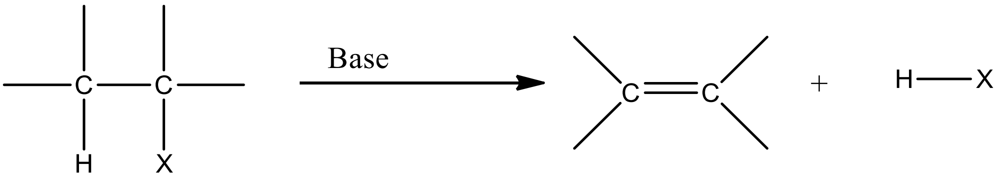
$3^\circ > 2^\circ > 1^\circ > CH_3X$

This can be attributed to the stability of the carbocation that is formed.

7. Favored by protic solvents.

4. Elimination Reactions

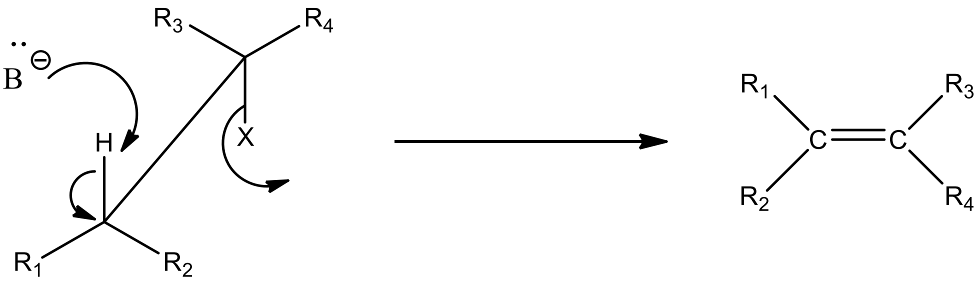
Example-7



The removal of adjacent hydrogen, a hydrogen and adjacent halide as well as vicinal halides to form unsaturated compound is generally called as elimination reaction. It proceeds via three kinds of mechanism.

4.1 Elimination Bimolecular- E2

Example-8



Key Features of E2 Mechanism

1. Single step reaction.

2. Rate=k [RX]

3. Single transition state with no intermediate.

4. No rearrangement

5. Strong bases are generally used as reagents.

6. Order or reactivity of alkyl halides:

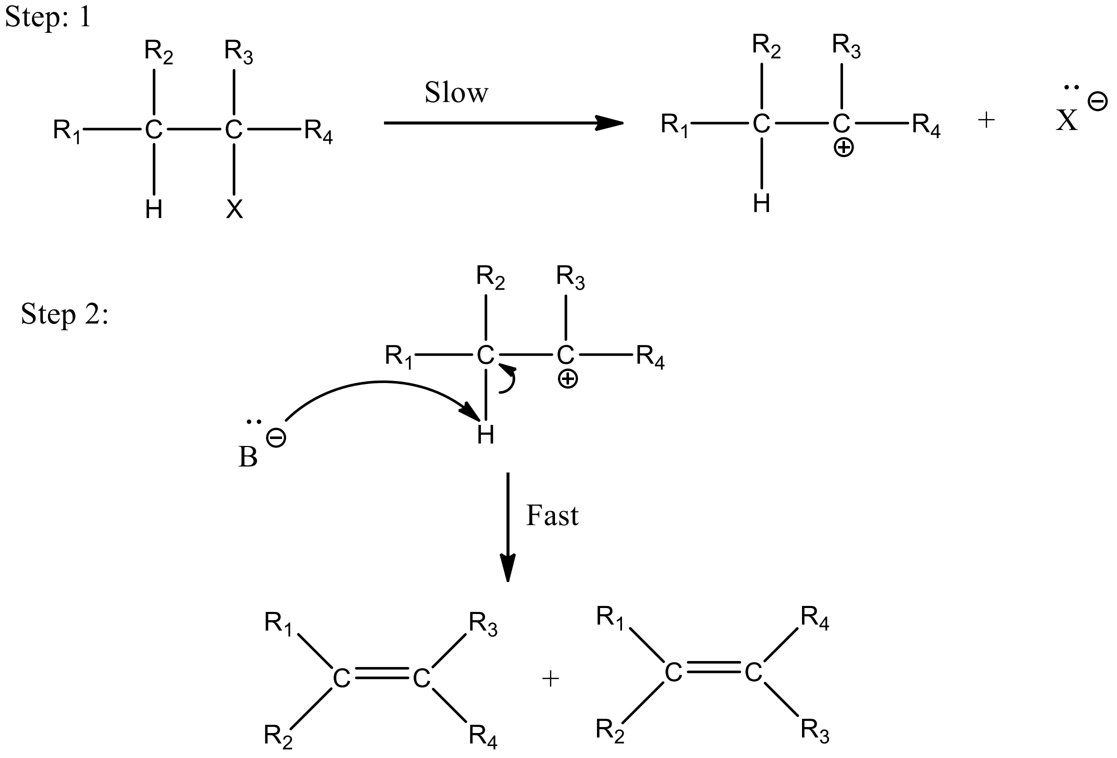
$3^{\circ} > 2^{\circ} > 1^{\circ}$

The number of alpha hydrogens will increase as we go from higher to lower alkene leading to alkene stability.

7. Favored by aprotic solvents.

4.2 Elimination Unimolecular-E1

Example-9



Key Features of E_1 Mechanism

1. It is a twostep reaction. First step involves formation of carbocation by loss of the leaving group and the second step is the deprotonation by using a nucleophilic base (generally weak).

2. $\text{Rate} = k[\text{RX}]$

3. Carbocation is formed as intermediate.

4. Rearrangement generally occurs until the carbocation is at its most stable position.

5. Observed in presence of weak bases.

6. Order or reactivity of alkyl halides:

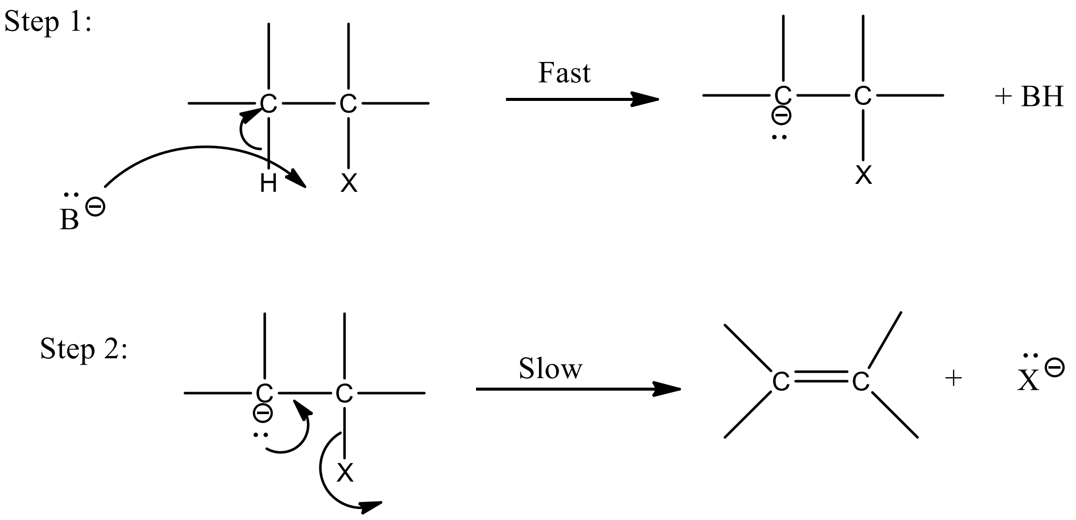
$3^{\circ} > 2^{\circ} > 1^{\circ}$

This can be attributed to the stability of carbocation formed as well as the stability of alkene formed.

7. Favored by protic solvents.

4.3 Elimination Unimolecular via Conjugate base E1cB

Example-10



Key Features of E1 Mechanism

1. It is a two-step reaction. First step is the formation of carbanion as intermediate and the second step is the loss of the leaving group.

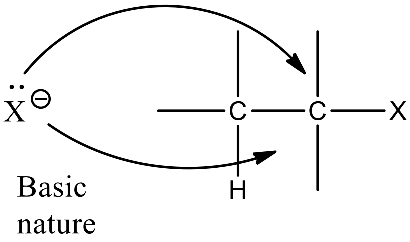
2. $\text{Rate} = k[\text{RX}][\text{Base}]$

3. Carbanion is formed as intermediate.

4. Occurs when a poor leaving group is present.

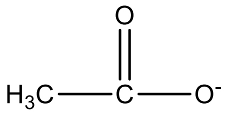
5. Substitution and elimination

There is some similarity between a base and nucleophile such that a base can also be a nucleophile. To get more insight on how elimination and substitution compete, we will analyze the properties of bases and nucleophiles:



5.1 Nucleophilicity vs Basicity

a. In the case of the same attacking group nucleophilicity and basicity is considered to be the same. Eg:



$$CH_3O^- > OH^- > H_3C-\overset{\overset{O}{\|}}{C}-O^-$$

b. Neutral nucleophiles are weaker than negatively charged nucleophiles. Eg:

$OH^- > H_2O$ Or $NH_2^- > NH_3$

c. Since larger atoms are more polarizable, the reason being the less attraction from the nucleus due to large size are better nucleophiles but these nucleophiles will be weak bases as they cannot form a strong bond with hydrogen atoms leading to strong conjugate acid formation. Also contrary to this strong base is the better nucleophile if the size of attacking groups is the same. e.g.

Acidic Strength:

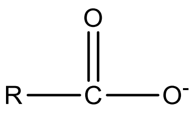
$CH_4 < NH_3 < H_2O < HF$

Basic Strength and Nucleophilicity:

${}^{0}CH_3 > {}^{0}NH_2 > {}^{0}OH > F^{0}$

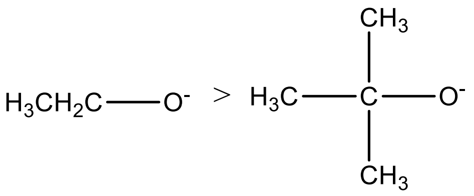
d. Nucleophilicity depends upon the nature of solvent if the sizes of attacking groups are different. However, Nucleophilicity is the same as basicity for gases.

e. With increase in stability of anion, nucleophilicity decreases.

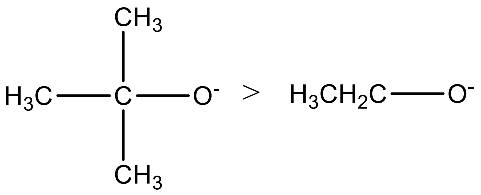


$R-\overset{\overset{O}{||}}{C}-O^-$ is a weaker nucleophile as it is resonance stabilized.

f. Nucleophilicity is controlled by steric factors



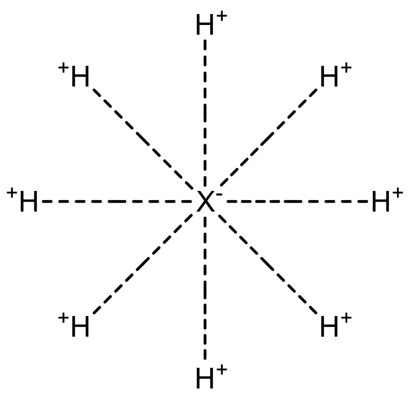
Nucleophilicity Order



Basicity Order

g. A strong base can be converted into a good leaving group. e.g.: Groups containing Oxygen such as hydroxide can be converted into a good leaving group in weak acid medium as it gets protonated and thus become a good leaving group.

h. Protic solvent: These solvents have a hydrogen atom attached to an atom of a strong electro-negative element (e.g. Oxygen). Molecules of protic solvent can, therefore form hydrogen bonds to nucleophiles as:



Small nucleophiles, which have a higher charge density than larger nucleophiles, are strongly solvated and this solvation prevents direct access to the nucleophilic center. Therefore, the smaller nucleophiles do not act as good nucleophiles like the larger nucleophiles. So, nucleophilicity is the opposite of basicity in protic solvents.

F^- Cl^- Br^- I^-

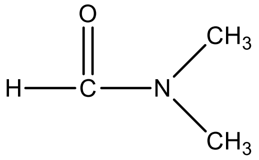
$\longleftarrow$

increasing basicity

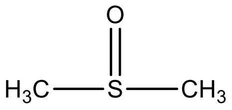
$\longrightarrow$

incresing nucleophilicity

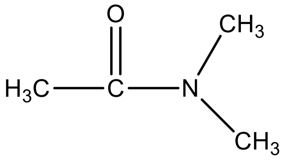
i. Aprotic solvents: Polar solvents that do not have H-atom, thus they are not able to form Hydrogen Bond. E.g.



N, N-Dimethyl formamide
(DMF)

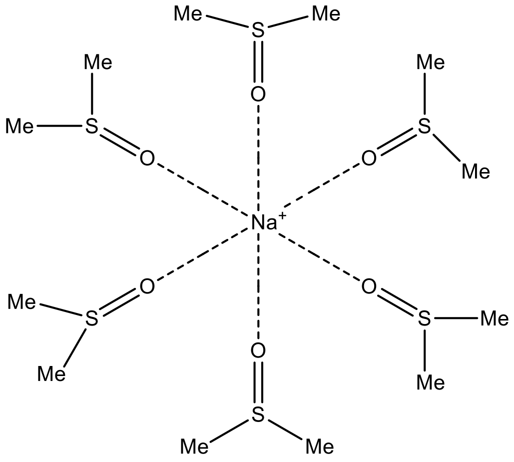


Dimethyl sulphoxide
(DMSO)



Dimethyl acetamide
(DMA)

These solvents dissolve ionic compounds and solvate the cations.



5.2 Saytzeff vs. Hoffmann Rule

According to position of double bond, two types of alkenes are formed and the rule that controls the position of bond are known as Saytzeff and Hoffman rule.

5.2.1 Saytzeff's Rule/Zaitsev Rule

According to this rule more stable alkene is formed, thus leading to formation of more substituted products. This reaction is said to be thermodynamically controlled

5.2.2 Hoffmann Rule

According to this less stable alkene should be formed, thus leading to formation of less substituted product. Here the product is formed by removal of more acidic β hydrogen, thus the reaction is said to be kinetically controlled.

5.3 Effect of Temperature

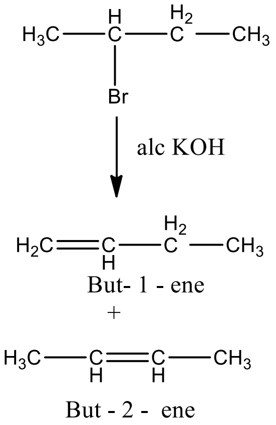
High temperature favours elimination while low temperature favours substitution reaction.

6. Stereochemistry

6.1 Regioselectivity

It is the preference of bond formation at a particular position or direction out of all the positions or directions that are present.

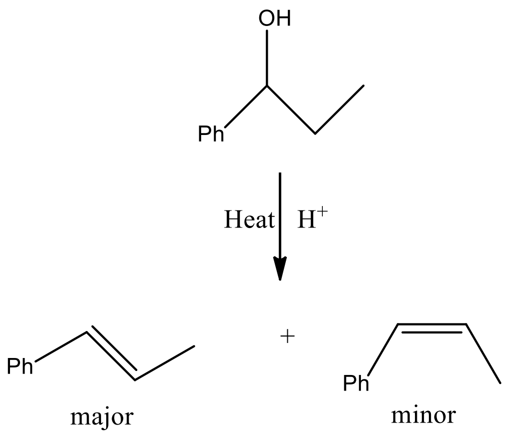
Example-11



6.2 Stereoselectivity

Stereoselective reactions are those reactions where the final product is a mixture of stereoisomers out of which one is the major and other is the minor product according to the reaction conditions. Either the pathway of lower activation energy (kinetic control) is preferred or the more stable product (thermodynamic control).

Example-12

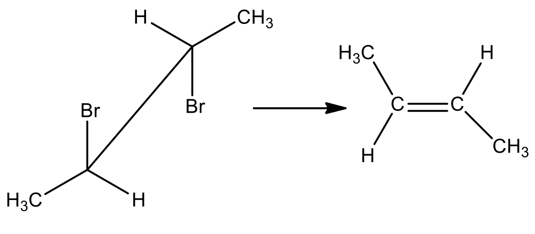


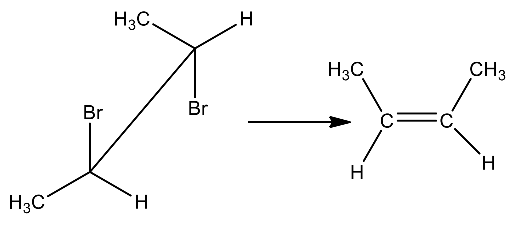
6.3 Stereospecificity

In this type of reactions, the initial reactant isomer decides the outcome of the reaction i.e. the final product is specified by the stereochemistry of the reactant.

The reaction gives a different diastereomer of the product from each stereoisomer of the starting material.

Example-13



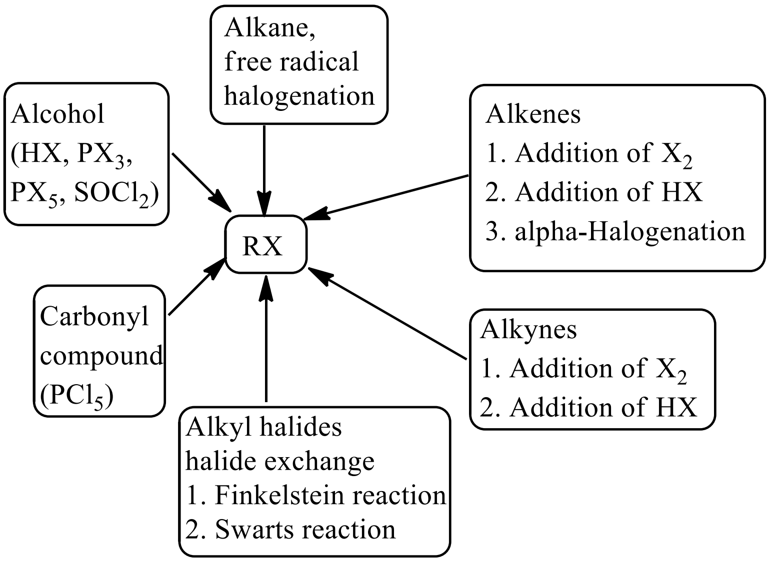


6.4 Chemoselectivity

If more than one type of functional groups are present, then the reagent attacks exclusively on a specific group leaving others as it is. Thesetypes of reactions are known as chemoselective reactions.

7. Alkyl Halides

7.1 Preparation of Alkyl Halides



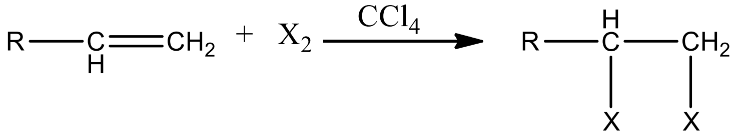
1. Alkanes

$$RH \xrightarrow{Cl_2} RCl + HCl$$

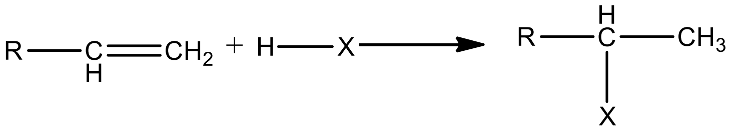
This method gives a mixture of mono, di and trihalides.

2. Alkenes

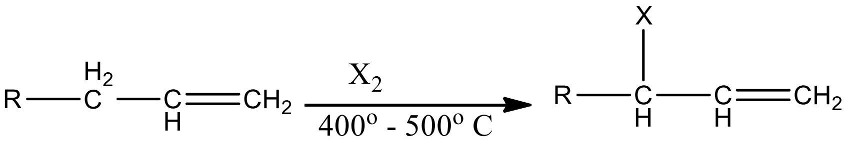
(i)

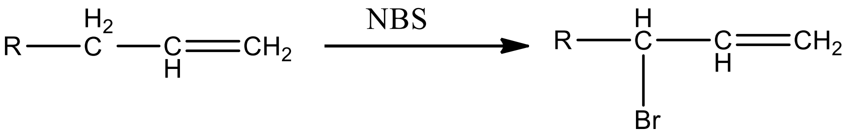


(ii)

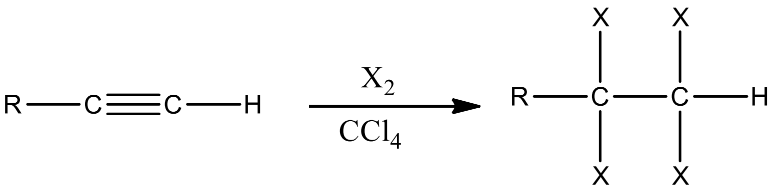


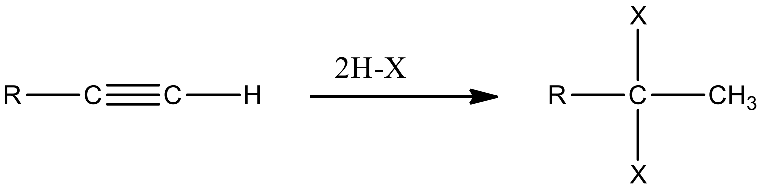
(iii)





3. Alkynes





4. Alkyl Halides

(i) Finkelstein Reaction

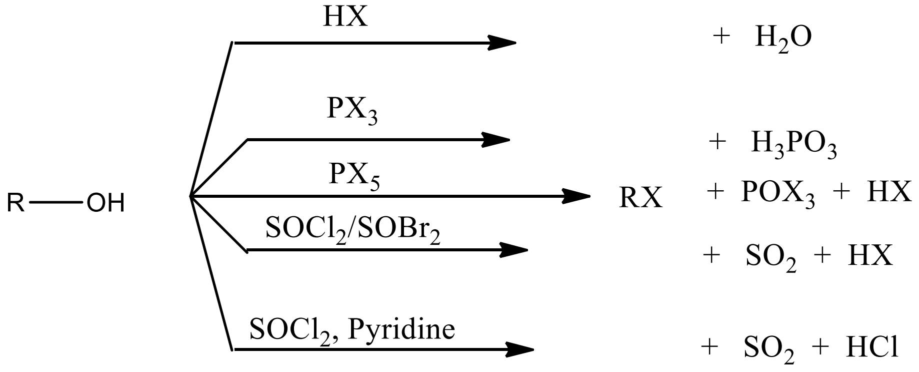
$\text{R-Br} + \text{NaI} \xrightarrow{\text{acetone}} \text{R-I} + \text{NaBr}$

$\text{R-Cl} + \text{NaI} \xrightarrow{\text{acetone}} \text{R-I} + \text{NaCl}$

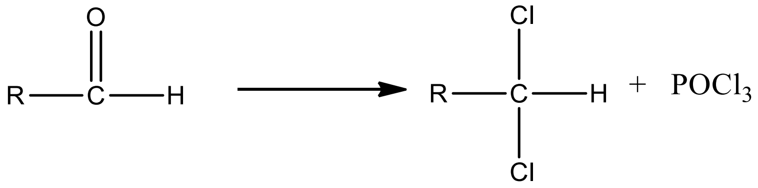
(ii) Swartz Reaction

$$\text{R-I/Br/Cl} + \text{AgF} \xrightarrow{\text{DMSO}} \text{R-F} + \text{AgI/Br/Cl}$$

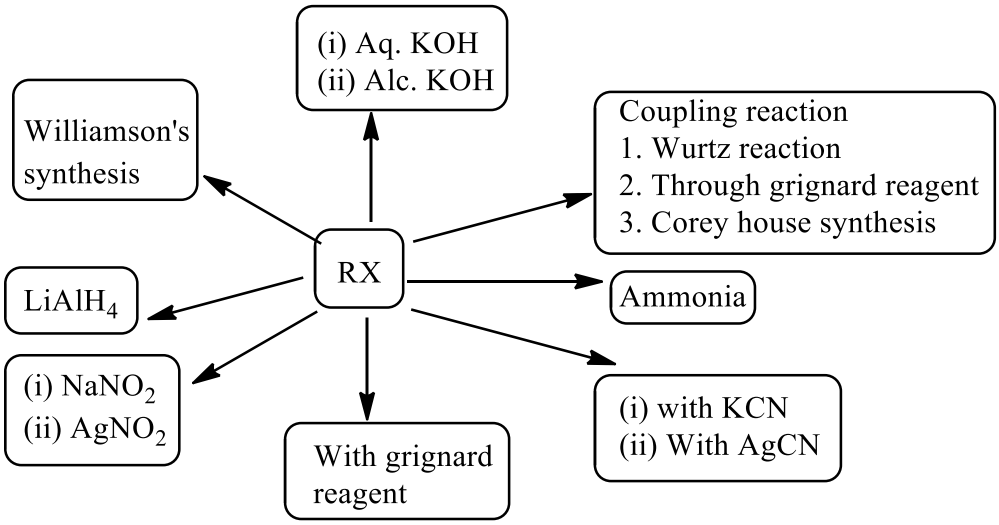
5. Alcohol



6. Carbonyl Compound



7.2 Reactions of Alkyl Halide



1. Coupling Reaction

(a) Wurtz Reaction

$$2\ RX + 2Na \xrightarrow{Et_2O} R\text{-}R + 2\ NaX$$

(b) Grignard Reagent

$$R\text{-}X + R\text{-}MgX \rightarrow R\text{-}R + MgX_2$$

(c) Corey-House Synthesis

$$R\text{-}X + 2\ Li \rightarrow R\text{-}Li + LiX$$

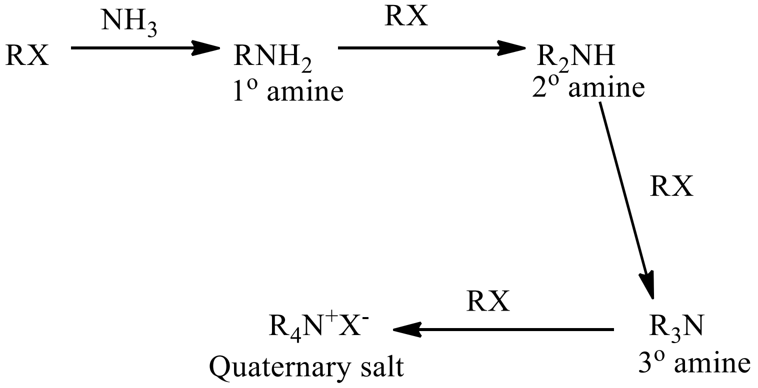
$$2\ R\text{-}Li + CuI \rightarrow R_2CuLi + LiI$$

$$R_2CuLi + R'\text{-}X \rightarrow R\text{-}R' + R\text{-}Cu + LiX$$

2. Amine Substitution

$$R\text{-}X + NH_3 \xrightarrow[\Delta]{C_2H_5OH} R\text{-}NH_2 + HX$$

Note: If alkyle halide is in excess, then 2° and 3° amines and even quaternary salts are also formed.



This reaction is called **Hofmann ammonolysis** of alkyl halides.

3. KCN

$$R\text{-}X + KCN \rightarrow R\text{-}CN + KX$$

4. AgCN

$$\text{R-X} + \text{AgCN} \rightarrow \text{R-N}\equiv\text{C}$$

5. $NaNO_2$

$$\text{R-X} + \text{NaNO}_2 \rightarrow \text{R-O-N=O} + \text{NaX}$$

6. $AgNO_2$

$$\text{RX} + \text{AgNO}_2 \rightarrow \text{R-NO}_2 + \text{AgX}$$

7. $LiAlH_4$

$$\text{R-X} + \text{LiAlH}_4 \rightarrow \text{R-H}$$

8. Williamson’s Ether Synthesis

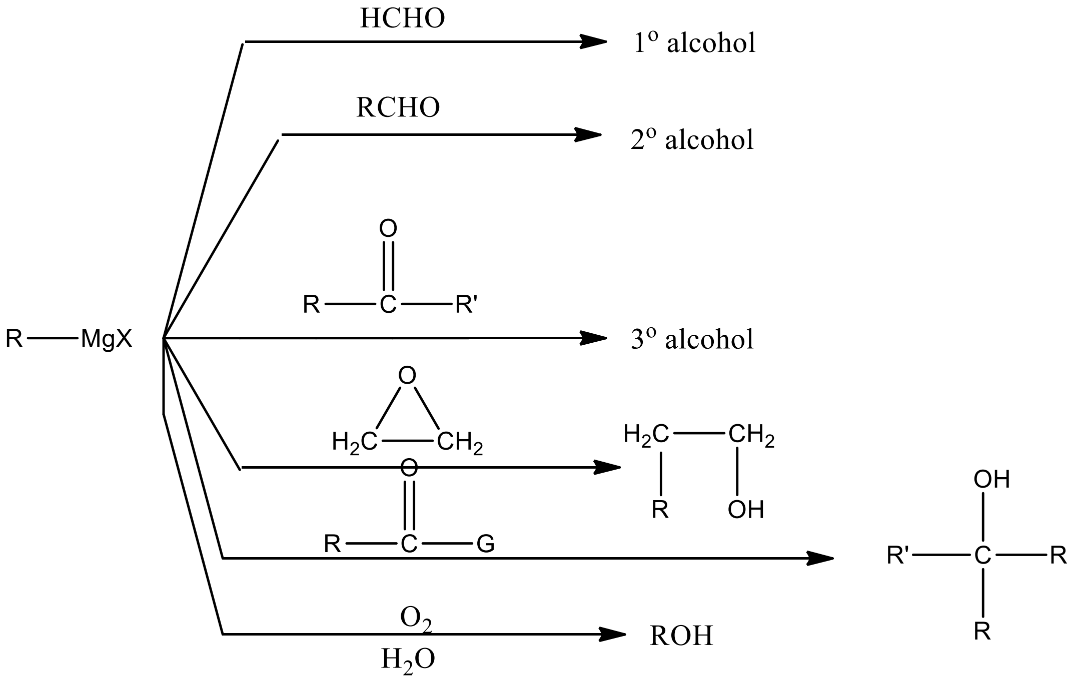
$$\text{R—X} + \text{R'—O—Na} \longrightarrow \text{R—O—R'}$$

9. Aq. KOH and Alc. KOH

$$\text{R-X} \xrightarrow{\text{aq. KOH}} \text{R-OH}$$

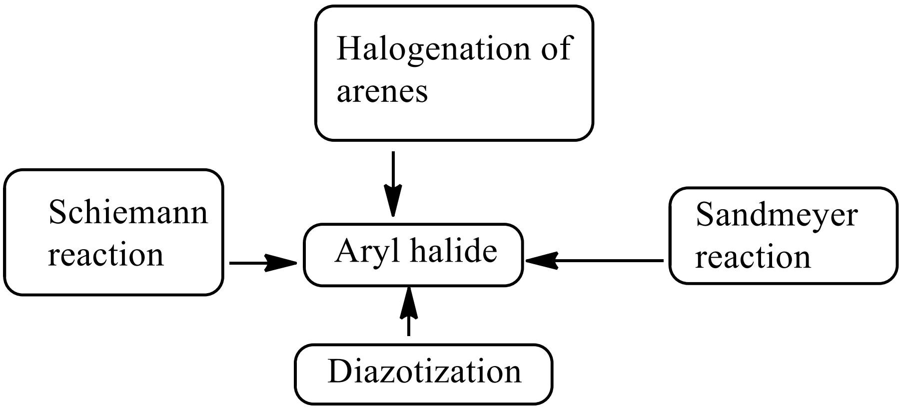
$$\text{R-X} \xrightarrow{\text{alc. KOH}} \text{alkene}$$

10. Reactions of R-MgX

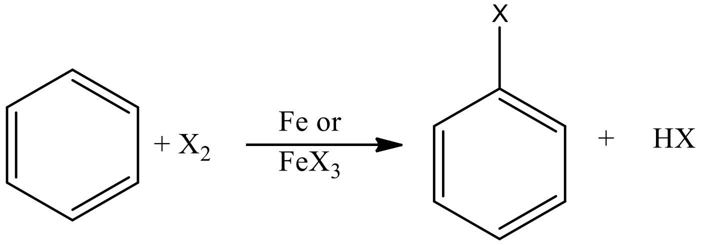


8. ArylHalide/Halorenes

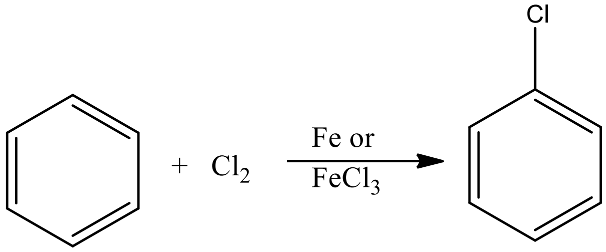
8.1 Preparation of Aryl Halide/Halorenes



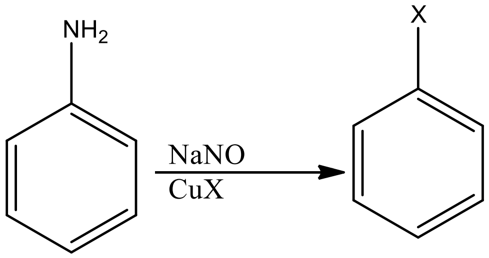
(a) Halogenation of Arenes



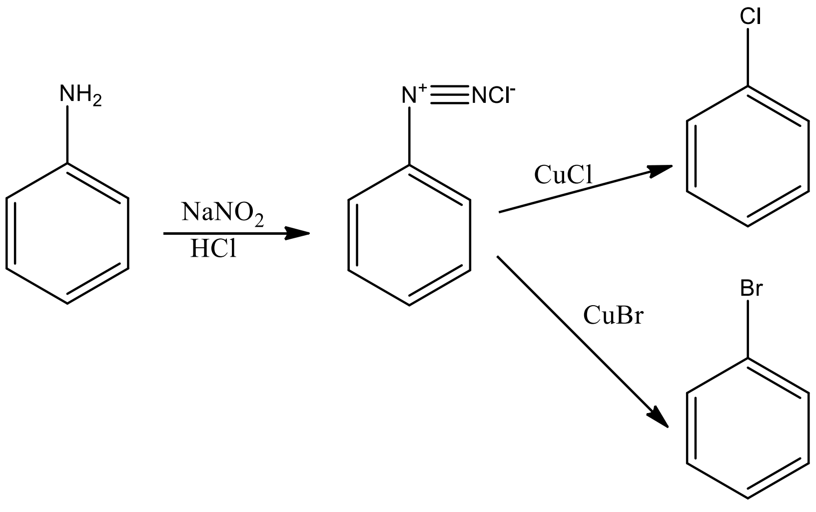
Example-14



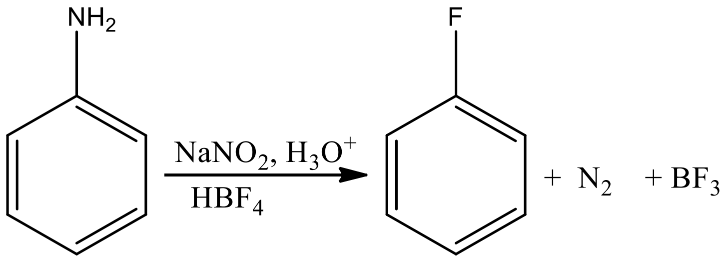
(b) Sandmeyer Reaction



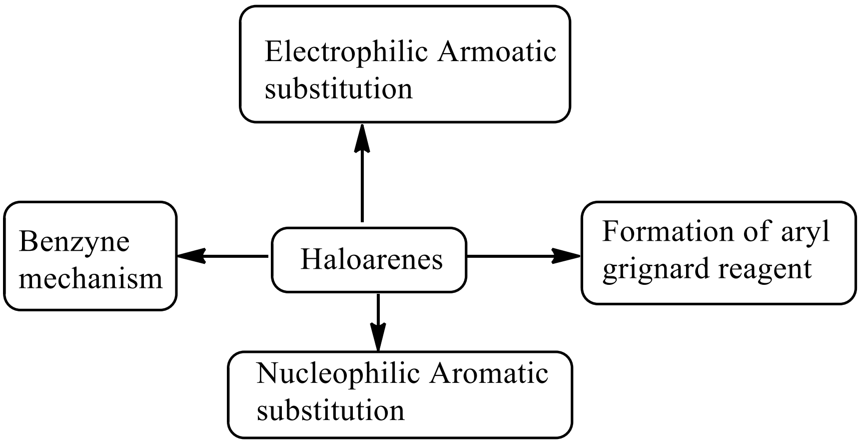
(c) Diazotiation



(d) Schiemann Reaction

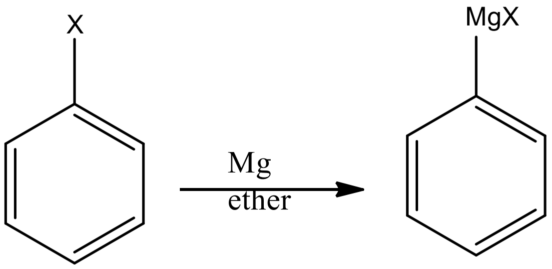


8.2 Reactions of Aryl Halide/Haloaranes

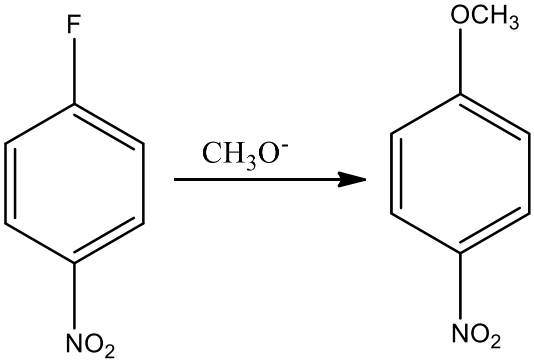


Electrophilic Aromatic Substitution Reaction: Halogens are weakly deactivating as they have strong induction effect and weak mesomeric effect. They are ortho/para directing.

(a) Formation of Aryl Grignard Reagent:

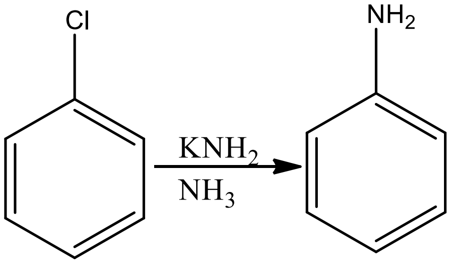


(b) S_NAr - Aromatic Nucleophilic Substitution Reaction



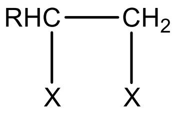
(c) Benzyne Mechanism(Elimination Addition Mechanism)

Strong bases such as Na, K and amide react readily with aryl halides.



9. Reactions of Special Alkyl Halides

9.1 Di-Halides

$RCHX_2$	Alkyidene Dihalides or Geminal Dihalides
 $RHC(X)-CH_2(X)$	Alkylene Dihalides or Vicinal(1,2) Dihalides

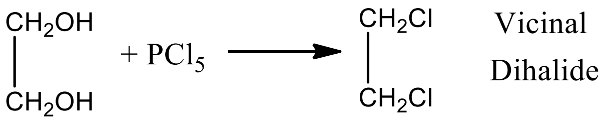
9.1.1 Preparation of:

(a) Halogenation of Alkenes and Alkynes

$CH_2{=}CH_2 + X_2 \rightarrow CH_2X\text{-}CH_2X$ (Vicinal Dihalide)

$CH{\equiv}CH + 2HX \rightarrow CH_3CHX_2$ (Geminal Dihalide)

(b) PCl_5 with Diols and Carbonyl Compounds



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + PCl_5 \longrightarrow \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$$

Vicinal Dihalide

$$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2$$ Gem Dihalide

9.1.2 Properties of some more reagents

(a) Alcoholic KOH: (Dehydrohalogenation)

$$XCH_2CH_2X \xrightarrow[KOH]{alcoholic} CH \equiv CH$$

$$CH_3CHX_2 \xrightarrow[KOH]{alcoholic} CH \equiv CH$$

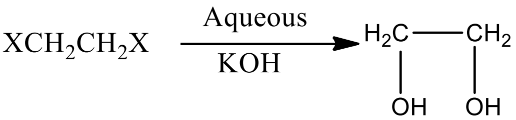
(b) Zinc Dust: (Dehalogenation)

$$XCH_2CH_2X \xrightarrow[Zn]{alcohol} CH_2{=}CH_2$$

$$CH_3CHX_2 \xrightarrow[Zn]{alcohol} CH_2{=}CH_2$$

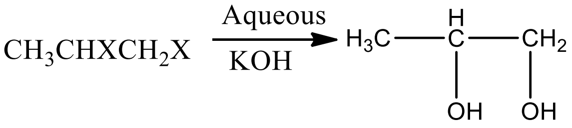
(c) Action of aq. KOH: (Alkaline Hydrolysis)

(i) Vicinal Dihalides



$$XCH_2CH_2X \xrightarrow[KOH]{Aqueous} \begin{matrix} H_2C & - & CH_2 \\ | & & | \\ OH & & OH \end{matrix}$$

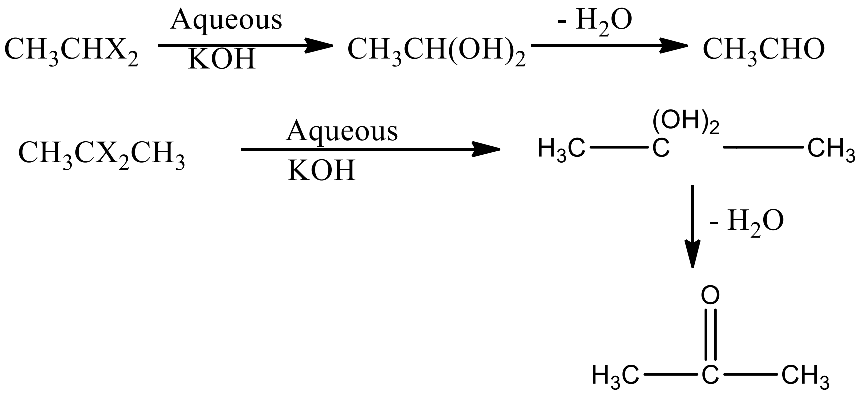
Ethylene Glycol



$$CH_3CHXCH_2X \xrightarrow[KOH]{Aqueous} \begin{matrix} & & H & & \\ H_3C & - & C & - & CH_2 \\ & & | & & | \\ & & OH & & OH \end{matrix}$$

Propan-1,2-diol

(ii) Gem Dihalides



Note: The above reaction is used to distinguish between gem and vicinal dihalides.

9.2 Tri- Halides and Tetra-Halides

$CHCl_3$ Chloroform (liquid)	$CHBr_3$ Bromoform (liquid)
CHI_3 Iodoform (yellow solid)	CCl_4 Carbon tetrachloride (liquid)

9.2.1 Chloroform: $CHCl_3$

(a) Preparation of chloroform

(i) Ethyl Alchohol: (using $NaOH/Cl_2$ or $CaOCl_2$)

$NaOH + Cl_2 \rightarrow NaOCl + HCl; NaOCl \rightarrow [\ O\ ]$

$C_2H_5OH \xrightarrow[\text{[O}]{}]Cl_2\ CH_3CHO \xrightarrow{Cl_2} CCl_3CHO + 3HCl$

$Ca(OH)_2$

$CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + Ca(HCOO)_2$

NaOH

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO \xrightarrow{\text{Hydrolysis}} CCl_3CH(OH)_2$$

$$CCl_3CH(OH)_2 \xrightarrow{\text{NaOH}} CHCl_3 + HCOONa + H_2O$$

Note: Pure form of chloroform is prepared from chloral b treating it with NaOH.

(ii) Methyl Ketones

$$CH_3COCH_3 + 3Cl_2 \rightarrow CCl_3COCH_3 \xrightarrow{Ca(OH)_2} CHCl_3 + (CH_3COO)_2Ca$$

(iii) Carbon Tetrachloride

$$CCl_4 + 2\ [\,H\,] \xrightarrow[\text{HCl}]{\text{Fe} + H_2O} CHCl_3 + HCl$$

(iv) Chlorination of Methane (Reaction Temperature = $370^{\circ}C$)

$$CH_4 + 3\ Cl_2 \xrightarrow[\text{Diffused Sunlight}]{370^{o}C} CHCl_3 + 3HCl$$

(b) Reactions

(i) Oxidation

Chloroform in presence of light and air (O_2) froms a highly poisonousgas, Phosgene.

$$2CHCI_3 + O_2 \xrightarrow{\text{light}} 2\ COCl_2 + 2\ HCl$$

To prevent the decomposition of chloroform 1% ethanol is added and chloroform is stored in brown bottle.

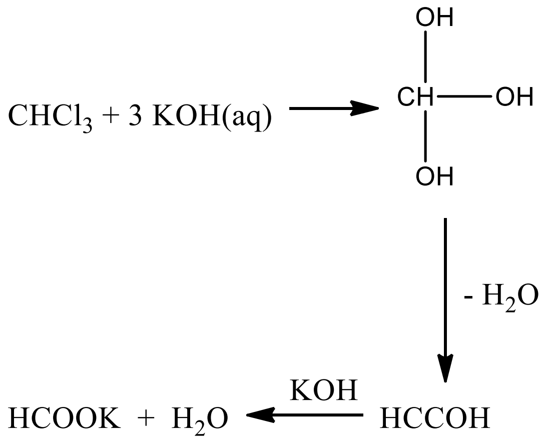
(ii) Carbylamine Reaction

$$RNH_2 + CHCl_3 + 3\ KOH \rightarrow RNC + 3H_2O + 3KCl$$

$$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3H_2O + 3KCl$$

This reaction is used as a test of primary aliphatic as well as secondary amines since carbylamines gives a pungent odour.

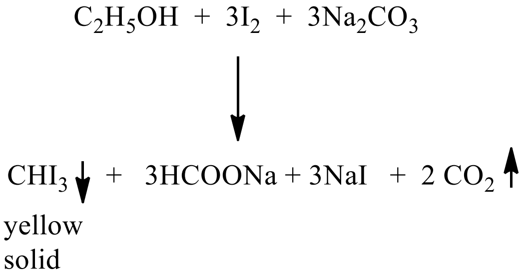
(iii) Hydrolysis



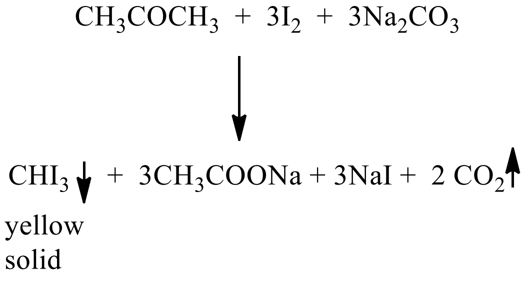
$$CHCl_3 + 3\,KOH(aq) \longrightarrow CH(OH)_3 \xrightarrow{-H_2O} HCOOH \xrightarrow{KOH} HCOOK + H_2O$$

9.2.2 Iodoform: CHI_3

(a) Preparation



$$C_2H_5OH + 3I_2 + 3Na_2CO_3 \longrightarrow CHI_3\downarrow + 3HCOONa + 3NaI + 2\,CO_2\uparrow$$



$$CH_3COCH_3 + 3I_2 + 3Na_2CO_3 \longrightarrow CHI_3\downarrow + 3CH_3COONa + 3NaI + 2\,CO_2\uparrow$$

Note- This above reaction is an important reaction used in practical chemistry which is known as Iodoform reaction. Iodoform is a yellow coloured solid. It is used to identify groups connected with $R-CH_3$ type of group such as ethyl alcohol, acetaldehyde, secondary alcohol, 2-ketones, $R(CH_3)CHOH$ (methyl alkyl carbinol) and methyl ketones ($RCOCH_3$), because all these form iodoform. The minor product of the iodoform reaction, sodium carboxylate is acidified to produce carboxylic acid (RCOOH).

9.2.3 Carbon Tetrachloride : CCl_4

(a) Preparation:

$$CH_4 + 4Cl_2 \xrightarrow[\text{diffused}]{hv} CCl_4 + 4HCl$$

$$CS_2 + 3Cl_2 \xrightarrow[Fe/I_2]{AlCl} CCl_4 + S_2Cl_2$$

Dfractional distillation is used to separate S_2Cl_2 . It is then treated with more CS_2 to give CCl_4. C washed with NaOH and distilled to obtain pure CCl_4.

$$2S_2Cl_2 + CS_2 \rightarrow CCl_4 + 6S$$

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[\text{70-100atm}]{400^oC} CCl_4 + HCl + C_2Cl_6$$

Note CCl_4 is a colourless and poisonous liquid which is insoluble in H_2O

It is a good solvent for grease and oils. CCl_4 is used in fire extinguisher for electric fires as Pyrene. It is also an insecticide for hookworms.

(b) Reactions:

(i) Oxidation

$$CCl_4 + H_2O \xrightarrow{500^oC} COCl_2 + 2HCl$$

(ii) Reduction

$$CCl_4 + 2[H] \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(iii) Hydrolysis

$$\begin{tikzcd}
CCl_4 + 4KOH \arrow[r] & C(OH)_4 \arrow[d] \\
K_2CO_3 + H2O & CO_2 \arrow[l, "2KOH"']
\end{tikzcd}$$

(iv) Action of HF

$CCl_4 + 4HF \xrightarrow{SbF_6} CCl_2F_2 + 2HCl$

9.2.4 Vinyl Chloride: $CH_2{=}CHCl$

Vinyl group $CH_2{=}CH-$

(a) Preparation

(i) $CH \equiv CH + HCl \rightarrow CH_2{=}CHCl$

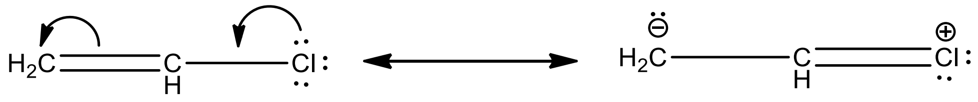
(ii) $ClCH_2CH_2Cl \xrightarrow{KOH(alc.)} CH_2{=}CHCl + KCl + H_2O$

(iii) $CH_2{=}CH_2 + Cl_2 \xrightarrow{600^oC} CH_2{=}CHCl + HCl$

(b) Reaction

$CH_2{=}CHCl + alc.KOH \rightarrow CH \equiv CH + HCl$

Vinyl Chloride is stable due to extended resonance of double bond with the halogen atom, So it does not undergo nucleophilic substitution.



9.2.5 Allyl chloride : $H_2C{=}CHCH_2Cl$

(a) Preparation

(i) $H_2C{=}CHCH_3 + Cl_2 \xrightarrow{500\text{-}600^oC} CH_2{=}CHCH_2Cl$

(ii) $CH_2{=}CHCH_2OH{+}PCl_5 \rightarrow CH_2{=}CHCH_2Cl + POCl_3{+}HCl$

(b) Reactions

(i) Addition Reactions

$CH_2{=}CH\text{-}CH_2Cl + Cl_2 \rightarrow CH_2ClCHClCH_2Cl$

$CH_2{=}CH\text{-}CH_2Br + HBr \rightarrow CH_3CHBrCH_2Br$

The addition follows Markonikov's rule. However in presence of peroxides, 1,3-dibromopropane is formed.

(ii) Nucleophilic Substitution Reactions

Since in allyl chloride, there is no resonance (unlike in vinyl chloride), nucleophilic substitution reactions take place with ease.

$$CH_2{=}CH\text{-}CH_2Cl \xrightarrow{KOH(aq)} CH_2{=}CHCH_2OH + KCl$$

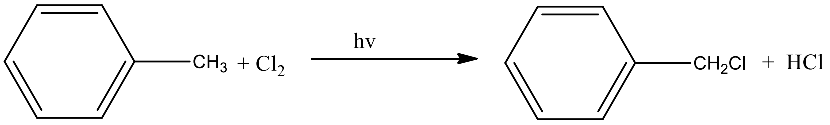
$$CH_2{=}CH\text{-}CH_2Cl \xrightarrow{NH_3} CH_2{=}CHCH_2NH_2 + HCl$$

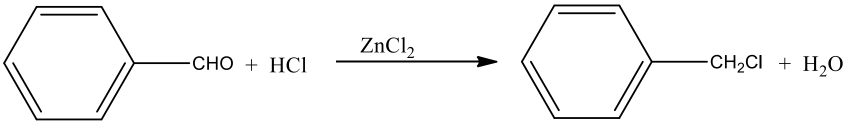
$$CH_2{=}CH\text{-}CH_2Cl \xrightarrow{KCN} CH_2{=}CHCH_2CN + KCl$$

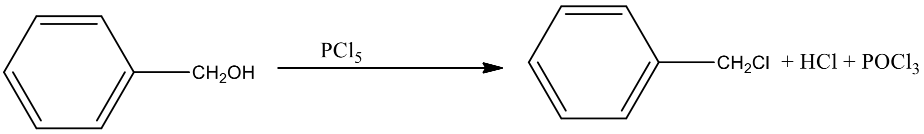
$$CH_2{=}CH\text{-}CH_2Cl + Mg \xrightarrow{\text{Dry ether}} CH_2{=}CHCH_2MgCl$$

9.2.6 Benzyl Chloride: $C_6H_5CH_2Cl$: $PhCH_2Cl$

(a) Preparation

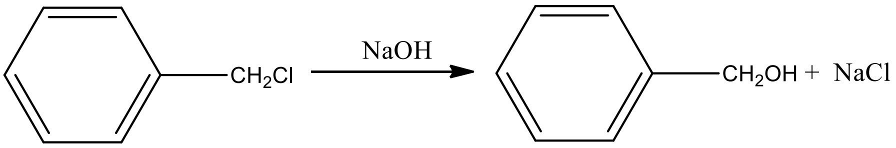


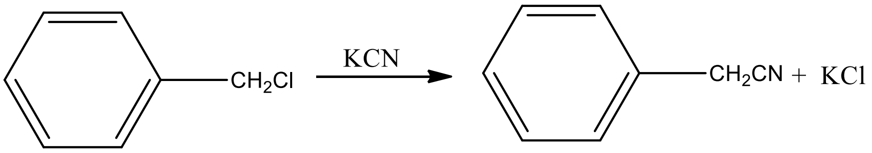


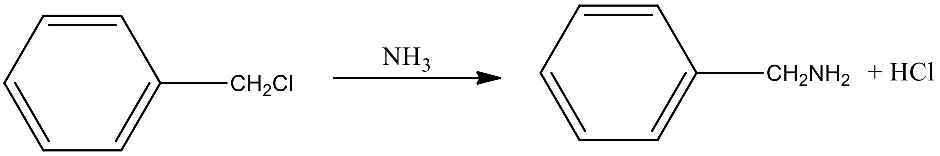


(b) Reactions

Benzyl halide undergo unimolecular nucleophilic substitution as the carbocation i.e. formed by loss of Chlorine is highly stable due to extended resonance, so the nucleophilic substitution easily takes place when compared to aryl halides.

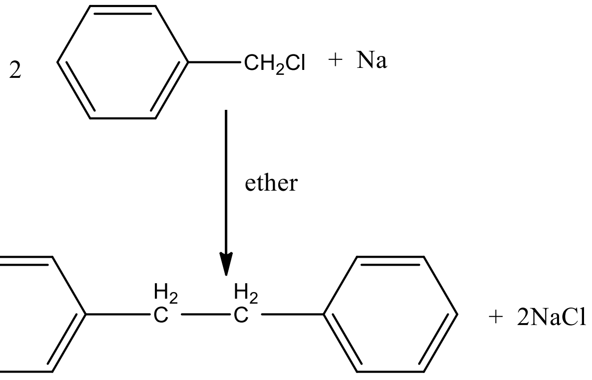




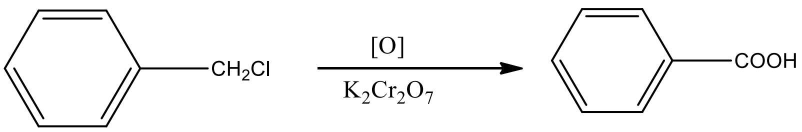


(i) Wurtz Reaction

Proceeds via free radical mechanism.



(ii) Oxidation



10. Chemistry of Grignard Reagent: R-Mg-X

10.1 Preparation

$$RX + Mg \xrightarrow[\text{ether}]{\text{reflux in}} R\text{-}Mg\text{-}X$$

Note: In preparation of Grignard reagent we can have any hydrocarbon group, it will not effect the reaction mechanism

10.1 Reactions

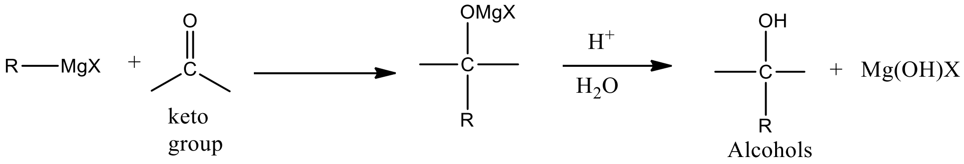
(a) Grignard reagent as a base reacts with compounds containing active H to give alkanes.

$$\text{R-MgI} + \text{HOH} \rightarrow \text{RH} + \text{Mg(OH)I}$$

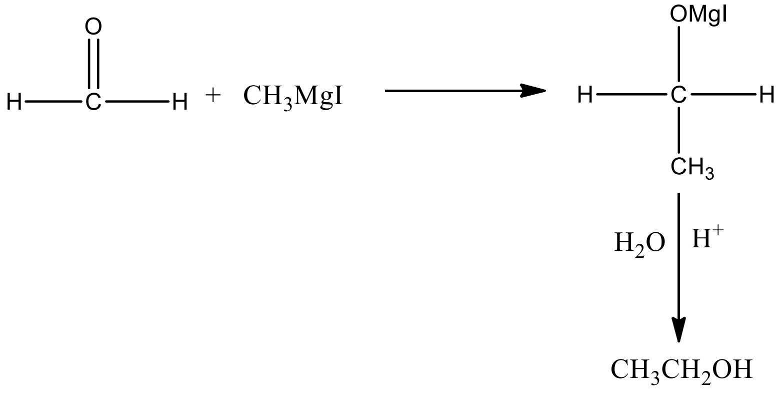
$$\text{R-MgI} + \text{R'OH} \rightarrow \text{RH} + \text{Mg(OR')I}$$

$$\text{R-MgI} + \text{R'NH-H} \rightarrow \text{RH} + \text{Mg(NHR')I}$$

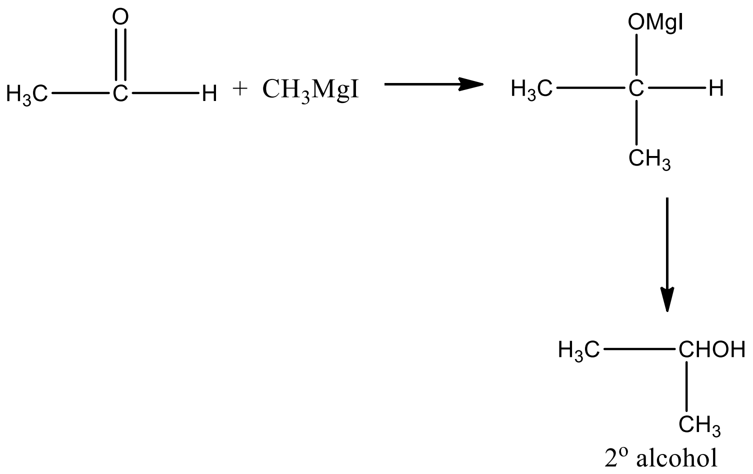
(b) Grignard reagent acts a strong nucleophile and shows nucleophilic additions to give various products. Alkyl group being electron rich (carbonian) acts as nucleophile in Grignard reagent.



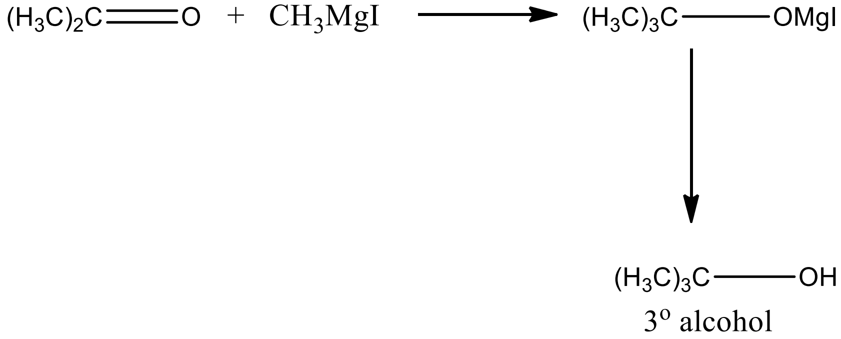
Example-15



Example-16

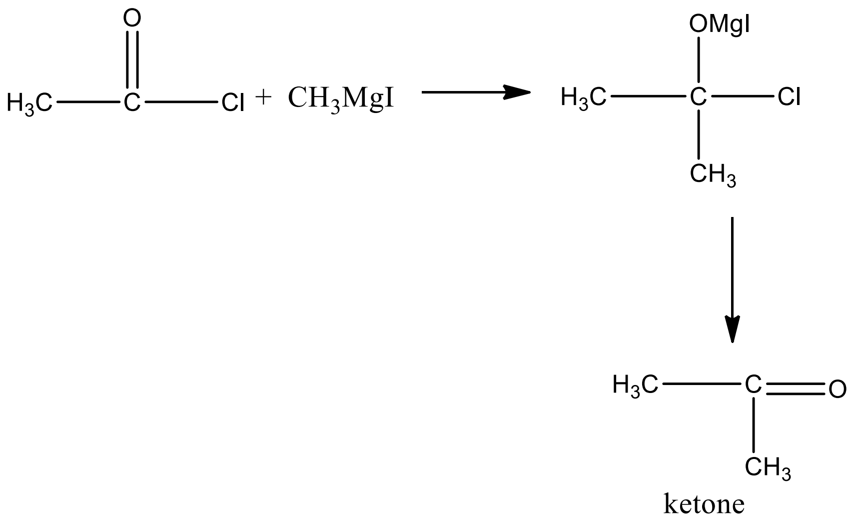


Example-17



(c) Acid Chloride

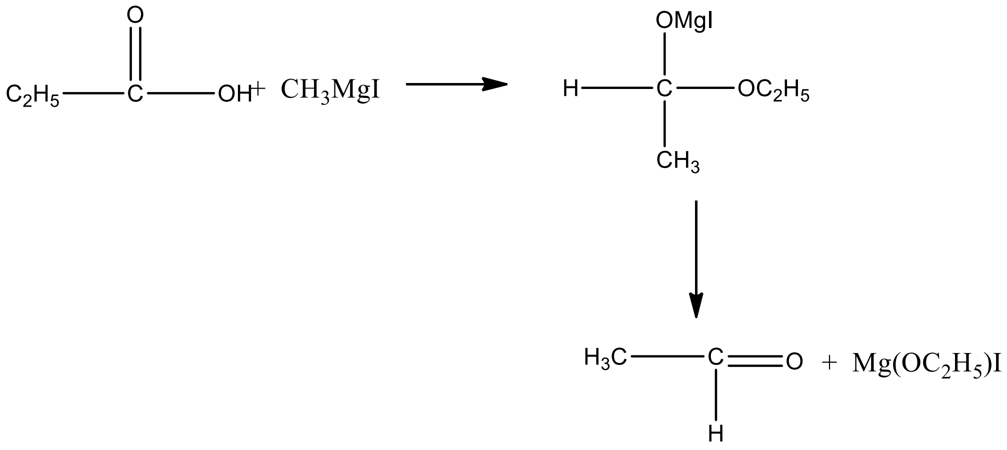
Example-18



Ketones (acetone) fromed further reacts with Grignard reagent to from 3° alcohols (tert. Butyl alcohol). However, with 1:1 mole ratio of acid halide andGrignard Reagent, one can prepare ketones.

(d) Esters

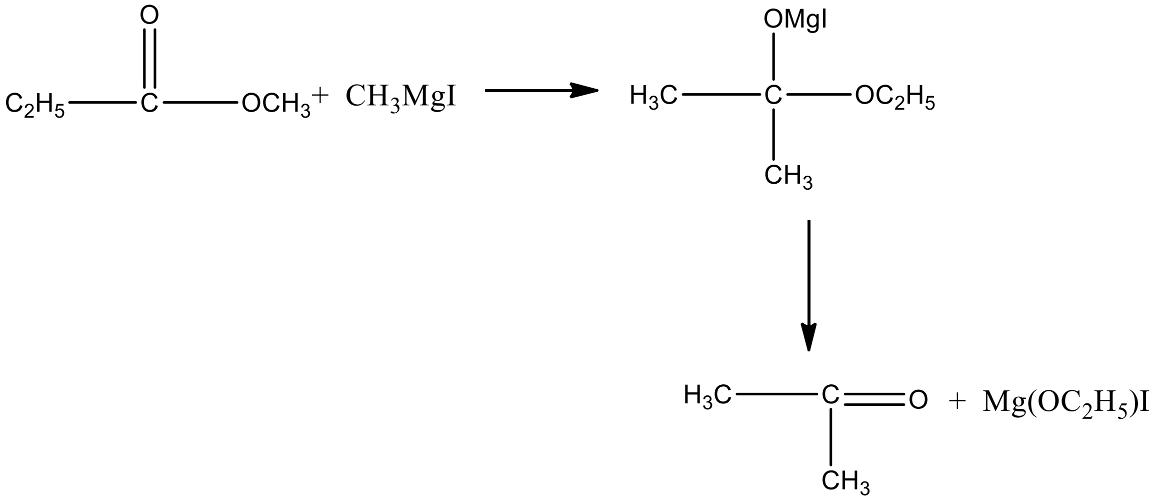
Example-19



Aldehyde

The further reaction of aldehyde with CH_3MgI will give secondary alcohol as the final product.

Example-20

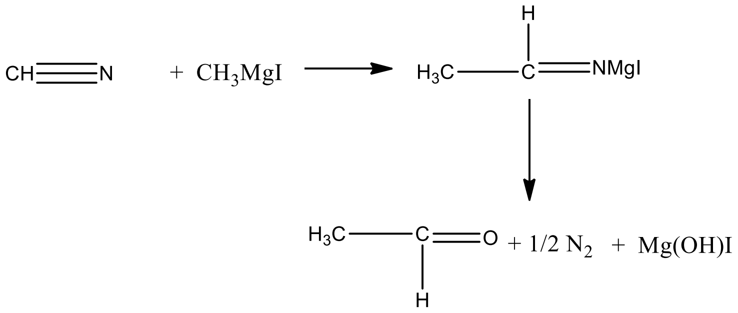


Ketone

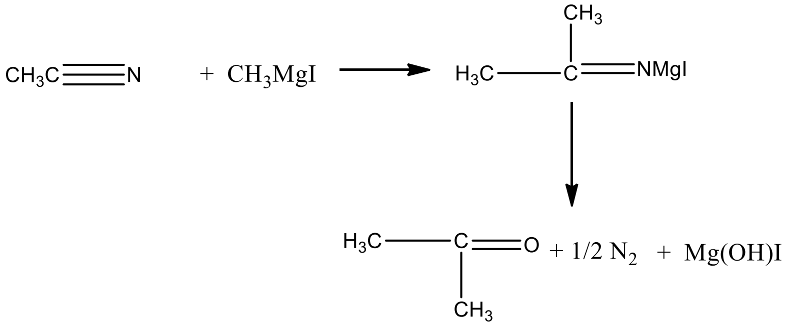
The ketones react further with CH_3MgI to give 3° alchohol, if present in excess. But 1:1 mole ratio of reactants will certainly give ketones.

(e) Cyanides

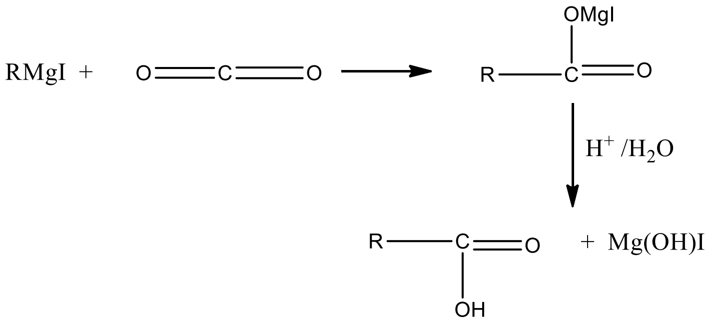
Example-21



Example-22

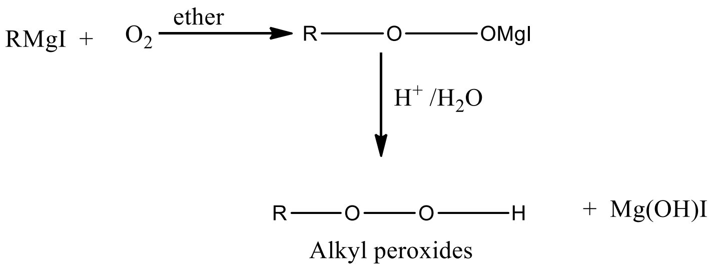


(a) CO_2

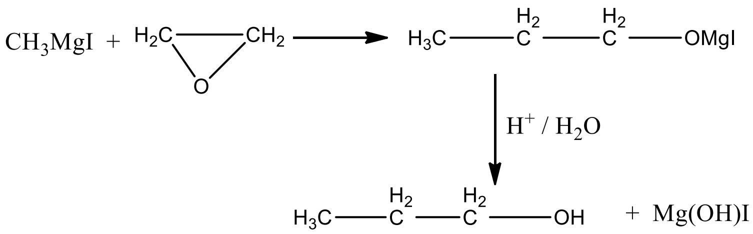


Carboxylic acid

(b) Oxygen



(c) Ethylene Oxide (Oxiranes)



(d) Alkynes

$$CH_3C\equiv C\text{-}H + CH_3MgI \rightarrow CH_3C\equiv C\text{-}MgI + CH_4$$

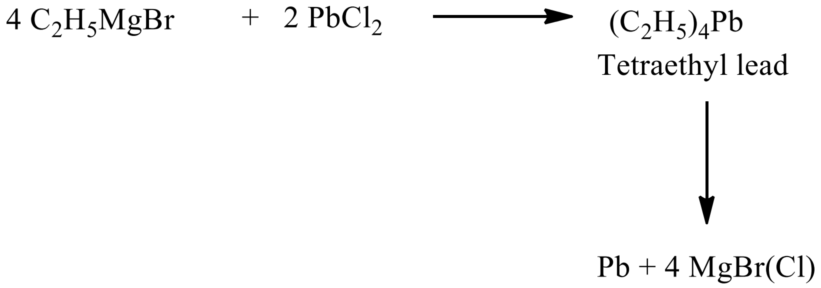
$$CH_3C\equiv C\text{-}MgI + CH_3I \rightarrow CH_3C\equiv C\text{-}CH_3 + MgI_2$$

(e) Alkyl Halides

$$R\text{-}MgI + CH_3CH_2Br \rightarrow CH_3CH_2R + Mg(Br)I$$

$$CH_3MgBr + CH_2{=}CHCH_2Br \rightarrow CH_3CH_2R + MgBr_2$$

(f) Inorganic Halides

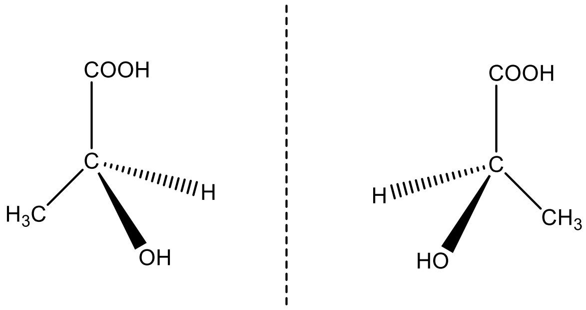


11. Some Important Concepts in Organic Chemistry:

- **Optical Activity:** The property due to which some compounds are able to rotate the plane of plane-polarised light when it is passed through their solution.

- **chirality and enantiomers:** The compounds when they are optically active are known as chiral molecule and they exist in pair such that they are mirror images of each other also known as enantiomers. If a mixture have enantiomers in equal quantity, then the mixture will have zero optical rotation and such mixtures are known as **racemic mixtures** and process of making such mixtures is known as **racemisation**.

Eg:

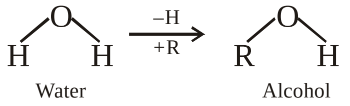


- **Retention:** The property due to which some elements are able to maintain both their absolute and relative configuration and position in space. In simple word the configuration of the stereocenter remains unchanged.

- **Inversion:** Here the absolute and relative configurations becomes reverse of each other which means their symmetry becomes different than what was it before.

ALCOHOL PHENOL ETHER

- Alcohols are derivatives of water molecule replacing one hydrogen atom by an alkyl group



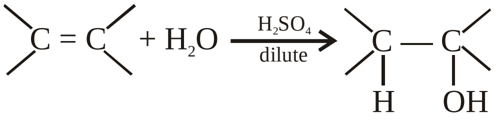
An alcohol is a compound containing one or more hydroxyl group (OH) directly attached to aliphatic carbon atoms.

The simplest alcohol is methyl alcohol, (CH_3OH) also called carbinol.

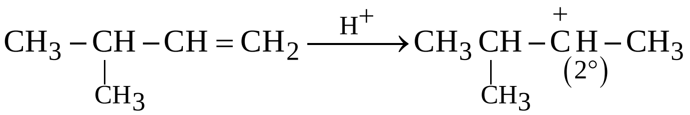
• GENERAL METHODS OF PREPARATION OF ALCOHOLS

(A) From alkanes by hydration (addition of water)

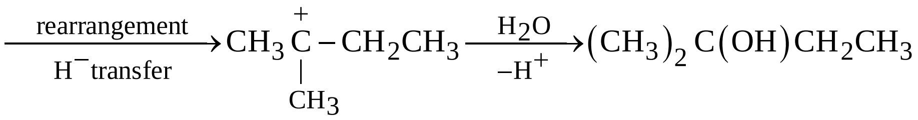
(i)



Acid catalyzed hydration follows Markonikov's rule but rearrangement may also take place. e.g.,

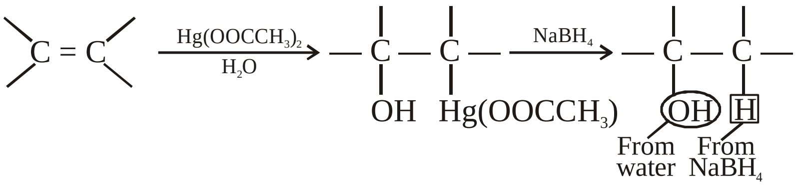


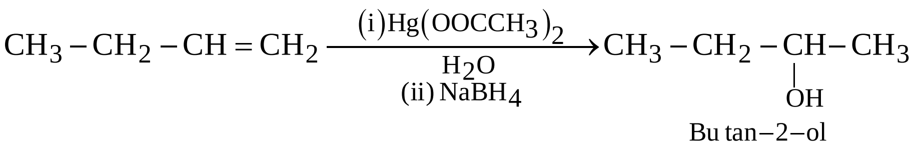
$$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH=CH_2\xrightarrow{H^+}CH_3\underset{\substack{|\\CH_3}}{CH}-\overset{+}{C}H-CH_3\;(2^\circ)$$



$$\xrightarrow[H^-\,\text{transfer}]{\text{rearrangement}}CH_3\underset{\substack{|\\CH_3}}{\overset{+}{C}}-CH_2CH_3\xrightarrow[-H^+]{H_2O}(CH_3)_2C(OH)CH_2CH_3$$

(ii) Hydration using mercuric acetate/$NaBH_4$ (oxymercuration-demercuration) follows Markovnikov's rule but no rearrangement.





$$CH_3-CH_2-CH=CH_2\xrightarrow[\substack{H_2O\\(ii)\,NaBH_4}]{(i)\,Hg(OOCCH_3)_2}CH_3-CH_2-\underset{\substack{|\\OH}}{CH}-CH_3$$

Bu tan−2−ol

(iii) Hydroboration oxidation using B_2H_6/H_2O_2 & OH^-, addition of water takes place according to anti Markonikov's rule

$$\underset{\text{Propene}}{CH_3-CH=CH_2}\xrightarrow{(BH_3)_2}\underset{\text{Trialkyl borane}}{(CH_3-CH_2-CH_2)_3-B}\xrightarrow[OH^-]{H_2O_2}\underset{\text{Propan}-1-\text{ol}}{CH_3CH_2CH_2OH}$$

(B) Reduction method

(i) $\left.\begin{array}{l} R-CHO \\ R-COCl \\ R-COOH \end{array}\right] \rightarrow$ All on reduction with $LiAlH_4 / H_2O$ or H_2 / Pd gives primary alcohols

While ketone RCOR' yields secondary alcohols.

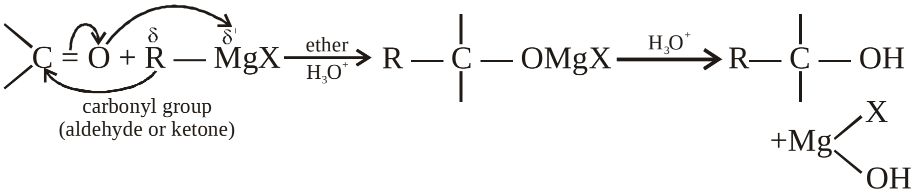
$NaBH_4$, reduces only aldehyde, ketones and acid halide.

$$\underset{\text{Ester}}{R-CO_2R'} \xrightarrow{Na/C_2H_5OH} RCH_2OH + R'OH$$

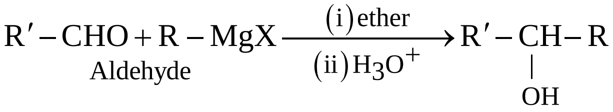
(C) From Grignard reagent (RMgX)

R—MgX is an organometallic compound. As carbon is more electronegative than metal, R group is present as negative group or Nu^- and attack at the e** deficient carbon.

The reaction is an example of nucleophilic addition reaction.

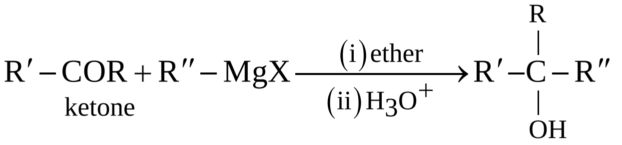


$$\underset{\text{Methanol}}{HCHO} + R-MgX \xrightarrow[(ii)H_3O^+]{(i)ether} \underset{1^\circ\text{ alcohol}}{R-CH_2OH}$$



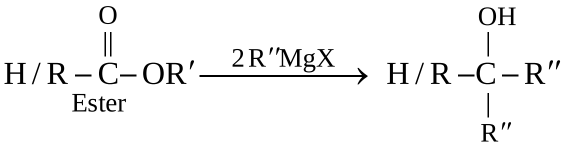
$$\underset{\text{Aldehyde}}{R'-CHO} + R-MgX \xrightarrow[(ii)H_3O^+]{(i)ether} R'-\underset{\underset{OH}{|}}{CH}-R$$

2° alcohol



$$\underset{\text{ketone}}{R'-COR} + R''-MgX \xrightarrow[(ii)H_3O^+]{(i)ether} R'-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-R''$$

3° alcohol



$$\underset{\text{Ester}}{H/R-\overset{\overset{O}{\|}}{C}-OR'} \xrightarrow{2R''MgX} H/R-\overset{\overset{OH}{|}}{\underset{\underset{R''}{|}}{C}}-R''$$

(Either 2° or 3° alcohol)

(D) Methanol is commercially prepared from CO + H_2 in the presence of Cu — ZnO — Cr_2O_3 as a catalyst at high temperature and pressure.

$CO + 2H_2 \rightarrow CH_3OH$ CH_3OH is called wood alcohol.

Ethanol is commercially manufactured by using fermentation process. Fermentation of sucrose gives ethanol.

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

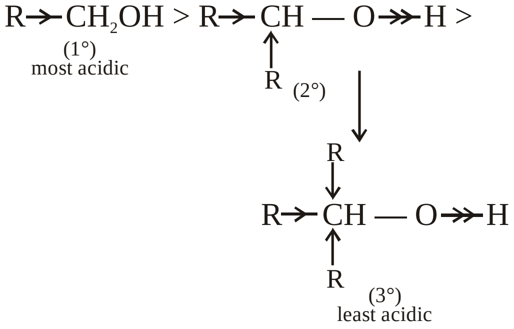
$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

(i) Boiling point : Alcohols have a higher boiling point than haloalkanes of same number of C-atom. This is due to the fact that alcohols are associated via intermolecular hydrogen bonding. B.P. of alcohols increases down the homologous series. For the same alcohol, as the branching increases, b.p. decreases due to decrease in surface area. Vander waal forces holding the molecules together decreases, b.p. decreases.

(ii) Solubility : Lower alcohols are completely miscible in water due to their ability to form hydrogen bonds with water.

The solubility of alcohols decreases down the homologous series, for the same alcohol, as the branching increases, solubility increases, t-butanol is more soluble in water than n-butanol.

(iii) Alcohols are weaker acids than water : O—H bond in alcohol is less polar as compared to O—H bond in water. The acidic strength of alcohols decreases as the number of e^- donating R groups increases at α-carbon.



The increasing O—H bond strength order is 1°RO—H < 2°RO—H < 3°RO—H and increasing C—O bond strength order is 3°R—OH < 2°R—OH < 1°R—OH

- Reactions of alcohols involving cleavage of O—H bond

(i) $\mathrm{RO-H} \xrightarrow{\mathrm{Na}} \mathrm{RO^{-}Na^{+}} + \frac{1}{2}\mathrm{H_2}$

(ii) $\underset{\text{only 1°alcohol}}{\mathrm{RO-H}} + \mathrm{R'-MgBr} \rightarrow \underset{\text{alkane}}{\mathrm{R'-H}} + \mathrm{RO-MgBr}$

- Reaction involving cleavage of C—O bond toward these type of reactions, the reactivity order is

  1°R—OH < 2°R—OH < 3°R—OH

  All these reactions require the presence of Lewis's acid because OH is not a good leaving group as it is a very strong base. Before removing OH, we have to decrease its basicity by developing a positive charge on oxygen and decreasing C—O bond strength.

(i) $\mathrm{R-OH} \xrightarrow{\mathrm{PCl_5}} \mathrm{R-Cl} + \mathrm{POCl_3} + \underset{\substack{\text{white}\\\text{fumes}}}{\mathrm{HCl}}$

(ii) $\mathrm{3R-OH} \xrightarrow[\mathrm{X=Cl,Br}]{\mathrm{PX_3}} \mathrm{3R-X} + \mathrm{H_3PO_3}$

(iii) $\mathrm{R-OH} \xrightarrow{\mathrm{P+I_2}} \mathrm{R-I} + \mathrm{H_3PO_3}$

(iv) $\mathrm{R-OH} \xrightarrow{\mathrm{SOCl_2}} \mathrm{R-Cl} + \mathrm{SO_2} + \mathrm{HCl}$

- Reaction with Lucas reagent

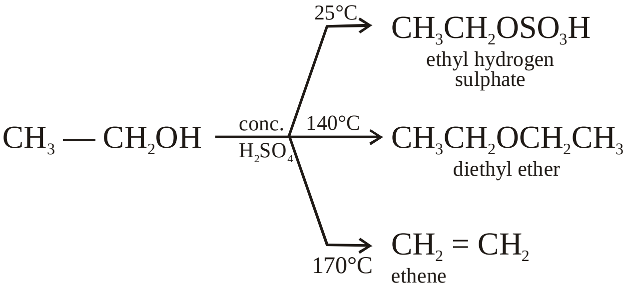
  Lucas reagent is conc. HCl/anhyd. $ZnCl_2$. The reagent is used to distinguish 1°, 2° and 3° alcohol.

  ⇒ 3° ROH gives cloudiness or turbidity with Lucas reagent immediately.

  ⇒ 2° R—OH gives cloudiness or turbidity after 5-10 minute.

  ⇒ 1° R—OH does not give cloudiness or turbidity at room temperature.

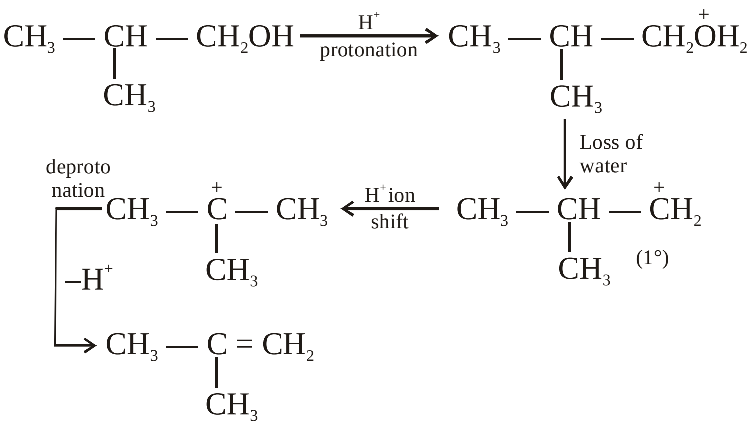
- Dehydration of alcohol (loss of H_2O) gives different products at different temperatures with conc. H_2SO_4. For example-



The ease of dehydration of three alcohols increases in the order

$$1° \text{ ROH} < 2° \text{ ROH} < 3° \text{ ROH}$$

- Dehydration of alcohol to alkene proceeds via the formation of carbonium ion (which can undergo rearrangement) e.g.

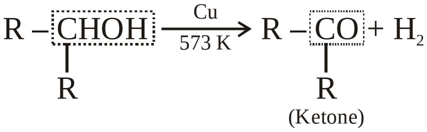


- Dehydrogenation (loss of H_2) with copper at 573K is used to distinguish 1°, 2° and 3° alcohol.

1° alcohol gives an aldehyde with same number of C-atoms

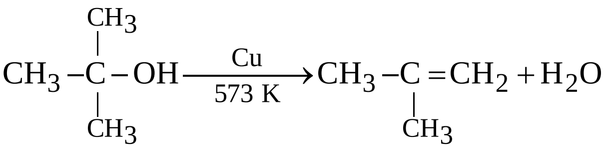
$$\underset{(1°)}{R – \boxed{CH_2OH}} \xrightarrow[573\text{ K}]{Cu} \underset{\text{an aldehyde}}{R – CHO} + H_2$$

2° alcohol gives ketones



$$R – \boxed{\underset{|\atop R}{CH}OH} \xrightarrow[573\text{ K}]{Cu} R – \underset{\underset{(\text{Ketone})}{|\atop R}}{\boxed{CO}} + H_2$$

3° alcohol undergo dehydration to form alkene (as there is no carbinol hydrogen)



$$CH_3 – \underset{CH_3}{\overset{CH_3}{C}} – OH \xrightarrow[573\text{ K}]{Cu} CH_3 – \underset{CH_3}{C} = CH_2 + H_2O$$

2−methyl propene−2−ol 2−methyl propene

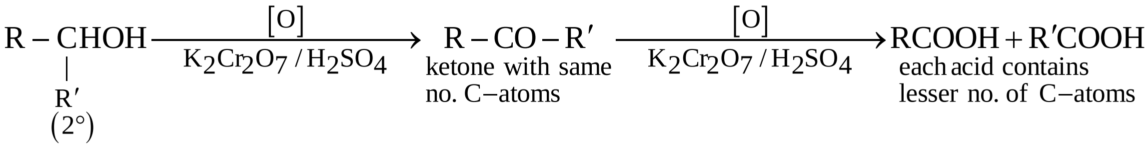
- Oxidation of alcohols involves the cleavage of O—H and C—H, final product of oxidation depends upon the structure of the alcohol and the oxidizing agent used.

The ease of oxidation follows a order

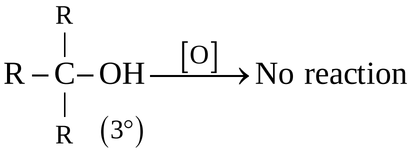
$$3°R — OH < 2°R—OH < 1°R — OH$$

(3° alcohols do not have any α-hydrogen)

$$R-CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{same no. of C-atoms}}{R-CHO} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{acid with same no. of carbon}}{R-CHO}$$

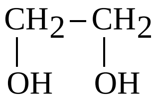


$$\underset{\underset{(2^\circ)}{R'}}{R-CHOH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{ketone with same no. C-atoms}}{R-CO-R'} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{each acid contains lesser no. of C-atoms}}{RCOOH+R'COOH}$$



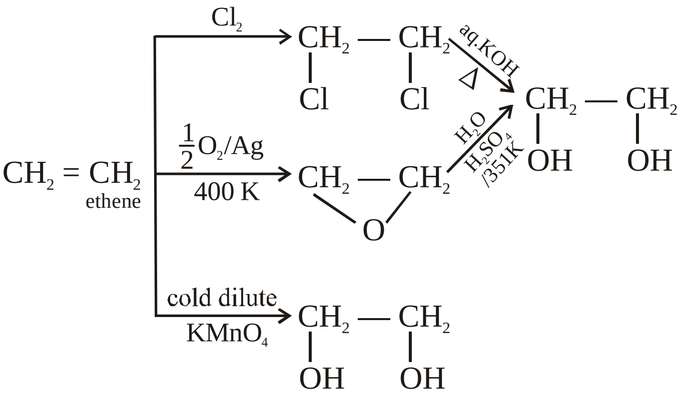
$$R-\overset{R}{\underset{R}{C}}-OH \xrightarrow{[O]} \text{No reaction} \quad (3^\circ)$$

- Properties and uses of methanol
  1. It is a colourless liquid and highly poisonous.
  2. It is completely soluble in water.
  3. It is used as solvent for paints, varnishes, and for making fomaldehyde.
- Ehtanol is a colourless liquid, higher b.p. than methanol. It is used as a solvent in paints industry. Denaturation of ethanol (or alcohol) means making it unfit for drinking purposes by adding $CuSO_4$ and pyridine.
- Ethylene glycol is an example of dihydric alcohol. Its IUPAC name is ehtane-1,2-diol. Its structureal formula is



$$\underset{OH}{CH_2}-\underset{OH}{CH_2}$$

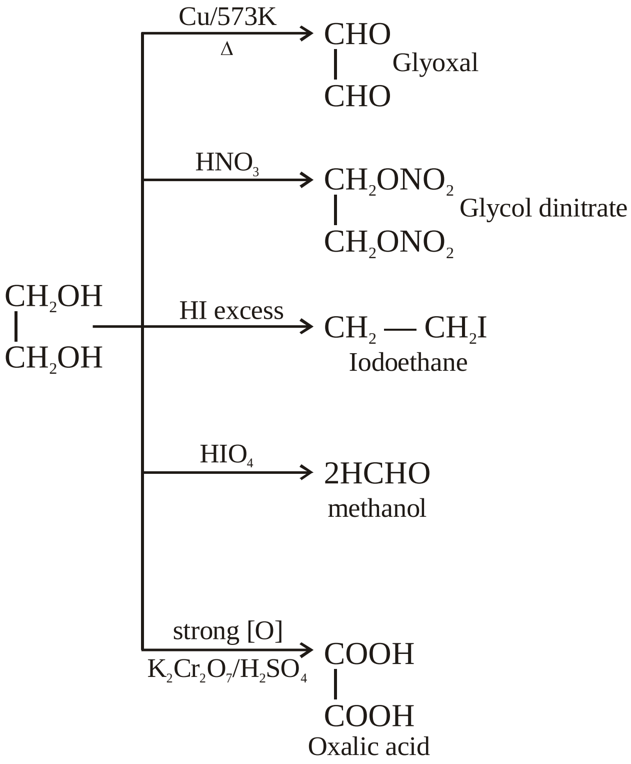
- Preparation of ethylene glycol



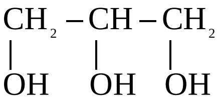
- Properties of ethylene glycol
  - (i) It is colourless syrupy liquid
  - (ii) It has a high b.p. than ehtanol due to more network of intermolecular hydrogen bonding.

Uses of ethylene glycol
  - (i) It is used as antifreeze in car radiator.
  - (ii) It is used in the preparation of polyester.
  - (iii) It is used as solvent.
- Reaction of Glycol

In glycol, both the OH groups are primary alcoholic groups.

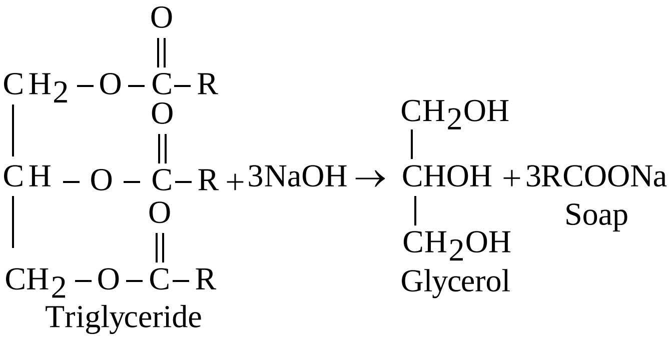


- Glycerol or glycerine is an example of trihydric alcohol. Its IUPAC name is propane-1,2,3-triol. Its structural formula is



$$\underset{\text{OH}}{\underset{|}{CH_2}}-\underset{\text{OH}}{\underset{|}{CH}}-\underset{\text{OH}}{\underset{|}{CH_2}}$$

- Glycerol is prepared commercially by the alkaline hydrolysis of fat or oil (which are called triglycerides).

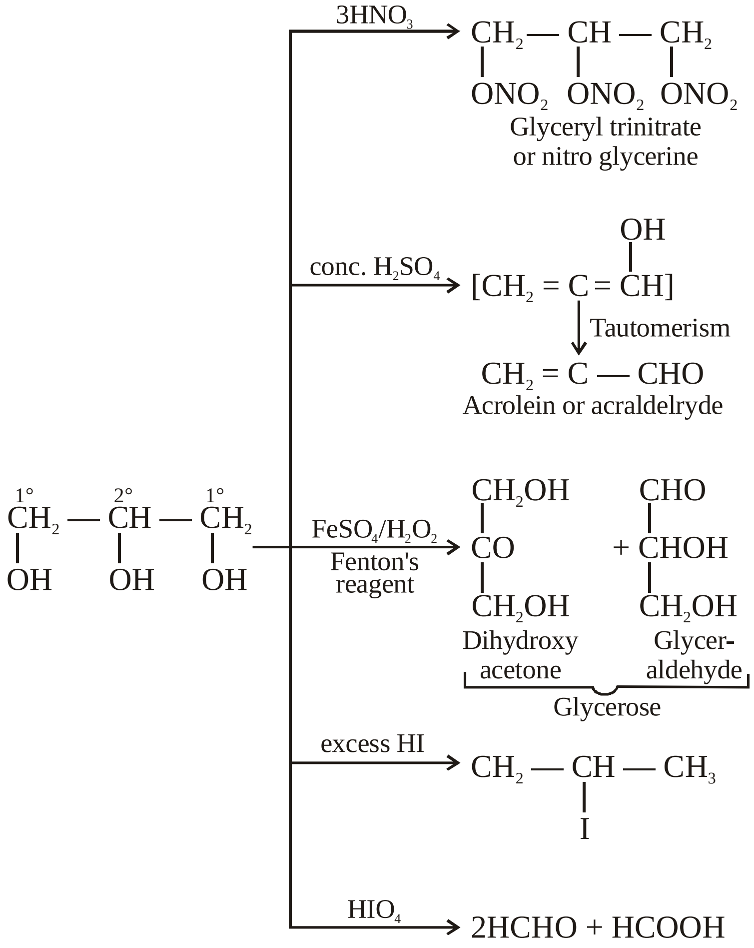


$$\begin{array}{l} CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \\ | \\ CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \\ | \\ CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \end{array} + 3NaOH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOONa$$

The alkaline hydrolysis of an ester is called saponification.

- Properties of Glycerol
  - (i) It is highly viscous liquid with high b.p. This is due to extensive network of inter molecular hydrogen bonding.
  - (ii) It is colourless, hygroscopic liquid.
  - (iii) Glycerol is used in the preparation of polyesters, dyanamite and for medicines, cosmetics and the textile processing.

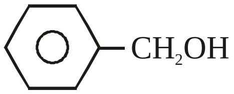
- Reactions of glycerol



PHENOL

- Phenols are compounds with an OH group attached directly to a carbon of an aromatic ring. The compound phenol is C_6H_5OH.

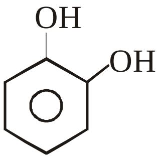
If OH group is present on the side chain, then it is called aliphatic alcohol. For example



- Phenols may be

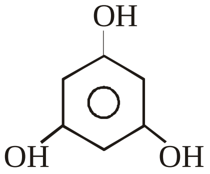
(i) monohydric,

(ii) dihydric,

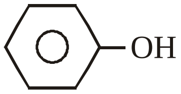


Catechol

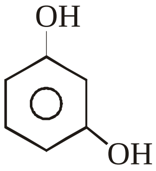
(iii) trihydric,



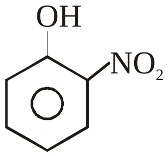
Phloroglucinol

- Phenol name for  is also accepted in IUPAC system. IUPAC and common names of some of the phenolic compounds are given below :

p-cresol
(4-methylphenol)

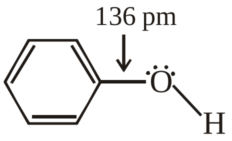


Resorcinol
(Benzene-1,3-diol)



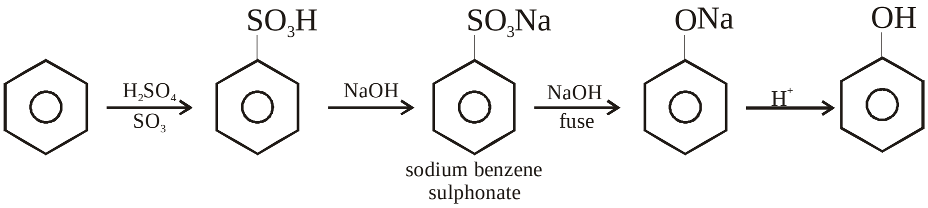
o-nitrophenol
(2-nitrophenol)

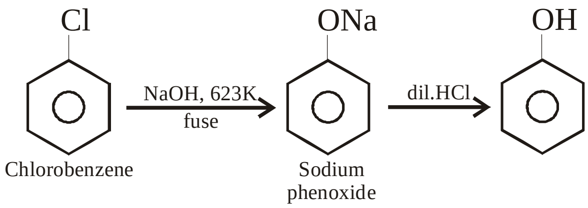
- The structure of phenol is



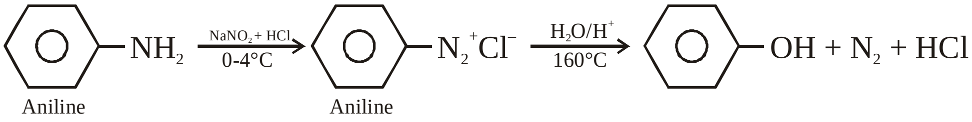
The C—O bond is slightly shorter than the C—O bond present in methanol. This is due to partial double bond character as lone pair of electrons on oxygen participates into resonance with the benzene ring.

- Preparation of phenol

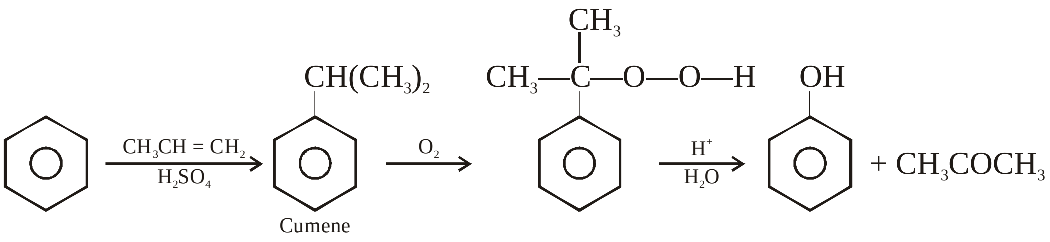
(i) 

(ii) 

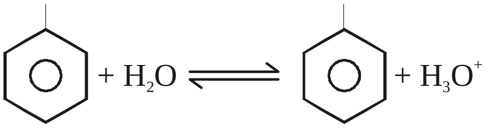
(DOW's process)

(iii) 

- Phenol is prepared commercially by cumene-phenol process.

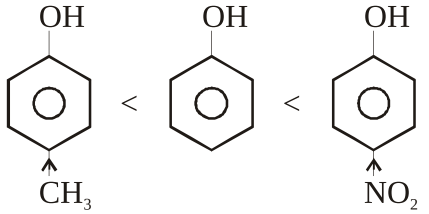


- Phenols have a higher boiling point than the corresponding hydrocarbon or aryl halides. This is due to the presence of intermolecular hydrogen bonding. Due to their ability to forms H-bonds with water, phenols are moderately soluble in H_2O.
- The phenols are acidic in nature and stronger acids than alcohols.

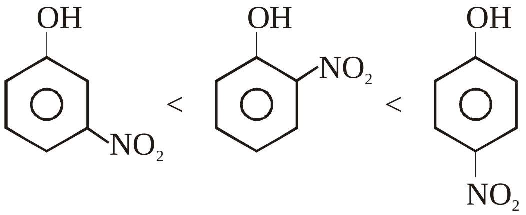


The pair of oxygen in phenol is delocalized with the benzene ring. As a result, the strength of O—H bond decreases and H as H^+ ion can easily be removed.

- The presence of electrons withdrawing group (EWG) like NO_2 group, increases the acidic strength and electron donating groups (EDG) like R group decreases the acidic strength. Therefore, the acidic strength order is



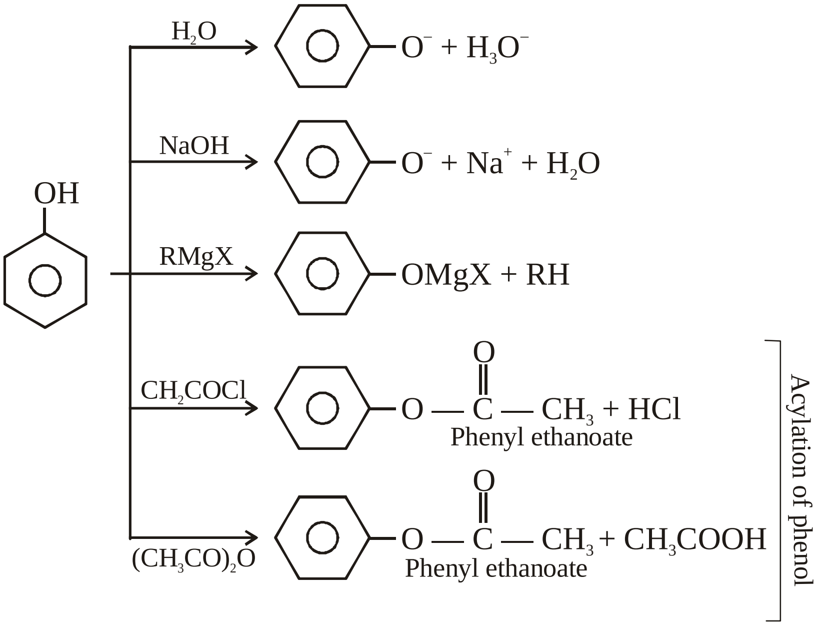
The increasing acidic strength order of the three nitrophenols is



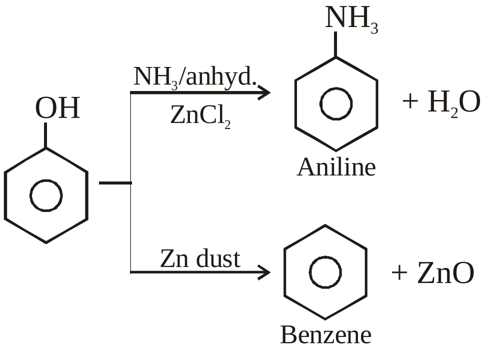
In m-nitro phenol, only –I effect no –R of NO_2 present. In o-nitro phenol. –I, –R effect of NO_2 both present but weaker than para as there exists an intra molecular hydrogen bonding.

p-nitrophenol is the strongest acid due to –R, –I effect of NO_2.

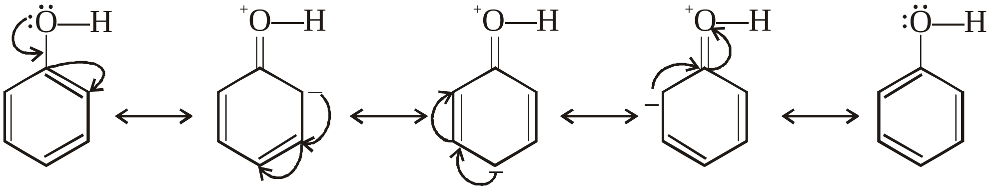
- Reaction of phenol involving the cleavage of O—H bond.



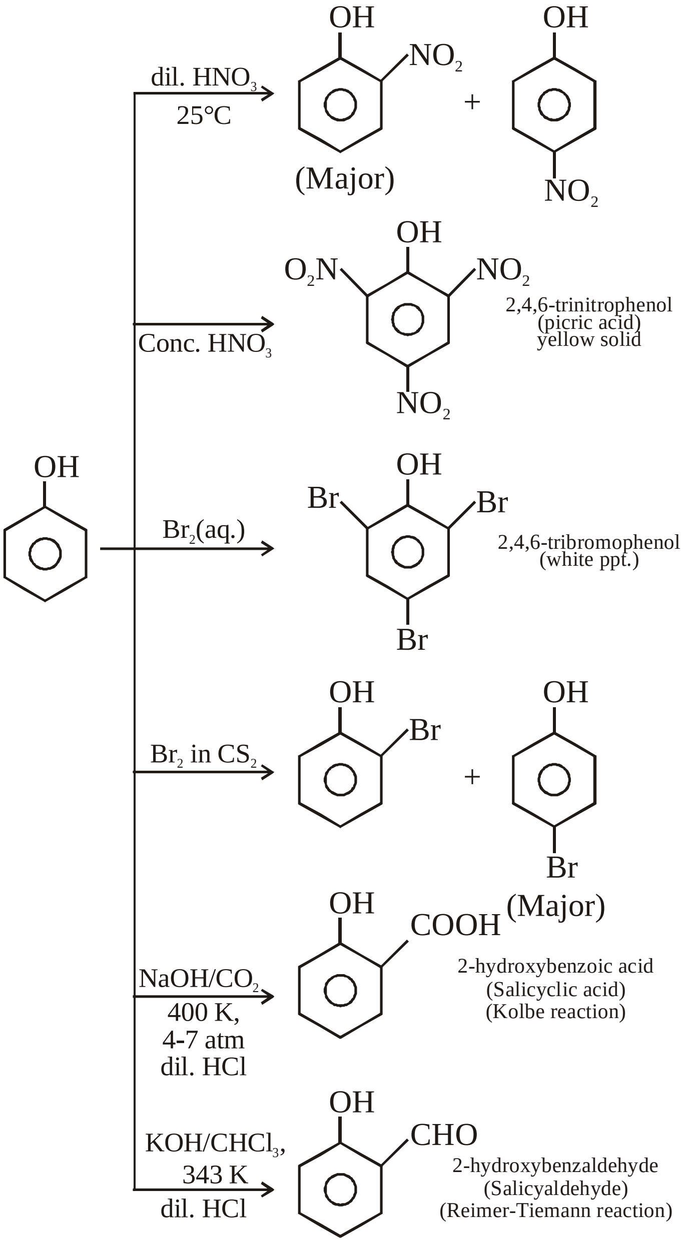
- Reactions of phenol involving cleavage of C—O bond



- The presence of OH group on benzene increases the electron density on the benzene ring making it more susceptible to attract by an electrophile. The reactions involving benzene ring are electrophilic substitution reactions. The presence of OH group makes the ortho and para-carbon of benzene more electron rich than meta position. The OH group is called o-, p-directing group.

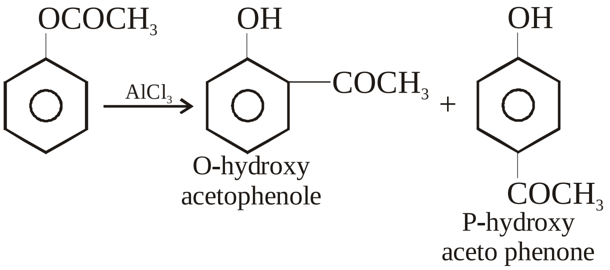


- Electrophilic substitution reactions of phenol



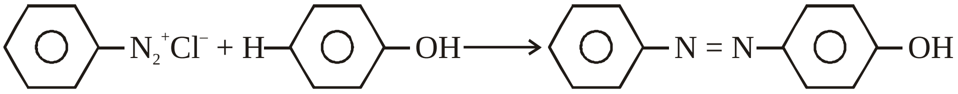
- Esters of phenol gives phenolic ketones on rearrangement in the presence of anhydrous $AlCl_3$. The reaction is called Fires rearrangement.

  Phenyl acetate yield phenolic ketones on treatment with anhydrous $AlCl_3$.



- Condensation reaction of phenol

  With benzene diazonium chloride (Diazo coupling)

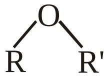


p-hydroxyazobenzene
(azodye)

- Uses of Phenol
  - (i) It is used as an antiseptic, disinfectant.
  - (ii) It is used in the preparation of dyes, drugs.
  - (iii) It is used in the preparation of bakelite, Novalac.

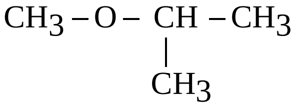
ETHERS

- Ethers are derivatives of water, H_2O, replacing both hydrogen by alkyl or aryl groups.

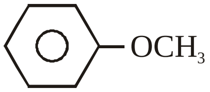


If R = R', then the ether is called simple ether. The common name is dialkyl ether. $CH_3CH_2OCH_2CH_3$ is diethyl ether.

If R $\neq$ R', then ether is called mixed ether. Then arrange the alkyl groups alphabetically and write a suffix ether.



$CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ is isopropyl methyl ether. In IUPAC system, ethers are called alkoxy alkane.

CH_3—OCH_2CH_3 is methoxy ethane and  OCH_3 is methoxy benzene. Its common name is methyl phenyl ether (anisole).

Phenetole is a common name of ethoxy benzene.

- Preparation of ethers
  - (i) Dehydration of 1° alcohols

$$2CH_3CH_2OH \xrightarrow[413]{H_2SO_4} CH_3CH_2OCH_2CH_3$$

2° and 3° alcohols on dehydration gives alkenes and not ethers.

  - (ii) From alkyl halides.

$$2RX \xrightarrow[dry]{Ag_2O} R_2O + 2AgX$$

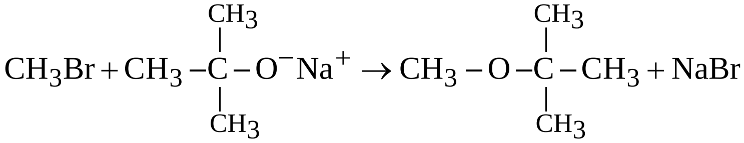
(iii) From alkyl halides using Williamson's synthesis (SN_2 reaction).

$$RX + NaOR' \longrightarrow R - O - R' + NaX$$

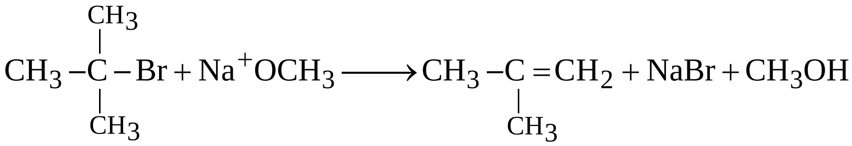
$(R = CH_3, 1°)$ sodium alkoxide

$(R' = 1°, 2°, 3°$ or Ar)

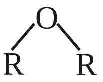
The important method to prepare any type of ether. With 3° RX, alkenes are formed as alkoxide ion is also a strong base, alkyl halide then undergoes elimination reaction.



$$CH_3Br + CH_3-\underset{CH_3}{\overset{CH_3}{|}}{C}-O^-Na^+ \rightarrow CH_3-O-\underset{CH_3}{\overset{CH_3}{|}}{C}-CH_3 + NaBr$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + Na^+OCH_3 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr + CH_3OH$$

- Ethers and monohydric alcohols are functional isomers but ethers have a lower b.p. than alcohols due to their inability to associate via intermolecular hydrogen bonding. Ethers are volatile.
- Ethers are polar in nature and have a net dipole moment even if the R groups are similar. This is due to their bent structure. 

  The oxygen atom is sp^3 hybridized and C—O—C bond angle is more than 109° due to the repulsions between the bulky large size R groups.
- Lower ethers (containing upto three carbon atoms) are completely miscible in water. The solubility of ethers decreases as the number of carbon atoms increases.
- Due to the presence of electron donating R groups and lone pair on oxygen atoms, ethers are Bronsted bases as well as Lewis bases.

$$R_2O + HX \rightarrow R_2OH^+X^-$$

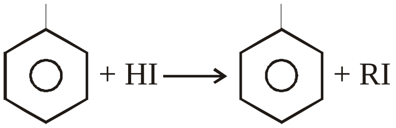
$(X = Cl, Br)$ dialkyl oxonium halide

$$\underset{\substack{\text{Lewis}\\\text{base}}}{R_2O} + \underset{\substack{\text{Lewis}\\\text{acid}}}{BF_3} \rightarrow [R_2O \rightarrow BF_3]$$

- Reactions of ethers involving C—O bond cleavage R—O—R + HI → ROH + RI simple ether

  For a given ether, the reactivity of hydrogen halides follows a order:

  HCl < HBr < HI (Strongest acid)
- In case of aromatic ether, reaction with HI results in the cleagvage of R—O bond because Ar—O bond has a double bond character and is strong. Also breaking R—O bond results in the formation of phenoxide ion which is resonance stabilized.

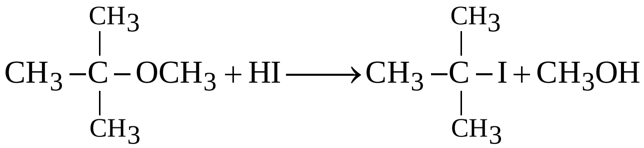


- In case of mixed ether with the different R groups, the product depends on the nature of R groups.

  When 1° or 2° R groups present, the lower R groups from alkyl iodide with HI (This is an S_N2 reaction)

$$CH_3OCH_2CH_3 + HI \rightarrow CH_3I + CH_3CH_2OH$$

When one of the R group is 3° R group, then tertiary alkyl iodide is formed with HI.

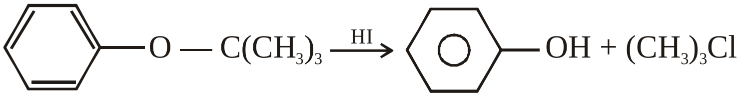


$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3+HI\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-I+CH_3OH$$

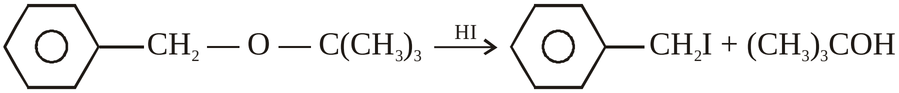
Because 3° carbonium ion is more stable.

Some more examples :

(i)



(ii)



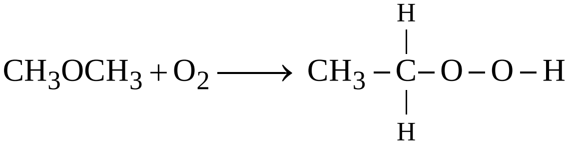
- The most important simple ether is ethoxy ethane. It is used as a solvent for oils, gums, resins, etc.

  It is also used as an inhalation anaesthetic. Ethrane and isoflurane are also used as anaesthetic. Phenyl ether used as a heat transfer medium because of its high boiling point.
- Some more reactions of ether

  (i) $R_2O+PCl_5 \rightarrow 2RCl+POCl_3$

  (ii) $R_2O+H_2O\xrightarrow{H^+}2ROH$

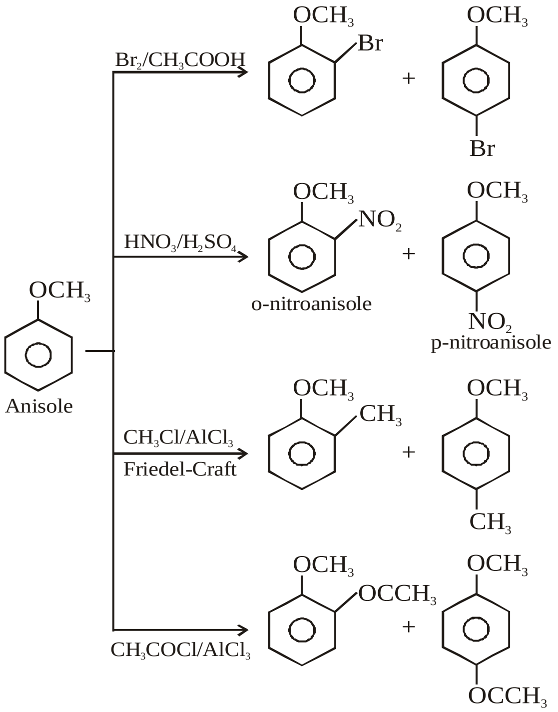
  (iii)



$$CH_3OCH_3+O_2\longrightarrow CH_3-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-O-O-H$$

dimethyl ether peroxide
(present as an impurity in ethers)

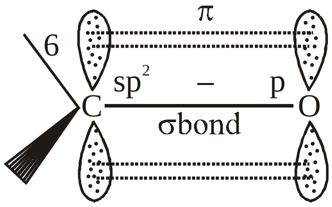
- RO-group on benzene ring is activating and o-, p-directing. Electrophilic substitution reactions of aromatic ether are



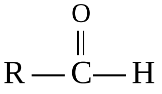
ALDEHYDES KETONES

STRUCTURE OF CARBONYL GROUPS :

The >C = O bond in aldehyde and ketones is made up of one σ and one π-bond around the carbon oxygen bond.

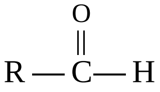


The electron cloud of the π-bond lies both above and below the C = O, σ bond



$R-\overset{\overset{\displaystyle O}{\|}}{C}-H$

Aldehyde



$R-\overset{\overset{\displaystyle O}{\|}}{C}-H$

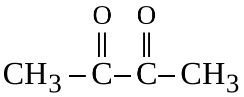
Ketone

NOMENCLATURE OF ALDEHYDE AND KETONES :

The suffix term for aldehyde is ‘al’ and for ketone is ‘one’.

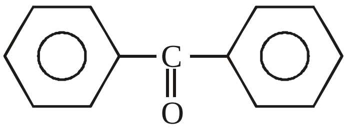
(a) $\underset{4}{C}H_3-\underset{3}{C}H=\underset{2}{C}H-\underset{1}{C}HO$

But – 2 – en – 1 – al

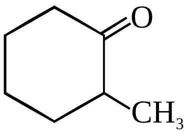
(b) 

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

Butane – 2, 3 – dione

(c) 

Benzophenone

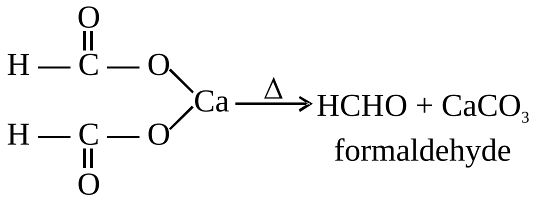
(d) 

2-Methyl-cyclohexanone

Aldehyde and ketones are functional isomers to each, due to which their properties largely resembles to each other.

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES:

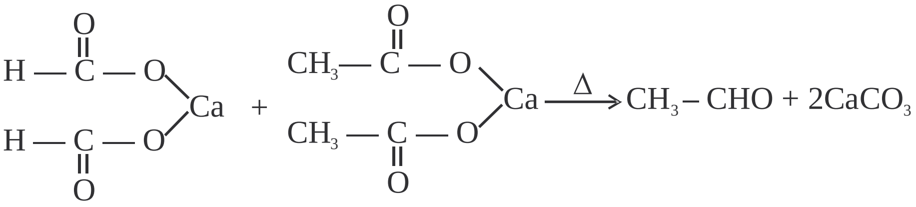
(1) By dry-distillation of calcium salt of carboxylic acids :

(a) 

$$\left.\begin{matrix}H-\overset{\overset{\displaystyle O}{\|}}{C}-O\\ H-\underset{\underset{\displaystyle O}{\|}}{C}-O\end{matrix}\right>Ca\xrightarrow{\Delta}\underset{\text{formaldehyde}}{HCHO}+CaCO_3$$

Calcium formate

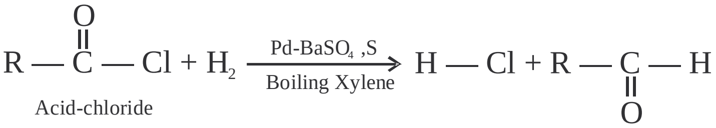
(b)



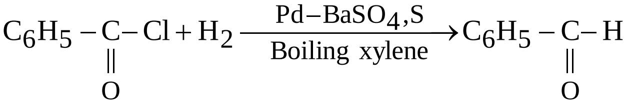
$$(HCOO)_2Ca + (CH_3COO)_2Ca \xrightarrow{\Delta} CH_3-CHO + 2CaCO_3$$

2. BY ROSENMUND'S REDUCTION:

Only aldehydes can be synthesised by this reaction.



$$\underset{\text{Acid-chloride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiling Xylene}]{\text{Pd-BaSO}_4\text{ ,S}} H-Cl + \underset{\text{Aldehydes}}{R-\underset{\underset{\displaystyle O}{\|}}{C}-H}$$

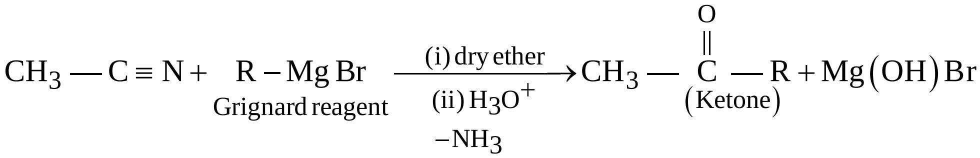


$$\underset{\text{Benzoyl chloride}}{C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiling xylene}]{\text{Pd}-\text{BaSO}_4\text{,S}} C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-H$$

Note : Formaldehydes can't be obtained by this method. Ketones also can't be synthesised by this reaction.

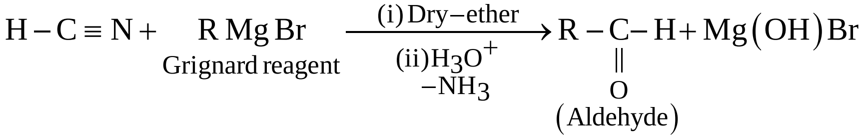
3. FROM NITRILES :

(a)



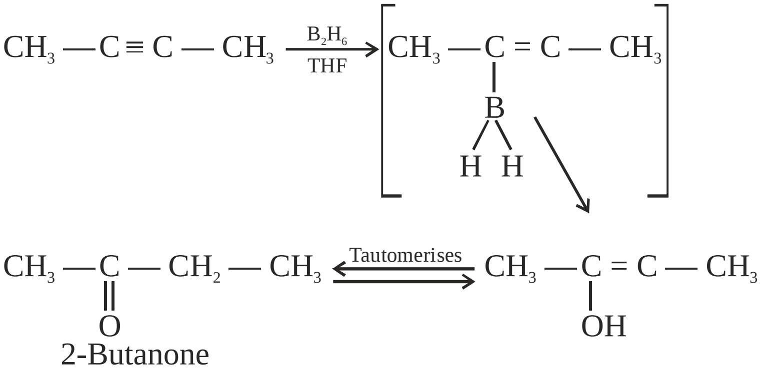
$$CH_3-C\equiv N + \underset{\text{Grignard reagent}}{R-MgBr} \xrightarrow[\substack{\text{(ii) }H_3O^+\\ -NH_3}]{\text{(i) dry ether}} CH_3-\underset{\text{(Ketone)}}{\overset{\overset{\displaystyle O}{\|}}{C}}-R + Mg(OH)Br$$

(b)



$$H-C\equiv N + \underset{\text{Grignard reagent}}{R\,MgBr} \xrightarrow[\substack{\text{(ii)}H_3O^+\\ -NH_3}]{\text{(i) Dry}-\text{ether}} \underset{\text{(Aldehyde)}}{R-\underset{\underset{\displaystyle O}{\|}}{C}-H} + Mg(OH)Br$$

4. BY HYDROBORATION - OXIDATION OF ALKYNES :

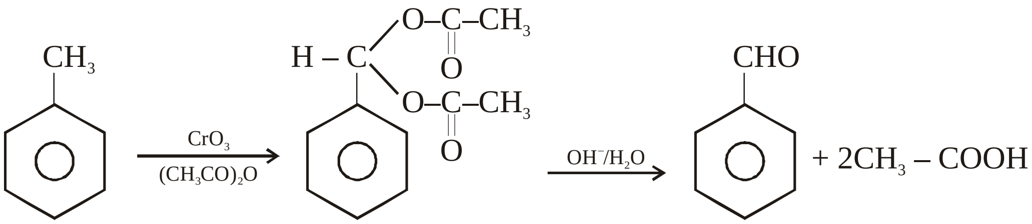


2-Butanone

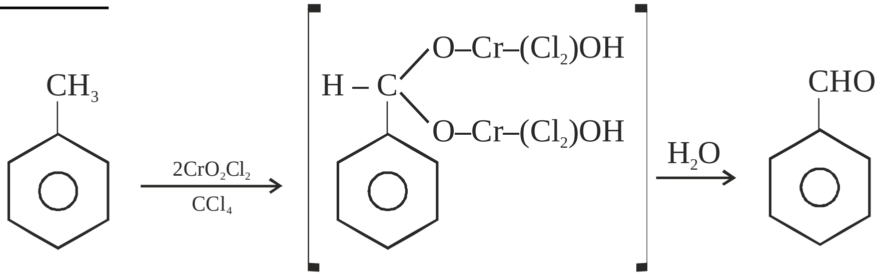
5. WACKER'S PROCESS :

$$CH_2=CH_2+H_2O+PdCl_2 \xrightarrow[\text{air}]{CuCl_2} CH_3CHO+Pd+2HCl$$

6. OXIDATION OF METHYL BENZENE :



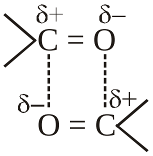
7. ETARD REACTION :



Physical Properties :

(1) Boiling - point :

Aldehyde and Ketone molecule are polar molecules due to the presence of carbonyl groups.



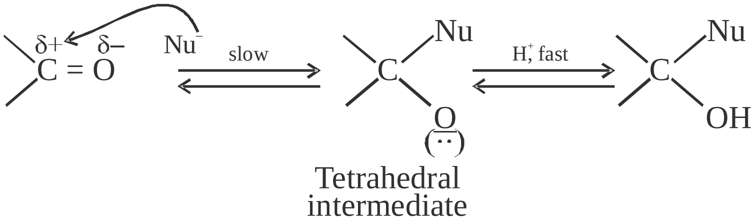
Dipole - Dipole interaction

Among isomeric aldehydes and ketones, ketone have slightaly higher boiling point value

Chemical properties of aldehyde and ketones :

Aldehydes and ketones are highly reactive due to the presence of polarized carbonyl groups. The reaction of aldehyde and ketones can be devided into following categories :

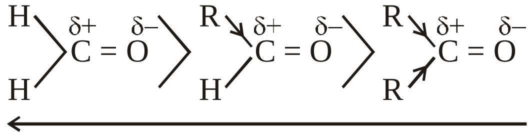
(1) Nucleophilic addition reactions :



The ability of the highly electronegative oxygen to retain the negative charge over it, causes the nucleophilic addition reaction at carbon. In addition, nucleophilic attack causes the formation of stable tetrahedral intermediate.

The relative reactivity of aldehydes and ketone is effected by at least given two factors :

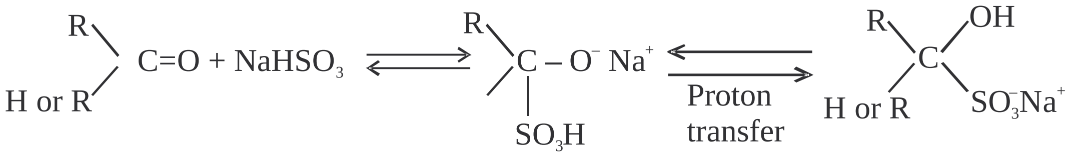
(i) Inductive effect (ii) Steric factors



Reactivity increases

SOME IMPORTANT NUCLEOPHILIC ADDITION REACTION :

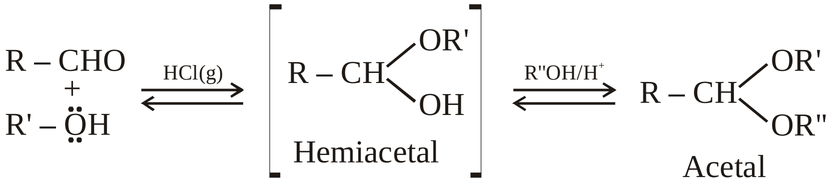
1. ADDITION OF SODIUM BISULPHITE



⇒ The position of equilibrium lies largely to the right for most aldehyde and for most of ketones it lies toward left.

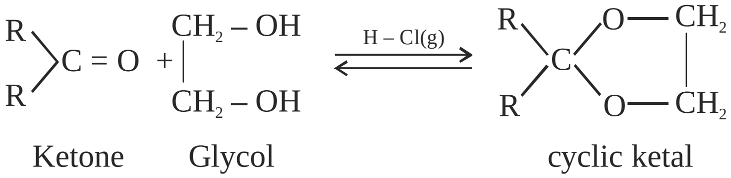
2. ADDITION OF ALCOHOL :

Aldehyde with one molecule of R–OH forms ‘hemiacetal’ and with another molecule it forms acetal.



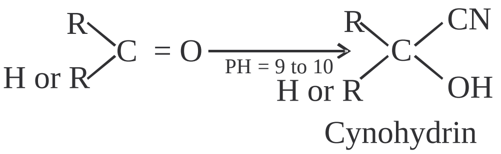
Ketone, similarly forms hemiketal and ketal.

3. WITH DIOL :



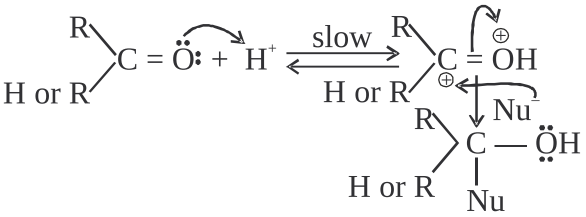
4. WITH HCN :

Cyanohydrins is formed



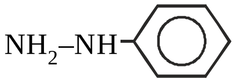
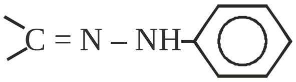
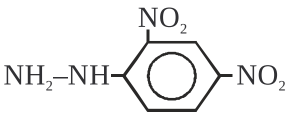
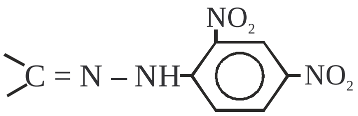
5. ADDITION OF AMMONIA DERIVATIVES :

The addition of ammonia derivative to aldehyde and ketone is catalysed by weak acids.



⇒ Due to protonation, the ease of nucleophilic addition becomes faster.

6.

AMMONIA DERIVATIVE USED		PRODUCT OBTAINED	
Strucutre	Name	Strucutre	Name
NH_2OH	Hydroxylamine	$>C=N-OH$	Oxime
NH_2-NH_2	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenyldrazine		Phenylhydrazone
	2,4-Dinitro-phenyldrazine		2,4-Dinitrophenyl-hydrazone
$NH_2CONHNH_2$	Semicarbazide	$>C=NNHCONH_2$	Semicarbazone

7. OXIDATION OF ALDEHYDE AND KETONES

Oxidation

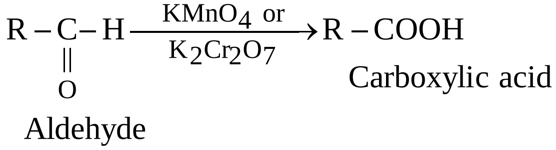
(A) Strong Oxidising agents

(1) $KMnO_4$ (2) $K_2Cr_2O_7$
(3) HNO_3

(B) Weak Oxidizing agents

(i) Fehling solution
(ii) Tollen's Reagent
(iii) Benedict solution

(A) Strong Oxidising agents :

(a) 

$$\underset{\text{Aldehyde}}{R-\underset{\underset{O}{\|}}{C}-H} \xrightarrow[K_2Cr_2O_7]{KMnO_4 \text{ or}} \underset{\text{Carboxylic acid}}{R-COOH}$$

(B) Oxidation by weak oxidising agents :

The given reactions are also used to distinguish between aldehyde and ketones.

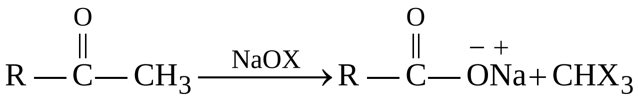
(i) By Tollen's reagent :

$$R-CHO+2\underset{\text{Tollen's reagent}}{\left[Ag\left(NH_3\right)_2\right]^+}+3OH^- \longrightarrow R-COO^-+2H_2O+4NH_3+\underset{\Rightarrow\text{Silver mirror test}}{2Ag\downarrow}$$

(ii) Fehling's solution :

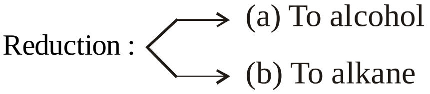
$$R-CHO+2Cu^{2+}+5OH^- \longrightarrow R-COO^-+\underset{\text{Brown}}{Cu_2O}+3H_2O$$

(C) Oxidation of methyl ketones by Haloform reaction :



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+CHX_3$$

8. REDUCITON :



Reduction : (a) To alcohol

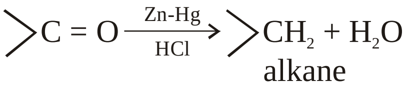
(b) To alkane

(A) To alcohols :

$$R-CHO \xrightarrow[NaBH_4]{LiAlH_4 \text{ or}} R-CH_2-OH$$

(B) To alkane :

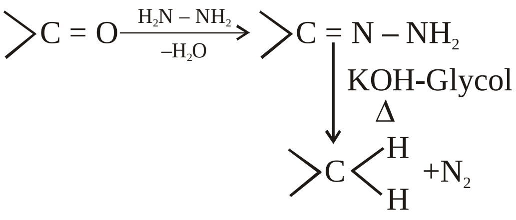
(i) Clemmenssen's reduction:



$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$$

alkane

(ii) Wolff-kishner reduction:

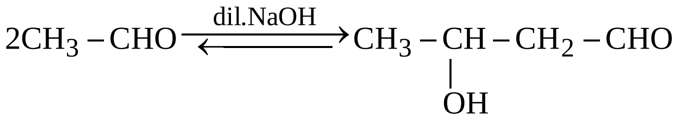


$$>C=O \xrightarrow[-H_2O]{H_2N-NH_2} >C=N-NH_2 \xrightarrow[\Delta]{KOH\text{-}Glycol} >C<^{H}_{H} + N_2$$

alkane

9. REACTION INVOLVING α-HYDROGEN (ALDOL-CONDENSATION REACTION) :

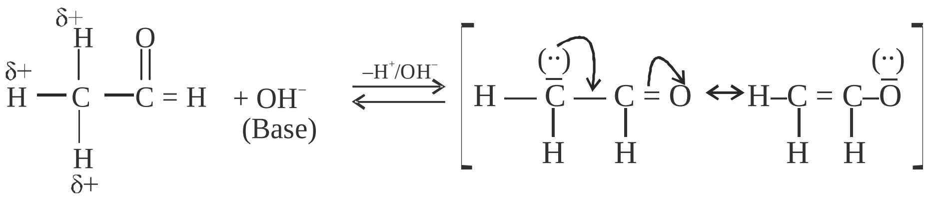
Aldehyde and Ketones having α H undergoes condensation in presence of these dilute base to form aldol. Thus reactions are also called as aldol condensation reactions.



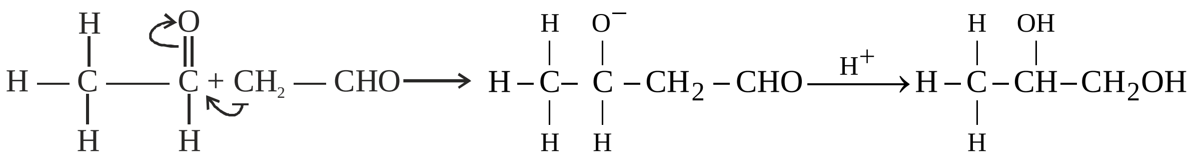
$$2CH_3-CHO \underset{}{\overset{dil.NaOH}{\rightleftharpoons}} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2-CHO$$

(Acetaldol)

Mechanism :



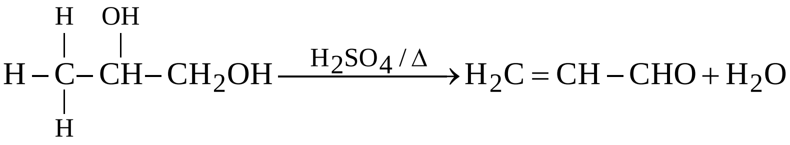
2nd Step :



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}}+CH_2-CHO \longrightarrow H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-CH_2-CHO \xrightarrow{H^+} H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2OH$$

[Aldol]

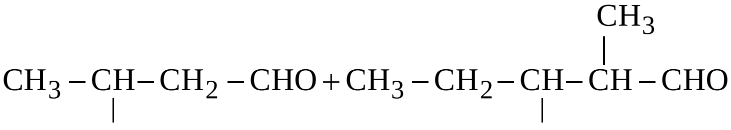
Note: The aldol formed may undergo dehydration in presence of dilute acids, upon heating.



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{OH}{CH}-CH_2OH \xrightarrow{H_2SO_4/\Delta} H_2C=CH-CHO+H_2O}$$

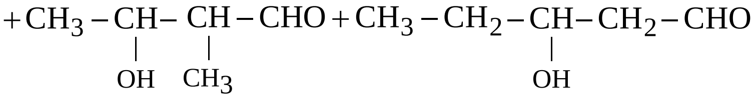
Cross Aldol condensation reaction:

$$\mathrm{CH_3-CHO+CH_3-CH_2-CHO \underset{}{\overset{Na-OH}{\rightleftarrows}}}$$



$$\mathrm{CH_3-\underset{OH}{CH}-CH_2-CHO+CH_3-CH_2-\underset{OH}{CH}-\overset{CH_3}{CH}-CHO}$$

self aldol products

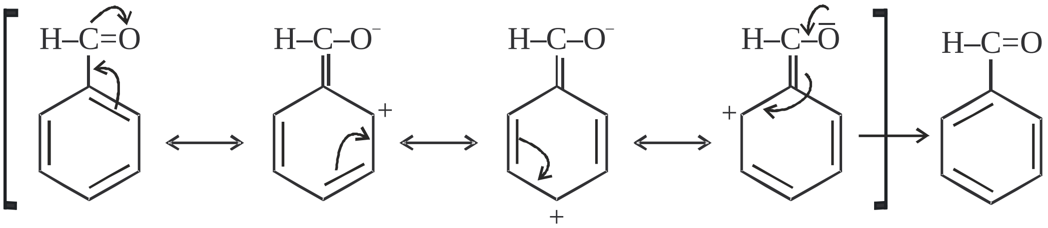


$$\mathrm{+CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CHO+CH_3-CH_2-\underset{OH}{CH}-CH_2-CHO}$$

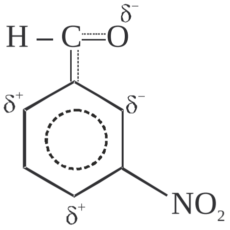
cross aldol products

Electrophilic Substitution reaction :

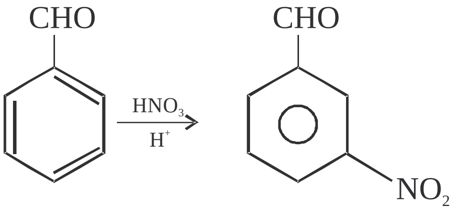
Aromatic aldehydes and ketones, gives rise to electrophilic substitution reaction at meta position. The carbonyl groups acts as deactivating, group for incoming electrophiles



Resonance hybrid:



(1) Nitration:



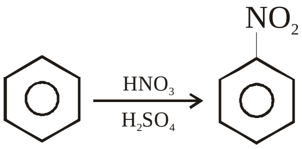
AMINES

NITRO COMPOUNDS

PREPARATIONS

(1) By direct nitration of Benzene:

Benzene undergoes electrophilic substitution reaction with HNO_3/H_2SO_4



The electrophile is NO_2^+ (nitronium ion) produced by the given reaction,

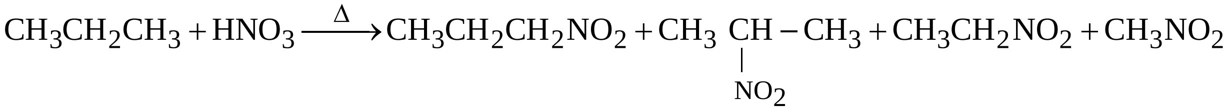
$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

In this reaction, HNO_3 acts as a base and H_2SO_4 acts as an acid.

During nitration, the number of solute particles increases (the Van't Hoff factor is greater than one), therefore, freezing point decreases.

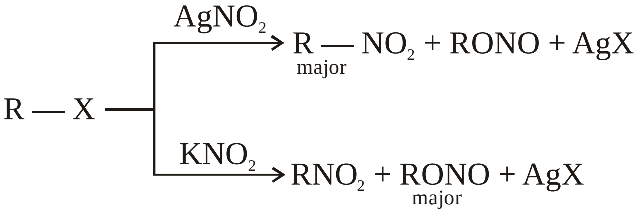
(2) Vapour phase nitration of alkane:

Alkane undergoes nitration at 475 K to 675 K in the presence of conc. HNO_3 and follows free radical mechanism. This is called vapour phase nitration and may results in the carbon-carbon cleavage.



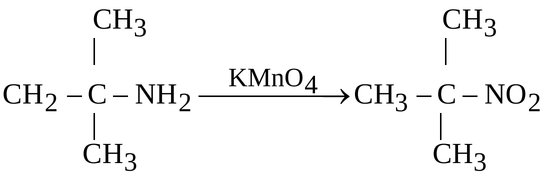
$$CH_3CH_2CH_3 + HNO_3 \xrightarrow{\Delta} CH_3CH_2CH_2NO_2 + CH_3\underset{\underset{NO_2}{|}}{CH} - CH_3 + CH_3CH_2NO_2 + CH_3NO_2$$

(3) From Halo compounds:



$$R - X \begin{cases} \xrightarrow{AgNO_2} \underset{major}{R - NO_2} + RONO + AgX \\ \xrightarrow{KNO_2} RNO_2 + \underset{major}{RONO} + AgX \end{cases}$$

(4) From amines:



$$CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - NH_2 \xrightarrow{KMnO_4} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - NO_2$$

PHYSICAL PROPERTIES :

(1) Nitroalkanes are colourless pleasant smelling liquids.

(2) Nitrobenzene is a yellow oily liquid, heavier than H_2O, smell of bitter almonds, steam volatile.

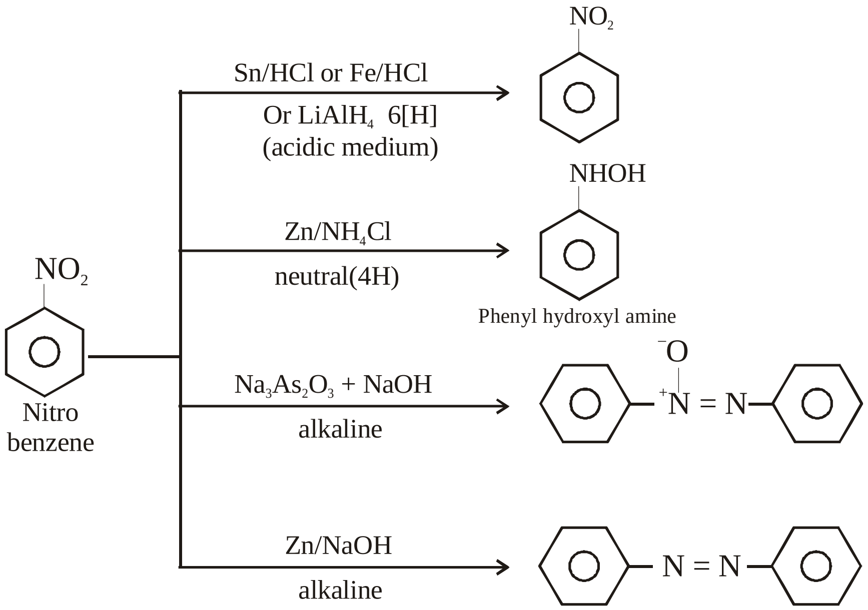
(3) Nitroalkanes are less soluble in water, b.p. are much higher than alkyl nitrites.

CHEMICAL PROPERTIES :

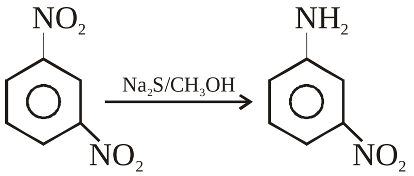
(1) Reduction :

Reduction of nitro alkane (or nitro benzene) gives variety of products depending upon the reducing agent used.

Nitrobenzene



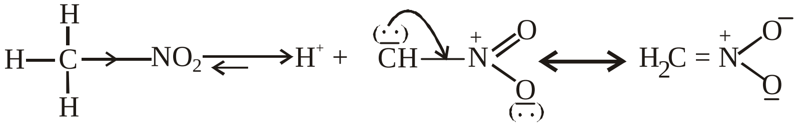
Note :- The reduction of selectively one nitro group in dinitrobenzene,can also be performed.



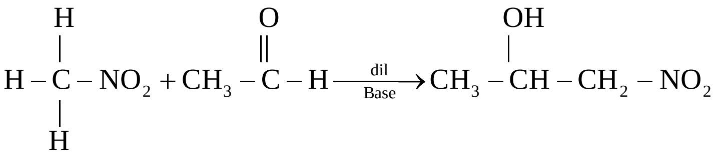
(2) Acidic αH of nitro alkanes :

Nitromethane contains acidic $\alpha-$hydrogen and can undergo condensation reaction with carbonyl compounds.

(a)

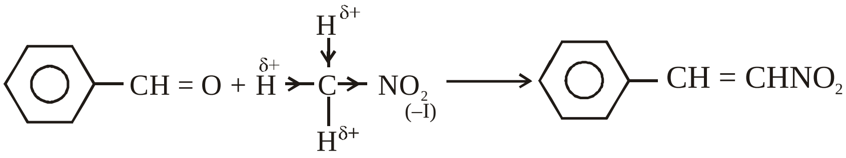


When Nitromethane is reacted with carbonyl molecules like acetaldehyde, than condensation product is formed. In given reaction, nitro methane releases proton and acetaldehyde



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-NO_2+CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H\xrightarrow[\text{Base}]{\text{dil}}CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-NO_2$$

(b)

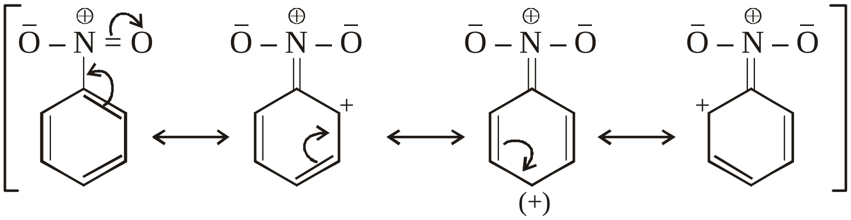


(3) With chlorine : nitromethane forms chloropicrin. (used as an insecticide)

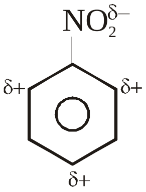
$$CH_3NO_2 \xrightarrow[NaOH]{3Cl_2} CCl_3NO_2$$

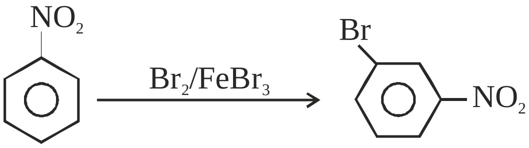
(4) Ring substitution in nitrobenzene : NO_2 group is m-directing and deactivating group, for incoming electrophiles.

Due to –M– effect, the ring gets partial +ve charge at ortho and para position.



Resonance hybrid structure :





CYANIDES AND ISOCYANIDES

Alkyl cyanides RCN and alkyl iso-cyanides (RNC) are isomers. CN^- and NC^- are ambident nucleophiles.

PREPARATION

(1) From alkyl halide:

$$R-X+alc.KCN \rightarrow \underset{(major)}{R-CN}+RNC$$

(2) From amides by dehydration:

$$R-CONH_2 \xrightarrow[Heat]{P_4O_{10}} R-CN+H_2O$$

(3) Using Grignard reagent:

$$R-MgX+\underset{\substack{cyanogen\\chloride}}{Cl-C\equiv N} \rightarrow R-CN+MgX\ Cl$$

(4) From oxime:

$$R-CH=NOH \xrightarrow[\Delta]{P_4O_{10}} R-CN+H_2O$$

PREPARATION OF RNC

(1) From RX:

$$RX+Ag\ CN(alc.) \rightarrow \underset{(major)}{R-NC}+RCN$$

(2) By carbylamine reaction:

$$R-NH_2+CHCl_3+3KOH\xrightarrow{\text{warm}}R-NC+3H_2O+3KCl$$

This reaction is given by only 1° amines. Hence is used as test for 1° amines. The reaction intermediate used in reaction is dichlorocarbene.

CHEMICAL PROPERTIES

(1) Hydrolysis:

(a) Cyanide:

$$R-CN\xrightarrow[H_2SO_4]{\text{dil.}}RCONH_2\xrightarrow[\substack{H_2SO_4\\ \text{acid}}]{\text{dil.}}RCOOH$$

(b) Hydrolysis of Isocyanide:

$$\underset{\substack{\text{Alkyl}\\ \text{isocyanides}}}{R-NC}\xrightarrow[H^+]{H_2O}RNH_2+HCOOH$$

Note : HCOOH gives silver mirror with tollen's reagent. Partial hydrolysis of RCN gives acid amides.

(2) Reduction

(a) Complete reduction:

(i) $$R-C\equiv N\xrightarrow[\text{reduction}]{\text{complete}}\underset{(1°\text{amine})}{R-CH_2-NH_2}$$

⇒ using $LiAlH_4$, H_2/Ni or Pt, the same result as above can be obtained.

(ii) $R-C\equiv N\xrightarrow{Na/C_2H_5OH}R-CH_2NH_2$, the reaction is known as Mendius reaction.

(b) Partial reduction:

$R-C\equiv N$ on partial reduction with $SnCl_2$/HCl followed by hydrolysis gives aldehyde (Stephen's reduction)

$$R-C\equiv N\xrightarrow{SnCl_2/HCl}RCH=NH\xrightarrow[H^+]{H_2O}RCHO$$

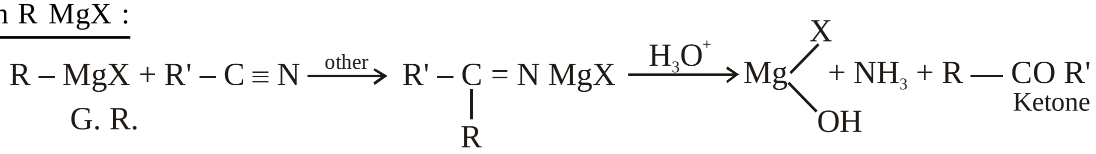
Note : RNC on reduction with H_2/Pt gives N-alkyl alkanamine.

$$R-NC\xrightarrow{H_2/Pt}R-NH\ CH_3$$

(3) Effect of heat at 250°C converts RNC into RCN :

$$R-CN\ f\ R-NC$$

(4) With R MgX :

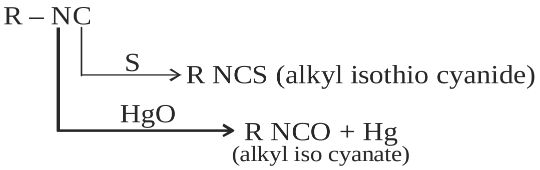


$$\underset{\text{G. R.}}{R-MgX}+R'-C\equiv N\xrightarrow{\text{other}}R'-\underset{\substack{|\\ R}}{C}=N\,MgX\xrightarrow{H_3O^+}Mg\begin{matrix}X\\ OH\end{matrix}+NH_3+\underset{\text{Ketone}}{R-CO\,R'}$$

(5) Addition reaction of RNC

RNC gives addition reaction due to the presence of lone pair of electron on carbon atom.

$R-\overset{+}{N}\equiv C:\Leftarrow$ structure of alkyl isocyanide.

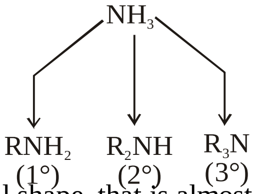


$$R-NC \xrightarrow{S} R\,NCS \text{ (alkyl isothio cyanide)}$$

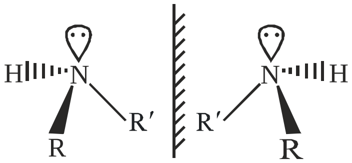
$$R-NC \xrightarrow{HgO} R\,NCO + Hg \text{ (alkyl iso cyanate)}$$

AMINES

Amines are derivatives of ammonia and are formed by the replacement of one or more hydrogen atom by R or aryl group.



Aliphatic amines have pyramidal shape, that is almost tetrahedral. Amines which have three different group attached to nitrogen, has chiral nitrogen. But, such optically active amines can't be resolved into its enantiomers because of rapid inter convertion of enantiomers to its mirror image.

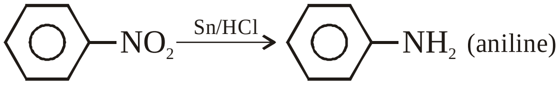


But on the other hand quaternary ammonium salt having four different groups attached to nitrogen show optically activity and its enantiomers can be resolved.

Preparation of Amines

(1) Reduction:

(i) $R-NO_2 \xrightarrow[\text{Sn / HCl}]{\text{Fe / HCl or}} R-NH_2$ $(1° \text{ amine})$



$$C_6H_5-NO_2 \xrightarrow{Sn/HCl} C_6H_5-NH_2 \text{ (aniline)}$$

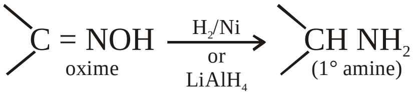
(ii) From Amides:

$$\underset{(\text{amides})}{R-CONH_2} \xrightarrow{LiAlH_4} \underset{(1° \text{ amine})}{RCH_2NH_2}$$

(iii) From Nitrites:

$$\underset{\text{nitriles}}{R-CN} \xrightarrow{LiAlH_4} \underset{(1° \text{ amine})}{R\,CH_2NH_2}$$

(iv) From oximes:



$$\underset{\text{oxime}}{>C=NOH} \xrightarrow[LiAlH_4]{H_2/Ni \text{ or}} \underset{(1° \text{ amine})}{>CH\,NH_2}$$

(2) From Hydroxy compound:

$$R-OH+NH_3 \xrightarrow[\text{or } ThO_2]{Al_2O_3,\Delta} RNH_2+H_2O$$

(3) Preparation of amines with step down:

(i) By Hofmann bromamide reaction:

$$R-CONH_2 \xrightarrow{Br_2/KOH} R\ NH_2 + KBr + K_2CO_3 + H_2O$$

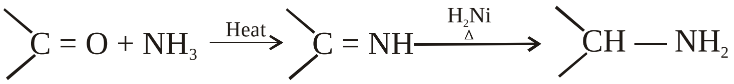
(ii) By Curtius rearrangement:

$$R-COCl \xrightarrow[Heat]{NH_3} R\ NH_2 + HCl + N_2$$

(iii) (Schmidt reaction)

$$R\ COOH + HN_3 \rightarrow R\ NH_2 + N_2 + CO_2$$

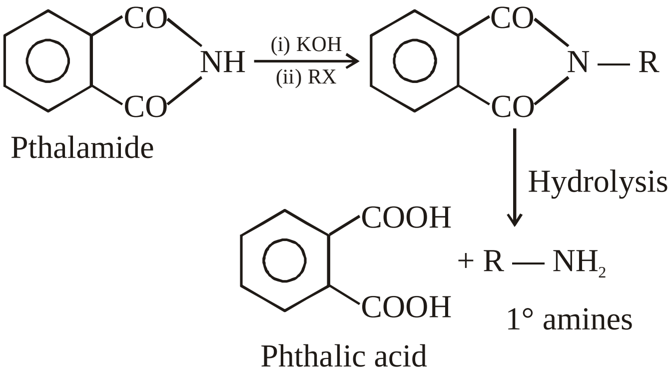
(4) Reductive aminationof aldehydes and ketones:



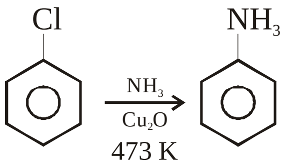
The reaction can also be used to prepare secondary and tertiary amines.

(5) Gabriel phthalimide synthesis:

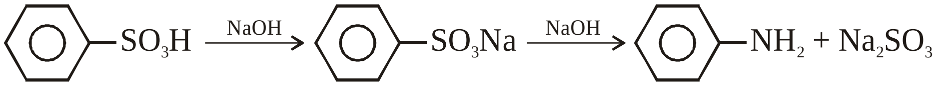
Exclusively for the preparation of primary amines.



(6) From Chlorobenzene by S_N reaction :



(7) Preparation of aniline from benzene sulphonic acid:



PROPERTIES OF AMINES

(1) Boiling Point : Out of isomeric amines, the b.p. order is 3° < 2° < 1°

(2) Solubility : Lower amines are soluble in water due to H-bonding and solubility decreases down the homologous series. Out of the three isomeric amines, the solubility order is
3° < 2° < 1°

BASICITY OF AMINES:

(i) Amines are basic in nature due to the presence of lone pair of electron on N-atom. Amines are weak bases as they give OH^- ion in aq. solution

$$R\ NH_2 + H_2O \rightleftharpoons R\ NH_3^+ + OH^-$$

where, $$\boxed{K_b = \frac{\left[RNH_3^+\right]\left[OH^-\right]}{\left[RNH_2\right]}}$$

K_b = base dissociation constant.

- Basicity increases as K_b value increases.
- Basicity $\propto K_b \propto pK_a \propto \frac{1}{pk_b}$

(ii) Except for amines containing $(CH_3)_3$ C group, all lower aliphatic amines are stronger bases than NH_3 because of the +I effect of alkyl group.

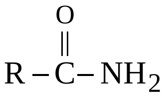
As the number of R group at N-atom increases, basicity should also increase, but the observed basicity order in case of lower member is

$$2° > 1° > 3°$$

This anamalous behaviour is due to steric factor. In 3° amines, the alkyl groups are so larger in size that amine comes under strain and becomes energetically unfavourable to accept any extra H^+ ion.

(iii) The order of basic nature is

R group	Basic strength order
CH_3—	$2° > 1° > 3° > NH_3$
C_2H_5—	$2° > 3° > 1° > NH_3$
$(CH_3)_2CH$	$2° > 1° > NH_3 > 3°$
$(CH_3)_3C$	$NH_3 > 1° > 2° > 3°$

(iv) Amides  $R-\overset{\overset{O}{\|}}{C}-NH_2$ are weaker bases than amines due to the delocalization of lone pair on N with carbonyl group.

(v) As the % character in N-atom increases, basicity decreases.

$$CH_3CH_2NH_2 \rightarrow N\left(sp^3\right) \rightarrow \text{ 25\% s-character}$$

$$CH_3CH = NH_2 \rightarrow N\left(sp^2\right) \rightarrow \text{ 33\% s-character}$$

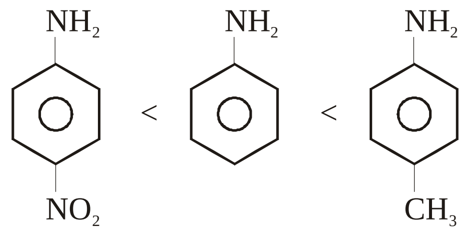
$$CH_3C \equiv N \rightarrow N\left(sp\right) \rightarrow \text{ 50\% s-character}$$

The basicity order is

$$CH_3C \equiv N < CH_3CH = NH < CH_3CH_2 - NH_2$$

(vi) Aniline is a weaker base than ethylamine because the lone pair on N is involved into resonance with the benzene ring. The electron density on N-atom decreases, basicity decreases.

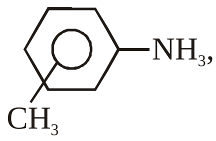
⇒ The presemce pf EDG increases the basicity and EWG decreases the basicity of aniline.



increasing basicity order

(vii) N-alkylated anilines are stronger bases than aniline because of steric hindrance. The basic character order is $C_6H_5N(C_2H_5)_2 > C_6H_5NHC_2H_5 > C_6H_5N(CH_3)_2 > C_6H_5NHCH_3 > C_6H_5NH_2$

(viii) In toluidines

$\Rightarrow$ 

, the basicity order is

p > m > o

$\longleftarrow$

(ix) In nitro anilines : The order is, p > m > o

$\longleftarrow$

REACTION OF AMINES:

(1) Amines are basic in nature, dissolves in HCl to form salt:

$$RNH_2 + HCl \rightarrow RNH_3^+Cl^-$$

$$C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+Cl^-$$

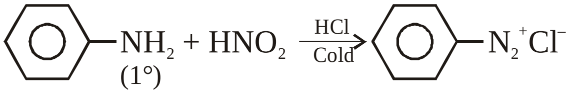
(2) In H_2O, amines gives OH^- which reacts with $FeCl_3$ to give reddish brown ppt. of $Fe(OH)_3$:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$FeCl_3 + 3OH^- \rightarrow Fe(OH)_3 + 3Cl^-$$

(3) With HNO_2 ($NaNO_2$ + HCl):

(i) (a) $\underset{1^0}{RNH_2} + HNO_2 \rightarrow ROH + H_2O + N_2 \uparrow (1°)$

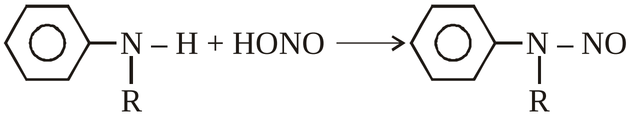


benzene diazonium chloride

This reaction is used to distinguish primary aliphatic amine and aniline.

(ii) 2° amine (aliphatic and aromatic) both form nitroso compound.

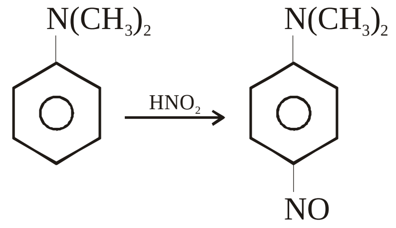
(a) $R_2NH + HONO \rightarrow R_2N — NO$

(b) 

$$C_6H_5-\underset{R}{\underset{|}{N}}-H + HONO \longrightarrow C_6H_5-\underset{R}{\underset{|}{N}}-NO$$

(iii) 3° aliphatic amines form salts with HNO_2 whereas 3° aromatic amine undergo electrophilic substitution reaction:

$$R_3N + HNO_2 \rightarrow R_3NH^+ONO^-$$



$$C_6H_5N(CH_3)_2 \xrightarrow{HNO_2} p\text{-}ON-C_6H_4-N(CH_3)_2$$

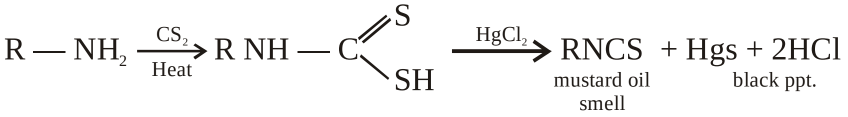
(4) Carbylamine reaction (Isocyanide Test):

This reaction is used to distinguish primary amines from secondary and tertiary. The reaction is given by both aliphatic and aromatic primary amines, only.

$$\underset{}{R-NH_2} + \underset{(alc.)}{3KOH} + CHCl_3 \xrightarrow{\text{warm}} \underset{\text{foul smell}}{R-NC} + 3KCl + 3H_2O$$

(Carbyl amine)

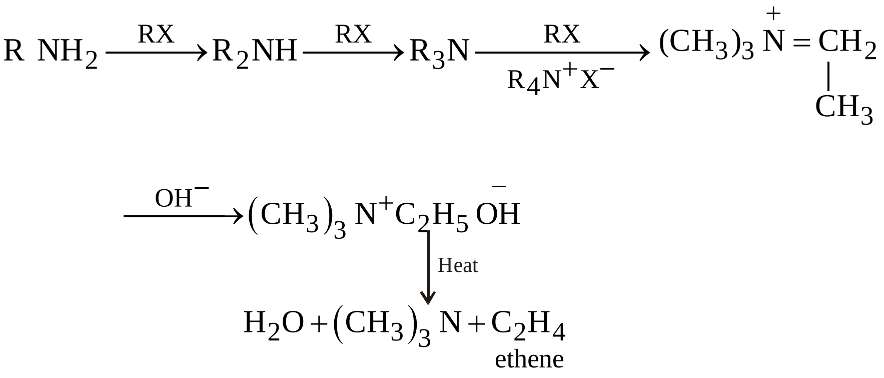
(5) Hofmann's mustard oil reaction for primary amines:



$$R-NH_2 \xrightarrow[\text{Heat}]{CS_2} R\,NH-C(=S)SH \xrightarrow{HgCl_2} \underset{\substack{\text{mustard oil}\\\text{smell}}}{RNCS} + \underset{\text{black ppt.}}{Hgs} + 2HCl$$

Note: Secondary amines →no black ppt.

(6) Alkylation of amine (Hofmann exhaustive alkylation):

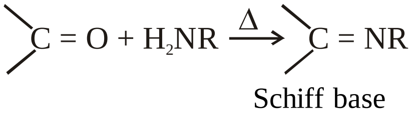


$$R\ NH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow[R_4N^+X^-]{RX} (CH_3)_3\overset{+}{N}=\underset{\underset{CH_3}{|}}{CH_2}$$

$$\xrightarrow{OH^-} (CH_3)_3N^+C_2H_5\overset{-}{O}H \xrightarrow{\text{Heat}} H_2O + (CH_3)_3N + \underset{\text{ethene}}{C_2H_4}$$

⇒ This is called Hofmann elimination. In this method, the alkene is obtained with lesser number of alkyl group.

(7) With aldehyde and ketones, amine form Schiff base:

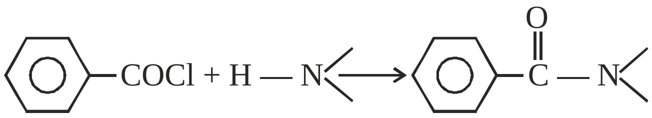


$$>C=O + H_2NR \xrightarrow{\Delta} \underset{\text{Schiff base}}{>C=NR}$$

(8) With RMgX:

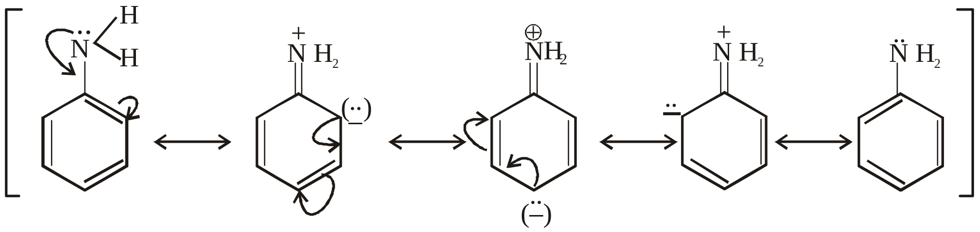
$$\rangle N-H + R-MgX \longrightarrow \rangle N-MgX + \underset{\text{alkane}}{RH}$$

(9) Benzoylation of amines is known as Schotten-Bauman reaction :

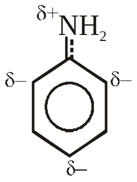


REACTION OF ANILINE :

Aniline is ortho-para directing group for incoming electrophiles because of + R or +M effect.



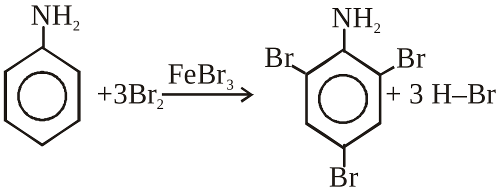
RESONANCE HYBRID STRUCUTRE



ELECTROPHILIC SUBSTITUTION REACTION

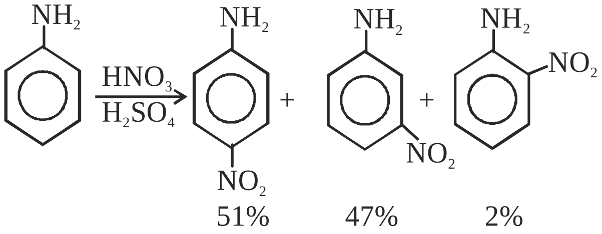
Anniline ring is largely activating for incoming electrophiles

1. Bromination:

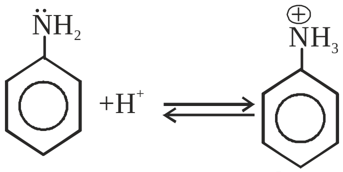


2,4, 6 Tribromo-aniline

2. Nirtration:



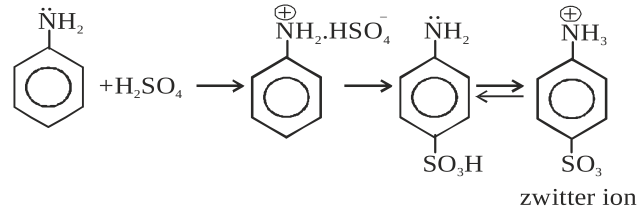
⇒ The meta proudct is formed, due to the formation of anilinium ion.



Annilinium ion

⇒ Anilinium ion is meta directing

Sulphonation:

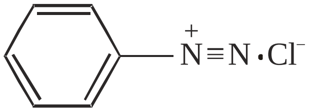


DIAZONIUM SALT

PREPARATION

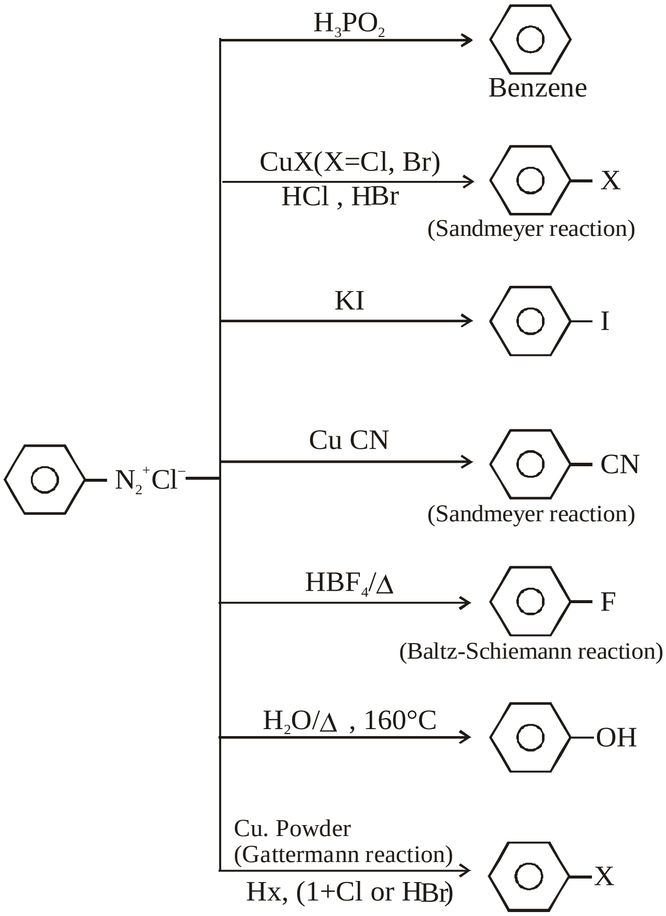
This reaction is given by compounds in which the —NH_2 group is directly bonded to the benzene ring. The aniline is treated with $NaNO_2$ and HCl at 0 to –4° C.

Structure of benzene diazonium chloride is



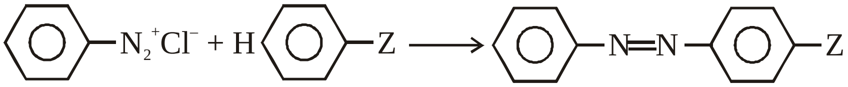
Benzene diazonium chloride gives various types of reaction

FEW CHEMICAL REACTIONS OF DIAZONIUM SALT:



(2) Coupling reaction

It involves the retention of diazonium group. No nitrogen gas is evolved. These is an examples of electrophilic substitution reaction.

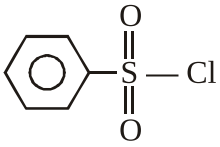


(Z=OH, OR,
NH_2, NHR, NR_2)

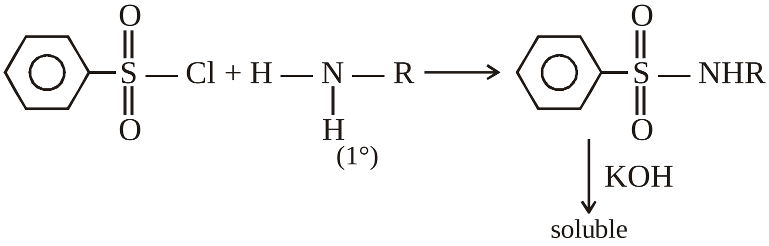
TEST FOR AMINES

(1) Hinsberg's test

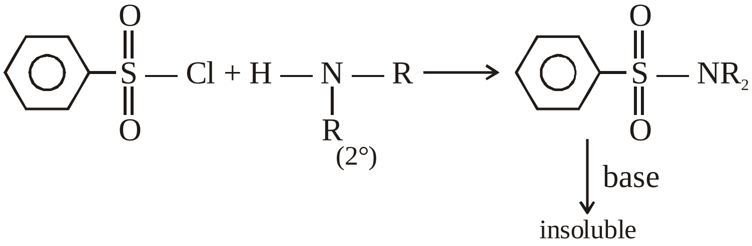
Hinsberg's reagent is benzene sulphonyl chloride.



1° amine gives a base soluble product with Hunsberg's reagent.



2° amine gives a base insoluble product with Hinsberg's reagent.



3° amines do not react with Hinsberg's reagent.

Biomolecules

The hydrates of carbon was originally defined as carbohydrates, with general formula of Cn(H_2O)y. But this defination has found several limitations today.

(i) Carbon do not forms hydrates

(ii) There are number of organic molecules having Cn(H_2O)y formula but are not carbohydrates.

e.g. (a) Formaldehyde (HCHO) : CH_2O

(b) Acetic acid CH_3COOH : $C_2H_4O_2$ etc.

(iii) A number of carbohydrates do not have Cn(H_2O) formula.

e.g. (i) Rhamnose - $C_6H_{12}O_5$

(ii) Deoxyribose - $C_5H_{10}O_4$

MODERN DEFINITION :

Polyhydroxy aldehyde or Ketone or substances which gives these on hydrolysis is called carbohydrates. They have at least one chiral carbon is general

CLASSIFICATION :

TYPE : 1

Carbohydrates

(1) Monosaccharides	(2) Oligosaccharides	(3) Polysaccharides
Simplest carbohydrates which can't be hydrolysed into simpler molecules Gen. formula = $(CH_2O)_n$ n = 3 to 7.	* oligo = few Carbohydrates which on hydrolysis gives 2 to 10 molecules of carbohydrates	Carbohydrates which on hydrolysis gives number of carbohydrates. e.g. $(C_6H_{10}O_5)$n n = 100 to 3000

TYPE : 2

Carbohydrates

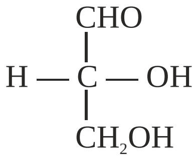
(i) Sugar	(ii) Non-Sugar
All the Mono and Oligosaccharides have sweet taste and these are collectively called sugars. They are crystalline in nature.	Polysaccharides are tasteless and are called non-sugar. They are amorphous in nature.

TYPE : 3

Carbohydrates

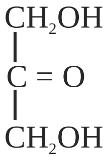
(i) Reducing	(ii) Non-Reducing
All those carbohydrates which has aldehydic or ketonic group in their hemiacetal and hemiketal structures have the ability to reduce Tollen's Reagent or Fehling solution. They are called Reducing sugar. * All Monosaccharides whether aldose or ketose are reducing sugars.	The carbohydrates which can not reduce Tollen's reagent or Fehling solutions are called as Non-reducing. * All Polysaccharides are non reducing. e.g. Starch, Cellulose, dextrins, Glycogens etc.

Simplest Triose : The simplest monosaccharides are triose.



$$\begin{array}{c} CHO \\ | \\ H - C - OH \\ | \\ CH_2OH \end{array}$$

Aldotriose
Glyceraldehyde



$$\begin{array}{l} CH_2OH \\ | \\ C = O \\ | \\ CH_2OH \end{array}$$

Aldoketose
Dihydroxy acetone

GLUCOSE

* They are also called as Grape sugar or Dextrose. It is present in sweet fruits.
Molecular formula — $C_6H_{12}O_6$
It is aldohexose sugar

PREPARATION OF GLUCOSE :

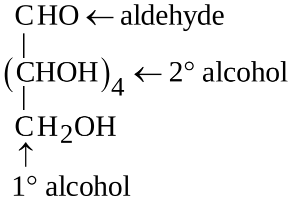
(i) From Sucrose (Cane - Sugar) : By acidic hydrolysis.

$$C_{12}H_{22}O_{11} \xrightarrow{H_3O^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) From Starch : Commercial method.

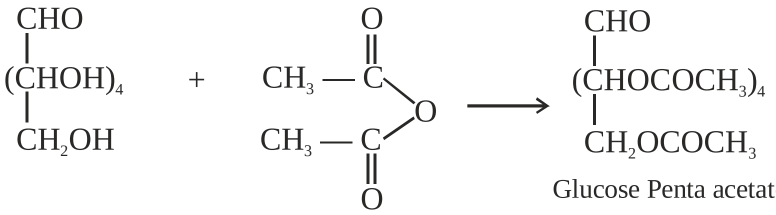
$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{393K.Boil}]{nH_3O^+} n\ \underset{\text{Glucose}}{C_6H_{12}O_6}$$

CHEMICAL REACTION OF GLUCOSE :



$$\begin{array}{l} CHO \leftarrow \text{aldehyde} \\ | \\ (CHOH)_4 \leftarrow 2^\circ \text{ alcohol} \\ | \\ CH_2OH \\ \uparrow \\ 1^\circ \text{ alcohol} \end{array}$$

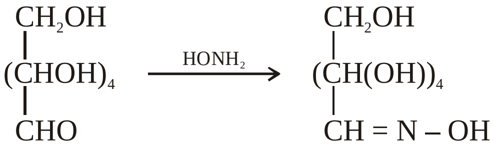
1. Reaction with Acetic anhydride : Acetylation



$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array} + \begin{array}{c}CH_3-\overset{\displaystyle O}{\overset{\|}{C}}\\ \quad\quad\;\; \rangle O\\CH_3-\underset{\displaystyle O}{\underset{\|}{C}}\end{array} \longrightarrow \begin{array}{c}CHO\\|\\(CHOCOCH_3)_4\\|\\CH_2OCOCH_3\end{array}$$

Glucose Penta acetate

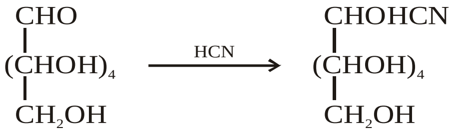
2. Reaction with hydrosylamines :



$$\begin{array}{c}CH_2OH\\|\\(CHOH)_4\\|\\CHO\end{array} \xrightarrow{HONH_2} \begin{array}{c}CH_2OH\\|\\(CH(OH))_4\\|\\CH=N-OH\end{array}$$

Glucose monoxime

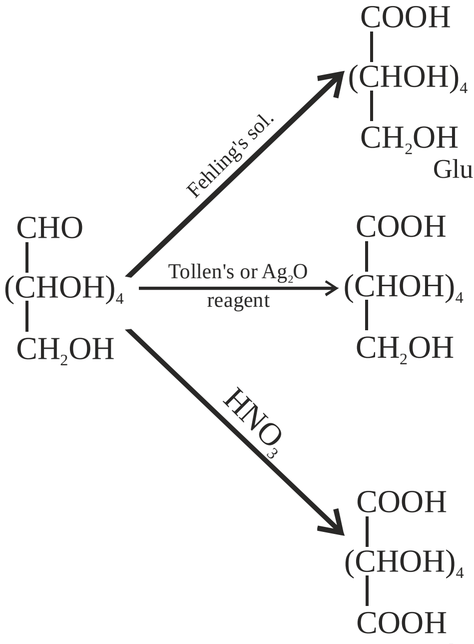
3. Reaction with HCN :



$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array} \xrightarrow{HCN} \begin{array}{c}CHOHCN\\|\\(CHOH)_4\\|\\CH_2OH\end{array}$$

Glucose cyanohydrin

4. Oxidation :



$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array} \xrightarrow{\text{Fehling's sol.}} \begin{array}{c}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}$$

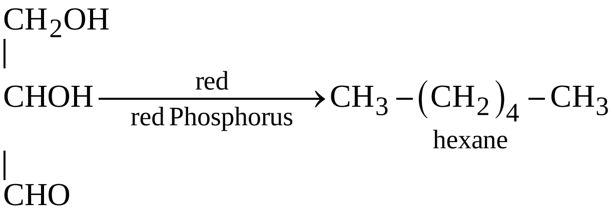
Gluconic acid

$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array} \xrightarrow[\text{reagent}]{\text{Tollen's or } Ag_2O} \begin{array}{c}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}$$

$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array} \xrightarrow{HNO_3} \begin{array}{c}COOH\\|\\(CHOH)_4\\|\\COOH\end{array}$$

saccharic acid

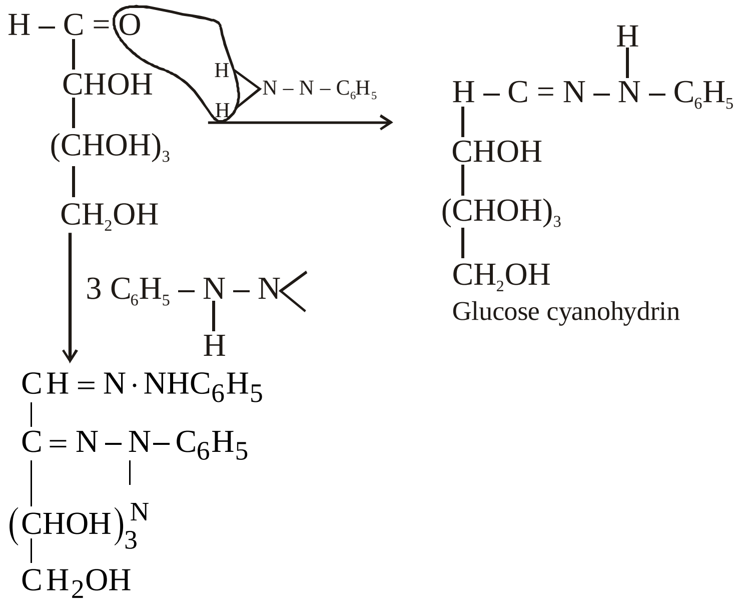
5.Reduction :



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CHO\end{array} \xrightarrow[\text{red Phosphorus}]{\text{red}} CH_3-(CH_2)_4-CH_3$$

hexane

6. Reaction with Phenyl hydrazine :


Glucose cyanohydrin

Glucose dihydrazone (Osazone)

7. Action of Alkali : Lobry de Bruyn-van Ekenstein reaction

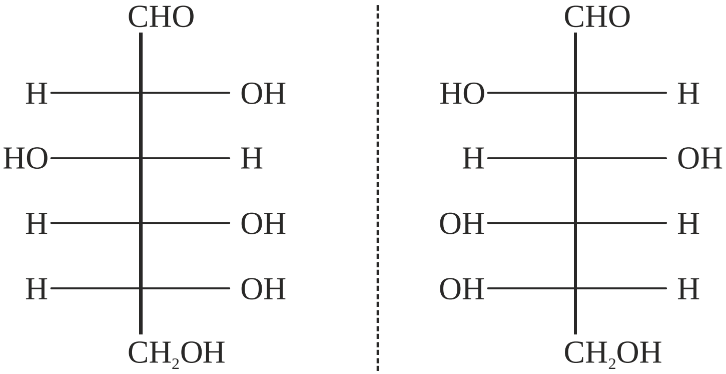
D — Glucose $\rightleftharpoons$ D — Mannose $\rightleftharpoons$ D — Fructose

On adding concentrated solution of NaOH this occurs.

⇒ It is probably on account of this isomerisation, that fructose reduces Fehling's solution and Tollen's Reagent in alkaline medium.

Structure of Glucose

Open-chain strs :


D-Glucose

L-Glucose

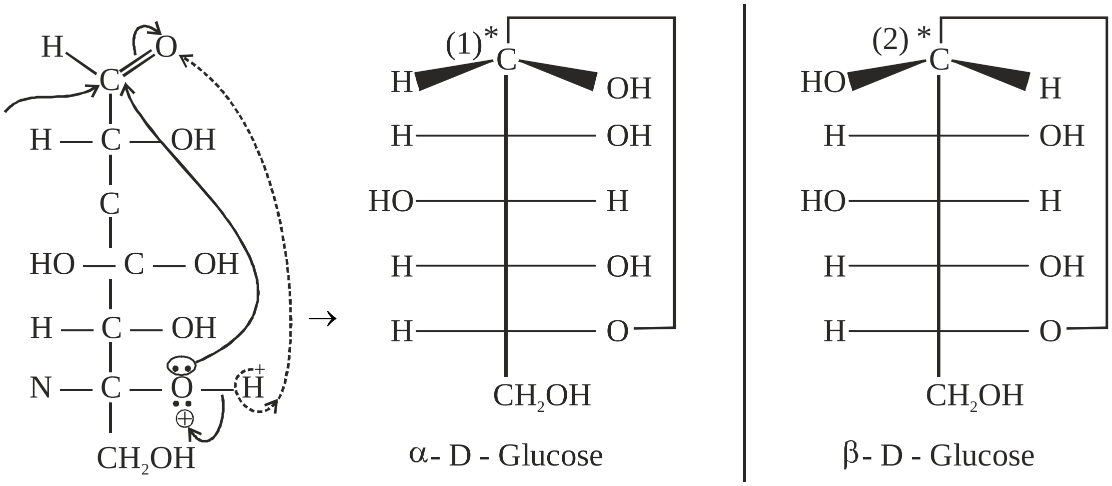
Limitationof open-chain strs :

(i) Glucose doesn't undergo characteristic reaction of aldehydes such as
  (a) Glucose does not reacts with $NaHSO_3$ (sodium bisulphate)
  (b) Glucose does not responds to schiff's test.
(ii) Glucose doesn't reacts with G.R.

Cyclic structures of Glucose :

$\alpha - D$ and $\beta - D$ Glucose : (Hemiacetal structures)

- In α-D-Glucose OH group is towards right while in β-D-Glucose the OH group is towards left at C_1.



α- D - Glucose

β- D - Glucose

ANOMERS :

"The stereo isomers which differs in configuration at "C_1" is called anomers".

The "Cl" is also called as anomeric carbon or Glycosidic carbon.

Note :'α' and 'β - D' Glucose are not enantiomers, since the configuration at other carbon remains same.

Mutarotation :

When Glucose is crystallized from a concentrated solution at 300 K, α form of D-Glucose is isolated. But, from a hot saturated solution (aqueous) at a temperature in excess of 100°C, the β-Glucose is obtained.

Term	α	β
M.pt :	146°C	150°C
Sp. rotation :	+111°	+19.2°

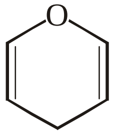
If eithe of the two forms is dissolved in water and allowed to stand, the specific rotation of the solution slowly changes and reaches a constant value of +52.5°.

"The spontaneous change in specific rotation of an optically active compound is called muta rotation".

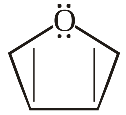
$$\boxed{\underset{\text{glu cos e}}{\alpha-D-(+)} \rightleftharpoons \underset{\text{Mixture}}{\text{Equilibrium}} \rightleftharpoons \underset{\text{Glucose}}{B-D+ve}}$$

Haworth structures of Glucose : The molecules of glucose and fructose can exist in any of the two cyclic structures.

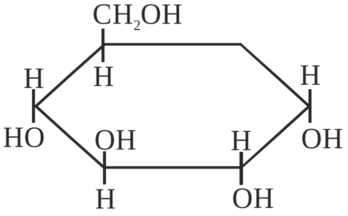
(a) Pyranose structure	(b) Furanose structure
Six membered ring	5 Membered Ring
Derived from pyran	Derived from furan



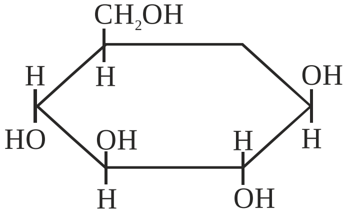
Pyran



Furan



α –D Glucose



β –D Glucose

OLIGOSACCHARIDES

These are carbohydrates which gives 2 to 10 molecules of monosaccharides.

* In some standard text (particularly in Biology) n = 2 to 7 has been frequentaly used.

Example

(1)	Disaccharides	:	Sucrose, Maltose, Lactose
(2)	Trisaccharides	:	Raffinose
(3)	Tetrasaccharides	:	Stachyrose

Disaccharides :

Gives two molecules of same or different monosaccharides.

General formula :

Formula : $C_{12} H_{22} O_{11}$

Examples and its monomers :

(1) Sucrose $\xrightarrow[H_3O^+]{\text{Invertase}}$ Glucose + Fructose

(2) Maltose $\xrightarrow[\text{Maltase}]{H_3O^+}$ Glucose + Glucose

(3) Lactose $\xrightarrow[\text{Lactase}]{H_3O^+}$ Glucose + Galactose

- The disaccharides can be reducing or non reducing. If carbonyl group is free, sugar is reducing.

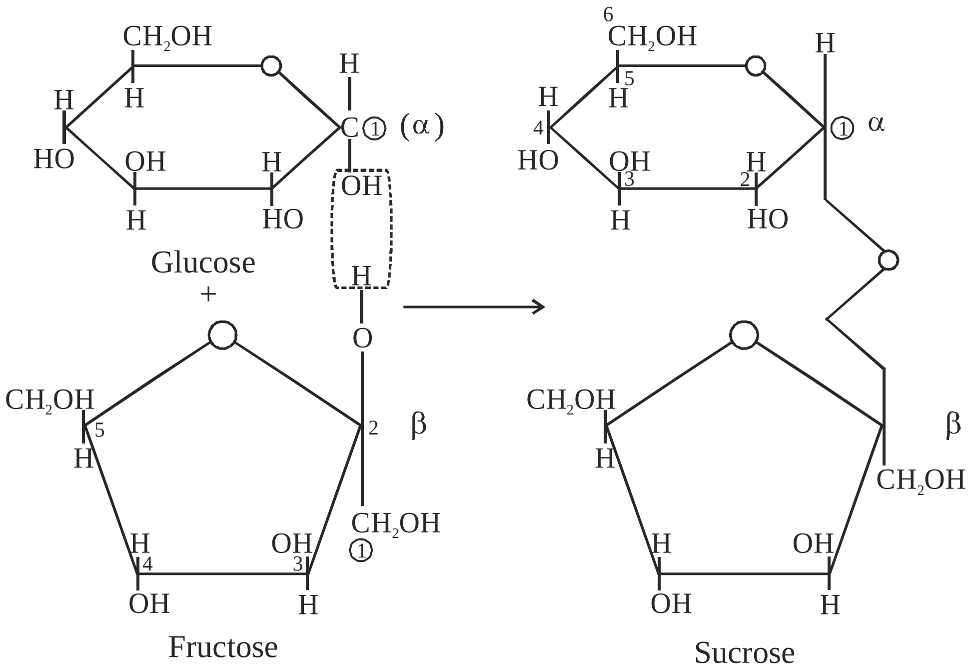
Sucrose or cane sugar or Table Sugar :

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_3O^+} \underset{\text{D}-\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{D}-\text{Fructose}}{C_6H_{12}O_6}$$

Specific rotation + 66.5° +52.5° –92.4°

Since the laevorotation of fructose is more than the dextro rotation of glucose, the resulting solution will be laevo rotatory. This overall process is called inversion of sugar.

HAWORTH STRUCTURE OF SUCROSE :



- Determination of ring size by spectral methods has revealed that, in sucrose glucose is in its pyranose form and fructose it is furanose form.
- There is thus, α,β glucosidic bond between glucose and fructose as monomers.

POLYSACCHARIDES :

Polysaccharides are formed when large number of monosaccharide joins together with simultaneous elimination of water molecules.

Some common polysaccharides are :

(i) Cellulose (ii) Starch (iii) Glycogen (iv) Dextrin

STARCH :

(i) It is also called as Amylum.

General formula - $(C_6H_{10}O_5)_n$

where, $n \cong 100 \text{ to } 300$

It is the chief food storage material in plants.

(ii) Starch is white amorphous powder which is sparingly soluble in water.

(iii) <u>Hydrolysis of starch :</u>

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{or Diastase}]{H_3O^+} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

$$\downarrow \text{Maltose}$$

$$\text{D}-\text{Glucose}$$

(iv) Starch does not reduce Fehling solution or Tollen's reagent and does not form osazone. This clearly suggests that all hemiacetal hydroxy group of glucose unit at C_1 is involved in glycosidic linkage.

(v) Starch is a mixture of two poly saccharides Amylose and Amylopectins.

Natural starch has

Amylose : 10 to 20%

Amylopectin : 80 to 90%

CELLULOSE :

(i) It is the major constituent material of plant cell wall. In general, wood contains 50% cellulose and cotton contains 90-95% cellulose.

(ii) It is a colourless, amorphous solid which can be decomposed by heating.

(iii) It is almost linear and its individiual monomeric units are joined through multiple H-bond.

(iv) Cellulose does not reduce Fehling solution, Tollen's reagent and does not forms osazone.

(v) Large population of cellulotic bacteria is present in the stomach of ruminant mammals. These bacteria causes decomposition of cellulose in stomach cellulose is digested as glucose in ruminant mammals.

(vi) Human does not have any system to digest cellulose.

(vii) Structure of Cellulose : Cellulose is a straight chain polymer of D-glucose which are joined by $\beta -$ Glucosidic bond b/w C_1 of one glucose and C_4 of other glucose.

PROTEINS

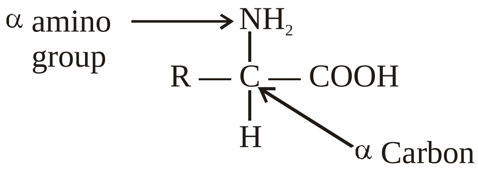
Proteins are vital chemical substance essential for the growth and maintenance of life. Chemically proteins are condensation polymers in which the monomeric unit is α amino acids. All proteins contain the elements like carbon, hydrogen, oxygen nitrogen and sulphur in major.

HYDROLYSIS OF PROTEINS

$$\text{Protein} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha - \text{Amino acids}$$

α Amino acids :

α amino acids are the building block of proteins.



$$R - \overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - COOH$$

The total of 2O amino acids has been isolated by hydrolysis of various proteins.

Classification of α Amino acids :

Amino acids

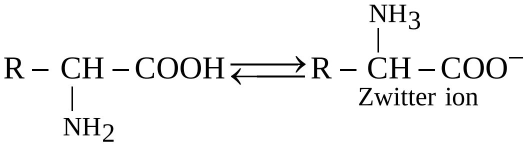
Essential	Non-essential
The amino acids which can't be synthesised in human body is called essential amino acids * They arey 10.	The amino acids which can be synthesised in human body is called non-essential amino acids. * They are also 10.

α - Amino acids

(a) Neutral	(b) Alkaline	(c) Acidic
Has one NH_2 group and one COOH group.	Two NH_2 group and one COOH group	Has two COOH group and one NH_2 group

Zwitterion ion structure :

α - amino acid largely exists as dipolar ion.

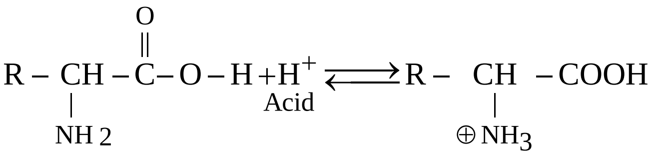


$$R-\underset{\underset{NH_2}{|}}{CH}-COOH \rightleftharpoons R-\overset{\overset{NH_3}{|}}{CH}-COO^-$$

Zwitter ion

Electrical behaviour of Amino acids :

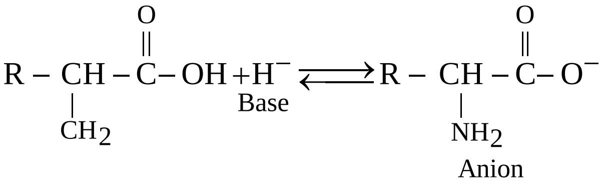
(a) In acidic solution : α amino acid exist as cations and thus will migrat towards the cathode under electrical field.



$$R-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-O-H+\underset{Acid}{H^+} \rightleftharpoons R-\underset{\underset{\oplus NH_3}{|}}{CH}-COOH$$

The cation will migrat towards cathode.

(b) In alkaline solution : α Amino acid exist as



$$R-\underset{\underset{CH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-OH+\underset{Base}{H^-} \rightleftharpoons \underset{Anion}{R-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-O^-}$$

The anion will migrat towards +ve electrode i.e. Anode.

Iso electric point :

The pH at which amino acid has no net migration towards any of the electrode under influence of electric field is called isoelectric point.

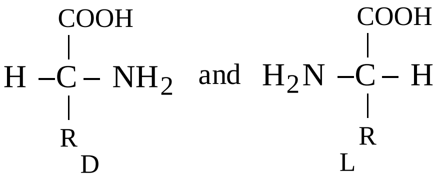
Each amino acid has a characteristic isoelectric point.

Amino acid	Iso electric point (pH)
(1) Neutral	Slightly less than 7($\cong$ 6.1)
(2) Acidic	3.2 to 3.5
(3) Alkaline	7.6 to 10.8

At isoelectric point amino acids have least solubility.

D, L Nomenclature of Amino acids :

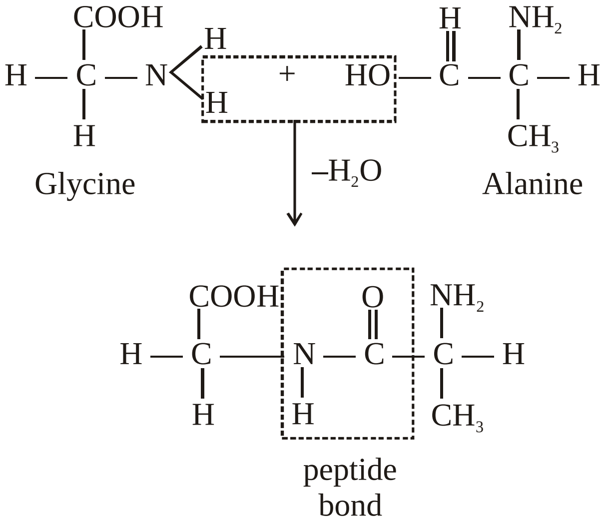
Au amino acids except glycine is chiral and has two stereo isomeric forms.



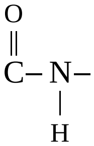
All naturally occuring amino acid belongs to L series.

Peptide bond :

Peptides are organic amides formed by the condensation of amino group of one α amino acid and carboxylic acid of other amino acid, by simultaneous elimination of water.

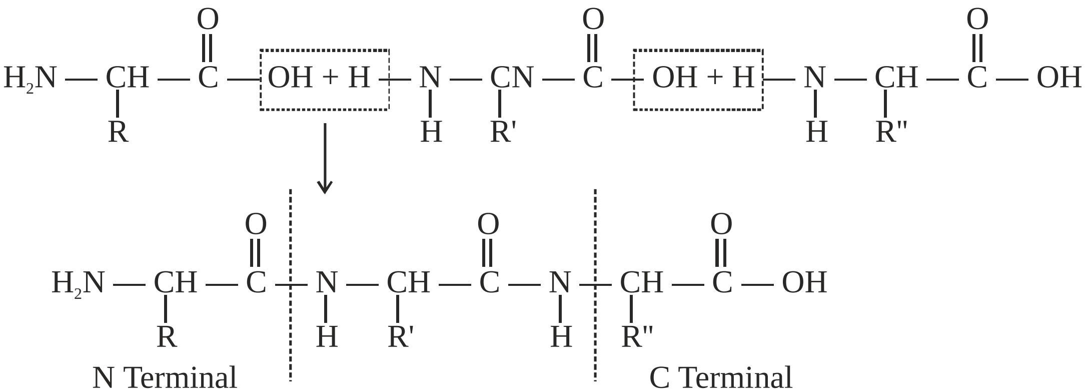


[Gly - Ala]

* Thus  $\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-$ linkage is called the peptide bond.

Poly peptides :

If large number of α amino acids are joined together by peptide bonds, the polyamide is formed. Such polyamides are called polypeptides.



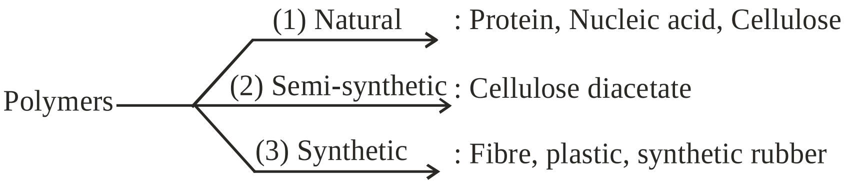
POLYMERS

POLYMERS

The small molecules that combines with each other to form a macromolecule is called monomer, The macromolecule formed is called polymer.

CLASSIFICATION OF POLYMERS :

(a) Based on source of availability :



: Protein, Nucleic acid, Cellulose

: Cellulose diacetate

: Fibre, plastic, synthetic rubber

(b) Based on mode of polymerisation :

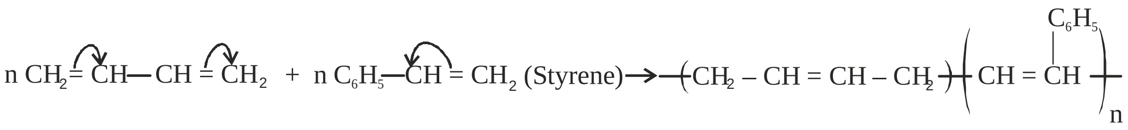
(1) Homo-polymer (2) Addition or Condensation.

Homopolymer and copolymer : Homopolymers one polymers having single type of monomers.

$$n\,CH_2 = CH_2 \longrightarrow \left(CH_2 - CH_2 \right)_n$$

Polythene

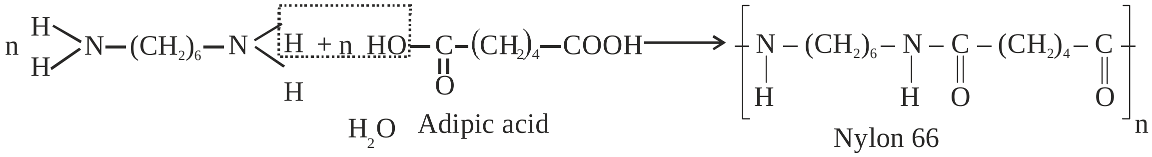
- While the polymers of two or more than two types of monomers is called co-polymers.
  e.g.



$$n\,CH_2=CH-CH=CH_2 \;+\; n\,C_6H_5-CH=CH_2 \text{ (Styrene)} \longrightarrow \left[\left(CH_2-CH=CH-CH_2 \right) - \left(CH=\overset{C_6H_5}{\overset{|}{CH}} \right) \right]_n$$

(3) Addition Polymers : This polymers is formed by monomer molecules having double or triple bond.
e.g. Polythene.

(4) Condensation Polymers : This polymer is formed by condensation of monomer with simultaneous loss of small molecules like. H_2O, NH_3, alcohol etc.
e.g. Nylon 66.



$$n\;\begin{matrix}H\\H\end{matrix}\!>N-(CH_2)_6-\underset{H}{N}<\boxed{H \;+ n\;HO}-\underset{\|\;O}{C}-(CH_2)_4-COOH \longrightarrow \left[\underset{|\;H}{N}-(CH_2)_6-\underset{|\;H}{N}-\underset{\|\;O}{C}-(CH_2)_4-\underset{\|\;O}{C} \right]_n$$

H_2O Adipic acid

Nylon 66

(c) Classification of polymers on the basis of Molecular force:

(i) Elastomers (ii) Fibre (iii) Thermoplast (iv) Thermosetting

(1) Elastomers : Polymers are held by weakest force.

⇒ These weakest force causes stretching of the strected polymer to its normal size.

e.g. ⟶ valcanized rubber.

(2) Fibre : Has high tensile strength

⇒ Has stronger intermolecular forces like H-bond

⇒ Imparts crystalline nature, due to which it has sharp M.Pt. e.g. → Fibre

(3) Thermoplastics : Has intermediate force between elastomer and fibre

⇒ Has no cross-links. e.g. → Polyethylene, Polystyrene.

(4) Thermosetting : This is relatively low molecular mass polymers of semi-fluids which on heating in a mould becomes infusible hard mass.

⇒ This happen due to extensive cross linking.

⇒ Has three dimensional network of bonds. e.g. → Bakelite.

General Methods of Polymerisation :

1. Addition 2. Condensation

1. Addition :

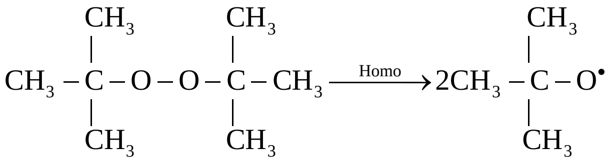
The monomers are unsaturated alkene, alkadiene or their derivatives.

⇒ The addition polymers can be classified into three types on the basis of its monomers.

1. Radical 2. Carbocation 3. Carbanion

- The addition polymerisation is also called as chain growth polymerisation, because it takes place through stages leading to increase in chain-length and the each stage produces relatively reactive intermediate which is used in next step.

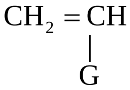
(1) Free-Radical Addition Polymers : The free-radical polymers take place through initiator. Initiator generates radical. e.g.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{Homo}} 2CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\bullet}$$

Initiator (In)

Vinyl Polymensation : Obtained from

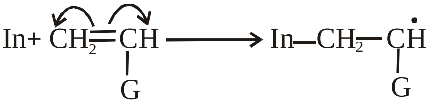


$$\underset{\qquad\quad G}{CH_2=CH}$$

Its formation can be depicted by given mechanism

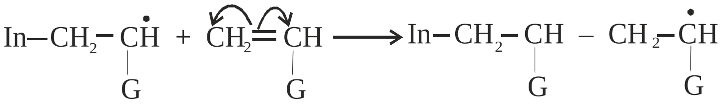
1st Step: Chain initiator step :

$$\text{Initiator} \longrightarrow \text{In}^{\bullet}$$



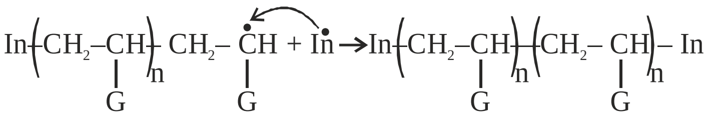
$$\text{In}+ CH_2=\underset{G}{CH} \longrightarrow \text{In}-CH_2-\underset{G}{\overset{\bullet}{CH}}$$

2nd Step: Chain Propagation :



$$\text{In}-CH_2-\underset{G}{\overset{\bullet}{CH}} + CH_2=\underset{G}{CH} \longrightarrow \text{In}-CH_2-\underset{G}{CH}-CH_2-\underset{G}{\overset{\bullet}{CH}}$$

3rd Step : Termination :



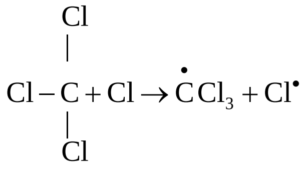
$$\text{In}\left(CH_2-\underset{G}{CH}\right)_n CH_2-\underset{G}{\overset{\bullet}{CH}} + \overset{\bullet}{\text{In}} \rightarrow \text{In}\left(CH_2-\underset{G}{CH}\right)_n\left(CH_2-\underset{G}{CH}\right)_n-\text{In}$$

Concept of chain transfer agents :

Some times some other compounds present may compete with the parent addition chain reactions and it initiates its non chain growth to simultaneously stop the normal polymerisation. Such reagents are called chain transfer agents and it includes CCl_4.

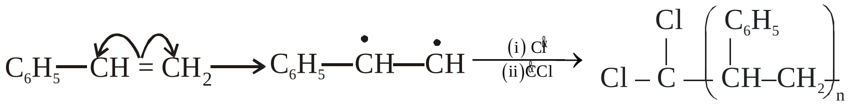
$\underset{\text{(Styrene)}}{C_6H_2-CH=CH_2}$, with normal initiator will form polystyrene but due to the presence of CCl_4 the different polymeric product is formed.

1st Step :



$$Cl-\underset{Cl}{\overset{Cl}{C}}+Cl\rightarrow\dot{C}Cl_3+Cl^{\bullet}$$

2nd Step :



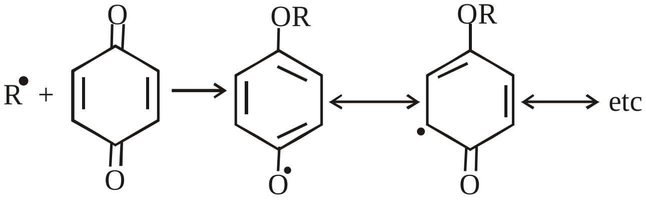
$$C_6H_5-CH=CH_2\longrightarrow C_6H_5-\dot{C}H-\dot{C}H\xrightarrow[(ii)\,CCl]{(i)\,Cl^{\bullet}}Cl-\overset{Cl}{C}-\left(\overset{C_6H_5}{CH}-CH_2\right)_n$$

Chain Inhibitors :

If the chain transfer agent forms a radical which is highly unreactive, the reaction chain gets terminated. Such compounds inhibit the polymerisation and they are -

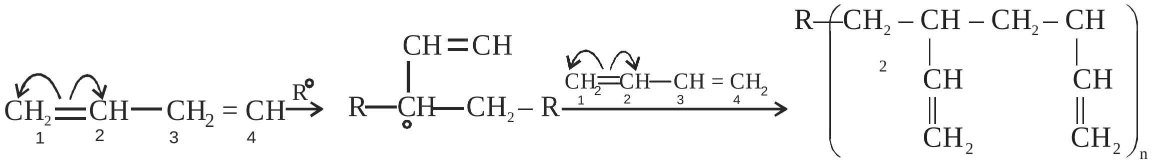
(a) Phenol (b) Some amines (c) Quinoline

If the chain transfer agent is, Banzoquinone,

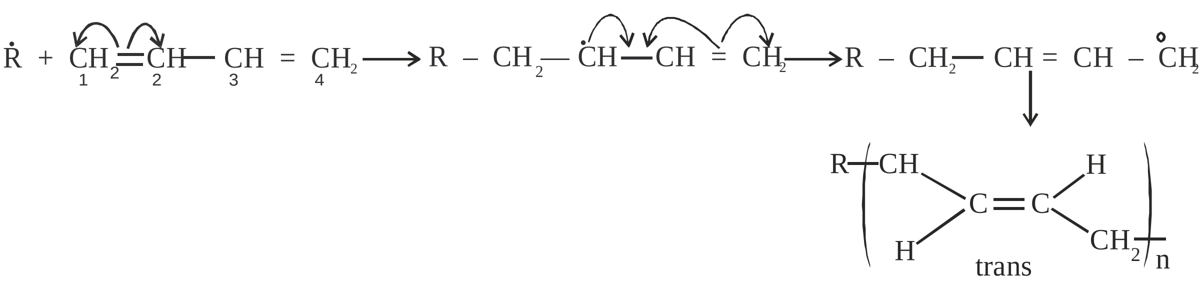


Conjugated dienes : (1) 1, 2 diene (2) 1, 4 diene

(1) 1, 2 Polymerisation :

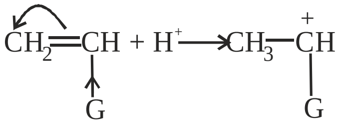


2. 1, 4 Polymers



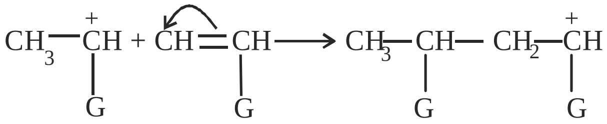
Cationic Addition Polymers :

(a) Chain reaction :



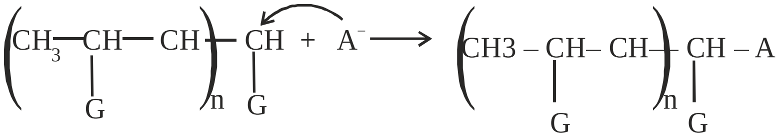
$$CH_2=\underset{\substack{|\\G}}{CH} + H^+ \longrightarrow CH_3-\overset{+}{\underset{\substack{|\\G}}{CH}}$$

(b) Chain Propagation :



$$CH_3-\overset{+}{\underset{\substack{|\\G}}{CH}} + CH=\underset{\substack{|\\G}}{CH} \longrightarrow CH_3-\underset{\substack{|\\G}}{CH}-CH_2-\overset{+}{\underset{\substack{|\\G}}{CH}}$$

(c) Chain termination : By Anions



$$\left(CH_3-\underset{\substack{|\\G}}{CH}-CH\right)_n-\overset{+}{\underset{\substack{|\\G}}{CH}} + A^- \longrightarrow \left(CH3-\underset{\substack{|\\G}}{CH}-CH\right)_n-\underset{\substack{|\\G}}{CH}-A$$

SOME COMMERCIALLY IMPORTANT

S.No.	Name of Polymer	Structure	Monomer	Uses
1.	Polythene	$(CH_2-CH_2)_n$	$CH_2=CH_2$	As insulator, anticorrsoive, packing material, household and laboratory wares.
2.	Polyvinylchloride (PVC)	$\left(CH_2-\overset{\substack{Cl\\|}}{CH}\right)_n$	$CH_2=CHCl$	In manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
3.	Polytetrafluoro ethylene (PTFE) or Teflon	$(CF_2-CF_2)_n$	$CF_2=CF_2$	As lubricant, insulator and making cooking wares.
4.	Neoprene	$\left(CH_2-\underset{\substack{|\\Cl}}{C}=CH-CH_2\right)_n$	$CH_2=\underset{\substack{|\\Cl}}{C}-CH=CH_2$	As insulator, making conveyor belts and printing rollers.

CHEMISTRY IN EVERYDAY LIFE

DRUGS :

Chemical compounds used for the treatment of diseases are called drugs or medicines.

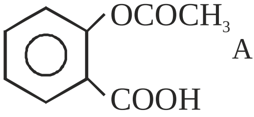
TYPE OF DRUGS:

1. Antipyretics :

Chemical substaces used to bring down body temperature in case of high fever. e.g. Paracetamol, Aspirin.

2. Analgesics :

Drugs used for relieving pain. Some analgesics have antipyretic properties too e.g. Aspirin, Ibuprofen, analgin. The structure of aspirin is:



Aspirin (2-Acetoxy benzoic acid)

3. Tranquilizers :

Drugs used for treatment of stress, mild and severe mental diseases by inducing a sense of well being, also called psychotherapeutic drugs.

Hypnotic tranquilizers : sleep producing transquilizers are barbiturates

4. Antiseptics and Disinfectants

Antiseptics : Chemicals which kill or prevent the growth of micro organisms and are harmless to human living tissue. e.g. Dettol (Mixture of chloroxylenol and terpeneol)

5. Anti fertility drugs :

Steroids are active ingredients of the oral contraceptive pill functioning as anti fertility agent. Oral contraceptive pill controls the female menstrual cycle and ovulation and prevents pregnancy.

The birth control pill is a mixture of synthetic estrogen and progesterone derivatives.

⇒ Mifepristone is a synthetic steroid that blocks the effects of progesterone and is used “morning after pill” in many countries.

6. Antihistamines (Anti-allergic drugs) :

Drugs which combat the effects of histamine, a chemical released by certain cells of the body during allergic reaction.

They help cure allergies like skin rashes, conjunctivitis (inflammation of conjuctiva of eye), rhinitis (inflammation of nasal mucosa), sneezing, nasal discharge, itching of eyes, nose and throat. Antiallergic drugs are diphenylhydramine, chlorpheniramine, and promethazine.

7. Antibiotics :

A substance (produced wholly or partly by chemical synthesis), which in low concentration inhibits the growth or destroyes microorganisms by intervening in their metabolic cycle.

Bactericidal antibiotics	Bacterisotatic antibiotics
Penicillin	Erythromycin
Aminoglycosides	Tetracycline
Ofloxacin	Chloramphenicol

8. Sulpha drugs :

Acts against disease causing microbes, e.g. sulphanilamide, sulphadiazine, sulphaguanidine.

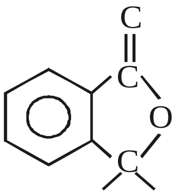
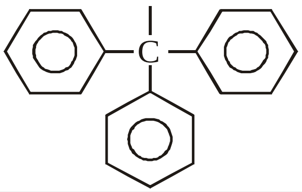
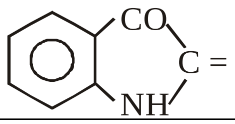
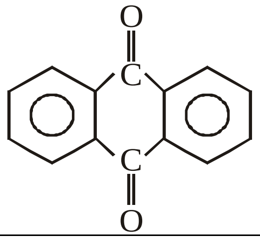
9. Antacids :

Chemicals which remove excess said and secretion pH to appropriate level in stomach. Antacids are used to cure acid gastritis, e.g., magnesium hydroxide, magnesium carbonate, magnesium trisilicate, aluminium hydroxide gel, sodium bicarbonate, aluminium phosphate, omeprazole, lansoprazole.

DYES

A dye is a coloured substance that can be applied in solution or dispersion to a substrate, giving it a coloured appearance. The substrate may be fibre, paper, leather, hair, fur, plastic, wax, and foodstuff. Earliest known dyes-indigo (a blue dye) and alizarin (a red dye).

CLASSIFICATION OF DYES BASED ON CONSTITUTION

Class of the Dye	Functional group present	Name of the Dye
AzO	—N=N—	Aniline yellow Orange-I Methyl orange Congo red
Nitro	$—NO_2$	Martius yellow
Phthalein		Phenolphthalein
Triphenyl methane		Magneta, Malachite green
Indigoid		Indigo
Anthraquinoid		Alizarin