HANDBOOK OF CHEMISTRY

ALLEN™
CAREER INSTITUTE
KOTA (RAJASTHAN)
Path to Success

CHAPTER 1

MOLE CONCEPT

SOME USEFUL CONVERSION FACTORS

$1\ \text{Å} = 10^{-10}\ \text{m}$, $1\ \text{nm} = 10^{-9}\ \text{m}$
$1\ \text{pm} = 10^{-12}\ \text{m}$
$1\ \text{litre} = 10^{-3}\ \text{m}^3 = 1\ \text{dm}^3$
$1\ \text{atm} = 760\ \text{mm or torr}$
$= 101325\ \text{Pa or Nm}^{-2}$
$1\ \text{bar} = 10^5\ \text{Nm}^{-2} = 10^5\ \text{Pa}$
1 calorie = 4.184 J
$1\ \text{electron volt(eV)} = 1.6022 \times 10^{-19}\ \text{J}$
$(1\ \text{J} = 10^7\ \text{ergs})$
(1 cal > 1 J > 1 erg > 1 eV)

ATOMIC MASS OR MOLECULAR MASS

Mass of one atom or molecule in a.m.u.
$C \rightarrow 12\ \text{amu}$
$H_2O \rightarrow 18\ \text{amu}$

ACTUAL MASS

mass of one atom or molecule in grams
$C \rightarrow 12 \times 1.6 \times 10^{-24}\ \text{g}$
$H_2O \rightarrow 18 \times 1.6 \times 10^{-24}\ \text{g}$

RELATIVE ATOMIC MASS OR RELATIVE MOLECULAR MASS

Mass of one atom or molecule w.r.t. 1/12th of ^{12}C atom
$C \rightarrow 12$
$H_2O \rightarrow 18$
It is unitless

GRAMS ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one mole of atom or molecule
$C \rightarrow 12\ \text{g}$
$H_2O \rightarrow 18\ \text{g}$
It is also called molar mass

DEFINITION OF MOLE

One mole is a collection of that many entities as there are number of atoms exactly in 12 gm of C-12 isotope.
The number of atoms present in exactly 12 gm of C-12 isotope is called Avogadro's number $[N_A = 6.022 \times 10^{23}]$

$$1\text{u} = 1\ \text{amu} = (1/12)^{\text{th}} \text{ of mass of 1 atom of } C^{12} = \frac{1\text{g}}{N_A} = 1.66 \times 10^{-24}\ \text{g}$$

For elements

- 1 g atom = 1 mole of atoms = N_A atoms
- g atomic mass (GAM) = mass of N_A atoms in g.
- Mole of atoms = $\dfrac{\text{Mass(g)}}{\text{GAM or molar mass}}$

For molecule

- 1 g molecule = 1 mole of molecule = N_A molecule
- g molecular mass (GMM) = mass of N_A molecule in g.
- Mole of molecule = $\dfrac{\text{Mass(g)}}{\text{GMM or molar mass}}$

For ionic compounds

- 1 g formula unit = 1 mole of formula unit = N_A formula unit.
- g formula mass (GFM) = mass of N_A formula unit in g.
- Mole of formula unit = $\dfrac{\text{Mass(g)}}{\text{GFM or molar mass}}$

1 mole of substance

- Contains 6.022×10^{23} particles
- Weighs as much as molecular mass / atomic mass/ionic mass in grams
- If it is a gas, one mole occupies a volume of 22.4 L at 1 atm & 273 K or 22.7 L at STP

Average or mean molar mass

The average molar mass of the different substance present in the container $M_{avg} = \dfrac{M_1 n_1 + M_2 n_2 + ...}{n_1 + n_2 + ...}$

Here M_1, M_2 are molar mass of substances and n_1, n_2 are mole of substances present in the container.

DENSITIES

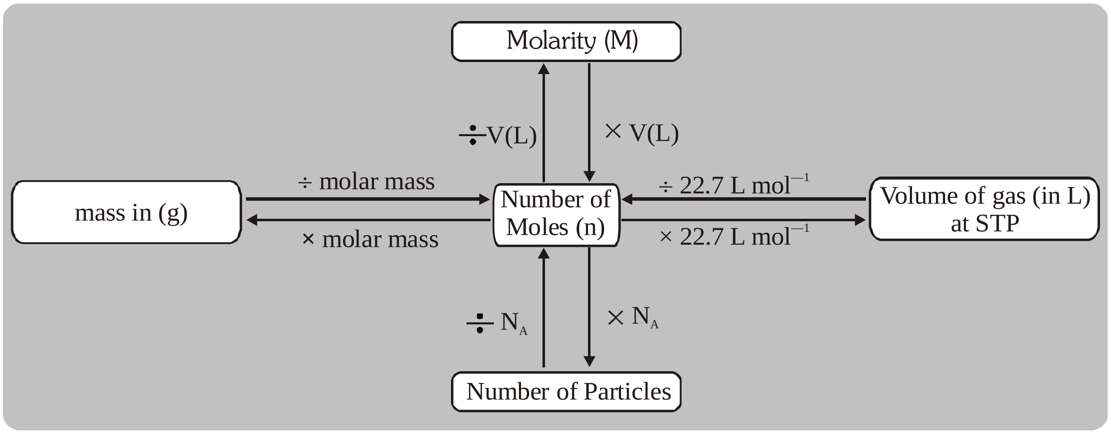
$$\text{Density} = \frac{\text{Mass}}{\text{volume}}$$

$$\text{Relative Density} = \frac{\text{Density of any substance}}{\text{Density of reference substance}}$$

VAPOUR DENSITY

Ratio of density of vapour to the density of hydrogen at similar pressure and temperature.

$$\text{Vapour density} = \frac{\text{Molar mass}}{2}$$



STOICHIOMETRY BASED CONCEPT

$aA + bB \rightarrow cC + dD$

- a,b,c,d, represents the ratios of moles, volumes [for gaseous] molecules in which the reactants react or products formed.
- a,b,c,d, does not represent the ratio of masses.
- The stoichiometric amount of components may be related as

$$\frac{\text{Moles of A reacted}}{a} = \frac{\text{Moles of B reacted}}{b} = \frac{\text{Moles of C reacted}}{c} = \frac{\text{Moles of D reacted}}{d}$$

- Amounts may also be related using POAC method. Moles of reactants and products may be related directly using conservation of suitable atoms.

❐ [Concept of limiting reagent]

If data of more than one reactant is given then first convert all the data into moles then divide the moles of reactants with their respective stoichiometric coefficient. The reactant having minimum ratio will be L.R. then find the moles of product formed or excess reagent left by comparing it with L.R. through stoichiometric concept.

◘ PERCENTAGE YIELD :

In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical amount of the product. The amount of the product that is actually obtained is called the actual yield. Knowing the actual yield and theorectical yield the percentage yield can be calculate as :

$$\boxed{\%\,\text{yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100}$$

The percentage yield of any product is always equal to the percentage extent of that reaction.

☐ DEGREE OF DISSOCIATION, (α) :

It represents the mole of substance dissociated per mole of the substance taken.

A → n particles; $\alpha = \dfrac{M_o - M}{(n-1).M}$

where, n = number of product particles per particle of reactant

M_o = Molar mass of 'A'

M = Molar mass of final mixture

Dissociation decreases the average molar mass of system while association increases it.

☐ PERCENTAGE PURITY :

The percentage of a specified compound or element in an impure sample may be given as

$$\boxed{\textbf{\% purity} = \frac{\textbf{Actual mass of compound}}{\textbf{Total mass of sample}} \times 100}$$

If impurity is unknown, it is always considered as inert (unreactive) material.

PERCENTAGE DETERMINATION OF ELEMENTS IN COMPOUNDS

- Mass % of an element in a compound

$$= \frac{\text{atomicity of an element} \times \text{atomic mass of an element}}{\text{molecular mass of compound}} \times 100$$

- Methods for organic compounds :

(a) **Liebig's method :** (*For Carbon and hydrogen*)

$$(w)\text{Organic Compound} \xrightarrow[\text{CuO}]{\Delta} (w_1)CO_2 + H_2O(w_2)$$

$\% \text{ of C} = \dfrac{w_1}{44} \times \dfrac{12}{w} \times 100$; $\% \text{ of H} = \dfrac{w_2}{18} \times \dfrac{2}{w} \times 100$

where w_1 = wt. of CO_2 produced, w_2 = wt. of H_2O produced,
w = wt. of organic compound taken

(b) **Duma's method :** (*for nitrogen*)

(w) Organic Compound $\xrightarrow[\text{CuO}]{\Delta}$ N_2 → (P, V, T given)

use PV = nRT to calculate moles of N_2, n.

$\therefore$ % of N = $\dfrac{n \times 28}{w} \times 100$

(c) **Kjeldahl's method :** (*for nitrogen*)

(w)O.C.+H_2SO_4 → $(NH_4)_2SO_4$ $\xrightarrow{\text{NaOH}}$ NH_3 + H_2SO_4 →[molarity and volume (V in L) consumed given]

⇒ % of N = $\dfrac{MV \times 2 \times 14}{w} \times 100$

where M = molarity of H_2SO_4. Some N containing compounds do not give the above set of reaction as in Kjeldahl's method.

(d) **Sulphur :**

(w) O.C. + HNO_3 → H_2SO_4 + $BaCl_2$ → (w_1) $BaSO_4$

⇒ % of S = $\dfrac{w_1}{233} \times \dfrac{32}{w} \times 100\%$

where w_1 = wt. of $BaSO_4$, w = wt. of organic compound

(e) **Phosphorus :**

$O.C + HNO_3 \rightarrow H_3PO_4 + [NH_3 + \text{magnesium ammonium molybdate}] \rightarrow MgNH_4PO_4$

$\xrightarrow{\Delta} Mg_2P_2O_7$

$$\% \text{ of } P = \frac{w_1}{222} \times \frac{2 \times 31}{w} \times 100$$

(f) **Carius method :** (*Halogens*)

$O.C. + HNO_3 + AgNO_3 \rightarrow AgX$

If X is Cl then colour = white

If X is Br then colour = dull yellow

If X is I then colour = bright yellow

Flourine can't be estimated by this

$$\% \text{ of } X = \frac{w_1}{(\text{Mol. wt. of AgX})} \times \frac{1 \times (\text{At. wt. of X})}{w} \times 100$$

EMPIRICAL AND MOLECULAR FORMULA

- **Empirical formula :** Formula depicting constituent atoms in their simplest ratio.
- **Molecular formula :** Formula depicting actual number of atoms in one molecule of the compound.
- The molecular formula is generally an integral multiple of the empirical formula.

i.e. molecular formula = empirical formula × n

$$\text{where } n = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$$

EXPERIMENTAL METHODS TO DETERMINE ATOMIC & MOLECULAR MASSES

- **For determination of atomic mass :**

Dulong's & Petit's law :

Atomic weight of metal × specific heat capacity (cal/gm°-C) ≈ 6.4.

It should be remembered that this law is an empirical observation and this gives an approximate value of atomic weight. This law gives better result for heavier solid elements, at high temperature conditions.

- **Experimental methods for molecular mass determination.**

(a) **Victor Meyer's Method :**

Victor -Mayer's method is used to determine molecular weight of volatile compound.

(b) **Silver Salt Method :**

$$\text{Organic acid } (H_nA) \xrightarrow{AgNO_3} \underset{(W\ gm)}{\text{Silver Salt}} \xrightarrow{\text{Ignite}} \underset{(x\ gm)}{Ag}$$

Molar mass of acid = $\frac{108 \times nW}{x} - n \times 108 + n \times 1 = n\left(\frac{108W}{x} - 107\right) gmol^{-1}$

(c) **Chloroplatinate Salt Method :**

$$\underset{\substack{\text{Organic base} \\ (\text{Acidity}=n)}}{B} \xrightarrow[\text{conc.HCl}]{H_2PtCl_6} \underset{\substack{\text{Platinic chloride salt} \\ (W\ gm)}}{B_2(H_2PtCl_6)_n} \xrightarrow{\text{Ignite}} \underset{(x\ gm)}{Pt}$$

Molar mass of base = $\frac{1}{2}$ **(Molar mass of salt – n × Molar mass of H_2PtCl_6)**

$$= \frac{1}{2}\left(\frac{W \times 195 \times n}{x} - n \times 410\right) = \frac{n}{2}\left(\frac{w \times 195}{x} - 410\right) gmol^{-1}$$

CONCENTRATION TERMS

Concentration Type	Mathematical Formula	Concept
Percentage by mass	$\%\left(\frac{w}{w}\right)=\frac{\text{Mass of solute}\times 100}{\text{Mass of solution}}$	Mass of solute (in gm) present in 100 gm of solution.
Volume percentage	$\%\left(\frac{v}{v}\right)=\frac{\text{Volume of solute}\times 100}{\text{Volume of solution}}$	Volume of solute (in cm^3) present in 100 cm^3 of solution.
Mass-volume percentage	$\%\left(\frac{w}{v}\right)=\frac{\text{Mass of solute}\times 100}{\text{Volume of solution}}$	Mass of solute (in gm) present in 100 cm^3 of solution.
Parts per million	$\text{ppm}=\frac{\text{Mass of solute}\times 10^6}{\text{Mass of solution}}$	Parts by mass of solute per million parts by mass of the solution
Mole fraction	$X_A=\frac{\text{Mole of A}}{\text{Mole of A}+\text{Mole of B}+\text{Mole of C}+....}$ $X_B=\frac{\text{Mole of B}}{\text{Mole of A}+\text{Mole of B}+\text{Mole of C}+....}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M=\frac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$	Moles of solute in one liter of solution.
Molality	$m=\frac{\text{Mole of solute}}{\text{Mass of solvent(Kg)}}$	Moles of solute in one kg of solvent

☐ ***MIXING OF SOLUTIONS :***

It is based on law of conservation of moles.

(i) **Two solutions having same solute :** Final molarity = $\frac{\text{Total moles}}{\text{Total volume}}=\frac{M_1V_1+M_2V_2}{V_1+V_2}$

(ii) **Dilution Effect :** Final molarity, $M_2=\frac{M_1V_1}{V_1+V_2}$

☐ **VOLUME STRENGTH OF H_2O_2 SOLUTION :**

Labelled as 'volume H_2O_2' means volume of O_2 (in litre) at 1 bar & 273 K that can be obtained from 1 litre of such a sample when it decomposes according to

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

- Volume Strength of H_2O_2 solution = 11.35 × molarity

☐ PERCENTAGE LABELLING OF OLEUM :

Labelled as '% oleum' means maximum amount of H_2SO_4 that can be obtained from 100 gm of such oleum (mixture of H_2SO_4 and SO_3) by adding sufficient water. For example, 109 % oleum sample means, with the addition of sufficient water to 100 gm oleum sample 109 gm H_2SO_4 is obtained.

% labelling of oleum sample = (100 + x)%

x = mass of H_2O required for the complete conversion of SO_3 in H_2SO_4

- % of free SO_3 in oleum = $\left(\frac{40}{9}\times x\right)\%$

EUDIOMETRY

Some basic assumptions related with calculations are:

1. Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.

$$\begin{array}{lll} N_2\,(g) + & 3H_2\,(g) \longrightarrow & 2NH_3\,(g) \\ 1\text{ vol.} & 3\text{ vol.} & 2\text{ vol.} \end{array}$$

Problem may be solved directly is terms of volume, in place of mole.

The stoichiometric coefficients of a balanced chemical reactions gives the ratio of volumes in which gaseous substances are reacting and products are formed at same temperature and pressure.

2. The volumes of solids or liquids is considered to be negligible in comparison to the volume of gas. It is due to the fact that the volume occupied by any substance in gaseous state is even more than thousand times the volume occupied by the same substance in solid or liquid states.

$$\begin{array}{lll} 2H_2\,(g) + & O_2\,(g) \longrightarrow & 2H_2O\,(l) \\ 2\text{ mole} & 1\text{ mole} & 2\text{ mole} \\ 2\text{ vol.} & 1\text{ vol.} & 0\text{ vol.} \end{array}$$

3. Air is considered as a mixture of oxygen and nitrogen gases only. It is due to the fact that about 99% volume of air is composed of oxygen and nitrogen gases only.

4. Nitrogen gas is considered as an non- reactive gas.

5. The total volume of non-reacting gaseous mixture is equal to sum of partial volumes of the component gases ***(Amagat's law)***.

$V = V_1 + V_2 + ...$

Partial volume of gas in a non-reacting gasesous mixture is its volume when the entire pressure of the mixture is supposed to be exerted only by that gas.

6. The volume of gases produced is often given by certain solvent which absorb contain gases.

Solvent	**Gases absorb**
KOH	CO_2, SO_2, Cl_2
Ammonical Cu_2Cl_2	CO
Turpentine oil	O_3
Alkaline pyrogallol	O_2
water	NH_3, HCl
$CuSO_4/CaCl_2$	H_2O

THERMODYNAMICS

DEFINITION

Deals with interaction of one body with another in terms of energy.

System : Part of universe under investigation

Surrounding : Rest part of universe except system.

Boundary : Devide system & surrounding

SYSTEM

Open	Closed	isolated
Energy and matter can exchange	Only energy can exchange	Neither energy nor matter

State function	Path function
Properties which depends only on initial & final state of system & not on process or path. e.g. U, H etc.	Depends on path or process. e.g. work, heat

THERMODYNAMIC PROPERTIES

Extensive	Intensive
Properties which are dependent of matter (size & mass) present in system	Properties which are independent of matter (size & mass) present in system.

Extensive Properties	Intensive Properties
Volume	Molar volume
Number of moles	Density
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy (S)	Viscosity
Enthalpy (H)	Free energy per mole
Internal energy (E & U)	specific heat
Heat capacity	Pressure
	Temperature
	Boilling point, freezing point etc

PROCESSES

Isothermal	**Isochoric**	**Isobaric**	**Adiabatic**	**Cyclic**
T = const.	V = const.	P = const.	No heat exchange dq = 0	Initial & final state of system are same

Reversible process	**Irreversible process**
• Slow process	• Fast process
• At any time system and surrounding are in equilibrium.	• No equilibrium between system and surrounding
• $P_{sys} = P_{surr} \pm dP$	• $P_{sys} = P_{surr} \pm \Delta P$

HEAT (q)

Energy exchange due to temperature difference :

$q = C\Delta T$, $q = nC_m\Delta T$, $q = ms\Delta T$

C = heat capacity

Cm = molar heat capacity

s = specific heat capacity

m = Amount of substance

General values of C_V & C_P for an ideal gas can be taken as follows.

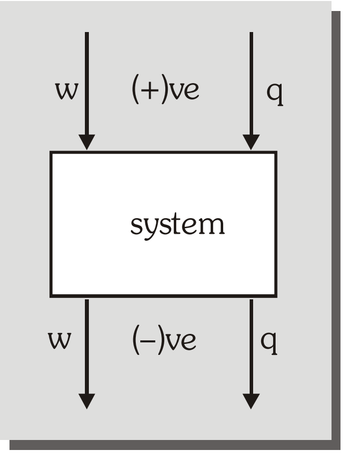
Atomicity		n_{tr}	n_{Rot}	n_{Vib}	C_V		C_P		γ	
						Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono		3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di		3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3	3R	6R	4R	7R	$\frac{4}{3}$	$\frac{7}{6}$

* $$\gamma_{mix} = \frac{n_1C_{P_1} + nC_{P_2}....}{n_1C_{V_1} + nC_{V_2}....}$$

WORK (W)

Reversible	Irreversible
$W_{rev} = -\int_{V_1}^{V_2} P_{ext} \cdot dV$	$W_{irr} = -P_{ext}(V_2 - V_1)$

SIGN CONVENTION



❑ INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{nuclear} + ...$

U is a state function & is an extensive property.

$\Delta U = U_{final} - U_{initial}$

For a given closed system

$U = f(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

FIRST LAW OF THERMODYNAMICS (FLOT)

Law of conservation of energy

$$\boxed{\Delta U = q + W}$$

❑ ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** (H) as.

$H = U + PV$

$\Delta H = \Delta U + \Delta(PV)$

at constant pressure $\Delta H = \Delta U + P\,\Delta V$

combining with first law. $\Delta H = q_p$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

* For a given closed system H = f(P, T) $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

☐ RELATIONSHIP BETWEEN ΔH & ΔU

The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids) $\Delta H = \Delta U + \Delta(PV)$

If substance is not undergoing chemical reaction or phase change. $\Delta H = \Delta U + nR\Delta T$

In case of chemical reaction $\Delta H = \Delta U + (\Delta n_g)RT$

WORK DONE IN VARIOUS PROCESS

Isochoric	**Isobaric**	**Free expansion**
$W = 0$ $\Delta U = q = nC_V\Delta T$	$W = -P_{ex}(V_2 - V_1)$	$P_{ext} = 0$ $W = 0, \Delta U = 0, q = 0$

ISOTHERMAL

$dT = 0$; $\Delta U = 0$ (for ideal gas); $q = -W$

Reversible Isothermal	**Irreversible Isothermal**
$W_{rev}, iso = -nRT\ell n\left(\frac{V_2}{V_1}\right)$ $= -nRT\ell n\left(\frac{P_1}{P_2}\right)$	$W_{irr}, iso = -P_{ext}\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right]$

ADIABATIC :

$q = 0 \Rightarrow \boxed{\Delta U = W = nC_V\Delta T \Rightarrow W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}}$

$\gamma = \frac{C_P}{C_V} \Rightarrow C_P$ = molar heat capacity at constant P.

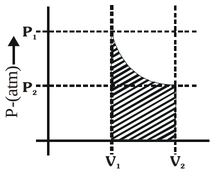
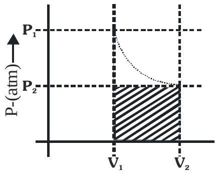
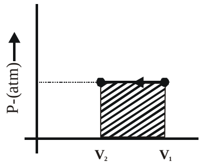
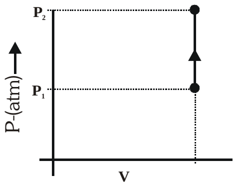
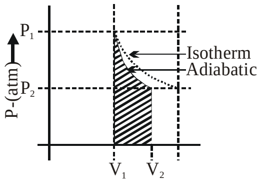
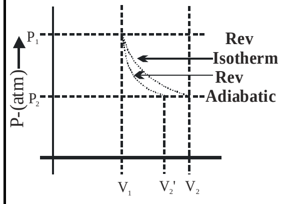
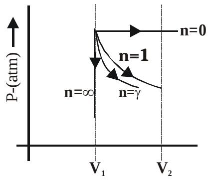
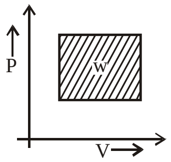
$C_P - C_V = R \Rightarrow C_V$ = molar heat capacity at constant V.

For Reversible adiabatic :
PV^γ = constant (Ideal gas)
$TV^{\gamma-1}$ = constant (Ideal gas)

For irrversible adiabatic process :

$\Delta U = -P_{ext}(V_2 - V_1)$

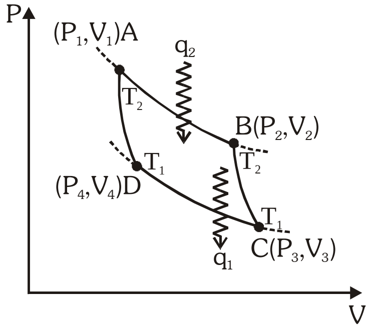
$n\,C_{Vm}(T_2 - T_1) = -P_{ext.}\,nR\left(\frac{T_2}{P_2} - \frac{T_1}{P_1}\right)$

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal	$w = -nRT\ln\frac{V_2}{V_1}$ $= -nRT\ln\frac{P_1}{P_2}$	$q = nRT\ln\left(\frac{V_2}{V_1}\right)$ $q = nRT\ln\left(\frac{P_1}{P_2}\right)$	0 process	0	
Irreversible isothermal	$w = -P_{ext}\left(V_2 - V_1\right)$ $= -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$	$q = P_{ext}\left(V_2 - V_1\right)$	0	0	
Isobaric process	$w = -P_{ext}\left(V_2 - V_1\right)$ $= -\ nR\Delta T$	$q = \Delta H = nC_P\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Isochoric process	w = 0	$q = \Delta U = nC_V\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Reversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	q = 0 PV^{γ}=constant $TV^{\gamma-1}$=constant $TP^{1-\gamma/\gamma}$=constant	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Irreversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	q = 0 $nC_v(T_2 - T_1)$ = $-P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Polytropic	$w = \frac{P_2V_2 - P_1V_1}{n - 1}$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$q = \int_{T_1}^{T_2} C_V dT$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Cyclic Process	Area encolsed in PV-diagram For clockwise it is –ive it is +ive	q = –w	0	0	

❑ SPONTANEOUS PROCESS :

A process which takes place on it's own (without any external assistance). The driving force of a spontaneous process is large or finite.

❑ CARNOT CYCLE



AB – Isothermal reversible expansion $q_2 = -w_{AB} = nRT_2 \ln \frac{V_2}{V_1}$

BC – adiabatic reversible expansion $w_{BC} = nC_V(T_1 - T_2)$

CD – Isothermal reversible compression $q_1 = -w_{CD} = nRT_1 \ln\left(\frac{V_4}{V_3}\right)$

DA – adiabatic reversible compression $w_{DA} = nC_V(T_2 - T_1)$

carnot efficiency $\eta = \frac{-w_{\text{Total}}}{q_2} = \frac{q_1+q_2}{q_2} = \frac{T_2-T_1}{T_2}$

$$\frac{q_1}{T_1}+\frac{q_2}{T_2}=0 \text{ for rev. cycle}$$

$$\oint \frac{q_{rev}}{T} = \oint dS = 0$$

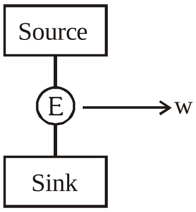
Entropy (denoted by S) is state function

$$\Delta S = \int \frac{q_{rev}}{T}$$

The direction of a spontaneous process and that it eventually reaches equilibrium, can be understood on the basis of entropy concept introduced through the second law of thermodynamics.

☐ STATEMENTS OF SECOND LAW OF THERMODYNAMICS

(i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.



(ii) In an irreversible process entropy of universe increases but it remains constant in a reversible process.

$\Delta S_{syt} + \Delta S_{sur} = 0$ for rev. process

$\Delta S_{syt} + \Delta S_{surr} > 0$ for irrev. process

$\Delta S_{syt} + \Delta S_{surr} \geq 0$ (In general)

☐ PHYSICAL SIGNIFICANCE OF ENTROPY

One can think entropy as a measure of the degree of randomness or disorder in a system. The greater the disorder in a system, the higher is the entropy.

(i) The entropies of substance follow the order,

$S(g) > S(l) > S(s)$

(ii) If more no. of gaseous moles are present on product side, $\Delta_r S$ will be +ive (since gas is more disordered than solid or liquid).

(iii) Entropy rises with increasing mass, other thing being same e.g. atomicity in gas phase.

e.g. $F_2(g)$ $S° = 203$ J/K-mole

$Cl_2(g)$ $S° = 223$ J/K-mole

$Br_2(g)$ $S° = 245$ J/K-mole

(iv) Entropy increases with chemical complexity

For $CuSO_4.nH_2O$

n = 0	n = 1	n = 3	n = 5
S° = 113	150	225	305

☐ CALCULATION OF ENTROPY CHANGE FOR AN IDEAL GAS

General Expression

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

* Reversible & irreversible isothermal expansion or contraction of an ideal gas

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

* Isobaric heating or cooling :

$$\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right)$$

* Isochoric heating or cooling :

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$$

* Adiabatic process :

$\Delta S = nC_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$ for irreversible process

$\Delta S = 0$ for reversible adiabatic compression and expansion.

❑ ENTROPY CALCULATION

Process	$\Delta S_{Sys.}$	$\Delta S_{Surr.}$
Isothermal reversible	$\Delta S_{Sys.} = nR\ell n\frac{V_2}{V_1}$	$\Delta S_{Surr.} = -\Delta S_{Sys.}$
Isothermal irreversible	$\Delta S_{Sys.} = nR\ell n\frac{V_2}{V_1}$	$\Delta S_{Surr.} = \frac{-q_{Sys}}{T} = \frac{W_{Sys}}{T} = \frac{-P_{ext}(V_2 - V_1)}{T}$
Adiabatic reversible	$\Delta S_{Sys.} = 0$	$\Delta S_{Surr.} = 0$
Adiabatic irreversible	$\Delta S_{Sys.} = nC_P\ell n\frac{T_2}{T_1} + nR\ell n\frac{P_1}{P_2}$	$\Delta S_{Surr.} = 0$
Isochoric reversible	$\Delta S_{Sys.} = nC_V\ell n\frac{T_2}{T_1}$	$\Delta S_{Surr.} = -\Delta S_{Sys.}$
Isochoric irreversible	$\Delta S_{Sys.} = nC_V\ell n\frac{T_2}{T_1}$	$\Delta S_{Surr.} = \frac{-q_{sys}}{T_{surr}} = \frac{-nC_V\Delta T}{T_{surr}}$

❑ THIRD LAW OF THERMODYNAMICS

''At absolute zero, the entropy of a perfectly crytalline substannce is zero'', which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{rev}}{T}$$

Since $S_{0K} = 0$

$$S_T = \int_0^T \frac{q_{rev}}{T}$$

Absolute entropies of various substances have been tabulated and these value are used to calculate entropy changes for the reactions by the formula;

$$\Delta S_r = \Sigma S \text{ (products)} - \Sigma S \text{ (reactants)}$$

❑ VARIATION OF ΔS_r WITH TEMPERATURE & PRESSURE :

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_P)_r \ln\frac{T_2}{T_1}$$

$$(\Delta S_r)_{p_2} - (\Delta S_r)_{p_1} = \Delta n_g R \ln\frac{p_1}{p_2}$$

Similarly

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1)$$ **{Krichoff's equation}**

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_V)_r (T_2 - T_1)$$

❑ GIBBS FREE ENERGY (G) AND SPONTANEITY :

A new thermodynamic state function G, the Gibbs free energy is defined as :

$$G = H - TS$$

at constant temperature and pressure

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

If $(\Delta G)_{T,P} < 0$ Process is irreversible (spontaneous)

$(\Delta G)_{T,P} = 0$ Process is reversible

$(\Delta G)_{T,P} > 0$ process is impossible (non spontaneous)

The use of Gibbs free energy has the advantage that it refers to the system only (and not surroundings).

To summaries, the spontaneity of a chemical reaction is decided by two factors taken together

(i) The enthalpy factor

(ii) The entropy factor

The equation $\Delta G = \Delta H - T\Delta S$ takes both the factors into consideration.

$(\Delta H_r)_{T,P}$	$(\Delta S_r)_{T,P}$	(ΔG_r)	Remarks
– ve	+ ve	Always –ve	Reaction is spontaneous
+ ve	– ve	Always +ve	Reaction non spontaneous
+ ve	+ ve	At low temperature, ΔG = + ve	Non spontaneous
		At high temperature, ΔG = – ve	Spontaneous
– ve	– ve	At low temperature, – ve	Spontaneous
– ve	– ve	At high temperature, + ve	Non spontaneous

☐ VARIATION OF GIBB'S FUNCTION (G) WITH TEMPERATURE AND PRESSURE :

$$G = H - TS$$

$$= U + PV - TS$$

$$dG = \cancel{dU} + P\cancel{dV} - T\cancel{d}S + VdP - SdT$$

$$dG = VdP - SdT$$

* At constant temperature

$\Delta G = VdP$

or $\left(\frac{\partial G}{\partial P}\right)_T = V$

* At constant pressure

$\Delta G = -SdT$

$\left(\frac{\partial G}{\partial T}\right)_P = -S$

Relationship between ΔG & W_{non-PV}

$dU = q + W_{PV} + W_{non-PV}$

for reversible process at constant T & P

$dU + pdV - TdS = W_{non-PV}$

$dH - TdS = W_{non-PV}$

$(dG_{system})_{T,\,P} = W_{non-PV}$

$(dG_{system})_{T,P} = (W_{non-PV})_{system}$

Non-PV work done by the system = decrease in gibbs free energy

☐ SOME FACTS TO BE REMEMBERED :

(a) Standard condition

- * For gases/solid / liquid

  P = 1 bar

- * For ion / substance in solution

  Concentration = 1M

(b) $\Delta G_r = (\Delta G_f)_{product} - (\Delta G_f)_{reactant}$

$\Delta H_r = (\Delta H_f)_{product} - (\Delta H_f)_{reactant}$

$\Delta S_r = (\Delta S_f)_{product} - (\Delta S_f)_{reactant}$

(All above equation will be derived in thermochemistry)

Relationship between , ΔG^o and equilibrium constant

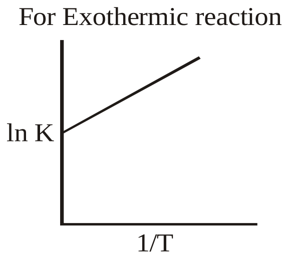
$\Delta G = \Delta G^o + RT\,ln Q$

At equilibrium $\Delta G = 0$

$\Delta G^o = -RT\,ln\,Keq$

$\Delta H^o - T\Delta S^o = -RT\,\ln Keq$

$$\ln K_{eq} = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$



$$\ln K_1 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_2}$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

CHAPTER 3

THERMOCHEMISTRY

ENTHALPY OF REACTION (ΔH_R)

Amount of heat evolved or absorbed during a reaction at constant pressure.

ENTHALPY OF FORMATION ($\Delta_f H$)

(May be endothermic or exotherm ic)

Change in enthalpy when one mole of a substance is formed from its constituent elements present in standard state.

* For elements $\Delta_f H^o = 0$ (for standard state)

Ex. $\Delta_f H^o\ [O_2(g)] = 0$, $\Delta_f H^o = S_{8(rhombic)} = 0$

$\Delta_f H^o\ [P_{4\ (white)}] = 0$, $\Delta_f H^0 = C_{(graphite)} = 0$

ENTHALPY OF COMBUSTION ($\Delta_C H$)

(always exothermic)

Change in enthalpy when 1 mole of a substance is completely burnt in oxygen.

$$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)\ ;\ \Delta_C H_{[C_2H_6(g)]}$$

$$\Delta_r H^\circ = \sum \Delta_C H^\circ\,(\text{react.}) - \sum \Delta_C H^\circ\,(\text{prod.})$$

$$\text{Calorific value} = \frac{\Delta H_{comb}}{\text{molecular wt}}$$

ENTHALPY OF TRANSITION

Enthalpy change when one mole of one allotropic form changes to another.

$$C_{(graphite)} \rightarrow C_{(diamond)}\quad \Delta_{tran}H^\circ = 1.9\ \text{kJ mol}^{-1}$$

$H_2O_{(\ell)} \rightarrow H_2O_{(g)};\ \Delta_{vap}H^o\ (H_2O_{(\ell)})$

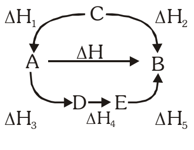
$H_2O_{(S)} \rightarrow H_2O_{(\ell)};\ \Delta_{fus}H^o\ (H_2O_{(s)})$

$H_2O_{(S)} \rightarrow H_2O_{(g)};\ \Delta_{sub}H^o\ (H_2O_{(s)})$

LAWS OF THERMOCHEMISTRY

$$\text{(i)}\quad \left.\begin{matrix} A \rightarrow B & \Delta_r H = x\ \text{kJ mol}^{-1} \\ B \rightarrow A & \Delta_r H = -x\ \text{kJ mol}^{-1} \end{matrix}\right\}\text{Lavoisier \& Laplace law}$$

(ii) Hess Law of Constant Heat summation



$\Delta H = \Delta H_1 + \Delta H_2$

or $\Delta H = \Delta H_3 + \Delta H_4 + \Delta H_5$

or $\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$

BOND ENTHALPY

Average amount of enthalpy required to dissociate one mole gaseous bond into separate gaseous atoms.

$$\Delta rH = \begin{pmatrix}\text{Sum of bond enthalpy} \\ \text{of gaseous reactant}\end{pmatrix} - \begin{pmatrix}\text{Sum of bond enthalpy} \\ \text{of gaseous product}\end{pmatrix}$$

RESONANCE ENERGY

$$\Delta H^o_{resonance} = \Delta_f H^\circ\ (\text{experimental}) - \Delta_f H^\circ\,(\text{calculated})$$
$$= \Delta_C H^\circ\,(\text{calculated}) - \Delta_C H^\circ\,(\text{experimental})$$

ENTHALPY OF NEUTRALIZATION (ΔH_{neut})

(Always exothermic)

Change in enthalpy when one gram equivalent of an acid is completely neutralized by one g-equivalent of a base in dilute solution.

SA + SB → salt + water ; ΔH^o_{neut}

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)}$;

$\Delta H = -13.7\ \text{kCal eq}^{-1} = 57.3\ \text{kJ eq}^{-1}$

In case of weak acid / base or both $|\Delta H^o_N| < 13.7\frac{\text{Kcal}}{\text{eq}}$ and the difference is enthalpy of ionisation of ionisation of weak species except in case of HF when $|\Delta H_N| > 13.7$ due to hydration of F^-.

ENTHALPY OF ATOMISATION (ΔH_{atom})

(always endothermic)

Change in enthalpy when one mole of gaseous molecules converts into gaseous atoms.

ENTHALPY OF SOLUTION (ΔH_{sol})

(may be endo or exothermic)

Change in enthalpy when 1 mol of a substance is dissolved in excess of water so that further dilution does not involve any heat change.

$$CuSO_{4(s)} \xrightarrow{aq} CuSO_{4(aq)};\Delta H^o_{(sol.)}$$

ENTHALPY OF HYDRATION (ΔH_{hydra})

(always exothermic)

Enthalpy change when 1 mole of anhydrous salt combine with requisite amount of water to form hydrated salt.

$$\underset{\text{(anhy. salt)}}{CuSO_{4(s)}} + 5H_2O_{(\ell)} \rightarrow \underset{\text{(hydra.salt)}}{CuSO_4\,.5H_2O_{(s)}};\Delta H^o_{hyd}$$

ENTHALPY OF HYDROGENATION (ΔH_{hydro}) (Always exothermic)

Enthalpy change during the complete hydrogenation of one mole unsaturated organic compound into its saturated compound.

$$\underset{(= \text{ or } \equiv \text{ bond})}{\text{unsaturated organic compound}} \xrightarrow{\Delta} \underset{(-\text{bond})}{\text{saturated organic compound}}$$

$$C_2H_2 + 2H_2 \rightarrow C_2H_6;\ \Delta H_{hydro}$$

NOTE :

If in a reaction heat of reactant & products are given then heat of that reaction can be measured as follows:

(a) For heat of combustion & for bond enthalpy

$$\Delta_r H = \sum(\Delta H_C)_{reactant} - \sum(\Delta H_C)_{product}$$

(b) For heat of formation

$$\Delta_r H = \sum(\Delta H_f)_{product} - \sum(\Delta H_f)_{reactant}$$

IMPORTANT NOTES

CHAPTER 4

CHEMICAL EQUILIBRIUM

- Equilibrium represents the state of a process in which the measurable properties like :- temperature, pressure, color, concentration of the system do not show any change with the passage of time.
- Equilibrium is a dynamic process, chemical equilibrium can be approached from both sides.
- The state of equilibrium is not affected by the presence of catalyst. It only helps to attain the equilibrium state in less or more time.
- Equilibrium can be attained both in homogeneous & heterogenous system.

Consider a reversible reaction,

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$$

AT EQUILIBRIUM STATE

Rate of forward reaction (r_f)

= rate of backward reaction (r_b)

So, at equilibrium,

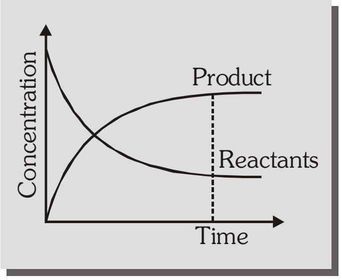
$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{K_f}{K_b}$$ In terms of active mass

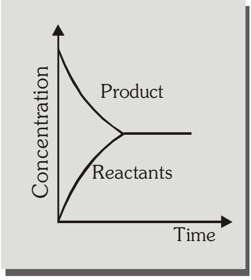
$$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b}$$ In terms of partial pressure

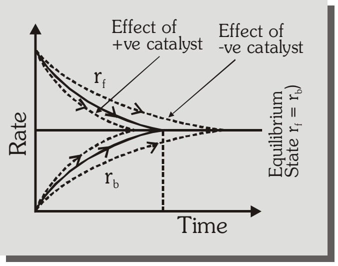
$$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b}$$ In terms of mole fraction

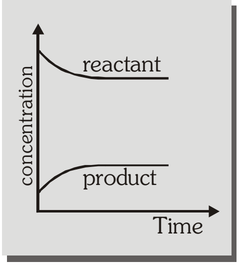
- Partial pressure of solid is taken as unity & in calculation of partial pressure of solids, their number of moles are not considered.
- $K_P = K_C(RT)^{\Delta ng}$ then $K_P = K_C$
  when $\Delta n_g = 0$ then $K_P = K_C$
  when $\Delta n_g > 0$ then $K_P > K_C$
  when $\Delta n_g < 0$ then $K_P < K_C$
- While determining Δn_g take only gaseous species.
- The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

GRAPHS









- **Unit of Equilibrium constant:**

$$K_C = (\text{mol L}^{-1})^{\Delta n_g}\ ;\ K_P = (\text{atm})^{\Delta n_g}$$

- **Application of K_C or K_P**
  - More is the value of K_P or K_C more is the extent of reaction.
  - Stability of reactant increases when value of K decreases
  - Stability of Product increases when value of K increases.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

Equilibrium constant depends upon temperature & way of writing the reaction

(i) Temperature :

Let K_1 & K_2 be equilibrium constant at T_1 & T_2 then

$$\text{Log}\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^o}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

(Van't Hoff equation)

(ii) Way of writing the reaction :

For $A + B \rightleftharpoons C + D$ $K_C = K$ then

(a) $C + D \rightleftharpoons A + B$; $K'_C = \frac{1}{K}$

(b) $nA + nB \rightleftharpoons nC + nD$, $K''_C = K^n$

when n=2, then $K''_C = K^2$

$n = \frac{1}{3}$ then $K''_C = K^{1/3}$

(c) $A \rightleftharpoons B$ $K_C = K_1$

$B \rightleftharpoons C$ $K_C = K_2$

$C \rightleftharpoons D$ $K_C = K_3$ then

$A \rightleftharpoons D$ $K_C = K_1 \times K_2 \times K_3$

(d) $A \rightleftharpoons B$ $K_C = K_1$

$2C \rightleftharpoons 2B$ $K_C = K_2$

$D \rightleftharpoons C$ $K_C = K_3$ then

$A \rightleftharpoons D$ $K_C = \frac{K_1}{\sqrt{K_2} * K_3}$

- **Predicting the direction of reaction :**

Reaction Quotient (Q) is expressed in the same way as for equilibrium constant, except that the concentrations may not necessarily be at equilibrium.

In general for the reversible reaction :

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$Q = \frac{[P_c]^c [P_D]^d}{[P_A]^a [P_B]^b} \text{ (in terms of pressure)}$$

If $Q = K_{eq}$ then system is in equilibrium

If $Q > K_{eq}$ then system proceed in backward direction to attain equilibrium.

If $Q < K_{eq}$ then system proceed in forward direction to attain equilibrium.

- **Degree of dissociation (α)**

$$\frac{\text{No. of moles of reactant dissociated}}{\text{No. of mole of reactant present initially}}$$

- **Degree of Dissociation from Vapour pressure**

$n_1A \rightleftharpoons n_2B + n_3C$

$\alpha = \frac{n_1}{\Delta n}\left(\frac{D_T - D_0}{D_0}\right)$; $\Delta n = (n_2 + n_3) - (n_1)$

D_T = theoretical vapour density = $\frac{\text{Molecular weight}}{2}$

D_0 = Observed vapour density

PHYSICAL EQUILIBRIUM

Physical reaction :

Those reactions in which change in only & only physical states of substances takes place without any chemical change.

(i) Ice-water system (melting of ice) :

$$\underset{\text{(more volume)}}{Ice_{(s)}} + Heat \rightleftharpoons \underset{\text{(less volume)}}{water_{(\ell)}}$$

It is an endothermic process & there is decrease in volume. Thus, the favourable conditions for melting of ice are high temperature, & High-pressure.

(ii) Water -Water vapour system (vapourisation of water) :

$$\underset{\text{(less volume)}}{water_{(\ell)}} \rightleftharpoons \underset{\text{(more volume)}}{vapour_{(g)}}$$

It is an endothermic process & there is increase in volume. Thus, the favourable conditions for vaporisation of water are high temperature, & low-pressure.

(iii) Solubility of gases in liquids :

$Gas_{(g)} + water_{(\ell)} \rightleftharpoons \text{Aqueous solution}_{(\ell)}$

When a gas dissolve in liquid, these is decrease in volume. Thus, increase in pressure will favour the dissolution of a gas in liquid.

LE-CHATELIER'S PRINCIPLE

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

CHEMICAL EQUILIBRIUM

S. No.	**Effect due to change in**		**$\Delta n_g = 0$** **$A \rightleftharpoons B$**	**$\Delta n_g > 0$** **$A \rightleftharpoons 2B$**	**$\Delta n_g < 0$** **$2A \rightleftharpoons B$**
a)	Concentration	(i) ↑ [A] (ii) ↓ [A]	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
b)	Pressure	(i) ↑ in pressure (ii) ↓ in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
c)	Temperature	(i) ↑ in Endothermic (ii) ↑ in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
d)	Dissociation	(i) ↑ in pressure (ii) ↑ in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Increases	Dissociation Increases Dissociation Decreases
e)	Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Increases Unchanged	Dissociation Decreases Unchanged

IONIC EQUILIBRIUM

☐ CLASSIFICATION OF SUBSTANCES

On the basis of their dissociation nature :

(i) Strong electrolytes : Substances which are largely dissociated and are strong electrolytes. e.g. HCl, H_2SO_4, HNO_3 etc.

(ii) Weak electrolytes Substances which dissociate only to a small extent in aqueous solution. e.g. HCN, H_3BO_3 etc.

(iii) Non electrolytes Which do not dissociate.

☐ pH CALCULATUION

Case (i) **A weak acid in water**

(a) if $\alpha = \sqrt{\frac{K_a}{C}}$ is < 0.1, then $[H^+] \approx \sqrt{K_aC}$.

(b) **General Expression :** $[H^+] = 0.5(-K_a + \sqrt{K_a^2 + 4K_aC})$

Similarly for a weak base, substitute $[OH^-]$ and K_b instead of $[H^+]$ and K_a respectively in these expressions.

Case (ii) **A weak acid and a strong acid :** Due to strong acid degree of dissociation of weak acid decreases.

Case (iii) **Two (or more) weak acids**

The accurate treatement yields a cubic equation. Assuming that acids dissociate to a negligible extent [i.e. $C - x \approx C$] $[H^+] = (K_1C_1 + K_2C_2 + ... + K_w)^{1/2}$

Case (iv) **When dissociation of water becomes significant:**

Dissociation of water contributes significantly to $[H^+]$ or $[OH^-]$ only when for

(i) ***Strong acids (or bases) :***

$10^{-8}M < C < 10^{-6}M$. Neglecting ionisation of water at 10^{-6}M causes 1% error (approvable). Below 10^{-8}M, contribution of acid (or base) can be neglected and pH can be taken to be practically 7.

(ii) ***Weak acids (or bases) :*** When $K_aC < 10^{-12}$, then consider dissociation of water as well.

Case (v) **pH of solution involving a polyprotic acid or base** depend upon K_1 , K_2 . Succesive dissociation can be neglected.

$$K_1 = \frac{x^2}{c - x}$$

❑ SALT HYDROLYSIS

The phenomenon of interaction of cations and anions of a salt with H_2O in order to produce acidic nature or alkaline nature is known as salt hydrolysis.

$$\text{Salt + Water} \rightleftharpoons \text{Acid + Base}$$

The process of salt hydrolysis is actually the reverse process of neutralization.

(i) ***Salts of strong acids and strong bases*** do not undergo hydrolysis.

(ii) ***Salts of a strong acids and weak bases*** give an acidic solution.

e.g. NH_4Cl when dissolved, it dissociates to give NH_4^+ ions.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ ; \qquad K_h = [NH_3][H_3O^+] / [NH_4^+] = K_w/K_b$$

Important ! In general : K_a(of an acid). K_b(of its conjugate base) = K_w

If the degree of hydrolysis(h) is small (<<1), $h = \sqrt{K_h/C}$.

$$pH = \frac{1}{2}(pk_w - pk_b - \log C)$$

Otherwise $h = \dfrac{-K_h + \sqrt{K_h^2 + 4K_hC}}{2C}$, $[H^+] = Ch$

(iii) ***Salts of strong base and weak acid*** give a basic solution (pH>7) when dissolved in water, e.g. NaCN, $CN^- + H_2O \rightleftharpoons HCN + OH^-$

$[OH^-] = Ch$, $h = \sqrt{K_h/C}$

$$pH = \frac{1}{2}(pk_w + pk_a + \log C)$$

(iv) ***Salts of weak base and weak acid***

Assuming degree of hydrolysis to be same for the both the ions,

$K_h = K_w / (K_a.K_b)$, $[H^+] = [K_a\, K_w/K_b]^{1/2}$

$$pH = \frac{1}{2}(pk_w + pk_a - pk_b)$$

(v) ***Amphiprotic salts***

e.g. $NAHCO_3$

$$pH = \frac{1}{2}(pk_1 + pk_2)$$

Note: Exact treatment of case (iv) & (v) is difficult to solve. So use this assumption in general cases. Also, degree of anion or cation will be much higher in the case of a salt of weak acid and weak base. This is because each of them gets hydrolysed, producing H^+ and OH^- ions. These ions combine to form water and the hydrolysis equilibrium is shifted in the forward direaction.

❑ BUFFER SOLUTIONS

A solution whose pH does not change significantly on addition of a small amount of acid or alkali.

Type of Buffers

1. Simple buffers

(i) A salt of weak acid and weak base in water e.g. CH_3COONH_4, NH_4CN

(ii) Proteins and amino acids

2. Mixed buffers

These are of two types :

(i) **Acidic buffer mixtures ; A weak acid with its conjugate base :**

$NaHCO_3 + H_2CO_3$(H_2CO_3 ; is weak acid and HCO_3^- is its conjugate base);

$CH_3COOH + CH_3COONa$; $NaH_2PO_4 + H_3PO_4$.

The pH of the buffer solution of this category not necessarily lie in between 0 to 7. It may be in the range of 7 to 14 depending upon the dissociation constant of acid.

Henderson's Equation

$pH = pK_a + \log\{[salt] / [acid]\}$ for weak acid with its conjugate base.

(ii) **Basic buffer mixtures ; A weak base with its conjugate Acid :**

$NH_4OH + NH_4Cl$ (NH_4OH is weak base and NH_4^+ is its conjugate acid.)

Henderson's Equation

$pOH = pK_b + \log\{[salt] / [base]\}$ for weak base with its conjugate acid.

Important : For good buffer capacity, [salt] : [acid] ratio should be as close to one as possible. In such a case, $pH = pK_a$. (This also is the case at midpoint of titration)

Buffer capacity = (no. of moles of acid (or base) added to 1L) / (change in pH)

❑ INDICATORS

Indicator is a substance which indicates the point of equivalence in a titration by undergoing a change in its colour. They are weak acids or weak bases.

Theory of Indicators. The ionized and unionized forms of indicators have different colours. If 90 % or more of a particular form (ionised or unionised) is present, then its colour can be distinclty seen.In general, for an indicator which is weak acid, $HIn \rightleftharpoons H^+ + In^-$, the ratio of ionized to unionized form can be determined from

$$pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

So, for detectable colour change, $pH = pK_a \pm 1$

This roughly gives the range of indicators. Ranges for some popular indicators are

Table 1 : Indicators

Indicators	**pH range**	**Colour**	
		acid medium	**basic medium**
Methyl Orange	3.1-4.4	pink	yellow
Methyl red	4.2-6.3	red	yellow
Litmus	5.5-7.5	red	blue
Phenol red	6.8-8.4	yellow	red
Phenolphathlene	8.3-10	colourless	pink
Thymol blue	1.2-2.8	red	yello

Equivalence point. The point at which exactly equivalent amounts of acid and base have been mixed.

Acid Base Titration. For choosing a suitable indicator titration curves are of great help. In a titration curve, change in pH is plotted against the volume of alkali to a given acid. Four cases arise.

(a) **Strong acid vs strong base.** The curve is almost vertical over the pH range 3-10.

(b) **Weak acid vs strong base.** The curve is almost vertical over the pH range 5-10. So, phenolphathlene is suitable.

(c) **Weak base vs strong acid .** The curve is almost vertical over the pH range 9-3. Methyl red or methyl orange suitable.

(d) **Weak acid vs weak base.** No sharp change in pH. No suitable indicator.

☐ SOLUBILITY PRODUCT (K_{sp}).

For sparingly soluble salts (eg. $Ag_2C_2O_4$) an equilibrium which exists is

$$Ag_2C_2O_4 \rightleftharpoons 2Ag^+ (aq.)\ C_2O_4^{2-} (aq.)$$

$$\text{Then } K_{sp} = [Ag^+]^2[C_2O_4^{2-}]$$

Common ion effects. Suppression of dissociation by adding an ion common with dissociation products. e.g. Ag^+ or $C_2O_4^{2-}$ in the above example.

Simultaneous solubility. $AgCl \rightleftharpoons Ag^+ + Cl^- \quad K_{sp_1}$

$$AgBr \rightleftharpoons Ag^+ + Br^- \quad K_{sp_2}$$

Precipitation. Whenever the product of concentrations (raised to appropriate power) exceeds the solubility product, precipitation occurs.

Effect of complex formation on solubility.

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq) \qquad K_{sp}$$

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_{form}$$

Effect of hydrolysis on solubility

$$MA\ (s) \rightleftharpoons M^+\ (aq) + A^-\ (aq)\ K_{sp}$$

$$A^-\ (aq) + H_2O \rightleftharpoons HA + OH^- \ \frac{K_w}{K_a}$$

$$S = \sqrt{K_{sp}\left(1 + \frac{[H^+]}{K_a}\right)}$$

THE ATLAS

Ionic Equilibrium

The concept of ionic equilibria as equilibria involving ions in solution

(i) Arrhenius theory of electrolytes.
(ii) Ostwards dilution law for weak electrolyte $K_a = \left(\frac{\alpha^2}{1-\alpha}\right)\left(\frac{1}{V}\right)$

(iii) Acid & Bases
(a) Arrhenius H^+/OH^- theory.
(b) Bronsted lowery - protonic concept.
(c) Lewis concept - electronic concept of acids and bases.

Some basic concept

pH scale : $pH = -\log[H^+]$.
(i) Water as amphiprotic solvent.
(ii) Autoionization of water : $K_w = [H^+][OH^-]$.
(iii) $K_a[H_2O] = K_w/[H_2O]$
(iv) Change in pH of neutral H_2O with temperature.

Homogenons Ionic equilibria

(i) Acid/ base equilibrium
(a) Strong acid $[H^+]=c/2+\sqrt{\frac{c^2}{4}+K_w}$;c=conc. of (acid)
(b) pH due to polyprotic weak acids
(c) Weak monobasic acid $[H^+] = \sqrt{K_a.c}$ (if $\alpha < 0.1$)
(d) Mixture of S.A. & W.A.
(e) Mixture of two W.A. $[H^+]=\sqrt{K_1c_1+K_2c_2}$
(f) Buffer solutions : $pH = pK_a + \log\left(\frac{salt}{acid}\right)$

$pOH = pK_b + \log\left(\frac{salt}{base}\right)$

(g) Salt hydrolysis – (W.A. & S.B) $pH=\frac{1}{2}(pK_w + pK_a + \log c)$

(W.B & S.A.) $pH = \frac{1}{2}(pK_w - pK_b - \log c)$

(W.A. & W.B.) $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

Heterogenons equilibria

Solubility of sparingly soluble salt's (AB, AB_2, A_xB_y)$K_{sp} = (S^{x+y})X^xY^y$
(i) Effect of pH on solubility.
(ii) Simultaneous solubility.

Application of both heterogenous and homogenous equilibrium

(i) Extent of hydrolysis in buffer solution.
(ii) Change in solubility due to complex formation.
(iii) Solubility and hydrolysis.

REDOX

❑ OXIDISING AND REDUCING AGENT

- **Oxidising agent or Oxidant :**

  Oxidising agents are those compound which can oxidise others and reduced itself during the chemical reaction. Those reagents whose O.N. decrease or which gain electrons in a redox reaction are termed as oxidants

e.g. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, conc. H_2SO_4 etc, are powerful oxidising agents.

- **Reducing agent or Reductant :**

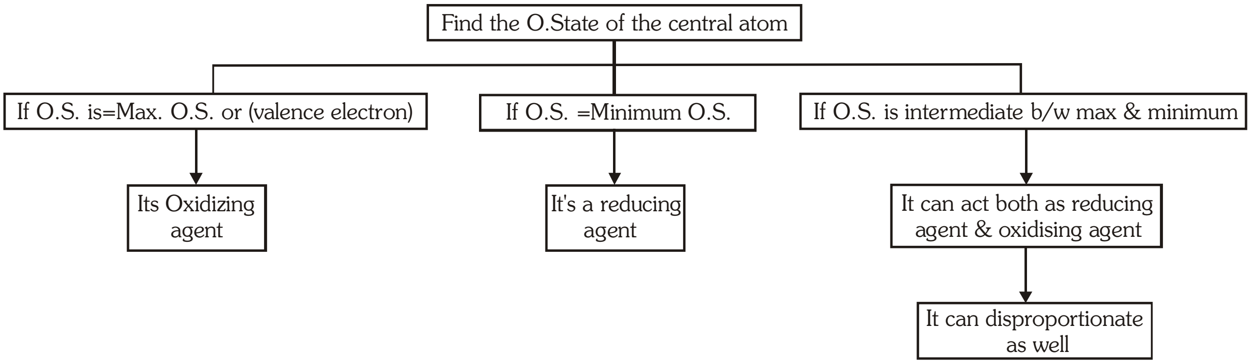
  Redusing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

e.g. KI, $Na_2S_2O_3$ are powerful reducing agents.

Note : There are some compounds also which can work both oxidising agent and reducing agent.

e.g. H_2O_2, NO_2^-

❑ HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR REDUCING AGENT



❑ REDOX REACTION

A reaction in which oxidation and reduction simultaneously take place.

In all redox reactions the total increase in oxidation number must equal the total decrease in oxidation number.

e.g. $10\overset{+2}{Fe}SO_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

Equivalent weight (E) :

$$\text{Eq. wt (E)} = \frac{\text{Molecular weight}}{\text{valency factor (v.f)}} = \frac{\text{Mol. wt.}}{\text{n} - \text{factor}}$$

$$\text{no of Equivalents} = \frac{\text{mass of a sample}}{\text{eq. wt. of that species}}$$

- Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.

(c) Eq. wt. of oxidising / reducing agents in redox reaction :

The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.

(a) Equivalent wt. of an oxidant (get reduced)

$$= \frac{\text{Mol.wt.}}{\text{No. of electrons gained by one mole}}$$

❑ n-FACTOR IN VARIOUS CASES

In Non Redox Change

- **n-factor for element :** Valency of the element
- **For acids :** Acids will be treated as species which furnish H^+ ions when dissolved in a solvent.

  The n-factor of an acid is the no. of acidic H^+ ions that a molecule of the acid would give when dissolved in a solvent (Basicity).

  For example, for HCl (n = 1), HNO_3 (n = 1), H_2SO_4 (n = 2), H_3PO_4 (n = 3) and H_3PO_3 (n = 2)
- **For bases :** Bases will be treated as species which furnish OH^- ions when dissolved in a solvent . The n-factor of a base is the no. of OH^- ions that a molecule of the base would give when dissolved in a solvent **(Acidity)**.

  For example, NaOH (n = 1), $Ba(OH)_2$ (n = 2), $Al(OH)_3$ (n = 3), etc.
- **For salts :** A salt reacting such that no atom of the salt undergoes any change in oxidation state.

  For example, $2AgNO_3 + MgCl_2 \rightarrow Mg(NO_3)_2 + 2AgCl$

  In this reaction, it can be seen that the oxidation state of Ag, N, O, Mg and Cl remains the same even in the product. The n-factor for such a salt is the total **charge on cation or anion.**

In Redox Change

For oxidizing agent or reducing agent n-factor is the **change in oxidation number per mole of the substance.**

❑ SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQ. WT.

Species	Changed to	Reaction	Electrons exchanged or change in O.N.	Eq. wt.
MnO_4^-(O.A.)	Mn^{+2} in acidic medium	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	5	$E = \frac{M}{5}$
MnO_4^-(O.A.)	MnO_2 in neutral medium	$MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$	3	$E = \frac{M}{3}$
MnO_4^-(O.A.)	MnO_4^{2-} in basic medium	$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	1	$E = \frac{M}{1}$
$Cr_2O_7^{2-}$(O.A.)	Cr^{3+} in acidic medium	$CrO_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	6	$E = \frac{M}{6}$
MnO_2(O.A.)	Mn^{2+} in acidic medium	$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	2	$E = \frac{M}{2}$

Cl_2(O.A.) in bleaching powder	Cl^-	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	2	$E = \frac{M}{2}$
$CuSO_4$(O.A.) in iodometric titration	Cu^+	$Cu^{2+} + e^- \longrightarrow Cu^+$	1	$E = \frac{M}{1}$
$S_2O_3^{2-}$ (R.A.)	$S_4O_6^{2-}$	$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$	2 (for two molecules)	$E = \frac{2M}{2} = M$
H_2O_2(O.A.)	H_2O	$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	2	$E = \frac{M}{2}$
H_2O_2(R.A.)	O_2	$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in H_2O_2 is –1 per atom)	2	$E = \frac{M}{2}$
Fe^{2+}(R.A.)	Fe^{3+}	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	1	$E = \frac{M}{1}$

☐ NORMALITY

Normality of solution is defined as the number of equivalent of solute present in one litre (1000 mL) solutions. Let a solution is prepared by dissolving W g of solute of eq. wt. E in V mL water.

- No. of equivalent of solute = $\frac{W}{E}$
- V mL of solution have $\frac{W}{E}$ equivalent of solute
- 1000 mL solution have $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) =** $\frac{W \times 1000}{E \times VmL}$
- **Normality (N) = Molarity × Valence factor**

  Normality (N) = molarity × Valence factor (n)

  or N × V (in mL) = M × V (in mL) × n

  or milli equivalents = millimoles × n

☐ LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

According :

(i) $aA + bB \rightarrow mM + nN$

m.eq of A = m.eq of B = m.eq of M = m.eq of N

(ii) In a compound M_xN_y

m.eq of M_xN_y = m.eq of M = m.eq of N

Solved Examples :

Iodimetric Titration

These are the titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in KI solution :

$KI + I_2 \longrightarrow KI_3$ (Potassium triiodide)

This solution is first standardized before using with the standard solution of substance such as sulphite, thiosulphate, arsenite etc, are estimated.

In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

☐ SOME IODOMETRIC TITRATIONS (TITRATING SOLUTIONS IS $Na_2S_2O_3.5H_2O$)

Estimation of	**Reaction**	**Relation between O.A. and R.A.**
I_2	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$ or $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	$I_2 = 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $Na_2S_2O_3$ = M/1
$CuSO_4$	$2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + 2K_2SO_4 + I_2$ $Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$ (White ppt.)	$2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $CuSO_4$ = M/1
$CaOCl_2$	$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$ $CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ $Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	Eq. wt. of $CaOCl_2$ = M/2
MnO_2	$MnO_2 + 4HCl\,(conc) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$ or $MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$ $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of MnO_2 = M/2
IO_3^-	$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$ Eq. wt. of IO_3^- = M/6

ELECTROCHEMISTRY

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment.**

Electrochemical Cells can be classified as:

(i) **Electrolytic Cells** in which a non–spontaneous reaction is driven by an external source of current.

(ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

Note: In a **galvanic cell**, cathode is positive with respect to anode.

In a **electrolytic cell**, anode is made positive with respect to cathode.

REPRESENTATION OF A CELL (IUPAC CONVENTIONS):

Let us illustrate the convention taking the example of Daniel cell.

(i) Anodic half cell is written on left and cathodic half cell on right hand side.

$$Zn(s) \mid ZnSO_4\,(sol) \parallel CuSO_4\,(sol) \mid Cu(s)$$

(ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.

(iii) EMF (electromotive force) may be written on the right hand side of the cell.

(iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

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

(v) Inert electrodes are represented in the bracket

$$Zn \mid ZnSO_4 \parallel H^+ \mid H_2, Pt$$

RELATIONSHIP BETWEEN ΔG AND ELECTRODE POTENTIAL

Let n, Faraday charge is taken out from a cell of e.m.f. (E) then electrical work done by the cell may be calculated as,

Work done = Charge x Potential = nFE

From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion

$\therefore\ \Delta G = -nFE$

Under standard state $\qquad \Delta G^0 = -nFE^0 \qquad$ (i)

(i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from e(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.

(ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.

Reactions	**ΔG**	**E**
Spontaneous	(–)	(+)
Non- spontaneous	(+)	(–)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E^0 (i.e., standard reduction potential of cathode- standard reduction potential of anode) in e (i) we may get ΔG^0.

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). EMF is called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

E_{cell} = reduction potential of cathode – Reduction potential of anode

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$E°_{cell}$ = Standard reduction potential of cathode – Standard

NERNST EQUATION

Walter Nernst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G° + RT \ln Q \qquad ..(A)$$

where ΔG and $\Delta G°$ are free energy and standard free energy change; 'Q' is reaction quotient.

$\therefore$ $-\Delta G = nFE$ and $-\Delta G° = nFE°$

Thus from E (i),we get $-nFE = -nFE° + RT \ln Q$

At 25°C, above equation may be written as $\mathbf{E = E^0 - \frac{0.0591}{n} \log Q}$

Where 'n' represents number of moles of electrons involved in process.

E, E° are e.m.f. and standard e.m.f. of the cell respectively.

In general , for a redox cell reaction involving the transference of n electrons

$aA + bB \longrightarrow cC + dD$, the EMF can be calculated as:

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

(ii) Determination of equilibrium constant : We know, that

$$E = E^0 - \frac{0.0591}{n} \log Q \qquad ..(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. E = 0

$\therefore$ From E (i), we have

$$0 = E^0 - \frac{0.0591}{n} \log K_{eq} \quad \text{or} \quad K_{eq} = \text{anti} \log \left[\frac{nE^0}{0.0591} \right]$$

(iii) **Heat of Reaction inside the cell:** Let n Faraday charge flows out of a cell of e.m.f. E, then

$$-\Delta G = nFE \qquad \text{(i)}$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad \text{(ii)}$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_p = \Delta H - nFT\left[\frac{\partial E}{\partial T}\right]_p$$

$$\therefore \qquad \Delta H = -nFE + nFT\left[\frac{\partial E}{\partial T}\right]_p$$

(iv) **Entropy change inside the cell :** We know that G = H - TS or $\Delta G = \Delta H - T\Delta S$ ...(i)

where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change.

According to Gibbs Helmoholtz equation,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad \text{....(ii)}$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T\left[\frac{\partial \Delta G}{\partial T}\right]_p \quad \text{or} \quad \Delta S = -\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

$$\text{or} \qquad \Delta S = nF\left[\frac{\partial E}{\partial T}\right]_p$$

CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell .

(i) **Electrode Gas concentration cell :**

$Pt, H_2(P_1) \mid H^+(C) \mid H_2(P_2), Pt$

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process : $1/2H_2(p_1) \rightarrow H^+(c) + e^-$ (Anode process)

$$\begin{array}{c} H^{+}(c)+e^{-}\rightarrow 1/2H_2(p_2) \\ \hline 1/2H_2(p_1)\rightleftharpoons 1/2H_2(p_2) \end{array} \qquad \therefore \qquad E=-\frac{2.303RT}{F}\log\left[\frac{p_2}{p_1}\right]^{1/2}$$

or $$E=\left[\frac{2.303RT}{2F}\right]\log\left[\frac{p_2}{p_1}\right]$$, At $25^{0}C$, $$E=\frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$$

For spontanity of such cell reaction, $p_1 > p_2$

(ii) Electrolyte concentration cells:

$Zn(s) \mid ZnSO_4\ (C_1) \parallel ZnSO_4\ (C_2) \mid Zn(s)$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,

$Zn(s)\rightarrow Zn^{2+}(C_1)+2e$ (Anodic process)

$$\begin{array}{c} Zn^{2+}(C_2)+2e\longrightarrow Zn(s) \\ \hline Zn^{2+}(C_2)\rightleftharpoons Zn^{2+}(C_1) \end{array}$$ (Over all process)

$\therefore$ From Nernst equation, we have

$$E=0-\frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right] \quad \text{or} \quad E=\frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

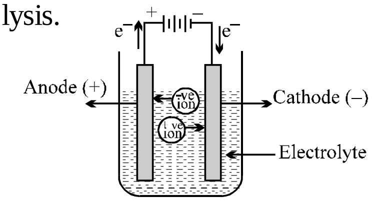
For spontanity of such cell reaction, $C_2 > C_1$

ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell



Electrolytic cell

ELECTRODES

The metal strip at which positive current enters is called ***anode***; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

FARADAY’S LAWS OF ELECTROLYSIS:

(i) **First law of electrolysis :**

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

W = weight liberated, Q = charge in coulomb

$$w = ZQ$$

Z = electrochemical equivalent

when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

Let 1 ampere current is passed till ‘t’ seconds .

Then, $Q = It \quad \therefore \quad w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

(ii) *Second law of electrolysis :*

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e. $w_1/w_2 = E_1/E_2$

CONDUCTANCE

Introduction:

Both metallic and electrolytic conductors obey Ohm's law

i.e. $V = IR$

where V = Potential difference in volt; I = Current in ampere ; R = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho\frac{l}{A} \qquad (\rho = \text{Specific resistance})$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm^2.

Unit of R is ohm and unit of specific resistance is ohm cm

Reciprocal of resistance is called as *conductance* and reciprocal of specific resistance is called as *specific conductance*.

$$\frac{1}{R} = \frac{1}{\rho}\frac{A}{l} \quad \text{or} \quad C = K\frac{A}{l}$$

where C = conductance ohm^{-1} ; K = specific conductance ohm^{-1}cm^{-1} .

Mho and siemens are other units of conductance

$$K = \frac{l}{A}C$$

Specific conductance= Cell constant × Conductance

SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM^3 OF AN ELECTROLYTE SOLUTION.

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by $\wedge$.

$$\wedge = K \text{ x } V$$

$$(\wedge = \text{ohm}^{-1} \text{ cm}^{-1} \text{ x cm}^3 = \text{ohm}^{-1} \text{ cm}^2)$$

Usually concern ration of electrolyte solution is expressed as C gm equivalent per litre.

Thus, $V=\dfrac{1000}{C}$

$\{\text{Volume having 1 gm equivalent electrolyte in the solution}\}$ Thus, $\wedge = K \times \dfrac{1000}{C}$

2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by $\wedge_m$.

$$\wedge_m = K \quad V$$

Usually concentration of electrolyte solution is expressed as ‘M’ gm mole elecrtrolyte per litre.

Thus, $V=\dfrac{1000}{M}$

Hence, $\wedge_m = K x \dfrac{1000}{M}$

Relation between $\wedge$ and $\wedge_m$: $\wedge_m = n \times \wedge$

Application of Kohlrausch's law :

(A) Determination of $\wedge_m^0$ of a weak electrolyte:

In order to calculate $\wedge_m^0$ of a weak electrolyte say CH_3COOH, we determine experimentally $\wedge_m^0$ values of the following three strong electrolytes:

(a) A strong electrolyte containing same cation as in the test electrolyte, say HCl

(b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa

(c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\wedge_m^0$ of CH_3COOH is then given as:

$$\wedge_m^0 (CH_3COOH) = \wedge_m^0 (HCl) + \wedge_m^0 (CH_3COONa) - \wedge_m^0 (NaCl)$$

Proof :

$\wedge_m^0$ (HCl) = $\lambda_H^0 + \lambda_{Cl^-}$ ....(i)

$\wedge_m^0$ (CH_3COONa) = $\lambda^0_{CH_3COO^-} + \lambda_{Na^+}$ ....(ii)

$\wedge_m^0$ (NaCl) = $\lambda^0_{Na^+} + \lambda^0_{Cl^-}$ ....(iii)

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\wedge_m^0 (HCl) + \wedge^0_{(CH_3COONa)} - \wedge^0_{(NaCl)} = \lambda^0_{(H^+)} + \lambda^0_{(CH_3COO^0)} = \wedge_{0(CH_3COOH)}$$

(B) Determination of degree of dissociation (α) :

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\wedge_m}{\wedge_m^0}$$

(C) Determination of solubility of sparingly soluble salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to $\wedge_m^0$ as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (D).

$$\wedge_m^0 = \frac{1000\kappa}{C},$$

where C is the molarity of solution and hence the solubility.

CHEMICAL KINETICS

- **Rate of reaction** (ROR) $= \dfrac{\text{Rate of disappearance of reactant (appearance of products)}}{\text{Stoichiometric coefficient of reactant (products)}}$

- **For a reaction :**

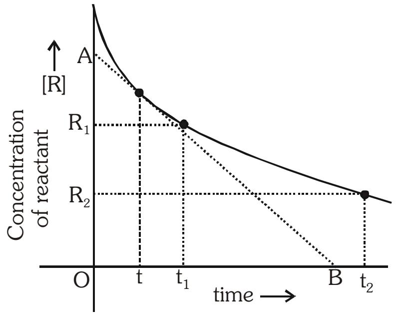
  $aA + bB \longrightarrow cC + dD$

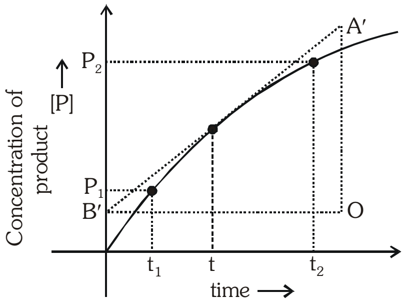
- **Instantaneous rate :** $-\dfrac{1}{a}\left(\dfrac{d[A]}{dt}\right) = -\dfrac{1}{b}\left(\dfrac{d[B]}{dt}\right) = \dfrac{1}{c}\left(\dfrac{d[C]}{dt}\right) = \dfrac{1}{d}\left(\dfrac{d[D]}{dt}\right)$

  Relationship between rate of reaction and rate of disappearence of reactant (rate of appearance of product).

◆ **Average rate :** $-\dfrac{1}{a}\left(\dfrac{\Delta[A]}{\Delta t}\right) = -\dfrac{1}{b}\left(\dfrac{\Delta[B]}{\Delta t}\right) = \dfrac{1}{c}\left(\dfrac{\Delta[C]}{\Delta t}\right) = \dfrac{1}{d}\left(\dfrac{\Delta[D]}{d\Delta t}\right)$

⇒ Graphical method for determining rate :





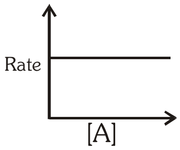
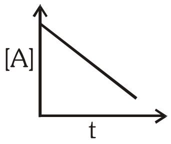
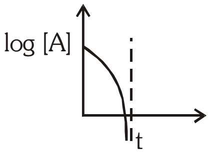
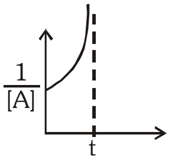
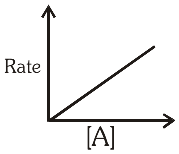
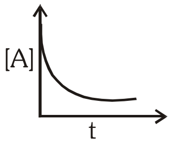
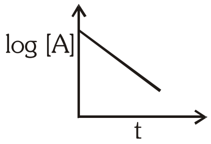
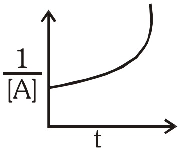
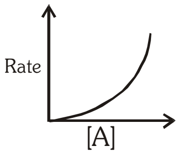
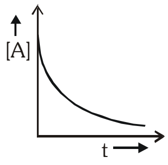
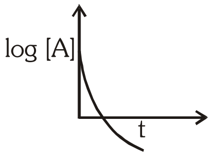
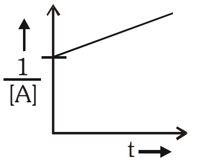
Avg. Rate $= -\left(\dfrac{[R]_2 - [R]_1}{t_2 - t_1}\right) = \dfrac{([P]_2 - [P]_1)}{t_2 - t_1}$

Instantaneous rate $= -\left(\dfrac{OA}{OB}\right) = +\dfrac{OA'}{OB'} = \pm$ slope of tangent

- **Important kinetic expression for reaction of type A ⟶ B :**

Order	Zero	1st	2nd	nth
Differential rate law	Rate = k	Rate= k[A]	Rate = $k[A]^2$	Rate = $k[A]^n$
Integrated rate law	$[A_0]-[A] = kt$	$kt = \text{In}\dfrac{[A]_0}{[A]}$	$kt = \dfrac{1}{[A]} - \dfrac{1}{[A]_0}$	$kt = \dfrac{1}{(n-1)}\left[\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A]_0^{n-1}}\right]$
Half life ($t_{1/2}$)	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{\ln 2}{k}$	$t_{1/2} = \dfrac{1}{[A]_0 k}$	$t_{1/2} = \dfrac{1}{k(n-1)}\left[\dfrac{2^{n-1}-1}{[A_0]^{n-1}}\right]$
($t_{3/4}$)	$t_{3/4}$=1.5 $t_{1/2}$	$t_{3/4}$= 2 $t_{1/2}$	$t_{3/4}$ = 3 $t_{1/2}$	$t_{3/4}$= $(2^{n-1} + 1)$ $t_{1/2}$

- **Graphs of various order**

Order	Rate vs [A]	[A] vs t	log [A] vs t	$\frac{1}{[A]}$ vs t
Zero order				
First order				
Second order				

Where

$[A]_0 \Rightarrow$ initial concentration

$[A] \Rightarrow$ concentration at time t

$t_{1/2} \Rightarrow$ time taken for initial concentration of reactant to finish by 50%

$t_{3/4} \Rightarrow$ time taken for initial concentration of reactant to finish by 75%

- **Monitoring Kinetics Experimently :**

The kinetics of reaction can be followed (i.e. order, rate constant etc. can be established) by measuring a property which changes with time.

e.g. (i) Total pressure in a gaseous reaction.

$$k = \frac{1}{t}\ln\left(\frac{P_0}{P_0 - x}\right)$$

- **Examples : (For Monitoring Kinetics Experimently)**

(i) Inversion of cane sugar :

$$\underset{\substack{\text{Sucrose} \\ \text{dextro-rotatory} \\ (+66.5^\circ)}}{C_{12}H_{22}O_{11}\,(aq)} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{Glucose} \\ \text{dextro-rotatory} \\ (+52.5^\circ)}}{C_6H_{12}O_6(aq)} + \underset{\substack{\text{Fructose} \\ \text{laevo-rotatory} \\ (-92^\circ)}}{C_6H_{12}O_6(aq)}}_{\text{(Laevo-rotatory)}}$$

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

$\mathbf{r_0}$ = rotation at time, t = 0

$\mathbf{r_t}$ = rotation at time, t = t

$\mathbf{r_\infty}$ = rotation at time, t = ∞

(ii) **Acidic hydrolysis of ethyl acetate** :

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

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

$\mathbf{V_0}$ = Volume of NaOH solution used at time, t = 0

$\mathbf{V_t}$ = Volume of NaOH solution used at time, t = t

$\mathbf{V_\infty}$ = Volume of NaOH solution used at time, t = ∞

Note : Here NaOH acts as a reagent. Acetic acid is one of the product the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution.

➢ **Important characteristics of first order reaction :**

◆ $t_{1/2}$ is independent of initial concentration.

◆ In equal time interval, reactions finishes by equal fraction.

	t = 0	t = t	t = 2t	t = 3t ....
Reactant conc.	a_0	a_0x	a_0x^2	a_0x^3........

x = fraction by which reaction complete in time 't'.

◆ Graph of ln[A] vs t is straight line with slope = $\frac{k}{2.303}$

◆ Graph of [A] vs t is exponentially decreasing.

➢ **Zero order :**

- $t_{1/2}$ of zero order is directly proportional to initial concentration.
- In equal time interval, reaction finishes by equal amount.

t = 0	t = t	t = 2t	t = 3t .....
C_0	$C_0 - x$	$C_0 - 2x$	$C_0 - 3x$....

- Graph of [A] vs t is straight line.

A zero order reaction finishes in $\boxed{t = \frac{[A]_0}{k}}$

➢ **Temperature dependence :**

– Arrhenious equation : $k = A.e^{-Ea/RT}$

– E_a = minimum energy over and above the avg. energy of reactant which must be possesed by reacting molecule for collision to be succesful.

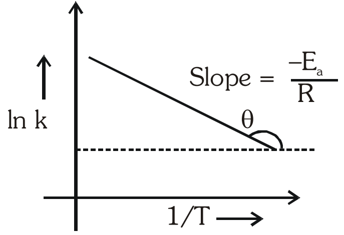
– A = frequency factor - proportional to number of collisions per unit volume per second.

– $e^{-Ea/RT}$= Fraction of collision in which energy is greater than E_a.

– A and E_a are constant i.e. do not vary with temperature

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

Graph : Graphical determination of E_a.

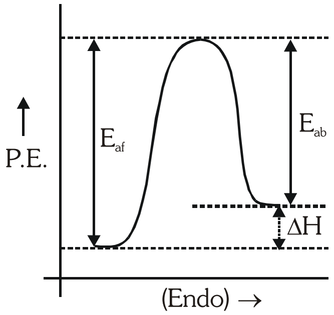


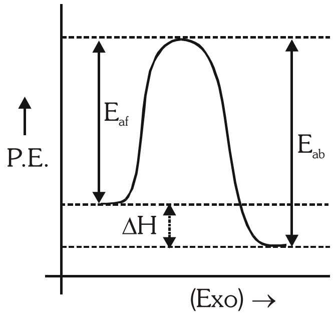
Temperature coefficient $= \frac{k_{T+10}}{k_T}$

By default T = 298 K

Variation of rate constant with temparture ⇒ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

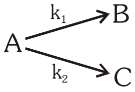
- **Endothermic and exothermic reactions :**





$$\boxed{\Delta H = E_{af} - E_{ab}}$$

- **Parallel reaction :**



(i) Rate = $(k_1 + k_2)$ [A] - (differential rate law)

(ii) $\frac{k_1}{k_2} = \frac{[B]}{[C]}$

(iii) $t_{1/2} = \frac{0.693}{k_1 + k_2}$

(iv) % of B = $\frac{k_1}{k_1 + k_2} \times 100$; % of C = $\frac{k_2}{k_1 + k_2} \times 100$

(v) $[A] = [A]_0 e^{-(k_1+k_2)t}$

- **Pseudo-order reaction :**

Rate law → rate = $k\,[A]^m\,[B]^n$

Pseudo rate law :

rate = $k_1\,[A]^m$

[B] assumed constant in two cases :

(i) B in large excess (ii) B → CATALYST

RADIOACTIVITY

- **All nuclear reactions are first order :**

Two types of nuclear reaction : **(a)** Artifical radioactivity **(b)** Radioactivity (spont.)

First order

$\lambda t = 2.303 \log \frac{N_0}{N_t}$

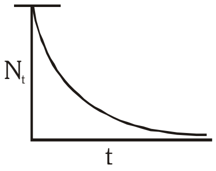
$\lambda \rightarrow$ Decay constant

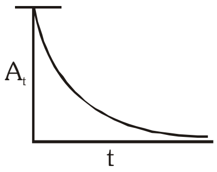
$N_0 \rightarrow$ Initial nuclei

$N_t \rightarrow$ Nuclei at 't'

Activity = $A_t = \frac{-dN_t}{d_t} = \lambda N_t$; Nuclei/sec.

A_t = Rate of decay





$\Rightarrow \quad t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$

- **α decay** = ${}^{4}_{2}He$ Particles at high velocity

${}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + \alpha$

To ↓ size of large nuclei

- **β decay** = ${}^{0}_{-1}e$ at high velocity

${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}P + {}^{0}_{-1}e$

To ↓ $\frac{n}{P}$ ratio.

Nuclear change in β decay

${}^{1}_{0}n \longrightarrow {}^{1}_{1}P + {}^{0}_{-1}e$

- **γ-decay :**

Photons from excited nuclei after α – or β – decay
No effect on n/p ratio
High energy e/m radiation.

Mean life , $t_{avg} = \frac{1}{\lambda}$

◆ $\left({}^{0}_{+1}\beta\right)$ **Positron decay**

$p \longrightarrow n + {}^{0}_{+1}\beta$

* Those nucleus which have low value of of n/p ratio (lie below the stability belt) undergoes ${}^{0}_{+1}\beta$ decay.

◆ **K electron capture**

$$^{A}_{Z}X + ^{0}_{-1}e \longrightarrow ^{A}_{Z-1}Y$$

$$^{106}_{47}Ag + ^{0}_{-1}e \longrightarrow ^{106}_{46}Pd$$

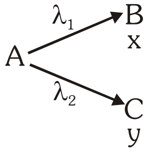
$$p + e \longrightarrow n$$

* Electron capture can occur when ever the mass of original neutral atom is larger than that of final atom.

* Those nucleus having low n/p ratio can capture K shell electron.

* X-rays are emitted during the process.

➢ **Parallel decay :**



$t = 0$ N_0

$t = t$ $N_0 - x - y$

$\lambda_{eff.} = \lambda_1 + \lambda_2$

$$\frac{1}{t_{eff.}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}$$

$\lambda \rightarrow$ No dependence on temp.

CHAPTER 10

LIQUID SOLUTION

- **Vapour Pressure :** Pressure of any volatile substance at any given temperature.

  T ↑ ⇒ V.P. ↑

  Attractive forces ↑ ⇒ V.P. ↓

- **Raoult's law :**

  Non volatile solute and volatile solvent solution.

  $\text{If} \begin{cases} B = \text{Non volatile solid} \\ P_B = 0 \end{cases}$

  $P_A = P_A^{\circ} X_A$

- **Colligative Properties :** Properties depends on no. of particles of Non volatile solute in solution.

  No. of particle of Non volatile solute ↑ ⇒ Colligative Properties ↑

  (1) Relative lowering of V.P. :

  $$\frac{P_A^{\circ} - P_A}{P_A^{\circ}} = i\frac{n_B}{n_A + n_B} \simeq i\frac{n_B}{n_A}$$

  Where n_B = mole of Non-volatile solute.

  i = Vant Hoff's factor.

  (2) Elevation in B.P. :

  $\Delta T_b = (T_b' - T_b) = i.\ k_b \times\ m.$

  where $K_b = \dfrac{RT_b^2}{1000 \times \ell_v}$

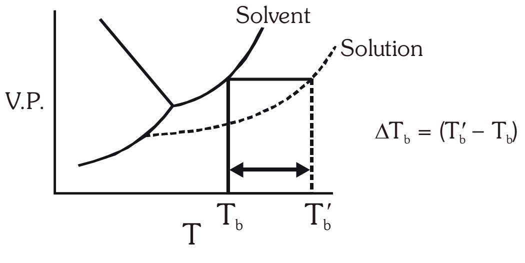
  where T_b = B.P. of pure solvent.

  ℓ_v = Latent heat of vapourization per gm

  K_b = molal elevation constant

  M = molar mass

  where $\ell_v = \left(\dfrac{\Delta H_{vap}}{M}\right)$



(3) **Depression** in FP.

$\Delta T_f = T_f - T_f' = i\ k_f \times m$

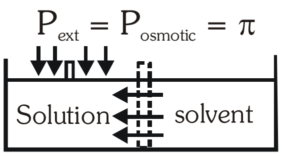
where $k_f = \dfrac{RT_f^2}{1000 \times \ell_f}$

T_f = f.p. of pure solvent

k_f = molal depression contsant

ℓ_f = latent heat of fusion per gm.

(4) Osmotic presssure :



$\pi \propto \left(P_A^\circ - P_A\right)$

π = iC. S.T.

where π = osmotic pressure

C = molarity (mole/lit)

S = R = const. for solution.

	Sol.(1)		Sol (2)	
If	π_1	=	π_2	Isotonic
If	π_1	>	π_2	$\begin{cases}\text{sol}^n(1) \text{ hypertonic} \\ \text{sol}^n(2) \text{ hypotonic}\end{cases}$

Van't Hoff factor for different Cases of solutes undergoing Ionisation and Association :

Solute	Example	Ionisation/association (x degree)	y*	van'thoff factor	Abnormal mol. wt. (m_1')
Non-electrolyte	urea-glucose, sucrose etc.	none	1	1	normal mol.wt. (m_1)
Binary electrolyte A^+B^-	NaCl, KCl, HCl CH_3COOH, $FeSO_4$ etc.	$\underset{1-x}{AB} \rightleftharpoons \underset{x}{A^+} + \underset{x}{B^-}$	2	(1 + x)	$\frac{m_1}{(1+x)}$
Ternary	K_2SO_4, $BaCl_2$,	$\underset{1-x}{A_2B} \rightleftharpoons \underset{2x}{2A^+} + \underset{x}{B^{2-}}$	3	(1+2x)	$\frac{m_1}{(1+2x)}$
electrolyte A_2B, AB_3	$K_3[Fe(CN)_6]$, $FeCl_3$	$\underset{1-x}{AB_3} \rightleftharpoons \underset{x}{A^{3+}} + \underset{3x}{3B^-}$	4	(1+3x)	$\frac{m_1}{(1+3x)}$
Associated Solute	benzoic acid in benzene	$2\,A \rightleftharpoons A_2$	$\frac{1}{2}$	$\left(1-\frac{x}{2}\right)=\left(\frac{2-x}{2}\right)$	$\frac{2m_1}{(2-x)}$
	forming dimer	$\underset{(1-x)}{A} \rightleftharpoons \frac{1}{2}\underset{x/2}{A_2}$			
	any solute	$nA \rightleftharpoons A_n$	$\frac{1}{n}$	$\left[1+\left(\frac{1}{n}-1\right)x\right]$	$\left[\frac{m_1}{1+\left(\frac{1}{n}-1\right)x}\right]$
	forming polymer A_n	$\underset{(1-x)}{A} \rightleftharpoons \frac{1}{n}\underset{x/2}{A_n}$			
General	one mole of solute giving y mol of products	$A \rightleftharpoons yB$	y	[1+(y–1)x]	$\frac{m_1}{[1+(y-1)x]}$

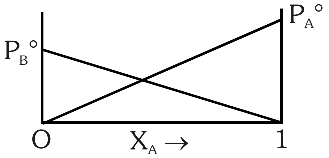
*** number of products from one mole solute**

Raoult's law :

(1) Volatile binary liquid mix :

Volatile liq.	A	B	
Mole fraction	X_A/Y_A	X_B/Y_A	$\Rightarrow$ liq/vapour
V.P. of pure liq.	P_A°	P_B°	

Binary liquid solution :

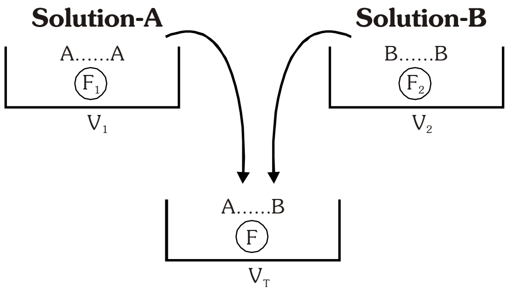


By Raoult's law $\Rightarrow P_T = P_A^\circ X_A + P_B^\circ X_B = P_A + P_B$ ......(i)

By Dalton's law $\Rightarrow P_A = Y_A P_T$ ......(ii)

$P_B = Y_B P_T$ ......(iii)

➢ **Ideal and Non-Ideal solution :**



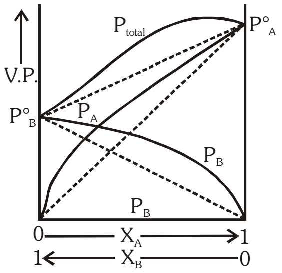
Ideal solution : $\left\{\begin{matrix}F_1 \simeq F_2 \simeq F \\ V_T = V_1 + V_2\end{matrix}\right. \Rightarrow \Delta H_{solution}=0$

Non-Ideal solution :

(1) **Solution showing +ve deviation :**

$F < F_1$ & F_2

$V_T > V_1 + V_2 \Rightarrow \Delta H_{solution} > 0$

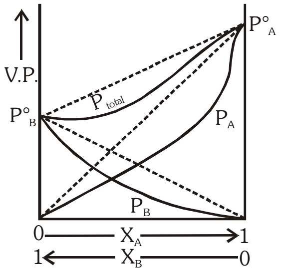


(2) **Solution showing –ve deviation :**

$\Rightarrow F > F_1$ & F_2

$\Rightarrow V_T < (V_1 + V_2)$

$\Rightarrow \Delta H_{solution} < 0$



DEVIATION FROM RAOULT'S LAW

	Positive deviation **(ΔH=+ve)**	**Negative deviation** **(ΔH=–ve)**	**Zero deviation** **(ΔH=0)**
(i)	ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(ii)	acetone + carbon disulphide n-hexane + n-heptane	benzene + chlorform	
(iii)	acetone + benzene	nitric acid + chloroform	ethyl bromide + ethyl iodide
(iv)	ethanol + aceton	acetone + aniline	chlorobenzene + bromo benzene
(v)	ethanol + water	water + nitric acid	
(vi)	carbon tetrachloride chloroform	diethyl ether + chloroform	

- **Azeotropic mixtures :**

  Some liquids on mixing form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. Azeotropic mixture cannot be separated by fractional distillation.

- **Types of Azeotropic mixtures**

(i) Minimum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviation. For example (95.5%) + water (4.5%) + water boils at 351.15 K.

(ii) Maximum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point are more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.

SOLID STATE

Distinction between Crystalline and Amorphous Solids

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

TYPES OF THE CRYSTALLINE SOLID

Types of Solid	Constituent Particles	Bonding/ Attractive forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular Solids						
(i) Non polar	Molecules	Disppersion or London forces	Ar, CCl_4, H_2, I_2 CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic Solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulator in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic Solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network Solids	Atoms	Covalent bonding	SiO_2 (quartz) SiC, C (diomond) AIN,	Hard	Insulators	Very high
			C(graphite)	Soft	Conductor	

THE SEVEN CRYSTAL SYSTEMS

	Name of System	Axes	Angles	Bravais Lattices
1.	Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred = 3
2.	Tetragonal	a= b ≠ c	$\alpha = \beta = \gamma = 90°$	Primitive, Body centred = 2
3.	Rhombohedral or Trigonal	a = b= c	$\alpha = \beta = \gamma \neq 90°$	Primitive = 1
4.	Orthorhombic or Rhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$	Primitive, Face-centred, Body centred End centred =
5.	Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90°$; $\beta \neq 90°$	Primitive, End - centred = 2
6.	Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive = 1
7.	Hexagonal	a = b ≠ c	$\alpha = \beta = 90°$ $\gamma = 120°$	Primitive = 1 Total = 14

CUBIC UNIT CELL

Unit cell	**Relation between r and a**	**Packing fraction**	**Co-ordinatin number**	**Effective number of particle**
Simple cubic Body centred	$r = \frac{a}{2}$	52.4%	6	1
cubic	$r = \frac{a\sqrt{3}}{4}$	68%	8	2
Face centred cubic	$r = \frac{a\sqrt{2}}{4}$	74%	12	4

Density : d = $\frac{ZM}{N_{A\ x}a^3}\ gm/cm^3$

Where Z = effective number of particle

M= molar mass

N_A = Avogarodro's number

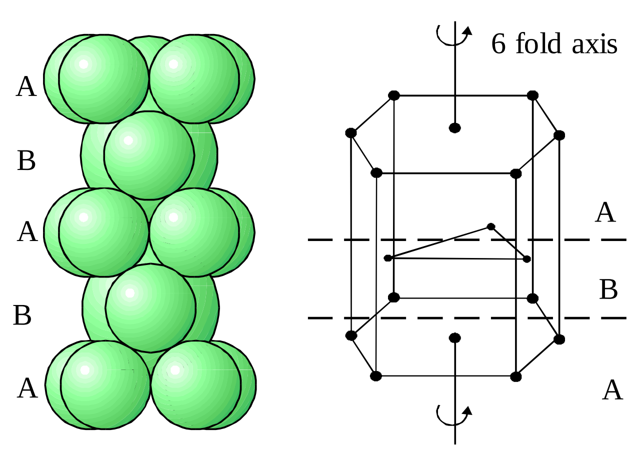
a = edge length (cm)

Three dimensional close packing :

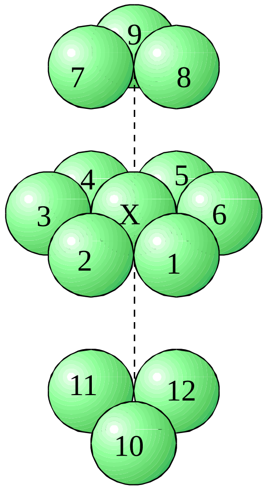
- **Hexagonal close packing (HCP) :**

  Effective number of particle = 6
  Effective number of octahedral void = 6
  Effective number of tetrahedral void = 12
  Packing fraction
  = 74% ; co-ordination number = 12

  $a = \frac{r}{2}$; $b = 4\sqrt{\frac{2}{3}}r$



ABABAB... or hexagonal close packing (hcp) of spheres



Coordination number of hcp and ccp structure

- **Cubic close packing (CCP) :**

Effective number of particle = 4

Effective number of octahedral void = 4

Effective number of tetrahedral void = 8

Packing fraction = 74% ;

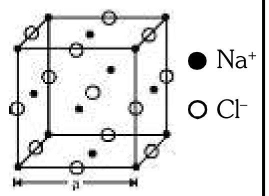
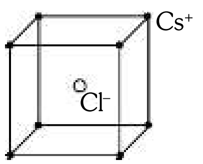
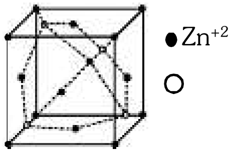
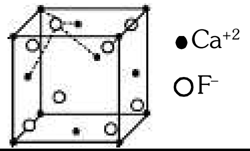
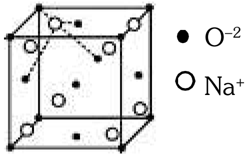
co-ordination number =12

$$\frac{a\sqrt{2}}{4} = r$$

- **Different type of voids and their radius ratio :**

Limiting radius ratio = r/R	**Limiting radius ratio for various types of sites**		
	Coordination Number of cation	**Structural Arrangement (Geometry of voids)**	**Example**
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 - 0.732	4	Square planaer	–
0.414 - 0.732	6	Octahedral	NaCl, MgO_2
0.732 - 1.000	8	Cubic	CsCl

TYPES OF IONIC CRYSTAL

	Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.C.	Examples	
1.	NaCl (1 : 1) (Rock Salt Type)	C.C.P. $\langle$ Na^+ → Every element of C.C.P. Cl^- → At every OHV	6 : 6	$4Na^+ + 4Cl^-$ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of II–A (Some exception) AgF, AgCl, AgBr, NH_4X	
2.	CsCl Type (1 : 1)	B.C.C. $\langle$ Cs^+ → at every corner Cl^- → at Body centre or at cubic void	8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CaS	
3.	Zns Type (1 : 1) (Zinc Blende Type) (Sphalerite)	C.C.P. $\langle$ Zn^{+2} → Every element of C.C.P. S^{-2} → At 50% of T.H.V. or at alternate tetrahedral voild	4 : 4	$4Zn^{+2} + 4S^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI	
4.	CaF_2 Type (1 : 2) (Fluorite Type)	C.C.P. $\langle$ Ca^{+2} → Every element of C.C.P. F^- → At every T.H.V.	$4Ca^{+2}, 8F^-$ 8 : 4	$4Ca^{+2} + 8F^-$ $4CaF_2$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2 $CaCl_2$, CaF_2	
5.	Na_2O Type (2 : 1) (Antiflourine)	C.C.P. $\langle$ Na^+ → At every T.H.V. O^{-2} → Every element of C.C.P.	$8Na^+, 4O^{-2}$ 4 : 8	$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S Na_2O, Na_2S K_2O, K_2S	
6.	ZnS Type (1 : 1) (Wurtzite) another geometry of Zns	H.C.P. $\langle$ Zn^{+2} → Every element of H.C.P. S^{-2} → 50% of T.H.V. or (at alternateT.H.V.)	4 : 4	$6Zn^{+2} + 6S^{-2}$ 6ZnS (6)	Same as sphalerite	

GASEOUS STATE

GAS LAW

- **Boyle's law :** $V \propto \frac{1}{P}$ (n, T = const) $\boxed{P_1V_1 = P_2V_2}$
- **Charle's law :** $V \propto T$ (n, P = const) $\frac{V_2}{V_1} = \frac{T_2}{T_1}$
- **Gay lussac's law:** $P \propto T$ (n, V = const) $\frac{P_2}{P_1} = \frac{T_2}{T_1}$
- **Avogadro's law :**

$V \propto$ moles $\propto$ number of molecules (P, T = const)

Ideal gas equation PV = nRT

R = 0.0821 lit atm mol^{-1} K^{-1}

R = 8.314 J K^{-1} mol^{-1} or 8.314 , N×m K^{-1} mol^{-1}

R = 2 cal K^{-1} mol^{-1}, R = 8.314 × 10^7 erg K^{-1} mol^{-1}

GRAHAM'S DIFFUSION LAW

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}\ ;\ r \propto \frac{1}{\sqrt{VD}}\ ;\ r \propto \frac{1}{\sqrt{M_w}}\ \text{(P, T = constant)}$$

$$VD = \frac{d_{gas}}{dH_2} = \frac{M_w}{2}$$

Rate of diffusion

$$r = \frac{\ell_{\text{diffused gas}}}{t_{\text{time taken}}}\ ;\ r = \frac{V_{\text{diffused gas}}}{t_{\text{time taken}}}\ ;\ r = \frac{n_{\text{diffused gas}}}{t_{\text{time taken}}}$$

(Where, ℓ = distance travelled by diffused gas)

KINETIC GAS EQUATION : PV = 1/3 mN V^2_{rms}

DALTON'S LAW OF PARTIAL PRESSURE

$$P_{mixture} = \underbrace{P_1 + P_2 + P_3}_{\text{Partial pressure}} \text{............(T \& V const)}$$

$P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapours}}$

It is applicable for non reacting gases.

Methods of determination of partial pressure

(P_A & P_B are partial pressure)

- from ideal gas equation

  $P_AV = n_A RT$ & $P_BV = n_B RT$

- In the form of mole fraction.

  $P_A = X_A P_T = \frac{n_A}{n_t} P_T$; $P_B = X_B P_T = \frac{n_B}{n_t} P_T$

  $[X_A + X_B = 1]$

  P_T = sum of partial pressure of al gases

- In the form of volume fraction

  $P_A = \frac{V_A}{V} P_T$ & $P_B = \frac{V_A}{V} P_T$

- If individual pressure and individual volume are given

$P_A = \frac{V_A}{V} P_1$ and $P_B = \frac{V_B}{V} P_2$

P_1, P_2 = pressure of gases before mixing

P_A, P_B = pressure of gases after mixing

AVERAGE KINETIC ENERGY (KE_{av})

$KE_{av} = \frac{3}{2}$ nRT (n moles)

$KE_{av} = \frac{3}{2}$ RT (1 mol or N_A molecules)

$KE_{av} = \frac{3}{2}$ KT (1 molecule)

K = 1.38 × 10^{-23} JK^{-1} $molecule^{-1}$

K is called Boltzman's constant

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + \ldots v_n^2}{N}} \qquad v_{av} = \frac{v_1 + v_2 + v_3 \ldots . v_n}{N}$$

$$v_{rms} = \sqrt{\frac{3RT}{Mw}} \qquad v_{av} = \sqrt{\frac{8}{\pi}\frac{RT}{Mw}} \qquad v_{mp} = \sqrt{\frac{2RT}{Mw}}$$

$$v_{rms} = \sqrt{\frac{3PV}{Mw}} \qquad v_{av} = \sqrt{\frac{8}{\pi}\frac{PV}{Mw}} \qquad v_{mp} = \sqrt{\frac{2PV}{Mw}}$$

$$v_{rms} = \sqrt{\frac{3P}{d}} \qquad v_{av} = \sqrt{\frac{8}{\pi}\frac{P}{d}} \qquad v_{mp} = \sqrt{\frac{2P}{d}}$$

$$v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$$
$$= 1 : 0.92 : 0.82$$

$$v_{mp} : v_{av} : v_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$
$$= 1 : 1.128 : 1.224$$

Compressibility factor (z) = $\frac{(V_m)obs}{V_i} = \frac{P(V_m)obs}{RT}$

If z = 1, the gas show ideal gas behaviour.
If z > 1, the gas show positive deviation.
If z < 1, the gas show negative deviation.

VANDERWAAL'S EQUATION

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$P_i = P_R + \frac{an^2}{V^2} \Rightarrow P_i > P_R$$

a↑ force of attraction↑

liquification↑;

b↑, effective size of molecule ↑,

incompressible vol ↑,

compressible vol ↓

- ♦ At high pressure, Vanderwaal's eq^n is

$$\boxed{PV_m - Pb = RT}$$

- ♦ At low pres. or Moderate pressure Vanderwaal's eq^n is

$$\boxed{PV_m + \frac{a}{V_m} = RT}$$

- ♦ At very low pressure, high temp. Vander waal's Equation is

$$\boxed{VP = nRT}$$

Ideal gas behavior.

- ♦ Gases having ↑value of a; will have ↑T_C; ↑rate of liquefaction.

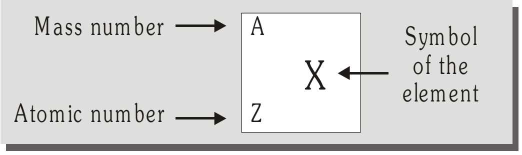
IMPORTANT NOTES

ATOMIC STRUCTURE

IMPORTANT DEFINITIONS

Proton (m_p) /anode rays	**Neutron (m_n)**	**Electron(m_e) / cathode rays**
mass =1.67 × 10^{-27} kg	mass = 1.67 × 10^{-27} kg	mass = 9.1 × 10^{-31} kg
mass = 1.67 × 10^{-24} g	mass = 1.67 × 10^{-24} g	mass = 9.1 × 10^{-28} g
mass = 1.00750 amu	mass = 1.00850 amu	mass = 0.000549 amu
e/m value is dependent on the nature of gas taken in discharge tube.		e/m of electron is found to be independent of nature of gas & electrode used.

REPRESENTATION OF AN ELEMENT



Terms associated with elements :

- Atomic Number (Z) : = No. of protons

  Electron = Z – C (charge on atom)
- Mass number (A) =Total number of neutron and proton present

  A = Number of proton + Number of Neutrons
- **Isotopes :** Same atomic number but different mass number

  Ex. : $_6C^{12}$, $_6C^{13}$, $_6C^{14}$
- **Isobars :** Same mass number but different atomic number

  Ex. $_1H^3$, $_2He^3$
- **Isodiaphers :** Same difference of number of Neutrons & protons

  Ex. $_5B^{11}$, $_6C^{13}$
- **Isotones** : Having same number of neutron

  Ex. $_1H^3$, $_2He^4$
- **Isosters**: They are the molecules which have the same number of atoms & electrons

  Ex. CO_2, N_2O
- **Isoelectronic**:Species having same no. of electrons

  Ex. Cl^-, Ar

ATOMIC MODELS

- **Thomson** : An atom considered to be positively charged sphere where e^- is embedded inside it.
- **Drawback** : Cannot explain stability of an atom.
- **Rutherford Model of an atoms :**

  Electron is revolving around the nucleus in circular path.

  $R_N = R_0(A)^{1/3}$, $R_0 = 1.33 \times 10^{-13}$ cm

  [A = mass number, R_N = Radius of nucleus]

SIZE OF NUCLEUS

- The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.
- Thus, diameter (size) of the atom is 1,00,000 times the diameter of the nucleus.

ELECTROMAGNETIC SPECTRUM

- RW →MW →IR →Visible →UV →X-rays →CR (Radiowaves →Microwaves →Infrared rays →Visible rays →Ultraviolet rays →X-rays →Cosmic rays)
- Wavelength decreases ⟶
- Frequency increases ⟶
- • $c = \nu\lambda$ • $\lambda = \frac{c}{\nu}$ • $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$

  • $T = \frac{1}{\nu}$ • $E = \frac{hc}{\lambda} = h\nu$, h = 6.626 × 10^{-34} Js

  • $E(ev) = \frac{12400}{\lambda(\text{Å})}$

  •Total amount of energy transmitted

  $E = nh\nu = \frac{nhc}{\lambda}$

BOHR'S ATOMIC MODEL

Theory based on quantum theory of radiation and the classical laws of physics

- $\frac{K(Ze)(e)}{r^2} = \frac{mv^2}{r}$
- $mvr = \frac{nh}{2\pi}$ or $mvr = n\hbar$
- Electron remains in stationary orbit where it does not radiate its energy.
- **Radius :** $r = 0.529 \times \frac{n^2}{Z} \text{Å}$
- **Velocity :** $v = 2.188 \times 10^6 \frac{Z}{n} ms^{-1}$
- Energy(KE + PE)

  =Total energy = $-13.6 \times \frac{Z^2}{n^2}$ eV/atom
- $TE = -\frac{KZe^2}{2r}$, $PE = \frac{-KZe^2}{r}$, $KE = \frac{KZe^2}{2r}$

  PE = –2KE, KE = –TE, PE = 2TE
- Revolutions per sec = $\frac{v}{2\pi r}$
- Time for one revolution = $\frac{2\pi r}{v}$
- Energy difference between n_1 and n_2 energy level

$$\Delta E = E_{n_2} - E_{n_1} = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \frac{eV}{atom} = IE \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where IE = ionization energy of single electron species.

- **Ionization energy** $= E_\infty - E_{G.S.} = 0 - E_{G.S.}$

  $E_{G.S.}$ = Energy of electron in ground state

HYDROGEN SPECTRUM

- **Rydberg's Equation** :

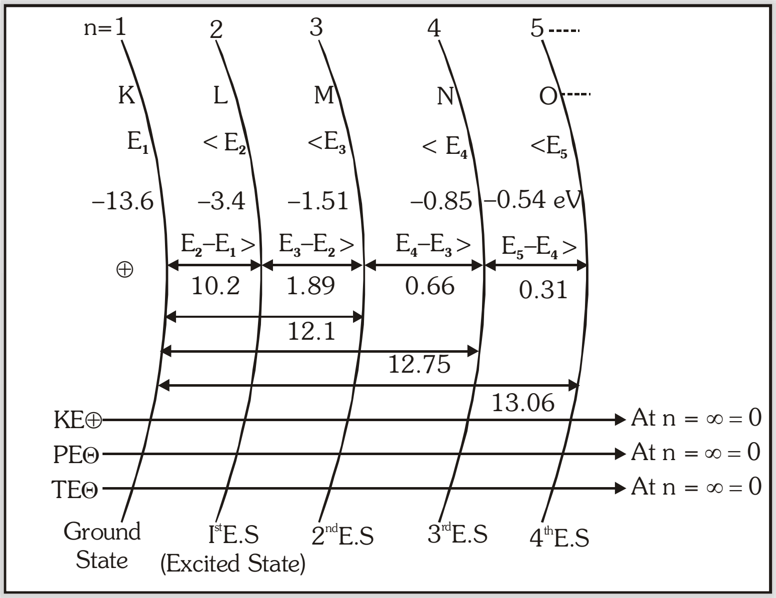
$$\frac{1}{\lambda} = \bar{v} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$$

$R_H \cong 109700 \text{ cm}^{-1}$ = Rydberg constant

- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_α line means n_2 =n+1; also known as line of longest λ, shortest ν, least E
- Similarly H_β line means $n_2 = n_1 + 2$
- When electrons de-excite from higher energy level (n) to ground state in atomic sample, then number of spectral lines observed in the spectrum $= \frac{n(n-1)}{2}$
- When electrons de-excite from higher energy level (n_2) to lower energy level (n_1) in atomic sample, then number of spectral line observed in the spectrum

$$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

- No. of spectral lines in a particular series = $n_2 - n_1$



DE-BROGLIE HYPOTHESIS

- All material particles posses wave character as well as particle character.
- $\lambda = \frac{h}{mv} = \frac{h}{p}$
- The circumference of the nth orbit is equal to n times of wavelength of electron i.e., $2\pi r_n = n\lambda$

  Number of waves = n = principal quantum number
- Wavelength of electron $(\lambda) \cong \sqrt{\frac{150}{V(\text{volts})}}$ Å
- $\lambda = \frac{h}{\sqrt{2mKE}}$

HEISENBERG UNCERTAINTY

- According to this principle, " it is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy"

  If one of them is measured with greater accuracy, the other becomes less accurate.
- $\Delta x.\Delta p \geq \frac{h}{4\pi}$ or $(\Delta x)(\Delta v) \geq \frac{h}{4\pi m}$

  where Δx =Uncertainty in position

  Δp = Uncertainty in momentum

  Δv = Uncertainty in velocity

  m = mass of microscopic particle
- Heisenberg replaced the concept of orbit by that of orbital.

QUANTUM NUMBER

- **Principal Quantum number (By Bohr)**
  - ⇒ Indicates = Size and energy of the orbit, distance of e^- from nucleus
  - ⇒ Values n = 1, 2, 3, 4, 5.....................
  - ⇒ Angular momentum = $n \times \frac{h}{2\pi}$
  - ⇒ Total number of e^-s in an orbit = $2n^2$
  - ⇒ Total number of orbitals in an orbit = n^2
  - ⇒ Total number of subshell in an orbit = n
- **Azimuthal/Secondary/Subsidiary/Angular momentum quantum number (ℓ)**
  - ⇒ Given by = Sommerfeld
  - ⇒ Indicates = Sub shells/sub orbit/sub level
  - ⇒ Values ⇒ 0, 1..............(n–1)
  - ⇒ Indicates shape of orbital/Sub shell

Value of n	Values of ℓ [Shape]	Initial from word
eg.	ℓ = 0 (s) [Spherical]	Sharp
If n = 4	ℓ=1 [p] [Dumb bell]	Principal
	ℓ=2 [d] [Double dumb bell]	Diffused
	ℓ=3 [f] [Complex]	Fundamental

- ⇒ Total no. of e^-s in a suborbit = 2(2l + 1)
- ⇒ Total no. of orbitals in a suborbit = (2l + 1)
- ⇒ Orbital angular momentum

$$= \sqrt{\ell(\ell+1)}\frac{h}{2\pi} = \sqrt{\ell(\ell+1)}\hbar$$

h = Planck's constant

- ⇒ For H & H like species all the subshells of a shell have same energy.

  i.e. 2s = 2p 3s = 3p = 3d
- **Magnetic Quantum number (m)**
  - ⇒ Given by Linde
  - ⇒ Indicates orientation of orbitals i.e. direction of electron density.
  - ⇒ Value of m = –ℓ ....0.........+ℓ
  - ⇒ Maximum no of e's in an orbital = 2 (with opposite spin)

    m for p sub shell = p_x p_y p_z

    –1 +1 0

m for d sub shell =

d_{xy} d_{yz} d_{z^2} d_{xz} $d_{x^2-y^2}$

–2 –1 0 +1 +2

- **Spin Quantum Number (m_s or s)**

  Given by Uhlenback & Goudsmit

  Values of s = ±½

  Total value of spin in an atom = ±½ ×number of unpaired electrons

  Spin Angular momentum = $\sqrt{s(s+1)}\frac{h}{2\pi}$

RULES FOR FILLING OF ORBITALS

- **Aufbau principle :** The electrons are filled up in increasing order of the energy in subshells. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$
- **(n + ℓ) rule :** The subshell with lowest (n + ℓ) value is filled up first, but when two or more subshells have same (n + ℓ) value then the subshell with lowest value of n is filled up first.
- **Pauli exclusion principle :** Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.
- **Hund's rule of maximum multiplicity :** Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.

SURFACE CHEMISTRY

CLASSIFICATION BASED ON INTERACTION OF PHASES :-

LYOPHILIC AND LYOPHOBIC SOLS

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols (solvent - liking).

For example - dispersion of gelatin, starch, gum and proteins in water.

Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called Lyophobic colloidal (Solvent hating) solutions.

COMPARISION OF LYOPHOBIC AND LYOPHILIC SOLS

Property	Lyophilic sol (Emulsoid)	Lyophobic sol (suspensoid)
1. Preparation	Can be easily prepared by shaking or warming the substance with solvent	Can not be prepared easily, special methods are required
2. Stability	are more stable	are less stable
3. Reversibility	are reversible	are irreversible
4. viscosity	viscosity is much higher than that of solvent	viscosity is nearly same as that of the solvent
5. Surface tension	Surface tension is usually low	Surface tension is almost same as that of solvent
6. Hydration or solvation	These are highly solvated as the particles have great affinity for solvent	These are less solvated as the particles have less affinity for the solvent
7. Charge	The particles have little charge or no charge at all	The particles carry a characteristic charge- either positive or negative
8. Visibility	Particles can not be seen under microscope	Particles can be seen under microscope
9. Coagulation or precipitation	Precipitated by high concentration of electrolytes	Precipitated by low concentration of electrolytes
10. Tyndall effect	Less Scattering	More Scattering
11. Migration in electric field	may or may not migrate as they may or may not carry charge.	migrate towards anode or cathode as these particles carrry charge.
12. General Ex.	**Mostly of organic nature** Ex. Gelatin, Starch, Gum, Albumin & Cellulose Solution	**Mostly of Inorganic nature** Ex. Transiton metal salt in water like Gold, As etc.

PEPTIZATION

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptization. The electrolyte used is called a **Peptizing agent.**

Hardy Schulze Rule - This rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion.

The higher the valency of the flocculating ion, the greater is its precipitating power. Thus for the precipitation of As_2S_3 sol (–ve) the precipitating power of Al^{3+}, Ba^{2+}, and Na^+ ions is in the order

$Al^{3+} > Ba^{2+} > Na^+$

Similarly for precipitating $Fe(OH)_3$ sol (positive) the precipitating power of $[Fe(CN)_6]^{-3}$, SO_4^{2-} and Cl^- ions is in the order

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

The minimum concentration of an electrolyte in milli moles required to cause precipitation of 1 litre sol in 2 hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

$$\text{Flocculation value } \alpha \frac{1}{\text{Flocculation power}}$$

GOLD NUMBER

The number of **milligrams** of a hydrophilic colloid that will just prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 10% NaCl solution is known as **Gold number** of that protector (Lyophilic colloid).

The precipitation of the gold sol is indicated by a colour change from red to blue when the particle size just increases.

The **smaller the gold number** of a protective Lyophilic colloid, **greater is its protection power.**

Note : Gelatin and startch have the maximum & minimum protective powers.

$$\text{Protection Capacity} \propto \frac{1}{\text{Protection Number (Gold number)}}$$

TYPES OF COLLOIDS ACCORDING TO THEIR SIZE

Multi Molecular	**Macro Molecular**	**Associated colloids**
Formation by aggregation of a large number of atoms or smaller molecules of substance.	Formation by aggregation of big size molecules. These are polymers with high molecular mass.	These are the substances which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal solutions. These associated particles are also called micelles.
Ex. → **Gold Sol (Au)** **Sulphur sol (S_8)**	Ex. → **Starch, Cellulose, Protein etc.**	Ex. → **Soap & Detergent**

COMPARISON OF PHYSI-SORPTION AND CHEMI-SORPTION

	Physical Adsorption	**Chemical Adsorption (Activated ad.)**
1.	It is caused by intermolecular vander waal's forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	Heat of adsorption is low. (– 20 to –40 KJ/mol) (Enthalpy)	Heat of adsorption is high. (–80 to –240 KJ/mol) (Enthalpy)
5.	No appreciable activation is energy involved.	High activation energy involved.
6.	It forms multimolecular layers on adsorbent surface.	It forms unimolecular layer under high pressure.

Critical temperature increases
Ease of liquification increases
Extent of adsorption increases
(true for physisorption)

GENERAL CHARACTERISTICS OF CATALYSTS

(i) A catalyst remains unchanged in mass and chemical composition but can change their physical state.

(ii) Only a very small amount of catalyst is sufficient to catalyse a reaction.

(iii) A catalyst does not initiate a reaction.

(iv) Solid catalyst is more efficient when used in finely divided form.

(v) Generally catalyst does not change the nature of products.

(vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time.

(vii) The catalyst are generally specific in nature.

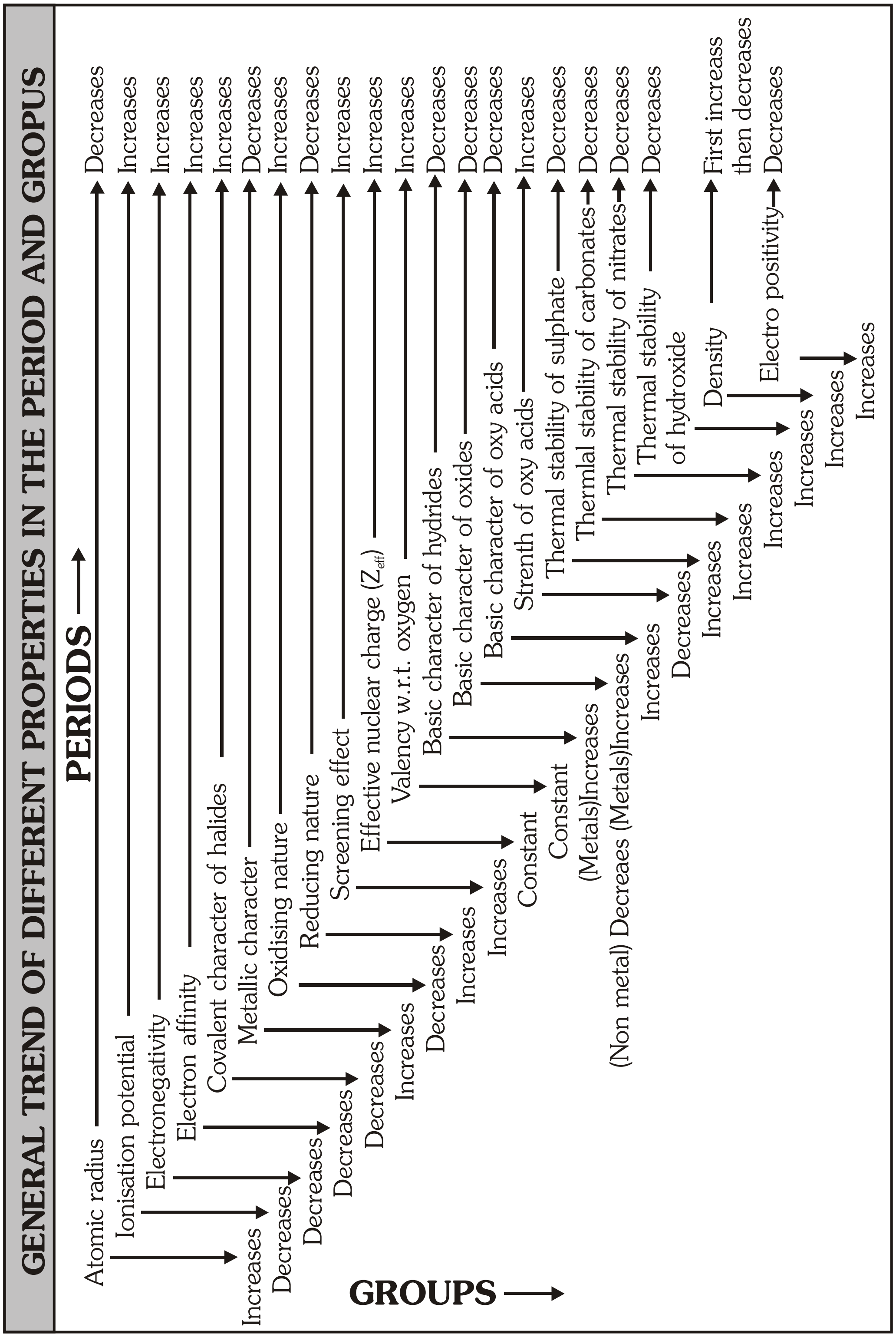
(viii) Changes rate constant of reaction.

(ix) Does not change free energy of reaction.

(x) Participates in mechanism of reaction.

IMPORTANT NOTES

Some Important Increasing Order



GENERAL TREND OF DIFFERENT PROPERTIES IN THE PERIOD AND GROPUS

Atomic radius	Decreases	Increases
Ionisation potential	Increases	Decreases
Electronegativity	Increases	Decreases
Electron affinity	Increases	Decreases
Covalent character of halides	Increases	Decreases
Metallic character	Decreases	Increases
Oxidising nature	Increases	Decreases
Reducing nature	Decreases	Increases
Screening effect	Increases	Increases
Effective nuclear charge (Z_{eff})	Increases	Constant
Valency w.r.t. oxygen	Increases	Constant
Basic character of hydrides	Decreases	(Metals)Increases
Basic character of oxides	Decreases	(Non metal) Decreaes (Metals)Increases
Basic character of oxy acids	Decreases	Increases
Strenth of oxy acids	Increases	Decreases
Thermal stability of sulphate	Decreases	Increases
Thermlal stability of carbonates	Decreases	Increases
Thermal stability of nitrates	Decreases	Increases
Thermal stability of hydroxide	Decreases	Increases
Density	First increass then decreases	Increases
Electro positivity	Decreases	Increases

CHAPTER
1

PERIODIC PROPERTIES

Periodicity :

Repetition of properties after regular interval is known as periodicity and these properties are known as periodic properties.

1. Effective Atomic Number
2. Atomic Radius
3. Ionisation Potential
4. Electron Affinity
5. Electro Negativity

ATOMIC RADIUS

Distance between centre of nucleus to outermost electron.

Accurate value of atomic radius cannot be measured therefore operational definations are used.

(i) Covalent radius
(ii) Metallic radius
(iii) Vander Waal's radius

$r_{cov} < r_{metallic} < r_{vw}$

Vander wall radius mainly used for noble gases.

Factors Affecting atomic radius :

(1) AR $\propto$ Number of shells

(2) AR $\propto \frac{1}{Z_{eff}}$

Periodic trends :

(1) Generally increases on moving down the group

(2) Generally decrease when we are moving left to right in the period.

Note :

Atomic radius of Al > Ga : Due to poor sheilding of 3d subshell electron

Atomic radius of 4d ≈ 5d series element due to lanthanide constraction

Lanthanide Contraction - decrease in atomic/ionic radius with increase in atomic number of lanthanide.

Actinide Contraction - decrease in atomic/ionic radius with increase in atomic number of actinide.

Ionic Radius:

$$A^+ \longleftarrow A \longrightarrow A^-$$

Z_{eff}	$A^+ > A > A^-$
Ionic radius	$A^+ < A \;\; < A^-$

Factors affecting ionic radius

(+) charge ↑	ionic radius ↓
(–) charge ↑	ionic radius ↑
Z_{eff} ↑	ionic radius ↓
n ↑	ionic radius ↑

⇒ In isoelectronic species (+) charge ↑ Ionic radius ↓
(–) charge ↑ Ionic radius ↑

eg. : $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{+2} > Al^{+3}$
$K^+ > Li^+ > Mg^{+2} > Al^{+3}$

IONIZATION ENERGY

Energy required to remove to loosely bonded e^- from isolated gaseous atom.

Successive I.E. :

$I.E_1$, $I.E_2$, ... combinedly termed as successive I.E.

$$A_{(g)} \xrightarrow{IE_1} A^{+}_{(g)} \xrightarrow{IE_2} A^{+2}_{(g)} \xrightarrow{IE_3} A^{+3}_{(g)} \xrightarrow{IE_3}$$

$IE_1 < IE_2 < IE_3$ .....

Factors affecting :

(1) IE $\propto Z_{eff}$ (2) IE $\propto \frac{1}{\text{size}}$

(3) IE $\propto$(+)charge, (4) IE $\propto \frac{1}{(-)\text{charge}}$

(5) half filled and full filled configration (affected upto 4th period)

(6) nature of subshell (affected upto 4th period)

Periodic trend (s & p-block) :

(1) Generally decrease on moving down the group

(2) Generally increase when we are moving left to right in the period.

Note : upto 4th period (Ionization Energy)
$ns^1 < np^1 < ns^2 < np^2 < np^4 < np^3 < np^5 < np^6$

Note : after 4th period (Ionization Energy)
$ns^1 < ns^2 < np^1 < np^2 < np^3 < np^4 < np^5 < np^6$

Al < Ga (Poor sheilding of 3d subshell e^-)

$$\left.\begin{array}{l} Tl > In \\ Pb > Sn \end{array}\right\} \text{due to lanthanide contraction}$$

Periodic trend (d-block) :

(1) Generally increases on moving down the group

(2) Generally increase when moving left to right in the period.

Sc > Y > La, Ag < Cu < Au, Cd < Zn < Hg

Application of ionization energy :

IE↑	Metallic Character ↓
IE↑	Electropositive Character ↓
IE↑	Reducing Property ↓

Note : Number of valence e^- = highest jump in successive IE

eg. : $IE_1 < IE_2 < IE_3 <<< IE_4 < IE_5$

Highest jump between IE_3 & IE_4 therefore V e^- is 3

Electron affinity & Electron gain enthalpy :

Electron affinity	Electron gain enthalpy
$A_{(g)} \xrightarrow{+e^-} A^-_{(g)}$	$A_{(g)} + e^- \longrightarrow A^-$
amount of energy released when an e^- is added to isolated gaseous atom.	Change in enthalpy when an e^- is added to isolated gaseous atom. $\Delta H_{eg} = H_P - H_R$

Successive electron affinity :

$$A_{(g)} \xrightarrow{EA_1} A^-_{(g)} \xrightarrow{EA_2} A^{2-}_{(g)} \xrightarrow{EA_3} A^{3-}_{(g)}$$

EA_1 is generally exothermic except N, Be, Mg and Noble gas

EA_2, EA_3 ..... always endothermic

Factors affecting :

(1) $EA \propto Z_{eff}$

(2) $EA \propto \frac{1}{\text{size}}$

(3) Nature of subshell

(4) half and full filled

Periodic trend :

(1) Generally decreases on moving down the group

(2) Generally increase when moving left to right in the period.

Note : IIIrd period element having greater EA than IInd period element except alkali metal.

O < Te < Se < S , I < Br < F < Cl

Note : $|IE_A| = |EA_{A^+}|$ and $|EA_A| = |IE_{A^-}|$

Electronegativity :

Tendency to attract shared pair of e^- towards itself in covalent bond.

Factors affecting :

(1) $EN \propto Z_{eff}$

(2) $EN \propto \frac{1}{\text{size}}$

(3) $EN \propto \frac{1}{(-)\text{charge}}$

(4) $EN \propto (+)$charge,

(5) $EN \propto$ % s-characters of hybrid orbital

Periodic trend :

(1) Generally decreases on moving down the group

(2) Generally increase when moving left to right in the period.

Application of electronegative

(1) Polarity of bond

$\Delta EN = 0$ non-polar bond

$\Delta EN \neq 0$ polar bond

(2) Bond parameter

$\Delta EN \uparrow$ Ionic character $\uparrow$

$\Delta EN \uparrow$ bond length $\downarrow$

$\Delta EN \uparrow$ bond strength $\uparrow$

(3) Nature of oxide & oxyacid :

E.N. of central atom increase acidic character of oxide and oxyacid increases.

Some Important Increasing Order

1. Abundance of Elements

(i)	Elements on earth crust	- Fe, Al, Si, O
(ii)	Metals on earth crust	- Ca, Fe, Al
(iii)	Non-metals	- Si, O
	In atmosphere	- O, N
	In universe	- He, Si, H

2. Atomic / Ionic Size

(i) Mg^{2+}, Na^+, F^-, O^{2-}, N^{3-}

(Hint : Isoelectronic series)

(ii) Ca^{2+}, Ar, Cl^-, S^{2-}

(iii) O, C, S, Se

(iv) B, Be, Li, Na

(v) F, O, F^-, O^{2-}

3. Ionization Energy

(i) Na, Al, Mg, Si

(ii) Li, B, Be, C, O, N, F, Ne, He (Ist I.P.)

(iii) Be, C, B, N, F, O, Ne, He, Li (IInd I.P.)

4. Electron Affinity

(i) I, Br, F, Cl

(ii) Cu, Ag, Au (EA, of Au is very high = 222 kJ mol^{-1})

(iii) O, S, F, Cl

(iv) N, P, O, S

5. Electonegativity

(i) As, P, S, Cl

(ii) I, Br, Cl, F

(iii) C, N, O, F

6. Hydration of Ions/Hydration Energry

(i) Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}, Be^{+2}

(ii) Cs^+, Rb^+, K^+, Na^+, Li^+

(iii) Na^+, Mg^{+2}, Al^{+3}

7. Ionic Radii in water

(i) Cs^+, Rb^+, K^+, Na^+, Li^+

(ii) Li^+, Be^{+2}

(iii) Na^+, Mg^{+2}, Al^{+3}

8. Molar Conductivity in Water

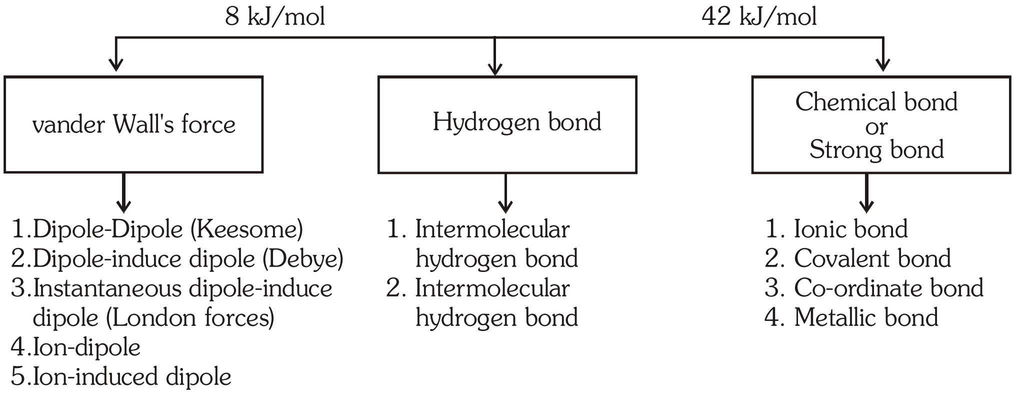
Li^+, Na^+, K^+, Rb^+, Cs^+

IMPORTANT NOTES

CHEMICAL BONDING

CHEMICAL BOND :

1. The force of attraction which hold togather atom, molecule or ions with in chemical species.
2. It is always exothermic process.



vander Wall's force
1. Dipole-Dipole (Keesome)
2. Dipole-induce dipole (Debye)
3. Instantaneous dipole-induce dipole (London forces)
4. Ion-dipole
5. Ion-induced dipole

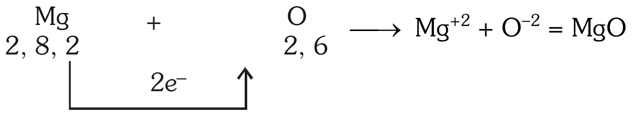
Hydrogen bond
1. Intermolecular hydrogen bond
2. Intermolecular hydrogen bond

Chemical bond or Strong bond
1. Ionic bond
2. Covalent bond
3. Co-ordinate bond
4. Metallic bond

❑ ELECTROVALENT OR IONIC BOND

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electons from one atom to another is called as Ionic or electrovalent bond.

Ionic bonds are non-directional.



$$\underset{2,\,8,\,2}{Mg} + \underset{2,\,6}{O} \longrightarrow Mg^{+2} + O^{-2} = MgO$$

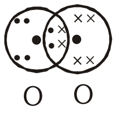
electrovalency of Mg = 2

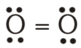
electrovalency of O = 2

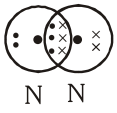
❑ COVALENT BOND

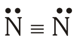
A covalent bond is formed by the mutual sharing of electrons between two atoms to complete their octet.(Except H which completes its duplet)

H_2 molecule





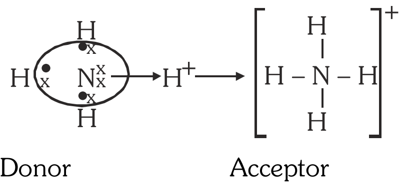




❑ COORDINATE BOND (DATIVE BOND)

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.

(i) NH_4^+ (ammonium ion)



(ii) $F_3B + :NH_3 \longrightarrow (F_3B \leftarrow NH_3)$

EXCEPTION OF OCTET RULE

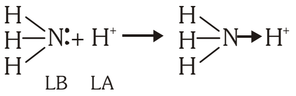
(a) electron deficient	**(b)** electron rich	**(c)** odd electron species
Central atom:	Central atom:	Central atom :
No. of electron < 8	No. of electron > 8	has odd electron
BeH_2	PCl_5 , IF_7	NO, NO_2, ClO_2
BF_3, BCl_3, BBr_3, BI_3	SF_6, XeF_2	ClO_3
$AlCl_3$, $AlBr_3$, AlI_3		

CO-ORDINATE BOND (DATIVE BOND)

In this type of bond, shared pair of electron donates by one species but shared by both

- For this type of sharing
- One species - must have lone pair - act as donar known as Lewis base - acquire +ve charge.
- Another species - must have vacant orbital act as acceptor known as Lewis acid - acquire -ve charge.

Eg.



Similarly

$H_2O + H^+ \longrightarrow H_3O^+$

$BF_3 + F^- \longrightarrow BF_4^-$

$NH_3 + BF_3 \longrightarrow F_3B.NH_3$

- Donor atom follow octet rule

MODERN APPROACH OF COVALENT BOND

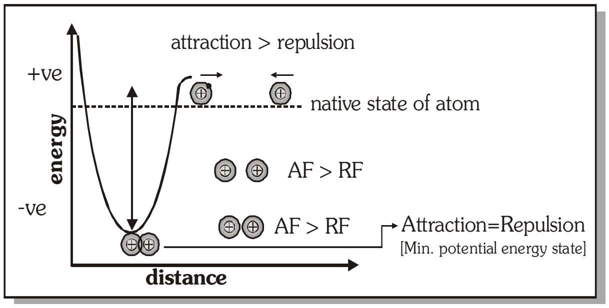
Consider wave mechanical model of atom means electron has dual nature; wave nature as well as particle nature considered by these theories, there are two theories in this approach.

1. Valence Bond Theory **2. Molecular Orbital Theory**

VALENCE BOND THEORY

Proposed by Heitler & London as per VBT bonding takes place for attaining stability.

$$\text{Stability} \propto \frac{1}{\text{Potential energy}}$$



- Bond formation is an exothermic process.
- During this process some extent of electron cloud merge into each other; this part is known as overlapped region & this process is known as overlapping.

Atom ⟨ Nucleus
Shell - subshell - orbital - electron - cloud

- Only those orbitals of valence shell can exhibit overlapping which has
  - Unpaired electron

For example
H—Cl bond form by overlapping of 1s - 3p orbitals.
$H \rightarrow 1s^1$
$Cl \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5$

  - Opposite spin

- **Strength of Covalent Bond**
  Strength of covalent bond ∝ extent of overlapping.

  1. NATURE OF ORBITALS
  (a) No. of shell : lower the number of shell higher overlapping.

$$\text{Bond Strength} \propto \frac{1}{\text{No. of shell}} / \text{size of orbitals}$$

$$\boxed{1\text{-}1 > 1\text{-}2 > 2\text{-}2 > 2\text{-}3}$$

- **Exception :** $Cl_2 > Br_2 > F_2 > I_2$ due to
  O—O < S—S lp-lp
  N—N < P—P repulsion

(b) Type of Sub-shell

Valence shell contain subshell s & p

s-non-directional
p-directional

Directional orbital has higher extent of overlapping

Possible combination & strength of overlapping

s-s < s-p < p-p

** This factor is applicable when number of shell is same otherwise shell factor prominent

2s - 2s < 2s-2p < 2p-2p sub-shell factor

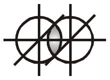
1s - 1s > 1s-2s > 1s-3s shell factor

2. PATTERN OF OVERLAPPING

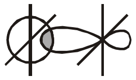
(a) Axial overlapping :

Along the internuclear axis; form sigma (σ) bond, strong bond.

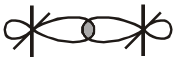
s-s



s-p



p-p

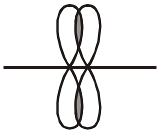


(b) Co-lateral overlapping

Side wise overlapping has less extent of overlapping form π- bond

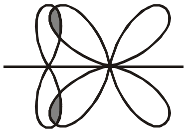
Weak bond

p-p overlapping



Internuclear axis
$p\pi$ - $p\pi$
bond

p-d overlapping



$p\pi$ - $d\pi$
bond

- In case of multiple bond between two atom one bond is sigma and rest are pi-bonds.
- VBT was not able to define geometry of molecule therefore a new concept came into existence known as hybridisation.

HYBRIDISATION

- Intermixing of atomic orbitals and formation of new orbital, these orbitals are known as hybrid orbital and this concept is known as hybridisation.
- It is hypothetical concept.
- Only those orbitals can participate in hybridisation which has slight difference in energy.
- No. of hybrid orbitals : No. of atomic orbitals participate in intermixing
- Hybrid orbitals oriented at maximum possible distance three dimensionally.
- On the basis of type of orbitals participating in hybridisation, we can divide hybridisation into following categories.

S.No.	Type of orbital	No. of hybrid orbital	3D orientation	Example
1.	one s + one p	2; sp	Linear	BeH_2, $BeCl_2$
2.	one s + two p	3; sp^2	Triangular	BCl_3, BF_3
3.	one s + three p	4; sp^3	Tetrahedral	CH_4, CCl_4
4.	one s + three p + one d	5; sp^3d	Triangular bipyramidal	PCl_5
5.	one s + three p + two d	6; sp^3d^2	Octahedral	SF_6
6.	one s + three p + three d	7; sp^3d^3	Pentagonal bipyramidal	IF_7

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

○ Given by Nyholm & Gillespie to define shape of molecule.

○ Shape of molecule define on the basis of electron pairs orientation present on central atom.

○ Electron pairs present on central atom repel each other therefore these electron pair occupy such position on central atom; where they experience minimum repulsion at maximum possible distance three dimensionally.

○ **Order of replusion :** $\boxed{\text{lp-lp > lp-bp > bp-bp}}$ $\boxed{\text{mb-mb > mb-sb > sb-sb}}$ (mb = multiple bond; sb = single bond)

TYPE OF HYBRIDISATION & POSSIBLE STRUCTURE

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridisation	2	-	Linear	BeF_2, CO_2, CS_2,$BeCl_2$
2. (a) sp^2-hybridisation	3	-	Trigonal planar	BF_3, $AlCl_3$, BeF_3^-
(b) sp^2-hybridisation	2	1	V-shape,Angular	NO_2^-, SO_2, O_3
3. (a) sp^3-hybridisation	4	0	Tetrahedral	CH_4, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-1}, SO_4^{-2}, $AlCl_4^-$
(b) sp^3-hybridisation	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3O^+, PCl_3, XeO_3,$N(CH_3)_3$, CH_3^-
(c) sp^3-hybridisation	2	2	V-shape	H_2O, NH_2^-
			Angular	OF_2, Cl_2O, SF_2, I_3^+
4. (a)sp^3d-hybridisation	5	-	Trigonal bipyramidal	PCl_5, SOF_4, AsF_5
(b) sp^3d-hybridisation	4	1	See-Saw, folded square distorted tetrahedral	SF_4, PF_4^-, AsF_4^- SbF_4^-, XeO_2F_2
(c) sp^3d-hybridisation	3	2	almost T-shape	ClF_3, ICl_3
(d) sp^3d-hybridisation	2	3	Linear	I_3^-, Br_3^-, ICl_2^-, ClF_2^-, XeF_2
5. (a) sp^3d^2-hybridisation	6	-	Square bipyramidal/octahedral	PCl_6^-, SF_6
(b) sp^3d^2-hybridisation	5	1	Square pyramidal/distorted octahedral	$XeOF_4$, ClF_5, SF_5^-, XeF_5^+
(c) sp^3d^2-hybridisation	4	2	Square planar	XeF_4
6. (a) sp^3d^3-hybridisation	7	-	Pentagonal bipyramidal	IF_7
(b) sp^3d^3-hybridisation	6	1	distorted octahedral /capped octahedral	XeF_6
			Pentagonal planar	
(c) sp^3d^3-hybridisation	5	2		XeF_5^-

DIPOLE MOMENT

Measurement of Polarity in a molecule

$\boxed{\vec{\mu} = q \times d}$ debye = esu-cm
1D = 10^{-18} esu.cm

(A) Identification of polar or Non-polar molecule.

Molecule : Symmetrical distribution of electron cloud- Non-polar.
Molecule : Unsymmetrical distribution of electron cloud- Polar.

Diatomic Molecule

(a) Homoatomic $\Delta EN = 0 \rightarrow \vec{\mu} = 0 \rightarrow$ Non-polar
H_2, F_2, Cl_2, N_2 etc.

(b) Heteroatomic $\Delta EN \neq 0 \rightarrow \vec{\mu}_{net} = 0 \rightarrow$ polar
HF > HCl > HBr > HI

Polyatomic molecule :

$\mu_R \rightarrow$ Vector sum of bond moment

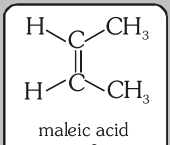
$\mu_R \rightarrow \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

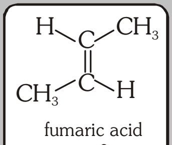
Important Order

$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$
$NH_3 > SbH_3 > AsH_3 > PH_3$
$H_2O > H_2S$
$CH_3Cl > CH_3F > CH_3Br > CH_3I$
$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

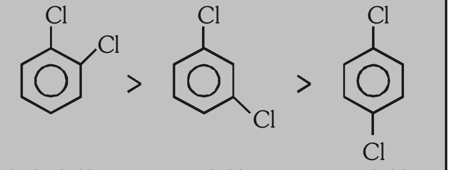
Applications

Predict shape and polarity of molecule
Symmetrical geometry → $\mu=0$ → non-polar
Unsymmetrical geometry → $\mu \neq 0$ → polar
Distinguish between cis & trans form


maleic acid
$\mu \neq 0$


fumaric acid
$\mu=0$

Dipole moment in Aromatic Compounds



Orthodichloro benzene **metadichloro benzene** **paradichloro benzene**

$$\mu \propto \frac{1}{\text{bond angle}}$$

HYDROGEN BONDING

⇒ It is dipole-dipole type of interaction.

⇒ Electrostatic force of attraction between hydrogen (covalently bond with F/N/O) & highly electronegative atom.

⇒ Hydrogen bond
- → Intermolecular hydrogen bond → between the molecules
- → Interamolecular hydrogen bond → within the molecules

* Intromolecular H-bonding takes places mainly in ortho derivatives of benzene.

Note :

1. Boric acid solid at room temperature (with 2D sheet structure) due to intermolecular hydrogen bonding.
2. In vapour state or in non-polar solvent CH_3COOH as dimer due to intermolecular hydrogen bonding.
3. In vapour phase HF exist as dimer and $(HF)_6$, due to intermolecular hydrogen bonding.
4. Due to intermolecular hydrogen bonding ice has 3D network structure with tetrahedral unit and having open cage structure.
   The density of ice is less than water.
5. DNA having hydrogen bonds.
6. In hydrated chloral intramolecular hydrogen bond is present.

Strength

Intermolecular H-bond > Intramolecular H-bond

● Intramolecular H-bonding takes place in ortho derivatives only.

Applications of H-bonding

Physical State (densile nature)	∝	H-bond
Melting Point (mp)	∝	H-bond
Boiling Point (bp)	∝	H-bond
Viscosity	∝	H-bond
Surface Tension	∝	H-bond
Volatility	∝	1/H-bond
Vapour Pressure	∝	1/H-bond

☐ MOLECULAR ORBITAL THEORY (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

(i) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(iii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**

(iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

Formation of Molecular Orbitals : Linear Combination of Atomic Orbitals(LCAO)

Case I : When two waves are in same phase (constructive interference) the wave adds up and amplitude of new wave is the sum of wave functions of individual atomic orbitals.

$\psi_{MO} = \psi_A + \psi_B$ (Bonding M.O.)

Case II : When two waves are out of phase, the waves are substracted from each other so that the amplitude of new wave is :

$\psi^*_{MO} = \psi_A - \psi_B$ (Antibonding M.O.)

Condition for combination atomic orbitals :

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent.

Energy level diagram from MOs :

Molecular orbital energy diagram for up to N_2 (molecule having ≤ 14 electrons)

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

Molecular orbital energy diagram for O_2 and F_2 (molecule having > 14 electrons)

$\sigma_{1s} < \sigma^*_{1s}\ ; < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

$\sigma *, \pi *$ = antibonding molecular orbital

σ, π = bonding molecular orbital

Rules of Filling up of Molecular Orbital with Electrons :

(1) The molecular orbital with lower energy will be filled first. (Aufbau Principle)

(2) The molecular orbital can accommodate maximum only two electrons. (Pauli's exclusion principle)

(3) If the two MOs have same energy then molecular orbital will first get singly filled and after that pairing will start. (Hunds Rule)

❑ BOND ORDER

Bond order (B.O.) is defined as follows Bond order (B.O.) = $\frac{1}{2}$ $(N_b - N_a)$

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative value (i.e., $N_b < N_a$) (i.e., $N_b = N_a$) bond order means an unstable molecule. If bond order zero then molecular does not exist.

❑ NATURE OF THE BOND

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

❑ BOND-LENGTH

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

❑ MAGNETIC NATURE

If one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule. Otherwise diamagnetic (eg : $N_{2)}$

Fractional bond order it will be always paramagnetic.

Sr. No.	**No. of electrons in molecules**	N_b	N_a	**B.O.**	**Paramagnetic / diamagnetic**
1	1	1	0	½	paramagnetic
2	2	2	0	1	diamagnetic
3	3	2	1	0.5	paramagnetic
4	4	2	2	0	——
5	5	3	2	½	paramagnetic
6	6	4	2	1	diamagnetic
7	7	4	3	½	paramagnetic
8	8	4	4	0	——
9	9	5	4	½	paramagnetic
10	10	6	4	1	paramagnetic
11	11	7	4	1.5	paramagnetic
12	12	8	4	2	both bond are π C_2 molecule
13	13	9	4	2.5	paramagnetic
14	14	10	4	3	diamagnetic
15	15	10	5	2.5	paramagnetic
16	16	10	6	2	paramagnetic
17	17	10	7	1.5	paramagnetic
18	18	10	8	1	diamagnetic
19	19	10	9	0.5	paramagnetic
20	20	10	10	0	——

In case of same bond order, stability depends upon No. of anti-bonding electrons

$$\text{Stability} \propto \frac{1}{\text{No. of anti-bonding } e^-}$$

BONDING PARAMETER

1. Bond length : Internuclear distance

Factor affecting Bond length

(i) Atomic size : bond length $\propto$ size [No. of shell]

(ii) ΔEN, Bond length $\propto \frac{1}{\Delta EN}$

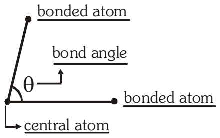
$$\boxed{d_{A-B} = r_A + r_B - 0.09 \times \Delta EN \text{ Å}}$$

(iii) Bond order : Bond length $\propto \frac{1}{\text{B.O.}}$

(iv) Hybridisation : Bond length $\propto \frac{1}{\text{\%age of s-character}}$

Bond Angle :

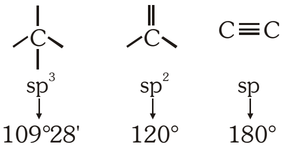
Angle between two adjacent bond is known as bond angle.



FACTORS AFFECTING BOND ANGLE

(i) Hybridisation

Bond angle $\propto$ %age of s-character



(ii) No. of lp/bp

[when hybridisation is same]

Bond angle $\propto \frac{1}{lp}$ Eg. : $CH_4 > \ddot{N}H_3 > H_2\ddot{O}:$

(iii) Type of Central atom: Applicable when :

* hybridisation same * No. of lp/bp same

Bond angle $\propto$ EN of central atom

Eg. $NH_3 > PH_3 > AsH_3 > SbH_3$

(iv) Type of bonded atom : Applicable when

* hybridisation - same

* No. of lp/bp - same

* Central atom - same

Bond angle $\propto$ size of bonded species

Eg. $OF_2 < OCl_2 < OBr_2 < OI_2$

Note :

Regular geometry / same hybridisation/ bond angle same

$BF_3 = BCl_3 = BBr_3 = BI_3$

IONIC BOND

Extreme polar covalent bond is an Ionic Bond.
Therefore Ionic Bond ΔEN - Must be higher
one specie - lower EN - metal
one specie - higher EN - non metal
Eg. NaCl, KF
Formation of Ionic Bond takes place in following step.

$$\underset{\text{Solid}}{\text{Metal (M)}} \xrightarrow[\substack{\Delta H = +ve \\ \text{S.E.}}]{\text{Sublimation}} M(g) \xrightarrow[\substack{\Delta H = +ve \\ \text{I.E.}}]{\text{Ionisation}} M^{+}_{(g)} \; ; \; \underset{\substack{\text{Non metal} \\ \text{molecule}}}{X_2} \xrightarrow[\substack{\Delta H = +ve \\ \text{B.D.E.}}]{\text{Dissociation}} X \xrightarrow[\substack{\Delta H = -ve \\ \text{electron gain} \\ \text{enthalpy}}]{+e^{-}} X^{-}_{(g)}$$

$$M^{+}_{(g)} + X^{-}_{(g)} \xrightarrow[\substack{\Delta H = -ve \\ \text{lattice energy}}]{} MX_{(solid)}$$

$\Delta H_{formation} = \Delta H_{Sub} + \text{I.E.} + ½\,\text{BDE} + \Delta H_{eg} + U$
bond formation is always an exothermic process.
$\Delta H_{formation} = —ve$

ΔH_{Sub}: should be lower
I.E. : should be lower
B.D.E. : should be lower
ΔH_{eg} : should be higher
U : should be higher

PROPERTIES OF IONIC SALT

General Properties :

Hard, Solid, Brittle (strong electrostatic attraction between ions)
Non directional nature (ionic compound do not exhibit stereo isomerism)
Higher Melting Point / Boiling Point
Isomorphism : $MgSO_4.7H_2O$; $ZnSO_4.7H_2O$; $FeSO_4.7H_2O$

Specific Properties

- Conduction
  - Molten state
  - Aqueous medium
- Solubility
- Covalent Character

Molten state

Ionic conduction $\propto \frac{1}{\text{Ionic radius}}$

Eg. : LiCl, NaCl, KCl, RbCl, CsCl
Ionic Radius : $Li^{+} <<< Cs^{+}$
Conductance : CsCl < RbCl < KCl < NaCl < LiCl

Aqueous medium

Ionic mobility $\propto \frac{1}{\text{Ionic radius}}$

Hyd. radius : $Cs^{+} <<< Li^{+}(aq)$
conductance : LiCl < NaCl < KCl < RbCl < CsCl

COVALENT CHARACTER / FAJAN'S RULE

Ionic potential of cation(ϕ) $\propto \frac{\text{charge of cation}}{\text{size of cation}}$

Polarisibility of anion ∝ size of anion ∝charge of anion

Condition for polarisation
- Smaller cation
- Large anion
- Higher charge

FACTORS AFFECTING POLARISATION

(1) Poliarisation ∝ charge of cation or anion

Eg. (i) $\overset{+2}{Cr}O < \overset{+3}{Cr_2}O_3 < \overset{+6}{Cr}O_3$ Covalent character ↑

(ii) $\overset{+2}{SF_2} < \overset{+4}{SF_4} < \overset{+6}{SF_6}$ Covalent character ↑

(iii) $Li\overset{-1}{F} < Li_2\overset{-2}{O} < Li_3\overset{-3}{N}$ Covalent character ↑ (anion charge↑)

(2) Polarisation ∝ $\frac{\text{size of anion}}{\text{size of cation}}$

Eg.

(i) LiF < LiCl<LiBr<LiI — anion size ↑ polarisability↑ covalent character↑

(ii $BeCl_2>MgCl_2>CaCl_2>SrCl_2>BaCl_2$ — cation size ↑ polarisation↓ covalent character↓

SOLUBILITY

For s-block
same group cation depends upon
Lattice Energy and Hydration Energy

Increasing order of solubility

(i) $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $BeCO_3$
(ii) $Be(OH)_2$, $Sr(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
(iii) $BaSO_4$, $SrSO_4$, $CaSO_4$, $MgSO_4$, $BeSO_4$
(iv) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, $CsCO_3$
(v) LiOH, NaOH, KOH, RbOH, CsOH
(vi) LiF, LiCl, LiBr, LiI
(vii) LiF, NaF, KF, RbF, CsF
(viii) BaF_2, SrF_2, MgF_2, CaF_2, BeF_2
(ix) CaF_2, $CaCl_2$, $CaBr_2$, Cal_2

For all **solubility ∝ $\frac{1}{\text{cov. char.}}$**

solubility in org. solvent ∝cov. char∝$\frac{1}{\text{ionic char}}$

[CCl_4, benzene, ether, alcohol, acetone]

Eg. (i) $PbF_2 > PbCl_2 > PbCl_2 > PbI_2$
(Anion size↑, cov. char.↑, solubility ↓)
(ii) $Fe^{+2}(OH)_2 > Fe^{+3}(OH)_3$
(+) charge↑, PP↑, CC ↑, solubility ↓
(iii) $ZnCl_2 > CdCl_2 > HgCl_2$
Z_{eff}↑, PP↑, CC ↑, solubility ↓
(iv) $Na_2SO_4 > MgSO_4$
(+)charge↑, PP↑, CC ↑, solubility ↓
(v) $ZnCl_2 > CdCl_2 > HgCl_2$
Z_{eff}↑, PP↑, CC ↑, solubility ↓
(vi) NaCl > CuCl
PP↑, CC ↑, solubility ↓
(vii) AgF > AgCl > AgBr > AgI
Anionic Size↑, PP ↑, CC↑, solubility ↓

HYBRIDISATION OF FOLLOWING SPECIES IN SPECIFIED STATE

Species	Cationic part	Anionic part
PCl_5	PCl_4^+ (sp^3)	PCl_6^- (sp^3d^2)
PBr_5	PBr_4^+ (sp^3)	Br^-
XeF_6	XeF_5^+ (sp^3d^2)	F^-
N_2O_5	NO_2^+ (sp)	NO_3^- (sp^2)
I_2Cl_6 (liquid)	ICl_2^+ (sp^3)	ICl_4^- (sp^3d^2)
Cl_2O_6	ClO_2^+ (sp^2)	ClO_4^- (sp^3)
I_2 (molten state)	I_3^+ (sp^3)	I_3^- (sp^3d)

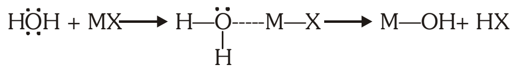
SILICATES

Silicates	Sharing of O-atom / Basic Tetrahedral unit	Contribution of O-atom/Basic Tetrahedral unit	General formula
Ortho	0	4	SiO_4^{4-}
Pyro	1	3.5	$Si_2O_7^{6-}$
Cyclic	2	3	$(SiO_3)_n^{2n-}$
Single chain (pyroxene)	2	3	$(SiO_3)_n^{2n-}$
Double chain (Amphibole)	(3, 2) avg. = 2.5	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(Si_4O_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(Si_2O_5)_n^{2n-}$
3D	4	2	$(SiO_2)_n$

HYDROLYSIS

Hydro - Water
lysis - break down

Break down of a molecule through water and formation of new product is known as hydrolysis.

- It is nucleophilic substitution reaction.
- 

$$H\ddot{O}H + MX \longrightarrow H-\ddot{O}\text{-----}M-X \longrightarrow M-OH + HX$$

molecule Intermediate Product

extent of hydrolysis ∝ covalent character.

$BeCl_2 + 2HOH \rightarrow Be(OH)_2 + 2HCl$

$BCl_3 + 3HOH \rightarrow B(OH)_3 + 3HCl$

$AlCl_3 + 3HOH \rightarrow Al(OH)_3 + 3HCl$

$SiCl_4 + 4HOH \rightarrow Si(OH)_4 + 4HCl$

$SF_6 + H_2O \rightarrow$ No hydrolysis
due to crowding

$CCl_4 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

$BF_3 + 3HOH \rightarrow B(OH)_3 + 3HF$

$3BF_3 + 3HF \rightarrow 3H^+ [BF_4]^-$

$4BF_3 + 3H_2O \rightarrow 3H[BF_4]$

(partially hydrolysis)

Similarly

$SiF_4 + 4HOH \rightarrow Si(OH)_4 + 4HF$

$2SiF_4 + 4HF \rightarrow H_2^+[SiF_6]^{2-}$

hydrolysis followed by
Lewis acid-base reaction.

15th Group Halides

$NF_3 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

$NCl_3 + HOH \longrightarrow NH_3 + 3HOCl$

$PCl_3 + HOH \longrightarrow H_3PO_3 + 3HCl$

$AsCl_3 + HOH \longrightarrow As(OH)_3 + 3HCl$

$SbCl_3 + HOH \longrightarrow SbOCl + 2HCl$
(partial hydrolysis)

$BiCl_3 + HOH \longrightarrow BiOCl + 2HCl$
(partial hydrolysis)

$PCl_5 + HOH \longrightarrow \underset{\text{partial}}{POCl_3} \xrightarrow{H_2O} \underset{\text{completely}}{H_3PO_4}$

Hydrolysis of higher covalent character containing salt

$Be_2C + 4HOH \longrightarrow 2Be(OH)_2 + CH_4$

$Mg_2C_3 + 4HOH \longrightarrow 2Mg(OH)_2 + C_3H_4$

$CaC_2 + 2HOH \longrightarrow Ca(OH)_2 + C_2H_2$

$Al_4C_3 + 12HOH \longrightarrow 4Al(OH)_3 + 3CH_4$

$Mg_3N_2 + 6HOH \longrightarrow 3Mg(OH)_2 + 2NH_3$

$AlN + 3HOH \longrightarrow Al(OH)_3 + NH_3$

$Ca_3P_2 + 6HOH \longrightarrow 3Ca(OH)_2 + 2PH_3$

$LiH + HOH \longrightarrow LiOH + H_2$

$CaH_2 + 2HOH \longrightarrow Ca(OH)_2 + H_2$

Hydrolysis of Interhalogen Compounds

$AX + HOH \longrightarrow HX + HOA$

$AX_3 + HOH \longrightarrow 3HX + HAO_2$

$AX_5 + HOH \longrightarrow 5HX\ \ HAO_3$

$AX_7 + HOH \longrightarrow 7HX + HAO_4$

HX Hydrohalic acid
HOA, HAO_2, HAO_3 HAO_4
oxyacid of halogen

Some specific hydrolysis

$XeF_2 \xrightarrow{HOH} Xe + 2HF + \frac{1}{2}O_2$

$6XeF_4 \xrightarrow{HOH} 4Xe + 2XeO_3 + 24HF + 3O_2$

$XeF_6 \xrightarrow{HOH} \underset{\text{partial}}{2HF + XeOF_4} \xrightarrow{HOH} \underset{\text{partial}}{2HF + XeO_2F_2} \xrightarrow{HOH} \underset{\text{complete}}{2HF + XeO_3}$

Back bonding :

It is type of π-interaction between lone pair & vacant orbital of adjacent atom in molecule.

Condition :

(i) One atoms must have lone pair and another atoms must have vacant orbital.

Type of back bond :

(i) (pπ – pπ) type of back bond
eg. BF_3, BCl_3, CF_2, CCl_2

(ii) (pπ – dπ) type of back bond
eg. CCl_3^-, $O(SiH_3)$, $N(SiH_3)_2$, SiH_5O^-, etc.

Application of back bonding :

Lewis acid character :

* $BF_3 < BCl_3 < BBr_3 < BI_3$
$BeF_2 < BeCl_2 < BeBr_2 < BeI_2$
$SiF_4 > SiCl_4 > SiBr_4 > SiI_4$

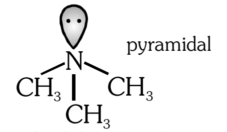
Lewis basic character :

$N(CH_3)_3 > N(SiH_3)_3$
$O(CH_3)_3 > O(SiH_3)_3$

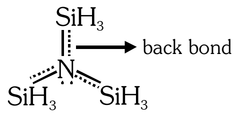
Note : Due to back bonding $\underline{B}_3N_3H_6$, $(\underline{B}O_2)_3^{3-}$, $\underline{N}(SiH_3)_3$ is planar around under lined atom.

Few more examples of back bonding

1. Shape of trimethyl amine pyramidal while shape of trisillyl amine is triangular planar.



No back bonding due to no vacant orbital in carbon.

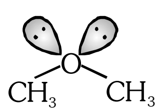


Trigonal Planar

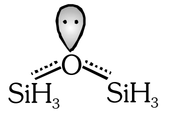
2. Lewis base strength

$\ddot{N}(CH_3)_3 > \underline{\ddot{N}(SiH_3)_3}$
lp involve in back bonding

3. Bond angle of $(CH_3)_2O$ is very less than $(SiH_3)_2O$



No back bonding
C : No vacant orbital



back bond effect of lp ↓
bond angle ↑

Chemical Species having multicentered bond

(3c-2e) bond is also termed as bannana bond.

Bridge bond is stronger than terminal bond.

Bridge bond is longer than terminal bond.

	Brigde bond	Hybridisation of central atom
Be_2Cl_4	(3c-4e)	sp^2
$(BeCl_2)_n$	(3c-4e)	sp^3
Al_2Cl_6	(3c-4e)	sp^3
I_2Cl_6	(3c-4e)	sp^3d^2
B_2H_6	(3c-2e)	sp^3
Be_2H_4	(3c-2e)	sp^2
$(BeH_2)_n$	(3c-2e)	sp^3
$(AlH_3)_n$	(3c-2e)	sp^3d^2
$Al_2(CH_3)_6$	(3c-2e)	sp^3

Odd e^- species : Total number of electron or valance electron in odd number.

	Hybridisation	Shape	Magnatic behaviour
NO_2	sp^2	V shape	Para
ClO_2	sp^2	V shape	Para
ClO_3	sp^3	Pyramidal	Para
$^{\bullet}CH_3$	sp^2	Trigonal planar	Para
$^{\bullet}CH_3$ / $^{\bullet}CHF_2$ / CH_2F	sp^3	Pramidal	Para

OXY-ACIDS

- ◆ Mainly oxy-acids are hydroxide of Non-metal oxides.
- ◆ No. of H^+ ion furnish by an oxyacid is known as their basicity. Oxyacid obtained by dissolving non-metal oxide in water.

  Eg. $CO_2 + HOH \rightarrow H_2CO_3$ or $OC(OH)_2$

  Here : $CO_2 \rightarrow$ Non metal oxide - Anhydride of carbonic acid

  $OC(OH)_2 \rightarrow$ Oxyacid
- ◆ $NO_2 \longrightarrow$ Mixed anhydride
- ◆ it gives $\longrightarrow HNO_2$ & HNO_3

Oxide	**Acid**	
◆ $N_2O_3 \longrightarrow$	HNO_2	— Nitrous acid
◆ $N_2O_5 \longrightarrow$	HNO_3	— Nitric acid
◆ $P_4O_{10} \longrightarrow$	H_3PO_4	— Phosphoric acid
◆ $SO_2 \longrightarrow$	H_2SO_3	— Sulphurous acid
◆ $SO_3 \longrightarrow$	H_2SO_4	— Sulphuric acid
◆ $Cl_2O_7 \longrightarrow$	$HClO_4$	— Perchloric acid

◆ Oxyacids of different elements

	Element	**Oxide**	**Oxyacid**	**Basicity**
1	Boron	B_2O_3	$B(OH)_3$ boric acid	Not protonic acid monobasic Lewis acid
2	Carbon	CO_2	H_2CO_3 carbonic acid	Two
3	Nitrogen		$H_2N_2O_2$ Hyponitrous acid HNO_2 Nitrous acid HNO_3 Nitric acid HNO_4 Pernitric acid	
4	Phosphorus		H_3PO_2 Hypophosphorus acid H_3PO_3 Ortho Phosphorus acid H_3PO_4 Ortho phosphoric acid HPO_3 Meta phosphoric acid $H_4P_2O_5$ Pyrophosphorus acid $H_4P_2O_7$ Pyrophosphoric acid $H_4P_2O_6$ Hypophosphoric acid	

Order of acidic strength

$H_3PO_2 > H_3PO_3 > H_3PO_4$

Reducing nature

$H_3PO_2 > H_3PO_3 > H_3PO_4$

OXYACIDS OF SULPHUR

1. Sulphurous acid - H_2SO_3
2. Sulphuric acid - H_2SO_4
3. Thiosulphuric acid - $H_2S_2O_3$
4. Peroxymonosulphuric (Caro's acid) - H_2SO_5 (Peroxide bond)
5. Peroxydisulphuric acid (Marshal's acid) - $H_2S_2O_8$ (Peroxide bond)
6. Pyrosulphurous acid - $H_2S_2O_5$ - (S-S linkage)
7. Pyrosulphuric acid - $H_2S_2O_7$ (S-O-S linkage)
8. Dithionus acid - $H_2S_2O_4$
9. Dithionic acid - $H_2S_2O_6$
10. Polythionic acid - $H_2(S)_nO_6$ (S-S linkage)

OXYACIDS OF HALOGEN (Cl)

1. Hypochlorous acid- HClO
2. Chlorous acid - $HClO_2$
3. Chloric acid - $HClO_3$
4. Perchloric acid - $HClO_4$

Order of acidic strength

$HClO < HClO_2 < HClO_3 < HClO_4$

Oxidising nature

$HClO > HClO_2 > HClO_3 > HClO_4$

ALLOTROPY

- Those substance which are made up of same elements but having different bonding arrangement are known as allotropes & this phenomenon known as allotropy.
- Those elements which exhibit higher tendency of catenation exhibit higher tendency of allotropy.
- Therefore carbon, phosphorus & sulphur exhibit maximum allotropy.

ALLOTROPES OF CARBON

DIAMOND

C-sp^3, tetrahedral structure
C-C bond length 1.54 Å
Compact 3 dimensional structure
Hardest substance
Very high mp (~ 3400°C)
Very high density
Non conductor
Very high refractive index
Exhibit total internal reflection
Shines brighty in light

GRAPHITE

Hexagonal layer structure

All sp^2 hybrid carbon

Unhybrid orbital electron form π–bond. This π–bond exhibit resonance and due to resonance there is mobility of electrons and it becomes conductor of electricity.

FULLERENE

Latest discovered allotrope of carbon it is found in chimney sooty particle.

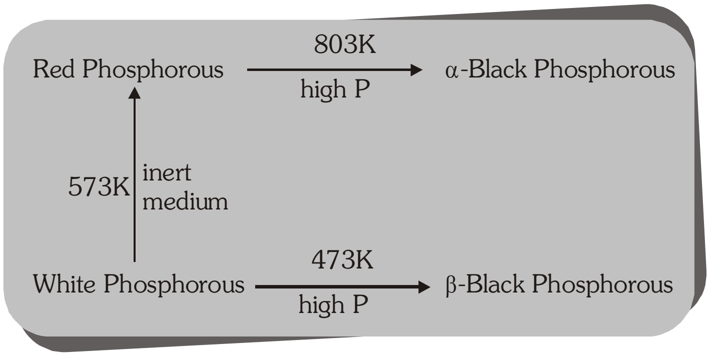
It contain C_{60}-$C_{320;}$ C : sp^2 hybrid
Contain pentagon & hexagonal structure
C_{60}: Buckminster fullerene soccer ball (football) or bucky ball.
C_{60} : 20 hexagon rings
12 pentagon rings
Purest form of carbon
No dangling bond

ALLOTROPES OF PHOSPHOROUS

(a) white phosphorous (b) Red phosphorous (c) Black phosphorous

White phosphorous	**Red Phosphorous**
Waxy solid	Brittle powder
Poisonous	Non poisonous
Soluble in CS_2, Insoluble in water	Insoluble in water & CS_2
Monomer of P_4	Polymer of P_4
Highly reactive due to bond angle strain	More stable than white phosphorous
It glows in dark due to slow oxidation (phosphorescence)	It does not glow in dark
It gives phosphine (PH_3) on reaction with NaOH	It gives hypo phosphoric acid on reaction with NaOH

Order of stability or MP or density → white < red < black



ALLOTROPES OF SULPHUR

S

Crystalline

Rhombic sulphur (α-S)
most stable form

Monoclinic sulphur (β-S)

$$\alpha\text{-S} \underset{<95^\circ,6^\circ C}{\overset{>95.6^\circ C}{\rightleftharpoons}} \beta\text{-S}$$

95.6℃ = transition Temp.
both are soluble in CS_2
but insoluble in water

Amorphous

Milk of sulphur
Plastic sulphur (γ-S)

Colloidal sulphur

$$\underset{RA}{H_2S} + \underset{OA}{2HNO_3} \xrightarrow[\text{Redox}]{} S + 2NO_2 + 2H_2O$$

(a)density of αS > βS (b)Both are puckered crown shape having S_8 units

(c) S_2 is paramagnetic sulphur which exist in vapour form at high temperature. (d)S_6 is chair form of S

Effect of Temperature

$S_{8(\alpha)} \xrightarrow{95.5^\circ C} S_{8(\beta)} \xrightarrow{119^\circ C} S_{(liq)} \xrightarrow{130\text{-}200^\circ C}$ Viscosity of liquid increase $\xrightarrow{>200^\circ C}$ Viscosity decrease

Some Important Increasing Order

1. Acidic property

(i) $SiO_2, CO_2, N_2O_5, SO_3$
(ii) $MgO, Al_2O_3, SiO_2, P_4O_{10}$
(iii) $HClO, HClO_2, HClO_3, HClO_4$
(iv) CH_4, NH_3, H_2O, HF
(v) SiH_4, PH_3, H_2S, HCl
(vi) H_2O, H_2S, H_2Se, H_2Te
(vii) HF, HCl, HBr, HI
(viii) $InCl_3, GaCl_3, AlCl_3$
(ix) BF_3, BCl_3, BBr_3, BI_3

2. Bond Angle

(i) CH_4, C_2H_4, C_2H_2
(ii) H_2O, NH_3, CH_4, CO_2
(iii) H_2O, NH_3, CH_4, BH_3
(iv) NO_2^-, NO_2, NO_2^+
(v) H_2Se, H_2S, H_2O
(vi) AsH_3, PH_3, NH_3
(vii) PF_3, PCl_3, PBr_3, PI_3
(viii) NF_3, NCl_3
(ix) NF_3, NH_3, NCl_3
(x) OF_2, OH_2, Cl_2O

3. Basic Character

(i) LiOH, NaOH, KOH, RbOH, CsOH
(ii) $Be(OH)_2, Mg(OH)_2, Ca(OH)_2, Ba(OH)_2$
(iii) BeO, MgO, CaO, SrO
(iv) $NiO, MgO, SrO, K_2O, Cs_2O$
(v) CO_2, B_2O_3, BeO, Li_2O
(vi) $SiO_2, Al_2O_3, MgO, Na_2O$
(vii) SbH_3, AsH_3, PH_3, NH_3
(viii) $F^-, OH^-, NH_2^-, CH_3^-$

4. Thermal Stability

(i) $Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3$
(ii) $BeCO_3, MgCO_3, CaCO_3, BaCO_3$
(iii) $Be(OH)_2, Mg(OH)_2, Ca(OH)_2, Sr(OH)_2, Ba(OH)_2$
Polarisation
(iv) LiOH, NaOH, KOH, RbOH, CsOH
(v) $BeSO_4, MgSO_4, CaSO_4$
(vi) CsH, RbH, KH, NaH, LiH
(vii) SbH_3, AsH_3, PH_3, NH_3
(viii) H_2Te, H_2Se, H_2S, H_2O
(ix) HI, HBr, HCl, HF

5. Ionic Character

(i) LiBr, NaBr, KBr, RbBr, CsBr
(ii) LiF, NaF, KF, RbF, CsF
(iii) $BeCl_2, MgCl_2, CaCl_2, SrCl_2, BaCl_2$
(iv) $BCl_3, AlCl_3, GaCl_3$
(v) VCl_4, VCl_3, VCl_2
(vi) AlF_3, MgF_2, NaF
(vii) AlN, Al_2O_3, AlF_3
(viii) HI, HBr, HCl, HF
(ix) CuCN, AgCN
(x) AgCl, KCl

6. Oxidizing Power

(i) $Cr_2O_7^{2-}, MnO_4^-$
(ii) MnO_4^{2-}, MnO_4^-
(iii) WO_3, MoO_3, CrO_3
(iv) $GeCl_4, SnCl_4, PbCl_4$
(v) I_2, Br_2, Cl_2, F_2
(vi) $Zn^{+2}, Fe^{+2}, Pb^{2+}, Cu^{2+}, Ag^+$

7. Melting Point

(i) Cs, Rb, K, Na, Li
(ii) Mg, Ba, Sr, Ca, Be
(iii) $CaI_2, CaBr_2, CaCl_2, CaF_2$
(iv) $BeCl_2, MgCl_2, CaCl_2, SrCl_2, BaCl_2$
(v) NaI, NaBr, NaCl, NaF
(vi) CsCl, RbCl, KCl, NaCl
(vii) $AlCl_3, MgCl_2, NaCl$

8. Density

(i) Na, Al, Fe, Pb, Au
(ii) Li, K, Na, Rb, Cs
(iii) Ca, Mg, Be, Sr, Ba
(iv) Highest Density = Os/Ir
(v) Lowest density = H
(vi) Metal of lowest Density = Li

9. Boiling Point

(i) PH_3, AsH_3, NH_3, SbH_3
(ii) H_2S, H_2Se, H_2O
(iii) HCl, HBr, HI, HF
(iv) NH_3, HF, H_2O
(v) He, Ne, Ar, Kr
(vi) H_2O, D_2O
(vii) H_2, Cl_2, Br_2

10. Electrical Conductivity

Cr, Pt, Fe, Al, Au, Cu, Ag

11. Reactivity with water

(i) Li, Na, K, Rb, Cs

(ii) Be, Mg, Ca, Sr, Ba

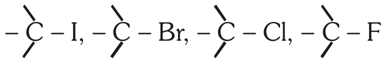
12. Extent of Hydrolysis

(i) CCl_4, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5

(ii) $BiCl_3$, $SbCl_3$, $AsCl_3$, PCl_3, NCl_3

13. Bond Strength

(i) HI, HBr, HCl, HF

(ii) 

(iii) N – N, N = N, N ≡ N

(iv) As – H, Sb – H, P – H, N – H

(v) N_2^{2-}, N_2^-, N_2^+, N_2

(vi) O_2^{2-}, O_2^-, O_2 , O_2^+, O_2^{2+}

LiI, LiBr, LiCl, LiF NaI, NaBr, NaCl, NaF

CsCl, RbCl, KCl, NaCl BaO, SrO, CaO, MgO

(vii) F_2, H_2, O_2, N_2

(viii) NO^-, NO, NO^+

(ix) I_2, F_2, Br_2, Cl_2

(x) O–O, S– S

(xi) F – F, O – O, N – N, C – C, H – H

14. Reducing Power

(i) $PbCl_2$, $SnCl_2$, $GeCl_2$

(ii) HF, HCl, HBr, HI

(iii) Ag, Cu, Pb, Fe, Zn

(iv) HNO_3, H_2SO_3, H_2S

(v) H_3PO_4, H_3PO_3, H_3PO_2

15. Covalent Character

(i) LiCl, $BeCl_2$, BCl_3, CCl_4

(ii) $SrCl_2$, $CaCl_2$, $MgCl_2$

(iii) $TiCl_2$, $TiCl_3$, $TiCl_4$

(iv) LiCl, LiBr, LiI

(v) Na_2O, Na_2S

(vi) AlF_3, Al_2O_3, AlN

(vii) HF, HCl, HBr, HI

16. Strength of Hydrogen bonding (X...H–X)

(i) S, Cl, N, O , F

(ii) NH_3, H_2O, HF

17. Reactivity with Hydrogen

(i) Cs, Rb, K, Na, Li

(ii) Ba, Sr, Ca, Mg, Be

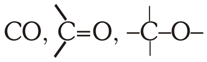
18. Reactivity Towards Air

Be, Mg, Cs, Sr, Ba

19. Bond Length

(i) N_2, O_2, F_2, Cl_2

(ii) N–N, C–N, C–C

(iii) 

(iv) NO^+, NO, NO^-

(v) O_2, O_3, H_2O_2 (O-O bond length)

(vi) CO, CO_2, CO_3^{-2}

(vii) N_2, N_2^-, N_2^{-2}

(viii) O_2^{+2}, O_2, O_2^-, O_2^{-2}

(ix) HF, HCl, HBr, HI

20. Dipole moments

(i) CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl

(ii) NF_3, NH_3, H_2O, HF

(iii) Cis-chloropropene, Trans-chloropropene

(iv) p, m, o-dichlorobenzene

(v) CH_3I, CH_3Br, CH_3F, CH_3Cl

(vi) NH_3, SO_2, H_2O, HF

(vii) H_2S, H_2O

(viii) HI, HBr, HCl, HF

(ix) PH_3, ASH_3, SbH_3, NH_3

(x) H_2O, H_2O_2

Group 15	Bond angle	Group 16	Bond angle
NH_3	107°°48'	H_2O	104°°28'
PH_3	93°°36'	H_2S	92°°
AsH_3	91°°48'	H_2Se	91°°
SbH_3	91°°18'	H_2Te	90.5°°

INERT PAIR EFFECT

- Inert pair effect the reluctance of ns electrons to take part in bond formation is called inert pair effect. This effect is more pronounced in heavier elements and that too for 13, 14 and 15 group. It results in the decrease in oxidation state by 2 units. For examples, Tl is more stable in oxidation state + 1 than the oxidation state +3.

  In p-block elements the stability of the lower oxidation state increases on descending the group.

Group 13	**Group 14**
B (+3)	C (+4)
Al (+3)	Si (+4)
Ga (+3), (+1)	Ge (+4), (+2)
In (+3), (+1)	Sn (+4), (+2)
Tl (+3), (+1)	Pb (+4), (+2)

Order of stability :

$Tl^{+1} > In^{+1} > Ga^{+1}$ (due to inert pair effect)

Order of stability :

$Pb^{+2} > Sn^{+2} > Ge^{+2}$ (due to inert pair effect)

Molecules that do not exist :

(1) SF_4, SF_6 & PF_5 exist while. OF_4, OF_6, NF_5 do not exist

(2) (a) PI_5(vap) & SCl_6 do not exist

(b) SCl_6 does not exist while $TeCl_6$ exist

(c) PI_5 (Solid) exist

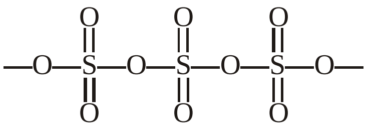
(3) SF_6, PF_5, XeF_6, XeF_4 & XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist

ALLOTROPIC FORM OF SO_3

SO_3 have three allotropic forms α-SO_3 , β-SO_3 and γ-SO_3

α-SO_3 ,

Cross linked solid

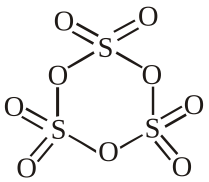


$$—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O—$$

,

Polymeric chain structure

β-SO_3



γ-SO_3

(S_3O_9)

cylic trimer

IMPORTANT NOTES

s-BLOCK ELEMENTS

ALKALI METALS

Physical properties :

General electronic configuration ns^1.

General oxidation state +1.

Atomic/Ionic size	$Li < Na < K < Rb < Cs$.
Density	$Li < K < Na < Rb < Cs$
Ionisation energy	$Li > Na > K > Rb > Cs$

Flame colour

Li	Crimsen red
Na	Golden yellow
K	Pale violet
Rb	Reddish violet
Cs	Blue

Basic nature increase down to the group

Reducing property :

$\xrightarrow{\text{Molten}}$ $Li < Na < K < Rb < Cs$

$\xrightarrow[\text{aqueous}]{}$ $Li > K \approx Rb > Cs > Na$

❒ **Chemical properties :**

With O_2: Lithium forms normal oxide [Li_2O]

Sodium forms peroxide (Na_2O_2)

K, Rb,Cs forms superoxide KO_2,RbO_2, CsO_2

$M_2O \xrightarrow{H_2O} M(OH)$

$M_2O_2 \xrightarrow{H_2O} M(OH) + H_2O_2$

$MO_2 \xrightarrow{H_2O} M(OH) + H_2O_2 + O_2$

With Water : $M + H_2O \longrightarrow MOH + H_2$

With Air :

$\xrightarrow{\text{Moist air } O_2} M_2O \xrightarrow{H_2O} MOH \xrightarrow{CO_2} M_2CO_3$

$\xrightarrow[\text{dry air}]{} M_2O + M_3N$

only Li gives nitride

With NH_3 :

$M + (X + Y)\,NH_3 \longrightarrow [Na(NH_3)_X]^+ + [e(NH_3)_Y]^-$

ammoniated e^-

Paramagnetic, blue colour. In excess of metal dimagnetic and copper bronze colour.

on standing

$Li + NH_3 \longrightarrow Li_2NH$ (Lithmide) $+ H_2$

$M(Na/K/Rb/Cs) + NH_3 \longrightarrow MNH_2$ (amide) $+ H_2$

With Halides :

$M + X_2 \longrightarrow MX$

K, Rb, Cs forms poly halide due to large size

SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM

(a) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(b) Lithium and magnesium react slowly with cold water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, Li_3N and Mg_3N_2.

(c) The oxides, Li_2O and MgO do not combine with excess oxygen to give a peroxide or a superoxide.

(d) The carbonates of lithium and magnesium decompose easily on heating to form the oxide and CO_2. Solid bicarbonates are not formed by lithium and magnesium.

(e) Both LiCl and $MgCl_2$ are soluble in ethanol.

(f) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates,

$LiCl.2H_2O$ and $MgCl_2.8H_2O$.

Carbonates :

Only Li_2CO_3 decomposes

$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$

Nitrates :

$LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$

$MNO_3 \xrightarrow{\Delta} MNO_2 + O_2$ (M = Na/K/Rb/Cs)

$Na_2CO_3.10H_2O$ (Washing Soda)

➢ In **Solvay's process**, CO_2 gas is passed through saturated brine (NaCl) solution when sparingly soluble $NaHCO_3$ separates out.

$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 \downarrow + NH_4Cl$

The $NaHCO_3$ formed above is calcined to form Na_2CO_3

$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + CO_2 + H_2O$

➢ The reactions taking place at different stages during the manufacture of Na_2CO_3 by Solvay process are given as under :

(a) $2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$

$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$

$2NaCl + 2NH_4HCO_3 \rightarrow 2NaHCO_3 + 2NH_4Cl$

(b) Ammonia recovery tower

$NH_4HCO_3 \xrightarrow{Heat} NH_3 + CO_2 + H_2O$

$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$

(c) Calcination of $NaHCO_3$

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

(i) **Efflorescence :** $Na_2CO_3.10H_2O$ when exposed to air it gives out nine out of ten H_2O molecules.

$Na_2CO_3.10H_2O \longrightarrow \underset{\text{(Monohydrate)}}{Na_2CO_3.H_2O} + 9H_2O$

This process is called efflorescence. Hence washing soda losses weight on exposure to air.

(ii) **Hydrolysis :**Aqueous solution of Na_2CO_3 is alkaline in nature due to anionic hydrolysis.

$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{-2}$ and

$CO_3^{-2} + H_2O \rightleftharpoons \underset{\text{(Carbonic acid)}}{H_2CO_3} + 2OH^-$

- Na_2CO_3 does not impart any colour to the flame but NaCl does because the thermal ionization of Na_2CO_3 does not take place at the temperature of flame of the burner.

❒ Reaction of NaOH :

(i) NaOH is **strong base**

$NaOH \xrightarrow{SiO_2} Na_2SiO_3 + H_2O$

$NaOH \xrightarrow{Al_2O_3} 2NaAlO_2 + H_2O$

(ii) **Reaction with non metals :** no reaction with H_2, N_2 and C

$NaOH \xrightarrow{\Delta/B} Na_3BO_3 + H_2$

$NaOH \xrightarrow{\Delta/Si} Na_2SiO_3 + H_2$

$NaOH \xrightarrow{\Delta/P_4} NaH_2PO_2 + PH_3$

$NaOH \xrightarrow{\Delta/S} Na_2S_2O_3 + Na_2S$

$X_2 \xrightarrow{NaOH\ (cold/dil)} NaX + NaOX$ (Sodium hypo halite)

$X_2 \xrightarrow{NaOH\ (Hot/conc.)} NaX + NaXO_3$ (Sodium Halate)

$(X_2 = Cl_2, Br_2, I_2)$

(iii) **Reaction with Metal :**

$NaOH \xrightarrow{\text{Alkali metal}}$ No reaction

$NaOH \xrightarrow{2Al + 2H_2O} 2NaAlO_2$ (Sodium meta aluminate) + H_2

$NaOH \xrightarrow{Be} Na_3BeO_2$ (Sodium Berrylate) + H_2

$NaOH \xrightarrow{Zn} Na_2ZnO_2$ (Sodium zincate) + H_2

$NaOH \xrightarrow{Sn} Na_2SnO_2$ (Sodium stannate) + H_2

$NaOH \xrightarrow{Pb} Na_2PbO_2$ (Sodium plumbite) + H_2

ALKALINE EARTH METALS

Physical properties : General electronic configuration ns^2.

General oxidation state +2.

Atomic/Ionic size $Be < Mg < Ca < Sr < Ba$

Ionisation energy $Be > Mg > Ca > Sr > Ba$

Flame Test :

Among alkaline earth metals, Be and Mg do not impart any characteristic colour to the flame due to more ionization energies.

Ca – Brick red

Sr – Crimson red

Ba - Apple green

Basic nature of oxide

Reducing property : Order of reducing property in aqueous and gaseous medium is

$Be^{+2} < Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$

Chemical properties :

With O_2 :

$$\underset{}{M} \xrightarrow{O_2} \underset{\text{(Be,Mg,Ca,Sr,Ba, oxide)}}{MO} \xrightarrow{O_2} \underset{\text{(Ca,Sr,Ba, peroxide)}}{MO_2}$$

With Water :

$$M + 2H_2O \rightarrow M(OH)_2 + H_2$$

With Air :

In moist air, except Be all the elements converts into carbonates.

In dry air gives nitride and oxide both

With NH_3 :

Only Ca, Sr and Ba gives deep blue-black solution of ammoniated electron.

Carbonates :

(i) Except $BeCO_3$, all the carbonates are stable towards heat

$$BeCO_3 \xrightarrow{\Delta} BeO + CO_2$$

(ii) Order of decreasing stability -

$$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$$

Nitrates :

(i) Alkaline earth metals forms $M(NO_3)_2$ type nitrates. (M –Alkaline earth metal).

(ii) All alkaline metals nitrates on heating gives oxides and $NO_2 + O_2$

$$M(NO_3)_2 \xrightarrow{\Delta} \text{Oxides} + NO_2 + O_2$$

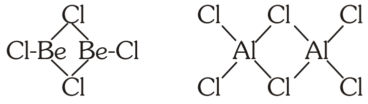
DIAGONAL SIMILARITY BETWEEN BERYLLIUM AND ALUMINIUM

In many of its properties, beryllium resembles aluminium. Thus –

(a) The two elements have same electronegativity and their charge/ radius ratios.

(b) Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalies to form soluble complexes, beryllates $[Be(OH)_4]^{2-}$ and aluminates, $[Al(OH)_4]^-$.

(c) The chlorides of both beryllium and aluminium



have bridged chloride structures in vapour phase.

(d) Salts of these metals form hydrated ions, Ex. $[Be(OH_2)_4]^{2+}$ and $[Al(OH_2)_6]^{3+}$ in aqueous solutions. Due to similar charge/ radius ratios of beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as $BeF_4^{\ 2-}$ and $[Be(C_2O_4)_2]^{2-}$ and aluminium forms octahedral complexes like AlF_6^{3-} and $[Al(C_2O_4)_3]^{3-}$.

- Be_2C on treatment with H_2O forms CH_4 while CaC_2 forms C_2H_2.

$$Be_2C + 2H_2O \rightarrow 2\,BeO + \underset{\text{methane}}{CH_4}$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

CHLORIDE OF ALKALINE EARTH METAL.

- $BeCl_2$ in the vapour phase above 900°C is monomeric ; below 900°C in the vapour exists as a mixture of monomer $BeCl_2$ and dimer Be_2Cl_4, in the solid state, has a polymeric structure and when dissolved in a coordinating solvent it exists as a monomer.

- Anhydrous $MgCl_2$ cannot be prepared by the simple heating of hydrated magnesium chloride $MgCl_2$, $6H_2O$, as it gets hydrolysed to magnesium oxide.

$$MgCl_2.6H_2O \xrightarrow{\text{Heat}} MgO + 2HCl + 2H_2O$$

- Out of the oxides of group 2 elements only BeO is extremely hard, non volatile, has high melting point and it is amphoteric.

ANALYTICAL DETECTION OF Mg

(i) Charcoal cavity test. On heating on a charcoal cavity with one drop of $Co(NO_3)_2$, a pink colour is imparted to the residue CoO.MgO.

(ii) The salt solution when mixed with NH_4Cl and NH_4OH and finally treated with soluble phosphates forms a white precipitate of magnesium ammonium phosphate.

$$MgSO_4 + Na_2HPO_4 + NH_4OH \rightarrow \underset{\text{white ppt.}}{Mg(NH_4)PO_4} + Na_2SO_4 + H_2O$$

CALCIUM CYANAMIDE

- Calcium cyanamide ($CaCN_2$) is prepared by heating a mixture of CaC_2 in an atmosphere of N_2 at 1270–1370K with CaF_2.

  $$CaC_2 + N_2 \xrightarrow[1270\text{–}1370K]{CaF_2} CaCN_2 + C$$

  Its trade name is Nitrolim.

- Calcium cyanamide ($CaCN_2$) is a slow acting manure and is preferred to soluble compounds like $NaNO_3$ or $(NH_4)_2SO_4$ since it confers fertility of a permanent nature. It is a nitrogenous fertiliser and undergoes a series of changes giving cyanamide, urea, NH_3 and finally the nitrates which are assimilable by plants.

  $$CaCN_2 + H_2O + CO_2 \rightarrow CaCO_3 + H_2NCN$$

  $$H_2NCN + H_2O \rightarrow \underset{\text{Urea}}{H_2NCONH_2}$$

  $$H_2NCONH_2 + H_2O \rightarrow CO_2 + 2NH_3$$

OXIDE OF CALCIUM

Quick lime (CaO) is obtained when limestone is heated at about 1000°C. On adding water, quick lime gives a hissing sound and forms calcium hydroxide, known as slaked lime. The paste of lime in water is called milk of lime while the filtered and clear solution is known as lime water. Chemically both are $Ca(OH)_2$. Quick lime is used for making caustic soda, bleaching powder, calcuim carbide, mortar, cement, glass, dye stuffs and purification of sugar.

Mortar : It is a building material. It consists slaked lime and silica in the ratio of 1:3. The mixture made a paste with water. It is called mortar.

PLASTER OF PARIS

- Gypsum ($CaSO_4 . 2H_2O$) found in nature, when heated, it first changes from monoclinic form to orthorhombic form without loss of water. At 120°C, it loses three-fourth of its water of crystallisation and forms hemihydrate ($CaSO_4 . \frac{1}{2}H_2O$) known as plaster of Paris.
- Plaster of Paris has the property of setting to a hard mass $CaSO_4 . 2H_2O$, slight expansion occurs during setting addition of alum to plaster of Paris makes the setting very hard. The mixture is known as **Keene cement.**

  Plaster of Paris is used for setting broken or disslocated bones, castes for statues, toys and in dentistry.

  When plaster of Paris is heated at 200°C, it forms anhydrous calcium sulphate which is known as dead plaster. It has no setting property.

CEMENT

- Cement is an important building meterial. The average composition of portland cement is : CaO 61.5%, SiO_2 22.5%, Al_2O_3 7.5%. Cement consists of :

  Tricalcium silicate $3CaO.SiO_2$
  Dicalcium silicate $2CaO.SiO_2$
  Tricalcium aluminate $3CaO.Al_2O_3$
  Tetracalcium alumino - ferrite $4CaO. Al_2O_3. Fe_2O_3$

  When cement is mixed with water, it sets to a hard mass, this is called setting. Setting is an exothermic process. During setting hydration occurs.

CALCIUM HYDROXYAPATITE

Hydroxyapatite, $Ca_9(PO_4)_6.Ca(OH)_2$ is the main component of tooth enamel. Cavities are formed when acids decompose this enamel. This can be prevented by converting the hydroxyapatite to more resistant enamel-fluorapatite, $Ca_9(PO_4)_6.CaF_2$.

HYDROLITH

- Hydrolith (CaH_2) is calcium hydride & on hydrolysis for calcium hydroxied & librate hydrogen.

IMPORTANT NOTES

CHAPTER 4

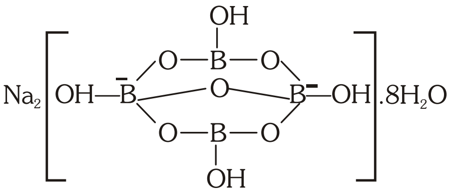
p-BLOCK

13th-GROUP

- Some important ores of Boron are given as under.
  - (i) Boric acid, H_3BO_3 (ii) Borax, $Na_2B_4O_7.10H_2O$ (iii) Colemanite, $Ca_2B_6O_{11}.5H_2O$
- Some important minerals of aluminium are given as under.
  - (i) Corundum, Al_2O_3 (ii) Bauxite, $Al_2O_3.2H_2O$ (iii) Cryolite, Na_3AlF_6
  - (iv) Feldspar, $KAlSi_3O_8$

BORAX $Na_2[B_4O_5(OH)_4].8H_2O$

$Na_2[B_4O_5(OH)_4].8H_2O$



Properties :

(i) It is a white crystalline solid of formula $Na_2B_4O_7.10H_2O$. In fact it contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and correct formula; therefore, is $Na_2[B_4O_5(OH)_4].8H_2O$.

(ii) Hydrolysis

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

(iii) Heating

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} \underset{\text{Swells up}}{Na_2B_4O_7} \xrightarrow{\Delta} \underset{\substack{\text{Sodium}\\\text{metaborate}}}{2NaBO_2} + \underset{\substack{\text{Boric}\\\text{anhydride}}}{B_2O_3}$$

(iv) When borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

DIBORANE, B_2H_6

Preparation :

(i) $$\underset{\text{or } LiBH_4}{3LiAlH_4} + 4BF_3 \longrightarrow 3LiF + \underset{\text{or } 3(BF_3)}{3AlF_3} + 2B_2H_6$$

(ii) **Laboratory** method :

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

(iii) **Industrial scale** :

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Properties :

(i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.

(ii) Diborane catches fire spontaneously upon exposure to air.

(iii) Reaction with Oxygen :

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O \;;\; \Delta_cH^{\ominus} = -1976 \text{ kJ mol}^{-1}$$

(iv) Hydrolysis :

$$B_2H_6(g) + 6H_2O(\ell) \text{ (Cold is enough)} \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

$$B_2H_6 + HCl \text{ (dry)} \xrightarrow[AlCl_3]{\text{anh.}} B_2H_5Cl + H_2$$

(v) Reaction with Lewis Bases

(a) $B_2H_6 + 2NMe_3 \rightarrow 2BH_3.NMe_3$

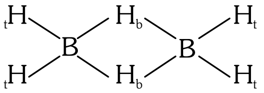
(b) $B_2H_6 + 2CO \rightarrow 2BH_3.CO$

(c) $3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\text{Heat}} 2B_3N_3H_6 + 12H_2$

(vi) Reaction with ROH :

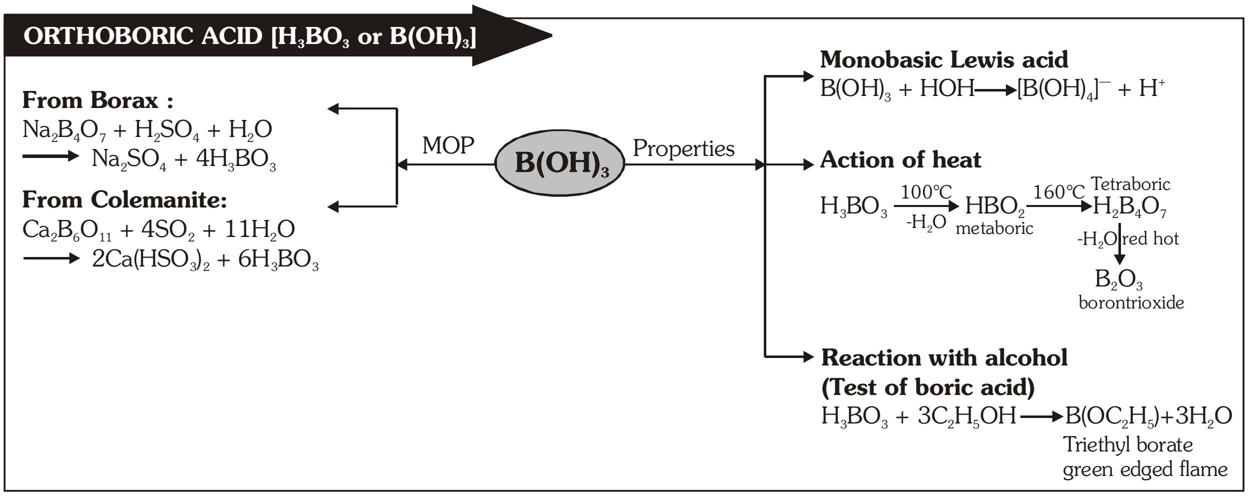
$B_2H_6 + 6ROH \rightarrow 2B(OR)_3 + 6H_2O$

Diborane, B_2H_6



dimer due to formation of
3 centre-2e-bond

Inorganic benzene



ORTHOBORIC ACID [H_3BO_3 or $B(OH)_3$]

From Borax :

$Na_2B_4O_7 + H_2SO_4 + H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

From Colemanite:

$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

MOP

$B(OH)_3$

Properties

Monobasic Lewis acid

$B(OH)_3 + HOH \longrightarrow [B(OH)_4]^- + H^+$

Action of heat

$H_3BO_3 \xrightarrow[-H_2O]{100°C} \underset{\text{metaboric}}{HBO_2} \xrightarrow{160°C} \overset{\text{Tetraboric}}{H_2B_4O_7} \xrightarrow[\text{red hot}]{-H_2O} \underset{\text{borontrioxide}}{B_2O_3}$

Reaction with alcohol
(Test of boric acid)

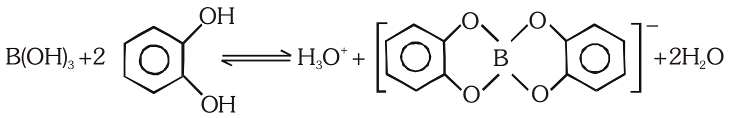
$H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)+3H_2O$

Triethyl borate
green edged flame

- Boric acid is a weak monobasic acid

$$B(OH)_3 + 2H_2O \Leftrightarrow H_3O^{\oplus} + [B\ (OH)_4]^{-1}$$
$$pKa = 9.25$$

- It is difficult to titrate boric acid against NaOH solutions and the end point cannot be located correctly However, it can be successfully titrated in the presence of polhydroxy alcohols (e.g. Glycerol, mannitol, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.



Boron is complex by these compounds. These complex ions cannot interact with H^+ ions as boron atom has already acquired it's maximum covalency of four. Consequently, boric acid in presence of polyhydroxy alcohols can be titrated against NaOH to a definite end point.

EXTRACTION OF ALUMINIUM

Al is usually extracted from Bauxite, $Al_2O_3.2H_2O$. First, bauxite is purified from the impurities (Red bauxite contains Fe_2O_3 as impurity while white bauxite contains silica as impurity). Red bauxite can be purified by Baeyer's process or Hall's process while white bauxite is purified by Serpeck's process.

- **Baeyer's process**, involves the roasting of the ore to convert FeO to Fe_2O_3 and then digested at 423K with conc. NaOH solution for a few hours when Al_2O_3 gets dissolved to give a solution of $[Al(OH)_4]^{-1}$

  The basic oxide impurities such as Fe_2O_3 are not affected.

  $$Al_2O_3 + 2OH^{-1} + 3H_2O \rightarrow \underset{\text{Aluminate ion}}{2Al(OH)_4^{-1}}$$

  Fe_2O_3 left undissolved is filtered off. The treatment of $Al(OH)_4^{-1}$. solution with a weak acid precipitate pure $Al(OH)_3$.

  $$Al(OH)_4^{-1} + H^+ \rightarrow \underset{\text{(White ppt.)}}{Al(OH)_3} + H_2O$$

  The $Al(OH)_3$ precipitate is removed by filtration and ignited to get alumina, Al_2O_3.

- **Hall's process**, Involves the fusion of the ore with Na_2CO_3 when soluble sodium meta aluminate, $NaAlO_2$ is produced. This is extracted with water when Fe_2O_3 is left as a residue.

  $$Al_2O_3 + Na_2CO_3 \rightarrow \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + CO_2$$

  The water extract is heated upto 333K and CO_2 is passed through it. $Al(OH)_3$ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_3.

  $$2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2Al(OH)_3 + Na_2CO_3$$

- **Serpeck's process** involves the heating of bauxite with coke in a current of N_2 at 2075K. The SiO_2 present in the ore is reduced to silicon which volatilizes off and alumina gives aluminium nitride. This can be hydrolysed to Al $(OH)_3$ which on fusion gives alumina.

  $$SiO_2 + 2C \rightarrow Si\uparrow + 2CO\uparrow$$

  $$Al_2O_3 + 3C + N_2 \rightarrow \underset{\text{Aluminium nitride}}{2AlN} + 3CO$$

  $$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

Electrolysis of Al_2O_3 to form aluminium. Pure alumina is dissolved in fused cryolite, Na_3AlF_6 at 1225 K by current of 100 amperes and 6 – 7 volts to get Al. The Al obtained is purified by Hoope's process.

ALUMINIUM TRIFLUORIDE

- **Aluminium trifluoride** (AlF_3) is different from other trihalides of Al in being insoluble and nonvolatile. In AlF_3 each Al is surrounded by a distorted octahedron of 6F atoms and 1 : 3 stoichiometry is achieved by the sharing of corner fluorine atoms between two octahedra.

ALUMINIUM CHLORIDE

- Aluminium chloride ($AlCl_3$) in the pure and anhydrous state is a white solid but commercial samples are yellowish due to the impurity of $FeCl_3$.
- Anhydrous $AlCl_3$, in the crystalline state possesses a closely packed layer structure with six coordinated aluminium octahedral arrangement.
- Anhydrous $AlCl_3$ has a very high affinity for water. On treating $AlCl_3$ with water the Cl^- ions go outside the coordination sphere to form $[Al(H_2O)_6]Cl_3$ with enthalpy of solution –330 KJ mol^{-1}. Due to this strong Al – O linkage hydrate cannot be dehydrated on heating to form $AlCl_3$.

  $$2[Al(H_2O)_6]\,Cl_3 \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$$

- Aluminium chloride, is a polymeric solid which exists as a dimer Al_2Cl_6 between 200–400°C and then monomer up to 800°C.
- **Thermite welding**, Aluminium has got a very high affinity for oxygen.

  $$4Al + 3O_2 \rightarrow 2Al_2O_3.$$
  $$\Delta H = -3230 \text{ KJ mol}^{-1}$$

  It, therefore, displaces metals less electropositive than itself from oxides. The large amount of heat produced is used in welding rails or heavy machinery without removing them from their position. This is called thermite welding or Gold Schmidt's aluminothermic process. In this process, a mixture of Ferric oxide (3 parts) and aluminium powder (1 part) called thermite is used.

- **Boron nitride** (BN), has a structure similar to that of graphite.
- Green edged flame test for borate (BO_3^{3-}) ion. A mixture of C_2H_5OH and BO_3^{3-} salt with conc. H_2SO_4 burns with green edge flame due to the formation of ethyl borate.

  $$H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{Ethyl borate}}{B(OC_2H_5)_3} + 3H_2O$$

- **Charcoal cavity test for aluminium.** On heating with Na_2CO_3 and a drop of cobalt nitrate solution a blue coloured residue to **cobalt metaaluminate** (Thenard's blue) is obtained.

ALUMS [$M_2SO_4.M_2'(SO_4)_3.24H_2O$]

Alums are the double salts of Type
[$M_2SO_4.M_2'(SO_4)_3.24H_2O$]

M : Monovalent Cation:
Na^+, K^+, Rb^+, Cs^+, NH_4^+

M' : Trivalent cation :
Al^{3+}, Fe^{3+} & Cr^{3+}

Soda alum
$Na_2SO_4.Al_2(SO_4)_3.24H_2O$

Potash alum
$K_2SO_4.Al_2(SO_4)_3.24H_2O \xleftarrow{\text{example}} \textbf{Alum} \xrightarrow{\text{properties}}$

- aq. solution acidic
- Coagulant
- Mordant for dyeing
- Tanning of leather

Ammonium alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3.24H_2O$

Pseudo alums are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.

(i) $MnSO_4.\ Al_2(SO_4)_3.24H_2O$ (ii) $FeSO_4.\ Al_2(SO_4)_3.24H_2O$

They are not isomorphous with true alums.

IMPORTANT NOTES

GROUP 14 ELEMENTS

1. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states.

2. Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).

3. Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.

4. SiO only exists at high temperature.

5. The dioxides — CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

6. Tin decomposes steam to form dioxide and dihydrogen gas.

7. All halide of 14th group are covalent. Exceptions are SnF_4 and PbF_4, which are ionic in nature.

8. Stability of dihalides increases down the group.

9. The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation.

➢ **Catenation** is the unique tendency of 14 group elements to form long chains of different sizes and shapes. The tendency to show catenation is directly related to the strength of bond. The bond energies of 14 group elements decrease as under :

	C–C	Si–Si	Ge–Ge	Sn–Sn	Pb–Pb
Bond energy (KJ mole^{-1})	348	222	167	155	–

This is the reason why carbon forms many chains, Si, a few and Ge and Sn form practically no chains.

➢ CO_2 is a gas while SiO_2 is a solid at room temperature.

➢ SiO only exists at high temperature

➢ CO_2 SiO_2 GeO_2 , GeO are acidic, PbO, PbO_2 is SnO and SnO_2 are amphoteric and CO is neutral

⇒ Among 14th group element only Sn reacts with steam to produce H_2 gas.

⇒ Tetrahalide of 14th group element are covalent except SnF_4 and PbF_4

Stability of oxidationstate

⇒ C^{+4} >------------------> Pb^{+4} (Stability)

C^{+2} <------------------< Pb^{+2} (Stability)

⇒ Pb^{+4} compounds are strong oxidizing agent.

⇒ PbI_4 does not exist.

➢ Trimethylamine $(CH_3)_3N$ is pyramidal while Trisilylamine $N(SiH_3)_3$ is planar due to back bonding.

SILICONES (ORGANO SILICONE POLYMER)

➢ Silicones are polymeric organosilicon compounds containing Si–O–Si linkage. They have high thermal stability of Si–O–Si chains and are also called high temperature polymers.

General formula : $(R_2SiO)_n$. Where R = $-CH_3$, $-C_2H_5$,$-C_6H_5$

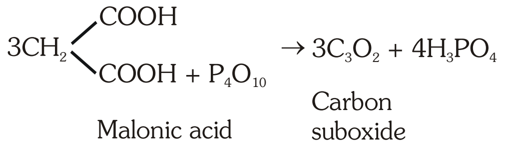
(i) $R_2SiCl_2 + 2H_2O \xrightarrow{-2HCl} R_2Si(OH)_2 \xrightarrow[-H_2O]{\Delta}$ Linear Silicones/Cyclic Silicones

(ii) $R_3SiCl + H_2O \xrightarrow{HCl} R_3Si(OH) \xrightarrow[-H_2O]{\Delta}$ Dimer Silicones

(iii) $RSiCl_3 + 3H_2O \xrightarrow{-3HCl} RSi(OH)_3 \xrightarrow[-H_2O]{\Delta}$ Crossed Linked Silicones

CARBON SUBOXIDE

- Carbon suboxide (C_3O_2) is an foul smelling gas which can be prepared by the dehydration of malonic acid with P_4O_{10}.



$$3CH_2\begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix} + P_4O_{10} \rightarrow 3C_3O_2 + 4H_3PO_4$$

Malonic acid Carbon suboxide

On heating upto 200°C, it decomposes into CO_2 and carbon.

$$C_3O_2 \xrightarrow{200°C} CO_2 + 2C$$

The molecule is throught to have a linear structure.

$$O = C = C = C = O$$

OXIDE OF LEAD

- $\underset{\text{massi cot}}{PbO} \overset{\text{Cool}}{\rightleftharpoons} \underset{\text{Lith arg e}}{PbO}$
- **Red lead (Pb_3O_4)** is considered to be mixture of lead monoxide and lead dioxide and it is written as (PbO_2.2PbO).
- **Lead dioxide (PbO_2).** It is a brown powder obtained by the treatment of red lead with HNO_3.

  $Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

  It is used as an active material of the positive plate in storage cells and finds use in match industry as an oxidizing agent.

REACTION OF LEAD OXIDES

Oxide	ex NaOH	HCl	H_2SO_4	HNO_3
PbO	Na_2PbO_2	$PbCl_2$	$PbSO_4$	$Pb(NO_3)_2$
PbO_2	Na_2PbO_3	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2$
Pb_2O_3	$Na_2PbO_2 + NaPbO_3$	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$
Pb_3O_4	$Na_2PbO_2 + Na_2PbO_3$	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$

TIN & ITS COMPOUNDS

- **Action of conc. HNO_3 on tin**

  (a) Dilute HNO_3

  $4Sn + 10HNO_3 \rightarrow 4\ Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

  (b) Hot conc. HNO_3

  $Sn + 4HNO_3 \rightarrow \underset{\text{Metastannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$

  Action of conc. NaOH on tin $\Rightarrow Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$

$SnCl_2$

- $SnCl_2.2H_2O$ on heating undergoes to form it's basic chloride Sn(OH).Cl. The anhydrous salt, therefore, be obtained by heating the hydrated salt in the presence of HCl vapour.
- Stannous chloride reduces mercuric chloride ($HgCl_2$) to a white precipitate of mercurous chloride (Hg_2Cl_2) which finally turns to metallic mercury (dark grey or black).

  $2Hg^{2+} + 3Cl^- + Sn^{2+} \rightarrow \underset{\text{Mercurous chloride}}{Hg_2Cl_2} + Sn^{+4}$

  $Hg_2Cl_2 + SnCl_2 \rightarrow \underset{\text{Black}}{2Hg\downarrow} + SnCl_4$

- **Mosaic gold** (SnS_2). Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold. It is prepared by heating mixture of tin fillings, sulphur and NH_4Cl in a retort.

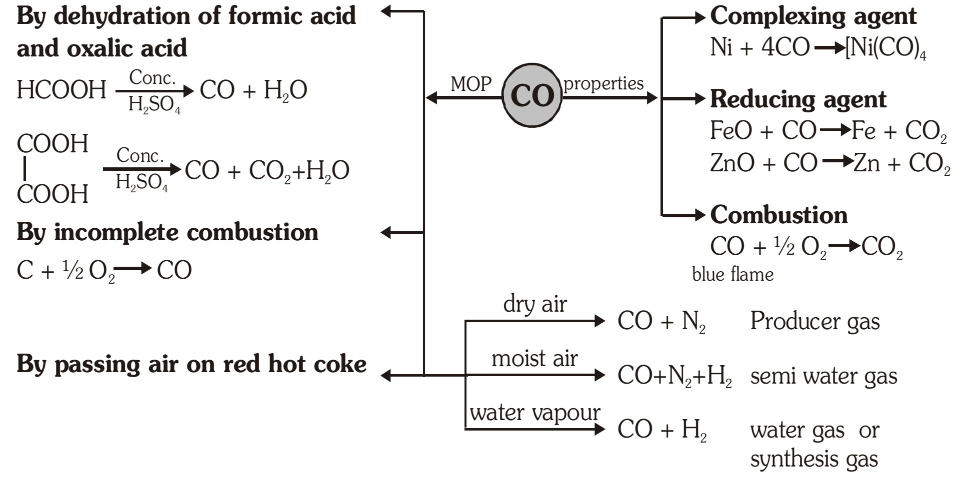
$$Sn + 4NH_4Cl \rightarrow (NH_4)_2SnCl_4 + H_2 + 2NH_3$$
$$2(NH_4)_2 SnCl_4 + 2S \rightarrow SnS_2 + (NH_4)_2 SnCl_6 + 2NH_4Cl$$

- **Tin Cry**. Tin metal when bent produces a cracking noise due to rubbing of metal crystals over one another.

CARBON MONOXIDE [CO]

Colorless odourless, tasteless, neutral, poisionous gas

$\boxed{C\equiv O}$



MOP ← CO → properties

By dehydration of formic acid and oxalic acid

$$HCOOH \xrightarrow[H_2SO_4]{Conc.} CO + H_2O$$

$$\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow[H_2SO_4]{Conc.} CO + CO_2 + H_2O$$

By incomplete combustion

$$C + ½\,O_2 \longrightarrow CO$$

By passing air on red hot coke

dry air	$CO + N_2$	Producer gas
moist air	$CO + N_2 + H_2$	semi water gas
water vapour	$CO + H_2$	water gas or synthesis gas

Complexing agent

$$Ni + 4CO \longrightarrow [Ni(CO)_4$$

Reducing agent

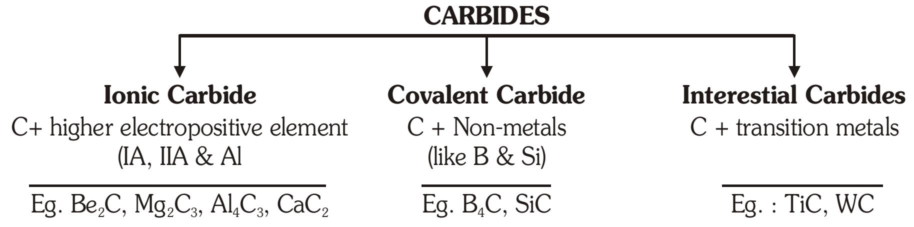
$$FeO + CO \longrightarrow Fe + CO_2$$
$$ZnO + CO \longrightarrow Zn + CO_2$$

Combustion

$$CO + ½\,O_2 \xrightarrow[\text{blue flame}]{} CO_2$$

CARBIDES

Binary compounds of carbon with other elements (except hydrogen) are known as carbides



CARBIDES

Ionic Carbide	**Covalent Carbide**	**Interestial Carbides**
C+ higher electropositive element (IA, IIA & Al	C + Non-metals (like B & Si)	C + transition metals
Eg. Be_2C, Mg_2C_3, Al_4C_3, CaC_2	Eg. B_4C, SiC	Eg. : TiC, WC

GROUP 15 ELEMENTS

NITROGEN FAMILY

1. Nitrogen and phosphorus are **non-metals**, arsenic and antimony **metalloids** and bismuth is a **typical metal**.

2. Except nitrogen all the elements show allotropy.

3. Bismuth hardly forms any compound in –3 oxidation state.

4. The only well characterised Bi (V) compound is BiF_5.

5. In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

(i) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

6. In case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid.

7. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

8. In case of nitrogen, only NF_3 is known to be stable.

9. Trihalides except BiF_3 are predominantly covalent in nature.

⇒ The only well characterised Bi (V) compound in BiF_5

⇒ All the oxidation states from +1 to + 4 tend to disproportionate in acidic solution :

exp: $3HNO_2 \longrightarrow HNO_3 + 2NO$

⇒ All the intermidiate oxidation states disproportionate into +5 and – 3

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

$$H_3PO_2 \xrightarrow{\Delta} H_3PO_4 + PH_3$$

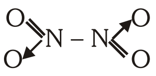
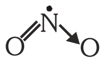
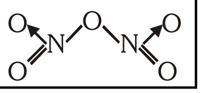
⇒ Hydride of 15th group elements :

$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$	Basic character
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$	Stability
$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$	Boiling Point
$PH_3 < AsH_3 < SbH_3 < NH_3$	Melting Point
$NH_3 > PH_3 > AsH_3 > SbH_3$	Bond Energy

⇒ Penta oxide of 15th group element is acidic. N_2O_3, P_2O_3 are acidic, As_2O_3, Sb_2O_3 are amphoteric with Bi_2O_3 is basic.

⇒ Trihalide of 15th group elements are covalent except BiF_3

STRUCTURE OF OXIDES OF NITROGEN AND PHOSPHORUS
NITROGEN

Oxide of Nitrogen	*Oxid. state*	*Physical appearance*	*Structure*
N_2O nitrous oxide	+1	Colourless gas	$N \equiv N \rightarrow O$
NO Nitric oxide	+2	Colourless gas	$N = O$
N_2O_3 Dinitrogen trioxide	+3	Blue colour solid	
N_2O_4 Dinitrogen tetraoxide	+4	Colourless solid	
NO_2 Nitrogen dioxide	+4	Brown gas	
N_2O_5 Dinitrogen pentaoxide	+5	Colourless solid	

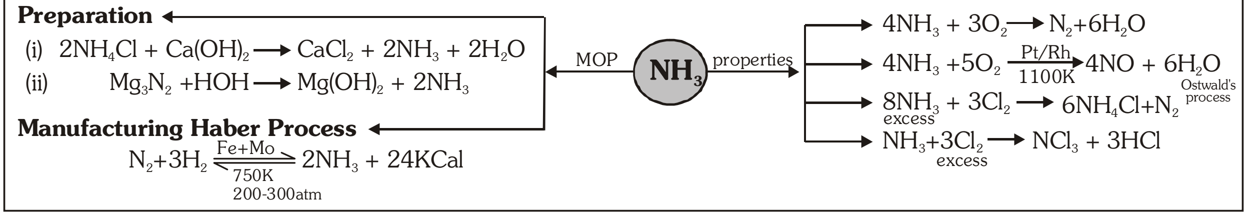
Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen oxide]	N_2O	+1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$	Blue solid, acidic blue liquid (–30ºC)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	Colourless solid/ liquid, acidic
Dinitrogen pentaoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

COMPOUNDS OF NITROGEN FAMILY

AMMONIA (NH_3)

Colorless, Pungent Smell, basic in nature liquified easily, uses as coolant



Preparation

(i) $2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$

(ii) $Mg_3N_2 + HOH \longrightarrow Mg(OH)_2 + 2NH_3$

Manufacturing Haber Process

$$N_2 + 3H_2 \underset{750K}{\overset{Fe+Mo}{\rightleftharpoons}} 2NH_3 + 24KCal$$

200-300atm

$4NH_3 + 3O_2 \longrightarrow N_2 + 6H_2O$

$4NH_3 + 5O_2 \xrightarrow[1100K]{Pt/Rh} 4NO + 6H_2O$ Ostwald's process

$\underset{excess}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

$NH_3 + \underset{excess}{3Cl_2} \longrightarrow NCl_3 + 3HCl$

NITRIC ACID (HNO_3)

Prepration :

Ostwald's process :

(i) $4NH_3(g) + \underset{\text{(From air)}}{5O_2(g)} \xrightarrow[500K,\,9bar]{Pt/Rh-gauge\ catalyst} 4NO(g) + 6H_2O(g)$

(ii) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

(iii) $3NO_2(g) + H_2O(\ell) \longrightarrow 2HNO_3(aq) + NO(g)$

Properties :

HNO_3, nitric acid was earlier called as aqua fortis (meaning strong water).

It usually acquires yellow colour. due to its decomposition by sunlight into NO_2.

It acts as a strong oxidising agent.

Reaction with $FeSO_4$:

$FeSO_4 + 8\ HNO_3 \rightarrow Fe_2(SO_4)_3 + 2NO + 4H_2O$

Reaction with non-metals :

Non-metals converted into highest oxyacids by hot and conc.

HNO_3. NO_2 gas is evolved (S to H_2SO_4; P to H_3PO_4; C to H_2CO_3; I_2 to HIO_3; As to H_3AsO_4; Sb to H_3SbO_4 and Sn to H_2SnO_3). Most of the metals except noble metals are attacked by HNO_3. It plays double role in action on metals, i.e., it acts as an acids as well as an oxidising agent.

Reaction with metals :

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

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

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

$Zn + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2+ metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O + metal nitrate
	Pb, Cu, Ag	NO + metal nitrate
Conc. HNO_3	Sn	$NO_2 + H_2SnO_3$ (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni, Cr, Al	rendered passive

PHOSPHINE (PH_3)

Preparation :

(i) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

(ii) $PH_4I + NaOH \longrightarrow NaI + H_2O + PH_3$

Laboratory preparation :

$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

Uses :

As Holme's signals in deep seas and oceans.
For the production of smoke screens.

Physical properties :

Colourless gas having smell of garlic or rotten fish, slightly soluble in water and slightly heavier than air.

Chemical properties :

(i) $2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$

(ii) $4PH_3 \xrightarrow{713K} P_4 + 6H_2$

(iii) $PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

Oxoacids of Phosphorus

Name	Formula	Oxidation state of Phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorus (Phosphinic)	H_3PO_2	+ 1	One P — OH Two P — H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+ 3	Two P — OH One P — H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P — OH Two P — H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P — OH Two P = O One P — P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+ 5	Three P — OH One P = O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P — OH Two P = O One P — O — P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+ 5	Three P — OH Three P = O Three P — O — P	phosphorous acid + Br_2, heat in a sealed tube

- Acidity of oxides and the solubility of 15 group oxides decreases from N to Bi. For example, N_2O_3, N_2O_5,P_4O_6,P_4O_{10}, As_4O_6 and As_4O_{10} are acidic and dissolve water forming acids. Sb_4O_6 and Sb_4O_{10} are weakly acidic and insoluble in water Bi_2O_3 is a basic oxide and is insoluble in water.
- On heating, phosphorus acid, H_3PO_3 decomposes into phosphine (PH_3) and phosphoric acid (H_3PO_4).

$$4H_3PO_3 \xrightarrow{\text{Heat}} 3H_3PO_4 + PH_3$$

$$2H_3PO_2 \xrightarrow{\text{Heat}} H_3PO_4 + PH_3$$

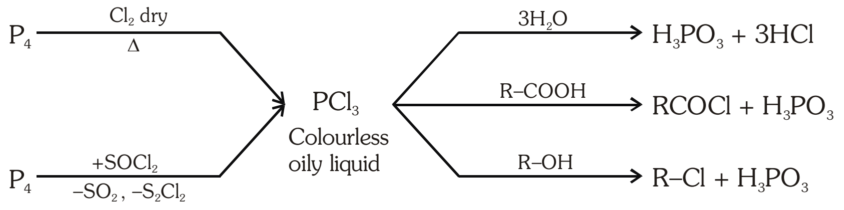
- **Holme's signals.** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2. The mixture burns with a bright luminous flame and it acts as a signal for approaching ships.

$$Ca_3P_2 + 6H_2O + 3Ca(OH)_2 + 2PH_3$$

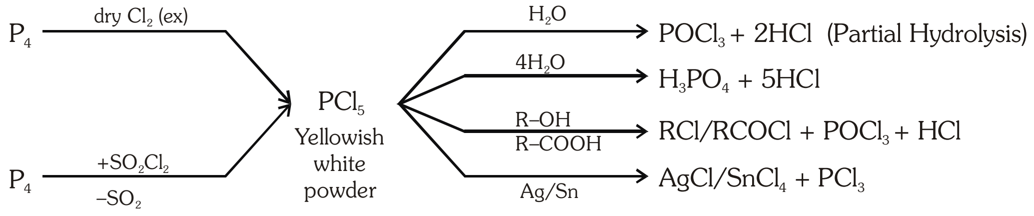
$$CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

- **Smoke screens,** involve the use of calcium phosphide, Ca_3P_2. The PH_3 gas obtained from Ca_3P_2 catches fire to give the needed smoke.
- **Phosphatic slag or Thomas slag or Basic slag** is obtained as a biproduct in the manufacture of steel and is probably a double salt of tricalcium phosphate and calcium silicate.

PCl_3



PCl_5



GROUP 16 ELEMENTS

OXYGEN FAMILY

1. Oxygen is the most abundant of all the elements on earth crust.

2. Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal.

3. Polonium hardly shows –2 oxidation state.

4. Reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent.

5. Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.

6. The well known monohalides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below : $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$

❐ The weakening of M–H bond with the increase in the size of M (not the electronegativity) explains the increasing acidic character of hydrides down the group.

❐ ***Halides* :** All these elements form a number of halides. The halides of oxygen are not very stable. Selenium does not form dihalides.

e.g. OF_2, Cl_2O_6, I_2O_5, etc.

SODIUM THIOSULPHATE $Na_2S_2O_3.5H_2O$

➢ **Preparation :**

(a) $Na_2SO_3 + S \xrightarrow{\text{Boil}} Na_2S_2O_3$

(b) $4S + 6NaOH \xrightarrow{\text{Boil}} Na_2S_2O_3 + 2Na_2S + 3H_2O$

(c) $2Na_2S + 3SO_2 \xrightarrow{\text{Boil}} 2Na_2S_2O_3 + S$

(d) Spring's reaction

$Na_2S + Na_2SO_3 + I_2 \xrightarrow{\text{Heat}} Na_2S_2O_3 + 2NaI$

➢ **Concentrated $Na_2S_2O_3$** does not give a white ppt. with $AgNO_3$. This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.

$$3S_2O_3^{2-} + Ag_2S_2O_3 \rightarrow \underset{\text{soluble}}{2[Ag(S_2O_3)_2]^{3-}}$$

Reaction with oxidizing agent :

(i) $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$

(ii) $2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$

This reaction forms the basis of iodometric estimation of $Cr_2O_7^{2-}$ and Cu^{2+} salts.

(iii) $3S_2O_3^{2-} + 2Fe^{3+} \Leftrightarrow \underset{\text{Violet}}{[Fe(S_2O_3)_2]^{-1}}$

The violet colour disappears quickly due to the reduction of ferric chloride by $S_2O_3^{2-}$ ions,

$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{+2} + S_4O_6^{2-}$

(iv) $2CuCl_2 + 2Na_2S_2O_3 \rightarrow 2CuCl + Na_2S_4O_6 + 2NaCl$

(v) $AuCl_3 + 2S_2O_3^{2-} \rightarrow AuCl + S_4O_6^{2-} + 2Cl^-$

$AuCl + 2S_2O_3^{2-} \rightarrow [Au\ (S_2O_3)_2]^{3-} + Cl^-$

➢ **Sulphur trioxides** (SO_3) is a white crystalline solid with melting point 290K and boiling point 318K.

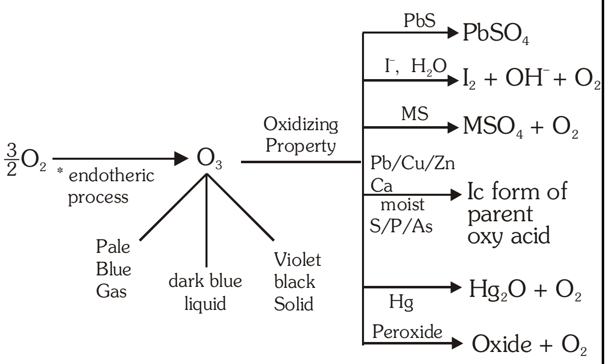
➢ SO_3 is prepared by the direct oxidation of SO_2 with atmospheric oxygen in presence of finally divided Pt or V_2O_5 at a pressure of 2 bar. and temperature 720K.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

➢ SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.

$SO_3 + H_2O \rightarrow H_2SO_4 + \text{heat}$

OZONE



* Fishy odour, Highly toxic.

Gases	**Absorbent**
O_3	Turpentine Oil/Oil of cinnamon.
NO	$FeSO_4$
SO_2	NaOH
CO	Cu_2Cl_2
O_2	Pyrogalol

HYDROGEN PEROXIDE

Preparation :

(i) $Na_2O_2 + H_2O$ (icecold) $\rightarrow NaOH + H_2O_2$

(ii) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

(Now a day conc. H_3PO_4 is used)

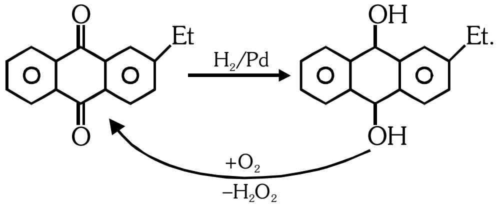
(iii) $2H_2SO_4 \rightarrow 2H^+ + 2HSO_4^-$

Anode : $2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$

Cathod : $2H^+ + e^- \rightarrow H_2$

$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$

(iv)



Properties :

Oxidizing property :

(i) $H_2O_2 \xrightarrow{PbS} PbSO_4$

(ii) $H_2O_2 \xrightarrow{BaSO_3} BaSO_4 + H_2O$

(iii) $H_2O_2 \xrightarrow{H_2S/HI} S/I_2 + H_2O$

(iv) $H_2O_2 \xrightarrow{F^{+2}/H^+} Fe^{+3} + H_2O$

(v) $H_2O_2 \xrightarrow{Cr^{+3}/OH^-} Cr^{+6} + H_2O$

Reducing property :

(i) $H_2O_2 \xrightarrow{Fe^{+3}/OH^-} Fe^{+2} + O_2$

(ii) $H_2O_2 \xrightarrow{Pb^+ \text{ Grids}} PbO$

(iii) $H_2O_2 \xrightarrow{Cl_2/Br_2} HX \downarrow + O_2$

(iv) $H_2O_2 \xrightarrow{MnO_4^-/OH^-} MnO_2 + O_2$

(v) $H_2O_2 \xrightarrow{MnO_4^-/H^+} Mn^{+2} + O_2$

(vi) $H_2O_2 \xrightarrow{Cr_2O_7^{2-}/H^+} Cr^{+2} + O_2$

- Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.

  $$2Hg + O_3 \rightarrow Hg_2O + O_2$$

  As a result of it, mercury looses it's meniscus and starts sticking to the glass.
- The bleaching action of ozone and H_2O_2 is permanent and is due to oxidation while that of SO_2 is temporary and is due to reduction.
- H_2O_2 is used to restore the colour of old lead paintings which have been blackened due to the formation of PbS by the action of H_2S present in the air.

  $$\underset{\text{Black}}{PbS} + 4H_2O_2 \rightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$$
- Antichlor action of H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl.

  $$H_2O_2 + Cl_2 \rightarrow 2HCl + O_2$$

$\Rightarrow NH_2.NH_2 + H_2O_2$ as rocket propellant.

Storage

H_2O_2 decomposes slowly on exposure to light.

$$2H_2O_2(\ell) \rightarrow 2H_2O(\ell) + O_2(g)$$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Acetanalide or Glycerol or Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

SULPHURIC ACID (H_2SO_4)

It is also known as oil of vitriol and king of chemicals.

Manufacture of sulphuric acid :

Lead chamber process :

The various steps involved are :

(a) Production of SO_2 : By burning S or iron pyrites.

$$S + O_2 \xrightarrow{\Delta} SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(b) Production of catalyst : Oxides of nitrogen.

$$2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_3$$

$$2HNO_3 \xrightarrow{\Delta} H_2O + NO + NO_2 + O_2$$

(c) Reaction in lead chamber

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$2NO + O_2 \longrightarrow 2NO_2 \text{ (used again)}$$

Contact process :

The steps involved are :

(a) Production of SO_2 : It is produced by burning sulphur or iron pyrites and purified by treating with steam to remove dust particles.

(b) Conversion of SO_2 to SO_3 : It is done in container or catalyst chamber after being pre-heated to 450°C.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + x \text{ cal}$$

Catalyst : Formerly, platinised asbestos was used which is costly and easily poisoned. These days V_2O_5 is used.

(c) SO_3 is absorbed by conc. H_2SO_4 and then water is added to produce the acid of desired concentration.

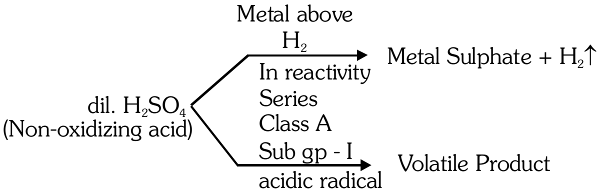
$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

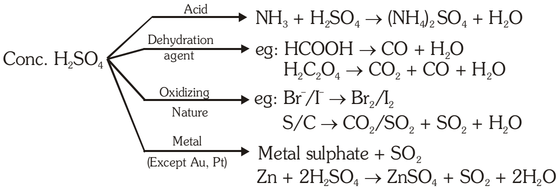
$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Properties : Its specific gravity is 1.8 and it is 98% by weight.

It is strong dibasic acid.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$





Uses :

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

GROUP 17 ELEMENTS

1. The electron affinity values (in KJ mol^{-1}) for 17 group element are given below :

F	Cl	Br	I
333	349	325	296

2. All halogens are coloured. For example, F_2 has yellow gas, Cl_2 greenish yellow gas, Br_2 red liquid and I_2 violet coloured solid.

3. They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is $F_2 > Cl_2 > Br_2 > I_2$

4. In general, a halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \text{ (X = Cl, Br or I)}$$
$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \text{ (X = Br or I)}$$
$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

5. **Reaction with water :**

$$2F_2(g) + H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$
$$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$$

(where X = Cl or Br)

$$4I^-\,(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(l)$$

6. Halogens form many oxides with oxygen but most of them are unstable.

7. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.

8. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF6 from spent nuclear fuel.

9. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br.

10. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

❒ ***Reactivity :*** All halogens are chemically very reactive elements. This is due to their low dissociation energy and high EN. Fluorine is the most reactive and iodine is the least reactive halogen.

INTERHALOGEN COMPOUNDS

❒ These compounds are regarded as halides of more electropositive (i.e. less elecronegative) halogens.

❒ Types of interhalogen compound :

AB type : ClF, BrF, BrCl, ICl, IBr

AB_3 type : ClF_3, BrF_3, ICl_3

AB_5 type : BrF_5, IF_5

AB_7 type : IF_7

HYDROGEN HALIDES

Bond strength, bond length and thermal stability :

- Since size of halogen atom increases from F to I down the group, bond length of H – X bond increases down the group.

  $\therefore$ reactivity and acidic character $\uparrow$.

  HF < HCl < HBr < HI.

- Bond strength is inversely, proportional to bond length i.e., larger the bond length, lower the bond strength is

  HF > HCl > HBr > HI.

- Higher the bond dissociation energy. greater will be thermal stability. Thus, thermal stability follows the order.

  HF > HCl > HBr > HI.

REDUCING CHARACTER :

The reducing character of hydrogen halides increases down the group as

HF < HCl < HBr < HI.

$$2HX \longrightarrow H_2 + X_2$$

A less thermally stable compound has more tendency to release hydrogen easily and show greater reducing property.

ACIDIC STRENGTH :

The acidic strength of these acids increases down the group and hence follows the order.

HF < HCl < HBr < HI.

Since H–I bond is weakest, it can be easily dissociated into H^+ and I^- ions while HF with greater bond dissociation energy can be dissociated with maximum difficulty.

HYDROCHLORIC ACID, (HCl)

Preparation : By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

By the direct combination of hydrogen and chlorine.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Sunlight}} 2HCl_{(g)}$$

Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.

Properties : Hydrogen chloride is a covalent compound but when dissolved in water it ionizes to form hydrogen ions and chloride ions.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Thus anhydrous HCl does not show acidic properties. Only aqueous HCl or in presence of moisture, HCl behaves as an acid.

Metal + Hydrochloric acid ⟶ Metal chloride + Hydrogen

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2\uparrow$$

It react with bases and basic oxides or hydroxides to form their respective chlorides and water.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

It reacts with metal carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites, etc, to form their respective chlorides.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

It reacts with silver nitrate and lead nitrate solution to form white precipitates.

$$AgNO_3 + HCl \longrightarrow HNO_3 + AgCl\downarrow$$

Reducing property :

HCl is a strong reducing agent.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

Uses :

In the production of dyes, paints, photographic chemicals, etc.

Used in the preparation of chlorides, chlorine, aqua-regia, etc.

Used as a laboratory reagent.

PSEUDO HALIDES

Pseudo halides are uninegative groups which show certain characteristics of halide ions. For example Cyanide (CN^-), Cyanate (OCN^-), Thiocyanate (SCN^-), Selencyanate ($SeCN^-$), Azide (N_3^-), Aziothio carbonate ($SCSN_3^-$) and isocyanate (ONC^-).

CHLORINE (Cl_2)

Preparation : By oxidation of conc. HCl.

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$$

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture :

Weldon's process : By heating pyrolusite with conc. HCl.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

Deacon process :

$$2HCl + O_2 \xrightarrow{CuCl_2} Cl_2 + H_2O$$

Properties : It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate $Cl_2.8H_2O$.

Bleaching action and oxidising property

(i) $Cl_2 + H_2O \longrightarrow HOCl + HCl$

$HOCl \longrightarrow HCl + [O]$

Coloured matter + nascent [O] → Colourless matter

The bleaching action of chlorine is permanent and is due to its oxidising nature.

(ii) $SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$

Action of hydrogen :

$$H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{U.V.light}} 2HCl$$

Displacement reactions :

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

Action of NaOH :

$$\underset{\text{(cold \& dil.)}}{2NaOH} + \underset{\text{dry}}{Cl_2^0} \rightarrow NaCl^{-1} + \underset{\text{sodium hypo chlorite}}{NaOCl^{+1}} + H_2O$$

$$\underset{\text{(hot and conc.)}}{6NaOH} + \underset{\text{(dry)}}{3Cl_2^0} \rightarrow 5NaCl^{-1} + \underset{\text{sodium chlorate}}{Na\overset{+5}{Cl}O_3} + 3H_2O$$

Addition reactions :

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

$$CO + Cl_2 \longrightarrow COCl_2$$

➢ **Test for chlorine :**

(a) It is a greenish yellow gas with irritating smell.

(b) It turns starch iodide paper blue.

(c) It bleaches litmus paper and indigo solution.

NOTE

- **Action of silica and glass** : Strong solution of HF attacks glass readily forming silicon fluoride which gives complex fluosilicic acid, H_2SiF_6 with excess HF.

  $SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O$

  $SiF_4 + H_2F_2 \rightarrow H_2SiF_6$

  This is called etching of glass.

- Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI_3.

  $$KI + I_2 \rightarrow KI_3$$

  The solution behaves as a simple mixture of KI and I_2.

OXY-ACID

- The acidic strength of the oxoacids of halogen decreases in the following order.

  $HClO_4 > HClO_3 > HClO_2 > HClO$

  The chlorine oxyanion in which the central atoms has highest oxidation number will have maximum number of oxygen atoms for participation in the extension of the π-bond. Thereby the charge on the ion is delocalized which greatly stabilizes the ion and thus decreases its tendency to accept a proton i.e., causes the ion to be very weak base with the result that the strength of the acid increases.

- The acidity of oxoacids of different halogens having the same oxidation number decreases with the increases in atomic numbers of the halogen

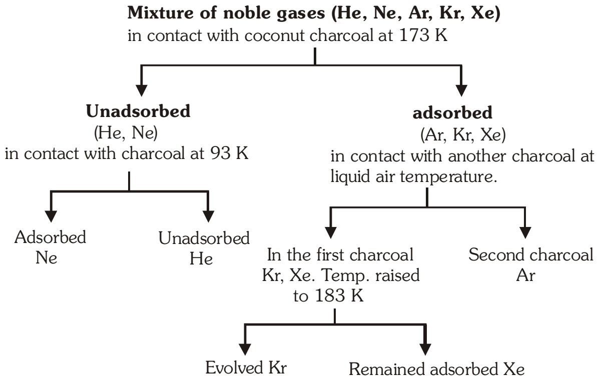
  $$HClO > HBrO > HIO$$

GROUP 18 ELEMENTS

1. Relative Abundance:
   Ar > Ne > Kr > He > Xe > Rn
2. Melting and Boiling point:
   Rn > Xe > Kr > Ar > Ne > He
3. He has the lowest boiling point among all element
4. Noble gases are monoatomic, colourless, odourless, spraingly soluble in water and diffusing through most commonly used laboratry materials.
5. $O_2[PtF_6]$ is the first noble gas compound.
6. Ar, Kr and Xe form clathrate compound when pass in ice with high pressure.
   $A.6H_2O$ (A = Ar/Kr/Xe)

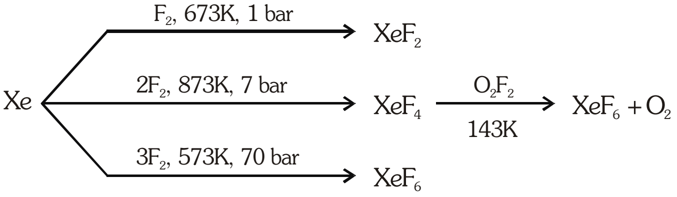
NOBLE GAS

- ➢ In Dewar's method, the separation of noble gases is summerized below



- ➢ The viscosity of He is extermely low, about 1/100th of hydrogen gas.

Prepration of Xe-Fluoride:



Properties:

Fluoride donor: Eg. $XeF_2 + \underset{(M=As/Sb/P)}{MF_5} \longrightarrow [XeF_4]^+ [MF_6]^-$

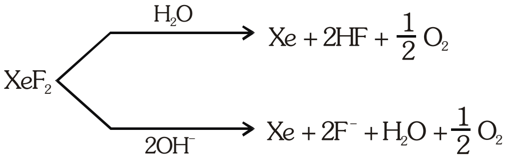
Fluoride acceptor: Eg. $XeF_6 + \underset{(M=Na/K/Rb/Cs)}{MF} \longrightarrow M^+[XeF_7]^-$

Fluorinating agents: Eg. $XeF_4 \xrightarrow{SF_4/Pt} PtF_4 / SF_6 + Xe$

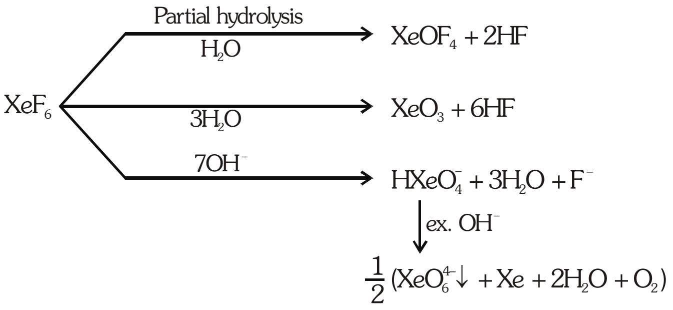
$XeF_2 + NO \longrightarrow 2NOF + Xe$

Reaction with SiO_2 : Eg. $2XeF_6 + SiO_2 \longrightarrow SiF_4 + XeOF_4$

Hydrolysis:



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



CHAPTER 5

COORDINATION CHEMISTRY

Addition compound

(two or more simple salt combining with fixed proportion of mass)

Double salt

* Loose their idenity in aqueous solution

eg. $KCl.MgCl_2.6H_2O$ carnalite salt

$K_2SO_4^-.Al_2(SO_4)_3.24H_2O$

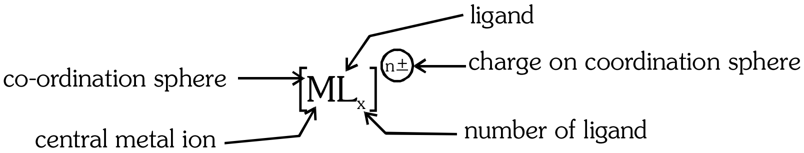
potash alum

C-ordination compound

* Retain their indenity in aqeous solution

eg. $K_4[Fe(CN)_6]$ Potassium hexacynidoferrate (II)

REPRESENTATION OF COMPLEX COMPOUND



Co-ordination number = Number of electron pair accepted by central metal ion.

LIGAND

Chemical species which can donates electron pair.

Calssification of the basis of denticity

(Denticity : = Number of electron pair donated by central metal atom or ion)

Monodentate (denticity = 1) :

eg. H^-, X^-, Py, N_2, N^{3-}, N_2H_4 etc.

Bidentate (denticity = 2) :

eg. en, pn, bn, ox^{2-}, $acac^{-1}$, gly^{-1}, dmg^{-1}

Polydentate (denticity = >2) :

eg. dien, $imda^{-2}$, trien, nta^{3-}, $EDTA^{4-}$

Ambidentate : Ligand which have more than one donor site but at the time of donation only atom can donate electron pair.

eg. : (CN^-, NC^-), (NO_2^-, ONO^-), (SCN^-, NCS^-), (OCN^-, NCO^-), $(S_2O_3^{2-}, SO_2S^{2-})$

Flexidentate ligand : Show more than one type of denticity.

eg. : CO_3^{2-}, SO_4^{2-}, CH_3COO^-

Note : Bidentate and Polydentate are also called chelating ligand.

* **Calssification on the basis of electron donating and accepting tandency**

Classsical ligand : H_2O, NH_3 etc.

Non-calssical ligand : CN^-, NO^+, NO, CO, PPh_3 etc

⇒ π-donor ligand ⇒ C_2H_4, C_2H_2 etc.

BONDING IN COORDINATION COMPOUND

Effective atomic number & Sidgwick rule :

Total number of electron present on central metal atom or ion after accepting the electron pair from ligand.

$$K_4[\overset{+2}{Fe}(CN)_6]$$

EAN = 26 – (+2) + 6(2) = 36

⇒ If EAN value is equal to atomic number of Noble gas then complex follow sidgwick rule of EAN.

⇒ In carbonyl complex if EAN value = Atomic number of Noble gas then carbonyl complex is more stable.

eg.	$[V(CO)_6]$	$[Cr(CO)_6]$	$[Mn(CO)_6]$
	act as oxidising agent	stable complex	act as reducing agent

⇒

Brown ring complex	37
Sodium nitroprusside	36
Zeise's Salt	84
$Mn_2(CO)_{10}$	36
$Fe_2(CO)_9$	36
$Co_2(CO)_8$	36

WERNER'S CO-ORDINATION THEORY :

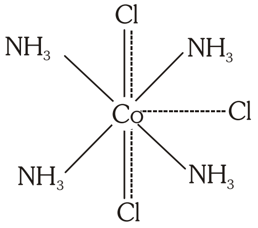
⇒ Metals possesses two types of valencies PV & SV.

⇒ PV is non-directional, represent by .... (doted line) is satisfied by negative charge species.

⇒ SV is directional, represent by ______ (solid line) and satisfied by negative or neutral species.

⇒ Now a days primary valency and secondary valency is consider as oxidation & co-ordination number respectively.

eg. $CoCl_3.4NH_3$
PV = 3, SV = 6
C.N. = 6, Oxidation state = +3



VBT :

⇒ Metal provoide hybridised vacant orbital for the acceptence of lone pair from ligand.

⇒ Hybridisation, shape and magnatic behaviour of complex depends upon the nature of ligand.

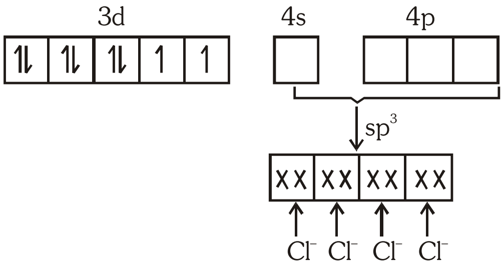
⇒ Strong field ligand pair up the unpaired e^- of central metal atom where as weak field ligand does not.

⇒ If unpaired e^- present in complex then complex is paramagnatic. If unpaired e^- is absent then diamagnatic.

eg. CN-4

$[NiCl_4]^{2-}$

NI^{+2} in $[NiCl_4]^2$



→ sp^3

→ Tetrahedral

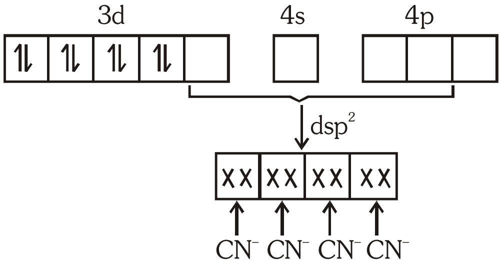
→ Paramagnatic

→ Outer Orbital complex

→ $\mu = \sqrt{8}$ BM

$[Ni(CN)_4]^{2-}$

NI^{+2} in $[Ni(CN)_4]^{2-}$



→ dsp^2

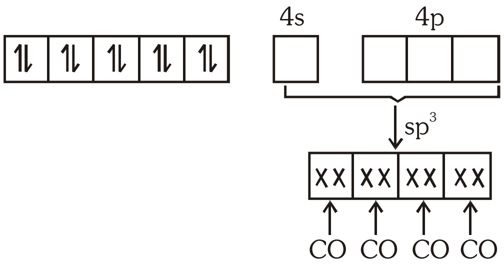
→ Square planar

→ Diamagnatic

→ Inner Orbital complex

$[Ni(CO)_4]$

NI^{+2} in $[Ni(CO)_4]$



→ sp^3

→ Tetrahedral

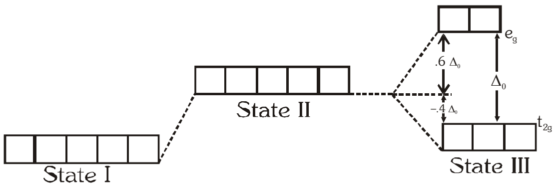
→ Diamagnatic

→ Outer Orbital complex

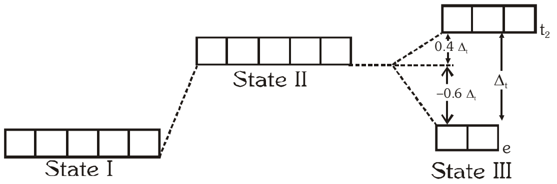
CRYSTAL FIELD THEORY

Crystal Field Theory : In the electric field of these negative charges, the five d orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

In octahedral :



In tetrahedral :



Orbitals which have same energy in a subshell are known as degenerate orbitals.

- **Series which shows the relative strength of ligands :**

  I^-(weakest) $< Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 <$ en $< CN^- <$ CO(strongest)

- **Crystal field stablisation energy (CFSE) :**

(i) For octahedral CFSE $=\left[-0.4\left(n_{t_{2g}}\right)+0.6\left(n_{eg}\right)\right]\Delta_0$ + Paring energy **(P.E.)** $\times x$

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals
n_{eg} = number of electron in eg orbitals
x = number of electron pair

(ii) For tetrahedral CFSE

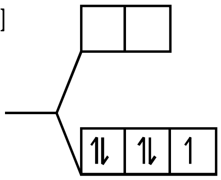
$=\left[-0.6\left(n_e\right)+0.4\left(n_{t_2}\right)\right]\Delta_t$ +Paring energy **(P.E.)** $\times x$

where n_{t_g} = number of electron in t_2 orbitals
n_e = number of electron in e orbitals
x = number of electron pair

⇒ Follow Hund's Pauli & Aufbau rule.

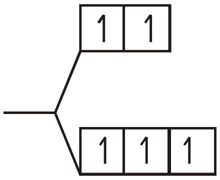
CN-6

eg. $K_3[Fe(CN)_6]$
Fe^{+3}
CN^- SFL
$\Delta_0 > P$



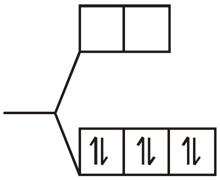
d^2sp^3, Octahedral
low spin complex,
inner orbital complex,
paramagnatic
$\mu=\sqrt{3}$ BM

$[Fe(F)_6]^{3-}$
Fe^{+3}
F-WFL
$\Delta_0 < P$



sp^3d^2, Octahedral
high spin complex,
outer orbital complex,
paramagnatic
$\mu=\sqrt{35}$ BM

$[IrF_6]^{3-}$
Ir^{+3}
$\Delta_0 > P$



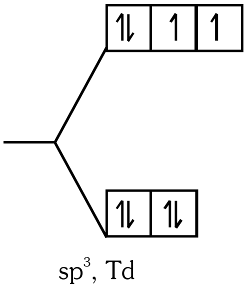
d^2sp^3, Octahedral
low spin complex,
inner orbital complex,
diamagnatic

Exeption :

$[Co(OX)_3]^{3-}$	d^2sp^3	diamagnatic
$[Co(H_2O)_6]^{3+}$	d^2sp^3	diamagnatic
$[NiF_6]^{2-}$	d^2sp^3	diamagnatic
$[Cr(NH_3)_6]^{2+}$	sp^3d^2	paramagnatic
$[Mn(NH_3)_6]^{2+}$	sp^3d^2	paramagnatic
$[Fe(NH_3)_6]^{2+}$	sp^3d^2	paramagnatic
$[CoL_6]^{4-}$ (L = NO_2^-/CN^-)	d^2sp^3	paramagnatic

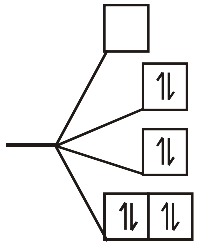
CN-4 :

eg. $[NiCl_4]^{2-}$



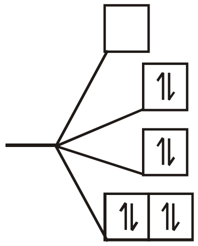
sp^3, Td
outer orbital complex,
paramagnatic
high spin complex

$[Ni(CN)_4]^{2-}$



dsp^2, sq. planar
inner orbital complex,
diamagnatic
low spin complex

$[AuCl_4]^-$



ds^2, sq. planar
inner orbital complex,
diamagnatic
low spin complex,

Exception :

1. d^3s hybridisation, Td, diamagnetic, inner orbital complex eg.

$$MnO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}, CrO_2Cl_2, CrO_2F_2, VO_4^{3-}$$

2. Tranference of electron
eg. Cu^{+2} in CN–4 with L
(where L = NO_2^- / CN^-/ NH_3 etc.)

➢ **Factor affecting splitting**

(i) Strength of ligand
(ii) Oxidation state of central metal ion
(iii) Transition series (d-series)
(iv) Geometry (number of ligands).
(v) Chelation

Colour of complexes

Colour

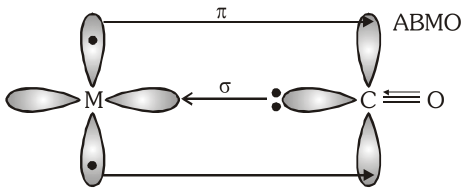
d-d tranistion	Charge transfer
→ d^1-d^9 complex can show colour.	→ Metal-metal charge transfers or metal ligand charge transfers
→ Complementry colour of absorb colour is observe	→ MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$
eg. : $[T_1(H_2O)_6]^{3+}$, $[Ni_1(H_2O)_6]^{2+}$ $[Cu(NH)_4]^{2+}$	brown ring complex sodium nitroprusside purssian blue, turnbull's blue

ORGANOMETALLIC COMPOUDS

Compounds in which the less E.N. (Ge, Sb, B, Si, P, As) central metal atoms are bonded directly to carbon atoms are called organometallic compounds.

- **σ-bonded compounds** formed by nontransition elements.
  R–Mg–X, $(CH_3–CH_2)_2Zn$, Ziegler natta catalyst, etc.
- **π-bonded organometallic compounds** are generally formed by transition elements e.g. Zeise's salt, ferrocene, dibenzene chromium, etc.
- **σ-and π-bonded organometallic compounds :** Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. $Ni(CO)_4$, $Fe(CO)_5$etc.

Synergic bonding



IUPAC nomenclature of complex compounds :

(A) For anionic complex (like $K_4[Fe(CN)_6]$)
Common name of normal cation (without numeral prefix) + name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + Ox. St (in roman number).
eg. : Potassium hexacyanoferrate (II)

(B) For cationic comlex like $[Cu(NH_3)_4]SO_4$
Name of ligands (with numeral prefix) + Common name of CMI + Ox. St (In roman number) + Name of anion (without numeral prefix)
eg. : Tetraammine copper (II) sulphate.

(C) For neutral complex (like $[Fe(CO)_5]$)
Name of ligands (with numeral prefix)
+ Common name of CMI + Ox. St.
(In roman number)
eg. : Pentacarbonyl iron (O)

(D) Rule same just apply alphabetical order when write the name of ligands.
e.g. $[Pt(NH_3)_2Cl_2]$
Diamminedichloroplatinum (II)

STRUCTURAL ISOMERISM

(i) **Ionisation isomerism :** Counter ion as a ligand & ligand act as counter ion.

$[Co\ (H_2O)_5Cl]\ SO_4 \leftrightarrow [Co(H_2O)_5SO_4]\ Cl$

(ii) **Hydrate isomersim :** Number of water molecule inside & outside the co-ordinate sphere are different.

$[Cr(H_2O)_6]Cl_3 \leftrightarrow [Cr\ (H_2O)_5\ Cl]\ Cl_2.H_2O \leftrightarrow [Cr\ (H_2O)_4\ Cl_2]\ Cl.2H_2O$

(iv) **Linkage :** Exihibit when ambidentate ligand is present in co-ordination sphere.

$[NC \rightarrow Ag \leftarrow CN]^- \leftrightarrow [NC \rightarrow Ag \leftarrow NC]^- \leftrightarrow [CN \rightarrow Ag \leftarrow NC]^-$

(iv) **Co-ordination isomerism :** Exihibit when both are cationic & anionic complex

$[Pt(NH_3)_4]\ [PtCl_4] \leftrightarrow [Pt(NH_3)_3Cl]\ [Pt(NH_3)Cl_3]$

STEREO ISOMERISM

STEREO ISOMERISM IN CO-ORDINATION COMPOUND

CN-4

* Square planar complex does not show optical isomerism.

* Square planar complex show optical activity if the co-ordinated ligand having chiral center.

* Square planar complex $[Ma_2b_2]^{n^\pm}$, $[Ma_2bc]^{n^\pm}$, $[Mabcd]^{n^\pm}$, $[M(AB)cd]^{n^\pm}$, $[M(AB)(CD)]^{n^\pm}$ show geometrical isomerism

* $[Mabcd]^{n^\pm}$ form two cis and one trans.

* Tetrahedral complex $[Mabcd]^{n^\pm}$, $[M(AB)cd]^{n^\pm}$ $[M(AB)(CD)]^{n^\pm}$ show optical isomerism

* Tetrahdral complex does not show geometrical isomerism.

CN-6

NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC COMPLEXES

Formula	Number of stereoisomers	Pairs of Enantiomers	Number of G.I.
Ma_4b_2	2	0	2
Ma_4bc	2	0	2
Ma_3b_3	2	0	2
Ma_3b_2c	3	0	3
Ma_3bcd	5	1	4
$Ma_2b_2c_2$	6	1	5
Ma_2b_2cd	8	2	6
Ma_2bcde	15	6	9
Mabcdef	30	15	15
M(AA)(BC)de	10	5	5
M(AB)(AB)cd	11	5	6
M(AB)(CD)ef	20	10	10
$M(AB)_3$	4	2	2

Note: Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.

IMPORTANT NOTES

d-BLOCK (Transition Elements)

DEFINITION

Trasition elements are those d-block elements which has partialy filled (n–1)d subshell either in their ground state or in their stable oxidation states. Therefore Zn, Cd & Hg – are d-block elements but not transition elements.

GENERAL ELECTRONIC CONFIGURATION

$ns^{0-2}\ (n-1)d^{1-10}$

$$\text{Exceptions}\begin{cases} Cr = 4s^1\ 3d^5 \\ Cu = 4s^1\ 3d^{10} \end{cases},\ Pd = 5s^0 4d^{10}$$

TRANSITION SERIES

1st	3d series	Sc_{21} — Zn_{30}	9 + 1 = 10
2nd	4d series	Y_{39} — Cd_{48}	9 + 1 = 10
3rd	5d series	La_{57}, Hf_{72} — Hg_{80}	9 + 1 = 10
4th	6d series	Ac_{89}, Unq $_{104}$— Uub_{112}	9 + 1 = 10

ATOMIC RADIUS

3d series Sc > Ti > V> Cr >Mn ≥Fe ≃ CO ≃ Ni≤Cu < Zn

In a group 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f electron. (Lanthanide contraction)

$$\boxed{3d < 4d \simeq 5d}$$

$$\text{e.g.: } Ti < Zr \simeq Hf \left| \begin{matrix}\text{Smallest radius} - Ni \\ \text{Largest radius} - La\end{matrix}\right.$$

Melting point :s-block metals < d-block metals

In a series on increasing number of unpaired e^- mpt increases and therefore m.p. increase upto Cr then decreases.

Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn

↓ Half filled d^5 ∴ weak metallic bond

↓ Fully filled d^{10} ∴ weak metallic bond

$$\text{Melting point}\left| \begin{matrix} Zn > Cd > Hg \\ Cu > Ag \le Au \end{matrix}\right. \quad \text{(data based)}$$

E.N. Exception Zn < Cd < Hg

Density : s-block metals < d-block metals.

3d series

Sc < Ti < V < Cr < Mn < Fe < Co ≤ Ni < Cu > Zn

Density in a Group 3d < 4d << 5d

Metallic character : They are solid, hard, ductile, malleable, good conductor of heat and electricity and exhibit metallic lusture, high tensile strength. Hg is liquid

$$\text{Electrical conductor } \underbrace{Ag > Cu > Au}_{d-block} > \underset{p-block}{Al}$$

OXIDATION STATE

Transition elements exhibit variable oxidation state due to small energy difference of ns and (n–1)d electrons.

- Sc(+3) and Zn(+2) exhibit only one oxidation state
- Common oxidation state is +2 & +3
- In 3d series highest oxidation state is +7 (Mn)
- In d-block series highest oxidation state is +8 (Os, Ru)
- In carbonyl compound the zero oxidation state of metals is stablize by synergic effects.
- Their higher oxidation states are more stable in fluoride and oxides.
- Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.

  eg. stable fluoride in higher oxidation state of Mn is MnF_4 while oxide is Mn_2O_7

⇒ Mn show maximum number of oxidation state (+2 to +7) among 3d series.

⇒ Beyong Mn trihalide are not observe except FeX_3 (X = Cl/Br/I) & CoF_3

⇒	V_2O_3 basic	V_2O_4 basic	V_2O_5 amphoteric
⇒	CrO basic	Cr_2O_3 amphoteric	CrO_3 acidic
⇒	MnO basic	MnO_2 amphoteric	Mn_2O_7 acidic

⇒ CuI_2 does not exist

$$CuI_2 \longrightarrow CuI + \frac{1}{2} I_2$$

⇒ In aqueous Cu^+ disproportinated into Cu & Cu^{+2}.

In p-block lower oxidation states of heavier elements are more stable while in d-block heavier element, higher oxidation state are more stable.

eg. In VIB gp Mo(+6) & W(+6) are more stable than Cr(+6)

MAGNETIC PROPERTY

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using formula $\mu = \sqrt{n(n+2)}$ Bohr magneton. (n is number of unpaired e^-.)

If n is 1 μ = 1.73 BM n is 2 μ = 2.84 BM n is 3 μ = 3.87 BM
n is 4 μ = 4.90 BM n is 5 μ = 5.92 BM

Substances that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block element and ions having d^0 and d^{10} configuration are diamagnetic.

COLOUR

Colour in transition metal ions is associated with d–d transition of unpaired electron from t_{2g} to e_g set of energies. This is achieved by absorption of light in the visible spectrum, rest of the light is no longer white.

Colourless – Sc^{3+}, Ti^{4+}, Zn^{2+} etc

Coloured – Fe^{3+} yellow , Fe^{2+} green, Cu^{2+} blue, Co^{3+} blue etc

ALLOYS

Solid mixture of metals in a definate ratio

(15% difference in metallic radius)

They are hard and having high melting point.

eg. Brass (Cu + Zn)
Bronze (Cu + Sn) etc.

Hg when mix with other metals form semisolid amalgam except Fe,Co,Ni, Pt.

Interstitial compounds :

When less reactive nonmetals of small atomic size eg. H, B, N, C, Trapped in the interstitial space of transition metals, interstitial compounds are formed, like :- TiC, Mn_4N, Fe_3H etc.

They are nonstoichiometric compounds.

They have high melting point than metals.

They are chemically inert.

CATALYTIC PROPERTIES

Most of the d-block compounds act as catalyst due to their variable oxidation state or complex formation tendency or adsorption on their surface. Example :

Contact proecess = V_2O_5

Haber process = $Fe_2O_3 + Al_2O_3 + K_2O$

Phenton reagent = $FeSO_4 + H_2O_2$

Decomposition of $KClO_3$ = MnO_2

Ostwald process = Pt/Rh

Zeigter Natta = $TiCl_4 + (C_2H_5)_3$ Al

Hydrogenation of Alkene = Ni/Pd

Wilkinson catalyst = RhCl + PPh_3

Important reactions of d-block elements

(a) $Cu^{2+} + 4I^- \longrightarrow Cu_2I_{2(s)} + I_2$

(b) $CuSO_4 + \underset{Excess}{KCN} \longrightarrow K_2SO_4 + \underset{Unstable}{Cu(CN)_2}$

$2Cu(CN)_2 \longrightarrow 2CuCN + \underset{Cyanogen}{(CN)_2}$

$CuCN + 3KCN \longrightarrow K_3[Cu(CN)_4]$

(c) $Cu \xrightarrow[\text{moist air}]{H_2O+CO_2} \underset{green}{CuCO_3.Cu(OH)_2}$

$Au \xrightarrow[(3HCl+HNO_3)]{\text{Aqua regia}} H[AuCl_4] + NOCl + H_2O$

(d) $AgNO_3(s) \xrightarrow{\text{Heating}} Ag + NO_2 + \frac{1}{2}O_2$

$AgCO_3(s) \xrightarrow{\text{Heating}} Ag + CO_2 + \frac{1}{2}O_2$

(e) $CuSO_4.5H_2O \xrightarrow{100°C} \underset{\text{light greenish blue}}{CuSO_4.H_2O} \xrightarrow{230°C} \underset{Colourless}{CuSO_4}$

$\xrightarrow{720°C} CuO + SO_2 + \frac{1}{2}O_2$

(f) $Hg_2Cl_2 + NH_4OH \longrightarrow Hg\begin{matrix}\diagup NH_2\\ \diagdown Cl\end{matrix} + \underset{Black}{Hg}$

(g) $NO_3^- / NO_2^- \xrightarrow{FeSO_4+H_2SO_4} \left[Fe(H_2O)_5 NO^+\right]SO_4$

Brown ring complex

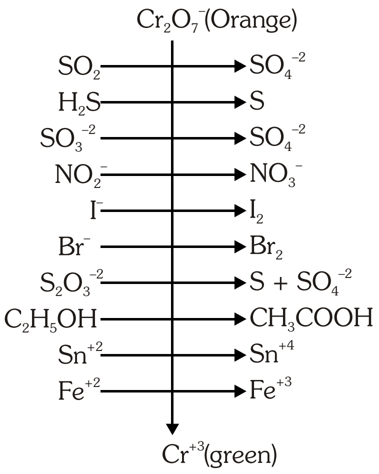
(h) $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

Photographic complex

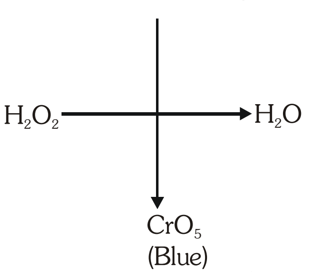
(i) Chemical volcano :

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

➢ Reactions of $Cr_2O_7^{-2}$:

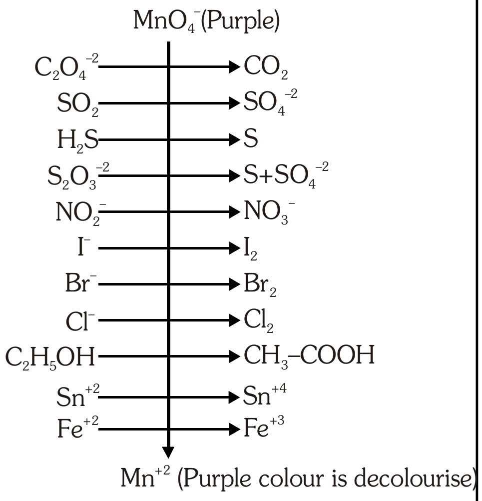


$\underset{Yellow}{CrO_4^{-2}} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{(Orange)}{Cr_2O_7^{-2}}$

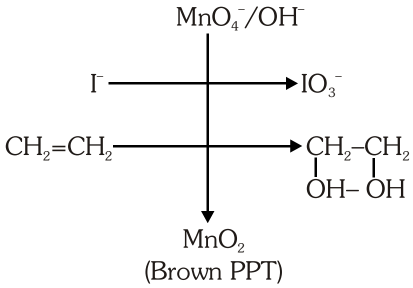


(Stablize in the presence of organic solvent such as pyridine etc.)

➢ Reaction of MnO_4^-



$\underset{purple}{MnO_4^-} \xrightarrow[\text{Basic solution}]{\text{Strongly } \Delta} \underset{green}{MnO_4^{-2}}$



IMPORTANT NOTES

CHAPTER 7

METALLURGY

- Bunch of process to extract metal from their respective ore

Ore : Minerals from which metal can be extracted economically :

Types of metallurgy

- **Pyrometallurgy**
  - Temp. is involved
  - For heavy metals
  - Fe, Zn, Cu, Hg, Sn, etc
- **Hydrometallurgy**
  - Solution is involved
  - According to E.C.S.
  - For metals placed below H
  - Cu, Ag, Au
- **Electro metallurgy**
  - Electric involved
  - IA, IIA, Al

Metallurgical process :

1. **Mining :** Ore obtain in big lumps (less reactive)
2. **Crushing/grinding/pulverization :** big lumps convert into powder (more reactive)
3. **Concentration :** To remove matrix/gangue from ore

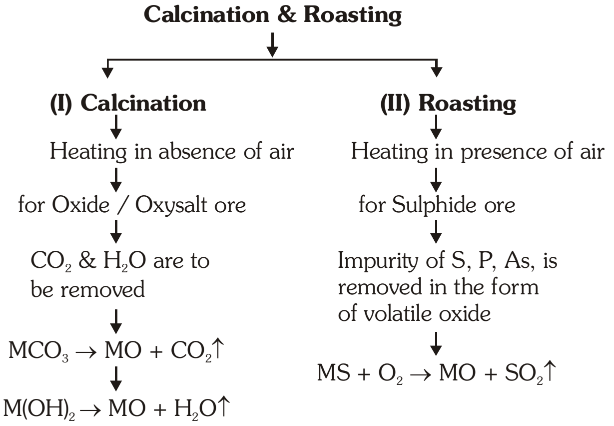
   To increase the concenration of ore particle in ore sample.

Concentration

- **(I) Physical process**
  - (a) Gravity separation /Hydraulic washing /Levigation
    - Based on difference in sp. gravity of metallic ore and impurity
    - for oxides/ carbonates ore
  - (b) Magnetic separation
    - Based on difference in mag. properties of metallic ore and impurity
    - Used to separate s & p block compound from transitional elements compounds
  - (c) Froath floatation
    - Based on difference in wetting properties
    - Sulphide ores
    - Frother - Pine oil
      Collector - Sodium ethyl xanthate
      depressant - NaCN
      Stablizer : Cresol or Aniline Derivative
- **(II) Chemical/leaching**
  - for $\boxed{\text{Al}}$ Ag, Cu
  - Dissolve in suitable solvent in which metallic ore is soluble & impurity is Insoluble

Ag, Au, are concentrated by cyanide process.

4.



5. Reduction : To obtains metal (95 to 98%) from oxidized metallic ore.

Self reduction :

⇒ Sulphide ore itself act as reducing agent.

eg. $PbS + 2PbO \xrightarrow{\Delta} 2Pb + SO_2$

⇒ Thermal decomposition

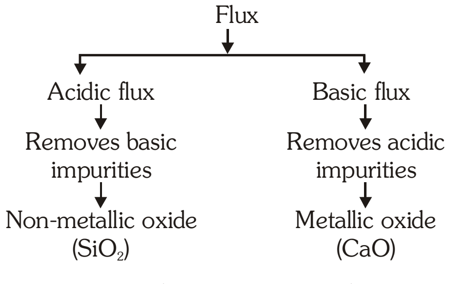
eg. $HgO \xrightarrow{\Delta} Hg + \frac{1}{2}O_2$

Carbon reduction (Smelting) : Reducing agent C/CO

eg. $Fe_2O_3 + 3CO \xrightarrow{250°-700°C} 2Fe + 3CO_2$

$ZnO + C \xrightarrow{\approx 1200°C} Zn + CO$

Flux - Substance to convert non-fusible impurities to fusible mass.



Imp. point – Above 710° C is reducing agent.
– Below 710°c CO is better reducing agent.

Aluminum reduction method : (Thermite process)

⇒ Al act as reducing agent

eg. $Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$

Thermite mixture mass ratio : Cr_2O_3 : Al = 3 : 1

METAL DISPLACEMENT REDUCTION

⇒ Metal placed below H. in E.C.S.

⇒ Ag, Au, Cu

Example of extraction of :

(i) Cynidation (Leaching Process)

$Ag_2S + 2NaCN \xrightarrow{O_2} 2Na[Ag(CN)_2] + Na_2SO_4$

$Au + 2KCN + H_2O \xrightarrow[air]{O_2} K[Au(CN)_2]$

NaCN / KCN → Leaching agent

O_2 → oxidizing agent

(ii) Recovery of Ag/Au (Metal displacement Reactions)

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

$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au\downarrow$

Zn → reducing agent

ELECTROLYTIC REDUCTION

⇒ For IA, IIA, Al

⇒ Electolysis of molten solution

Example :-

(i) Extraction of Al(Hall-Herault)

– Al can be extracted from Al_2O_3

– Na_3AlF_6 & CaF_2 act as auxilary electrolyte increase the conductivity & to reduce the fusion temp. of mixture

(ii) At cathode impure Al is collected and at anode O_2,CO, CO_2 is released.

(iii) Extraction of Na (Down cell process)

– Na can be extracted from NaCl

– Down Process Neutral flux ($CaCl_2$) to be added to decrease the fusion temp. of NaCl

– Neutral flux - substance used to increase the conductivity of NaCl

Auxilary Electrolyte – decrease the fusion temp. of ionic compounds of (IA, IIA, Al) which is more than the melting point of metal.

REFINING

To obtain metal (99.98%)

(I) **Physical process**

- (a) Liquation (Sn, Pb, Bi, Sb) ↓ Low m.p. metal
- (b) Distillation (Zn, Cd, Hg) ↓ Low b.p. metal ↓ Volatile metal
- (c) Zone refining/ Fractional crystallization (Ge, Ga, Si, Tl, B) ↓ Ultrapure metal

(II) **Chemical Process**

- (a) Cupellation ↓ For Ag or Au having the impurity of Pb $\xrightarrow{\Delta}$ Ag + PbO↑
- (b) Polling ↓ CuSn, Pb having the impurity of their own oxide ↓ Scum is form at the surface
- (c) Bessemerization ↓* Fe, Cu
  - * In Cu metallurgy it is not purification method.
  - * It is used to manufacture steel from cast iron.

(III) **Thermal decomposition (Vapour Phase Refining)**

- (a) Van. arkel de Boer (Ti, Zr, Hf, B, Th)

  Impure metal ↓ Pure metal

  $$\underset{\text{Impure}}{Ti} + I_2 \rightarrow \underset{\text{Volatile}}{TiI_4} \rightarrow \overset{\text{Pure}}{Ti} + 2I_2$$

  $$\text{Impurity} + I_2 \rightarrow \text{No reaction}$$

  (Or not form volatile product)

- (b) Mond's process (for Ni)

  $$\underset{\text{Impure metal}}{Ni + 4CO} \xrightarrow{\approx 50°C} \underset{\text{Volatile carbonyl}}{Ni(CO)_4} \xrightarrow{\approx 200°C} \underset{\text{(Pure metal)}}{Ni + 4CO}$$

  $$\text{Impurity} + CO \rightarrow X$$

(IV) **Electrolytic refining**

Anode – made up of impure metal

Cathode – pure metal

Impurity deposited below anode as anode mud or goes to electrolytic solution pure metal deposited at cathod.

THERMODYNAMICS PRINCIPLE OF METALLURGY

- The graphical representationof Gibbs energy was first used by H.I.T. Ellingham. This provide a sound basis for considering the choice of reducing agent in the reduction of oxides. this is known as Ellingham diagram such diagram help us in predicting the feasibility of thermal reduction of an ore.
- The criteria of feasibility is that at a given temperatue, Gibbs energy of reaction must be negative.
- At high temperature 'C' is the best reducing agent.
- At low temperature 'CO' is the best redusing agent.
- In blast fornace reduction takes plae at low temperature i.e. why CO is the reducing agent (For Fe).

A summary of the occurence and Extraction of some Metals is presented in the following table :

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Aluminium E°=-1.66	1. Bauxite, $Al_2O_3.xH_2O$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten $Na_3AlF_6 + CaF_2$	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required
Iron E°=-0.44	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 3. Limonite, $Fe_2O_3.3H_2O$ 4. Siderite, $FeCO_3$	Reduction of the oxide with CO and coke in Blast furnace	Bessemerization (impurites has more affinity for O_2 as compare to Fe)	Temperature approaching 2170K is required
Copper E°=-0.34	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O 5. Azurite, $2CuCO_3.Cu(OH)_2$	Roasting of sulphide partially and reduction	(i) Polling (ii) Electrolytic method.	It is self reduction in a specially designed converted. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc E°=-0.76	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO	Roasting of sulphide ore or calcination of $ZnCO_3$ followed by reduction with coke	The metal may be purifed by fractional distillation	For ZnO, carbon is better reducing agent then CO and Zn is obtain in vapours form $ZnO+C \xrightarrow{1673K} Zn + CO$
Mg E°=-2.36	1. Carnallite, $KCl.MgCl_2.6H_2O$ 2. Magnesite, $MgCO_3$	Electrolysis of fused $MgCl_2$ with KCl	-	$MgCl_2.6H_2O$ is heated in the excess current of dry HCl gas to produce anhydrous $MgCl_2$
Sn E°=-0.14	1. Cassiterite ,SnO_2 (Tin stone)	Reduction of the SnO_2 with carbon. $SnO_2+2C \rightarrow Sn+2CO$	Polling and Liquidation	Ore contain impurity of wolframite, $FeWO_4$ + $MnWO_4$ (magnetic sepration)
Pb E°=-0.13	1. Galena , PbS	Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon $PbS+2PbO \rightarrow 3Pb+SO_2$ $PbO+C \rightarrow Pb+CO$	Liquadation & electrolytic method.	-
Ag E°=0.80	1. Argentite- Ag_2S, native Silver	Hydro metallurgy $Ag_2S + 4NaCN \rightarrow 2NaAg(CN)_2 + N_2S$ $2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$	Cupelation & electrolytic method	In hydro mettallurgy Ag obtain in the form of dark amorphous ppt.
Au E°=1.40	Native ore	1. Amalgamation. 2.Cynide process	Cupelation & electrolysis method.	In hydro mettallurgy Au obtain in the form of dark amorphous ppt.

SALT ANALYSIS

Definition :

The branch of chemical analysis which aims to find out the constituents of a mixture of compound is known as Qualitative Analysis.

The identification of a substances usually involves its conversion into a new substance possessing characteristic properties with the help of one or more substance of known composition. The substance which is used to bring about such change is called a Reagent.

Salt Analysis

(A)
Analysis of Anion
✷ **by Wet Test**

(B)
Analysis of Cation
✷ **by Dry Test**
✷ **by Wet Test**

ANALYSIS OF ACIDIC RADICAL

Classification of acidic radical

Class - A **(Form volatile product with acid)**	**Class - B** **(Does not form volatile product with acid)**
Sub group-I : (Form volatile product with dil. HCl / dil. H_2SO_4) $CO_3^{2-}, HCO_3^-, SO_3^{2-}, HSO_3^-, S_2O_3^{2-}, S^{2-}, CH_3COO^-, NO_2^-$	**Sub group-I :** (Detected by precipitation reaction) $SO_4^{2-}, PO_4^{3-}, AsO_3^{3-}, AsO_4^{3-}$
Sub group-II : (Form volatile product with conc. H_2SO_4) $F^-, Cl^-, Br^-, I^-, NO_3^-, BO_3^{3-}, C_2O_4^{2-}$ + sub group-I	**Sub group-II :** (Detected by redox reaction) $CrO_4^{2-}, Cr_2O_7^{2-}, MnO_4^-$

⇒ CO_2 is colourless, odourless gas evolved with brisk effevesence, Detected by lime water test.

⇒ SO_2 is colourless, Suffocating gas with burning sulphur odour. Detected by lime water test or by passing in $Cr_2O_7^{2-}/H^+$ solution.

⇒ H_2S is a colourless gas with rotten egg odour.

⇒ CH_3COOH has colourless fumes having vinegar odour.

⇒ NO_2/Br_2 is brown gas.

⇒ I_2 is violet gas.

LIME WATER / BARYTA WATER TEST :

When CO_2 is passed in lime water or baryta water then white turbidity (milky appearance) is formed due to the formation of soluble carbonate but when excess of CO_2 is passed then white turbidity disappeared due to formation of soluble bicarbonate.

$$CO_2\uparrow + Ca^{2+} + 2OH^- \longrightarrow \underset{\text{White turbidity}}{CaCO_3\downarrow} + H_2O$$

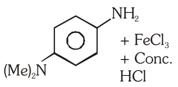
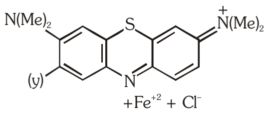
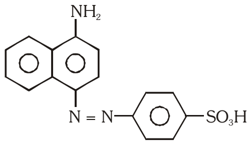
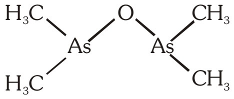
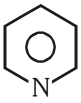
$$CaCO_3\downarrow + CO_2\uparrow + H_2O \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

Note : SO_2 also gives similar observation.

Acidic Radical Table

	dil. H_2SO_4	Conc. H_2SO_4	$CaCl_2$	$BaCl_2$	$HgCl_2$	$AgNO_3$	$Pb(OAc)_2$	MnO_4^- / H^+
CO_3^{2-}	$CO_2\uparrow$	$CO_2\uparrow$	$CaCO_3\downarrow$ white	$BaCO_3\downarrow$ white	$HgCO_3.3HgO\downarrow$ Reddish brown	$Ag_2CO_3\downarrow$	$PbCO_3.2Pb(OH)_2\downarrow$	—
$\Delta + HCO_3^-$	$CO_2\uparrow$	$CO_2\uparrow$	$CaCO_3\downarrow$	$BaCO_3\downarrow$	$HgCO_3.3HgO\downarrow$ Reddish brown	$Ag_2CO_3\downarrow$	$PbCO_3.2Pb(OH)_2\downarrow$	—
SO_3^{2-}	$SO_2\uparrow$	$SO_2\uparrow$	$CaSO_3\downarrow$ white	$BaSO_3\downarrow$ white	—	$Ag_2SO_3\downarrow$ white	$PbSO_3\downarrow$ white	SO_4^{2-}
$S_2O_3^{2-}$	$SO_2\uparrow + S\downarrow$	$SO_2\uparrow$	—	$BaS_2O_3\downarrow$ white	$HgS_2O_3\downarrow$ white	$Ag_2S_2O_3\downarrow$ white	$PbS_2O_3\downarrow$ white	$SO_4^{2-} + S\downarrow$
S^{2-}	$H_2S\uparrow$	$S\downarrow + SO_2\uparrow$	—	$BaS\downarrow$ black	$HgS\downarrow$ black	$Ag_2S\downarrow$ black	$PbS\downarrow$ black	$S\downarrow$
NO_2^-	$NO_2\uparrow$	$NO_2\uparrow$	—	—	—	$AgNO_2\downarrow$	—	NO_3^-
CH_3COO^-	$CH_3COOH\uparrow$	$CH_3COOH + SO_2\uparrow$	—	—	—	—	—	—
I^-		$I_2\uparrow$ violet	—	—	$HgI_2\downarrow$ scarlet red	$AgI\downarrow$ yellow	$PbI_2\downarrow$ dark yellow	$I_2\uparrow$
Cl^-		$HCl\uparrow$	—	—	—	$AgCl\downarrow$ white	$PbCl_2\downarrow$ white	$Cl_2\uparrow$
Br^-		$Br_2\uparrow$ brown	—	—	—	$AgBr\downarrow$ pale yellow	$PbBr_2\downarrow$ white	$Br_2\uparrow$
$C_2O_4^{2-}$	—	$CO_2\uparrow + CO\uparrow$	$CaC_2O_4\downarrow$ white	$BaC_2O_4\downarrow$ white	—	$Ag_2C_2O_4\downarrow$ white	—	$CO_2\uparrow$
BO_2^-	—	$H_3BO_3\uparrow$	$Ca(BO_2)_2\downarrow$ white	$Ba(BO_2)_2\downarrow$ white	—	$AgBO_2\downarrow$ white	—	—
NO_3^-	—	$NO_2\uparrow$	—	—	—	—	—	—
SO_4^{2-}	—	—	$CaSO_4\downarrow$ white	$BaSO_4\downarrow$ curdy white ppt	$HgSO_4.2HgO\downarrow$ yellow	—	$PbSO_4\downarrow$ white	—
PO_4^{3-}	—	—	$CaHPO_4\downarrow$ white	$BaHPO_4\downarrow$ white	—	$Ag_3PO_4\downarrow$ yellow	—	—
CrO_4^{2-}	—	—	—	$BaCrO_4\downarrow$ yellow	—	$Ag_2CrO_4\downarrow$ brick red	$PbCrO_4\downarrow$ yellow	—

SPECIFIC REACTION OF ACIDIC RADICAL

Anion	Reaction Name /with	Reagent	Product	Observation
S^{2-}	Sodium Nitro Prusside	$Na_2[Fe(CN)_5NO]$	$Na_4[(Fe(CN)_5NOS]$	Purple Complex
S^{2-}	Methylene blue Test			Methylene Blue
NO_2^-	Gries Illosavay Test	(i) Sulphanilic acid (ii)1, napthyl Amine		Red Azo dye
NO_2^-	Brown Ring Test	$FeSO_4$+dil.H_2SO_4	$[Fe(H_2O)_5NO]SO_4$	Brown Ring
CH_3COO^-	Cacodyl Test	As_2O_3		Nauseating odour
CH_3COO^-	$FeCl_3$ Sol^n	$FeCl_3+H_2O \xrightarrow{boil}$	$[Fe_3(OH)_2(CH_3OO)_6]^+$ ↓ boil $Fe(OH)_2(CH_3COO)$	Blood Red solution ↓ boiling Reddish Brown ppt.
NO_3^-	Brown Ring test	$FeSO_4$+Conc.H_2SO_4	$[Fe(H_2O)_5NO]SO_4$	Brown Ring
$C_2O_4^{2-}$	Mn^{+2} + NaOH	$NaOH + Mn^{+2} \xrightarrow[air]{\Delta}$	$[Mn(C_2O_4)_3]^{3-}$	Red Complex
Br^-	Layer Test	Cl_2 Water + CCl_4	$Br_2+ CCl_4$	Red layer
I^-	Layer Test	Cl_2 Water + CCl_4	$I_2 + CCl_4$	Violet Layer
I^-	$HgCl_2$	$HgCl_2$	HgI_2	Red/yellow
Cl^-	Chromyl Chloride Test	(i)$K_2Cr_2O_7(s)$ + conc.H_2SO_4 (ii) NaOH (iii) $Pb(CH_3COO)_2$ + CH_3COOH	CrO_2Cl_2 ↓ CrO_4^{2-} ↓ $PbCrO_4$	Reddish brown Vapour ↓ Yellow Solution ↓ Yellow PPt.
BO_3^{3-}	Green Flame Test	Conc. H_2SO_4 + R OH + Δ(Flame)	$B(OR)_3$	Green edge flame
BO_3^{3-}	Modified Green Flame Test	CaF_2 + Conc. H_2SO_4 + Δ	$BF_3\uparrow + Ca(HSO_4)_2$	Green flame
PO_4^{3-}	Ammonium molybdate	$(NH_4)_2MoO_4$ + dill HNO_3 + 30 – 40° C	$(NH_4)_3PO_4.12MoO_3$	Canary yellow ppt.
CrO_4^{2-} /Cr_2O_7	Acidic Solution of H_2O_2 + pyridine	$H_2O_2 + H^+ +$ 	CrO_5	Blue Solution

BASIC RADICAL ANALYSIS

Dry test of cation :

Flame test : used for s-block cation (except Be^{+2}, Mg^{+2})

Cation :	Li^+	Na^+	K^+	Ca^{+2}	Sr^{+2}	Ba^{+2}	Cu^{+2}
Observation : (Naked eye)	Caramine red	Golden yellow	Lilac	Brick Red	Crimson Red	Apple green	Green flame
Cobalt glass :		flame disappear	crimson red	Light Green	Purple	Bluish green	Green flame

Borax bead test :

⇒ Used for coloured cation (d-block cation)

⇒ Given salt heated on borax bead than metal metaborate are form.

⇒ Metal metaborate on heating show characteristic bead colour.

	Oxidizing flame		**Reducing flame**	
	Hot	Cold	Hot	Cold
Mn	Violet	Amethyst	Colourless	Colourless
Cr	Yellow	Green	Green	Green
Fe	Yellowish brown	Yellow	Green	Green
Co	Blue	Blue	Blue	Blue
Ni	Violet	Brown	Grey	Grey
Cu	Green	Blue	Colourless	Opaque red

Charcol cavity test :

Heat salt with Na_2CO_3 in charcoal cavity

Zn^{+2} In hot yellow and in cold white residue.

Pb^{+2} Yellow residue in hot and grey metal in cold.

As^{+3} White residue with garlic odour.

Cd^{+2} Brown residue.

If white residue is obtain then add. $Co(NO_3)_2$ and heat.

Zn^{+2}	ZnO.CoO	Rinmann's Green
Al^{+3}	$Al_2.O_3$	Thenard Blue
Mg^{+2}	MgO.CoO	Pink residue
Sn^{+2}	SnO.CoO	Bluish residue

Classification of Basic Radical

Group	**Basic Radical**	**Reagent used**	**Precipitate form**
Group-I	Pb^{+2}, Hg_2^{+2}	dil HCl	$\underbrace{AgCl \quad PbCl_2 \quad Hg_2Cl_2}_{\text{white ppt.}}$
Group-II	Cu^{+2}, Pb^{+2}, Hg^{+2}, Cd^{+2}, Bi^{+3}	H_2S+dil. HCl	$\underbrace{Cu_2S, PbS, HgS}_{\text{Black}}$, CdS, Bi_2S_3 yellow black
	Sn^{+2},Sn^{+4},As^{+3},As^{+5},Sb^{+3},Sb^{+5}		$\underset{\text{brown}}{SnS}$ $\underbrace{SnS_2 \quad As_2S_3\,As_2S_5}_{\text{yellow}}$ $\underbrace{Sb_2S_3Sb_2S_5}_{\text{orange}}$
Group-III	Cr^{+3}, Al^{+3}, Fe^{+3}	NH_4OH + NH_4Cl	brown $Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$ gelatinous reddish green white brown
Group-IV	Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}	H_2S+NH_4OH	$\underset{\text{white}}{ZnS}$ $\underset{\text{buff}}{MnS}$ $\underbrace{NiS \quad CoS}_{\text{black}}$
Group-V	Ca^{+2}, Sr^{+2}, Ba^{+2}	$(NH_4)_2CO_3$ +NH_4OH	$\underbrace{CaCO_3, SrCO_3, BaCO_3}_{\text{white}}$

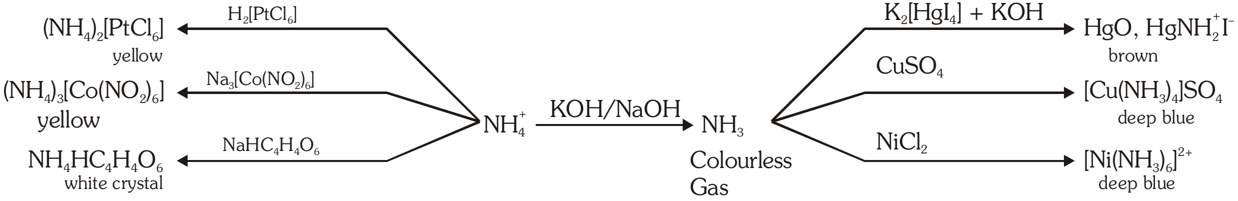
Test of Basic Radical

	Ag^+	Hg_2^{2+}	Pb^{2+}	Cu^{+2}	Hg^{+2}	Cd^{+2}	Al^{+3}	Cr^{+3}	Fe^{+3}	Fe^{+2}	Zn^{+2}	Mn^{+2}	Ni^{+2}	Co^{+2}
KI	AgI Yellow	Hg_2I_2 Green	PbI_2 Yellow	$CuI + I_3^-$ White solution	HgI_2 Scarlet Red	—	—	—	$FeI_2 + I_3^-$ yellowish brown sol.	—	—	—	—	—
ex KI	—	$Hg + [HgI_4]^{2-}$ Black	$[PbI_4]^{2-}$ soluble complex	—	$[HgI_4]^{2-}$ Solution	—	—	—	—	—	—	—	—	—
KCN	$AgCN$ White	$Hg + Hg(CN)_2$ Black	$Pb(CN)_2$ White	$CuCN + (CN)_2\uparrow$ White	—	$Cd(CN)_2$ White	—	—	$Fe(CN)_3$ Brown	$Fe(CN)_2$ yellowish brown	$Zn(CN)_2$ White	$Mn(CN)_2.Mn(OH)_2$ Pink	$Ni(CN)_2$ green	$Co(CN)_2$ Reddish Brown
ex KCN	$[Ag(CN)_2]^-$	—	—	$K_3[Cu(CN)_4]$ soluble complex	—	$[Cd(CN)_4]^{2-}$	—	—	$K_3[Fe(CN)_6]$ Yellow	$K_4[Fe(CN)_6]$ Pale yellow	—	—	$K_2[Ni(CN)_4]$ Soluble complex	$[Co(CN)_6]^{-4}$ Brown Solution
NaOH	Ag_2O Bhrown	Hg_2O Black	$Pb(OH)_2$ White	$Cu(OH)_2$ Pale Blue	HgO yellow	$Cd(OH)_2$ White	$Al(OH)_3$ Gelatinous white	$Cr(OH)_3$ Green	$Fe(OH)_3$ Reddish Brown ppt.	$Fe(OH)_2$ Dirty Green	$Zn(OH)_2$ White	$Mn(OH)_2$ Pink	$Ni(OH)_2$ Green	$Co(OH)Cl$ Blue
ex NaOH	—	—	$Na_2[Pb(OH)_4]$ soluble complex	—	—	—	$Na[Al(OH)_4]$ soluble complex	$Na[Cr(OH)_4]$ Yellow	—	—	$Na_2[Zn(OH)_4]$	—	—	$Co(OH)_2$ pink
NH_4OH	Ag_2O Broun	$Hg + HgO.HgNH_2^+NO_3^-$ black white	$Pb(OH)_2$ White	$Cu(OH)_2$ Pale Blue	$HgO.HgNH_2^+Cl^-$ White	$Cd(OH)_2$ White	$Al(OH)_3$ Gelatinous white	$Cr(OH)_3$ Green	$Fe(OH)_3$ Reddish Brown ppt.	$Fe(OH)_2$ Dirty Green	$Zn(OH)_2$ White	$Mn(OH)_2$	$Ni(OH)_2$ Green	$Co(OH)Cl$ Blue
ex NH_4OH	$[Ag(NH_3)_2]^+$	—	—	$[Cu(NH_3)_4]^{2+}$ Deep blue.	—	$[Cd(NH_3)_4]^{2+}$	—	$[Cr(NH_3)_6]^{3+}$ Pink/voilet	—	—	$[Zn(NH_3)_4]^{2+}$ White	—	$Ni[(NH_3)_6]^{2+}$ Deep blue	$[Co(NH_3)_6]^{2+}$ Yellow
$H_2S/^*(NH_4)_2S$	Ag_2S Black	$\underbrace{Hg + HgS}_{black}$	PbS Black	CuS Black	HgS Black	CdS Yellow	$Al(OH)_3$ Gelatinous white	$Cr(OH)_3$ Green	$FeS + S$ Black yellow	FeS Black	ZnS White	MnS Pink	NiS Black	CoS Black
K_2CrO_4	Ag_2CrO_4 Red	Hg_2CrO_4 Red	$PbCrO_4$ Yellow	—	—	—	—	—	—	—	—	—	—	—
$Na_2S_2O_3$	$Ag_2S_2O_3$ White	—	PbS_2O_3 White	$Cu_2S_2O_3$ White	HgS_2O_3 White	—	—	—	Fe^{+2} Green solution					
$K_4[Fe(CN)_6]$	$Ag_4[Fe(CN)_6]$ White	—	—	$Cu_2[Fe(CN)_6]$ Brown	—	$Cd_2[Fe(CN)_6]$	—	—	$Fe_4[Fe(CN)_6]_3$ Prussian blue	$K_2Fe[Fe(CN)_6]$ White	$K_2Zn_3[Fe(CN)_6]$ White	$Mn_2[Fe(CN)_6]$ White	$Ni_2[Fe(CN)_6]$ Light green	$Co_2[Fe(CN)_6]$ Green
$K_3[Fe(CN)_6]$	—	—	—	$Cu_3[Fe(CN)_6]_2$ Green	—	—	—	—	$Fe[Fe(CN)_6]$ Brown	$Fe_3[Fe(CN)_6]_2$ Turnbull's blue	—	—	—	—

Other important reaction of basic radical

Basic radical	Reagent	Product	Observation
Fe^{+3}	SCN^-	$[Fe(H_2O)_5(SCN)]^{2+}$	Blood red colouration
Ni^{+2}	dmg / NH_4^+	$[Ni(dmg)_2]$	Rosy red complex
Co^{+2}	KNO_2	$K_3[Co(NO_2)_6]$	Yellow ppt
Hg^{+2}	$SnCl_2$(ex)	Hg	Grey / black
K^+	$HClO_4$	$KClO_4$	White ppt

Test of NH_4^+



IMPORTANT NOTES

ENVIRONMENT POLLUTION

Pollutant :

Substance which cause pollution is known as pollutant.

Atomospheric pollution → Tropospheric pollution
Atomospheric pollution → Stratospheric pollution

⇒ Troposheric pollution occurs due to presence of undesirable solid or gaseous particles in air.

Gaseous pollutant :

SO_2 :

* Cause resipiratory diseases of anthma, bronchitis emphysema etc & irrataling to eyes.

NO_2 :

* Form by fossil fuel burn, Damage lungs.

* Higer concentration of NO_2 damage the leaves of plant and retard rate of photoshynthesis.

Hydrocarbon :

* Form by incomplete combustion of fuel of atomobile, Carcogonic.

Oxide of carbon :

CO :

* Blocks the delivery of oxygen to organs and tissues.

* Carboxy hemoglobine is 300 times more stable then oxy hemoglobin about 3-4% of carboxy hemoglobin the oxygen carrying capacity is highly reduced.

CO_2 :

* Main source is respiration, burning of fossil fuels, demposition of lime stone in cement industry.

* Increase of CO_2 cause global warming.

Global warming and Green House Effect :

Some of the gases such as CO_2, CH_4,O_3 CFC(s) and water vapour tapped the heat and does not radiates back to the atomosphere. This cause global warming.

Acid Rain :

* Normally the pH rain water is 5.6 due to the reaction between rain water and CO_2.

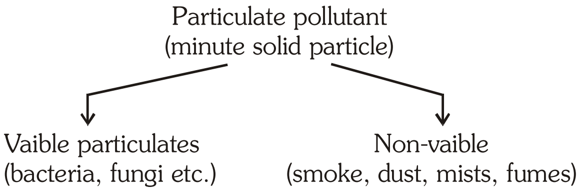
* When pH less then 5.6 then it is called acid rain.

* Source : burning of fuel (contain N & S) form SO_2 & NO_2.

* Harmful to agniculture, tree and plants.

* Taj Mahal affect by acid rain.

Particulat pollutant :



Smoke :

Solid/mixture of solid and liquid particles formed from burning of fossil fuel, oil smoke etc.

Dust :

Find solid particle over 1μm diameter, produced by crushin, grinding etc.

Mist :

Mist are produced by particle of spray liquid condensation of vapours, eg. herbiciaes mist etc.

Note : Pb is major air pollutant.

Smog (Smoke + fog) :

Classical smog :

(Smoke + fog + SO_2) also called reducing smog

Photochemical smog :

$$\text{hydrocarbon} + NO \xrightarrow{h\nu}$$

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \longrightarrow O_3$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

→ contribute to Haze

$(NO_2 + O_2)$ + hydrocarbon

→ CH_2O
formaldelyde
or
$CH_2 = CHCHO$
A.crotein
or
CH_3COONO_2
peroxy acetyl nitrate (PAN)

Stratospheric pollution :

Formation & decomposition of oxone.

$$O_2(g) \xrightarrow{UV} O(g) + O(g)$$

$$O_2(g) + O(g) \overset{UV}{\rightleftharpoons} O_3$$

Ozone is thermodynimcally unstable and thus dynamic equilibrium exist between production.

Ozone Hole :

The main reason of ozone layer depletion the release of CFC(s) (also called as freous)

Reaction of ozone depletion :

$$CF_2Cl_2(g) \xrightarrow{UV} \dot{Cl}(g) + \dot{C}FCl(g)$$

$$\dot{Cl}(g) + O_3(g) \longrightarrow \dot{Cl}O(g) + O_2(g)$$

$$\dot{Cl}O(g) + NO_2(g) \longrightarrow \dot{Cl}ONO_2(g)$$

$$\dot{Cl}(g) + CH_4(g) \longrightarrow \dot{C}H_3(g) + HCl(g)$$

$$ClONO_2(g) + H_2O(g) \longrightarrow HOCl(g) + HNO_3(g)$$

$$ClONO_2(g) + HCl(g) \longrightarrow Cl(g) + HNO_3(g)$$

$$HOCl \xrightarrow{h\nu} \dot{O}H(g) + \dot{C}l(g)$$

$$Cl_2(g) \longrightarrow 2\dot{C}l(g)$$

WATER POLLUTION

Cause of water pollution :

(i) Pathogen

(ii) Organic waste

(iii) Organic waste

BOD : The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical **Oxygen Demand (BOD).** Clean water wolud have BOD value of less than 5 ppm where as highly polluted water could have a BOD value of 17 ppm or more.

Fluoride : Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or 1 mg dm^{-3}.

However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth.

Lead : The prescribed upper limit concentration of lead in drinking water is about 50 ppb. Lead can damage kidney, liver, reproductive system etc.

Sulphate: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

Table

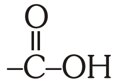
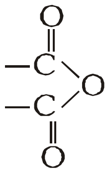
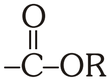
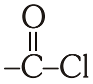
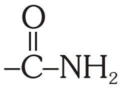
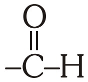
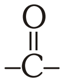
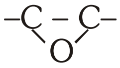
Maximum Prescribed Concentration of Some Metals in Drinking Water.

Metal	Maximum concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

IMPORTANT NOTES

TABLE FOR IUPAC NOMENCLATURE

The order of priority of functional groups used in IUPAC nomenclature of organic compounds.

Functional group	**Structure**	**Prefix**	**Suffix**
Carboxylic acid	 $-\overset{\overset{O}{\|}}{C}-OH$	Carboxy	- oic acid
Sulphonic acid	$-SO_3H$	Sulpho	sulphonic acid
Anhydride		×	oic-anhydride
Ester	 $-\overset{\overset{O}{\|}}{C}-OR$	Alkoxy carbonyl or Carbalkoxy	alkyl....oate
Acid chloride	 $-\overset{\overset{O}{\|}}{C}-Cl$	Chloroformyl or Chlorocarbonyl	- oyl chloride
Acid amide	 $-\overset{\overset{O}{\|}}{C}-NH_2$	Carbamoyl/ Amido	- amide
Carbonitrile/Cyanide	$-C\equiv N$	Cyano	nitrile
Aldehyde	 $-\overset{\overset{O}{\|}}{C}-H$	Formyl or Oxo	- al
Ketone	 $-\overset{\overset{O}{\|}}{C}-$	Keto or oxo	- one
Alcohol	$-OH$	Hydroxy	- ol
Thio alcohol	$-SH$	Mercapto	thiol
Amine	$-NH_2$	Amino	amine
Ether	$-O-R$	Alkoxy	–
Oxirane		Epoxy	–
Nitro derivative	$-NO_2$	Nitro	–
Nitroso derivative	$-NO$	Nitroso	–
Halide	$-X$	Halo	–
Double bond	$C=C$	–	ene
Triple bond	$C\equiv C$	–	yne

IMPORTANT NOTES

ISOMERISM

DEFINITION

Compounds having same molecular formula but differ in atleast one physical or chemical or biological properties are called isomers and this phenomena is known as isomerism.

Types of Isomerism : (A) Structural isomerism (B) Stereo isomerism

(A) STRUCTURAL ISOMERISM

Structural isomerism is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

TYPES OF STRUCTURAL ISOMERISM

CHAIN ISOMERISM

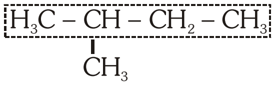
This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

Key points :

Parent carbon chain or side chain should be different.

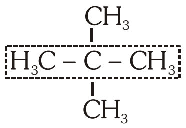
e.g. C_5H_{12} : $\boxed{CH_3-CH_2-CH_2-CH_2-CH_3}$

n-pentane



$\boxed{H_3C-\underset{CH_3}{CH}-CH_2-CH_3}$,

iso-pentane



$\boxed{H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3}$

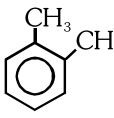
neo-pentane

POSITIONAL ISOMERISM

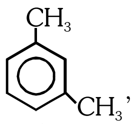
It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

Key point : Parent carbon chain remain same and substituent, multiple bond and functional group changes its position.

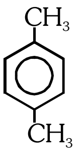
e.g. $C_6H_4(CH_3)_2$:



o-xylene



m-xylene



p-xylene

FUNCTIONAL ISOMERISM

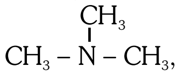
It occurs when compounds have the same molecular formula but different functional groups.

e.g. C_3H_9N : $CH_3-CH_2-CH_2-NH_2$,

1-propanamine

$CH_3-CH_2-NH-CH_3$,

N-methylethanamine



$CH_3-\overset{CH_3}{N}-CH_3$,

N, N-dimethylmethanamine

METAMERISM

This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

e.g. $C_4H_{10}O$:

$CH_3-O-CH_2-CH_2-CH_3$

n-propyl methylether

$CH_3-CH_2-O-CH_2-CH_3$

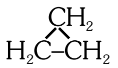
diethyl ether

RING-CHAIN ISOMERISM

In this type of isomerism, one isomer is open chain but another is cyclic.

e.g. C_3H_6 : $CH_3-CH=CH_2$

propene



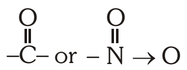
cyclopropane

- For chain, positional and metamerism, functional group must be same.
- Metamerism may also show chain and position isomerism but priority is given to metamerism.

TAUTOMERISM

This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

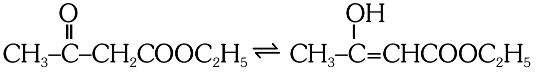
Conditions :



(i) Presence of $-\overset{O}{\overset{\|}{C}}-$ or $-\overset{O}{\overset{\|}{N}}\rightarrow O$

(ii) Presence of at least one α-H atom which is attached to a saturated C-atom.

e.g. Acetoacetic ester.



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5$

keto form enol form

ENOL CONTENT ENHANCE BY:

* Acidity of α-H of keto form

* Intra molecular H-Bonding in enol form

* Resonance in enol form

* Aromatisation in enol form

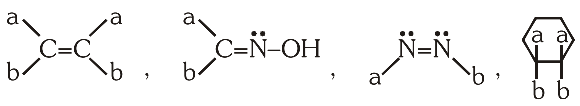
(B)STEREOISOMERISM

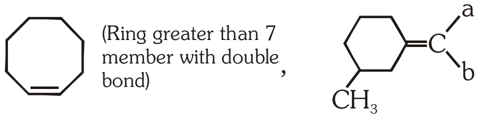
Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms or groups in 3D space are called stereoisomers and the phenomenon is called stereoisomerism.

TYPES OF STEREOISOMERISM

GEOMETRICAL ISOMERISM

It is due to restricted rotation and is observed in following systems

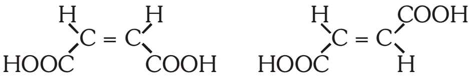




(Ring greater than 7 member with double bond),

- **Cis-trans isomerism :** The *cis* compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



cis
maleic acid

trans
fumaric acid

- General physical properties of geometrical isomer of but-2-ene

(i) Stability *trans* > *cis*

(ii) Dipole moment *cis* > *trans*

(iii) Boiling point *cis* > *trans*

(iv) Melting point *trans* > *cis*

Calculation of number of geometrical isomer

Unsymmetrical	2^n
Symmetrical	$2^{n-1} + 2^{m-1}$ $m = \frac{n}{2}$ (If n is even) $m = \frac{n+1}{2}$ (If n is odd)

* Where n = number of sites where GI is possible.

OPTICAL ISOMERISM

Compounds having similar molecular and structural formula but differing in the stereo chemical formula and behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomersim.

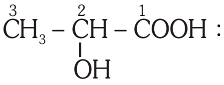
- ***Types of optical isomers***
  (1) Optically active
  - dextrorotatory (d)
  - laevorotatory (ℓ)

  (2) Optically inactive
  - meso
- ***Condition :***

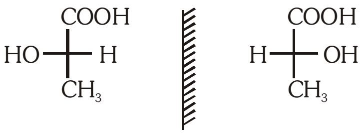
  Molecule should be asymmetric or chiral i.e. symmetry element (POS & COS) should be absent.
- The carbon atom linked to four different groups is called ***chiral carbon.***
- ***Fischer projection :*** An optical isomer can be represented by Fischer projection which is planar representation of three dimensional structure.

  Fischer projection representation of lactic acid

  (2-hydroxypropanoic acid)



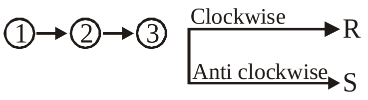
$$\overset{3}{C}H_3 - \underset{OH}{\overset{2}{C}H} - \overset{1}{C}OOH :$$



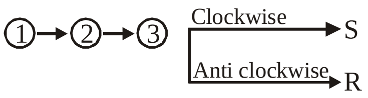
- ***Configuration of optical isomer :***
  (a) Absolute configuration (R/S system)
  (b) Relative configuration (D/L system)
- ***Determination of R/S configuration :***

Rule-1 Assign the priority to the four groups attached to the chiral carbon according to priority rule.

Rule-2 If lowest priority ④ is bonded to vertical line then moving



Rule-3 If lowest priority ④ is bonded to horizontal line then moving

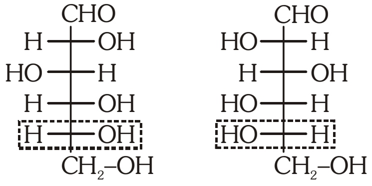


DETERMINATION OF D/L SYSTEM :

- Reference molecule glyceraldehyde
- It is used to assign configuration in carbohydrate, amino acid and similar compounds

Rule: Arrange parent carbon chain on the vertical line

- Placed most oxidised carbon on the top or nearest to top.
- On highest IUPAC numbered chiral carbon
  If OH group on RHS → D
  If OH group on LHS → L



D–Glucose L–Glucose

- **CIP SEQUENCE RULE :**
  The following rules are followed for deciding the precedence order of the atoms or groups :-
  - (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
  - (ii) In case of isotopes, isotopes having higher atomic mass is given priority.
  - (iii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2nd atom or subsequent atoms in group.
  - (iv) If there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated.
- Non-superimposable mirror images are called ***enantiomers*** which rotate the plane polarised light up to same extent but in opposite direction.
- ***Diastereomers*** are stereoisomers which are not mirror images of each other. They have different physical and chemical properties.
- ***Meso compounds*** are those compounds whose molecules are superimposable on their mirror images inspite of the presence of asymmetric carbon atom.
- An equimolar mixture of the enantiomers (d & ℓ) is called ***racemic mixture.*** The process of converting d- or ℓ- form of an optically active compound into racemic form is called ***racemisation.***
- The process by which dℓ mixture is separated into d and ℓ forms with the help of chiral reagents or chiral catalyst is known as ***resolution.***
- Compound containing chiral carbon may or may not be optically active but show optical isomerism.
- For optical isomer chiral carbon is not the necessery condition.

Calculation of number of optical isomers

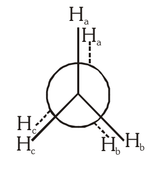
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2^n	Zero
Symmetrical If n = even	$2^{(n-1)}$	$2^{\frac{n}{2}-1}$
Symmetrical If n = odd	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

* Where n = no. of chiral carbon

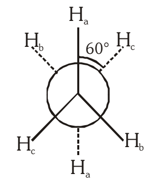
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomerism.

CONFORMATIONAL ISOMERISM

Newmann projection : Here two carbon atoms forming the σ bond are represented one by circle and other by centre of the circle. Circle represents rear side C and its centre represents front side carbon. The C–H bonds of front carbon are depicted from the centre of the circle while C–H bond of the back carbon are drawn from the circumference of the circle.

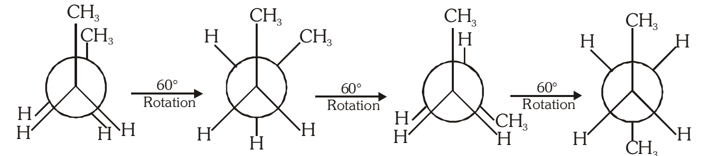


Eclipsed form (least stable)



Staggered form (most stable)

- ***Conformations of butane :*** $\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}H_2 - \overset{1}{C}H_3$



Fully eclipsed (less stable) Gauche (more stable) Partially Eclipsed form Anti Staggered-form (most stable)

- The order of stability of conformations of n-butane.
  Anti staggered>Gauche>Partially eclipsed>Fully eclipsed.
- Relative stability of various conformation of cyclohexane is
  Chair > twist boat > boat > half chair

IMPORTANT NOTES

REACTION MECHANISM

Electrophiles are electron deficient species.

eg. $H^{\oplus}$, $R^{\oplus}$, $NO_2^{\oplus}$, $X^{\oplus}$, PCl_3, PCl_5

($\overset{\oplus}{N}H_4$ and $H_3O^{\oplus}$ are not electrophile)

Nucleophiles are electron rich species.

e.g. $Cl^{\ominus}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{O}H$, $R\overset{\ominus}{O}$, $\overset{\ominus}{C}\ddot{N}$, NH_3, $\ddot{\underset{\cdot\cdot}{R}}OH$, $CH_2{=}CH_2$, $CH{\equiv}CH$

Relative electron withdrawing order (–I order)

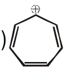
$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH > -X > -OR > -OH > -C{\equiv}CH > -NH_2 > -C_6H_5 > -CH = CH_2$

Relative electron releasing order (+I order)

$-\overset{\ominus}{N}H > -\overset{\ominus}{O} > -CO\overset{\ominus}{O} > 3°\text{ alkyl} > 2°\text{ alkyl} > 1°\text{ alkyl} > -CH_3$

RELATIVE STABILITY ORDER

(A) Stability of carbocation

(i)  $> (Ph)_3\overset{\oplus}{C} > (Ph)_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H_2 > CH_2 = CH-\overset{\oplus}{C}H_2$

(ii) $(CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2 = \overset{\oplus}{C}H > CH \equiv \overset{\oplus}{C}$

(B) Stability of free radical

$(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2 = CH-\dot{C}H_2 >$

$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

(C) Stability of Carbanion

$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2 = CH-\overset{\ominus}{C}H_2 >$

$\overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

BASIC STRENGTH $\propto K_b \propto \dfrac{1}{pK_b}$

- ***Basic strength of amine :-***

  In aqueous medium

  $R \Rightarrow -CH_3$ $2° > 1° > 3° > NH_3$

  $R \Rightarrow -CH_2CH_3$ $2° > 3° > 1° > NH_3$

  In gaseous medium

  $R \Rightarrow -CH_3$ $3° > 2° > 1° > NH_3$

  $R \Rightarrow -CH_2CH_3$ $3° > 2° > 1° > NH_3$
- ***Reactivity towards nucleophile (NAR)***

  (1) $HCHO > CH_3CHO > (CH_3)_2CO$

  (2) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$
- ***Reactivity order towards acyl nucleophilic substitution reaction***

  Acid chloride > anhydride > ester > amide
- ***Order of electronic effect***

  Mesomeric > Hyperconjugation > Inductive effect
- ***Stability of alkene $\propto$ no. of α-hydrogen***

$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > \underset{\text{trans form}}{RCH{=}CHR} > \underset{\text{cis form}}{RCH{=}CHR}$

$RCH{=}CH_2 > CH_2{=}CH_2$

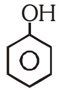
- ***Heat of hydrogenation*** $\propto \dfrac{1}{\text{Stability of alkene}}$

ACIDIC STRENGTH $\propto$ Stability of conjugate base

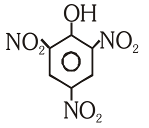
$$\propto K_a \propto \frac{1}{pK_a}$$

(i) $H_2O > CH \equiv CH > NH_3$

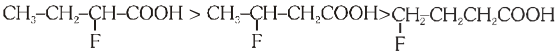
(ii) $CH \equiv CH > CH_2 = CH_2 > CH_3{-}CH_3$

(iii) $R{-}SO_3H > R{-}COOH >$  $> R{-}OH$

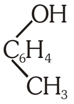
(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

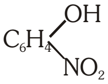
(v)  $> HCOOH > C_6H_5COOH > CH_3COOH$

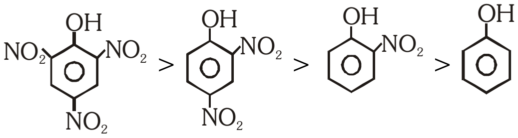
(vi) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

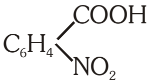
(vii) 

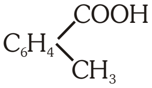
$CH_3{-}CH_2{-}\underset{F}{\underset{|}{C}}H{-}COOH > CH_3{-}\underset{F}{\underset{|}{C}}H{-}CH_2COOH > \underset{F}{\underset{|}{C}}H_2{-}CH_2CH_2COOH$

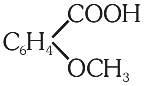
(viii)  $C_6H_4(OH)(CH_3)$ Phenol > m > p > o

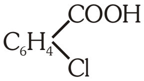
(ix)  $C_6H_4(OH)(NO_2)$ p > o > m > Phenol

(x) 

(xi)  $C_6H_4(COOH)(NO_2)$ o > p > m > benzoic acid

(xii)  $C_6H_4(COOH)(CH_3)$ o > benzoic acid > m > p

(xiii)  $C_6H_4(COOH)(OCH_3)$ o > m > benzoic acid > p

(xiv)  $C_6H_4(COOH)(Cl)$ o > m > p > benzoic acid

IMPORTANT NOTES

PRACTICAL ORGANIC CHEMISTRY

PURIFICATION METHODS

DISTILLATION TECHNIQUES

Type :

(A) SIMPLE DISTILLATION

Conditions

(i) When liquid sample has non volatile impurities

(ii) When boiling point difference is 30 K or more.

Examples

(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K)

(ii) Mixture of Ether (b.p. = 308K) & Toluene (b.p. = 384K)

(iii) Hexane (342K) and Toulene(384K)

(B) FRACTIONAL DISTILLATION

When b.p. difference is 10K

Examples

(i) Crude oil in petroleum industry

(ii) Acetone (329 K) and Methyl alcohol (338K)

(C) DISTILLATION UNDER REDUCED PRESSURE

(Vacuum distillation)

When liquid boils at higher temperature and it may decompose before b.p. is attained.

Example (i) Concentration of sugar juice

(ii) Recovery of glycerol from spent lye.

(iii) Glycerol

(D) STEAM DISTILLATION

When the substance is immiscible with water and steam volatile.

Example :

(i) Aniline is separated from water

(ii) Turpentine oil (iii) Nitro Benzene

(iv) Bromo Benzene (v) Naphthalene

(vi) o-Nitrophenol

$$\boxed{\underset{\text{Vapour pressure}}{P} = \underset{\text{Vapour pressure of Organic liquid}}{P_1} + \underset{\text{Vapour pressure of water}}{P_2}}$$

LASSAIGNE'S METHOD

(detection of elements)

Element	Sodium extract	Confirmed test
Nitrogen	$Na + C + N$ $\Delta\downarrow$ $NaCN$	$(NaCN+FeSO_4+NaOH)$ boil and cool $+FeCl_3+conc.\ HCl \rightarrow Fe_4[Fe(CN)_6]_3$ Prussian blue colour
Sulphur	$2Na + S$ $\Delta\downarrow$ Na_2S	(i) $Na_2S + Na_2[Fe(CN)_5NO]$ sodium nitrosopruside $\rightarrow Na_4[Fe(CN)_5NOS]$ a deep violet colour (ii) $Na_2S+CH_3COOH+(CH_3COO)_2Pb \rightarrow$ A black ppt. ($PbS\downarrow$)
Halogen	$Na + X$ $\Delta\downarrow$ NaX	$NaX + HNO_3 + AgNO_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 confirms I.
Nitrogen and sulphur together	$Na+C+N+S$ $\Delta\downarrow$ $NaCNS$ Sodium thiocyanate (Blood red colour)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Estimation of carbon and hydrogen - Leebig's method

$$C_xH_y + \underset{\text{excess}}{O_2} \longrightarrow xCO_2 + y/2\ H_2O$$

$$\%\text{ of } C = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of org. compd}} \times 100$$

$$\%\text{ of } H = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of org compd}} \times 100$$

Note : This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which is being absorbed in KOH and will increase the percentage of carbon and therefore following modification should be made.

ESTIMATION OF NITROGEN

Duma's method :

The nitrogen containing organic compound yields nitrogen gas on heating it with copper (II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.

$$\%\text{ of } N = \frac{28}{22400} \times \left(\frac{\text{Vol. of } N_2 \text{ collected at N.T.P.}}{\text{Wt. of organic compound}}\right) \times 100$$

Note : This method can be used to estimate nitrogen in all types of organic compounds

Kjeldahl's method :

In this method nitrogen containing compound is heated with conc. H_2SO_4 in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is

$$\%\text{ of } N = \frac{1.4 \times \text{volume of acid (ml)} \times \text{normality of acid}}{\text{wt of organic compound}}$$

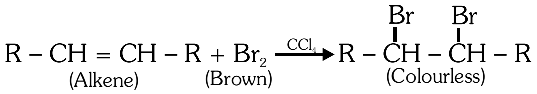
Note : This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (–N = N–) and nitrogen in the ring (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

IMPORTANT NOTES

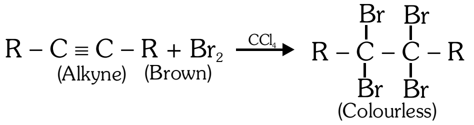
DISTINCTION BETWEEN PAIRS OF COMPOUNDS

UNSATURATION TEST

(a) Double/Triple bonded Compounds $(C = C)/(C \equiv C) + Br_2$ in CCl_4 (Brown colour) → Colourless compound

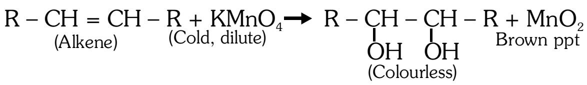


- $$\underset{\text{(Alkene)}}{R-CH=CH-R} + \underset{\text{(Brown)}}{Br_2} \xrightarrow{CCl_4} \underset{\text{(Colourless)}}{R-\overset{Br}{\overset{|}{C}H}-\overset{Br}{\overset{|}{C}H}-R}$$



- $$\underset{\text{(Alkyne)}}{R-C\equiv C-R} + \underset{\text{(Brown)}}{Br_2} \xrightarrow{CCl_4} \underset{\text{(Colourless)}}{R-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-R}$$

(b) Double/Triple bonded Compounds + Baeyer's reagent (Pink colour) ⟶ Brown precipitate

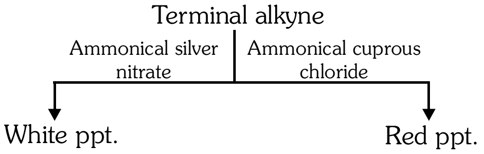


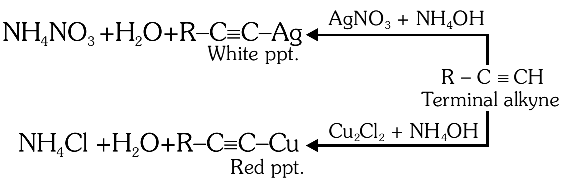
- $$\underset{\text{(Alkene)}}{R-CH=CH-R} + \underset{\text{(Cold, dilute)}}{KMnO_4} \rightarrow \underset{\text{(Colourless)}}{R-\underset{OH}{\underset{|}{C}H}-\underset{OH}{\underset{|}{C}H}-R} + \underset{\text{Brown ppt}}{MnO_2}$$
- $$R{-}C{\equiv}C{-}R' + \underset{\text{(Hot, dilute)}}{KMnO_4} \rightarrow \underset{\text{Brown ppt.}}{MnO_2} + RCOOH + R'COOH$$
- $$\underset{\text{(Alkyne)}}{R{-}C{\equiv}C{-}H} + \underset{\text{(Hot, dilute)}}{KMnO_4} \rightarrow \underset{\text{Brown ppt.}}{MnO_2} + \underset{\text{(Colourless)}}{RCOOH + CO_2 + H_2O}$$

Baeyer's reagent is cold, dilute $KMnO_4$ solution having pink colour.

Note : The above test are not given by Benzene. Although it has unsaturation.

TEST FOR TERMINAL ALKYNE





$$\underset{\text{White ppt.}}{NH_4NO_3 + H_2O + R{-}C{\equiv}C{-}Ag} \xleftarrow{AgNO_3 + NH_4OH} \underset{\text{Terminal alkyne}}{R-C\equiv CH}$$

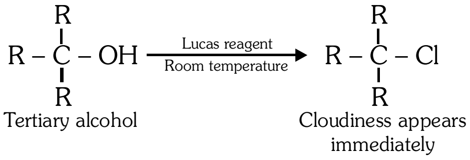
$$\underset{\text{Red ppt.}}{NH_4Cl + H_2O + R{-}C{\equiv}C{-}Cu} \xleftarrow{Cu_2Cl_2 + NH_4OH} \underset{\text{Terminal alkyne}}{R-C\equiv CH}$$

NATURE OF X-GROUP IN C–X BOND

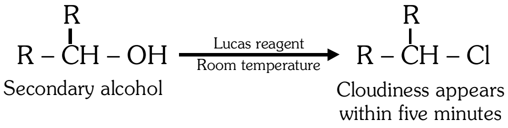
$$R{-}X + \text{aqueous } KOH \longrightarrow R{-}OH + KX \xrightarrow[AgNO_3]{HNO_3} \underset{\text{Precipitate}}{AgX}$$

If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOLS



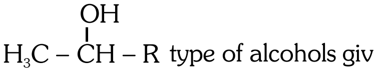
- $$\underset{\text{Tertiary alcohol}}{R-\overset{R}{\underset{R}{C}}-OH} \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} \underset{\text{Cloudiness appears immediately}}{R-\overset{R}{\underset{R}{C}}-Cl}$$



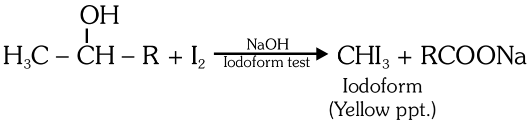
- $$\underset{\text{Secondary alcohol}}{R-\overset{R}{\overset{|}{C}H}-OH} \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} \underset{\text{Cloudiness appears within five minutes}}{R-\overset{R}{\overset{|}{C}H}-Cl}$$

- $$\underset{\text{Primary alcohol}}{R-CH_2-OH} \xrightarrow[\text{Heat}]{\text{Lucas reagent}} \underset{\text{Cloudiness appears after 30 minute}}{R-CH_2-Cl}$$

Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl.



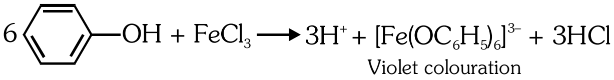
- $H_3C-\overset{OH}{\overset{|}{C}H}-R$ type of alcohols give iodoform test.



- $$H_3C-\overset{OH}{\overset{|}{C}H}-R + I_2 \xrightarrow[\text{Iodoform test}]{NaOH} \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3} + RCOONa$$

PHENOL

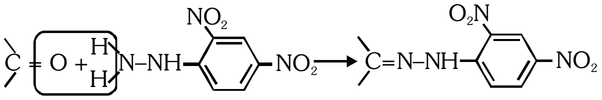
$$\text{Phenol} + \underset{\text{(neutral)}}{\text{ferric chloride}} \longrightarrow \text{Violet colouration}$$



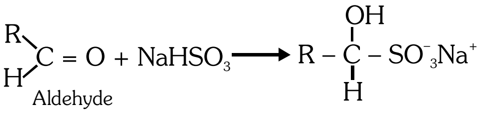
$$6\,C_6H_5{-}OH + FeCl_3 \rightarrow 3H^+ + \underset{\text{Violet colouration}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

CARBONYL GROUP

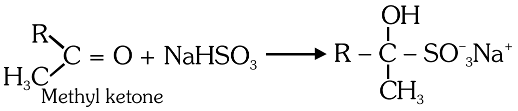
- Carbonyl compound + 2, 4-Dinitrophenylhydrazine → Yellow/orange crystal (Brady's reagent)



- All aldehydes and only aliphatic methyl ketones + $NaHSO_3$ → White crystalline bisulphite.



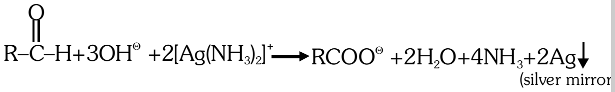
$$\underset{\text{Aldehyde}}{R(H)C=O} + NaHSO_3 \longrightarrow R-\overset{OH}{\underset{H}{C}}-SO_3^-Na^+$$



$$\underset{\text{Methyl ketone}}{R(H_3C)C=O} + NaHSO_3 \longrightarrow R-\overset{OH}{\underset{CH_3}{C}}-SO_3^-Na^+$$

ALDEHYDE GROUP

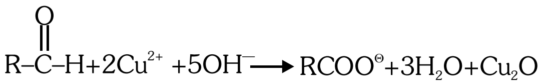
- Aldehyde + Tollen's reagent ⟶ Silver mirror



$$R-\overset{\overset{\displaystyle O}{||}}{C}-H + 3OH^{\ominus} + 2[Ag(NH_3)_2]^{+} \longrightarrow RCOO^{\ominus} + 2H_2O + 4NH_3 + 2Ag\downarrow$$

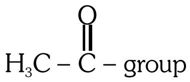
(silver mirror)

- Aldehyde+Fehling's solution → Reddish brown precipitate



$$R-\overset{\overset{\displaystyle O}{||}}{C}-H + 2Cu^{2+} + 5OH^{-} \longrightarrow RCOO^{\ominus} + 3H_2O + Cu_2O$$

(Reddish brown ppt)



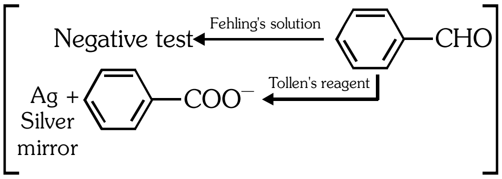
- $H_3C-\overset{\overset{\displaystyle O}{||}}{C}-$ group also give iodoform test

$$H_3C-\overset{\overset{\displaystyle O}{||}}{C}-R + I_2 + NaOH \xrightarrow{\text{Iodoform test}} CHI_3 + RCOONa$$

Iodoform
(Yellow ppt.)

AROMATIC ALDEHYDE GROUP

- Aromatic aldehyde + Tollen's reagent → Silver mirror
- Aromatic aldehyde + Fehling's solution → Negative test

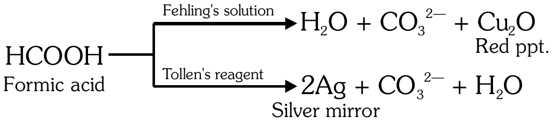


CARBOXYLIC GROUP

Carboxylic acid + Sodium bicarbonate → effervescence

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

FORMIC ACID



AMINES (1°)

$$\text{Primary amine} + KOH + CHCl_3 \xrightarrow[\text{reaction}]{\text{Carbylamine}} \text{Isonitrile}$$

(Offensive smell)

Amines (1°, 2° & 3°) (Hinsberg's test)

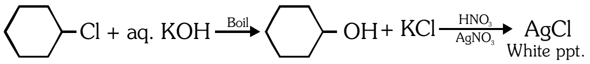
- Primary amine + Benzenesulphonyl chloride
  → Precipitate $\xrightarrow{KOH}$ soluble
- Secondary amine + Benzenesulphonyl chlorid
  ⟶ Precipitate $\xrightarrow{KOH}$ insoluble
- Tertiary amine + Benzenesulphonyl chloride → No reaction

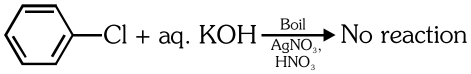
Note : Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and chlorobenzene

- $C_2H_5-Cl + aq.\ KOH \xrightarrow{\text{Boil}} C_2H_5-OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$ White ppt.

Chlorocyclohexane and chlorobenzene

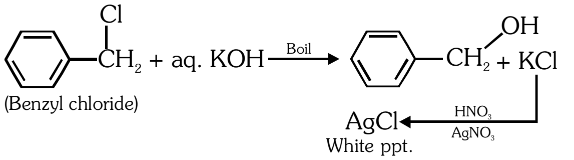


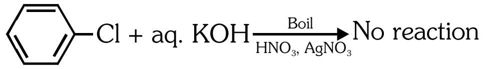


Chloroethane and bromoethane

- $C_2H_5-Cl + aq.\ KOH \xrightarrow{\text{Boil}} C_2H_5-OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$
  (Chloroethane) White ppt.
- $C_2H_5-Br + aq.\ KOH \xrightarrow{\text{Boil}} C_2H_5-OH + KBr \xrightarrow[AgNO_3]{HNO_3} AgBr$
  (Bromoethane) Yellow ppt.

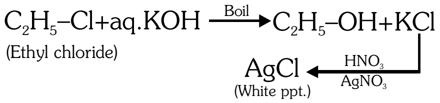
Benzyl chloride and chlorobenzene





Chlorobenzene

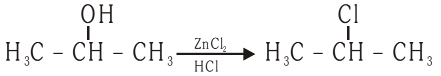
Ethyl chloride and vinyl chloride



- $H_2C=CH-Cl + aq.KOH \xrightarrow[HNO_3,\ AgNO_3]{\text{Boil}} \text{No reaction}$
  Vinyl chloride

n-Propyl alcohol and iso-propyl alcohol

- $CH_3CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2Cl$
  No cloudiness at room temp.



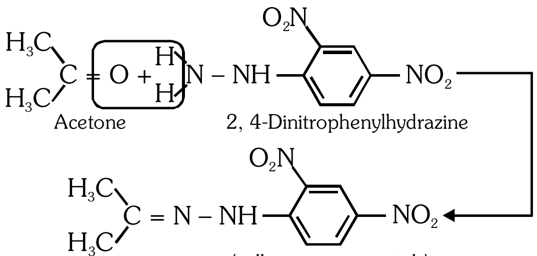
- $H_3C-\underset{}{\overset{\overset{\displaystyle OH}{|}}{CH}}-CH_3 \xrightarrow[HCl]{ZnCl_2} H_3C-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_3$

Cloudiness within 5 minutes

Ethyl alcohol and methyl alcohol (Iodoform test)

- $CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3} + HCOONa$
- $CH_3OH + 4I_2 + 6NaOH \longrightarrow$ No yellow ppt.

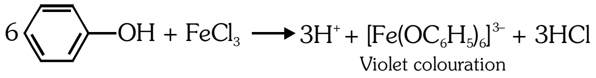
Ethyl alcohol and acetone (2, 4 – DNP)

- 

- $C_2H_5OH \xrightarrow{2,4-DNP}$ No reaction

Phenol and ethyl alcohol (Neutral $FeCl_3$)

- Phenol + Neutral ferric chloride ⟶ Violet colouration



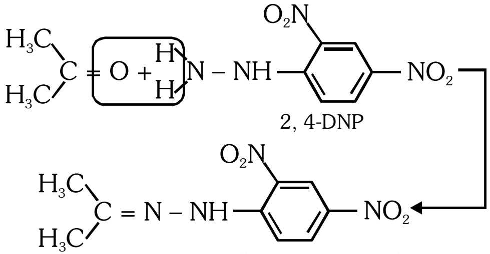
- CH_3CH_2OH + Neutral ferric chloride ⟶ No violet colouration

Benzoic acid and phenol ($NaHCO_3$)

- Benzoic acid + Sodium bicarbonate ⟶ effervescence
  $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$
- Phenol + Sodium bicarbonate → No effervescence

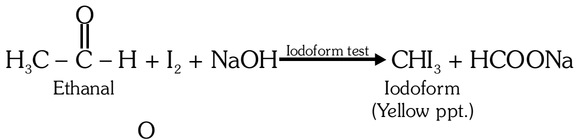
(Phenol is less acidic than benzoic acid)

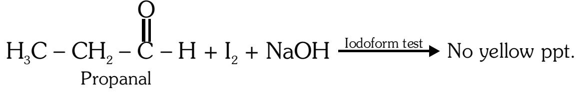
Propanone and propanol (2, 4 - DNP)

- 

- Propanol + 2,4-Dinitrophenylhydrazine ⟶ No crystals

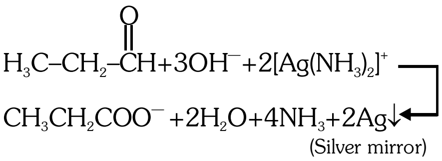
Ethanal and propanal (Iodoform test)

- 
$\underset{\text{Ethanal}}{H_3C-\overset{\overset{O}{\|}}{C}-H} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + HCOONa$

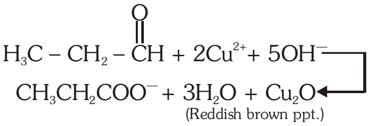
- 
$\underset{\text{Propanal}}{H_3C-CH_2-\overset{\overset{O}{\|}}{C}-H} + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Propanal and propanone (Tollen's and Fehling reagent)

- Propanal + Tollen's reagent ⟶ Silver mirror

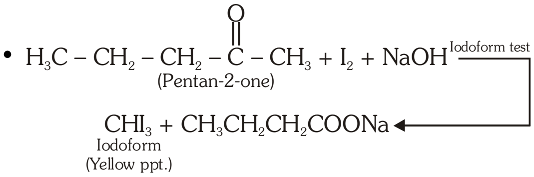

$H_3C-CH_2-\overset{\overset{O}{\|}}{C}H + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow CH_3CH_2COO^- + 2H_2O + 4NH_3 + \underset{\text{(Silver mirror)}}{2Ag\downarrow}$

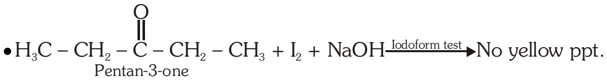
- Propanal + Fehling's solution → Reddish brown precipitate


$H_3C-CH_2-\overset{\overset{O}{\|}}{C}H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O + \underset{\text{(Reddish brown ppt.)}}{Cu_2O}$

- $$\begin{tikzcd} & \text{Negative test} \\ \text{Propanone} \arrow[ur, "\text{Fehling's solution}"] \arrow[dr, "\text{Tollen's reagent}"'] & \\ & \text{Negative test} \end{tikzcd}$$

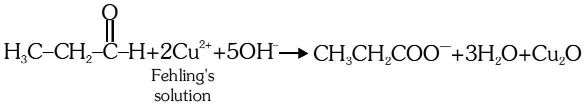
Pentan-2-one and pentan-3-one (Iodoform test)

- 
$\underset{\text{(Pentan-2-one)}}{H_3C-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + CH_3CH_2CH_2COONa$

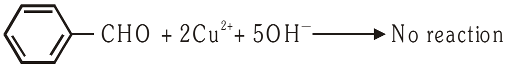
- 
$\underset{\text{Pentan-3-one}}{H_3C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3} + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Propanal and benzaldehyde (Fehling solution)

- Propanal + Fehling's solution → Reddish brown precipitate


$H_3C-CH_2-\overset{\overset{O}{\|}}{C}-H + \underset{\text{Fehling's solution}}{2Cu^{2+} + 5OH^-} \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$

- Benzaldehyde + Fehling's solution → No precipitate



Methanoic acid and ethanoic acid (Tollen's & Fehling solution)

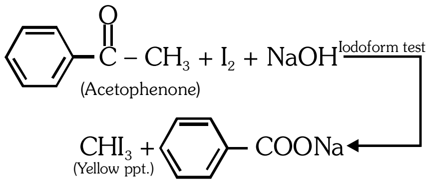
- $$\begin{tikzcd} & H_2O + CO_3^{2-} + Cu_2O \\ \underset{\text{Methanoic acid}}{HCOOH} \arrow[ur, "\text{Fehling's solution}"] \arrow[dr, "\text{Tollen's reagent}"'] & \\ & 2Ag\downarrow + CO_3^{2-} + H_2O \end{tikzcd}$$

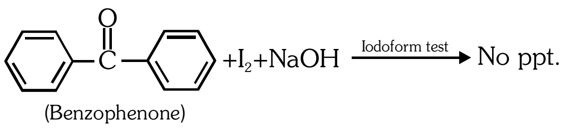
- $$\begin{tikzcd} & \text{No brown ppt.} \\ \text{Ethanoic acid} \arrow[ur, "\text{Fehling's solution}"] \arrow[dr, "\text{Tollen's reagent}"'] & \\ & \text{No silver mirror} \end{tikzcd}$$

Ethanal and methanal (Iodoform test)

- $CH_3CHO+I_2+NaOH \xrightarrow{\text{Iodoform test}} CHI_3+HCOONa$
  Ethanal — Iodoform (Yellow ppt.)
- $HCHO+I_2+NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.
  Methanal

Acetophenone and benzophenone (Iodoform test)



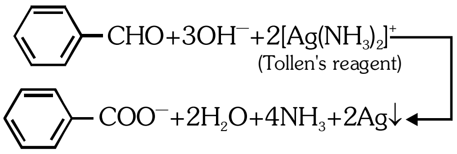


Benzoic acid and ethylbenzoate

- $C_6H_5COOH+NaHCO_3 \rightarrow C_6H_5COONa+CO_2\uparrow+H_2O$
  effervescence
- Ethyl benzoate + Sodium bicarbonate → No effervescence

Benzaldehyde and acetophenone (Tollen's test)

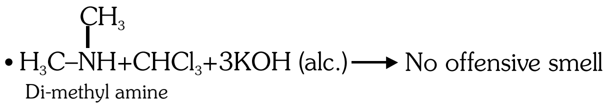
- Benzaldehyde + Tollen's reagent → Silver mirror



- Acetophenone + Tollen's reagent ⟶ No silver mirror

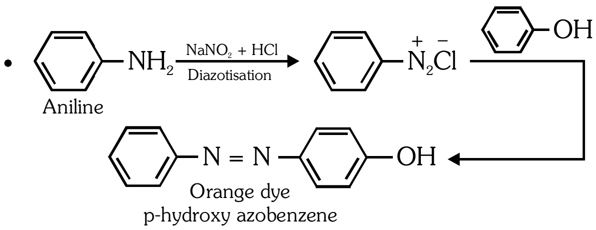
Methyl amine and dimethyl amine (Isocyanide test)

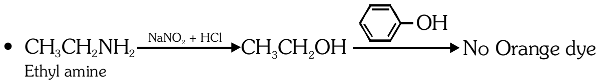
- $CH_3NH_2 + CHCl_3 + 3KOH \rightarrow CH_3NC + 3KCl + 3H_2O$
  Methyl amine — (alc.) — Methyl isocyanide (Offensive smell)



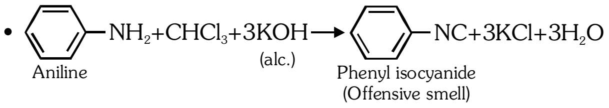
- $H_3C\text{–}NH(CH_3)+CHCl_3+3KOH \text{ (alc.)} \rightarrow$ No offensive smell
  Di-methyl amine

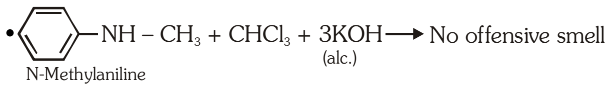
Aniline and ethyl amine (Diazotisation)



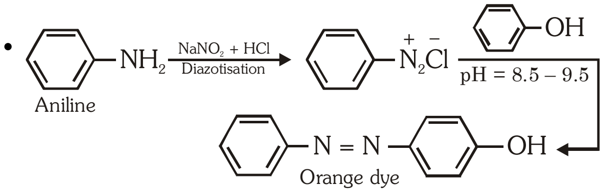


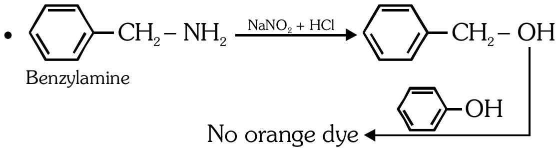
Aniline and N-methylaniline (Isocyanide test)





Aniline and Benzylamine (Diazotisation + phenol)





Glucose and fructose

- Glucose + Br_2 + H_2O ⟶ Gluconic acid + 2HBr
  (Brown colour) — (Colourless)
- Fructose + Br_2 + H_2O ⟶ Brown colour
  (Brown colour) — (no change in colour)

Glucose and sucrose

- Glucose + Tollen's reagent ⟶ Silver mirror
- Sucrose + Tollen's reagent ⟶ No silver mirror

Glucose and starch

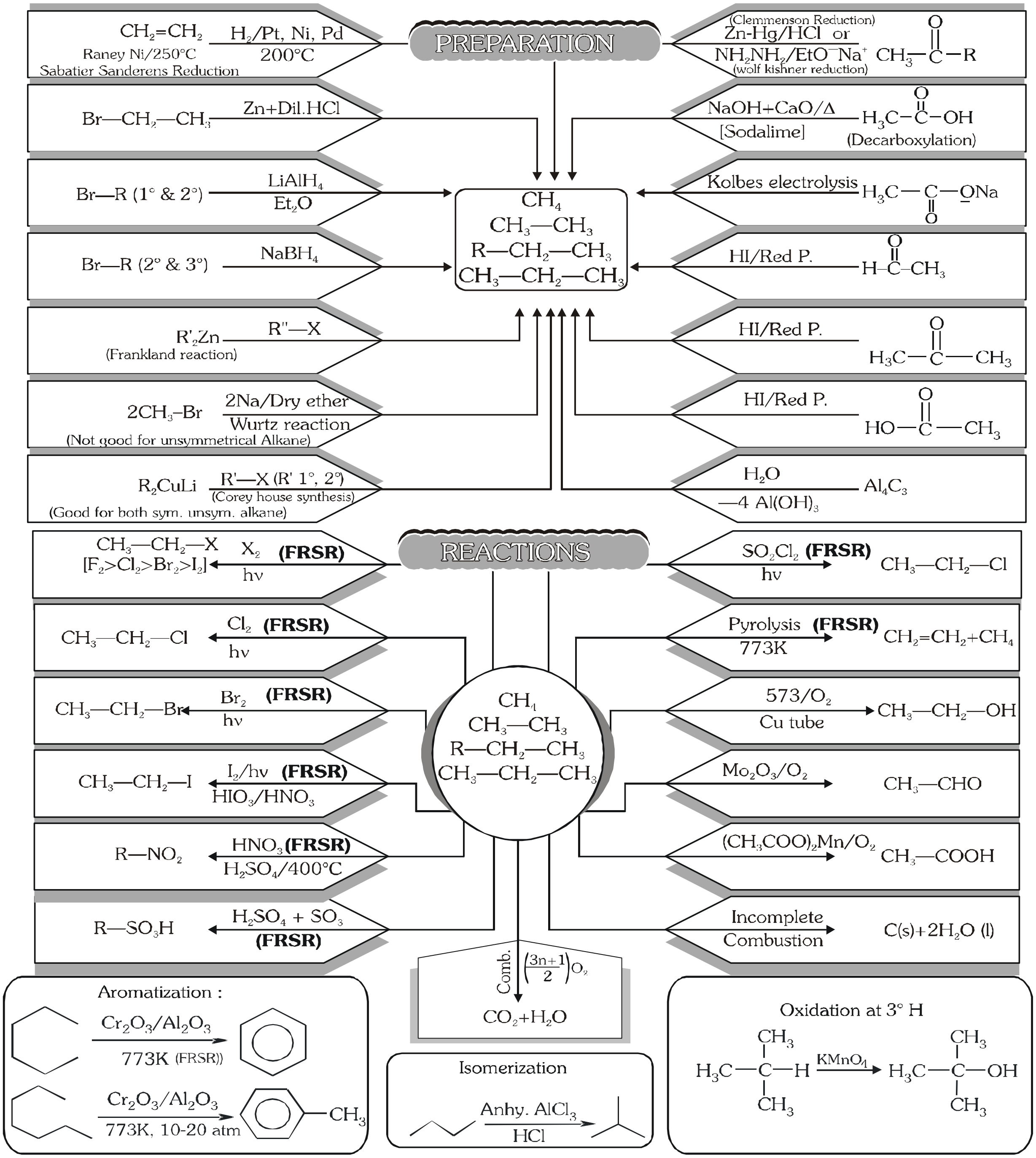
- Glucose + Fehling's solution ⟶ Red ppt.
- Starch + Fehling's solution ⟶ No red ppt.

OR

- Glucose + I_2 solution ⟶ No blue colour
- Starch + I_2 solution ⟶ Blue colour

IMPORTANT NOTES

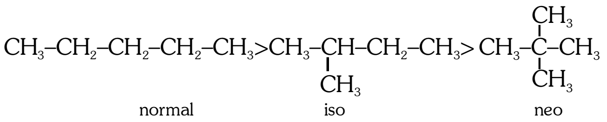
HYDROCARBON - ALKANE



- Reactivity of alkane towards free radical halogenation is ∝ stability of free radical
  $C_6H_5–CH_3 > CH_2=CH–CH_3 > (CH_3)_3CH$
  $> CH_3–CH_2–CH_3 > CH_3–CH_3 > CH_4$
- Reactivity of halogen towards free radical substitution
  $F_2 > Cl_2 > Br_2 > I_2$
- Knocking tendency of petroleum as fuel decrease with increase in side chain. Straight chain > Branched chain

Knocking tendency is in the order
Olefin > cycloalkane > aromatic

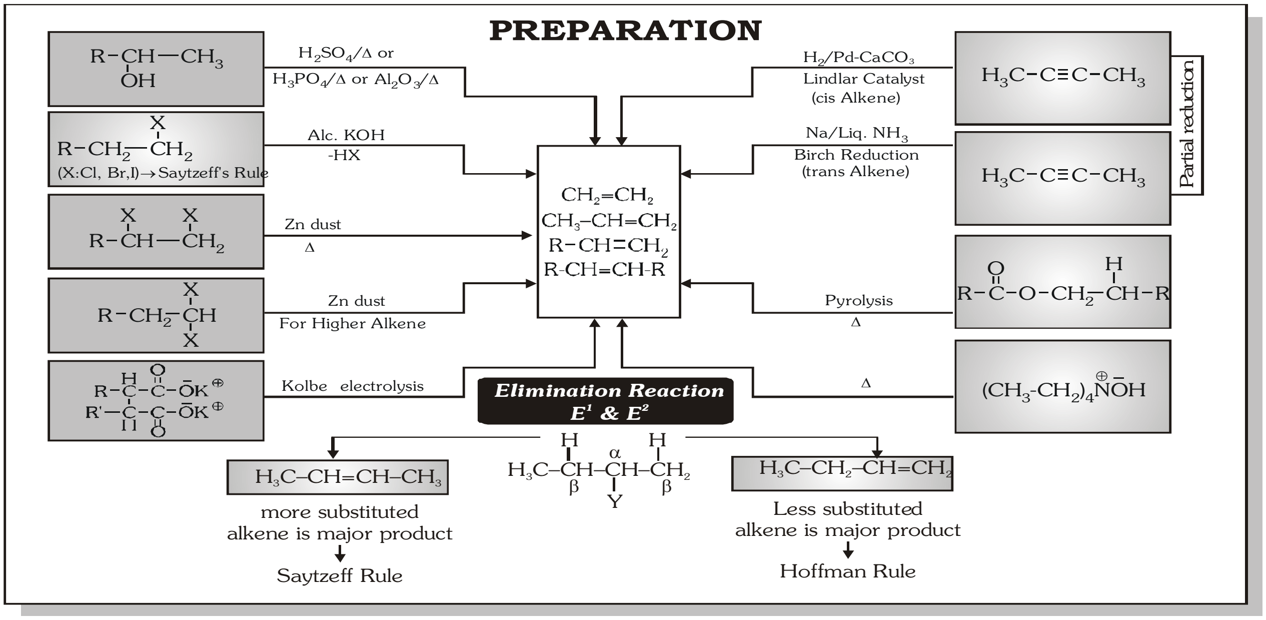
- Boiling point decrease with increase in number of side chain.

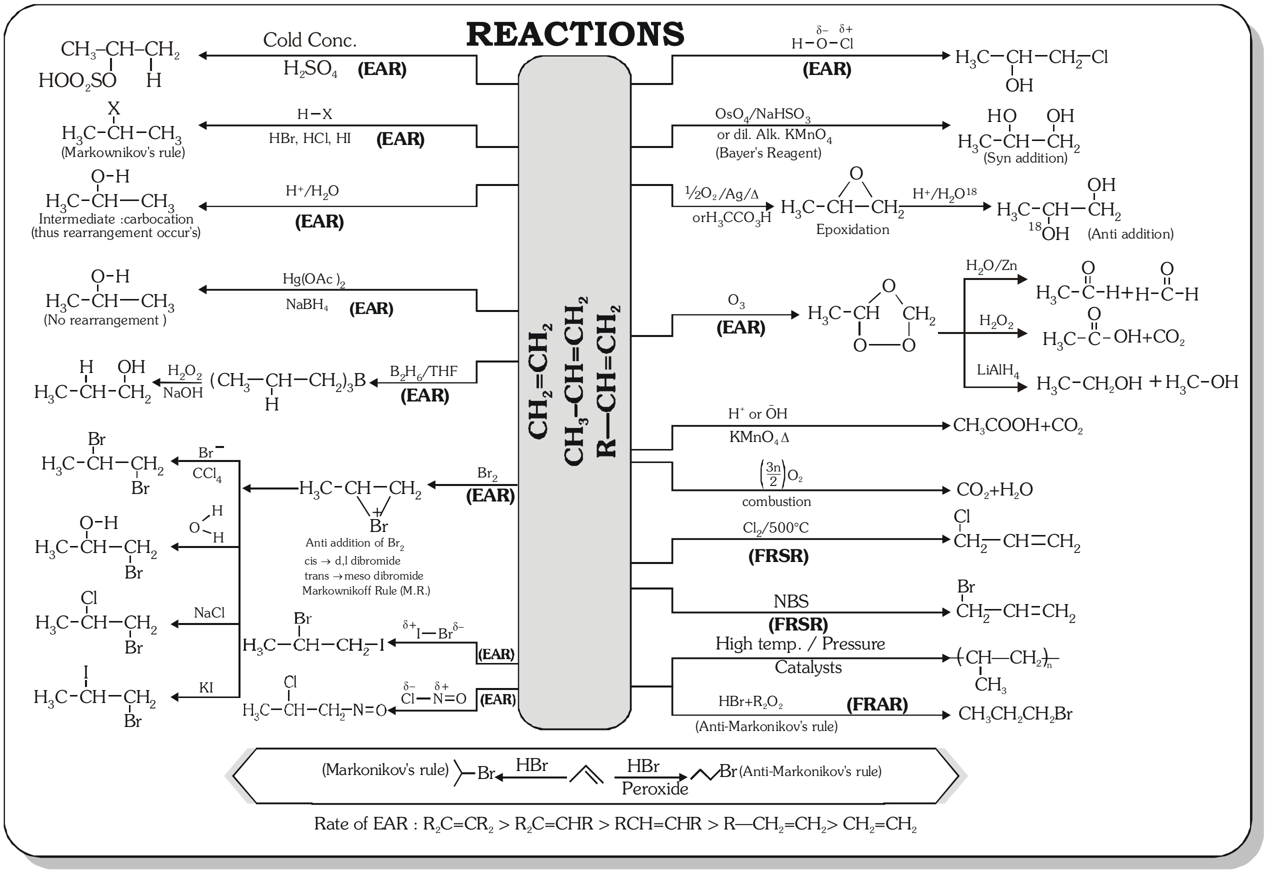


$CH_3–CH_2–CH_2–CH_2–CH_3 > CH_3–\underset{CH_3}{\underset{|}{C}H}–CH_2–CH_3 > CH_3–\overset{CH_3}{\underset{CH_3}{C}}–CH_3$

normal iso neo

HYDROCARBON - ALKENE





- Order of reactivity of olefins for hydrogenation $CH_2=CH_2$ > R–CH=CH_2 (Reverse of stability)
- Order of reactivity of alkene towards hydration $CH_3\text{-}\underset{CH_3}{C} = CH_2$ > CH_3–CH = CH_2 > CH_2 = CH_2

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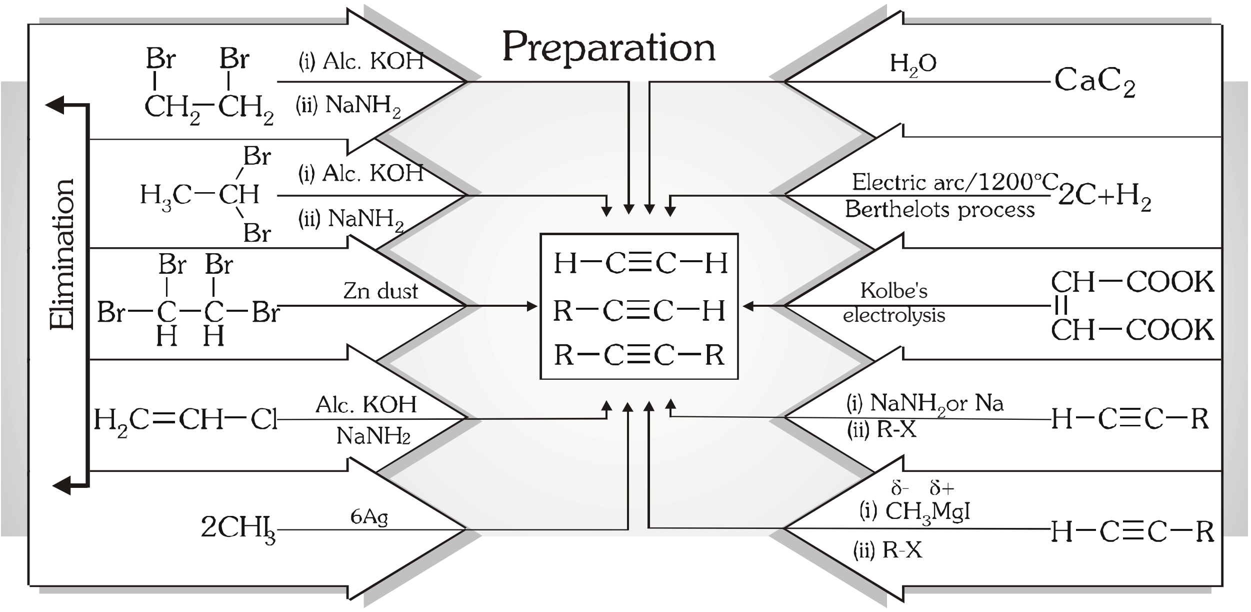
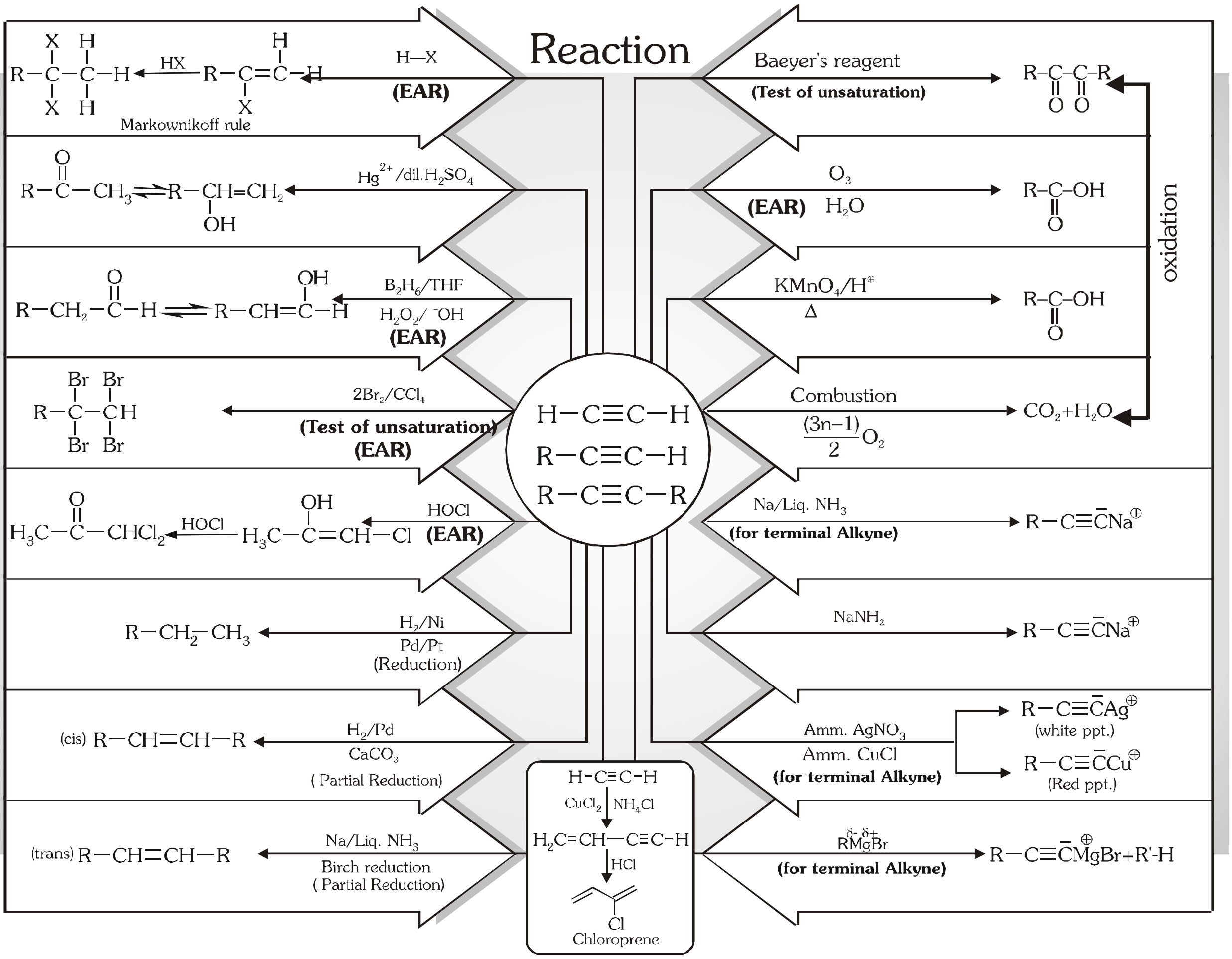
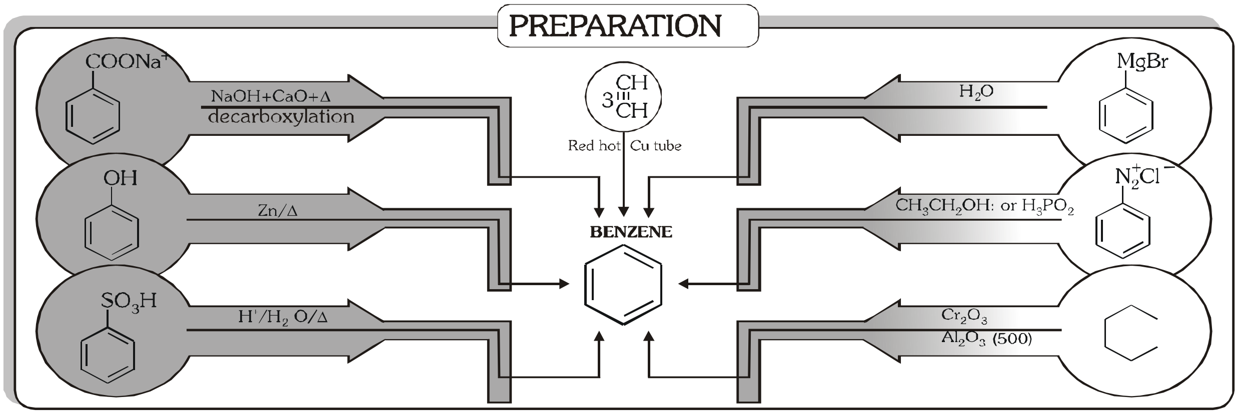
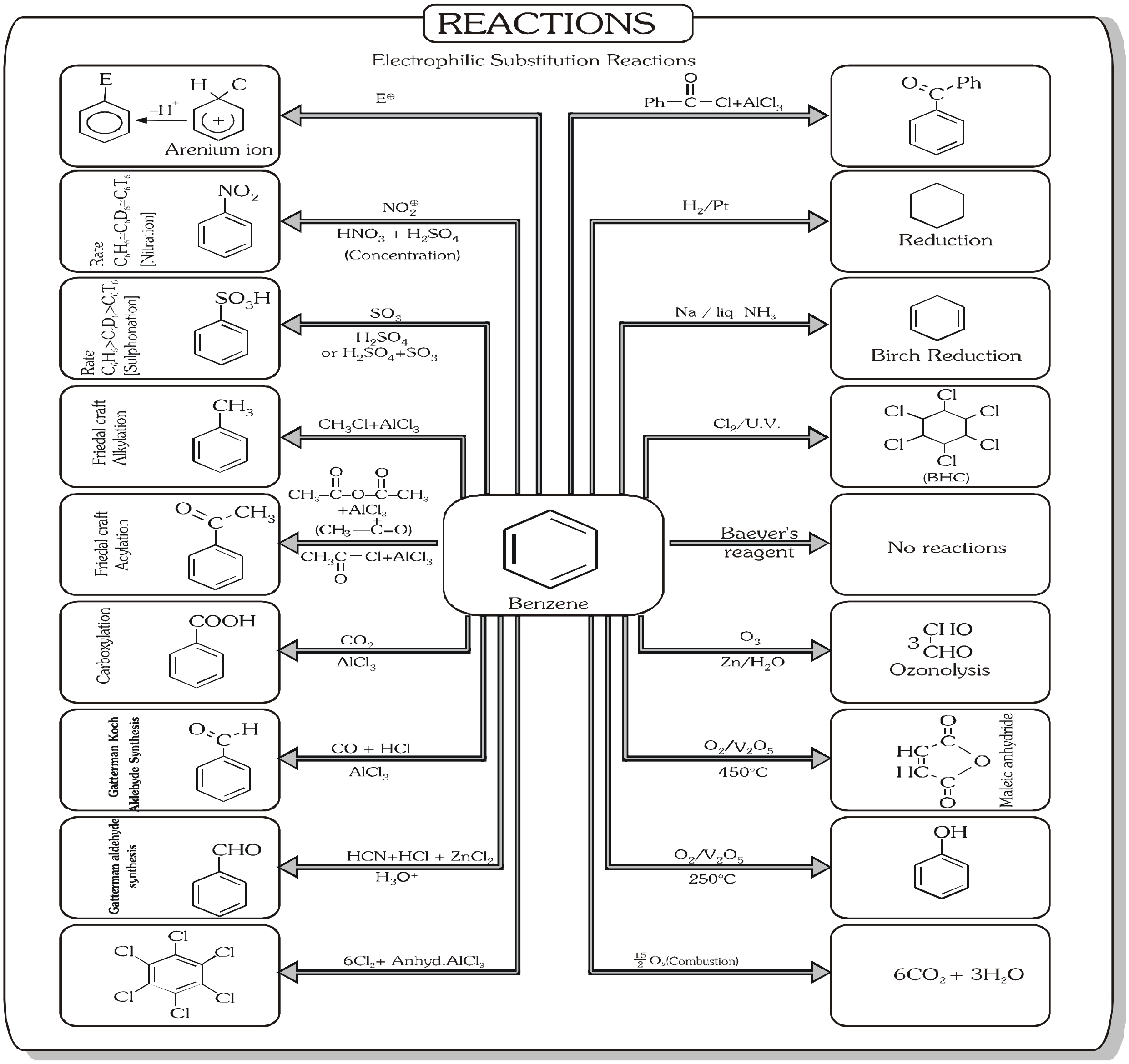
HYDROCARBON - ALKYNE





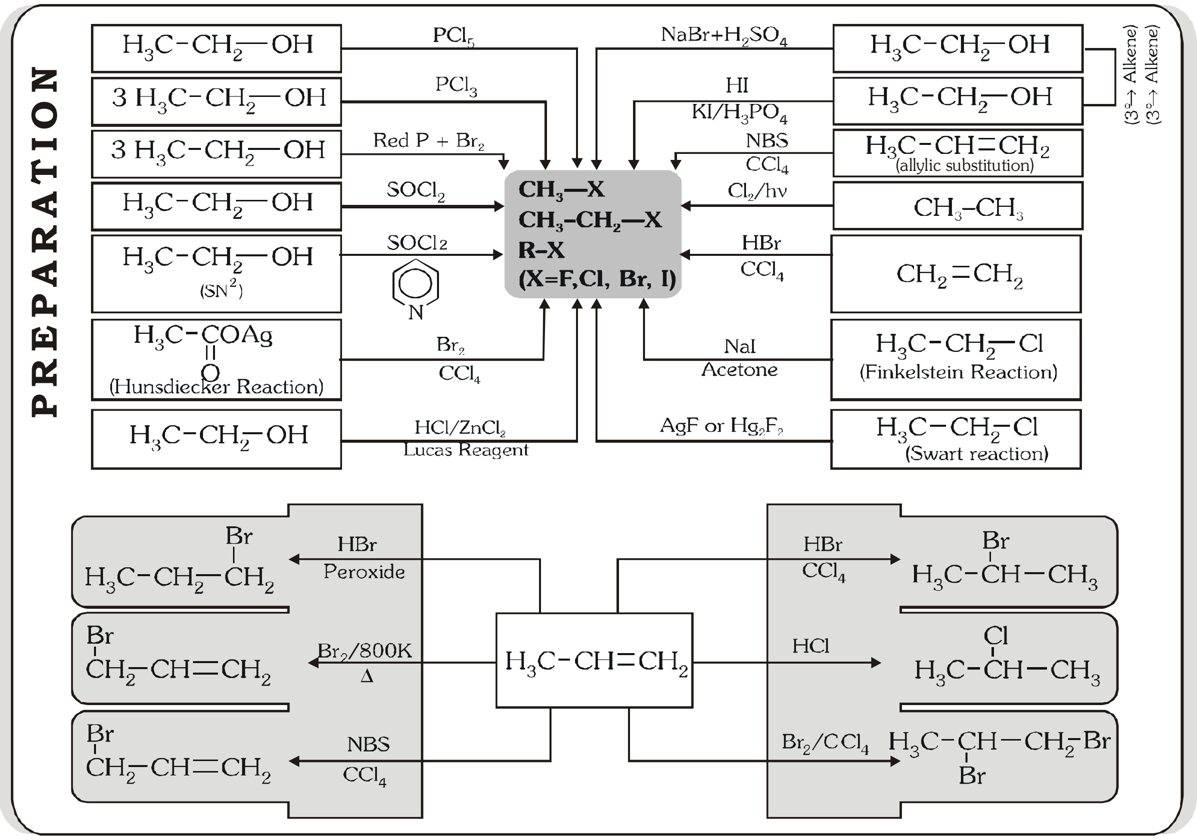
HYDROCARBON - BENZENE

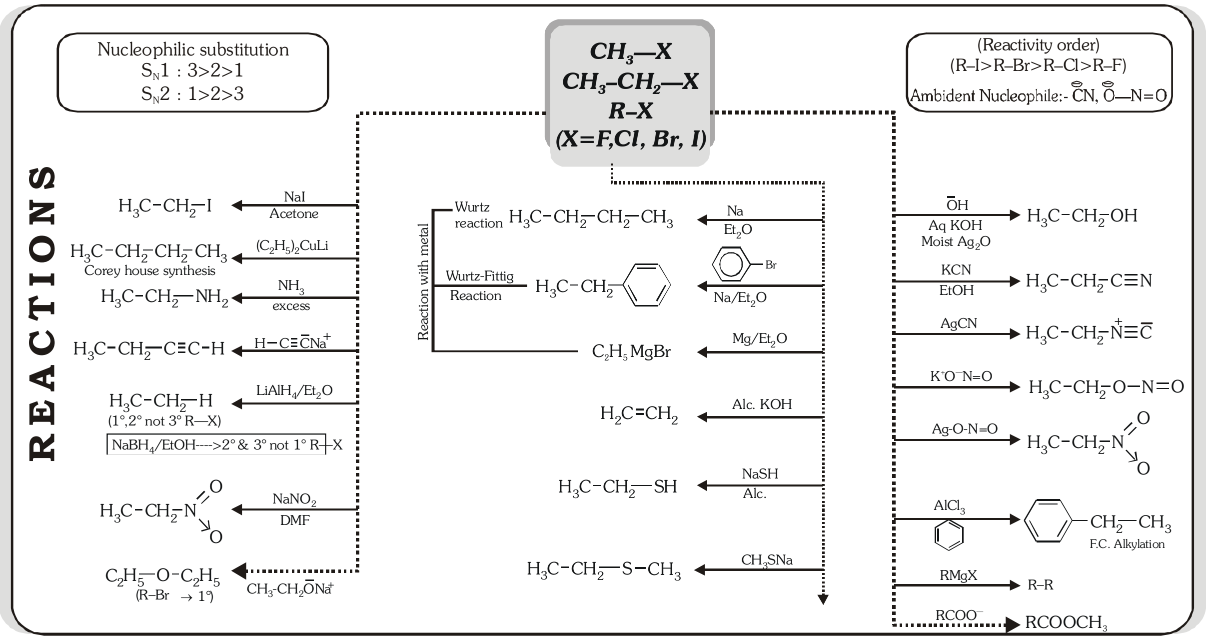




IMPORTANT NOTES

HALOALKANE



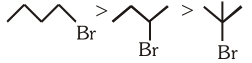


PHYSICAL PROPERTIES

(1) Dipole moment : $CH_3{-}Cl > CH_3{-}F > CH_3{-}Br > CH_3{-}I$

(2) Bond enthalpies : $CH_3{-}F > CH_3{-}Cl > CH_3{-}Br > CH_3{-}I$

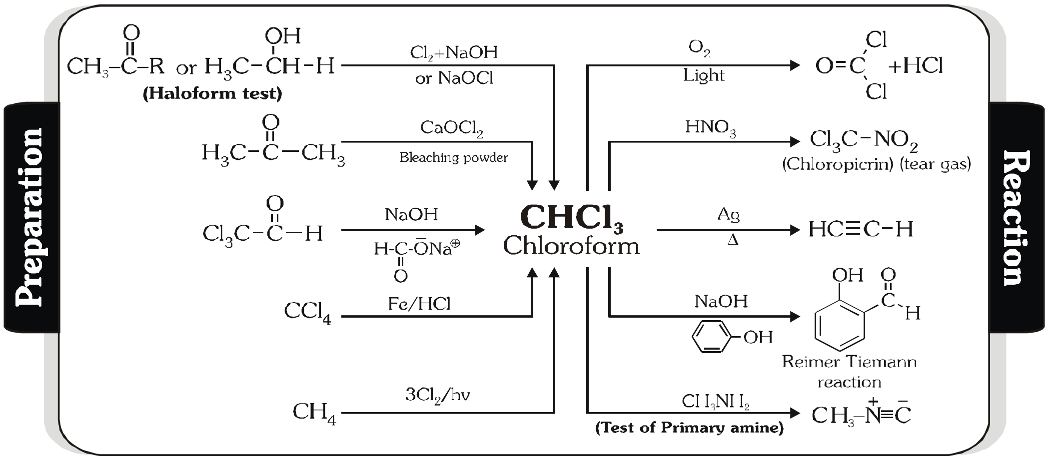
(3) Boiling point : $R{-}I > R{-}Br > R{-}Cl > R{-}F$



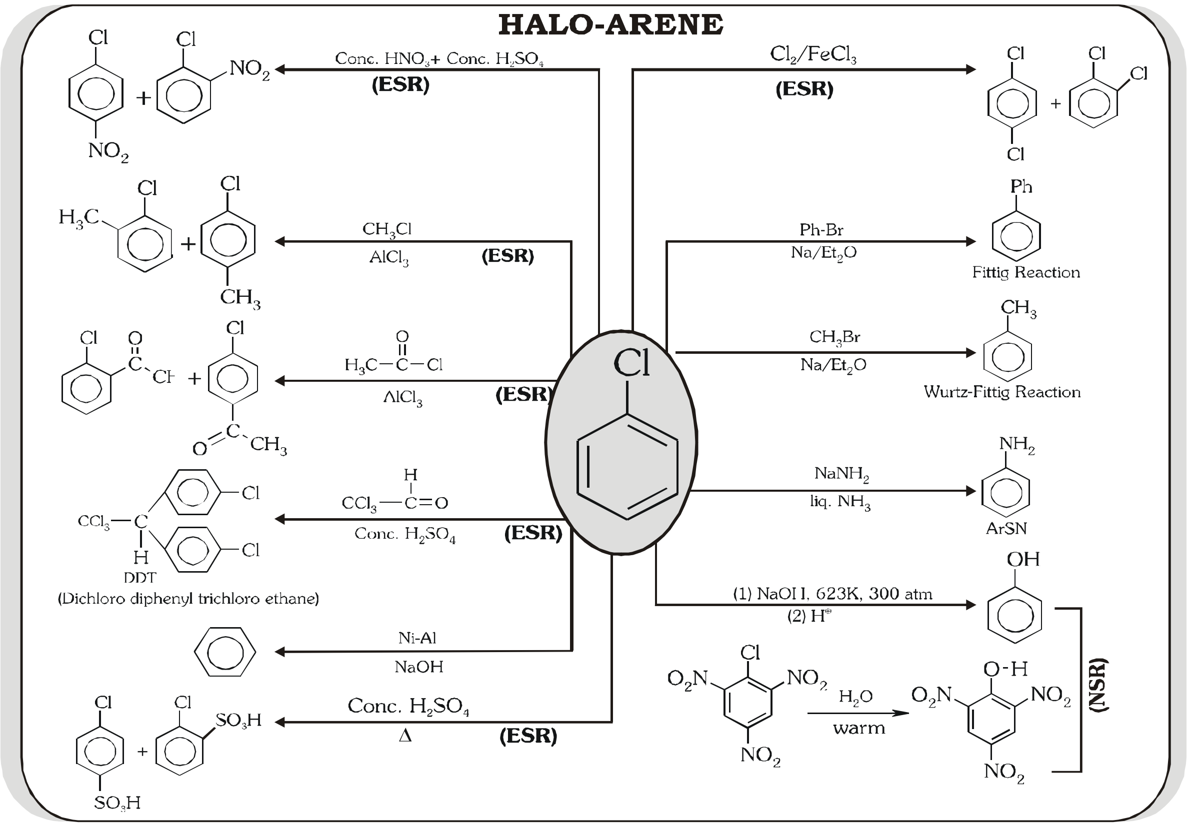
(4) Density : $n{-}C_3H_7Cl < n{-}C_3H_7Br < n{-}C_3H_7I$

(5) Solubility → sligthly soluble in water

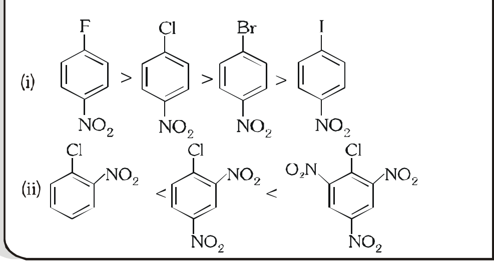
TRI-HALO ALKANE



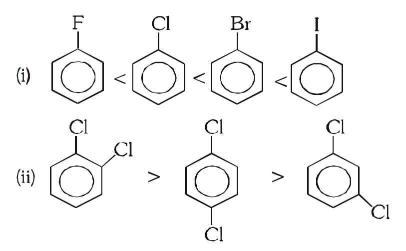
HALO-ARENE



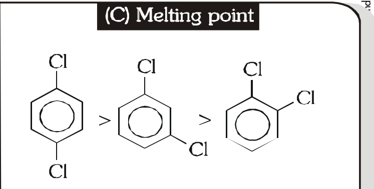
(A) [Reactivity toward Nucleophile]



(B) Boiling point



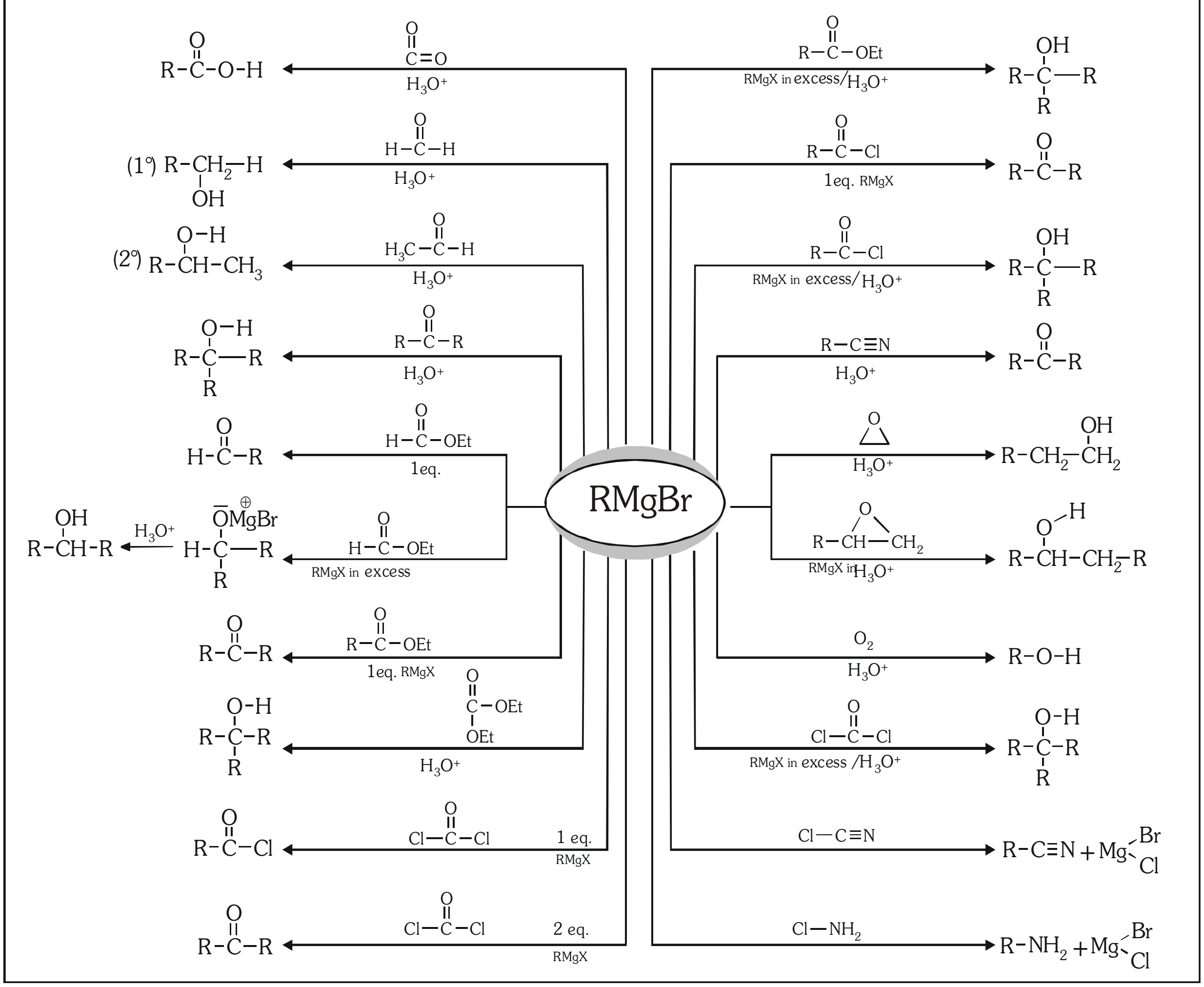
(C) Melting point



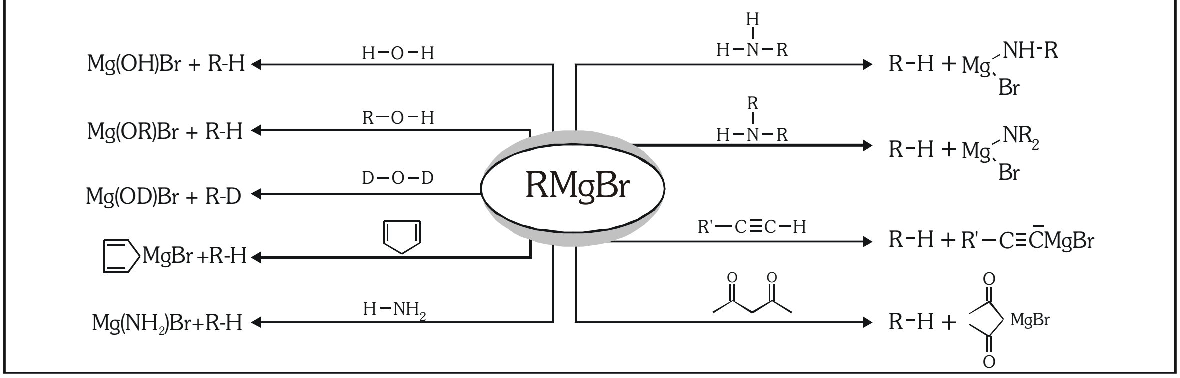
GRIGNARD REAGENT

REACTION

GRIGNARD REAGENT as Nucleophile

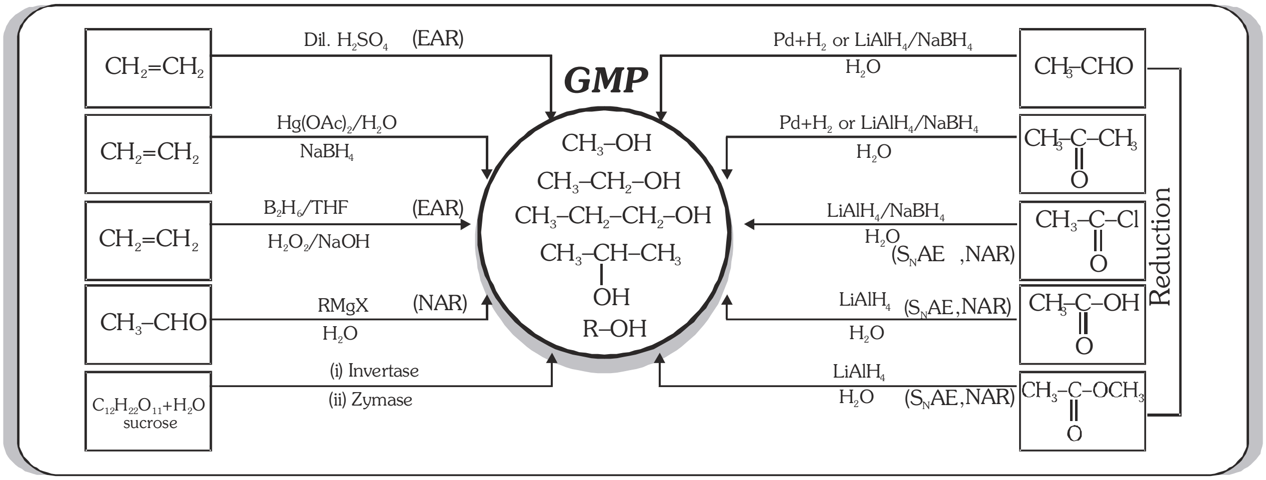


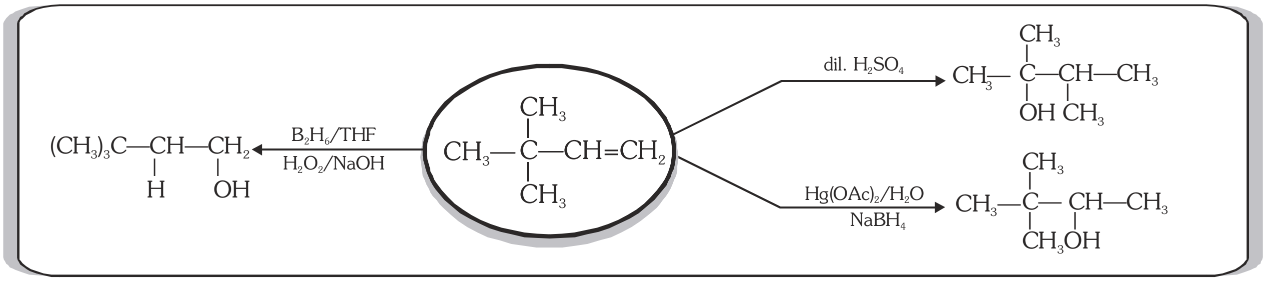
GRIGNARD REAGENT as BASE
(Active H-containing compound)

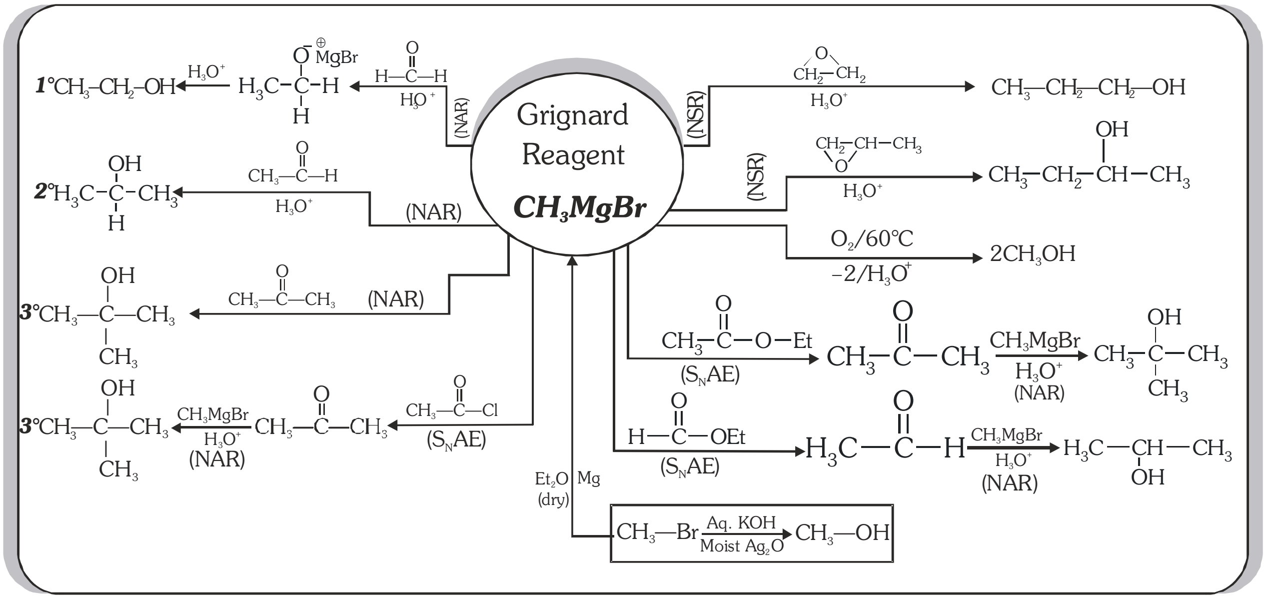


IMPORTANT NOTES

ALCOHOL



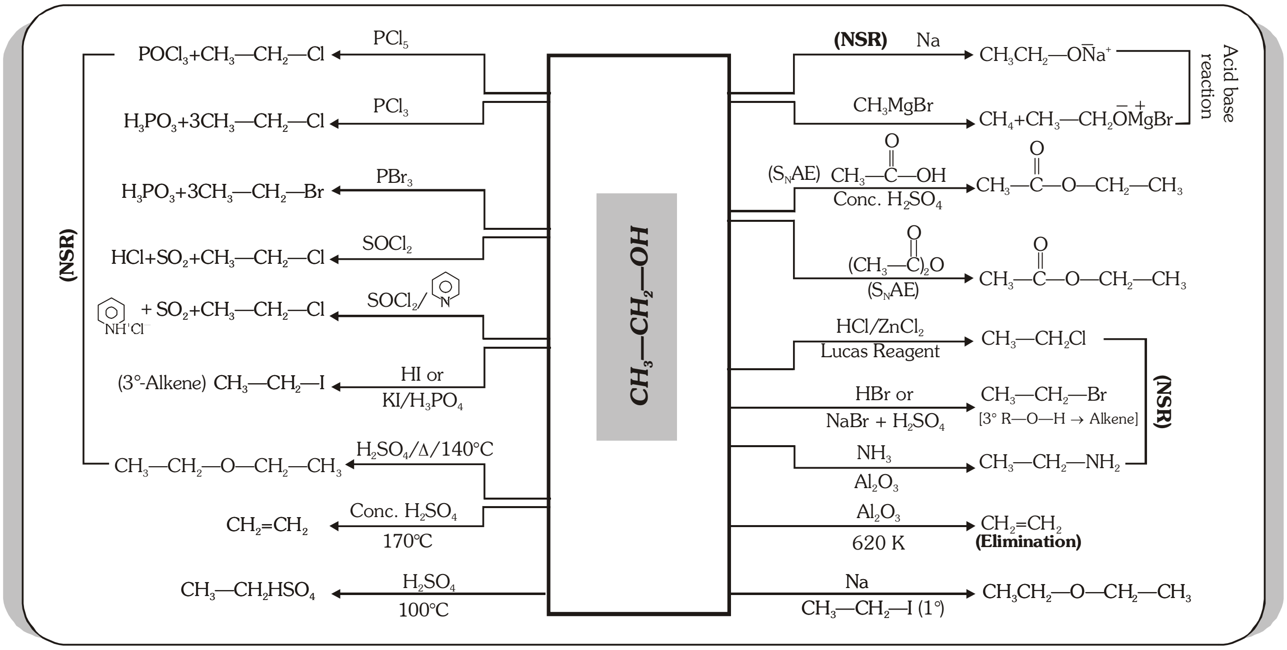




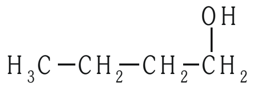
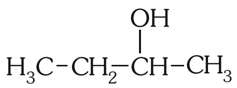
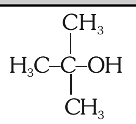
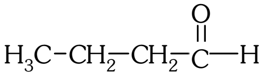
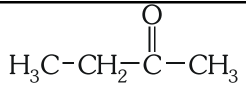
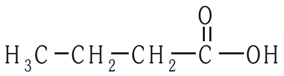
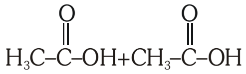
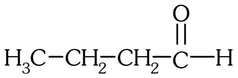
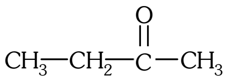
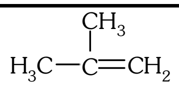
- Solubility of alcohol increase with increase in branching n < iso < neo (isomeric)
- Relative order of reactivity

(i) 1° > 2° > 3° (O–H bond fission) (ii) 3° > 2° > 1° (C–O bond fission) (iii) 3° > 2° > 1° (Dehydration)

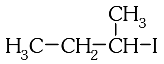
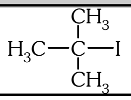
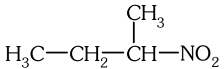
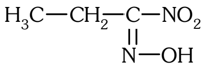
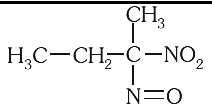
ALCOHOL



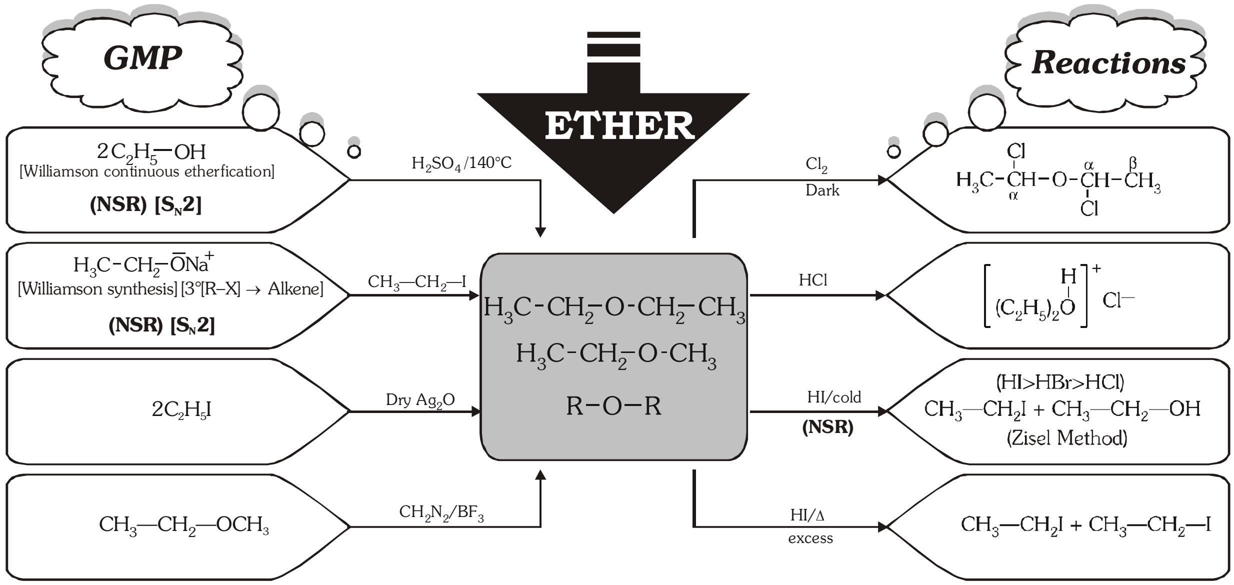
DEHYDROGENATIONS

Reagent	 $H_3C-CH_2-CH_2-\underset{}{\overset{OH}{CH_2}}$ 1° Alcohol	 $H_3C-CH_2-\overset{OH}{CH}-CH_3$ 2° Alcohol	 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$ 3° Alcohol
PCC/PDC Anhy. CrO_3	 $H_3C-CH_2-CH_2-\overset{O}{\overset{\|\|}{C}}—H$	 $H_3C-CH_2-\overset{O}{\overset{\|\|}{C}}-CH_3$	No reaction
$K_2Cr_2O_7/H^{\oplus}$ $KMnO_4/H^+/\overline{O}H/\Delta$ Jones Reagent	 $H_3C-CH_2-CH_2-\overset{O}{\overset{\|\|}{C}}—OH$	 $H_3C-\overset{O}{\overset{\|\|}{C}}-OH+CH_3-\overset{O}{\overset{\|\|}{C}}-OH$	No reaction
Cu/500°C	 $H_3C-CH_2-CH_2-\overset{O}{\overset{\|\|}{C}}—H$	 $CH_3—CH_2—\overset{O}{\overset{\|\|}{C}}—CH_3$	 $H_3C—\overset{CH_3}{C}=CH_2$
Lucas Reagent $HCl/ZnCl_2$	Cloudiness appear upon heating after 30 mins.	within five min.	Immediately

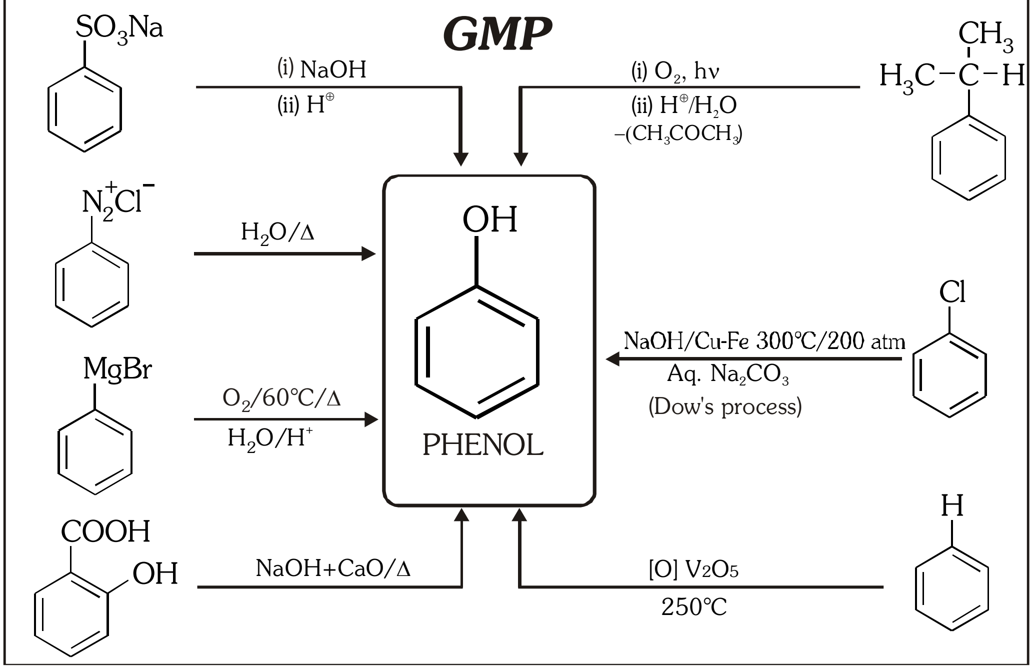
VICTOR MAYER'S TEST

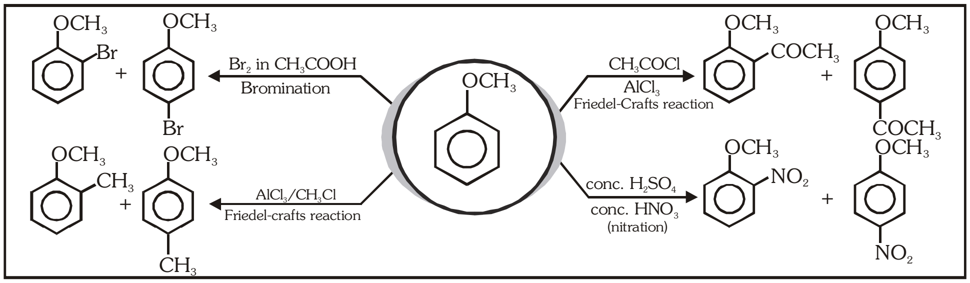
P/I_2	$CH_3–CH_2–CH_2–CH_2–I$	 $H_3C-CH_2-\overset{CH_3}{CH}-I$	 $H_3C—\overset{CH_3}{\underset{CH_3}{C}}—I$
$AgNO_2$	$CH_3–CH_2–CH_2–NO_2$	 $H_3C—CH_2—\overset{CH_3}{CH}—NO_2$	$(CH_3)_3C–NO_2$
HNO_2	 $H_3C—CH_2—\underset{N—OH}{\underset{\|\|}{C}}—NO_2$ Nitrolic acid	 $H_3C—CH_2—\overset{CH_3}{\underset{N=O}{C}}—NO_2$ Blue colour	No reaction : Colourless
NaOH	Red Color	No reaction	

ETHER

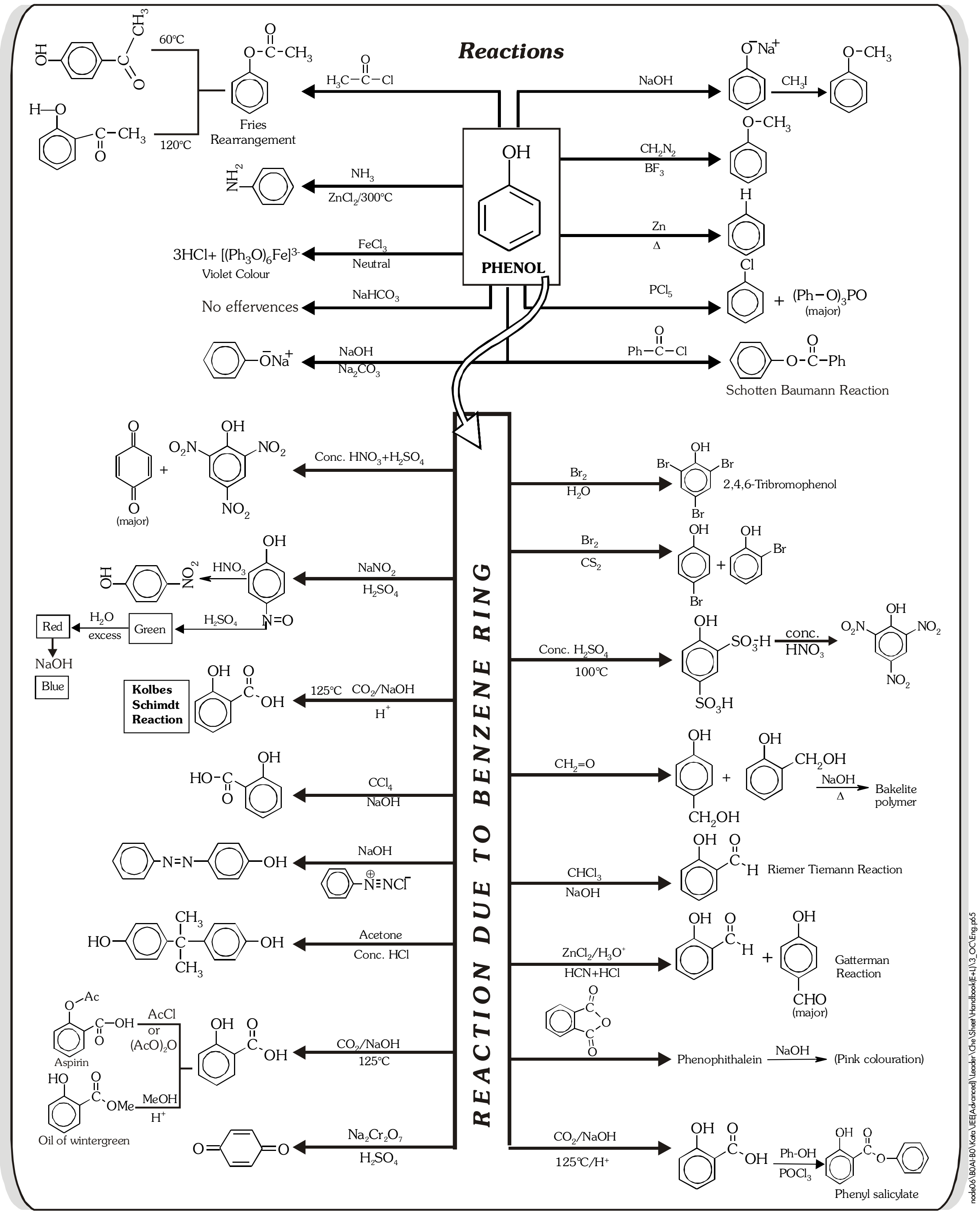


PHENOL





PHENOL



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Comparision of S_N1 and S_N2

	REACTIONS	S_N1	S_N2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	$k[RX][Nu:^{\ominus}]$
C	Stereochemistry	Racemisation	Inversion
D	Substrate (reactivity)	3°> 2°>1°>MeX	MeX >1°>2°>3°
E	Nucleophile	Rate Independent	Needs Strong Nu
F	Solvent	Good ionizing	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Comparision of E_1 and E_2

	REACTIONS	E1	E2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	$k[RX][B:^{-}]$
C	Stereochemistry	No special geometry	Anti-periplanar
D	Substrate	3° > 2°>>>1°	3° >2° >1°
E	Base Strength	Rate Independent	Needs Strong bases
F	Solvent	Good ionizing	Polarity not import
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Summary of S_N1, S_N2, E_1 and E_2 Reactions

RX	Mechanism	$\overset{\ominus}{Nu}/\overset{\ominus}{B}$	Solvent	Temp.
1°	S_N2	Better $\overset{\ominus}{O}H, C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E2	Strong & bulky base $(CH_3)_3C\overset{\ominus}{O}$		High
2°	S_N2	$H\overset{\ominus}{O}; C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E2	$(CH_3)_3C\overset{\ominus}{O}$		High
	(S_N1)	(Solvent	Polar aprotic	(Low)
	(E1)	(Solvent)		(High)
3°	S_N1	Solvent	Protic	Low
	E1	Solvent	Protic	High

	Primary (1°)	Secondary (2°)	Tertiary (3°)
Strong nucleophile	S_N2 >>E2	$S_N2 + E_2$ (if weak base, S_N2 favored)	E2
Weak nucleophile weak base	Mostly S_N2	Mostly S_N2/S_N1	Mostly S_N1 at low T mostly E1 at high T
Weak nucleophile strong base	Mostly E2	Mostly E2	E2

Order of reactivity of

Alkyl Halide towards

$S_N1 \propto$ Benzylic>Allylic>3°>2°>1°

$S_N1 \propto$ Stability of carbocation

$S_N2 \propto$ 1° > 2° > 3°

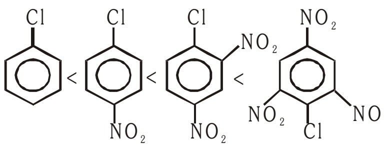
$$S_N2 \propto \frac{1}{\text{Steric hindrance}}$$

Reactivity order towards

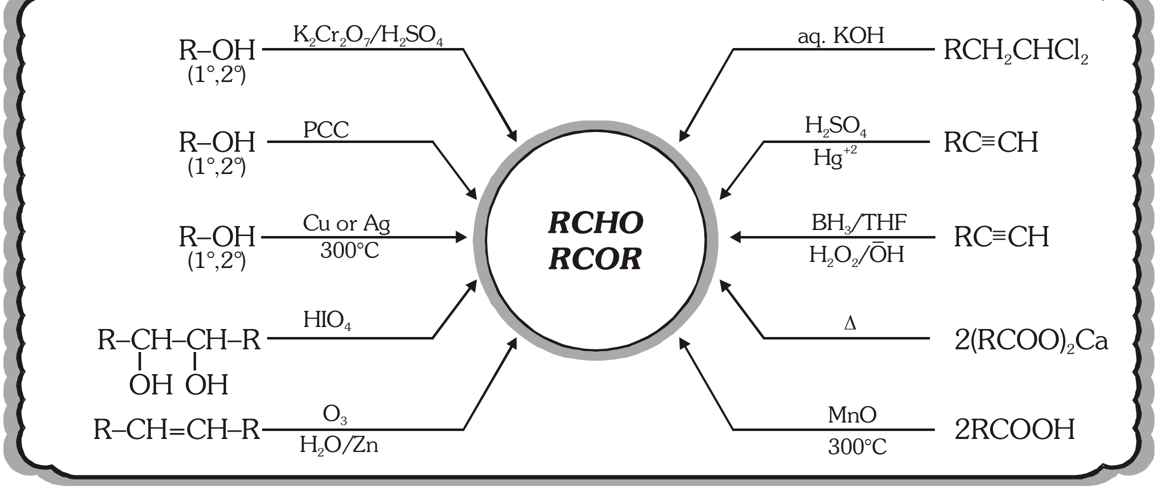
S_N1 or S_N2 and E_1 or E_2

R–I > R–Br > R–Cl > R–F

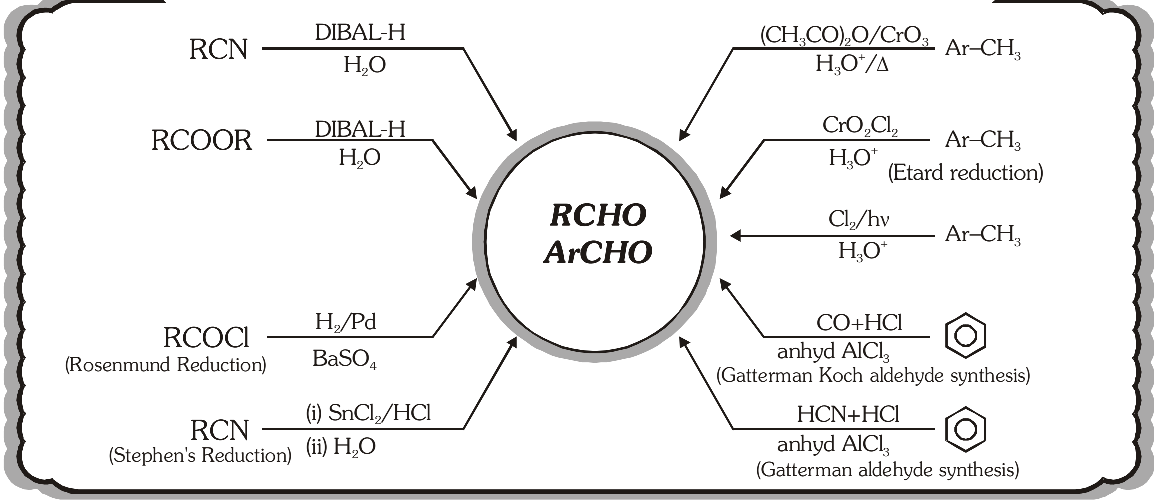
With increase in number of strong electron withrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitution increases.



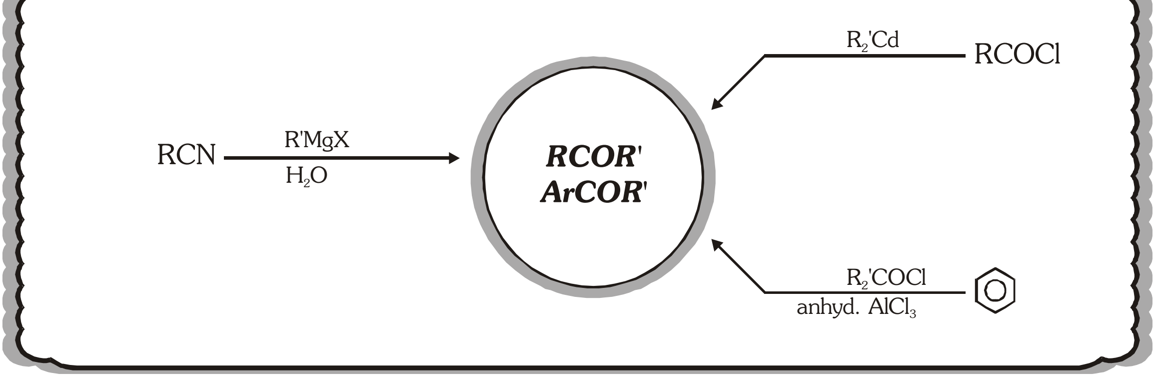
Preparation of Aldehyde & Ketone both



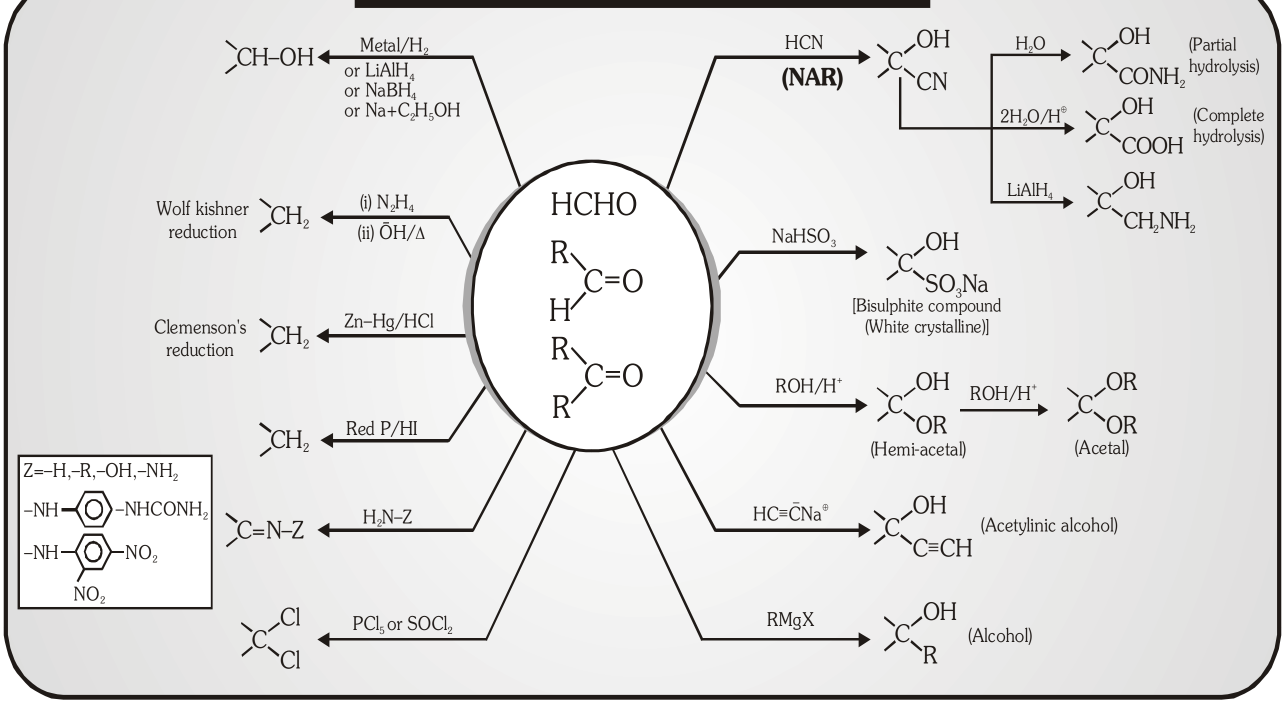
Preparation of Aldehyde only



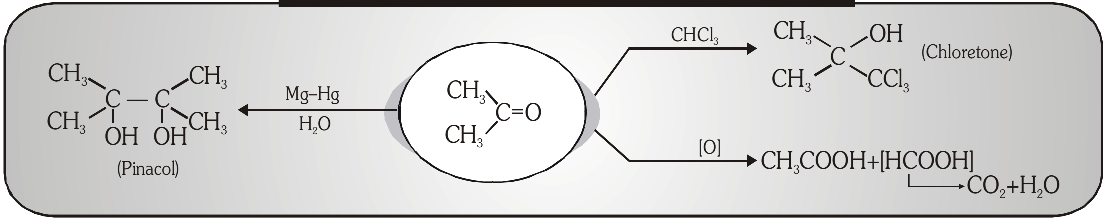
Preparation of Ketone only



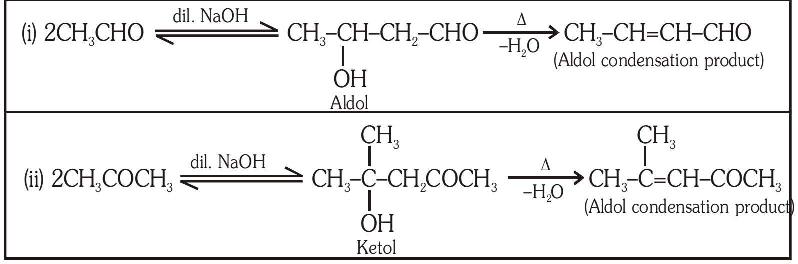
Reaction of Aldehyde & Ketone



Reaction of only Ketone



Aldol Reaction (Aldehyde or ketone with αH)



(i) $2CH_3CHO \overset{\text{dil. NaOH}}{\rightleftharpoons} CH_3\text{–}\underset{\underset{\text{Aldol}}{OH}}{CH}\text{–}CH_2\text{–}CHO \xrightarrow[-H_2O]{\Delta} CH_3\text{–}CH{=}CH\text{–}CHO$ (Aldol condensation product)

(ii) $2CH_3COCH_3 \overset{\text{dil. NaOH}}{\rightleftharpoons} CH_3\text{–}\overset{CH_3}{\underset{\underset{\text{Ketol}}{OH}}{C}}\text{–}CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3\text{–}\overset{CH_3}{C}{=}CH\text{–}COCH_3$ (Aldol condensation product)

Cannizzaro reaction (Aldehyde with no α H)

$$2HCHO \xrightarrow[\Delta]{\text{conc. NaOH}} CH_3OH + HCOO^-Na^+$$

TESTS

Tollen's test :-

$RCHO + 2[Ag(NH_3)_2]^+ + 3\ ^-OH \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$

(Given by Aliphatic and aromatic aldehyde)

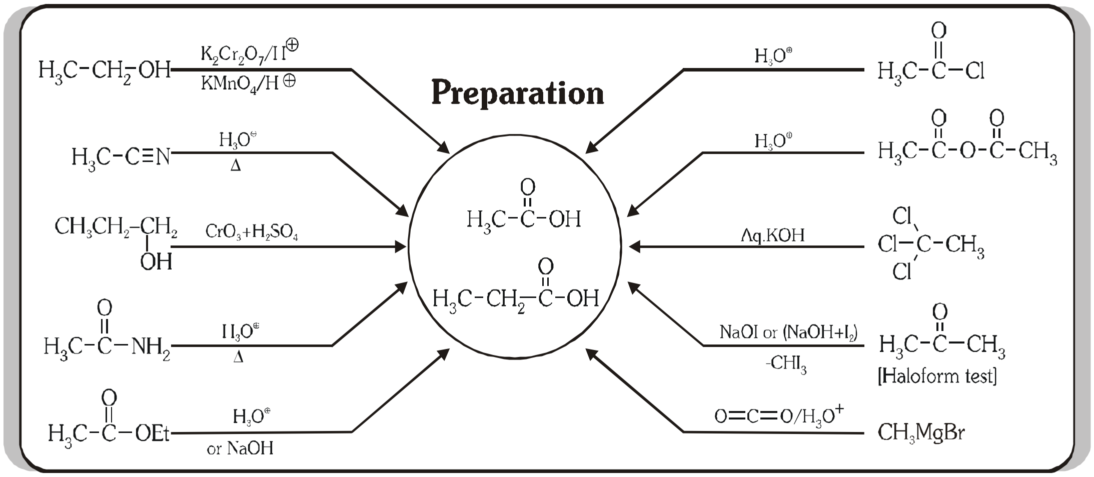
Fehling's test

$RCHO + 2Cu^{+2} + 5\ ^-OH \longrightarrow RCOO^- + Cu_2O + 3H_2O$

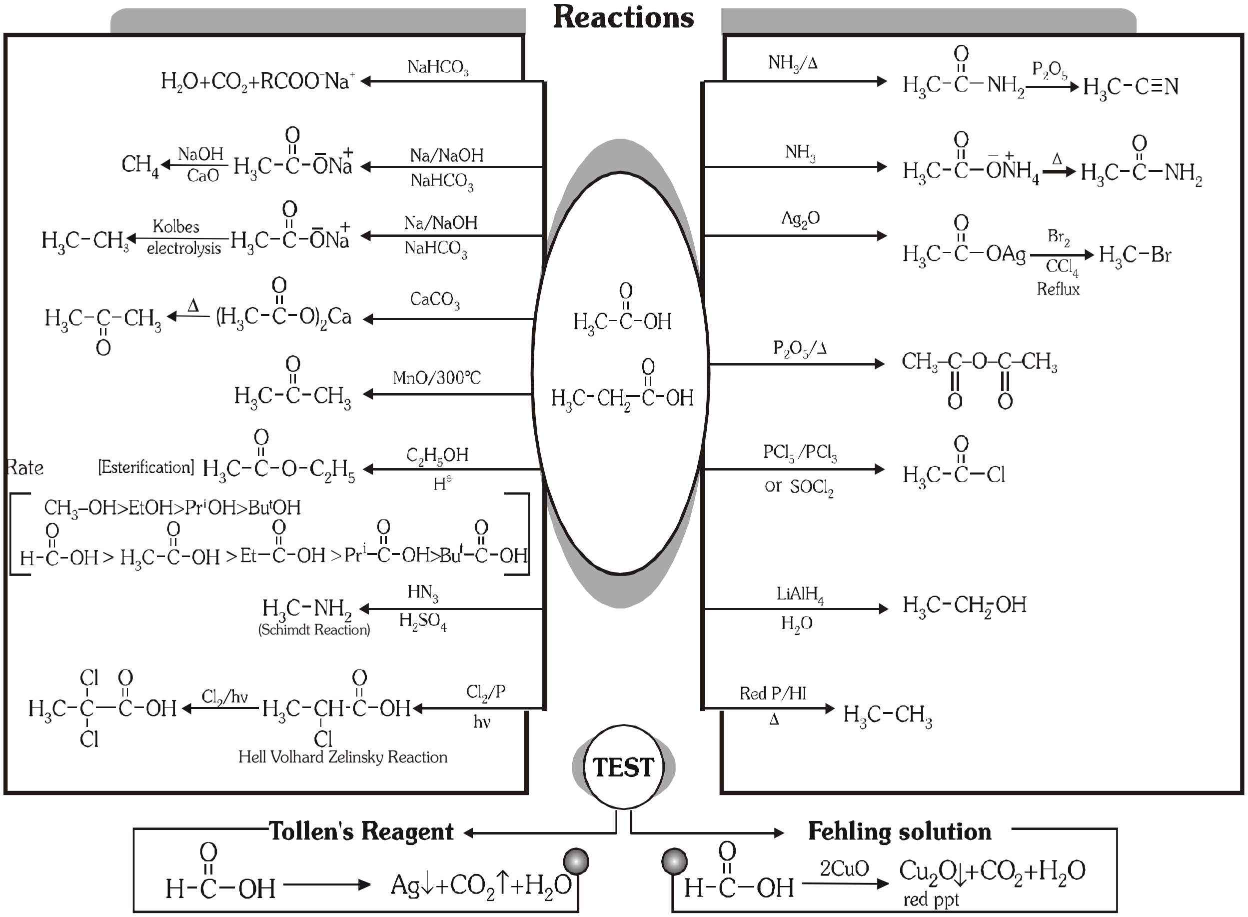
(Given by Aliphatic aldehyde) (Red-Brown ppt.)

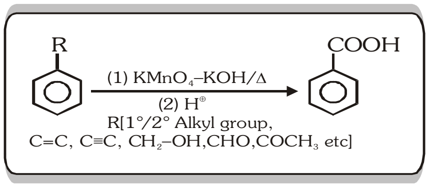
IMPORTANT NOTES

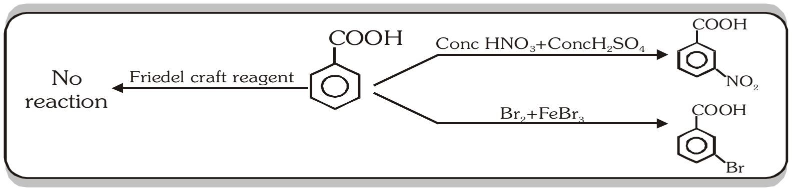
CARBOXYLIC ACID

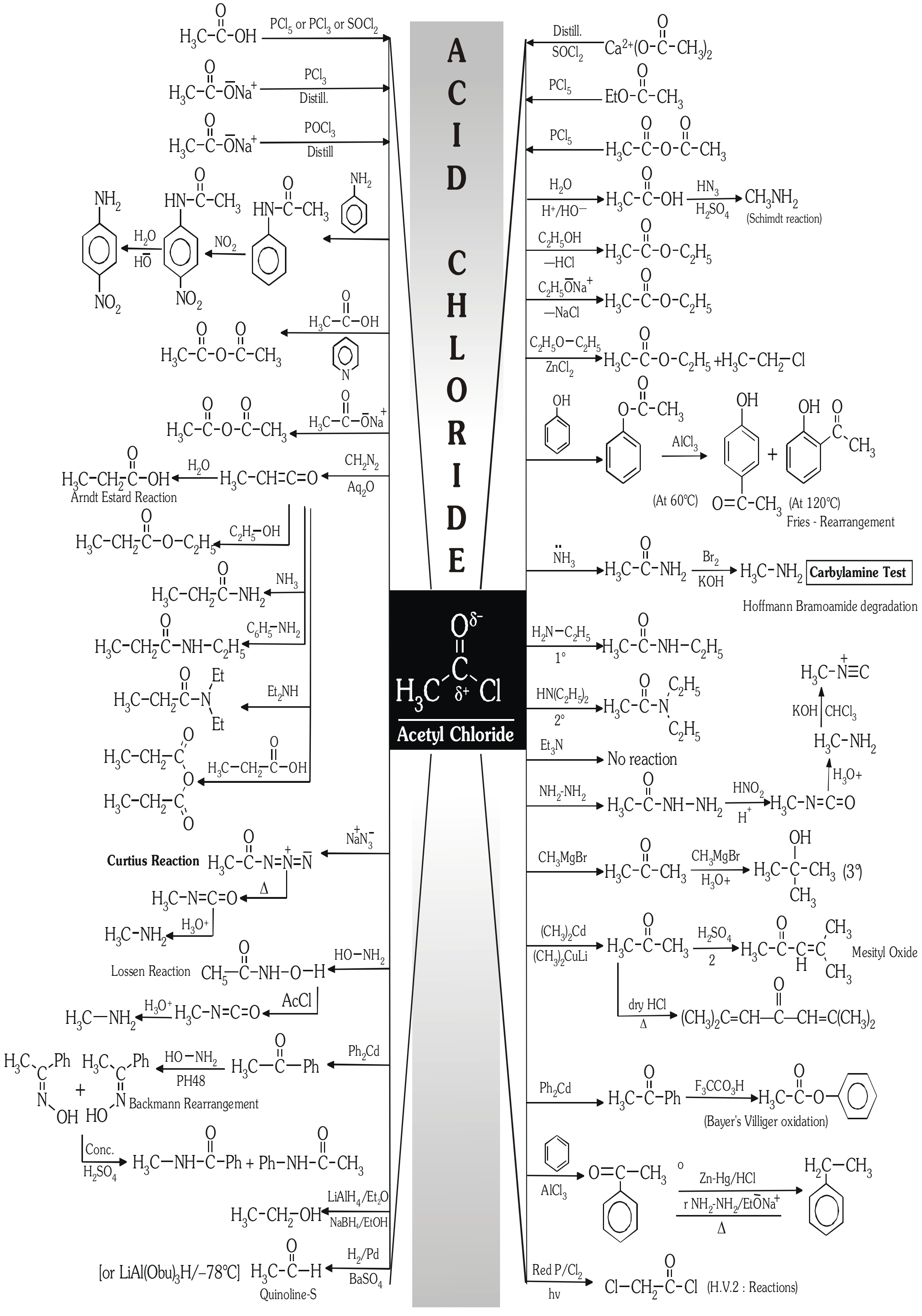


Reactions

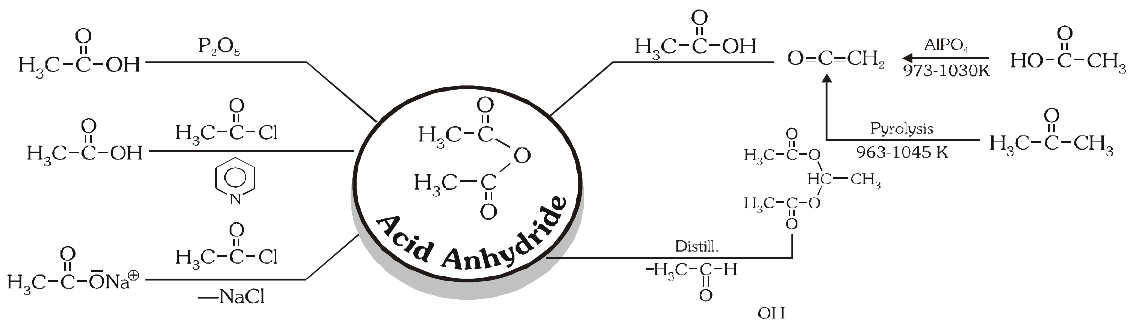


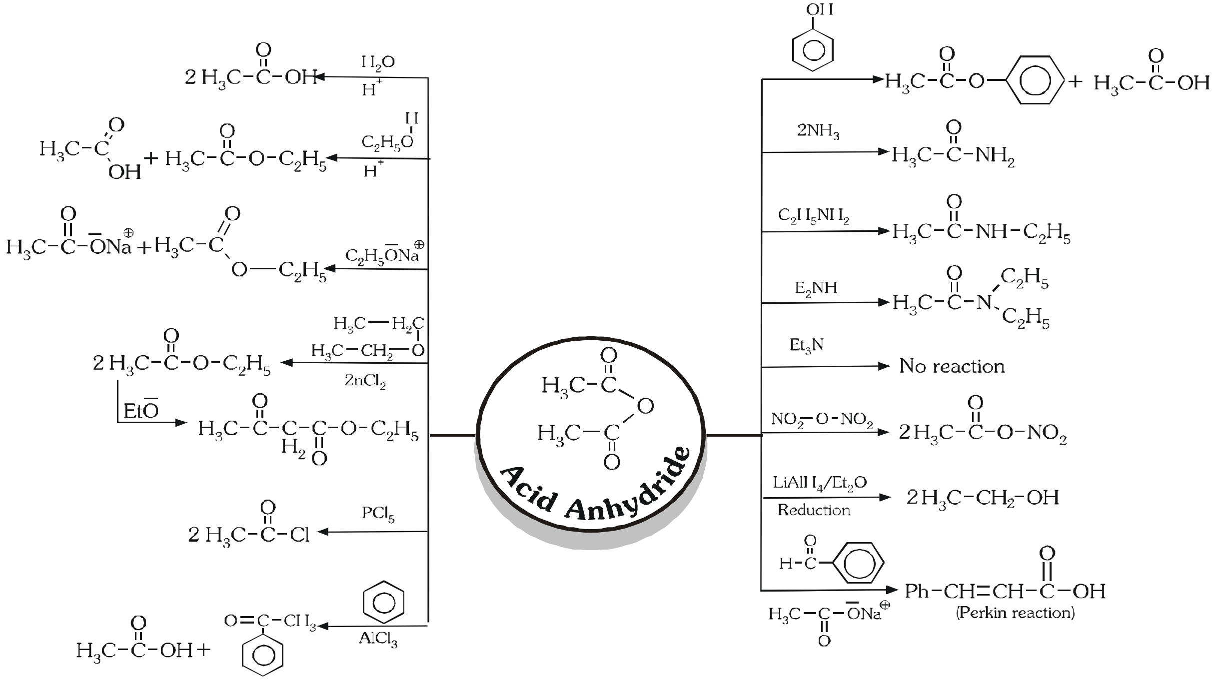





ACID CHLORIDE
$H_3C-C(=O^{\delta-})-Cl$ ($C^{\delta+}$)
Acetyl Chloride
$H_3C-C(=O)-OH$ PCl_5 or PCl_3 or $SOCl_2$
$H_3C-C(=O)-\bar{O}Na^+$ PCl_3 Distill.
$H_3C-C(=O)-\bar{O}Na^+$ $POCl_3$ Distill
NH_2 (aniline)
$HN-C(=O)-CH_3$ (acetanilide)
NO_2
H_2O / $H\bar{O}$
NH_2 / NO_2 (p-nitroaniline)
$H_3C-C(=O)-OH$ / pyridine (N)
$H_3C-C(=O)-O-C(=O)-CH_3$
$H_3C-C(=O)-\bar{O}Na^+$
$H_3C-C(=O)-O-C(=O)-CH_3$
CH_2N_2 / Aq_2O
$H_3C-CH=C=O$
H_2O
$H_3C-CH_2-C(=O)-OH$
Arndt Estard Reaction
C_2H_5-OH → $H_3C-CH_2-C(=O)-O-C_2H_5$
NH_3 → $H_3C-CH_2-C(=O)-NH_2$
$C_6H_5-NH_2$ → $H_3C-CH_2-C(=O)-NH-C_2H_5$
Et_2NH → $H_3C-CH_2-C(=O)-N(Et)_2$
$H_3C-CH_2-C(=O)-OH$ → $(H_3C-CH_2-C(=O))_2O$
$Na\overset{+}{N}_3^-$
Curtius Reaction $H_3C-C(=O)-N=\overset{+}{N}=\bar{N}$
Δ → $H_3C-N=C=O$
H_3O^+ → H_3C-NH_2
$HO-NH_2$
Lossen Reaction $CH_3-C(=O)-NH-O-H$
AcCl → $H_3C-N=C=O$ H_3O^+ → H_3C-NH_2
Ph_2Cd → $H_3C-C(=O)-Ph$
$HO-NH_2$ / PH48
$H_3C(Ph)C=N-OH$ + $H_3C(Ph)C=N-OH$
Backmann Rearrangement
Conc. H_2SO_4 → $H_3C-NH-C(=O)-Ph$ + $Ph-NH-C(=O)-CH_3$
$LiAlH_4/Et_2O$ / $NaBH_4/EtOH$ → H_3C-CH_2-OH
H_2/Pd / $BaSO_4$ / Quinoline-S → $H_3C-C(=O)-H$
[or $LiAl(Obu)_3H$/–78°C]
Distill. $SOCl_2$ ← $Ca^{2+}(O-C(=O)-CH_3)_2$
PCl_5 ← $EtO-C(=O)-CH_3$
PCl_5 ← $H_3C-C(=O)-O-C(=O)-CH_3$
H_2O / H^+/HO^- → $H_3C-C(=O)-OH$ HN_3 / H_2SO_4 → CH_3NH_2
(Schimdt reaction)
C_2H_5OH / —HCl → $H_3C-C(=O)-O-C_2H_5$
$C_2H_5\bar{O}Na^+$ / —NaCl → $H_3C-C(=O)-O-C_2H_5$
$C_2H_5O-C_2H_5$ / $ZnCl_2$ → $H_3C-C(=O)-O-C_2H_5$ + H_3C-CH_2-Cl
OH (phenol) → $O-C(=O)-CH_3$ (phenyl acetate)
$AlCl_3$
OH / $O=C-CH_3$ (At 60°C) + OH, $C(=O)CH_3$ (At 120°C)
Fries - Rearrangement
$\ddot{N}H_3$ → $H_3C-C(=O)-NH_2$ Br_2 / KOH → H_3C-NH_2
Carbylamine Test
Hoffmann Bramoamide degradation
$H_2N-C_2H_5$ 1° → $H_3C-C(=O)-NH-C_2H_5$
$HN(C_2H_5)_2$ 2° → $H_3C-C(=O)-N(C_2H_5)_2$
Et_3N → No reaction
$H_3C-\overset{+}{N}\equiv C$
KOH | $CHCl_3$
H_3C-NH_2
H_3O+
NH_2-NH_2 → $H_3C-C(=O)-NH-NH_2$ HNO_2 / H^+ → $H_3C-N=C=O$
CH_3MgBr → $H_3C-C(=O)-CH_3$ CH_3MgBr / H_3O+ → $H_3C-C(OH)(CH_3)-CH_3$ (3°)
$(CH_3)_2Cd$ / $(CH_3)_2CuLi$ → $H_3C-C(=O)-CH_3$ H_2SO_4 / 2 → $H_3C-C(=O)-CH=C(CH_3)_2$ Mesityl Oxide
dry HCl / Δ → $(CH_3)_2C=CH-C(=O)-CH=C(CH_3)_2$
Ph_2Cd → $H_3C-C(=O)-Ph$ F_3CCO_3H → $H_3C-C(=O)-O-C_6H_5$
(Bayer's Villiger oxidation)
benzene / $AlCl_3$ → $O=C-CH_3$ (acetophenone)
o
Zn-Hg/HCl
r $NH_2-NH_2/Et\bar{O}Na^+$
Δ
H_2C-CH_3 (ethylbenzene)
Red P/Cl_2 / hv → $Cl-CH_2-C(=O)-Cl$ (H.V.Z : Reactions)

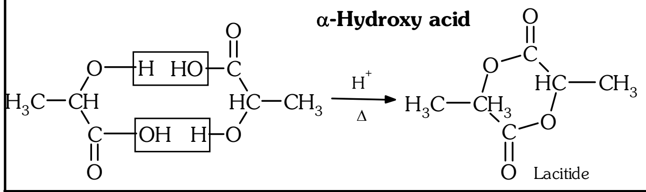
ACID anhydride



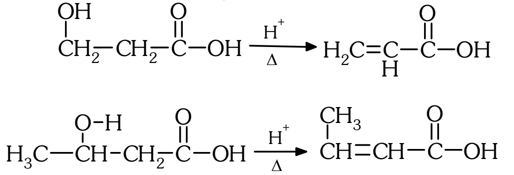


Heating effect

α-Hydroxy acid



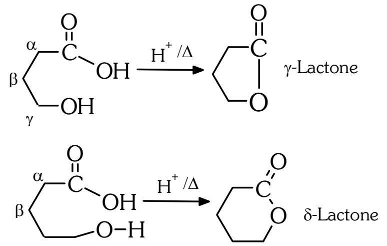
β-Hydroxy acid



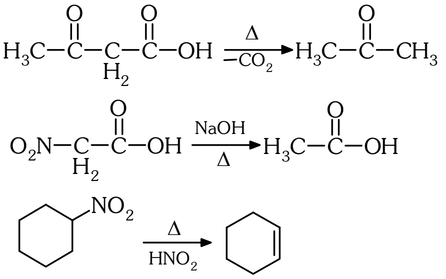
$$H_2\overset{OH}{C}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{H^+} H_2C=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-OH$$

$$H_3C-\overset{O-H}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{H^+} \overset{CH_3}{CH}=CH-\overset{O}{\overset{\|}{C}}-OH$$

γ & δ–Hydroxy acid

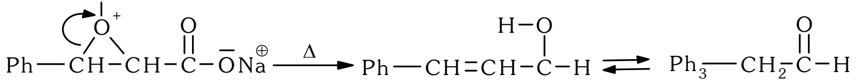


β –Keto acid:



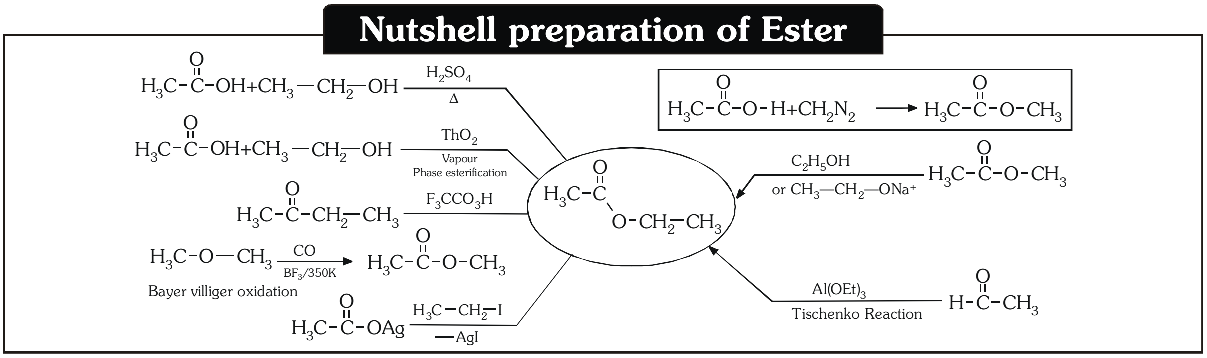
$$H_3C-\overset{O}{\overset{\|}{C}}-\underset{H_2}{C}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-CO_2]{\Delta} H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

$$O_2N-\underset{H_2}{C}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NaOH} H_3C-\overset{O}{\overset{\|}{C}}-OH$$

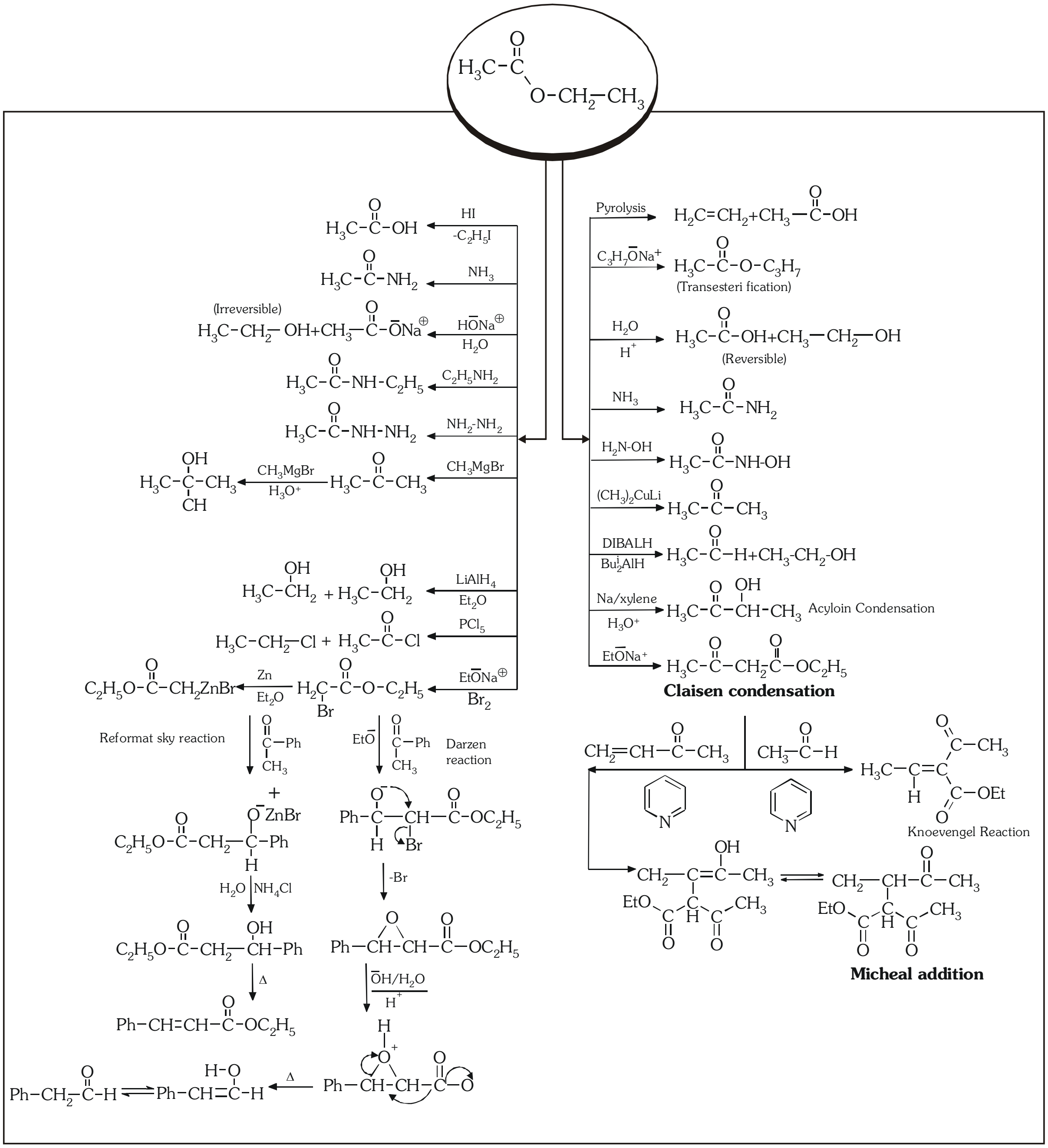


$$Ph-\overset{H-\overset{+}{O}}{CH}-CH-\overset{O}{\overset{\|}{C}}-\bar{O}Na^{\oplus} \xrightarrow{\Delta} Ph-CH=CH-\overset{H-O}{\overset{|}{C}}-H \rightleftharpoons Ph_3-CH_2-\overset{O}{\overset{\|}{C}}-H$$

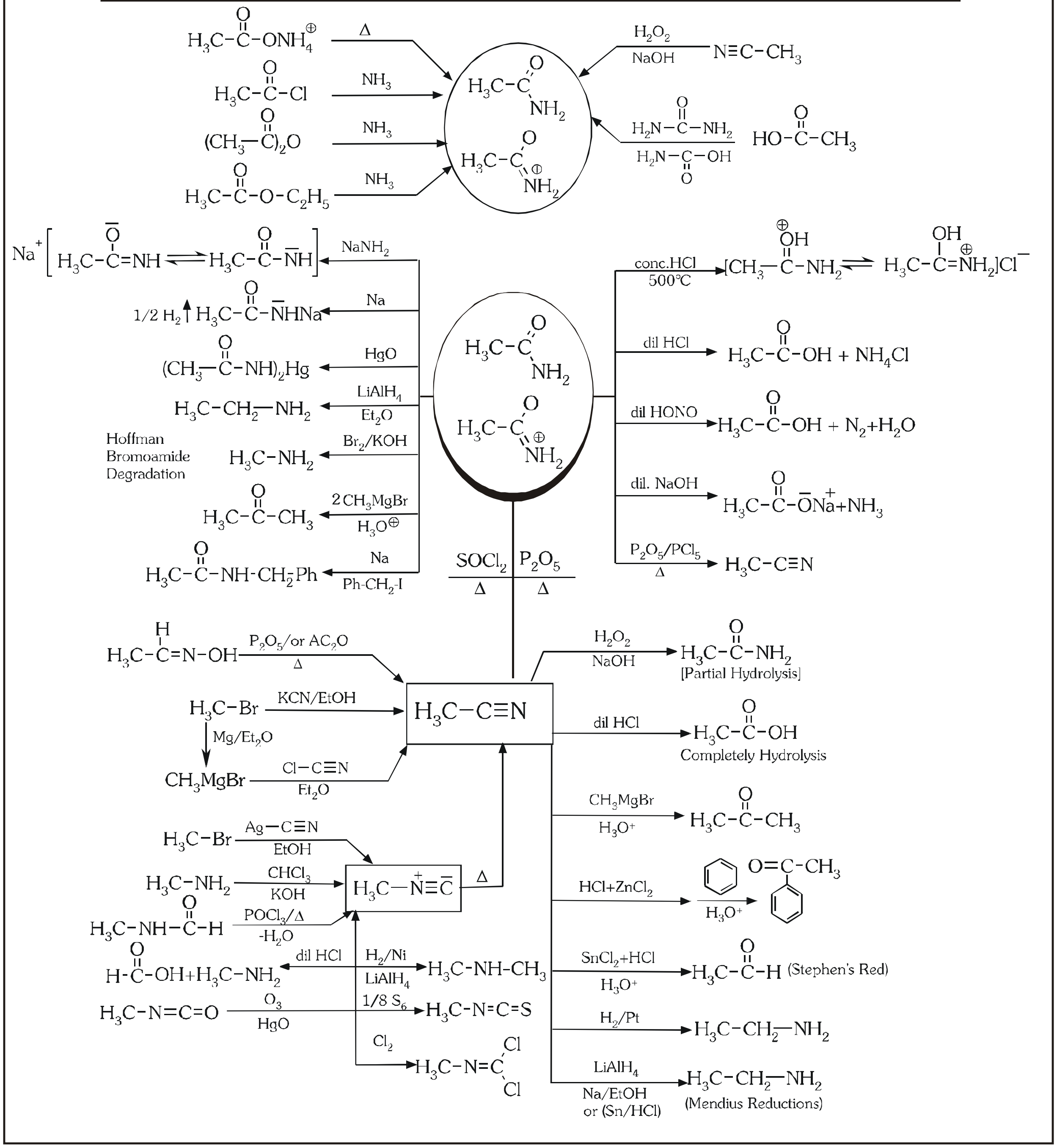
Nutshell preparation of Ester



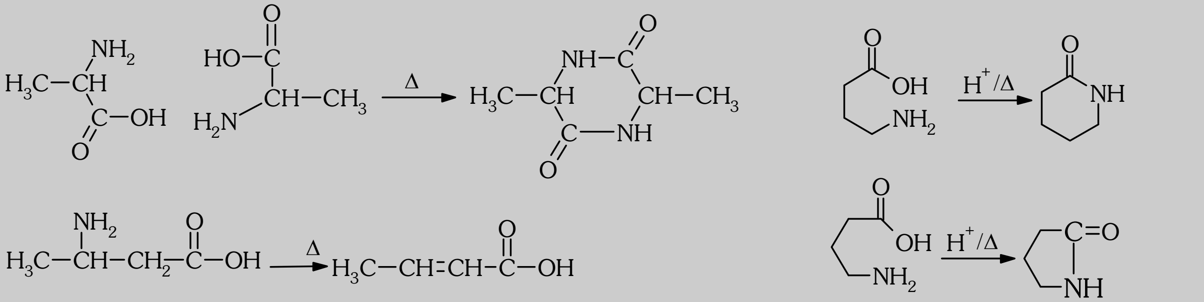
Nutshell chemical properties of Ester



Nutshell preview and review of Amide, Cyanide and Isocyanide



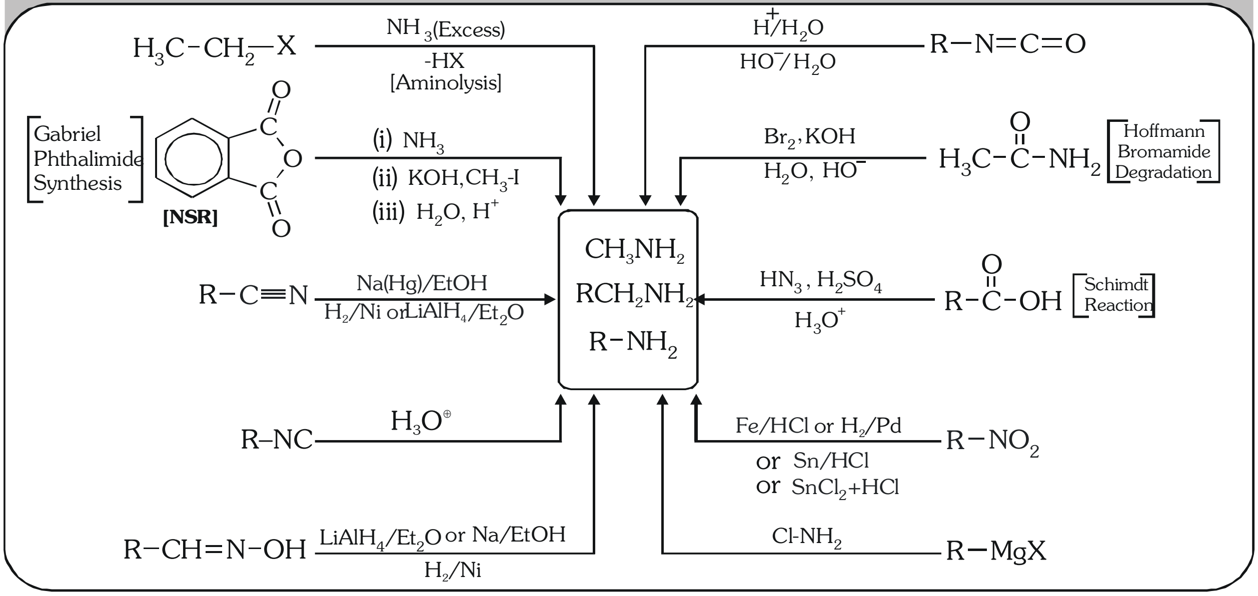
Amino Acid :



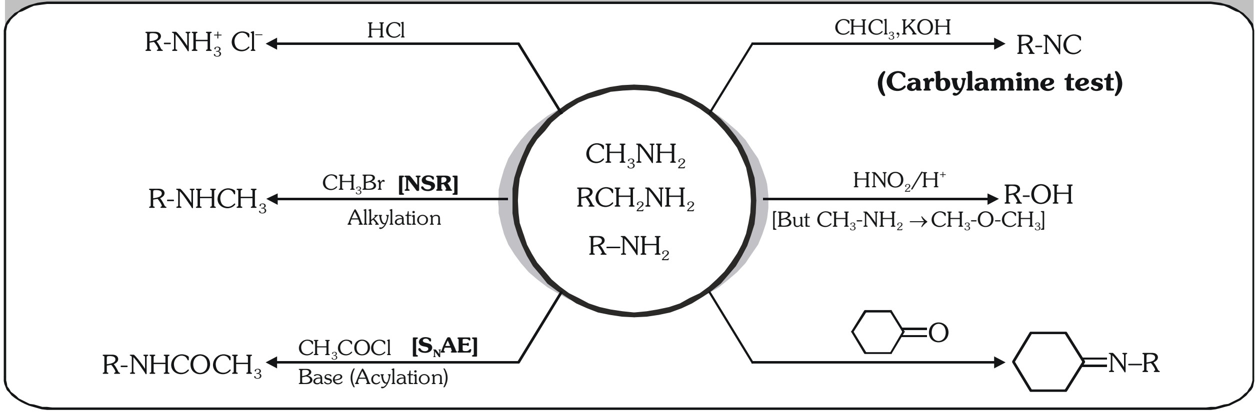
IMPORTANT NOTES

AMINES

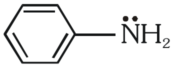
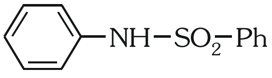
PREPARATION



REACTION

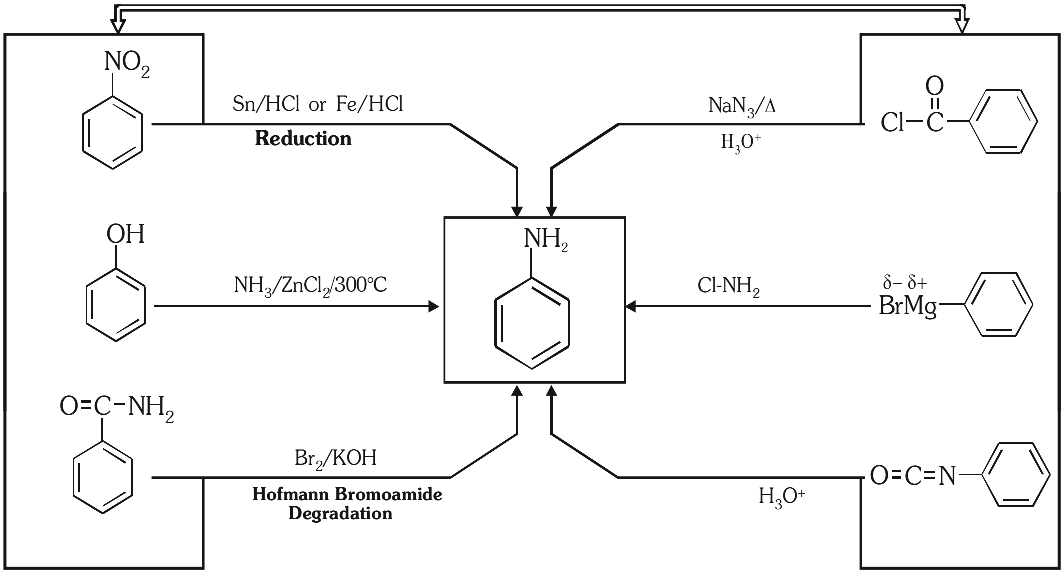


TEST

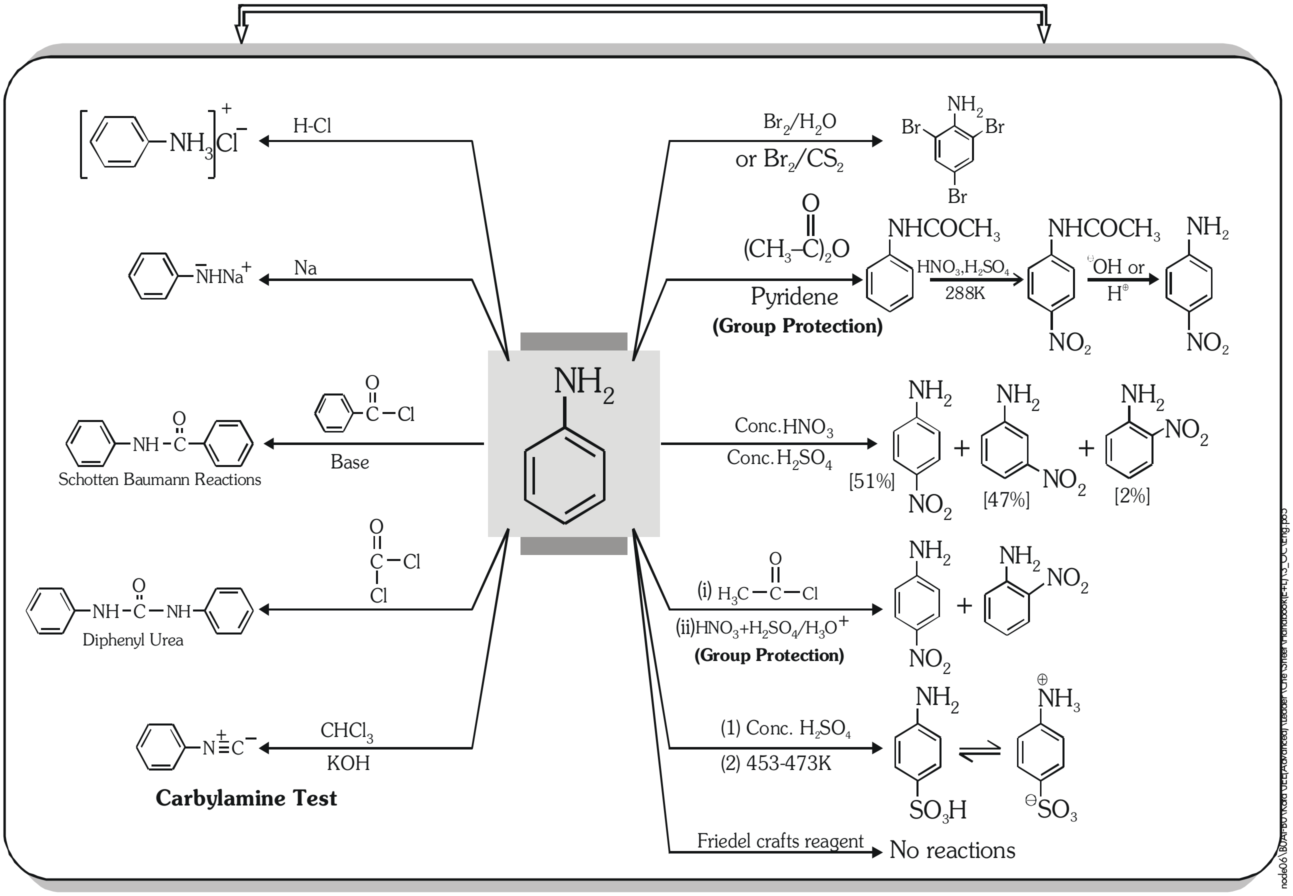
Reagent	$R-\ddot{N}H_2$(1°)	$R_2\ddot{N}H$(2°)	$R_3\ddot{N}$(3°)	
$Ph-SO_2Cl$ (Hinsberg reagent)	$R-\underset{H}{N}-SO_2-Ph$ soluble $\big\downarrow$ NaOH $[R-\overset{\ominus}{N}-SO_2-Ph]Na^+$	$R_2N-\underset{\downarrow O}{\overset{O \atop ||}{S}}-Ph$ $\big\downarrow$ NaOH Insoluble	No reaction	
$\overset{S \atop ||}{C}=S$ $\Delta/HgCl_2$ Mustard oil test	$R-NH-\overset{S \atop ||}{C}-SH$ $HgCl_2 \big\downarrow \Delta$ $R-N=C=S+HgS$	$R_2N-\overset{S \atop ||}{C}-SH$ $HgCl_2 \big\downarrow \Delta$ No reaction	No reaction	$\xrightarrow{KOH}$ Ph—N=C=S+HgS

ANILINE

PREPARATION

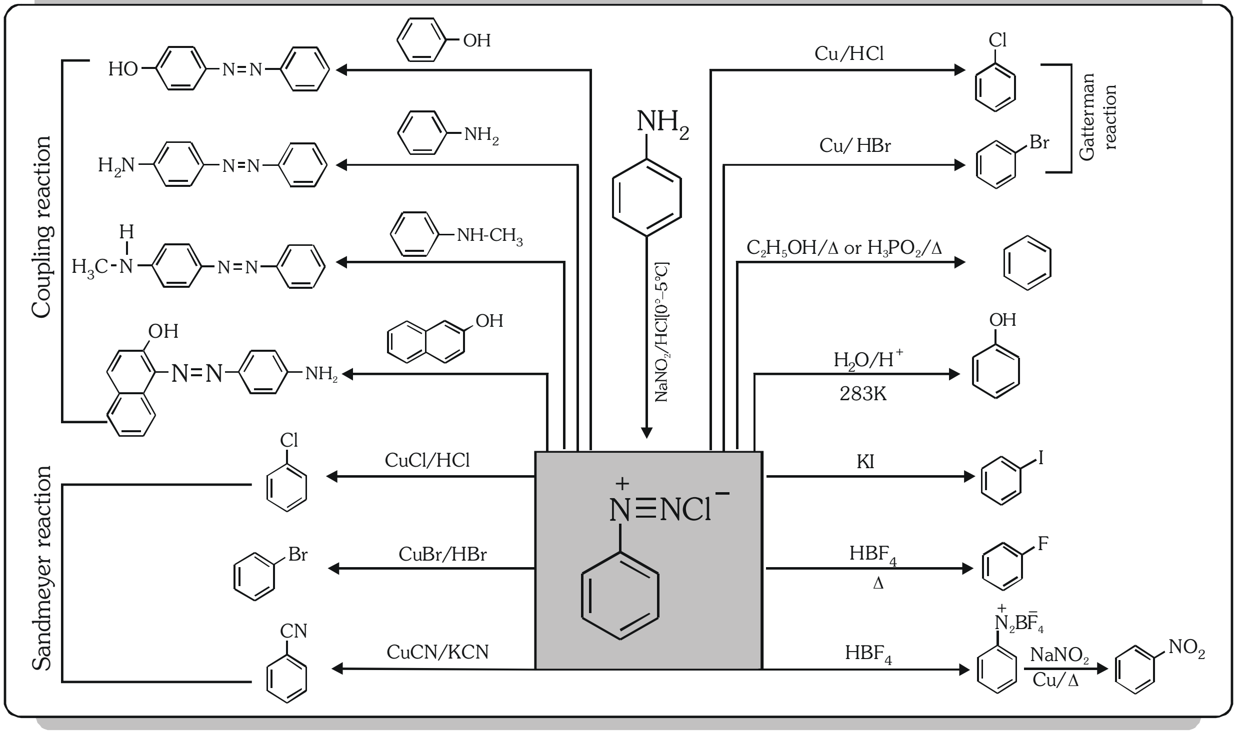


REACTION



BENZENE DIAZONIUM CHLORIDE

REACTION



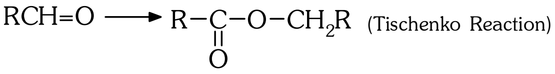
FrSR	Free Radical Substitution reaction
ESR	Electrophilic Substitution reaction
NSR	Nucleophilic Substitution reaction
S_NAE	Substitution Nucleophilic (addition elimination)
FrAR	Free radical addition reaction
NAR	Nucleophilic addition reaction
EAR	Electrophilic addition reaction
FrER	Free Radical Elimination reaction

IMPORTANT NOTES

Nutshell review & preview of
ORGANIC REAGENTS

1. **Alcoholic KOH**
R—X → Alkene ; Elimination

2. **Aluminium Ethoxide**

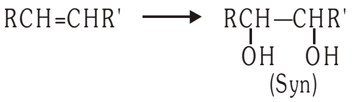


$RCH{=}O \longrightarrow R-\underset{\underset{O}{\|}}{C}-O-CH_2R$ (Tischenko Reaction)

(Aldehyde) (Ester)

3. **Aqueous KOH/NaOH**
R—X → ROH
Nucleophilic substitution reaction also used for Cannizzaro reaction with aldehyde.

4. **Baeyer's Reagent** (Alkaline cold dilute $KMnO_4$)



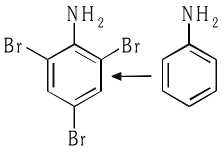
$RCH{=}CHR' \longrightarrow \underset{OH}{RCH}-\underset{OH}{CHR'}$

(Syn)

alkene ⟶ 1, 2 diol
(used to detect unsaturation)

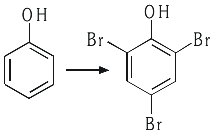
5. **Bromine water**
(i) used to detect unsaturation;

(ii)



2,4,6-tribromoaniline

(iii)

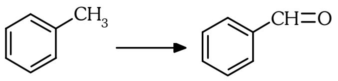


2,4,6-tribromophenol

6. **Benedict's solution**
Used to detect aldehyde group RCHO → RCO_2^-
[ketone gives -ve test]

7. **Cu_2Cl_2 + NH_4OH**
Used to Detect Terminal Alkyne
Red Precipitate observed

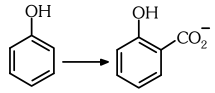
8. **CrO_2Cl_2**



Etard reaction

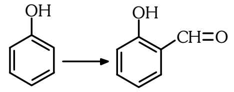
9. **CrO_3**
(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C{=}O$
(iii) $R_3COH \rightarrow$ no reaction

10. **CCl_4 + OH^-** (Reimer Tiemann)



+ p-Product

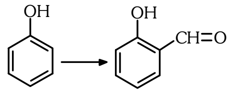
11. **CO + HCl + $AlCl_3$**



+ p-Product

Gatterman koch reaction

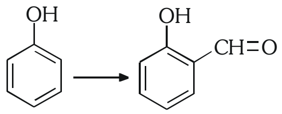
12. **HCN + HCl + $AlCl_3$**



Gatterman Aldehyde Synthesis

13. **$CHCl_3$ + KOH**

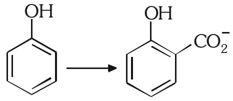
(i)



Reimer Tiemann reaction

(ii) $RNH_2 \rightarrow RNC$ ***(Carbyl amine reaction)***
(used to detect 1° Amine) (Isocyanide test)

14. **CO_2 + OH^- (high temp. + Pressure)**

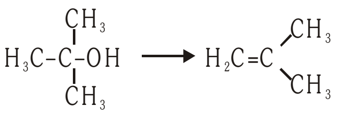


+ p–Product

Kolbe's reaction

15. **Cu/Δ**
(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C{=}O$

(iii)

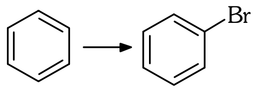


$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH \longrightarrow H_2C{=}C(CH_3)_2$

16. **2,4 – D.N.P.**
used to detect carbonyl group (orange ppt observed)

17. **DMSO**
Polar aprotic solvent: favour S_N2 mechanism

18. Fe+ $Br_2/FeBr_3$



19. Fehling solution

used to identify – CH=O group.
PhCHO gives –ve test
Observation: red ppt of Cu_2O formed

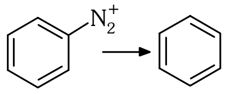
20. Grignard Reagent

Follows (i) Acid base reaction (ii) NAR (iii) NSR

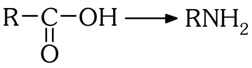
21. $H_2(Pd/CaCO_3)$ Quinoline (Lindlar catalyst)

R—C≡C—R→ R—CH=CH—R (cis)

22. H_3PO_2



23. HN_3 + H_2SO_4



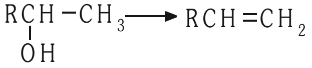
$R-\underset{\displaystyle O}{\underset{\|}{C}}-OH \longrightarrow RNH_2$

(Schmidt Reaction)

24. H_3PO_4/Δ

$H_3PO_4 \Rightarrow$ Same as H_2SO_4/Δ

25. H_2SO_4/Δ

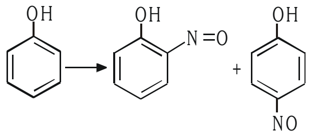


$R\underset{\displaystyle OH}{\underset{|}{C}H}-CH_3 \longrightarrow RCH=CH_2$

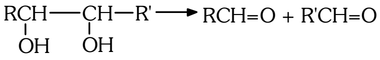
Saytzeff product; C^+ mechanism;
Rearranged alkene can be formed

26. HNO_2 ($NaNO_2$ + HCl)

(i) $RNH_2 \rightarrow R—OH$;
(ii) $PhNH_2 \rightarrow PhN_2^+$ (0 – 5°C)
(iii) $PhNH_2 \rightarrow PhOH$ (high temperature)

(iv) 

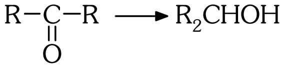
27. HIO_4 (Periodic acid)



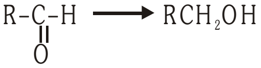
$R\underset{\displaystyle OH}{\underset{|}{C}H}—\underset{\displaystyle OH}{\underset{|}{C}H}—R' \longrightarrow RCH=O + R'CH=O$

Oxidative cleavage of diol

28. $H_2(Ni)$ can reduce

(i) 

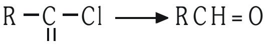
$R-\underset{\displaystyle O}{\underset{\|}{C}}-R \longrightarrow R_2CHOH$

(ii) 

$R-\underset{\displaystyle O}{\underset{\|}{C}}-H \longrightarrow RCH_2OH$

(iii) $RCN \rightarrow RCH_2NH_2$; $-C{\equiv}C- \rightarrow -CH_2-CH_2-$,
$-HC=CH- \rightarrow -CH_2—CH_2-$

29. $H_2(Pd/BaSO_4)$
Quinoline



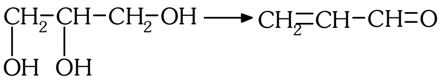
$R-\underset{\displaystyle O}{\underset{\|}{C}}-Cl \longrightarrow RCH=O$

(Rosenmund reduction)

30. Jones Reagent (CrO_3 + dil. H_2SO_4+ acetone)

(i) $RCH_2OH \rightarrow RCH=O$; (ii) $R_2CHOH \rightarrow R_2C=O$

31. $KHSO_4$ Dehydrating Reagent



$\underset{\displaystyle OH}{\underset{|}{C}H_2}-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-OH \longrightarrow CH_2=CH-CH=O$

32. $K_2Cr_2O_7/H^+$

(i) $RCH_2OH \rightarrow RCO_2H$; (ii) $R_2CHOH \rightarrow R_2C = O$

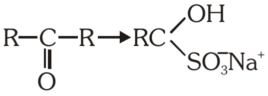
33. MnO_2

(i) $CH_3—CH=CH—CH_2—OH \rightarrow CH_3—CH=CH—CH=O$
(ii) $PhCH_2OH \rightarrow PhCH=O$
To oxidise allylic / benzylic hydroxyl group into corresponding carbonyl.

34. $NaHCO_3$

$$RCO_2H \xrightarrow{NaH\overset{14}{C}O_3} RCO_2^-Na^+ + \overset{14}{C}O_2 \uparrow$$

35. $NaHSO_3$

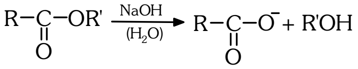


$R-\underset{\displaystyle O}{\underset{\|}{C}}-R \longrightarrow RC\begin{matrix} OH \\ SO_3^-Na^+ \end{matrix}$

[White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]

36. NaOH(aq)

(i) $R—X \rightarrow R—OH$

(ii) 

$R-\underset{\displaystyle O}{\underset{\|}{C}}-OR' \xrightarrow[(H_2O)]{NaOH} R-\underset{\displaystyle O}{\underset{\|}{C}}-O^- + R'OH$

Basic hydrolysis of ester

(iii) $HCHO \xrightarrow{OH^-} HCO_2^- + CH_3OH$ (cannizaro)

(iv) $H_3C-CH=O \xrightarrow[\Delta]{OH^-} H_3C-CH=CH-CH=O$
(Aldol condensation)

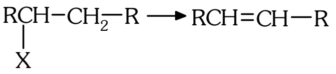
37. Ninhydrin

Detection of amino acid

Observation : Purple coloured ion

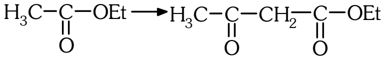
38. NaOR

Strong base :

(i) 

$$\underset{\substack{|\\ X}}{RCH}-CH_2-R \longrightarrow RCH=CH-R$$

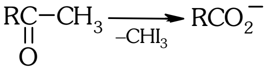
(Saytzeff Product : E_2 elimination)

(ii) 

$$H_3C-\underset{\substack{\|\\ O}}{C}-OEt \longrightarrow H_3C-\underset{\substack{\|\\ O}}{C}-CH_2-\underset{\substack{\|\\ O}}{C}-OEt$$

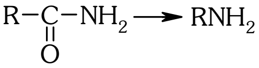
(claisen condensation) (β keto ester)

39. NaOH + X_2 or NaOX

(i) 

$$R\underset{\substack{\|\\ O}}{C}-CH_3 \xrightarrow[-CHI_3]{} RCO_2^-$$

(Haloform reaction)

(ii) 

$$R-\underset{\substack{\|\\ O}}{C}-NH_2 \longrightarrow RNH_2$$

(Hoffman Degradation)

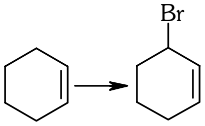
40. NaOH + CaO

$RCO_2H \rightarrow RH$

41. MnO / 300°C

used for $-CO_2$ & $-H_2O$ in carboxylic acid.

42. NBS

(i) 

; (ii) $PhCH_3 \rightarrow PhCH_2—Br$

43. $NaNO_2$ + HCl

$RNH_2 \rightarrow R—OH$

44. $NaNH_2$ in paraffin

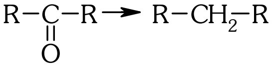
Non-terminal Alkyne →Terminal Alkyne

(2–Butyne → 1–butyne)

45. Na/EtOH

Reduce all except c/c double & triple bond

46. Zn(Hg) + HCl [Clemmensen's reduction]

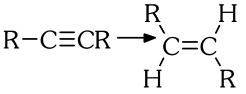


$$R-\underset{\substack{\|\\ O}}{C}-R \longrightarrow R-CH_2-R$$

47. NH_2 **$-NH_2/OH^-$** [Wolf Kishner reduction]

$R–CO–R \rightarrow R–CH_2–R$

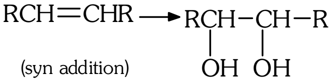
48. Na in Liq. NH_3 [Birch reduction]



$$R-C\equiv CR \longrightarrow \overset{R}{\underset{H}{>}}C=C\overset{H}{\underset{R}{<}}$$

(trans alkene)

49. OsO_4 + H_2O



$$RCH=CHR \longrightarrow R\underset{\substack{|\\ OH}}{CH}-\underset{\substack{|\\ OH}}{CH}-R$$

(syn addition)

50. O_3 : $R\text{-}CH=CH\text{-}R \xrightarrow[H_2O\backslash Zn]{O_3} R\text{-}CHO + R\text{-}CHO$

(Ozonolysis process)

51. Oxirane followed by H^+

$RMgX \rightarrow RCH_2—CH_2—OH$

52. PCC

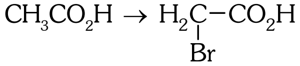
(i) $RCH_2OH \rightarrow RCHO$,

(ii) $R_2CHOH \rightarrow R_2C=O$

(iii) $R_3COH \rightarrow$ no reaction

(Mild oxidizing reagent)

53. P(red) + Br_2

(i) 

$$CH_3CO_2H \rightarrow H_2\underset{\substack{|\\ Br}}{C}-CO_2H$$

(HVZ reaction)

(ii) $ROH \rightarrow R—Br$

54. P (red) + HI

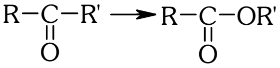
$CH_3CO_2H \rightarrow CH_3—CH_3$

$CH_3CH=O \rightarrow CH_3—CH_3$

$CH_3CH_2OH \rightarrow CH_3—CH_3$

(strong reducing agent can reduce any oxygen or halogen containing compound to alkane)

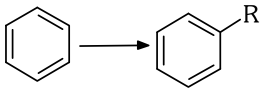
55. Perbenzoic acid [Baeyer Villiger Oxidation]



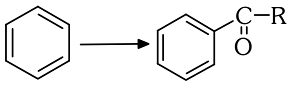
$$R-\underset{\substack{\|\\ O}}{C}-R' \longrightarrow R-\underset{\substack{\|\\ O}}{C}-OR'$$

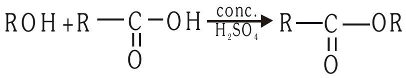
R' having more migrating tendency than R

56. RCl+$AlCl_3$ [Friedel craft alkylation]



57. RCOCl + $AlCl_3$ [Friedel craft acylation]



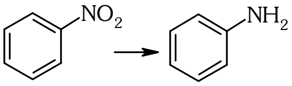
58. 

$$ROH + R-\underset{\overset{\|}{O}}{C}-OH \xrightarrow[H_2SO_4]{conc.} R-\underset{\overset{\|}{O}}{C}-OR$$

Ester formed (Esterification reaction)

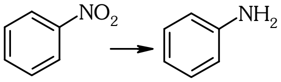
59. $SnCl_2$ + HCl

(i) R—N=N—R' → RNH_2 + $R'NH_2$

(ii) 

(iii) RCN → RCH=O [Stephen reduction]

60. Sn + HCl

(i) 

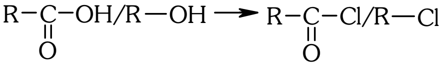
(ii) RCN → $R-CH_2NH_2$

61. Silver salt RCOOAg (Hunsdiecker reaction)

$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

62. AgOH/moist Ag_2O; $R_4\overset{+}{N}\overset{-}{X} \rightarrow R_4\overset{+}{N}\overset{-}{O}H$

63. $SOCl_2$



$$R-\underset{\overset{\|}{O}}{C}-OH/R-OH \longrightarrow R-\underset{\overset{\|}{O}}{C}-Cl/R-Cl$$

64. Tollens Reagent Test

(i) Terminal alkyne gives
(ii) Aldehyde Group gives
(iii) Ketone gives –ve test
(iv) α-hydroxy ketone gives
(v) HCOOH gives
(vi) Hemi acetal gives
(vii) PhNH–OH gives

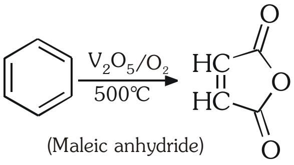
65. Benzene sulphonyl chloride

It is used to distinguish and separate (Hinsberg reagent) 1°, 2° and 3° amines.

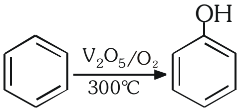
66. Tetra ethyl lead (TEL)

Used as antiknock compound

67. V_2O_5

(I) 

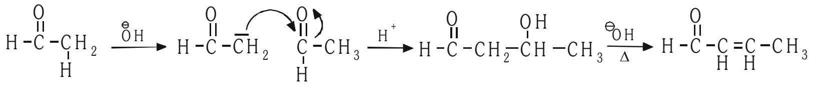
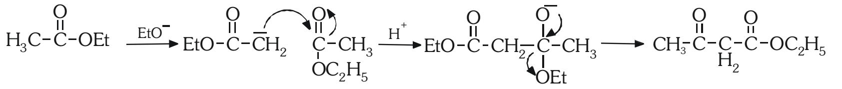
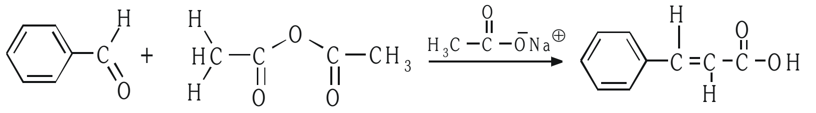
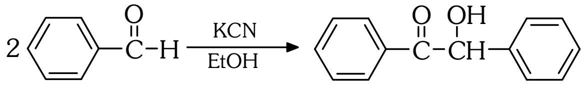
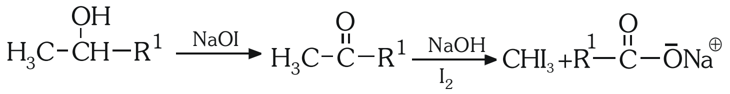
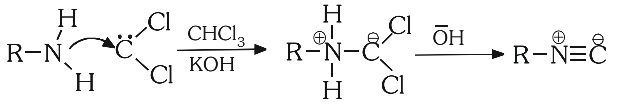
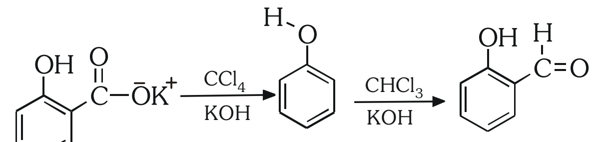
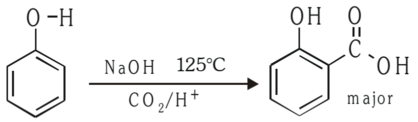
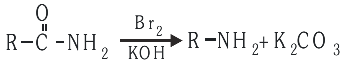
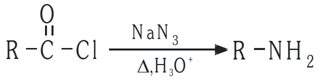
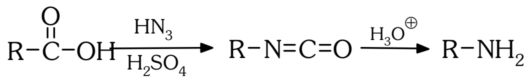
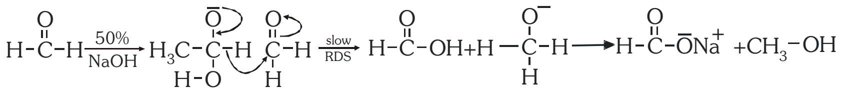
(Maleic anhydride)

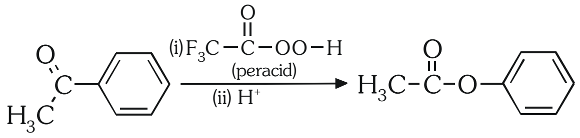
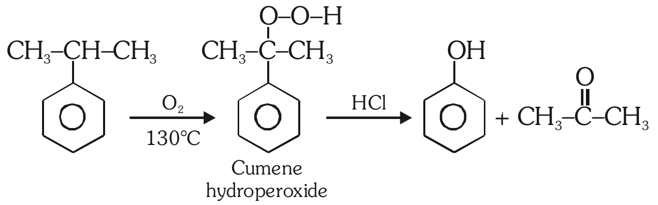
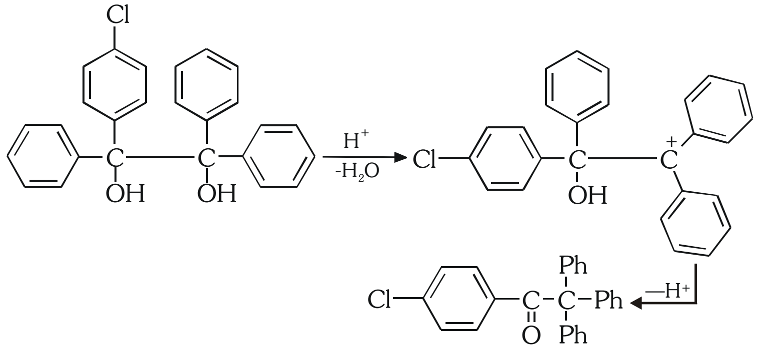
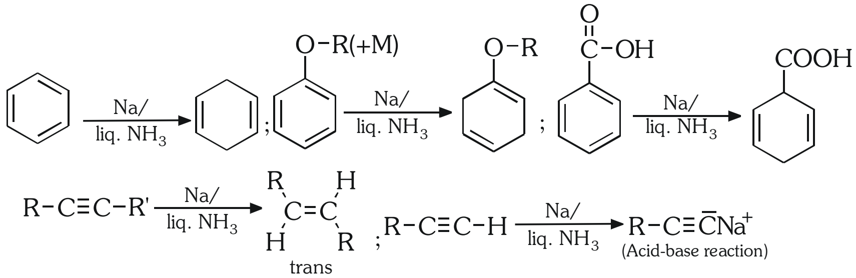
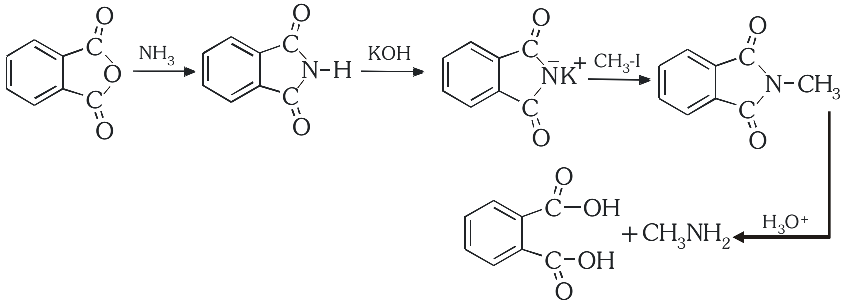
(II) 

IMPORTANT NOTES

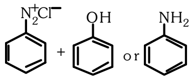
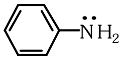
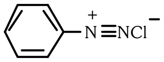
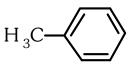
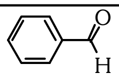
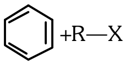
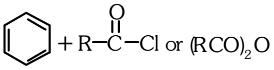
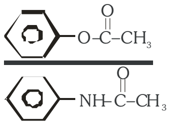
Nutshell review & preview of

ORGANIC NAME REACTIONS

• **Aldol Condensation**	 $H-\overset{O}{\overset{\|}{C}}-\underset{H}{CH_2} \xrightarrow{\overset{\ominus}{O}H} H-\overset{O}{\overset{\|}{C}}-\overline{C}H_2 \quad \underset{H}{\overset{O}{\overset{\|}{C}}}-CH_3 \xrightarrow{H^+} H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{\|}{C}H}-CH_3 \xrightarrow[\Delta]{\overset{\ominus}{O}H} H-\overset{O}{\overset{\|}{C}}-\underset{H}{C}=\underset{H}{C}-CH_3$
• **Claisen Condensation**	 $H_3C-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{EtO^-} EtO-\overset{O}{\overset{\|}{C}}-\overline{C}H_2 \quad \underset{OC_2H_5}{\overset{O}{\overset{\|}{C}}}-CH_3 \xrightarrow{H^+} EtO-\overset{O}{\overset{\|}{C}}-CH_2-\underset{OEt}{\overset{O^-}{C}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{H_2}{C}-\overset{O}{\overset{\|}{C}}-OC_2H_5$
• **Perkin Condensation**	 Cinnamic acid
• **Benzoin Condensation**	 Benzoin
• **Haloform Reaction**	 $H_3C-\overset{OH}{\overset{\|}{C}H}-R^1 \xrightarrow{NaOI} H_3C-\overset{O}{\overset{\|}{C}}-R^1 \xrightarrow[I_2]{NaOH} CHI_3+R^1-\overset{O}{\overset{\|}{C}}-\bar{O}Na^{\oplus}$
• **Carbylamine Test**	 Isocyanide
• **Reimer Tiemman Reaction**	 (Salicylaldehyde) (Salicylic acid)
• **Kolbe's Schimdt Reaction**	 (Salicylic acid)
• **Hoffmann Bromamide Degradation**	 $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[KOH]{Br_2} R-NH_2+K_2CO_3$
• **Curtius Reaction**	 $R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\Delta,H_3O^+]{NaN_3} R-NH_2$
• **Schimdt Reaction**	 $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_2SO_4]{HN_3} R-N=C=O \xrightarrow{H_3O^{\oplus}} R-NH_2$
• **Cannizzaro reaction**	 $H-\overset{O}{\overset{\|}{C}}-H \xrightarrow[NaOH]{50\%} H_3C-\underset{H-O}{\overset{\bar{O}}{C}}-H \quad \underset{H}{\overset{O}{C}}-H \xrightarrow[RDS]{slow} H-\overset{O}{\overset{\|}{C}}-OH+H-\underset{H}{\overset{O^-}{C}}-H \longrightarrow H-\overset{O}{\overset{\|}{C}}-\bar{O}Na^+ +CH_3-OH$

• ***Bayer villiger oxidation***	
• ***Cumene***	
• ***Pinacol-Pincolone rearrangement***	
• ***Birch Reduction***	
• ***Gabriel Synthesis***	

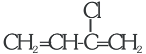
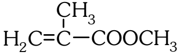
NAME REACTIONS

Name	**Reactant**	**Reagent**	**Product**
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl	Alkane
Coupling Reaction		NaOH (phenol) HCl (Aniline)	Azo Dye (Detection of OH or NH_2 gr)
Diazotization		$NaNO_2$ + HCl 0° – 5°C	
Etard reaction		CrO_2Cl_2/CS_2	 (Benzaldehyde)
Fittig Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation		Anhydrous $AlCl_3$	Alkyl Benzene
Friedel Craft acylation	 $+ R-\overset{O}{\overset{\|}{C}}-Cl$ or $(RCO)_2O$	Anhydrous $AlCl_3$	Acyl Benzene
Gattermann aldehyde synthesis	C_6H_6	HCN + HCl /$ZnCl_2/H_3O^+$	Benzaldehyde
Gattermann-Koch reaction	C_6H_6 (CO + HCl)	anhy $AlCl_3$	Benzaldehyde
Hell-Volhard-Zelinsky reaction	carboxylic acid having α-hydrogen atom	Br_2/ red P	α– halogenated carboxylic acid
Hoffmann mustard oil reaction	primary aliphatic amine + CS_2	$HgCl_2/\Delta$	$CH_3CH_2—N=C=S$ +HgS (black)
Hunsdiecker reaction	Ag salt of carboxylic acid	Br_2/CCl_4, 80°C	alkyl or aryl bromide
Kolbe electrolytic reaction	alkali metal salt of carboxylic acid	electrolysis	alkane, alkene and alkyne
Mendius reaction	alkyl or aryl cyanide	Na/C_2H_5OH	primary amine
Rosenmund reduction	acid chloride	H_2, $Pd/BaSO_4$ boiling xylene	aldehyde
Sabatier-Senderens reaction	Unsaturated hydrocarbon	Raney Ni/H_2, 200—300°C	Alkane
Sandmeyer reaction	$C_6H_5\overset{+}{N_2}Cl^-$	CuCl/HCl or CuBr/HBr or CuCN/KCN, heat	Halo or cyanobenzene
Gattermann Reaction	$C_6H_5N_2^+Cl^-$	Cu/HX(HBr/HCl)	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	NaOH + C_6H_5COCl	benzolytated product 
Stephen reaction	alkyl cyanide	(i) $SnCl_2/HCl$ (ii) H_2O	Aldehyde
Williamson synthesis	alkyl halide	sodium alkoxide or sodium phenoxide	Ether
Wurtz-Fittig reaction	alkyl halide + aryl halide	Na/dry ether	alkyl benzene

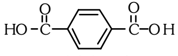
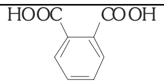
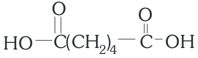
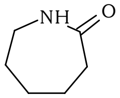
IMPORTANT NOTES

POLYMERS

ADDITION POLYMERS

S.No	Name of Polymer	Starting Materials	Nature of Polymer
I. Polyolefins			
1.	Polyethylene or Polyethene	$CH_2=CH_2$	Low density homopolymer (branched chain growth
2.	Polypropylene or Polypropene	$CH_3CH=CH_2$	Homopolymer, linear, chain growth
3.	Polystyrene	$C_6H_5CH=CH_2$	Homopolymer, linear, chain growth
II. Polydiences			
1.	Neoprene	 $CH_2=CH-\overset{Cl}{\overset{\vert}{C}}=CH_2$ Chloroprene or 2-Chloro-1,3-butadiene	Homopolymer, chain growth
2	Buna S (Styrene-Butadiene, Rubber) SBR or GRS	$CH_2=CH-CH=CH_2$ and $C_6H_5CH=CH_2$ 1,3-butadiene Styrene	Copolymer, chain growth
III. Polyacrylates			
1.	Polymethylmethacrylate (Flexiglass Lucite, Acrylite or Perspex PMMA	 $H_2C=\overset{CH_3}{\overset{\vert}{C}}-COOCH_3$	Homopolymer
2.	Polyethylacrylate	$H_2C=CH-COOC_2H_5$	Homopolymer
3.	Polyacrylonitrile or Orlon PAN	$CH_2=CH—CN$	Homopolymer
IV. Polyhalofins			
1.	Polyvinyl chloride PVC	$CH_2=CH—Cl$	Homopolymer, chain growth
2.	Polytetrafluoroethylene or Teflon PTFE	$F_2C=CF_2$	Homopolymer
3.	Polymonochlorotrifluoro-ethylene PCTFE	$ClFC=CF_2$	Homopolymer

CONDENSATION POLYMERS

S.No	Name of Polymer	Starting Materials	Nature of Polymer
I. Polyesters			
1.	Terylene or Dacron	$HO—CH_2-CH_2-OH$ Ethylene glycol or Ethane-1,2-diol And  Terephthalic acid or Benzene-1,4-dicarboxylic acid	Copolymer, step growth, linear
2.	Glyptal or Alkyl resin	$HO—CH_2—CH_2—OH$ and  Ethylene glycol Phthalic acid or Benzene-1,2-dicarboxylic acid	Copolymer, linear step growth
II. Polyamides			
1.	Nylon-6,6	 $HO-\overset{O}{\overset{\Vert}{C}}(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-OH$ and $H_2N-(CH_2)_6-NH_2$ Adipic acid Hexamethylenediamine	Copolymer, linear, step growth
2	Nylon-6,10	$H_2N(CH_2)_6NH_2$ and $HOOC(CH_2)_8COOH$ Hexamethylene diamine Sebacic acid	Copolymer, linear, step growth
3.	Nylon-6	 Caprolactum	Homopolymer, linear
Formaldehyde resins			
1.	Phenolformaldehye resin or Bakelite	Phenol and formaldehyde	Copolymer, step growth
2.	Melamine formaldehyde resin	Melamine and formaldehyde	Copolymer, step growth

IMPORTANT NOTES

CARBOHYDRATES

- Carbodydrates are defined as optically active polyhydroxy aldehydes or ketones or the compound which produce such units on hydrolysis.
- ***Monosaccharide*** **($C_nH_{2n}O_n$)** : single unit, can't be hydrolysed : Glucose and fructose.
- ***Oligosaccharides*** gives two to ten monosaccharides on hydrolysis.
- ***Disaccharides*** (by glycosydic linkage)

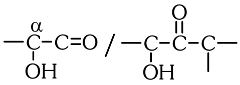
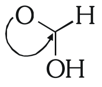
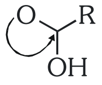
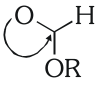
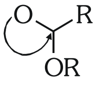
Sucrose $\xrightarrow{H_3O^+}$ α–D. Glucose + β–D. Fructose;

Maltose $\xrightarrow{H_3O^+}$ 2 α–D. Glucose unit

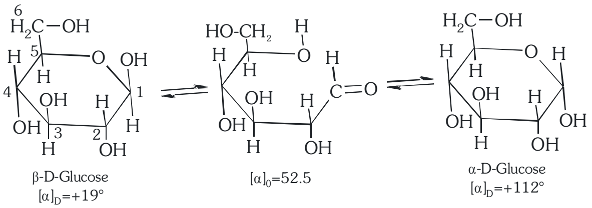
Lactose $\xrightarrow{H_3O^+}$ β–D. Glucose + β–D. Galactose

- ***Polysaccharide*** : Contain more than ten monosaccharide units

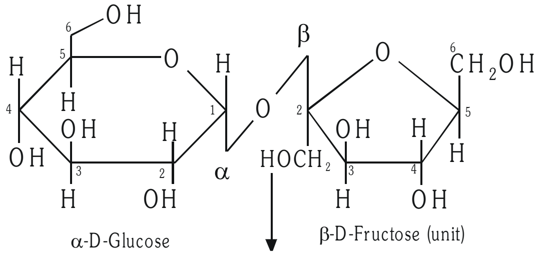
($C_6H_{10}O_5)_n$: Starch & cellulose.

TYPE OF SUGAR		
Give Test	***Reducing***	***Non Reducing***
Tollen's Reagent	+ve test	–ve test
Fehling Reagent	+ve test	–ve test
Benedict Test	+ve test	–ve test
Mutarotation	Yes	No
Functional Unit	 $-\underset{OH}{\overset{\alpha}{C}}-C=O$ / $-\underset{OH}{C}-\overset{O}{\overset{\Vert}{C}}-\underset{\vert}{C}-$  Hemiacetal  Hemiketal	  Acetal  Ketal
Example	All monosaccharides Glucose Fructose Mannose Galactose Disaccharide Maltose lactose	Disaccharide Sucrose Polysaccharide Starch cellulose

- ***Mutarotation:*** When either form of D-glucose is placed in aq. solution it slowly form the other via open chain aldehyde and gradual change in specific rotation until specific rotation (± 52.5°) is reached.

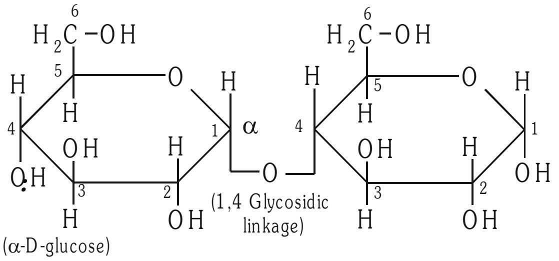


- ***Anomer's*** : Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new-asymmetric carbon is referred to as Anomeric carbon.
- ***Epimer's*** : Diastereomer's which differ in conformation at any one chiral carbon
  eg. D-Glucose & D-mannose
  D-Glucose & D-Galactose
- ***Sucrose :***



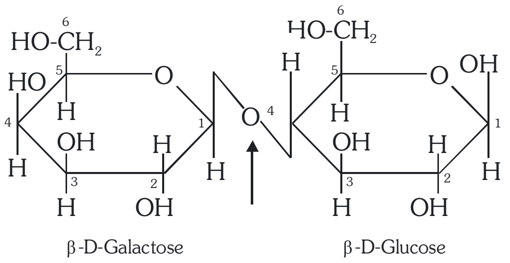
(1,2 Glycosidic linkage)

- ***Maltose***



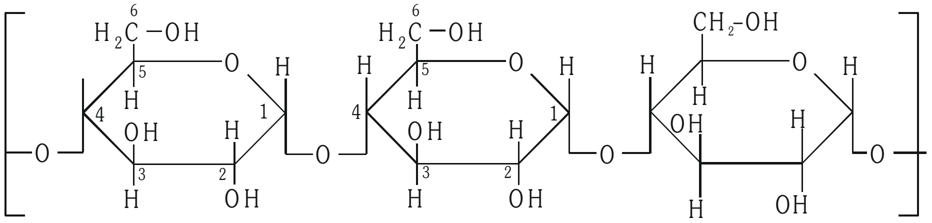
Two α-D-Glucose unit

- ***Lactose :***



(1,4 Glycosidic linkage)

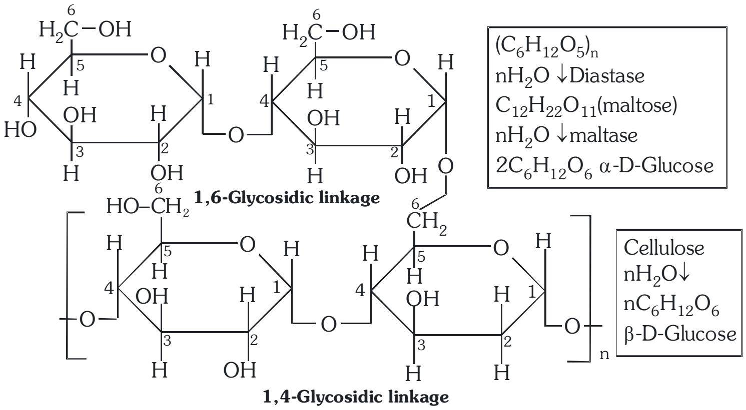
- ***Starch*** : (Amylose & Amylopectin)
- ***Amylose : (Straight Chain) :***



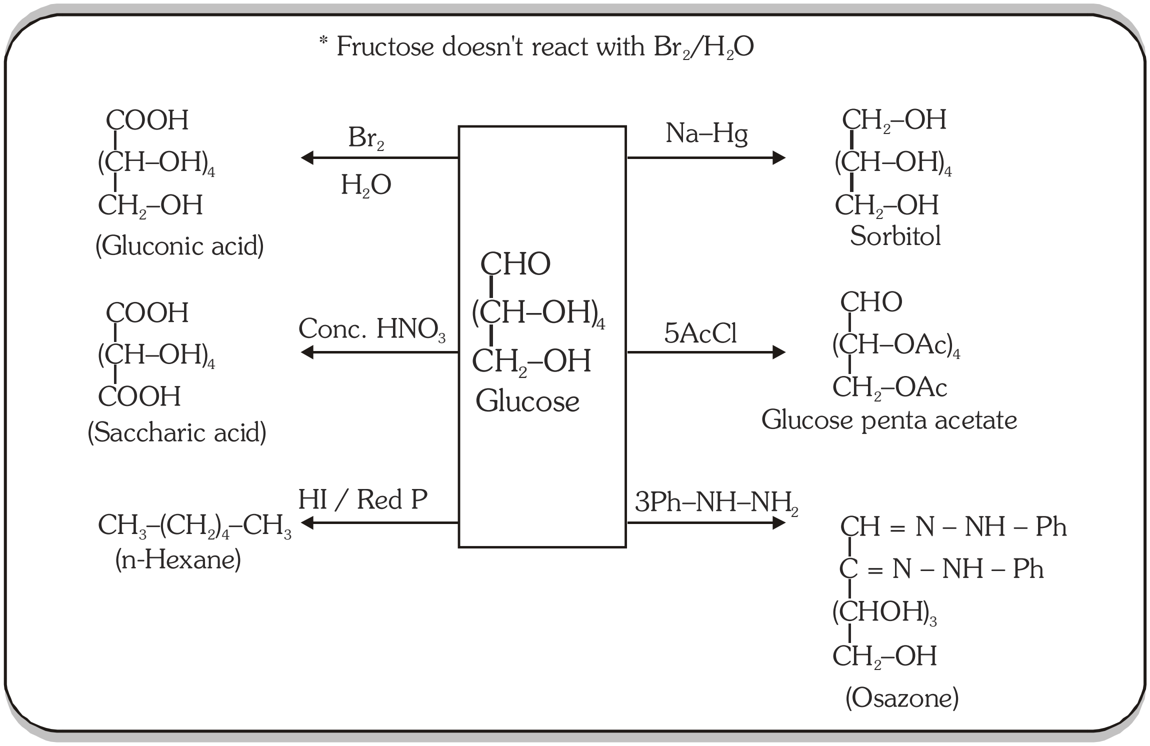
(α-1,4 Glycosidic linkage)

(i) Soluble in H_2O & gives blue colour with I_2

- ***Amylopectin (Branch chain) : $(C_6H_{12}O_5)_n$***



REACTION OF GLUCOSE (OPEN CHAIN STRUCTURE)



IMPORTANT NOTES