

HANDBOOK OF CHEMISTRY

E



S. No.	CONTENTS	Page No.
PHYSICAL CHEMISTRY		
1.	Mole Concept	01
2.	Thermodynamics	07
3.	Thermochemistry	18
4.	Chemical Equilibrium	20
5.	Ionic Equilibrium	23
6.	Redox	28
7.	Electrochemistry	32
8.	Chemical kinetics	39
9.	Radioactivity	43
10.	Liquid Solution	45
11.	Solid State	49
12.	Gaseous State (Ideal Gas)	53
13.	Atomic Structure	55
14.	Surface Chemistry	58
INORGANIC CHEMISTRY		
1.	Some Important Increasing order Periodic Properties	61 62
2.	Chemical Bonding	65
3.	s-Block elements	81
4.	p-Block elements	86
5.	Coordination Chemistry	104
6.	d-Block (Transition Elements)	110
7.	Metallurgy	114
8.	Salt Analysis	118
9.	Environment Pollution	124
ORGANIC CHEMISTRY		
1.	Table for IUPAC Nomenclature	127
2.	Isomerism	129
3.	Reaction Mechanism	133
4.	Practical Organic Chemistry	135
5.	Distinction b/w pair of compound	137
6.	Hydrocarbons	142
7.	Haloalkanes & Grignard Reagents	147
8.	Alcohol, Ether and Phenol	151
9.	Carboxylic Acid	159
10.	Amines	165
11.	Benzene diazonium chloride	167
12.	Organic Reagents	169
13.	Organic Name Reactions	174
14.	Polymers	178
15.	Carbohydrates	180

© All rights including trademark and copyrights and rights of translation etc. reserved and vested exclusively with **Allen Career Institute®**. No part of this publication may be copied, reproduced, adapted, abridged or translated, stored in any retrieval system, computer system, photographic or other system or transmitted in any form or by any means whether electronic, mechanical, digital, optical, photocopying, recording or otherwise, or stood in any retrieval system of any nature. Any breach will entail legal action and prosecution without further notice.

This study material is sold/distributed by Allen Career Institute® subject to the condition and undertaking given by the student that all proprietary rights (as defined under the Trademark Act, 1999 and Copyright Act, 1957) of the Study Materials and/or Test Series and/or the contents shall belong to Allen Career Institute's Tests and neither the Study Materials and/or Test Series and/or the contents nor any part thereof shall be reproduced, modify, re-publish, sub-license, upload on website, broadcast, post, transmit, disseminate, distribute, sell in market, stored in a retrieval system or transmitted in any form or by any means for reproducing or making multiple copies of it. Any violation or infringement of the propriety rights of Allen shall be specifically punishable under Section- 29 & 52 of the Trademark Act, 1999 and under Section- 51, 58 & 63 of the Copyright Act, 1957 and any other Act applicable in India. All disputes are subjected to the exclusive jurisdiction of courts, tribunals and forums at Kota, Rajasthan only.

Note:- Due care and diligence has been taken while editing and printing this book/study materials. Allen Career Institute shall not hold any responsibility for any mistake that may have inadvertently crept in. Allen Career Institute shall not be liable for any direct, consequential or incidental damages arising out of the use of this book.



MOLE CONCEPT

SOME USEFUL CONVERSION FACTORS

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

ATOMIC MASS OR MOLECULAR MASS

Mass of one atom or molecule in a.m.u.
 $\text{C} \rightarrow 12 \text{ amu}$
 $\text{H}_2\text{O} \rightarrow 18 \text{ amu}$

ACTUAL MASS

mass of one atom or molecule in grams
 $\text{C} \rightarrow 12 \times 1.6 \times 10^{-24} \text{ g}$
 $\text{H}_2\text{O} \rightarrow 18 \times 1.6 \times 10^{-24} \text{ g}$

RELATIVE ATOMIC MASS OR RELATIVE MOLECULAR MASS

Mass of one atom or molecule w.r.t.

$1/12^{\text{th}}$ of ^{12}C atom

$\text{C} \rightarrow 12$

$\text{H}_2\text{O} \rightarrow 18$

It is unitless



GRAMS ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one mole of atom or molecule

$\text{C} \rightarrow 12 \text{ g}$

$\text{H}_2\text{O} \rightarrow 18 \text{ g}$

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 [$N_A = 6.022 \times 10^{23}$]

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

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 =
$$\frac{\text{Mass(g)}}{\text{GAM or molar mass}}$$

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 =
$$\frac{\text{Mass(g)}}{\text{GMM or molar mass}}$$

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 =
$$\frac{\text{Mass(g)}}{\text{GFM or molar mass}}$$

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 $M_{\text{avg}} = \frac{M_1 n_1 + M_2 n_2 + \dots}{n_1 + n_2 + \dots}$

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

DENSITIES

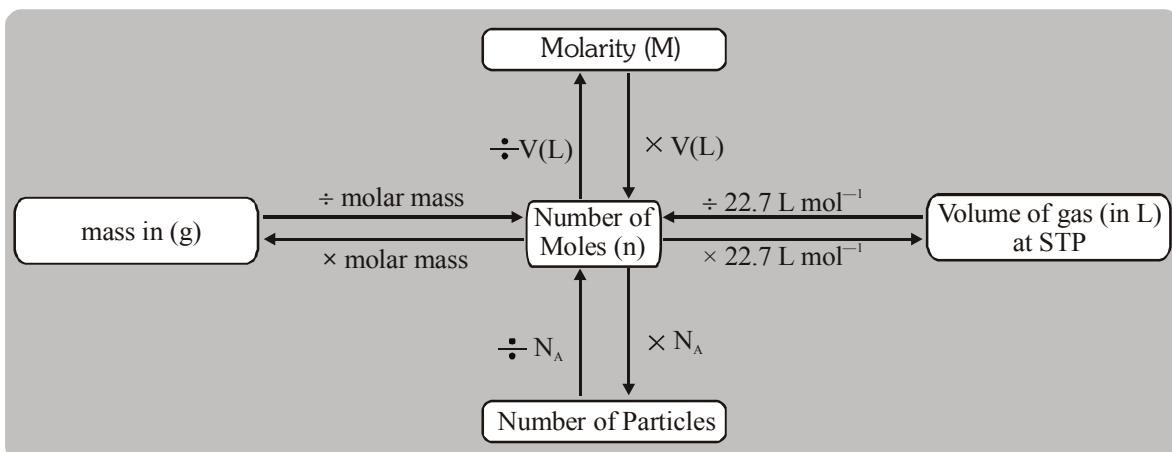
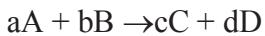
$$\text{Density} = \frac{\text{Mass}}{\text{volume}}$$

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

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**

- 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]

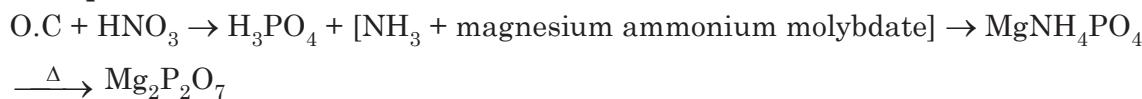
If data of more than one reactant is given then first convert all the data into moles then divide the moles of reactants with their respective stoichiometric coefficient. The reactant having minimum ratio will be L.R. then find the moles of product formed or excess reagent left by comparing it with L.R.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

PERCENTAGE YIELD :

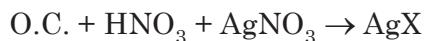
In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical amount of the product. The amount of the product that is actually obtained is called the actual yield. Knowing the actual yield and theoretical yield the percentage yield can be calculate as :

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

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

(e) **Phosphorus :**

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

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

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 \times 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 :

$$\text{Atomic weight of metal} \times \text{specific heat capacity (cal/gm}^{\circ}\text{-C}) \approx 6.4.$$

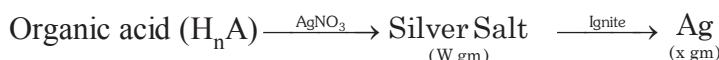
It should be remembered that this law is an empirical observation and this gives an approximate value of atomic weight. This law gives better result for heavier solid elements, at high temperature conditions.

- Experimental methods for molecular mass determination.**

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

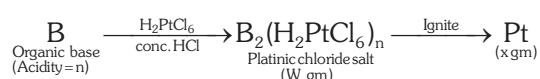
Victor -Mayer's method is used to determine molecular weight of volatile compound.

(b) **Silver Salt Method :**



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

(c) **Chloroplatinate Salt Method :**



$$\text{Molar mass of base} = \frac{1}{2} (\text{Molar mass of salt} - n \times \text{Molar mass of H}_2\text{PtCl}_6)$$

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

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	$X_A = \frac{\text{Mole of A}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$ $X_B = \frac{\text{Mole of B}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$	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 :**

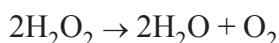
It is based on law of conservation of moles.

(i) **Two solutions having same solute :** Final molarity = $\frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$

(ii) **Dilution Effect :** Final molarity, $M_2 = \frac{M_1 V_1}{V_1 + V_2}$

□ **VOLUME STRENGTH OF H₂O₂ SOLUTION :**

Labelled as 'volume H₂O₂' means volume of O₂ (in litre) at 1 bar & 273 K that can be obtained from 1 litre of such a sample when it decomposes according to



- Volume Strength of H₂O₂ solution = $11.35 \times \text{molarity}$

□ 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.

$$\% \text{ labelling of oleum sample} = (100 + x)\%$$

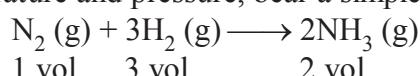
x = mass of H_2O required for the complete conversion of SO_3 in H_2SO_4

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

EUDIOMETRY

Some basic assumptions related with calculations are:

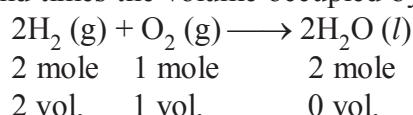
1. Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.



Problem may be solved directly in 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.



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*).

$$V = V_1 + V_2 + \dots$$

Partial volume of gas in a non-reacting gaseous 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
<p>Properties which depends only on initial & final state of system & not on process or path.</p> <p>e.g. U, H etc.</p>	<p>Depends on path or process.</p> <p>e.g. work, heat</p>

THERMODYNAMIC PROPERTIES

Extensive

Properties which are dependent
of matter (size & mass)
present in system

Intensive

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
	Boiling point, freezing point etc

PROCESSES

Isothermal $T = \text{const.}$	Isochoric $V = \text{const.}$	Isobaric $P = \text{const.}$	Adiabatic No heat exchange $dq = 0$	Cyclic Initial & final state of system are same
-----------------------------------	----------------------------------	---------------------------------	---	--

Reversible process	Irreversible process
<ul style="list-style-type: none"> Slow process At any time system and surrounding are in equilibrium. $P_{\text{sys}} = P_{\text{surr}} \pm dP$ 	<ul style="list-style-type: none"> Fast process No equilibrium between system and surrounding $P_{\text{sys}} = P_{\text{surr}} \pm \Delta P$

HEAT (q)

Energy exchange due to temperature difference :

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

C = heat capacity

C_m = 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.

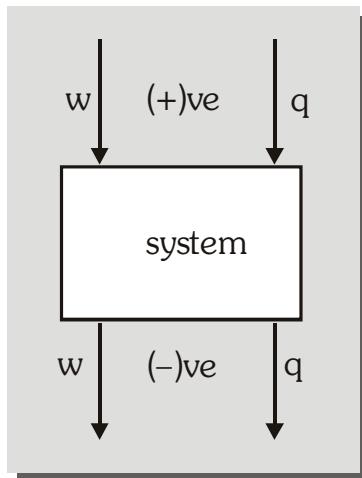
Atomicity	n_{tr}	n_{Rot}	n_{Vib}	C_v		C_p		γ	
					Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono	3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di	3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri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

$$* \quad \gamma_{\text{mix}} = \frac{n_1 C_{p1} + n_2 C_{p2} + \dots}{n_1 C_{v1} + n_2 C_{v2} + \dots}$$

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.

$$U = U_{\text{Kinetics}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

U is a state function & is an extensive property.

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

final 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

$$\Delta U = q + W$$

□ 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
$W_{rev}, iso=nRT\ln\left(\frac{V_2}{V_1}\right)$ $=-nRT\ln\left(\frac{P_1}{P_2}\right)$	$W_{irr}, iso=-P_{ext}\left[\frac{nRT}{P_2}-\frac{nRT}{P_1}\right]$

ADIABATIC :

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

$\gamma=\frac{C_p}{C_v} \Rightarrow C_p$ = molar heat capacity at constant P.

$C_p-C_v=R \Rightarrow C_v$ = molar heat capacity at constant V.

For Reversible adiabatic :

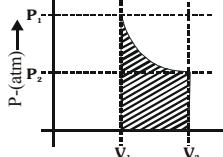
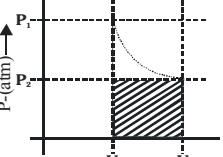
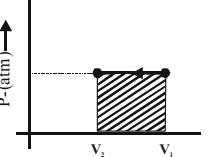
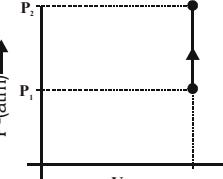
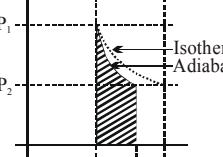
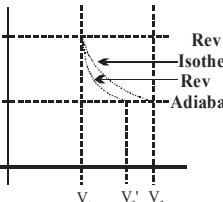
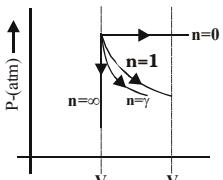
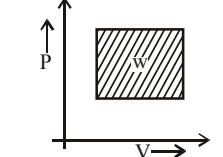
$PV^\gamma = \text{constant}$ (Ideal gas)

$TV^{\gamma-1} = \text{constant}$ (Ideal gas)

For irreversible adiabatic process :

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

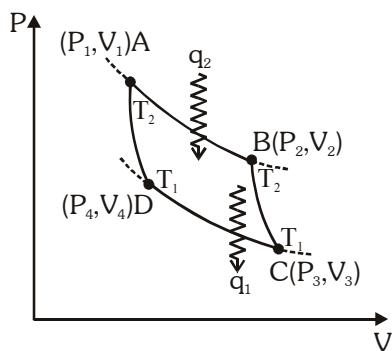
$$nC_{Vm}(T_2-T_1)=-P_{ext}nR\left(\frac{T_2}{P_2}-\frac{T_1}{P_1}\right)$$

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	$w = -P_{\text{ext}}(V_2 - V_1)$ $= -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$q = P_{\text{ext}}(V_2 - V_1)$	0	0	
Isobaric process	$w = -P_{\text{ext}}(V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_p \Delta T$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
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	$w = nC_v(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Irreversible adiabatic process	$w = nC_v(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $nC_v(T_2 - T_1) = -P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Polytropic	$w = \frac{P_2 V_2 - P_1 V_1}{n-1}$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$q = \int_{T_1}^{T_2} C_v dT$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Cyclic Process	Area enclosed in PV-diagram For clockwise it is -ive it is +ive	$q = -w$	0	0	

SPONTANEOUS PROCESS :

A process which takes place on its 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

$$w_{DA} = nC_v(T_2 - T_1)$$

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

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

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

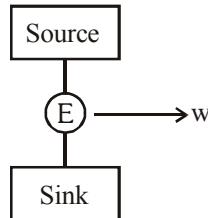
Entropy (denoted by S) is state function

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

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.

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0 \quad \text{for rev. process}$$

$$\Delta S_{\text{syst}} + \Delta S_{\text{surr}} > 0 \quad \text{for irrev. process}$$

$$\Delta S_{\text{int}} + \Delta S_{\text{trans}} \geq 0 \quad (\text{In general})$$

□ 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, $\Delta_f S$ 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. $F_2(g)$ $S^\circ = 203 \text{ J/K-mole}$

$$\text{Cl}_2(\text{g}) \quad S^\circ = 223 \text{ J/K-mole}$$

$\text{Br}_2(\text{g}) \quad S^\circ = 245 \text{ J/K-mole}$

- (iv) Entropy increases with chemical complexity

For $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$

n = 0 n = 1 n = 3 n = 5

$$S^\circ = 113 \quad 150 \quad 225 \quad 305$$

□ 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 :

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

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

□ ENTROPY CALCULATION

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

□ THIRD LAW OF THERMODYNAMICS

“At absolute zero, the entropy of a perfectly crystalline substance 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 values are used to calculate entropy changes for the reactions by the formula;

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

□ 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

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

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

□ 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 summarize, 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, $\Delta G = +$ ve	Non spontaneous
		At high temperature, $\Delta G = -$ 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 :

$$\begin{aligned} G &= H - TS \\ &= U + PV - TS \end{aligned}$$

$$dG = dU + PdV - TdS + VdP - SdT$$

$$dG = VdP - SdT$$

* At constant temperature

$$\Delta G = VdP$$

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

* At constant pressure

$$\Delta G = -SdT$$

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

Relationship between ΔG & $W_{\text{non-PV}}$

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

for reversible process at constant T & P

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

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

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

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

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

□ SOME FACTS TO BE REMEMBERED :

(a) Standard condition

* For gases/solid / liquid

$$P = 1 \text{ bar}$$

* For ion / substance in solution

$$\text{Concentration} = 1M$$

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

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

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

(All above equation will be derived in thermochemistry)

Relationship between ΔG° and equilibrium constant

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

At equilibrium $\Delta G = 0$

$$\Delta G^\circ = - RT \ln K_{\text{eq}}$$

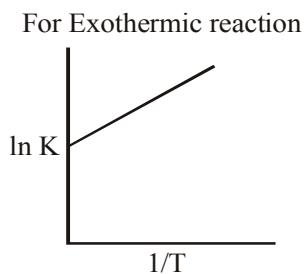
$$\Delta H^\circ - T\Delta S^\circ = - RT \ln K_{eq}$$

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

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

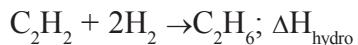
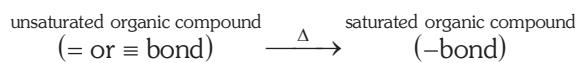
$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_2}$$

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



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

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



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

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

- (b) For heat of formation

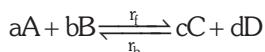
$$\Delta_r H = \sum (\Delta H_f)_{\text{product}} - \sum (\Delta H_f)_{\text{reactant}}$$

IMPORTANT NOTES

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,

**AT EQUILIBRIUM STATE**

Rate of forward reaction (r_f)

$$= \text{rate of backward reaction } (r_b)$$

So, at equilibrium,

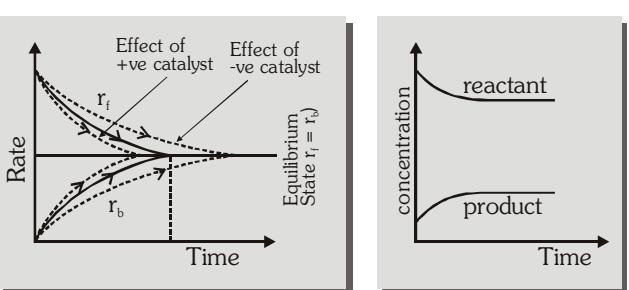
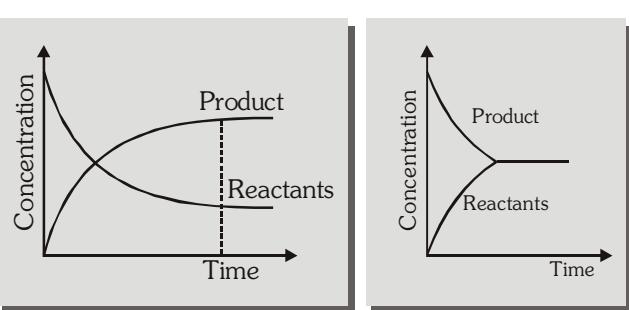
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{K_f}{K_b} \quad \text{In terms of active mass}$$

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

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

- Partial pressure of solid is taken as unity & in calculation of partial pressure of solids, their number of moles are not considered.

- $K_p = K_c (RT)^{\Delta n_g}$ 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.

PHYSICAL EQUILIBRIUM

Physical reaction :

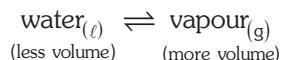
Those reactions in which change in only & only physical states of substances takes place without any chemical change.

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



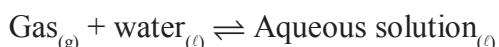
It is an endothermic process & there is decrease in volume. Thus, the favourable conditions for melting of ice are high temperature, & High-pressure.

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



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 :



When a gas dissolve in liquid, there 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) $\uparrow [A]$ (ii) $\downarrow [A]$	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
b)	Pressure	(i) \uparrow in pressure (ii) \downarrow in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
c)	Temperature	(i) \uparrow in Endothermic (ii) \uparrow in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
d)	Dissociation	(i) \uparrow in pressure (ii) \uparrow 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, H₂SO₄, HNO₃ etc.

(ii) Weak electrolytes Substances which dissociate only to a small extent in aqueous solution.
e.g. HCN, H_2BO_3 etc.

(iii) Non electrolytes Which do not dissociate.

pH CALCULATUION

Case (i) A weak acid in water

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

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

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 treatment yields a cubic equation. Assuming that acids dissociate to a negligible extent [i.e. $C - x \approx C$] $[H^+] = (K_1 C_1 + K_2 C_2 + \dots + K_w)^{1/2}$

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) :

$10^{-8} \text{M} < C < 10^{-6} \text{M}$. 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.

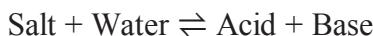
(ii)

pH of solution involving a polyprotic acid or base depend upon K_1 , K_2 . Successive dissociation can be neglected.

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

SALT HYDROLYSIS

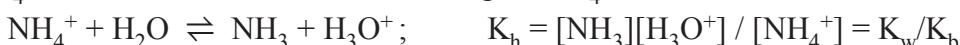
The phenomenon of interaction of cations and anions of a salt with H₂O in order to produce acidic nature or alkaline nature is known as salt hydrolysis.



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. NH₄Cl when dissolved, it dissociates to give NH₄⁺ ions.



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), $h = \sqrt{K_h/C}$.

$$\text{pH} = \frac{1}{2} (\text{pk}_w - \text{pk}_b - \log C)$$

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

- (iii) ***Salts of strong base and weak acid*** give a basic solution (pH>7) when dissolved in water, e.g. NaCN, CN⁻ + H₂O \rightleftharpoons HCN + OH⁻

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

$$\text{pH} = \frac{1}{2} (\text{pk}_w + \text{pk}_a + \log C)$$

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

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

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

$$\text{pH} = \frac{1}{2} (\text{pk}_w + \text{pk}_a - \text{pk}_b)$$

- (v) ***Amphiprotic salts***

e.g. NAHCO₃

$$\text{pH} = \frac{1}{2} (\text{pk}_1 + \text{pk}_2)$$

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 direction.

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. CH₃COONH₄, NH₄CN
- (ii) Proteins and amino acids

2. Mixed buffers

These are of two types :

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

$\text{NaHCO}_3 + \text{H}_2\text{CO}_3$ (H_2CO_3 is weak acid and HCO_3^- is its conjugate base);

$\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$; $\text{NaH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$.

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

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

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

$\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ (NH_4OH is weak base and NH_4^+ is its conjugate acid.)

Henderson's Equation

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

Important : For good buffer capacity, [salt] : [acid] ratio should be as close to one as possible. In such a case, $\text{pH} = \text{pK}_a$. (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 distinctly seen. In general, for an indicator which is weak acid, $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$, the ratio of ionized to unionized form can be determined from

$$\text{pH} = \text{pK}_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

So, for detectable colour change, $\text{pH} = \text{pK}_a \pm 1$

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
Phenolphthalein	8.3-10	colourless	pink
Thymol blue	1.2-2.8	red	yellow

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, phenolphthalein 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. $\text{Ag}_2\text{C}_2\text{O}_4$) an equilibrium which exists is



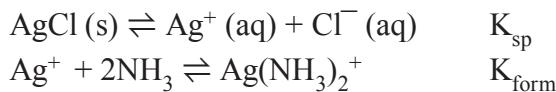
$$\text{Then } K_{sp} = [\text{Ag}^+]^2[\text{C}_2\text{O}_4^{2-}]$$

Common ion effects. Suppression of dissociation by adding an ion common with dissociation products. e.g. Ag^+ or $\text{C}_2\text{O}_4^{2-}$ in the above example.

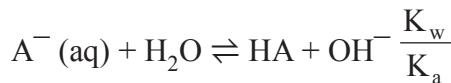
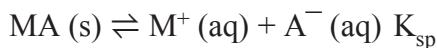


Precipitation. Whenever the product of concentrations (raised to appropriate power) exceeds the solubility product, precipitation occurs.

Effect of complex formation on solubility.



Effect of hydrolysis on solubility



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

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 : $\text{pH} = -\log[\text{H}^+]$.

- (i) Water as amphiprotic solvent.
- (ii) Autoionization of water : $K_w = [\text{H}^+][\text{OH}^-]$.
- (iii) $K_a[\text{H}_2\text{O}] = K_w / [\text{H}_2\text{O}]$
- (iv) Change in pH of neutral H_2O with temperature.

Homogenous Ionic equilibria

- (i) Acid/ base equilibrium
- (a) Strong acid $[\text{H}^+] = c/2 + \sqrt{\frac{c^2}{4} + K_w}$; $c = \text{conc. of (acid)}$
- (b) pH due to polyprotic weak acids
- (c) Weak monobasic acid $[\text{H}^+] = \sqrt{K_a \cdot c}$ (if $\alpha < 0.1$)
- (d) Mixture of S.A. & W.A.
- (e) Mixture of two W.A. $[\text{H}^+] = \sqrt{K_1 c_1 + K_2 c_2}$
- (f) Buffer solutions : $\text{pH} = \text{p}K_a + \log \left(\frac{\text{salt}}{\text{acid}} \right)$
 $\text{pOH} = \text{p}K_b + \log \left(\frac{\text{salt}}{\text{base}} \right)$
- (g) Salt hydrolysis – (W.A.&S.B) $\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log c)$
(W.B & S.A.) $\text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log c)$
(W.A. & W.B.) $\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a - \text{p}K_b)$

Heterogeneous equilibria

Solubility of sparingly soluble salt's
 $(AB, AB_2, A_xB_y) K_{sp} = (S^{x+y}) X^x Y^y$

- (i) Effect of pH on solubility.
- (ii) Simultaneous solubility.

Application of both heterogeneous 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 , $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , conc. H_2SO_4 etc, are powerful oxidising agents.

◆ Reducing agent or Reductant :

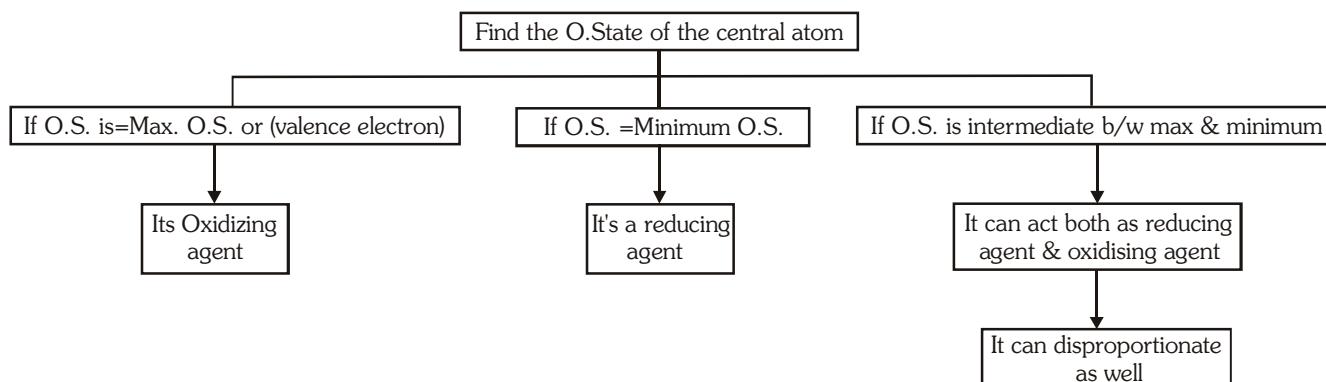
Reducing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

e.g. KI , $\text{Na}_2\text{S}_2\text{O}_3$ 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^-

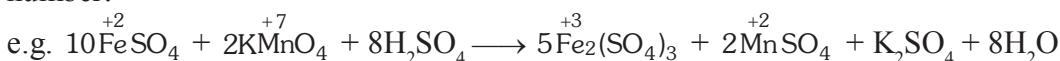
□ HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR REDUCING AGENT



□ 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.



Equivalent weight (E) :

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

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

- ◆ 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 ($n = 1$), $\text{Ba}(\text{OH})_2$ ($n = 2$), $\text{Al}(\text{OH})_3$ ($n = 3$), etc.

- ◆ **For salts :** A salt reacting such that no atom of the salt undergoes any change in oxidation state.

For example, $2\text{AgNO}_3 + \text{MgCl}_2 \rightarrow \text{Mg}(\text{NO}_3)_2 + 2\text{AgCl}$

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	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	5	$E = \frac{M}{5}$
MnO_4^- (O.A.)	MnO_2 in neutral medium	$\text{MnO}_4^- + 3\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{OH}^-$	3	$E = \frac{M}{3}$
MnO_4^- (O.A.)	MnO_4^{2-} in basic medium	$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	1	$E = \frac{M}{1}$
$\text{Cr}_2\text{O}_7^{2-}$ (O.A.)	Cr^{3+} in acidic medium	$\text{CrO}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	6	$E = \frac{M}{6}$
MnO_2 (O.A.)	Mn^{2+} in acidic medium	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	2	$E = \frac{M}{2}$

Cl_2 (O.A.) in bleaching powder	Cl^-	$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	2	$E = \frac{M}{2}$
CuSO_4 (O.A.) in iodometric titration	Cu^+	$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	1	$E = \frac{M}{1}$
$\text{S}_2\text{O}_3^{2-}$ (R.A.)	$\text{S}_4\text{O}_6^{2-}$	$2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$	2	$E = \frac{2M}{2} = M$
				(for two molecules)
H_2O_2 (O.A.)	H_2O	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	2	$E = \frac{M}{2}$
H_2O_2 (R.A.)	O_2	$\text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ (O.N. of oxygen in H_2O_2 is -1 per atom)	2	$E = \frac{M}{2}$
Fe^{2+} (R.A.)	Fe^{3+}	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$	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 $\frac{W \times 1000}{E \times \text{VmL}}$
- ◆ **Normality (N) = $\frac{W \times 1000}{E \times \text{VmL}}$**
- ◆ **Normality (N) = Molarity × Valence factor**
Normality (N) = molarity × Valence factor (n)
or $N \times V$ (in mL) = $M \times V$ (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) $a\text{A} + b\text{B} \rightarrow m\text{M} + n\text{N}$

$m.\text{eq of A} = m.\text{eq of B} = m.\text{eq of M} = m.\text{eq of N}$

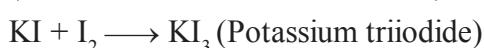
(ii) In a compound M_xN_y

$m.\text{eq of M}_x\text{N}_y = m.\text{eq of M} = m.\text{eq of N}$

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 :



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 $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

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



- (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.



- (v) Inert electrodes are represented in the bracket



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,

$$\text{Work done} = \text{Charge} \times \text{Potential} = nFE$$

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

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

$$\text{Under standard state} \quad \Delta G^0 = -nFE^0 \quad (\text{i})$$

- (i) From thermodynamics we know, $\Delta G =$ 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 $\Delta G = \text{positive}$, $E = \text{negative}$ 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.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad ..(A)$$

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

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^\circ = nFE^\circ$$

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

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

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:

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

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

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

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

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

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

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

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

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

- (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 Helmholtz equation,

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

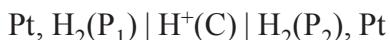
From Eqs. (i) and (ii), we have

$$\begin{aligned} -T\Delta S &= T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_p \\ \text{or} \quad \Delta S &= nF \left[\frac{\partial E}{\partial T} \right]_p \end{aligned}$$

CONCENTRATION CELL

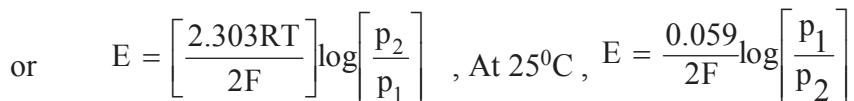
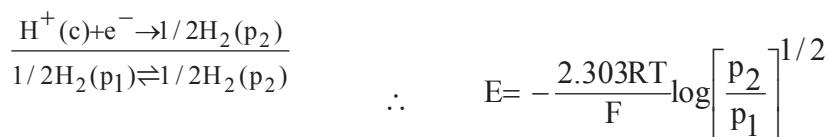
The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell .

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



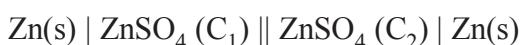
Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process : $1/2\text{H}_2(\text{p}_1) \rightarrow \text{H}^+(\text{c}) + \text{e}^-$ (Anode process)

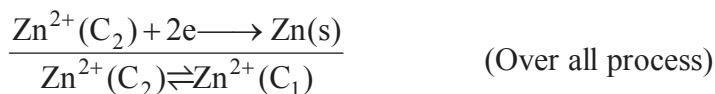


For spontaneity of such cell reaction, $p_1 > p_2$

(ii) Electrolyte concentration cells:



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



∴ 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 spontaneity 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

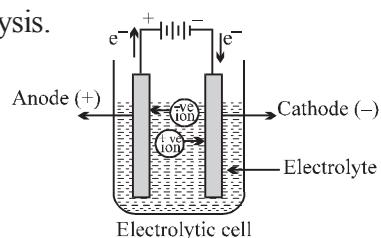
This cell converts electrical energy into chemical energy.

The entire assembly except that of the external battery is known as the electrolytic cell

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

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.

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

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm².

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*.

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

where C = conductance ohm⁻¹ ; K = specific conductance ohm⁻¹cm⁻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 CM³ 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 Λ .

$$\wedge = K \times V$$

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

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

$$\text{Thus, } V = \frac{1000}{C}$$

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

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 Λ_m :

$$\wedge_m = K - V$$

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

Thus,

Hence, $\lambda_m = Kx \frac{1000}{M}$

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

Application of Kohlrausch's law :

- (A) Determination of γ_m^0 of a weak electrolyte:

In order to calculate γ_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.

Δ_m^0 of CH_3COOH is then given as:

$$\Delta_m^0 (\text{CH}_3\text{COOH}) = \Delta_m^0 (\text{HCl}) + \Delta_m^0 (\text{CH}_3\text{COONa}) - \Delta_m^0 (\text{NaCl})$$

Proof :

$$\lambda_m^0 (\text{HCl}) = \lambda_{\text{H}}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \dots \dots \text{(i)}$$

$$\lambda_m^0 (\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots \dots \dots \text{(ii)}$$

$$\lambda_m^0 (\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \dots \dots \text{(iii)}$$

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

$$\lambda_m^0 (\text{HCl}) + \lambda_{(\text{CH}_3\text{COONa})}^0 - \lambda_{(\text{NaCl})}^0 = \lambda_{(\text{H}^+)}^0 + \lambda_{(\text{CH}_3\text{COO}^-)}^0 = \lambda_0^0 (\text{CH}_3\text{COOH})$$

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

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

(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 λ_m^0 as the saturated solution of a sparingly soluble salt is extremely dilute.

Hence from equation (D).

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

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

CHEMICAL KINETICS

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

➤ **For a reaction :**

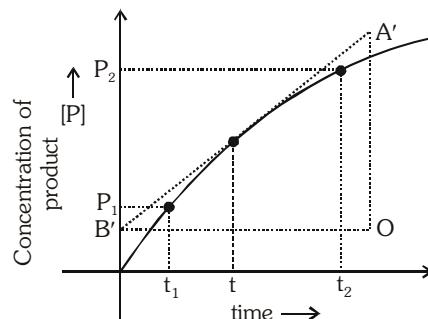
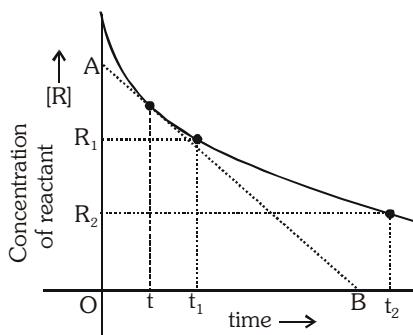


➤ **Instantaneous rate :** $-\frac{1}{a} \left(\frac{d[A]}{dt} \right) = -\frac{1}{b} \left(\frac{d[B]}{dt} \right) = \frac{1}{c} \left(\frac{d[C]}{dt} \right) = \frac{1}{d} \left(\frac{d[D]}{dt} \right)$

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

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

⇒ Graphical method for determining rate :



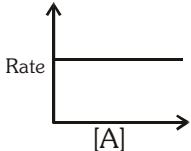
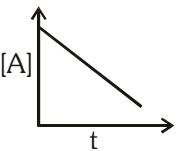
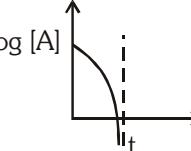
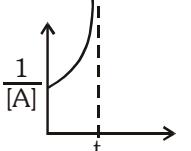
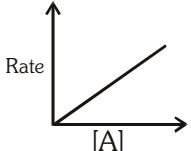
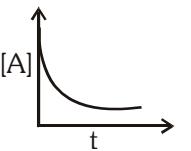
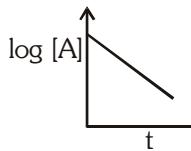
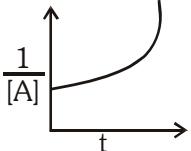
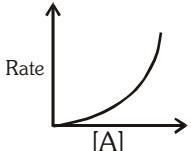
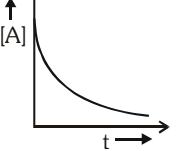
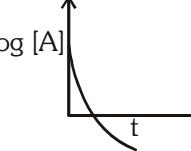
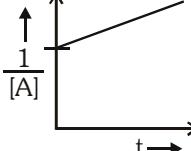
$$\text{Avg. Rate} = -\left(\frac{[R]_2 - [R]_1}{t_2 - t_1} \right) = \frac{([P]_2 - [P]_1)}{t_2 - t_1}$$

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

➤ **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	$[A_0] - [A] = kt$	$kt = \ln \frac{[A_0]}{[A]}$	$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$	$kt = \frac{1}{(n-1)} \left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$
Half life ($t_{1/2}$) ($t_{3/4}$)	$t_{1/2} = \frac{[A]_0}{2k}$ $t_{3/4} = 1.5 t_{1/2}$	$t_{1/2} = \frac{\ln 2}{k}$ $t_{3/4} = 2 t_{1/2}$	$t_{1/2} = \frac{1}{[A]_0 k}$	$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{[A]_0^{n-1}} \right]$ $t_{3/4} = (2^{n-1} + 1) t_{1/2}$

➤ 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 Experimentally :**

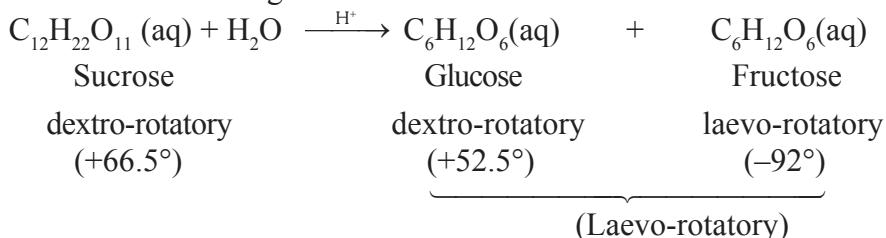
The kinetics of reaction can be followed (i.e. order, rate constant etc. can be established) by measuring a property which changes with time.

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 Experimentally)**

(i) Inversion of cane sugar :



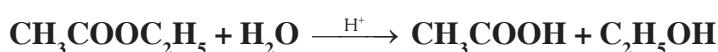
$$k = \frac{2.303}{t} \log \left(\frac{r_\infty - r_t}{r_\infty - r_0} \right)$$

\mathbf{r}_0 = rotation at time, $t = 0$

\mathbf{r}_t = rotation at time, $t = t$

r = rotation at time, $t = \infty$

(ii) Acidic hydrolysis of ethyl acetate :



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

V_0 = Volume of NaOH solution used at time, $t = 0$

V_t = Volume of NaOH solution used at time, $t = t$

V = Volume of NaOH solution used at time, $t = \infty$

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.

$$t = 0 \quad t = t \quad t = 2t \quad t = 3t \dots$$

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]

- **Zero order :**
 - $t_{1/2}$ of zero order is directly proportional to initial concentration.

In equal time interval, reaction finishes by

$$C = C - x \quad C = 2x \quad C = 3x$$

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

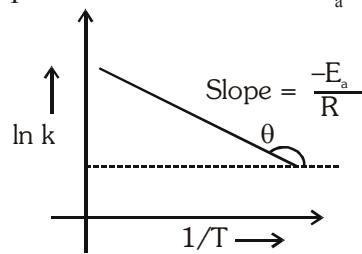
A zero order reaction finishes in $t = \frac{[A]_0}{k}$

Temperature dependence :

- Arrhenius equation : $k = A \cdot e^{-E_a/RT}$
 - E_a = minimum energy over and above the avg. energy of reactant which must be possessed by reacting molecule for collision to be successful.
 - A = frequency factor - proportional to number of collisions per unit volume per second.
 - $e^{-E_a/RT}$ = 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 .

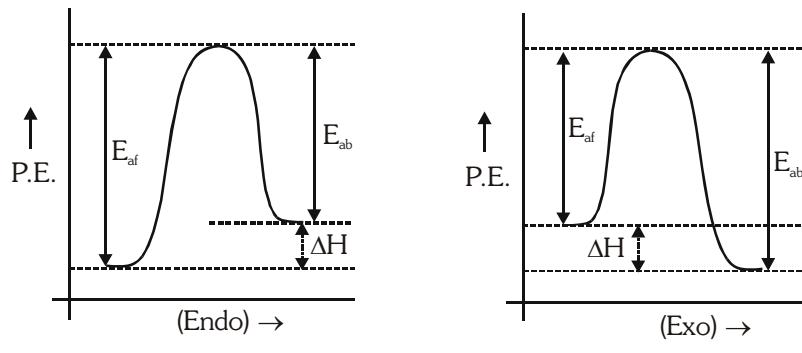


$$\text{Temperature coefficient} = \frac{k_{T+10}}{k_T}$$

By default $T = 298 \text{ K}$

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

➤ **Endothermic and exothermic reactions :**



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

➤ **Parallel reaction :** $A \xrightarrow{k_1} B$ $A \xrightarrow{k_2} C$

(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 \rightarrow 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 \rightarrow CATALYST

RADIOACTIVITY

- All nuclear reactions are first order :

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

First order

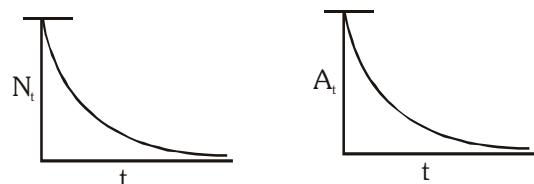
$$\lambda t = 2.303 \log \frac{N_0}{N_t} \quad \lambda \rightarrow \text{Decay constant}$$

$N_0 \rightarrow$ Initial nuclei

$N_t \rightarrow$ Nuclei at 't'

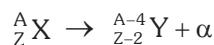
$$\text{Activity} = A_t = \frac{-dN_t}{dt} = \lambda N_t; \text{ Nuclei/sec.}$$

A_t = Rate of decay



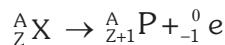
$$\Rightarrow t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$$

- **α decay** = ${}^4_2\text{He}$ Particles at high velocity



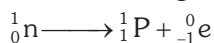
To ↓ size of large nuclei

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



To $\downarrow \frac{n}{P}$ ratio.

Nuclear change in β decay



- ## ➤ **γ -decay :**

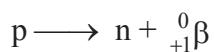
Photons from excited nuclei after α – or β – decay

No effect on n/p ratio

High energy e/m radiation.

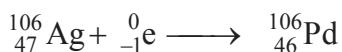
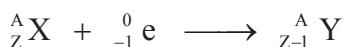
Mean life , $t_{avg} = \frac{1}{\lambda}$

- ### ◆ $\begin{pmatrix} 0 \\ \pm 1 \end{pmatrix} \beta$ Positron decay



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

◆ K electron capture



- * Electron capture can occur whenever 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 :

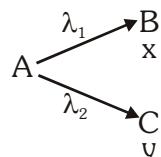
$$t = 0 \quad N_0$$

$$t = t \quad N_0 - x - y$$

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

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

$\lambda \rightarrow$ No dependence on temp.



LIQUID SOLUTION

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

$T \uparrow \Rightarrow V.P. \uparrow$

Attractive forces $\uparrow \Rightarrow V.P. \downarrow$

- **Raoult's law :**

Non volatile solute and volatile solvent solution.

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 $\uparrow \Rightarrow$ Colligative Properties \uparrow

(1) Relative lowering of V.P. :

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

Where n_B = mole of Non-volatile solute.

i = Vant Hoff's factor.

(2) Elevation in B.P. :

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

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

where T_b = B.P. of pure solvent.

ℓ_v = Latent heat of vapourization per gm

K_b = molal elevation constant

M = molar mass

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

(3) Depression in FP.

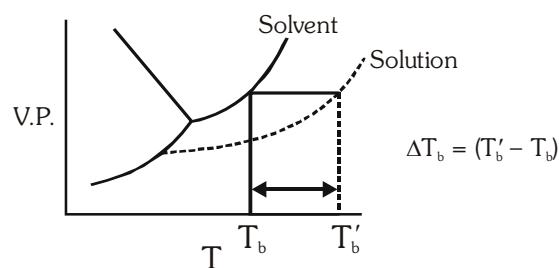
$$\Delta T_f = T_f - T_f' = i k_f \times m$$

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

T_f = f.p. of pure solvent

k_f = molal depression constant

ℓ_f = latent heat of fusion per gm.



(4) Osmotic pressure :

$$\pi \propto (P_A^o - P_A)$$

$\pi = iC \cdot S.T.$

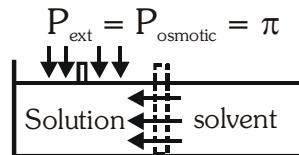
where π = osmotic pressure

C = molarity (mole/lit)

S = R = const. for solution.

$$\begin{array}{ll} \text{Sol.(1)} & \text{Sol (2)} \\ \text{If } \pi_1 = \pi_2 & \text{Isotonic} \end{array}$$

$$\text{If } \pi_1 > \pi_2 \quad \begin{cases} \text{sol}^o(1) \text{ hypertonic} \\ \text{sol}^o(2) \text{ hypotonic} \end{cases}$$



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

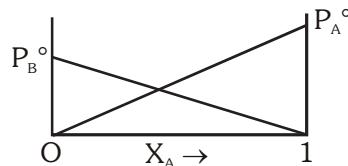
Solute	Example	Ionisation/association (x degree)	y*	van'thoff factor	Abnormal mol. wt. (m'_1)
Non-electrolyte	urea-glucose, sucrose etc.	none	1	1	normal mol.wt. (m_1)
Binary electrolyte A^+B^-	NaCl, KCl, HCl	$AB \rightleftharpoons A_x^+ + B_x^-$	2	$(1+x)$	$\frac{m_1}{(1+x)}$
Ternary electrolyte	CH_3COOH , $FeSO_4$ etc.				
Associated Solute	K_2SO_4 , $BaCl_2$,	$A_2B \rightleftharpoons 2A_{2x}^+ + B_{x}^{2-}$	3	$(1+2x)$	$\frac{m_1}{(1+2x)}$
	$K_3[Fe(CN)_6]$, A_2B , AB_3	$AB_3 \rightleftharpoons A_x^{3+} + 3B_x^-$	4	$(1+3x)$	$\frac{m_1}{(1+3x)}$
	FeCl ₃				
General	benzoic acid in benzene forming dimer	$2A \rightleftharpoons A_2$	$\frac{1}{2}$	$\left(1-\frac{x}{2}\right) = \left(\frac{2-x}{2}\right)$	$\frac{2m_1}{(2-x)}$
	any solute forming polymer A_n	$A_{(1-x)} \rightleftharpoons \frac{1}{2}A_{x/2}$	$\frac{1}{n}$	$\left[1 + \left(\frac{1}{n} - 1\right)x\right]$	$\left[\frac{m_1}{1 + \left(\frac{1}{n} - 1\right)x}\right]$
	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°



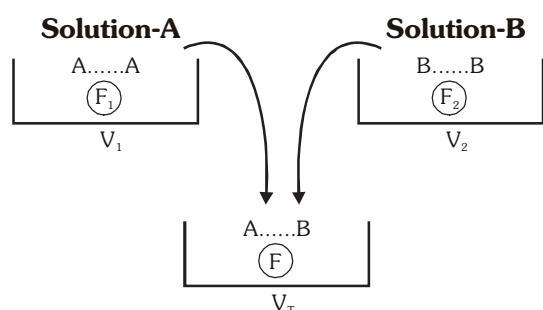
Binary liquid solution :

$$\text{By Raoult's law} \Rightarrow P_T = P_A^\circ X_A + P_B^\circ X_B = P_A + P_B \quad \dots\dots(i)$$

$$\text{By Dalton's law} \Rightarrow P_A = Y_A P_T \quad \dots\dots(ii)$$

$$P_B = Y_B P_T \quad \dots\dots(iii)$$

➤ Ideal and Non-Ideal solution :



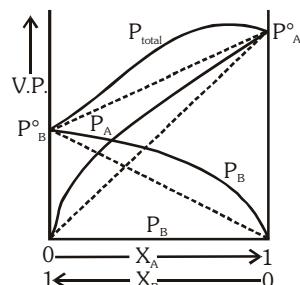
$$\text{Ideal solution : } \begin{cases} F_1 \approx F_2 \approx F \\ V_T = V_1 + V_2 \end{cases} \Rightarrow \Delta H_{\text{solution}} = 0$$

Non-Ideal solution :

- (1) Solution showing +ve deviation :

$$F < F_1 \& F_2$$

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

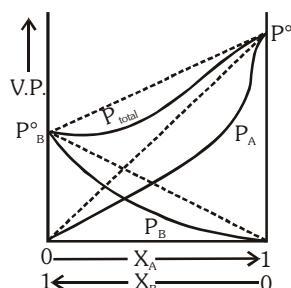


- (2) Solution showing -ve deviation :

$$\Rightarrow F > F_1 \& F_2$$

$$\Rightarrow V_T < (V_1 + V_2)$$

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



DEVIATION FROM RAOULT'S LAW

	Positive deviation ($\Delta H=+ve$)	Negative deviation ($\Delta H=-ve$)	Zero deviation ($\Delta H=0$)
(i)	ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(ii)	acetone + carbon disulphide n-hexane + n-heptane	benzene + chloroform	
(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 (ii) Polar (iii) Hydrogen bonded	Molecules	Dispersion or London forces	Ar, CCl_4 , H_2 , I_2 CO_2	Soft	Insulator	Very low
		Dipole-dipole	HCl , SO_2	Soft	Insulator	Low
		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 (diamond) AlN ,	Hard	Insulators	Very high
			C (graphite)	Soft	Conductor	

THE SEVEN CRYSTAL SYSTEMS

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

CUBIC UNIT CELL

Unit cell	Relation between r and a	Packing fraction	Co-ordination 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

$$\text{Density : } d = \frac{ZM}{N_A a^3} \text{ gm/cm}^3$$

Where Z = effective number of particle

M = molar mass

N_A = Avogadro's number

a = edge length (cm)

Three dimensional close packing :

➤ Hexagonal close packing (HCP) :

Effective number of particle = 6

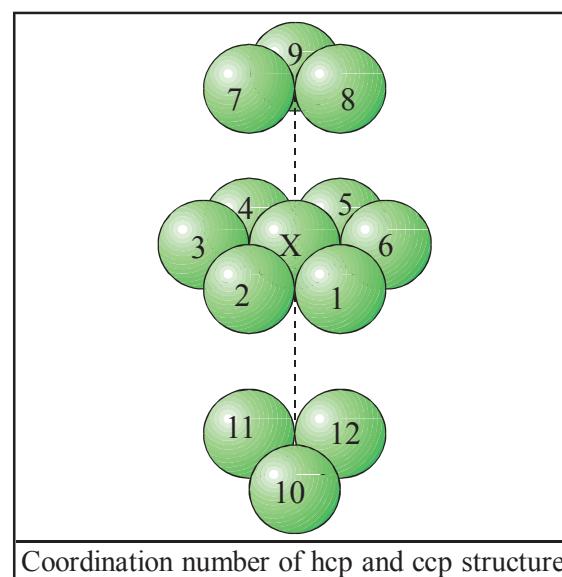
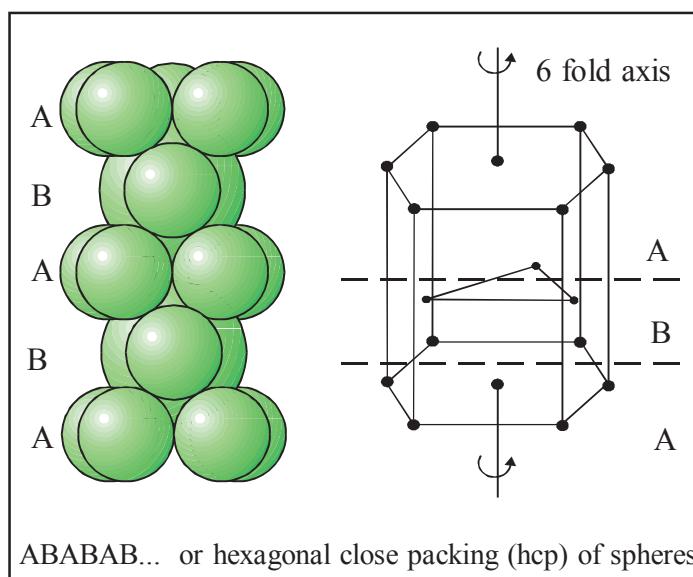
Effective number of octahedral void = 6

Effective number of tetrahedral void = 12

Packing fraction

= 74% ; co-ordination number = 12

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



➤ **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 planar	-
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. $\begin{cases} \text{Na}^+ \rightarrow \text{Every element of C.C.P.} \\ \text{Cl}^- \rightarrow \text{At every OHV} \end{cases}$	6 : 6	$4\text{Na}^+ + 4\text{Cl}^-$ 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. $\begin{cases} \text{Cs}^+ \rightarrow \text{at every corner} \\ \text{Cl}^- \rightarrow \text{at Body centre or at cubic void} \end{cases}$	8 : 8	$1\text{Cs}^+ + 1\text{Cl}^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CsS
3. Zns Type (1 : 1) (Zinc Blende Type) (Sphalerite)	C.C.P. $\begin{cases} \text{Zn}^{+2} \rightarrow \text{Every element of C.C.P.} \\ \text{S}^2 \rightarrow \text{At 50% of T.H.V. or at alternate tetrahedral void} \end{cases}$	4 : 4	$4\text{Zn}^{+2} + 4\text{S}^{2-}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
4. CaF ₂ Type (1 : 2) (Fluorite Type)	C.C.P. $\begin{cases} \text{Ca}^{+2} \rightarrow \text{Every element of C.C.P.} \\ \text{F}^- \rightarrow \text{At every T.H.V.} \end{cases}$	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 ₂ O Type (2 : 1) (Antifluorine)	C.C.P. $\begin{cases} \text{Na}^+ \rightarrow \text{At every T.H.V.} \\ \text{O}^{2-} \rightarrow \text{Every element of C.C.P.} \end{cases}$	8Na ⁺ , 4O ⁻² 4 : 8	$8\text{Na}^+ + 4\text{O}^{2-}$ 4Na ₂ O (4)	Li ₂ O, Li ₂ S Na ₂ O, Na ₂ S K ₂ O, K ₂ S
6. ZnS Type (1 : 1) (Wurtzite)	H.C.P. $\begin{cases} \text{Zn}^{+2} \rightarrow \text{Every element of H.C.P.} \\ \text{S}^{2-} \rightarrow \text{50% of T.H.V. or (at alternate T.H.V.)} \end{cases}$	4 : 4	$6\text{Zn}^{+2} + 6\text{S}^{2-}$ 6ZnS (6)	Same as sphalerite

GASEOUS STATE

GAS LAW	GRAHAM'S DIFFUSION LAW
<ul style="list-style-type: none"> ♦ Boyle's law : $V \propto \frac{1}{P}$ ($n, T = \text{const}$) $P_1 V_1 = P_2 V_2$ ♦ Charle's law : $V \propto T$ ($n, P = \text{const}$) $\frac{V_2}{V_1} = \frac{T_2}{T_1}$ ♦ Gay lussac's law: $P \propto T$ ($n, V = \text{const}$) $\frac{P_2}{P_1} = \frac{T_2}{T_1}$ ♦ Avogadro's law : $V \propto \text{moles} \propto \text{number of molecules}$ ($P, T = \text{const}$) Ideal gas equation $PV = nRT$ $R = 0.0821 \text{ lit atm mol}^{-1} \text{ K}^{-1}$ $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ or $8.314 \text{ N} \times \text{m K}^{-1} \text{ mol}^{-1}$ $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$, $R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$ 	<p>It is applicable for non reacting gases</p> $r \propto \frac{1}{\sqrt{d}}$; $r \propto \frac{1}{\sqrt{VD}}$; $r \propto \frac{1}{\sqrt{M_w}}$ ($P, T = \text{constant}$)

KINETIC GAS EQUATION : $PV = \frac{1}{3} mN V_{rms}^2$	
DALTON'S LAW OF PARTIAL PRESSURE	AVERAGE KINETIC ENERGY (KE_{av})
$P_{mixture} = P_1 + P_2 + P_3$(T & V const) Partial pressure	$KE_{av} = \frac{3}{2} nRT$ (n moles)
$P_{moist\ gas} = P_{dry\ gas} + P_{water\ vapours}$	$KE_{av} = \frac{3}{2} RT$ (1 mol or N_A molecules)
It is applicable for non reacting gases.	$KE_{av} = \frac{3}{2} KT$ (1 molecule)
Methods of determination of partial pressure (P_A & P_B are partial pressure)	$K = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$ K is called Boltzman's constant
◆ from ideal gas equation $P_A V = n_A RT$ & $P_B V = n_B RT$	$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + \dots v_n^2}{N}}$ $v_{av} = \frac{v_1 + v_2 + v_3 + \dots v_n}{N}$
◆ In the form of mole fraction.	$v_{rms} = \sqrt{\frac{3RT}{Mw}}$ $v_{av} = \sqrt{\frac{8}{\pi} \frac{RT}{Mw}}$ $v_{mp} = \sqrt{\frac{2RT}{Mw}}$
$P_A = X_A P_T = \frac{n_A}{n_t} P_T$; $P_B = X_B P_T = \frac{n_B}{n_t} P_T$ [$X_A + X_B = 1$] P_T = sum of partial pressure of all gases	$v_{rms} = \sqrt{\frac{3PV}{Mw}}$ $v_{av} = \sqrt{\frac{8}{\pi} \frac{PV}{Mw}}$ $v_{mp} = \sqrt{\frac{2PV}{Mw}}$
◆ In the form of volume fraction	$v_{rms} = \sqrt{\frac{3P}{d}}$ $v_{av} = \sqrt{\frac{8P}{\pi d}}$ $v_{mp} = \sqrt{\frac{2P}{d}}$
$P_A = \frac{V_A}{V} P_T$ & $P_B = \frac{V_B}{V} P_T$	$v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$ = 1 : 0.92 : 0.82
◆ If individual pressure and individual volume are given	$v_{mp} : v_{av} : v_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$ = 1 : 1.128 : 1.224
$P_A = \frac{V_A}{V} P_1$ and $P_B = \frac{V_B}{V} P_2$	Compressibility factor (z) = $\frac{(V_m)_{obs}}{V_i} = \frac{P(V_m)_{obs}}{RT}$
P_1, P_2 = pressure of gases before mixing P_A, P_B = pressure of gases after mixing	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↑

liquefaction↑;

$b \uparrow$, effective size of molecule \uparrow ,

incompressible vol \uparrow

compressible vol ↓

- ◆ At high pressure, Vanderwaal's eqⁿ is

$$PV_m - Pb = RT$$
 - ◆ At low pres. or Moderate pressure Vanderwaal's eqⁿ is

$$PV_m + \frac{a}{V_m} = RT$$
 - ◆ At very low pressure, high temp. Vander waal's Equation is

$$VP = nRT$$
 - ◆ Ideal gas behavior.
 - ◆ Gases having ↑value of a; will have ↑T_c; ↑rate of liquefaction.

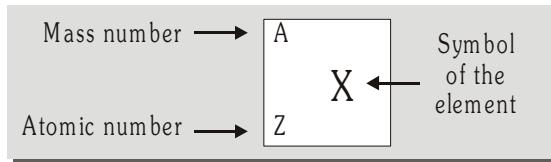
IMPORTANT NOTES

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
 $A = \text{Number of proton} + \text{Number of Neutrons}$
- **Isotopes :** Same atomic number but different mass number
Ex. : ${}_6^1\text{C}^{12}$, ${}_6^1\text{C}^{13}$, ${}_6^1\text{C}^{14}$
- **Isobars :** Same mass number but different atomic number
Ex. ${}_1^1\text{H}^3$, ${}_2^3\text{He}^3$
- **Isodiaphers :** Same difference of number of Neutrons & protons
Ex. ${}_5^1\text{B}^{11}$, ${}_6^1\text{C}^{13}$
- **Isotones :** Having same number of neutron
Ex. ${}_1^1\text{H}^3$, ${}_2^4\text{He}^4$
- **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.

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

[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

- $\text{RW} \rightarrow \text{MW} \rightarrow \text{IR} \rightarrow \text{Visible} \rightarrow \text{UV} \rightarrow \text{X-rays} \rightarrow \text{CR}$
(Radiowaves → Microwaves → Infrared rays → Visible rays → Ultraviolet rays → X-rays → Cosmic rays)
- Wavelength decreases
- Frequency increases
- $c = \lambda \nu$ $\lambda = \frac{c}{\nu}$ $\nu = \frac{c}{\lambda}$
- $T = \frac{1}{\nu}$ $E = \frac{hc}{\lambda} = h\nu$, $h = 6.626 \times 10^{-34} \text{ Js}$
- $E(\text{ev}) = \frac{12400}{\lambda(\text{\AA})}$
- 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

- $\frac{K(Ze)(e)}{r^2} = \frac{mv^2}{r}$
- $mvr = \frac{n\hbar}{2\pi}$ 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 :** $v = 2.188 \times 10^6 \frac{Z}{n} \text{ ms}^{-1}$
- Energy(KE + PE)
 $= \text{Total energy} = -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom}$
- $TE = -\frac{KZe^2}{2r}$, $PE = \frac{-KZe^2}{r}$, $KE = \frac{KZe^2}{2r}$
 $PE = -2KE$, $KE = -TE$, $PE = 2TE$
- 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
 $\Delta E = E_{n_2} - E_{n_1} = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV/atom}$
where IE = ionization energy of single electron species.
- **Ionization energy** $= E_\infty - E_{GS} = 0 - E_{GS}$.
 E_{GS} = Energy of electron in ground state

HYDROGEN SPECTRUM

- **Rydberg's Equation :**

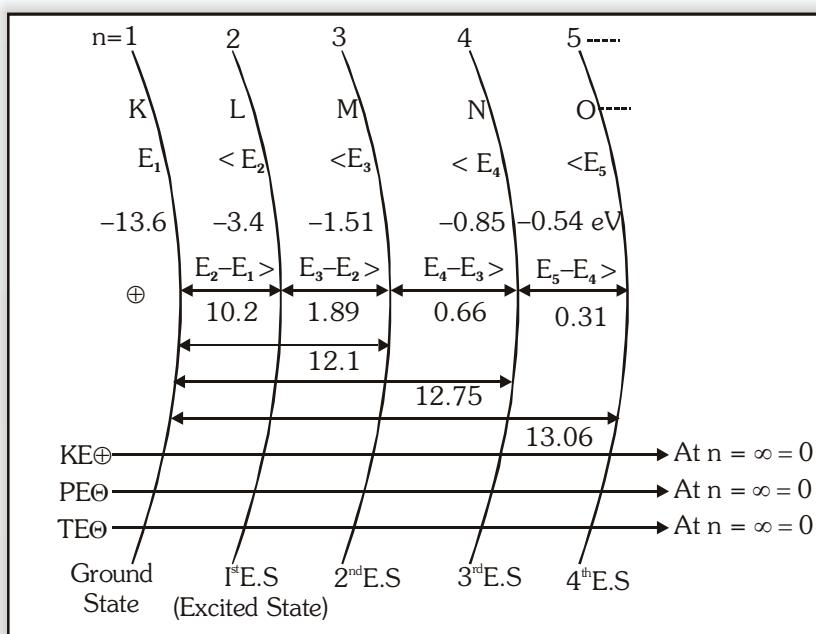
$$\frac{1}{\lambda} = \bar{v} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \times Z^2$$

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

- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H _{α} line means $n_2 = n_1 + 1$; also known as line of longest λ , shortest v , 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 (n₂) to lower energy level (n₁) 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 possess wave character as well as particle character.
 - $$\lambda = \frac{h}{mv} = \frac{h}{p}$$
 - The circumference of the n^{th} 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 (λ) $\cong \sqrt{\frac{150}{V(\text{volts})}} \text{ \AA}$
 - $$\lambda = \frac{h}{\sqrt{2mKE}}$$

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.
 - $$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \text{ or } (\Delta x)(\Delta v) \geq \frac{h}{4\pi m}$$

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 $n = 1, 2, 3, 4, 5, \dots$
 - ⇒ 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 $\Rightarrow 0, 1, \dots, (n-1)$
 - ⇒ Indicates shape of orbital/Sub shell

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

- ⇒ 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 $m = -l \dots 0 \dots +l$
 - ⇒ Maximum no of e's in an orbital = 2 (with opposite spin)

(with opposite spin)
 m for p sub shell = p_x p_y p_z
 -1 +1 0

m for d sub shell =

$$\begin{array}{ccccc} dxy & dyz & dz^2 & dxz & dx^2-y^2 \\ -2 & -1 & 0 & +1 & +2 \end{array}$$

Spin Quantum Number (m_s or s)

Given by Uhlenback & Goudsmit

Values of s = $\pm \frac{1}{2}$

Total value of spin in an atom = $\pm \frac{1}{2} \times$ number of unpaired electrons

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

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 $(n + \ell)$ value is filled up first, but when two or more subshells have same $(n + \ell)$ 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.

COMPARISON OF LYOPHOBIC AND LYOPHILIC SOLS

Property	Lyophilic sol (Emulsoid)	Lyophobic sol (susensoid)
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 carry charge.
12. General Ex.	Mostly of organic nature Ex. Gelatin, Starch, Gum, Albumin & Cellulose Solution	Mostly of Inorganic nature Ex. Transition 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_5S_3 sol (-ve) the precipitating power of Al^{3+} , Ba^{2+} , and Na^+ ions is in the order

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

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

$$[\text{Fe}(\text{CN})_6]^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$$

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.

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

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 starch have the maximum & minimum protective powers.

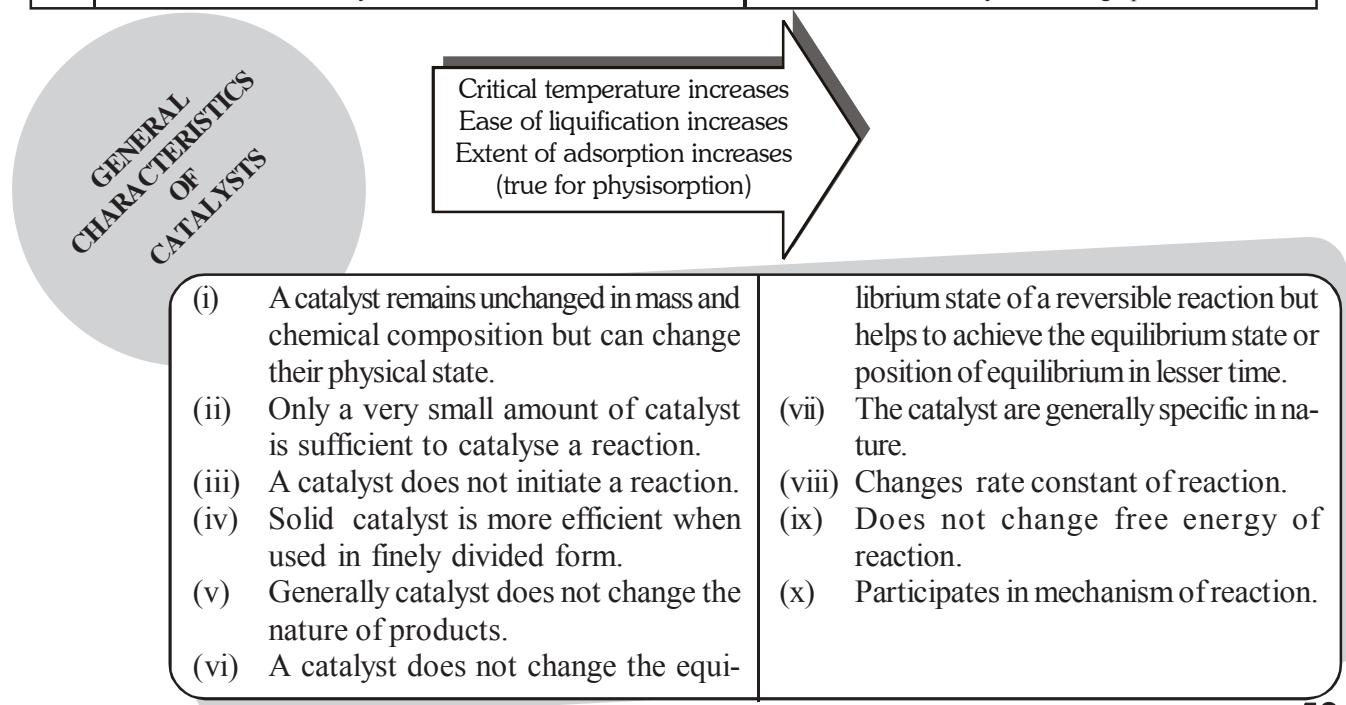
Protection Capacity $\alpha \frac{1}{\text{Protection Number}}$
(Gold number)

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

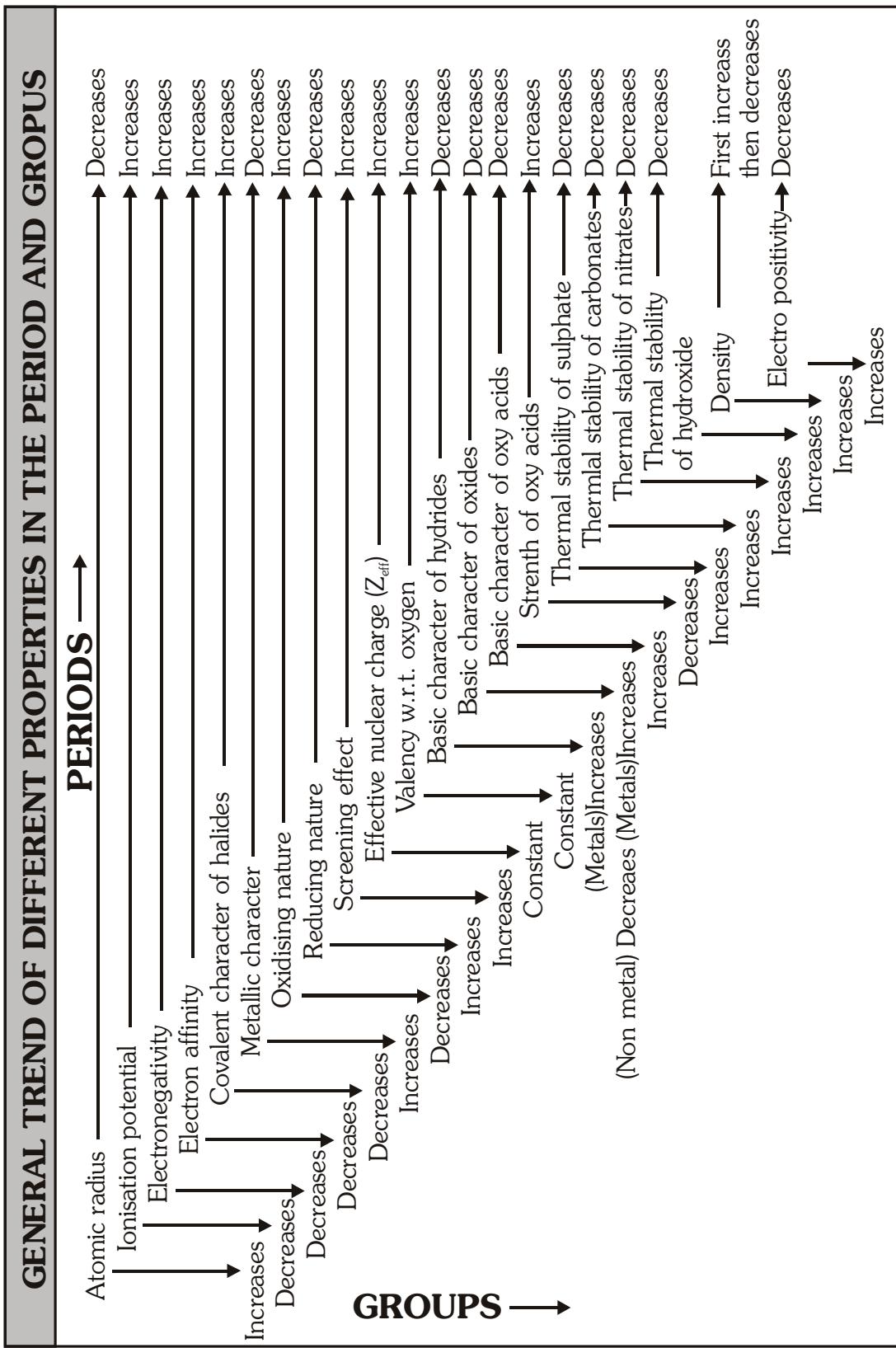
Physical Adsorption		Chemical Adsorption (Activated ad.)
1.	It is caused by intermolecular vander waal's forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	Heat of adsorption is low. (- 20 to -40 KJ/mol) (Enthalpy)	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.



IMPORTANT NOTES



Some Important Increasing Order



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 definitions are used.

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

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

Vander wall radius mainly used for noble gases.

Factors Affecting atomic radius :

$$(1) \text{ AR} \propto \text{Number of shells}$$

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

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 shielding of 3d subshell electron

Atomic radius of 4d \approx 5d series element due to lanthanide contraction

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:



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

Factors affecting ionic radius

- (+) charge \uparrow ionic radius \downarrow
- (-) charge \uparrow ionic radius \uparrow
- $Z_{\text{eff}} \uparrow$ ionic radius \downarrow
- $n \uparrow$ ionic radius \uparrow

\Rightarrow In isoelectronic species (+) charge \uparrow Ionic radius \downarrow
 (-) charge \uparrow Ionic radius \uparrow

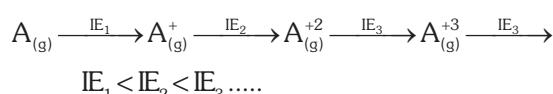
$$\text{eg.: } \text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{+2} > \text{Al}^{+3} \\ \text{K}^+ > \text{Li}^+ > \text{Mg}^{+2} > \text{Al}^{+3}$$

IONIZATION ENERGY

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

Successive I.E. :

$I\text{E}_1, I\text{E}_2, \dots$ combinedly termed as successive I.E.



Factors affecting :

- (1) $I\text{E} \propto Z_{\text{eff}}$
- (2) $I\text{E} \propto \frac{1}{\text{size}}$
- (3) $I\text{E} \propto (+)\text{charge}, \quad (4) I\text{E} \propto \frac{1}{(-)\text{charge}}$
- (5) half filled and full filled configuration (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)

$$\text{ns}^1 < \text{np}^1 < \text{ns}^2 < \text{np}^2 < \text{np}^3 < \text{np}^4 < \text{np}^5 < \text{np}^6$$

Note : after 4th period (Ionization Energy)

$$\text{ns}^1 < \text{ns}^2 < \text{np}^1 < \text{np}^2 < \text{np}^3 < \text{np}^4 < \text{np}^5 < \text{np}^6$$

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

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

Periodic trend (d-block) :

- (1) Generally increases on moving down the group
- (2) Generally increase when moving left to right in the period.

$$\text{Sc} > \text{Y} > \text{La}, \text{Ag} < \text{Cu} < \text{Au}, \text{Cd} < \text{Zn} < \text{Hg}$$

Application of ionization energy :

- $I\text{E} \uparrow$ Metallic Character \downarrow
- $I\text{E} \uparrow$ Electropositive Character \downarrow
- $I\text{E} \uparrow$ Reducing Property \downarrow

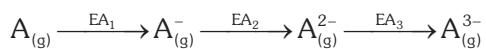
Note : Number of valence e^- = highest jump in successive IE

$$\text{eg.: } I\text{E}_1 < I\text{E}_2 < I\text{E}_3 <<< I\text{E}_4 < I\text{E}_5$$

Highest jump between $I\text{E}_3$ & $I\text{E}_4$ therefore V e^- is 3

Electron affinity & Electron gain enthalpy :

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

Successive electron affinity :

EA_1 is generally exothermic except N, Be, Mg and Noble gas
 EA_2, EA_3 always endothermic

Factors affecting :

- (1) $EA \propto Z_{\text{eff}}$
- (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.



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) $EN \propto Z_{\text{eff}}$
- (2) $EN \propto \frac{1}{\text{size}}$
- (3) $EN \propto \frac{1}{(-\text{charge})}$
- (4) $EN \propto (+\text{charge})$,
- (5) $EN \propto \% \text{ s-characters of hybrid orbital}$

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⁻, O²⁻

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. Electronegativity

- (i) As, P, S, Cl
- (ii) I, Br, Cl, F
- (iii) C, N, O, F

6. Hydration of Ions/Hydration Energy

- (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

- $Li^+, Na^+, K^+, Rb^+, Cs^+$

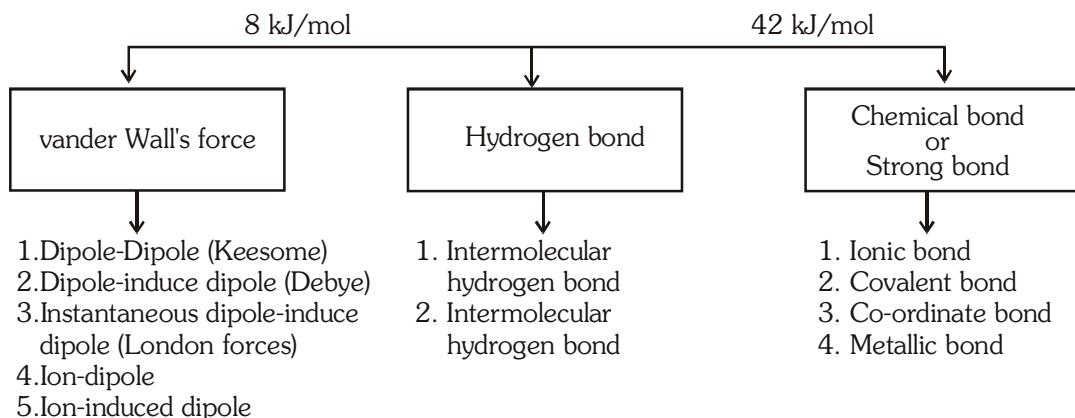
IMPORTANT NOTES



CHEMICAL BONDING

CHEMICAL BOND :

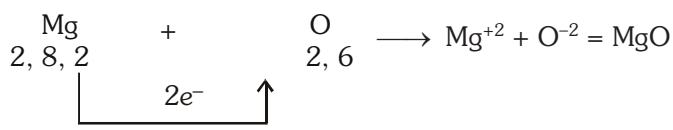
1. The force of attraction which hold together atom, molecule or ions within chemical species.
 2. It is always exothermic process.



ELECTROVALENT OR IONIC BOND

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called as Ionic or electrovalent bond.

Ionic bonds are non-directional.



electrovalency of Mg = 2
electrovalency of O = 2

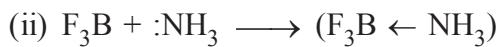
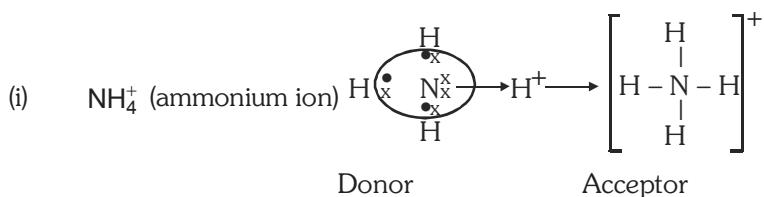
COVALENT BOND

A covalent bond is formed by the mutual sharing of electrons between two atoms to complete their octet.(Except H which completes its duplet)



COORDINATE BOND (DATIVE BOND)

The bond formed between two atoms in which contribution of an electron pair is made by one of them while the sharing is done by both.



EXCEPTION OF OCTET RULE

(a) electron deficient

Central atom:

No. of electron < 8

BeH₂

BF₃, BCl₃, BBr₃, BI₃

AlCl₃, AlBr₃, AlI₃

(b) electron rich

Central atom:

No. of electron > 8

PCl₅, IF₇

SF₆, XeF₂

(c) odd electron species

Central atom :

has odd electron

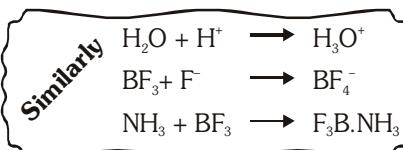
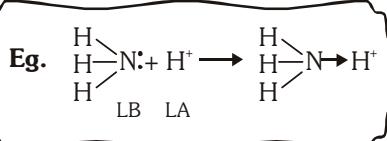
NO, NO₂, ClO₂

ClO₃

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 donor known as Lewis base - acquire +ve charge.
- Another species - must have vacant orbital act as acceptor known as Lewis acid - acquire -ve charge.



- Donor atom follow octet rule

MODERN APPROACH OF COVALENT BOND

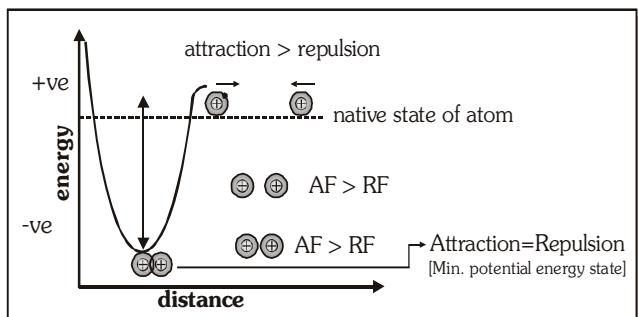
Consider wave mechanical model of atom means electron has dual nature; wave nature as well as particle nature considered by these theories, there are two theories in this approach.

1. Valence Bond Theory

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

2. Molecular Orbital Theory

- 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 → 1s¹
Cl → 1s²2s²2p⁶3s²3p⁵

- 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.

$$\text{Bond Strength} \propto \frac{1}{\text{No. of shell}} / \text{size of orbitals}$$

$$1-1 > 1-2 > 2-2 > 2-3$$

- **Exception :** Cl₂ > Br₂ > F₂ > I₂ 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 | Directional orbital has
p-directional 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

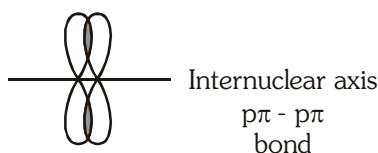
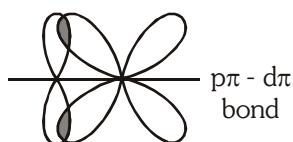
2. PATTERN OF OVERLAPPING**(a) Axial overlapping :**

Along the internuclear axis; form sigma (σ) bond, strong bond.

**(b) Co-lateral overlapping**

Side wise overlapping has less extent of overlapping form π - bond

Weak bond

p-p overlapping**p-d overlapping**

- 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 ³ d	Triangular bipyramidal	PCl ₅
5.	one s + three p + two d	6; sp ³ d ²	Octahedral	SF ₆
6.	one s + three p + three d	7; sp ³ d 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 repulsion :** lp-lp > lp-bp > bp-bp 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 (b) sp ² -hybridisation	3 2	- 1	Trigonal planar V-shape, Angular	BF ₃ , AlCl ₃ , BeF ₃ ⁻ NO ₂ ⁻ , SO ₂ , O ₃
3. (a) sp ³ -hybridisation (b) sp ³ -hybridisation (c) sp ³ -hybridisation	4 3 2	0 1 2	Tetrahedral Pyramidal V-shape Angular	CH ₄ , CCl ₄ , PCl ₄ ⁺ , ClO ₄ ⁻ , NH ₄ ⁺ , BF ₄ ⁻ , SO ₄ ⁻² , AlCl ₄ ⁻ NH ₃ , PF ₃ , ClO ₃ ⁻ , H ₃ O ⁺ , PCl ₃ , XeO ₃ , N(CH ₃) ₃ , CH ₃ H ₂ O, NH ₂ ⁻ OF ₂ , Cl ₂ O, SF ₂ , I ₃ ⁺
4. (a)sp ³ d-hybridisation (b) sp ³ d-hybridisation (c) sp ³ d-hybridisation (d) sp ³ d-hybridisation	5 4 3 2	- 1 2 3	Trigonal bipyramidal See-Saw, folded square distorted tetrahedral almost T-shape Linear	PCl ₅ , SOF ₄ , AsF ₅ SF ₄ , PF ₄ ⁻ , AsF ₄ SbF ₄ ⁻ , XeO ₂ F ₂ ClF ₃ , ICl ₃ I ₃ ⁻ , Br ₃ ⁻ , ICl ₂ ⁻ , ClF ₂ ⁻ , XeF ₂
5. (a) sp ³ d ² -hybridisation (b) sp ³ d ² -hybridisation (c) sp ³ d ² -hybridisation	6 5 4	- 1 2	Square bipyramidal/octahedral Square pyramidal/distorted octahedral Square planar	PCl ₆ ⁻ , SF ₆ XeOF ₄ , ClF ₅ , SF ₅ ⁻ , XeF ₅ ⁺ XeF ₄
6. (a) sp ³ d ³ -hybridisation (b) sp ³ d ³ -hybridisation (c) sp ³ d ³ -hybridisation	7 6 5	- 1 2	Pentagonal bipyramidal distorted octahedral /capped octahedral Pentagonal planar	IF ₇ XeF ₆ XeF ₅ ⁻

DIPOLE MOMENT

Measurement of Polarity in a molecule

$$\vec{\mu} = q \times d$$

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.

Diatomeric Molecule

(a) Homotomeric $\Delta EN = 0 \rightarrow \vec{\mu} = 0 \rightarrow$ Non-polar
H₂, F₂, Cl₂, N₂ etc.

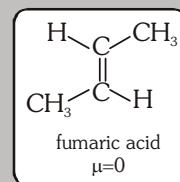
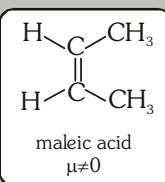
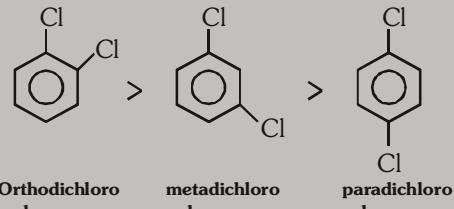
(b) Heterotomeric $\Delta EN \neq 0 \rightarrow \vec{\mu}_{net} = 0 \rightarrow$ polar
HF > HCl > HBr > HI

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 OrderNH₃ > NI₃ > NBr₃ > NCl₃ > NF₃NH₃ > SbH₃ > AsH₃ > PH₃H₂O > H₂SCH₃Cl > CH₃F > CH₃Br > CH₃ICH₃Cl > CH₂Cl₂ > CHCl₃ > CCl₄**Applications**

Predict shape and polarity of molecule
Symmetrical geometry $\rightarrow \mu=0 \rightarrow$ non-polar
Unsymmetrical geometry $\rightarrow \mu \neq 0 \rightarrow$ polar
Distinguish between cis & trans form

**Dipole moment in Aromatic Compounds**

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
Intramolecular hydrogen bond → within the molecules

- * Intramolecular H-bonding takes place 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 CH₃COOH 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 (dense nature) Melting Point (mp) Boiling Point (bp) Viscosity Surface Tension Volatility Vapour Pressure	∞ H-bond ∞ H-bond ∞ H-bond ∞ H-bond ∞ H-bond ∞ 1/H-bond ∞ 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.

$$\Psi_{MO} = \Psi_A + \Psi_B \quad (\text{Bonding M.O.})$$

Case II : When two waves are out of phase, the waves are subtracted from each other so that the amplitude of new wave is :

$$\Psi_{MO}^* = \Psi_A - \Psi_B \quad (\text{Antibonding M.O.})$$

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 N₂ (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 O₂ and F₂ (molecule having > 14 electrons)

$$\sigma_{1s} < \sigma_{1s}^* ; \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

σ^*, π^* = 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., O₂ molecule. Otherwise diamagnetic (eg : N₂)

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	$\frac{1}{2}$	paramagnetic
2	2	2	0	1	diamagnetic
3	3	2	1	0.5	paramagnetic
4	4	2	2	0	—
5	5	3	2	$\frac{1}{2}$	paramagnetic
6	6	4	2	1	diamagnetic
7	7	4	3	$\frac{1}{2}$	paramagnetic
8	8	4	4	0	—
9	9	5	4	$\frac{1}{2}$	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 $\propto \frac{1}{\Delta EN}$

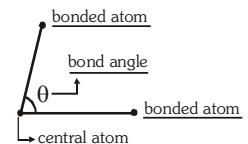
$$d_{A-B} = r_A + r_B - 0.09 \times \Delta EN \text{ Å}$$

(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 :

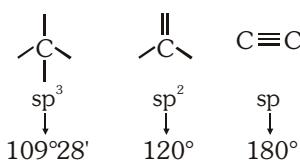
Angle between two adjacent bond is known as bond angle.



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. : CH₄ > NH₃ > H₂O:

(iii) Type of Central atom: Applicable when :

* hybridisation same * No. of lp/bp same

Bond angle \propto EN of central atom

Eg. NH₃ > PH₃ > AsH₃ > SbH₃

(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. OF₂ < OCl₂ < OBr₂ < OI₂

Note :

Regular geometry / same hybridisation/ bond angle same

BF₃ = BCl₃ = BBr₃ = BI₃

IONIC BOND

Extreme polar covalent bond is an Ionic Bond.

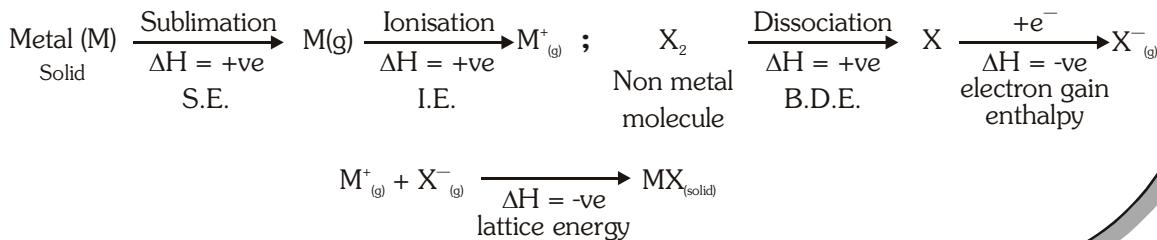
Therefore Ionic Bond ΔEN - Must be higher

one specie - lower EN - metal

one specie - higher EN - non metal

Eg. NaCl, KF

Formation of Ionic Bond takes place in following step.



$\Delta H_{\text{formation}} = \Delta H_{\text{Sub}} + \text{I.E.} + \frac{1}{2} \text{BDE} + \Delta H_{\text{eg}} + U$
bond formation is always an exothermic process.

$$\Delta H_{\text{formation}} = -ve$$

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 :

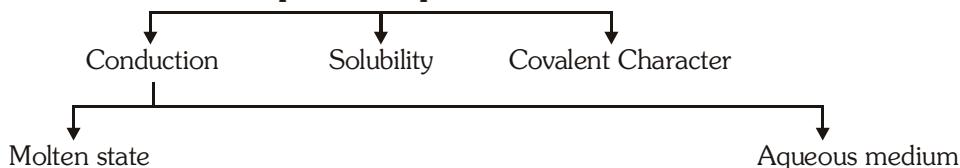
Hard, Solid, Brittle (strong electrostatic attraction between ions)

Non directional nature (ionic compound do not exhibit stereo isomerism)

Higher Melting Point / Boiling Point

Isomorphism : MgSO₄.7H₂O; ZnSO₄.7H₂O; FeSO₄.7H₂O

Specific Properties



$$\text{Ionic conduction} \propto \frac{1}{\text{Ionic radius}}$$

$$\text{Ionic mobility} \propto \frac{1}{\text{Ionic radius}}$$

Eg. : LiCl, NaCl, KCl, RbCl, CsCl

Hyd. radius : Cs⁺ <<< Li⁺(aq)

Ionic Radius : Li⁺ <<< Cs⁺

conductance : LiCl < NaCl < KCl < RbCl < CsCl

Conductance : CsCl < RbCl < KCl < NaCl < LiCl

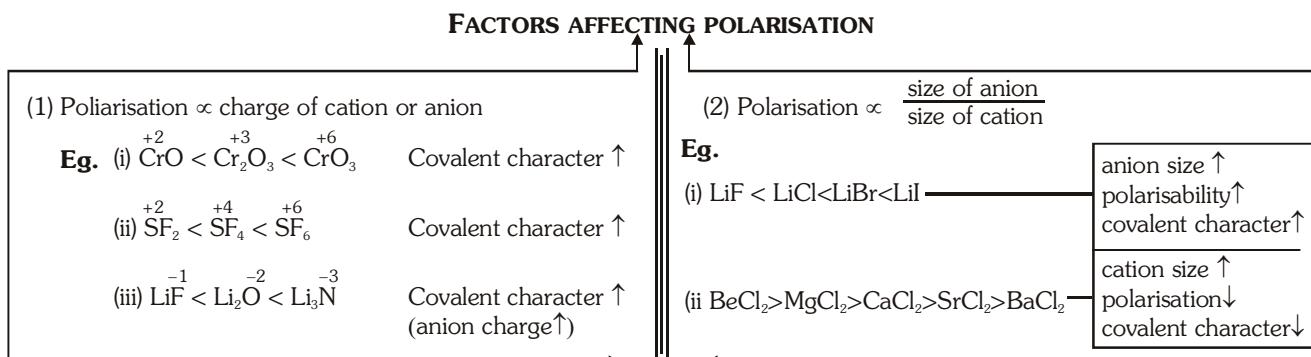
COVALENT CHARACTER / FAJAN'S RULE

$$\text{Ionic potential of cation}(\phi) \propto \frac{\text{charge of cation}}{\text{size of cation}}$$

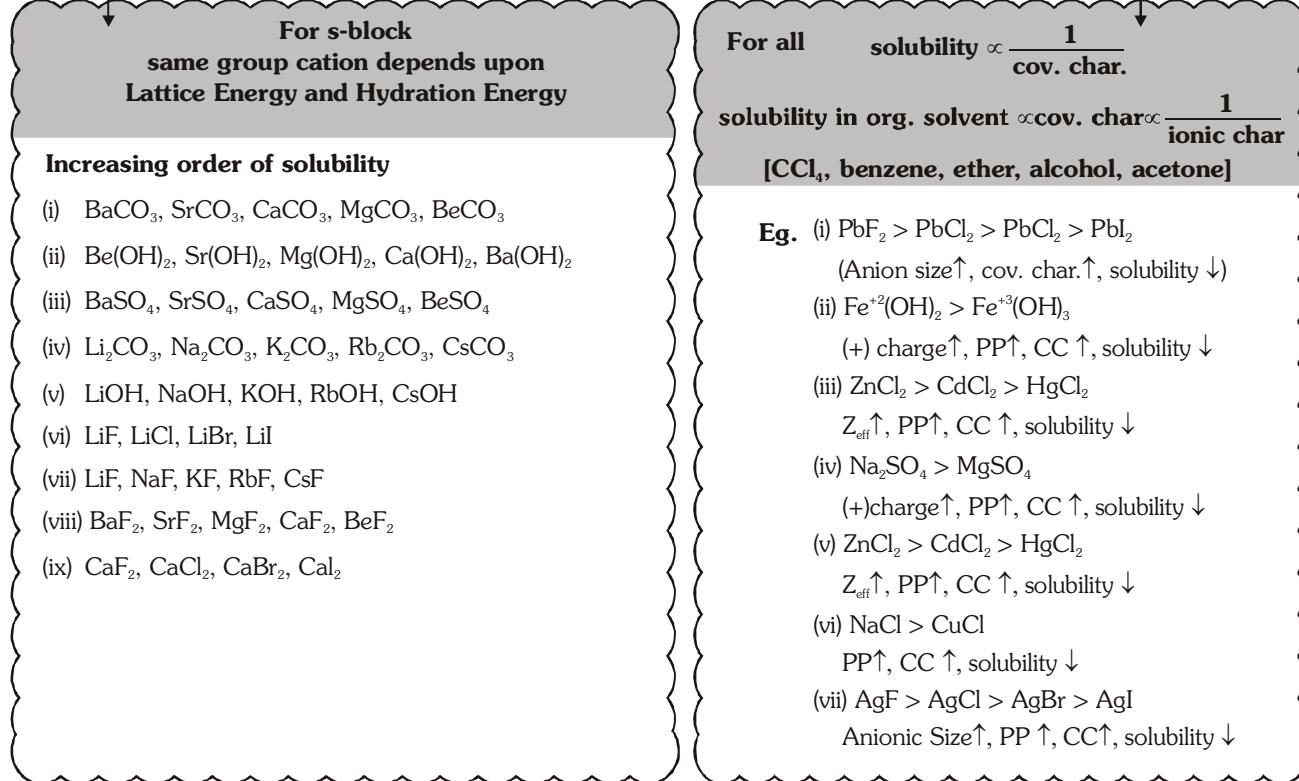
$$\text{Polarisability of anion} \propto \text{size of anion} \propto \text{charge of anion}$$

Condition for polarisation

- Smaller cation
- Large anion
- Higher charge



SOLUBILITY



HYBRIDISATION OF FOLLOWING SPECIES IN SPECIFIED STATE

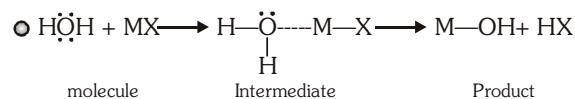
Species	Cationic part	Anionic part
PCl_5	$\text{PCl}_4^+ (\text{sp}^3)$	$\text{PCl}_6^- (\text{sp}^3\text{d}^2)$
PBr_5	$\text{PBr}_4^+ (\text{sp}^3)$	Br^-
XeF_6	$\text{XeF}_5^+ (\text{sp}^3\text{d}^2)$	F^-
N_2O_5	$\text{NO}_2^+ (\text{sp})$	$\text{NO}_3^- (\text{sp}^2)$
I_2Cl_6 (liquid)	$\text{ICl}_2^+ (\text{sp}^3)$	$\text{ICl}_4^- (\text{sp}^3\text{d}^2)$
Cl_2O_6	$\text{ClO}_2^+ (\text{sp}^2)$	$\text{ClO}_4^- (\text{sp}^3)$
I_2 (molten state)	$\text{I}_3^+ (\text{sp}^3)$	$\text{I}_3^- (\text{sp}^3\text{d})$

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	$\text{Si}_2\text{O}_7^{6-}$
Cyclic	2	3	$(\text{SiO}_3)_n^{2n-}$
Single chain (pyroxene)	2	3	$(\text{SiO}_3)_n^{2n-}$
Double chain (Amphibole)	(3, 2) avg. = 2.5	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(\text{Si}_4\text{O}_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(\text{Si}_2\text{O}_5)_n^{2n-}$
3D	4	2	$(\text{SiO}_2)_n$

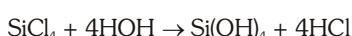
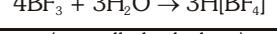
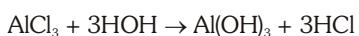
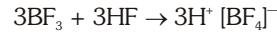
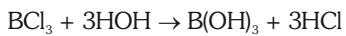
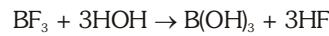
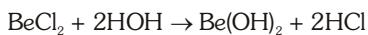
HYDROLYSIS
Hydro - Water
lysis - break down

Break down of a molecule through water and formation of new product is known as hydrolysis.

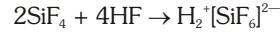
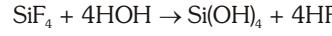
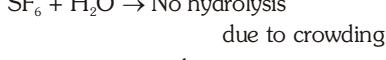
It is nucleophilic substitution reaction.



extent of hydrolysis \propto covalent character.



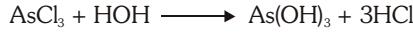
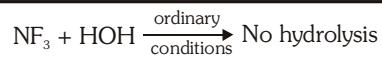
(partially hydrolysis)



hydrolysis followed by

Lewis acid-base reaction.

15th Group Halides



(partial hydrolysis)



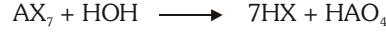
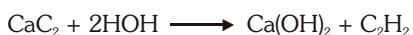
(partial hydrolysis)



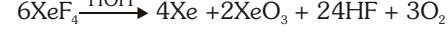
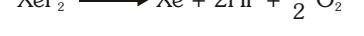
Hydrolysis of higher covalent character containing salt



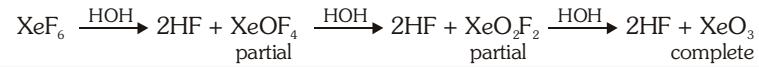
Hydrolysis of Interhalogen Compounds



HX Hydrohalic acid
HOA, HAO₂, HAO₃, HAO₄
oxyacid of halogen



Some specific hydrolysis



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) ($p\pi - p\pi$) type of back bond
eg. BF_3 , BCl_3 , CF_2 , CCl_2
- (ii) ($p\pi - d\pi$) type of back bond
eg. CCl_3^- , $\text{O}(\text{SiH}_3)$, $\text{N}(\text{SiH}_3)_2$, SiH_5O^- , etc.

Application of back bonding :**Lewis acid character :**

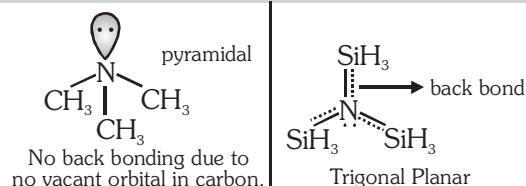
- * $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$
- $\text{BeF}_2 < \text{BeCl}_2 < \text{BeBr}_2 < \text{Bel}_2$
- $\text{SiF}_4 > \text{SiCl}_4 > \text{SiBr}_4 > \text{SiI}_4$

Lewis basic character :

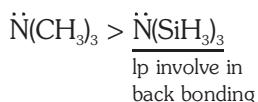
Note : Due to back bonding $\underline{\text{B}_3\text{N}_3\text{H}_6}$, $\underline{(\text{BO}_2)_3}^{3-}$, $\underline{\text{N}(\text{SiH}_3)_3}$ is planar around underlined atom.

Few more examples of back bonding

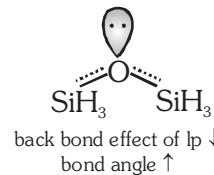
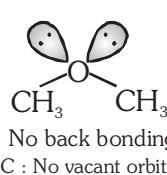
1. Shape of trimethyl amine pyramidal while shape of trisilyl amine is triangular planar.



2. Lewis base strength



3. Bond angle of $(\text{CH}_3)_2\text{O}$ is very less than $(\text{SiH}_3)_2\text{O}$

**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.

	Bridge bond	Hybridisation of central atom
Be_2Cl_4	(3c-4e)	sp^2
$(\text{BeCl}_2)_n$	(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
$(\text{BeH}_2)_n$	(3c-2e)	sp^3
$(\text{AlH}_3)_n$	(3c-2e)	sp^3d^2
$\text{Al}_2(\text{CH}_3)_6$	(3c-2e)	sp^3

Odd e^- species : Total number of electron or valance electron in odd number.

	Hybridisation	Shape	Magnetic behaviour
NO_2	sp^2	V shape	Para
ClO_2	sp^2	V shape	Para
ClO_3	sp^3	Pyramidal	Para
${}^*\text{CH}_3$	sp^2	Trigonal planar	Para
${}^*\text{CH}_3 / {}^*\text{CHF}_2 / \text{CH}_2\text{F}$	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
- $NO_2 \rightarrow$ Mixed anhydride
- it gives $\rightarrow HNO_2 & HNO_3$

Oxide Acid

- $N_2O_3 \rightarrow HNO_2$ — Nitrous acid
- $N_2O_5 \rightarrow HNO_3$ — Nitric acid
- $P_4O_{10} \rightarrow H_3PO_4$ — Phosphoric acid
- $SO_2 \rightarrow H_2SO_3$ — Sulphurous acid
- $SO_3 \rightarrow H_2SO_4$ — Sulphuric acid
- $Cl_2O_7 \rightarrow HClO_4$ — 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

- Sulphurous acid - H_2SO_3
- Sulphuric acid - H_2SO_4
- Thiosulphuric acid - $H_2S_2O_3$
- Peroxymonosulphuric (Caro's acid) - H_2SO_5 (Peroxide bond)
- Peroxydisulphuric acid (Marshal's acid) - $H_2S_2O_8$ (Peroxide bond)
- Pyrosulphurous acid - $H_2S_2O_5$ - (S-S linkage)
- Pyrosulphuric acid - $H_2S_2O_7$ (S-O-S linkage)
- Dithionous acid - $H_2S_2O_4$
- Dithionic acid - $H_2S_2O_6$
- Polythionic acid - $H_2(S)_nO_6$ (S-S linkage)

OXYACIDS OF HALOGEN (Cl)

- Hypochlorous acid- $HClO$
- Chlorous acid - $HClO_2$
- Chloric acid - $HClO_3$
- 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.

ALLOTROPIES OF CARBON**DIAMOND**

$C-sp^3$, tetrahedral structure
C-C bond length 1.54 \AA
Compact 3 dimensional structure
Hardest substance
Very high mp ($\sim 3400^\circ\text{C}$)
Very high density
Non conductor
Very high refractive index
Exhibit total internal reflection
Shines brightly 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

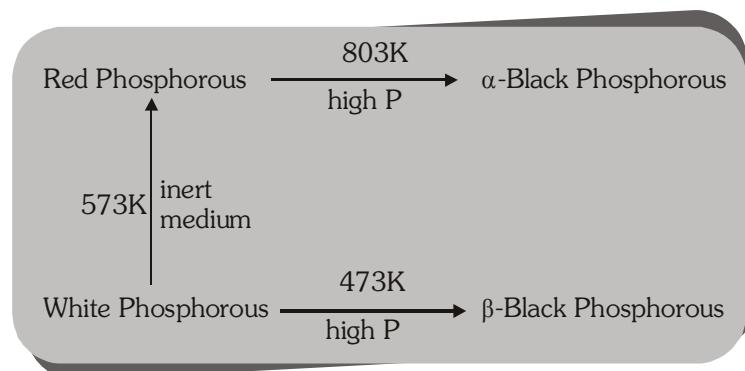
Latest discovered allotrope of carbon it is found in chimney sooty particle.
It contain $C_{60}-C_{320}$; $C : sp^2$ hybrid
Contain pentagon & hexagonal structure
 C_{60} : Buckminster fullerene soccer ball (football) or bucky ball.
 C_{60} : 20 hexagon rings
12 pentagon rings
Purest form of carbon
No 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



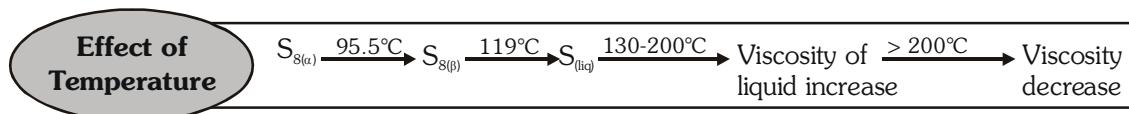
ALLOTROPES OF SULPHUR

S	
Crystalline	Amorphous
Rhombic sulphur (α -S) most stable form	Milk of sulphur Plastic sulphur (γ -S)
Monoclinic sulphur (β -S)	Colloidal sulphur
α -S $\xrightleftharpoons[<95.6^\circ\text{C}]{>95.6^\circ\text{C}}$ β -S	$\text{H}_2\text{S} + 2\text{HNO}_3 \xrightarrow[\text{RA}]{\text{OA}} \text{S} + 2\text{NO}_2 + 2\text{H}_2\text{O}$ Redox
95.6°C = transition Temp. both are soluble in CS_2 but insoluble in water	

(a) density of α S > β S

(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



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) $\text{Be}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$
- (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) $\text{Be}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$
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) $\text{Cr}_2\text{O}_7^{2-}$, 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) H₂, HBr, HCl, HF
- (ii) $\text{C}-\text{I}$, $\text{C}-\text{Br}$, $\text{C}-\text{Cl}$, $\text{C}-\text{F}$
- (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) F₂, H₂, O₂, N₂
- (viii) NO⁻, NO, NO⁺
- (ix) I₂, F₂, Br₂, Cl₂
- (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) NH₃, H₂O, 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) N₂, O₂, F₂, Cl₂
- (ii) N–N, C–N, C–C
- (iii) CO, $\text{C}=\text{O}$, $-\text{C}-\text{O}-$
- (iv) NO⁺, NO, NO⁻
- (v) O₂, O₃, H₂O₂ (O–O bond length)
- (vi) CO, CO₂, CO₃²⁻
- (vii) N₂, N₂⁻, N₂⁻²
- (viii) O₂⁺², O₂, O₂⁻, O₂⁻²
- (ix) HF, HCl, HBr, HI

20. Dipole moments

- (i) CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl
- (ii) NF₃, NH₃, H₂O, HF
- (iii) Cis-chloropropene, Trans-chloropropene
- (iv) p, m, o-dichlorobenzene
- (v) CH₃I, CH₃Br, CH₃F, CH₃Cl
- (vi) NH₃, SO₂, H₂O, HF
- (vii) H₂S, H₂O
- (viii) HI, HBr, HCl, HF
- (ix) PH₃, ASH₃, SbH₃, NH₃
- (x) H₂O, H₂O₂

Group 15**Bond angle Group 16****Bond angle**

NH ₃	107°48'	H ₂ O	104°28'
PH ₃	93°36'	H ₂ S	92°
AsH ₃	91°48'	H ₂ Se	91°
SbH ₃	91°18'	H ₂ Te	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

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)

Group 14**Order of stability :**

$\text{Ti}^{+1} > \text{In}^{+1} > \text{Ga}^{+1}$ (due to inert pair effect)

Order of stability :

$\text{Pb}^{+2} > \text{Sn}^{+2} > \text{Ge}^{+2}$ (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

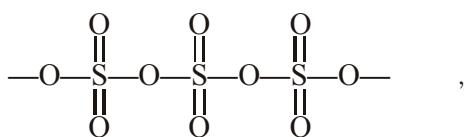
ALLOTROPIC FORM OF SO_3

SO_3 have three allotropic forms $\alpha\text{-SO}_3$, $\beta\text{-SO}_3$ and

$\gamma\text{-SO}_3$

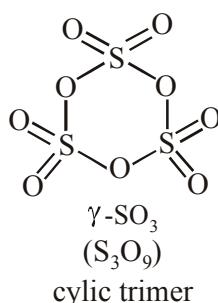
$\alpha\text{-SO}_3$

Cross linked solid



Polymeric chain structure

$\beta\text{-SO}_3$



$\gamma\text{-SO}_3$

(S_3O_9)

cyclic trimer

IMPORTANT NOTES

s-BLOCK ELEMENTS**ALKALI METALS****Physical properties :**

General electronic configuration ns^1 .

General oxidation state +1.

Atomic/Ionic size $Li < Na < K < Rb < Cs$.

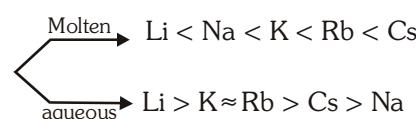
Density $Li < K < Na < Rb < Cs$

Ionisation energy $Li > Na > K > Rb > Cs$

Flame colour

Li	Crimsen red
Na	Golden yellow
K	Pale violet
Rb	Reddish violet
Cs	Blue

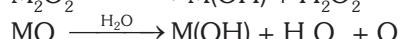
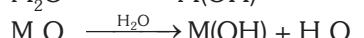
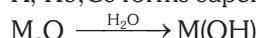
Basic nature increase down to the group

Reducing property :**□ Chemical properties :**

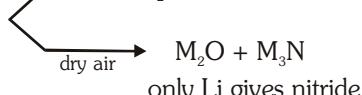
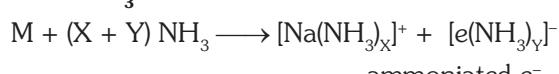
With O_2 : Lithium forms normal oxide [Li_2O]

Sodium forms peroxide (Na_2O_2)

K, Rb,Cs forms superoxide KO_2, RbO_2, CsO_2

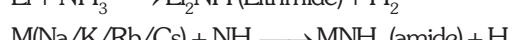
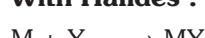


With Water : $M + H_2O \longrightarrow MOH + H_2$

With Air :**With NH_3 :**

Paramagnetic, blue colour. In excess of metal dimagnetic and copper bronze colour.

on standing

**With Halides :**

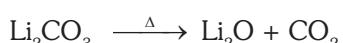
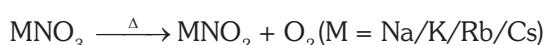
K, Rb, Cs forms poly halide due to large size

SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM

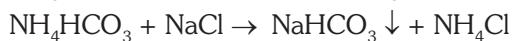
- (a) Both lithium and magnesium are harder and lighter than other elements in the respective groups.
- (b) Lithium and magnesium react slowly with cold water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, 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,
 $LiCl \cdot 2H_2O$ and $MgCl_2 \cdot 8H_2O$.

Carbonates :

Only Li_2CO_3 decomposes

**Nitrates :** **$Na_2CO_3 \cdot 10H_2O$ (Washing Soda)**

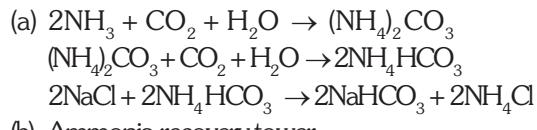
- In **Solvay's process**, CO_2 gas is passed through saturated brine ($NaCl$) solution when sparingly soluble $NaHCO_3$ separates out.



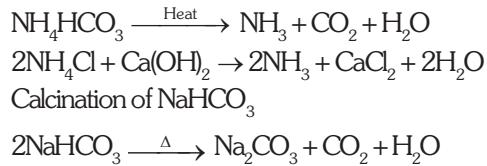
The $NaHCO_3$ formed above is calcined to form Na_2CO_3



- The reactions taking place at different stages during the manufacture of Na_2CO_3 by Solvay process are given as under :



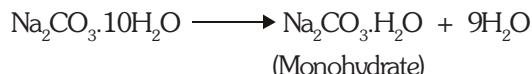
(b) Ammonia recovery tower



(c) Calcination of NaHCO_3

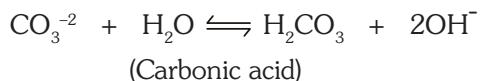


(i) **Efflorescence :** $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ when exposed to air it gives out nine out of ten H_2O molecules.



This process is called efflorescence. Hence washing soda losses weight on exposure to air.

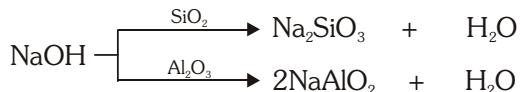
(ii) **Hydrolysis :** Aqueous solution of Na_2CO_3 is alkaline in nature due to anionic hydrolysis.



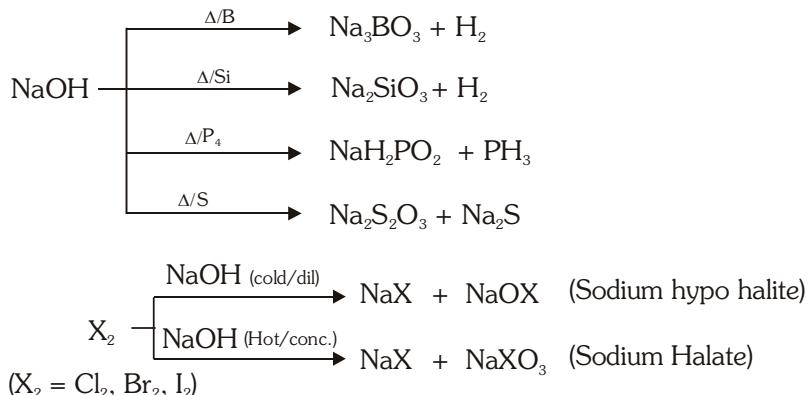
➤ Na_2CO_3 does not impart any colour to the flame but NaCl does because the thermal ionization of Na_2CO_3 does not take place at the temperature of flame of the burner.

Reaction of NaOH :

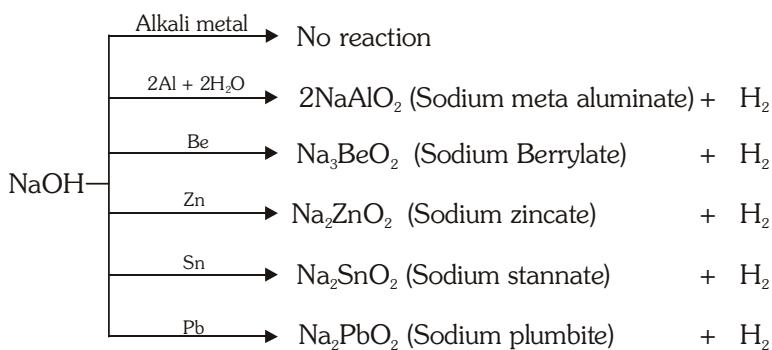
(i) NaOH is **strong base**



(ii) **Reaction with non metals :** no reaction with H_2 , N_2 and C



(iii) **Reaction with Metal :**



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

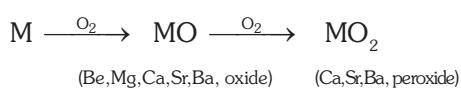
Basic nature of oxide

Reducing property : Order of reducing property in aqueous and gaseous medium is

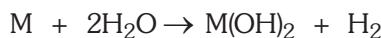
$Be^{+2} < Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$

Chemical properties :

With O₂ :



With Water :



With Air :

In moist air, except Be all the elements converts into carbonates.

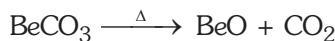
In dry air gives nitride and oxide both

With NH₃ :

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



- (ii) Order of decreasing stability -



Nitrates :

- (i) Alkaline earth metals forms $M(NO_3)_2$ type nitrates.

(M –Alkaline earth metal).

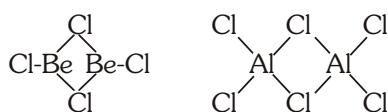
- (ii) All alkaline metals nitrates on heating gives oxides and $NO_2 + O_2$



DIAGONAL SIMILARITY BETWEEN BERYLLIUM AND ALUMINIUM

In many of its properties, beryllium resembles aluminium. Thus –

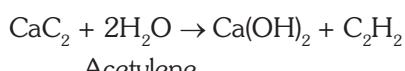
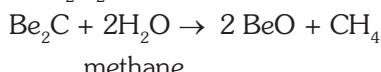
- (a) The two elements have same electronegativity and their charge/ radius ratios.
- (b) Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalies to form soluble complexes, beryllates $[Be(OH)_4]^{2-}$ and 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 $[Al(C_2O_4)_3]^{3-}$.

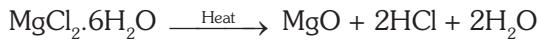
- Be_2C on treatment with H_2O forms CH_4 while CaC_2 forms C_2H_2 .



CHLORIDE OF ALKALINE EARTH METAL.

- $BeCl_2$ in the vapour phase above $900^\circ C$ is monomeric ; below $900^\circ C$ 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.

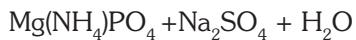
- Anhydrous $MgCl_2$ cannot be prepared by the simple heating of hydrated magnesium chloride $MgCl_2 \cdot 6H_2O$, as it gets hydrolysed to magnesium oxide.



- 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

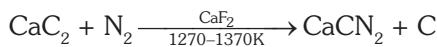
- (i) Charcoal cavity test. On heating on a charcoal cavity with one drop of $\text{Co}(\text{NO}_3)_2$, a pink colour is imparted to the residue $\text{CoO} \cdot \text{MgO}$.
- (ii) The salt solution when mixed with NH_4Cl and NH_4OH and finally treated with soluble phosphates forms a white precipitate of magnesium ammonium phosphate.



white ppt.

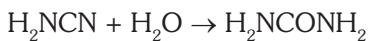
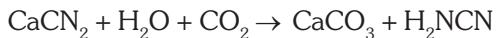
CALCIUM CYANAMIDE

- 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 .



Its trade name is Nitrolim.

- Calcium cyanamide (CaCN_2) is a slow acting manure and is preferred to soluble compounds like NaNO_3 or $(\text{NH}_4)_2\text{SO}_4$ 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.



Urea

**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 $\text{Ca}(\text{OH})_2$. Quick lime is used for making caustic soda, bleaching powder, calcium 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 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) 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 ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) known as plaster of Paris.
- Plaster of Paris has the property of setting to a hard mass $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 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 dislocated 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 material. The average composition of portland cement is : CaO 61.5%, SiO_2 22.5%, Al_2O_3 7.5%. Cement consists of :

Tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$

Dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$

Tricalcium aluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

Tetracalcium alumino - ferrite $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$

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, $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{Ca}(\text{OH})_2$ 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, $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaF}_2$.

HYDROLITH

- Hydrolith (CaH_2) is calcium hydride & on hydrolysis for calcium hydroxied & liberate hydrogen.

IMPORTANT NOTES

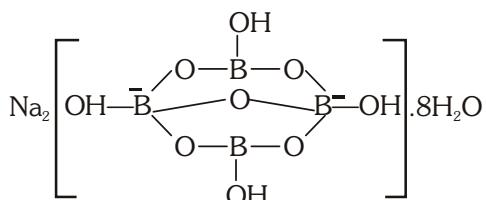


p-BLOCK

13th-GROUP

- Some important ores of Boron are given as under.
 - (i) Boric acid, H_3BO_3
 - (ii) Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
 - (iii) Colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

 - Some important minerals of aluminium are given as under.
 - (i) Corundum, Al_2O_3
 - (ii) Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
 - (iii) Cryolite, Na_3AlF_6
 - (iv) Feldspar, KAlSi_3O_8



Properties :

- Properties :**

 - (i) It is a white crystalline solid of formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In fact it contains the tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and correct formula; therefore, is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.
 - (ii) Hydrolysis

$$\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \rightarrow 2\text{NaOH} + 4\text{H}_3\text{BO}_3$$
 - (iii) Heating

$$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\Delta} \text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\Delta} \begin{matrix} 2\text{NaBO}_2 \\ \text{Sodium} \\ \text{metaborate} \end{matrix} + \begin{matrix} \text{B}_2\text{O}_3 \\ \text{Boric} \\ \text{anhydride} \end{matrix}$$
 - (iv) When borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $\text{Co}(\text{BO}_2)_2$ head is formed.



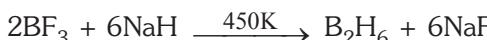
Preparation :

- (i) $3\text{LiAlH}_4 + 4\text{BF}_3 \longrightarrow 3\text{LiF} + 3\text{AlF}_3 + 2\text{B}_2\text{H}_6$
 or LiBH_4 or $3(\text{BF}_3)$

4



(iii) Industrial scale :



5



Properties :

- (i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.

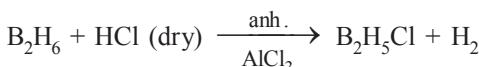
(ii) Diborane catches fire spontaneously upon exposure to air.

(iii) Reaction with Oxygen :

$$\text{B}_2\text{H}_6 + 3\text{O}_2 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} ; \Delta_c H^\ominus = - 1976 \text{ kJ mol}^{-1}$$

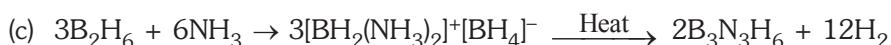
(iv) Hydrolysis :

$$\text{B}_2\text{H}_6(\text{g}) + 6\text{H}_2\text{O}(\ell) \text{ (Cold is enough)} \rightarrow 2\text{B}(\text{OH})_3(\text{aq}) + 6\text{H}_2(\text{g})$$

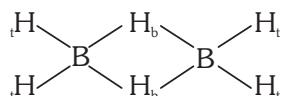
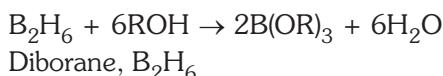


(v) Reaction with Lewis Bases

- $B_2H_6 + 2NMe_3 \rightarrow 2BH_3.NMe_3$
- $B_2H_6 + 2CO \rightarrow 2BH_3.CO$



(vi) Reaction with ROH :

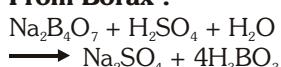


dimer due to formation of
3 centre-2e-bond

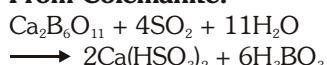
Inorganic benzene

ORTHOBORIC ACID [H_3BO_3 or $B(OH)_3$]

From Borax :

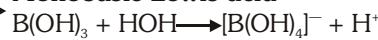


From Colemanite:

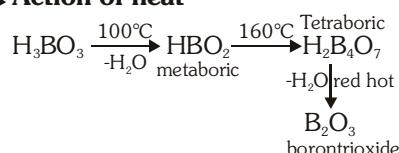


Properties

Monobasic Lewis acid

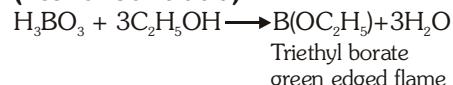


Action of heat

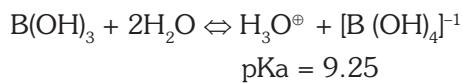


Reaction with alcohol

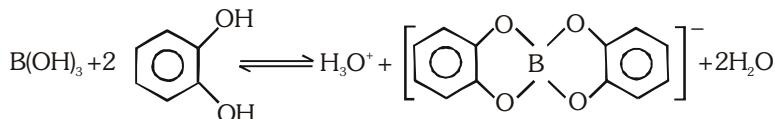
(Test of boric acid)



➤ Boric acid is a weak monobasic acid



➤ 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 polyhydroxy alcohols (e.g. Glycerol, mannitol, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.

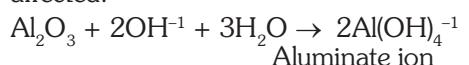


Boron is complex by these compounds. These complex ions cannot interact with H^+ ions as boron atom has already acquired its maximum covalency of four. Consequently, boric acid in presence of polyhydroxy alcohols can be titrated against NaOH to a definite end point.

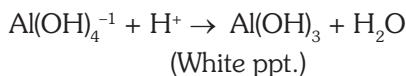
EXTRACTION OF ALUMINIUM

Al is usually extracted from Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. 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 $[\text{Al}(\text{OH})_4]^{-1}$. The basic oxide impurities such as Fe_2O_3 are not affected.

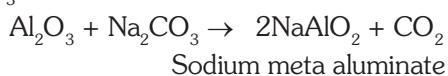


Fe_2O_3 left undissolved is filtered off. The treatment of $\text{Al}(\text{OH})_4^{-1}$ solution with a weak acid precipitate pure $\text{Al}(\text{OH})_3$.

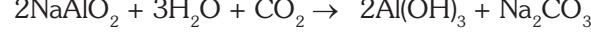


The $\text{Al}(\text{OH})_3$ precipitate is removed by filtration and ignited to get alumina, Al_2O_3 .

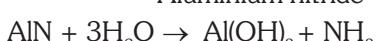
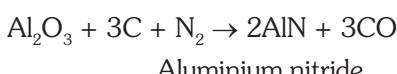
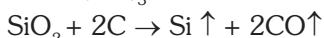
- **Hall's process**, Involves the fusion of the ore with Na_2CO_3 when soluble sodium meta aluminate, NaAlO_2 is produced. This is extracted with water when Fe_2O_3 is left as a residue.



The water extract is heated upto 333K and CO_2 is passed through it. $\text{Al}(\text{OH})_3$ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_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 $\text{Al}(\text{OH})_3$ which on fusion gives alumina.



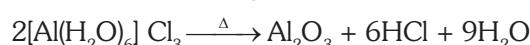
Electrolysis of Al_2O_3 to form aluminium. Pure alumina is dissolved in fused cryolite, Na_3AlF_6 at 1225 K by current of 100 amperes and 6–7 volts to get Al. The Al obtained is purified by Hooke's process.

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.

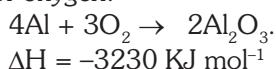
ALUMINIUM CHLORIDE

- 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 $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ 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 .



- 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.

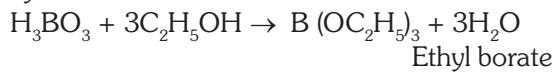
- **Thermite welding**, Aluminium has got a very high affinity for oxygen.



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 $\text{C}_2\text{H}_5\text{OH}$ and BO_3^{3-} salt with conc. H_2SO_4 burns with green edge flame due to the formation of ethyl borate.



- **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 $[M_2SO_4 \cdot M_2'(SO_4)_3 \cdot 24H_2O]$

Alums are the double salts of Type

M : Monovalent Cation:

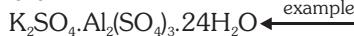
M' : Trivalent cation :

M' : Trivalent cation :
 Al^{3+} , Fe^{3+} & Cr^{3+}

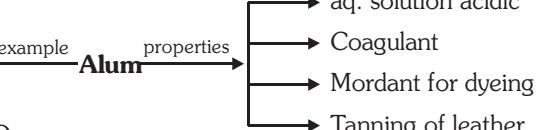
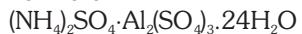
Soda alum



Potash alum



Ammonium alum



Pseudo alums are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.

(i) $\text{MnSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (ii) $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

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 — CO₂, SiO₂ and GeO₂ are acidic, whereas SnO₂ and PbO₂ 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 SnF₄ and PbF₄, 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.

- CO₂ is a gas while SiO₂ is a solid at room temperature.
- SiO only exists at high temperature
- CO₂ SiO₂ GeO₂ , GeO are acidic, PbO, PbO₂ is SnO and SnO₂ are amphoteric and CO is neutral
 ⇒ Among 14th group element only Sn reacts with steam to produce H₂ gas.
 ⇒ Tetrahalide of 14th group element are covalent except SnF₄ and PbF₄

Stability of oxidation state

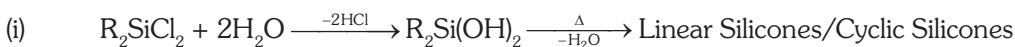
- ⇒ C⁺⁴ >-----> Pb⁺⁴ (Stability)
- ⇒ C⁺² <-----< Pb⁺² (Stability)
- ⇒ Pb⁺⁴ compounds are strong oxidizing agent.
- ⇒ PbI₄ does not exist.

- Trimethylamine (CH₃)₃N is pyramidal while Trisilylamine N(SiH₃)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 : (R₂SiO)_n. Where R = -CH₃, -C₂H₅, -C₆H₅



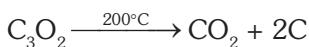
CARBON SUBOXIDE

- Carbon suboxide (C_3O_2) is a foul smelling gas which can be prepared by the dehydration of malonic acid with P_4O_{10} .



Carbon
suboxide

On heating upto 200°C, it decomposes into CO₂ and carbon.



The molecule is thought to have a linear structure.



OXIDE OF LEAD

- $\text{PbO}_{\text{massicot}} \xrightleftharpoons[\text{Litharge}]{\text{Cool}} \text{PbO}_{\text{Litharge}}$
 - **Red lead (Pb_3O_4)** is considered to be mixture of lead monoxide and lead dioxide and it is written as $(\text{PbO}_2 \cdot 2\text{PbO})$.
 - **Lead dioxide (PbO_2)**. It is a brown powder obtained by the treatment of red lead with HNO_3 .

$$\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \rightarrow 2\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$$

It is used as an active material of the positive plate in storage cells and finds use in match industry as an oxidizing agent.

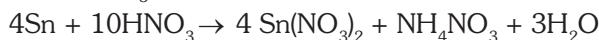
REACTION OF LEAD OXIDES

Oxide	ex NaOH	HCl	H_2SO_4	HNO_3
PbO	Na_2PbO_2	PbCl_2	PbSO_4	$\text{Pb}(\text{NO}_3)_2$
PbO_2	Na_2PbO_3	$\text{PbCl}_2 + \text{Cl}_2$	$\text{PbSO}_4 + \text{O}_2$	$\text{Pb}(\text{NO}_3)_2$
Pb_2O_3	$\text{Na}_2\text{PbO}_2 + \text{NaPbO}_3$	$\text{PbCl}_2 + \text{Cl}_2$	$\text{PbSO}_4 + \text{O}_2$	$\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2$
Pb_3O_4	$\text{Na}_2\text{PbO}_2 + \text{Na}_2\text{PbO}_3$	$\text{PbCl}_2 + \text{Cl}_2$	$\text{PbSO}_4 + \text{O}_2$	$\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2$

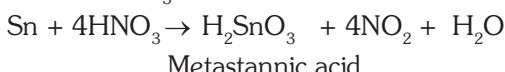
TIN & ITS COMPOUNDS

- ## ➤ Action of conc. HNO_3 on tin

(a) Dilute HNO_3

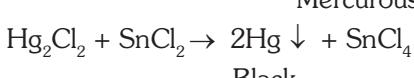
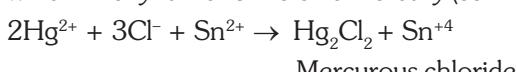


(b) Hot conc. HNO_3

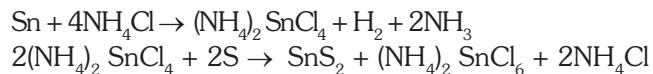


Action of conc. NaOH on tin $\Rightarrow \text{Sn} + 2\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SnO}_3 + 2\text{H}_2\uparrow$

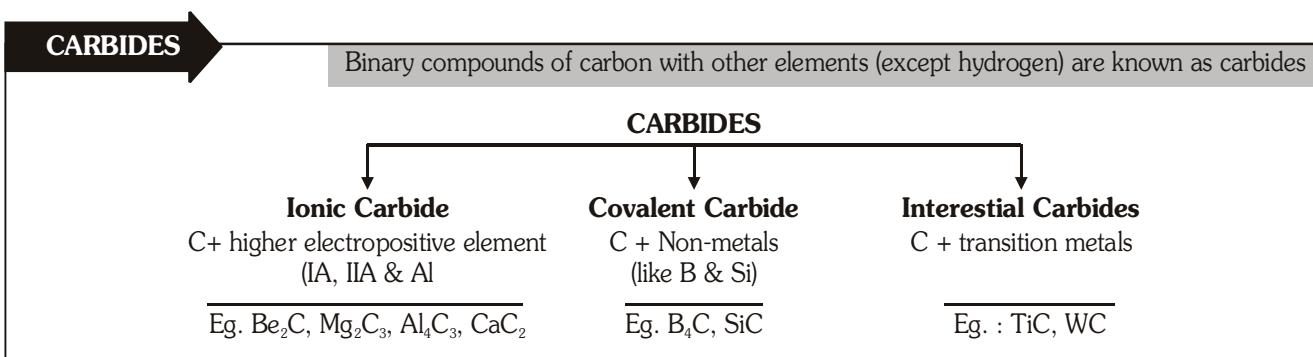
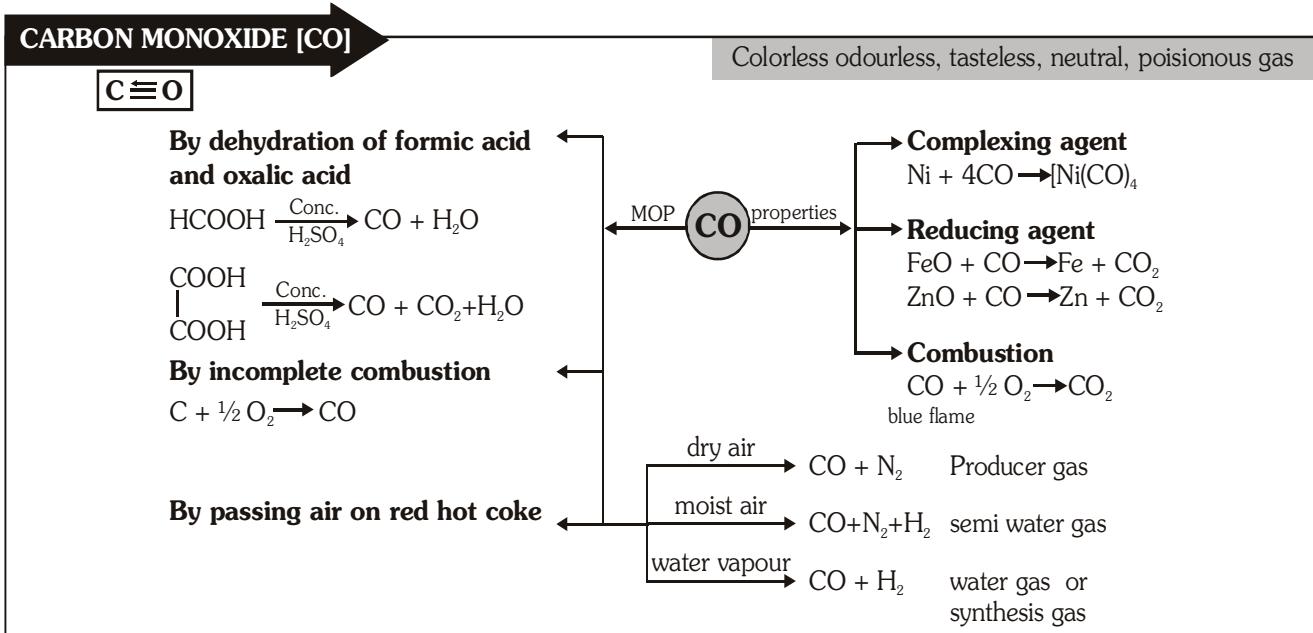
- $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ on heating undergoes to form its basic chloride $\text{Sn}(\text{OH})\text{Cl}$. The anhydrous salt, therefore, be obtained by heating the hydrated salt in the presence of HCl vapour.
 - Stannous chloride reduces mercuric chloride (HgCl_2) to a white precipitate of mercurous chloride (Hg_2Cl_2) which finally turns to metallic mercury (dark grey or black).



- **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.



- **Tin Cry.** Tin metal when bent produces a cracking noise due to rubbing of metal crystals over one another.



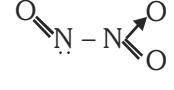
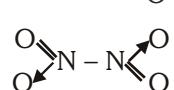
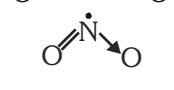
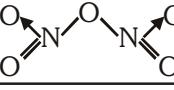
GROUP 15 ELEMENTS

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) $3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$
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 is BiF_5
 - ⇒ All the oxidation states from +1 to +4 tend to disproportionate in acidic solution :
 - exp: $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + 2\text{NO}$
 - ⇒ All the intermediate oxidation states disproportionate into +5 and -3
 - $4\text{H}_3\text{PO}_3 \xrightarrow{\Delta} 3\text{H}_3\text{PO}_4 + \text{PH}_3$
 - $\text{H}_3\text{PO}_2 \xrightarrow{\Delta} \text{H}_3\text{PO}_4 + \text{PH}_3$
 - ⇒ Hydride of 15th group elements :

$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 \geq \text{BiH}_3$	Basic character
$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$	Stability
$\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3 < \text{BiH}_3$	Boiling Point
$\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$	Melting Point
$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$	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

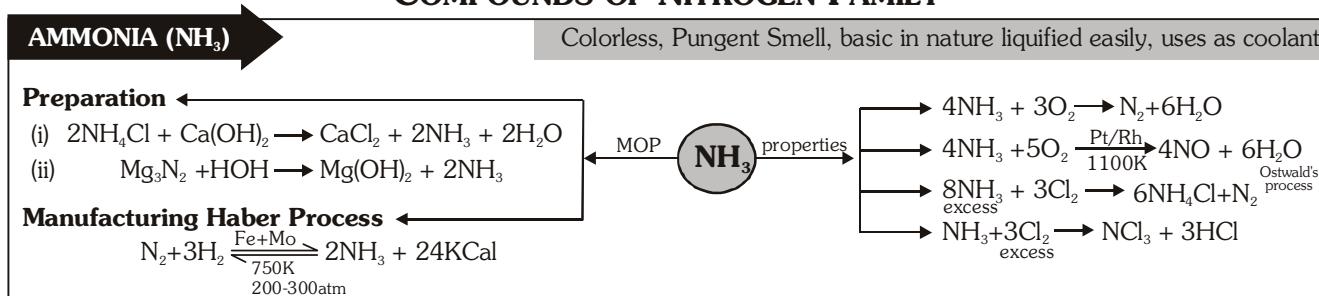
STRUCTURE OF OXIDES OF NITROGEN AND PHOSPHORUS NITROGEN

Oxide of Nitrogen	Oxid. state	Physical appearance	Structure
N_2O nitrous oxide	+1	Colourless gas	$\text{N} \equiv \text{N} \rightarrow \text{O}$
NO Nitric oxide	+2	Colourless gas	$\text{N} = \text{O}$
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 pentoxide	+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 ₂ O	+1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N ₂ O ₃	+3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$	Blue solid, acidic
Nitrogen dioxide [Nitrogen (IV) oxide]	NO ₂	+4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N ₂ O ₄	+4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$	Colourless solid/liquid, acidic
Dinitrogen pentaoxide [Nitrogen(V) oxide]	N ₂ O ₅	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic

COMPOUNDS OF NITROGEN FAMILY

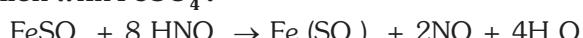

NITRIC ACID (HNO₃) →

Preparation :
Ostwald's process :

- (i) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \xrightarrow[\text{From air}]{\substack{\text{Pt/Rh-gauge catalyst} \\ 500\text{K}, 9\text{bar}}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- (ii) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- (iii) $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$

Properties :

HNO₃, nitric acid was earlier called as aqua fortis (meaning strong water). It usually acquires yellow colour due to its decomposition by sunlight into NO₂. It acts as a strong oxidising agent.

Reaction with FeSO₄ :

Reaction with non-metals :

Non-metals converted into highest oxyacids by hot and conc.

HNO₃, NO₂ gas is evolved (S to H₂SO₄; P to H₃PO₄; C to H₂CO₃; I₂ to HIO₃; As to H₃AsO₄; Sb to H₃SbO₄ and Sn to H₂SnO₃). Most of the metals except noble metals are attacked by HNO₃. 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 HNO₃(dilute) → 3Cu(NO₃)₂ + 2NO + 4H₂O
- Cu + 4HNO₃(conc.) → Cu(NO₃)₂ + 2NO₂ + 2H₂O
- 4Zn + 10HNO₃(dilute) → 4 Zn(NO₃)₂ + 5H₂O + N₂O
- Zn + 4HNO₃(conc.) → Zn(NO₃)₂ + 2H₂O + 2NO₂

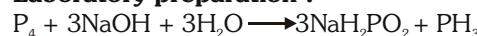
Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2 + metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O + metal nitrate
	Pb, Cu, Ag	NO + metal nitrate
Conc. HNO_3	Sn	NO_2 + H_2SnO_3 (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni, Cr, Al	rendered passive

PHOSPHINE (PH_3)

Preparation :

- (i) $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
(ii) $\text{PH}_3\text{I} + \text{NaOH} \rightarrow \text{NaI} + \text{H}_2\text{O} + \text{PH}_3$

Laboratory preparation :



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.

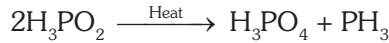
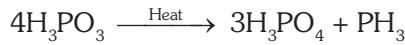
Chemical properties :

- (i) $2\text{PH}_3 + 4\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$
(ii) $4\text{PH}_3 \xrightarrow{713\text{K}} \text{P}_4 + 6\text{H}_2$
(iii) $\text{PH}_3 + 4\text{Cl}_2 \rightarrow \text{PCl}_5 + 3\text{HCl}$

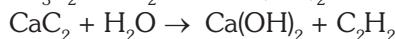
Oxoacids of Phosphorus

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	$\text{P}_2\text{O}_3 + \text{H}_2\text{O}$
Pyrophosphorous	$\text{H}_4\text{P}_2\text{O}_5$	+ 3	Two P — OH Two P — H Two P = O	$\text{PCl}_3 + \text{H}_3\text{PO}_3$
Hypophosphoric	$\text{H}_4\text{P}_2\text{O}_6$	+ 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	$\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$	+ 5	Four P — OH Two P = O One P — O — P	heat phosphoric acid
Metaphosphoric*	$(\text{HPO}_3)_n$	+ 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).

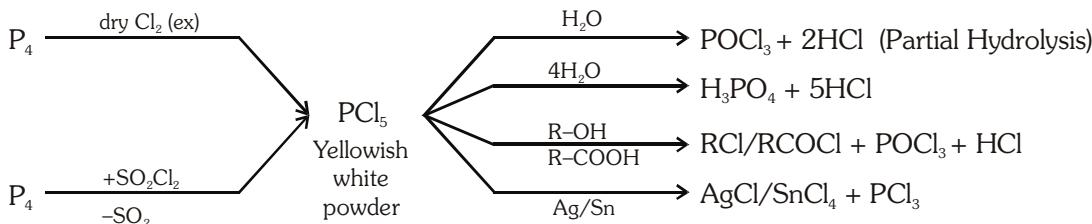
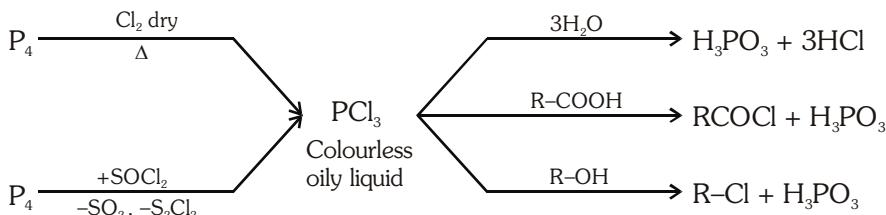


- **Holme's signals.** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2 . The mixture burns with a bright luminous flame and it acts as a signal for approaching ships.



- **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.



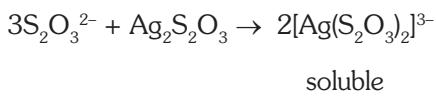
GROUP 16 ELEMENTS**OXYGEN FAMILY**

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 : $2\text{Se}_2\text{Cl}_2 \rightarrow \text{SeCl}_4 + 3\text{Se}$
- 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 $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ **Preparation :**

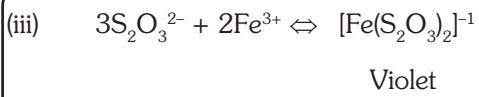
- (a) $\text{Na}_2\text{SO}_3 + \text{S} \xrightarrow{\text{Boil}} \text{Na}_2\text{S}_2\text{O}_3$
- (b) $4\text{S} + 6\text{NaOH} \xrightarrow{\text{Boil}} \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O}$
- (c) $2\text{Na}_2\text{S} + 3\text{SO}_2 \xrightarrow{\text{Boil}} 2\text{Na}_2\text{S}_2\text{O}_3 + \text{S}$
- (d) Spring's reaction
$$\text{Na}_2\text{S} + \text{Na}_2\text{SO}_3 + \text{I}_2 \xrightarrow{\text{Heat}} \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaI}$$

Concentrated $\text{Na}_2\text{S}_2\text{O}_3$ 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.

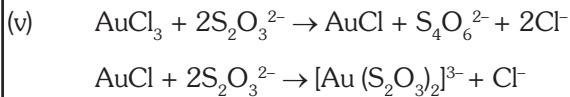
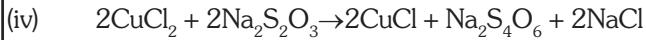
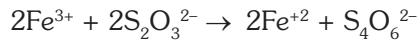
**Reaction with oxidizing agent :**

- (i) $\text{Na}_2\text{S}_2\text{O}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl} + \text{S}$
- (ii) $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$
Sodium tetrathionate

This reaction forms the basis of iodometric estimation of $\text{Cr}_2\text{O}_7^{2-}$ and Cu^{2+} salts.

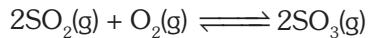


The violet colour disappears quickly due to the reduction of ferric chloride by $\text{S}_2\text{O}_3^{2-}$ ions,

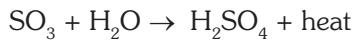


Sulphur trioxides (SO_3) is a white crystalline solid with melting point 290K and boiling point 318 K.

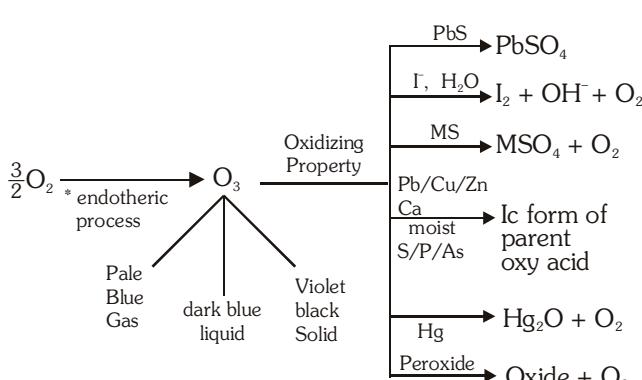
SO_3 is prepared by the direct oxidation of SO_2 with atmospheric oxygen in presence of finely divided Pt or V_2O_5 at a pressure of 2 bar. and temperature 720 K.



SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.



OZONE



* Fishy odour, Highly toxic.

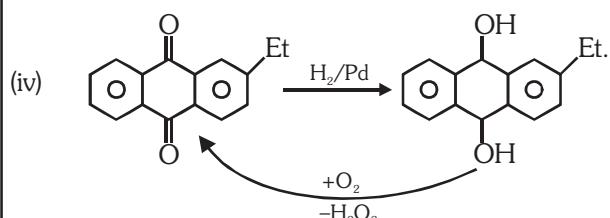
Gases Absorbent

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 : $2H^+ + e^- \rightarrow H_2$
 $H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$



Properties :

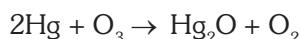
Oxidizing property :

- (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) $H_2O_2 \xrightarrow{\text{Pb+ Grids}} PbO$
- (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) $H_2O_2 \xrightarrow{Cr_2O_7^{2-}/H^+} Cr^{+2} + O_2$

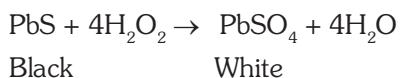
➤ Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.



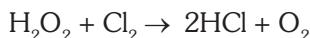
As a result of it, mercury loses its meniscus and starts sticking to the glass.

➤ 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.



➤ Antichlor action of H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl.



$\Rightarrow NH_2.NH_2 + H_2O_2$ as rocket propellant.

Storage

H_2O_2 decomposes slowly on exposure to light.



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.

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, F₂ has yellow gas, Cl₂ greenish yellow gas, Br₂ red liquid and I₂ 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 F₂ > Cl₂ > Br₂ > I₂
 4. In general, a halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \quad (X = Cl, Br \text{ or } I)$$

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \quad (X = Br \text{ or } I)$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$
 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 OF₂ and O₂F₂. However, only OF₂ 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. O₂F₂ oxidises plutonium to PuF₆ 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. I₂O₅ 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 electronegative) halogens.
- Types of interhalogen compound :
 - AB type : ClF, BrF, BrCl, ICl, IBr
 - AB₃ type : ClF₃, BrF₃, ICl₃
 - AB₅ type : BrF₅, IF₅
 - AB₇ type : IF₇

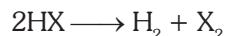
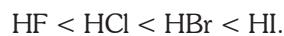
HYDROGEN HALIDES

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.
∴ reactivity and acidic character ↑.
 $HF < HCl < HBr < HI$.
- 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 :

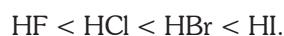
The reducing character of hydrogen halides increases down the group as



A less thermally stable compound has more tendency to release hydrogen easily and show greater reducing property.

ACIDIC STRENGTH :

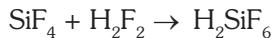
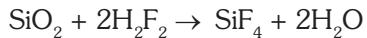
The acidic strength of these acids increases down the group and hence follows the order.



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.

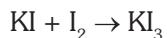
NOTE

- **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.



This is called etching of glass.

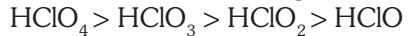
- Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI_3 .



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.



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.

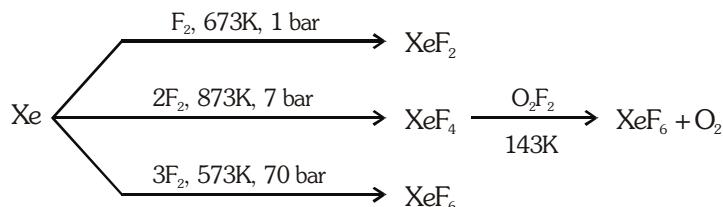
The acidity of oxoacids of different halogens having the same oxidation number decreases with the increases in atomic numbers of the halogen



GROUP 18 ELEMENTS

1. Relative Abundance:
 $\text{Ar} > \text{Ne} > \text{Kr} > \text{He} > \text{Xe} > \text{Rn}$
 2. Melting and Boiling point:
 $\text{Rn} > \text{Xe} > \text{Kr} > \text{Ar} > \text{Ne} > \text{He}$
 3. He has the lowest boiling point among all elements.
 4. Noble gases are monoatomic, colourless, odourless, sparingly soluble in water and diffusing through most commonly used laboratory materials.
 5. $\text{O}_2[\text{PtF}_6]$ is the first noble gas compound.
 6. Ar, Kr and Xe form clathrate compound when passed in ice with high pressure.
 $\text{A.6H}_2\text{O}$ ($\text{A} = \text{Ar/Kr/Xe}$)

Preparation of Xe-Fluoride:



Properties:

Fluoride donor: Eg. $\text{XeF}_2 + \text{MF}_5 \xrightarrow{\text{(M=As/Sb/P)}} [\text{XeF}_4]^+ [\text{MF}_6]^-$

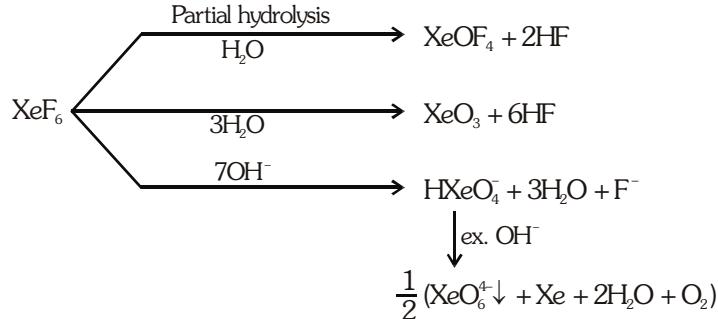
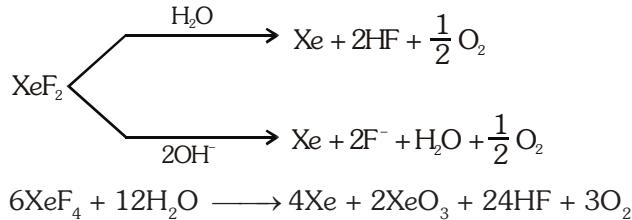
Fluoride acceptor: Eg. $\text{XeF}_6 + \text{MF} \xrightarrow{\text{(M=Na/K/Rb/Cs)}} \text{M}^+[\text{XeF}_7^-]$

Fluorinating agents: Eg. $\text{XeF}_4 \xrightarrow{\text{SF}_4 / \text{Pt}} \text{PtF}_4 / \text{SF}_6 + \text{Xe}$



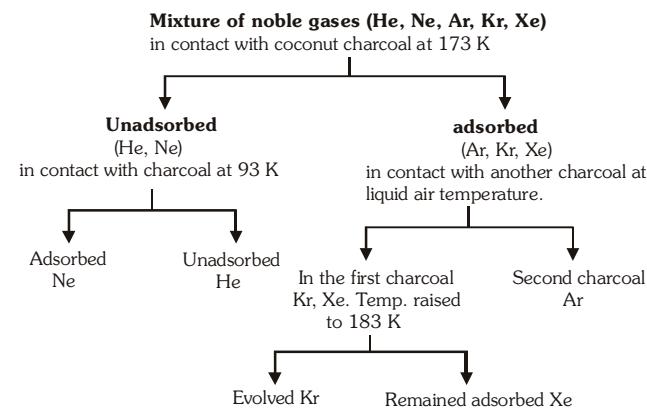
Reaction with SiO_2 : Eg. $2\text{XeF}_6 + \text{SiO}_2 \longrightarrow \text{SiF}_4 + \text{XeOF}_4$

Hydrolysis:



NOBLE GAS

- In Dewar's method, the separation of noble gases is summarized below



- The viscosity of He is extremely low, about $1/100^{\text{th}}$ of hydrogen gas.

COORDINATION CHEMISTRY

Addition compound

(two or more simple salt combining with fixed proportion of mass)

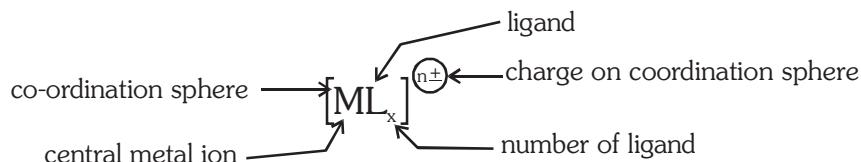
Double salt

- * Loose their identity in aqueous solution
- eg. $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ carnalite salt
- $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- potash alum

C-ordination compound

- * Retain their identity in aqueous solution
- eg. $\text{K}_4[\text{Fe}(\text{CN})_6]$ Potassium hexacyanoferrate (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.

Classification 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, ox²⁻, acac⁻¹, gly⁻¹, dmgo⁻¹

Polydentate (denticity = >2) :

eg. dien, imda⁻², trien, nta³⁻, EDTA⁴⁻

Ambidentate : Ligand which have more than one donor site but at the time of donation only atom can donate electron pair.

eg. : (CN^-) , (NO_2^-) , (ONO^-) , (SCN^-) , (NCS^-) , (OCN^-) , (NCO^-) , $(\text{S}_2\text{O}_3^{2-})$, $(\text{SO}_2\text{S}^{2-})$

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.

* Classification on the basis of electron donating and accepting tendency

Classical ligand : H_2O , NH_3 etc.

Non-classical ligand : CN^- , NO^+ , NO , CO , PPh_3 etc

\Rightarrow π -donor ligand $\Rightarrow \text{C}_2\text{H}_4$, 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.



$$\text{EAN} = 26 - (+2) + 6(2) = 36$$

\Rightarrow If EAN value is equal to atomic number of Noble gas then complex follow sidgwick rule of EAN.

\Rightarrow In carbonyl complex if EAN value = Atomic number of Noble gas then carbonyl complex is more stable.

eg.	$[\text{V}(\text{CO})_6]$	$[\text{Cr}(\text{CO})_6]$	$[\text{Mn}(\text{CO})_6]$
	act as oxidising agent	stable complex	act as reducing agent

\Rightarrow Brown ring complex 37

Sodium nitroprusside 36

Zeise's Salt 84

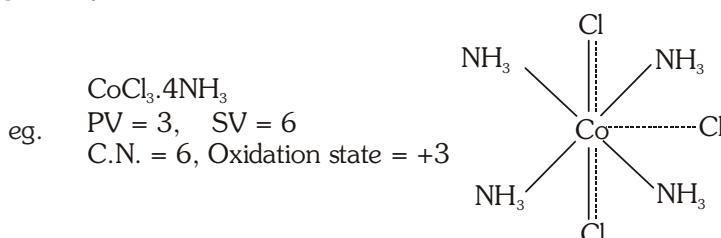
$\text{Mn}_2(\text{CO})_{10}$ 36

$\text{Fe}_2(\text{CO})_9$ 36

$\text{Co}_2(\text{CO})_8$ 36

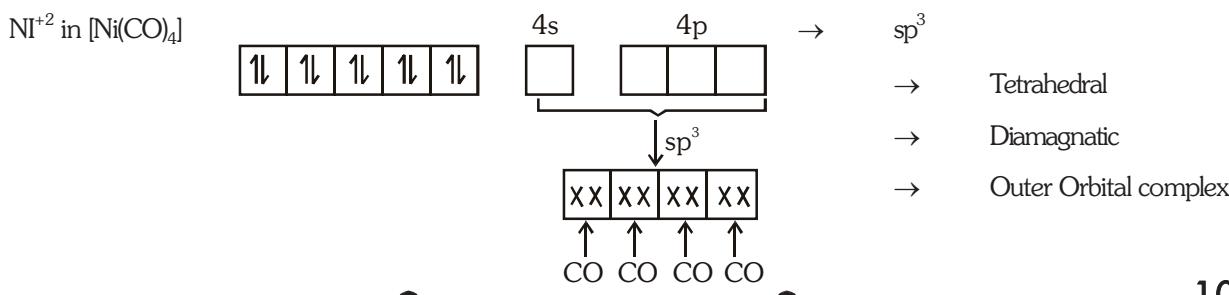
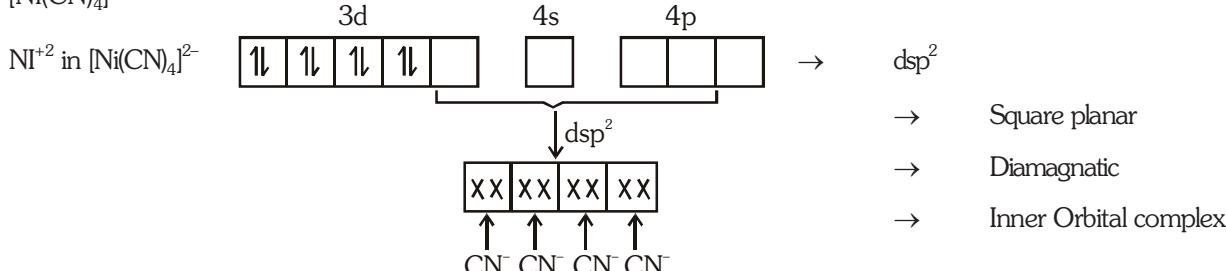
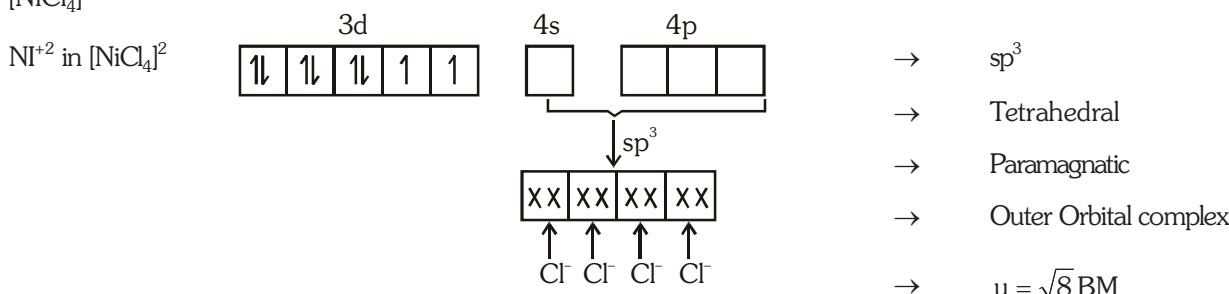
WERNER'S CO-ORDINATION THEORY :

- ⇒ Metals possesses two types of valencies PV & SV.
- ⇒ PV is non-directional, represent by (dotted 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.

**VBT :**

- ⇒ Metal provide hybridised vacant orbital for the acceptance of lone pair from ligand.
- ⇒ Hybridisation, shape and magnetic 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 paramagnetic. If unpaired e^- is absent then diamagnetic.

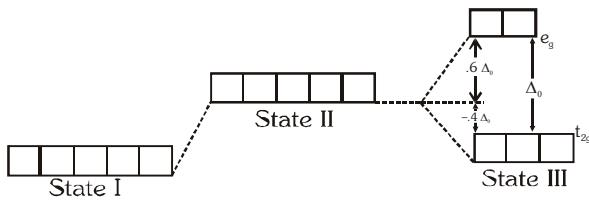
eg. CN_4^4



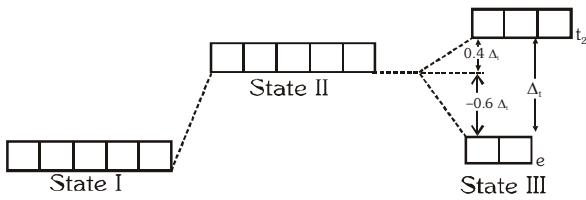
CRYSTAL FIELD THEORY

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 :

Γ (weakest) < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < $\text{C}_2\text{O}_4^{2-}$ < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO(strongest)

➤ Crystal field stabilisation energy (CFSE) :

(i) For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{eg})]\Delta_0 + \text{Paring energy (P.E.)} \times x$

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

= $[-0.6(n_e) + 0.4(n_t)]\Delta_t + \text{Paring energy (P.E.)} \times x$

where n_t = number of electron in t orbitals
 n_e = number of electron in e orbitals
 x = number of electron pair

⇒ Follow Hund's Pauli & Aufbau rule.

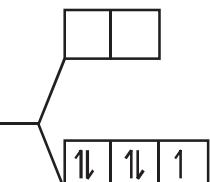
CN-6

eg. $\text{K}_3[\text{Fe}(\text{CN})_6]$

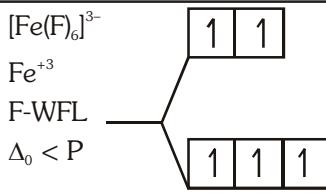
Fe^{+3}

CN-SFL

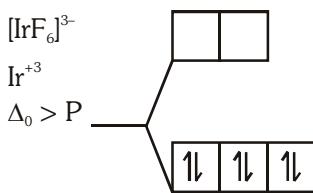
$\Delta_0 > P$



d^2sp^3 , Octahedral low spin complex, inner orbital complex, paramagnetic $\mu = \sqrt{3}$ BM



sp^3d^2 , Octahedral high spin complex, outer orbital complex, paramagnetic $\mu = \sqrt{35}$ BM

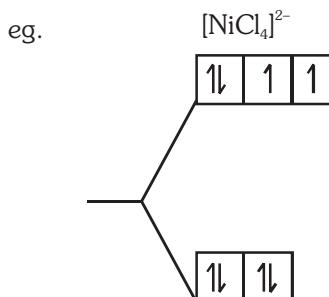


d^2sp^3 , Octahedral low spin complex, inner orbital complex, diamagnetic

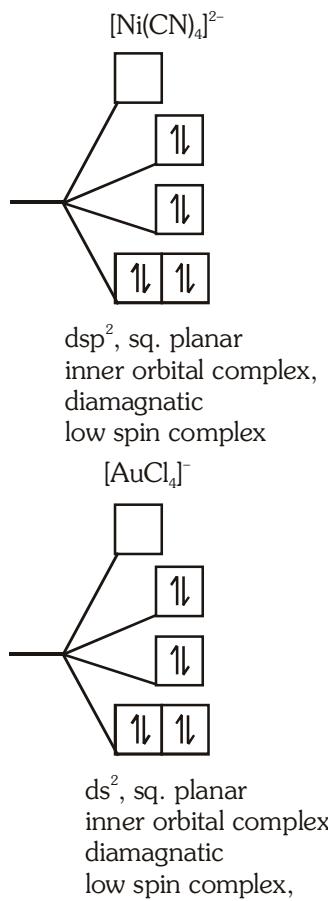
Exception :

$[\text{Co}(\text{OX})_3]^{3-}$	d^2sp^3	diamagnetic
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	d^2sp^3	diamagnetic
$[\text{NiF}_6]^{2-}$	d^2sp^3	diamagnetic
$[\text{Cr}(\text{NH}_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[\text{Mn}(\text{NH}_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[\text{Fe}(\text{NH}_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[\text{CoL}_6]^{4-}$ ($L = \text{NO}_2^-/\text{CN}^-$)	d^2sp^3	paramagnetic

CN-4 :



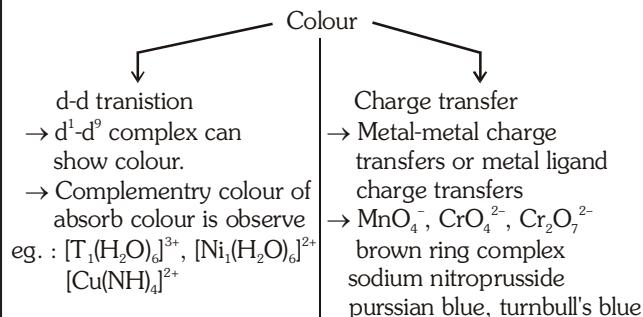
sp^3 , Td outer orbital complex, paramagnetic high spin complex

**Exception :**

1. d^3 's hybridisation, Td , diamagnetic, inner orbital complex
eg. MnO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, CrO_2Cl_2 , CrO_2F_2 , VO_4^{3-}
2. Tranference of electron
eg. Cu^{+2} in $\text{CN}-4$ with L
(where $\text{L} = \text{NO}_2^- / \text{CN}^- / \text{NH}_3$ etc.)

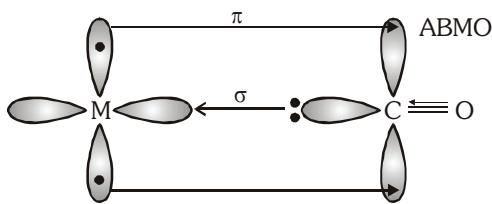
➤ Factor affecting splitting

- (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**ORGANOMETALLIC COMPOUNDS**

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.
 $\text{R}-\text{Mg}-\text{X}$, $(\text{CH}_3-\text{CH}_2)_2\text{Zn}$, 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. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ etc.

Synergic bonding**IUPAC nomenclature of complex compounds :**

- (A) For anionic complex (like $\text{K}_4[\text{Fe}(\text{CN})_6]$)
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 complex like $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
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 $[\text{Fe}(\text{CO})_5]$)
Name of ligands (with numeral prefix) + Common name of CMI + Ox. St.
(In roman number)
eg. : Pentacarbonyl iron (0)
- (D) Rule same just apply alphabetical order when write the name of ligands.
e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
Diamminedichloroplatinum (II)

STRUCTURAL ISOMERISM

(i) **Ionisation isomerism** : Counter ion as a ligand & ligand act as counter ion.



(ii) **Hydrate isomersim** : Number of water molecule inside & outside the co-ordinate sphere are different.



(iv) **Linkage** : Exhibit when ambidentate ligand is present in co-ordination sphere.



(iv) **Co-ordination isomerism** : Exhibit when both are cationic & anionic complex

**STEREO ISOMERISM****STEREO ISOMERISM IN CO-ORDINATION COMPOUND****CN-4**

* Square planar complex does not show optical isomerism.	* Tetrahedral complex $[\text{Mabcd}]^{n^\pm}$, $[\text{M(AB)cd}]^{n^\pm}$ $[\text{M(AB)(CD)}]^{n^\pm}$ show optical isomerism
* Square planar complex show optical activity if the co-ordinated ligand having chiral center.	* Tetrahedral complex does not show geometrical isomerism.
* Square planar complex $[\text{Ma}_2\text{b}_2]^{n^\pm}$, $[\text{Ma}_2\text{bc}]^{n^\pm}$, $[\text{Mabcd}]^{n^\pm}$, $[\text{M(AB)cd}]^{n^\pm}$, $[\text{M(AB)(CD)}]^{n^\pm}$ show geometrical isomerism	
* $[\text{Mabcd}]^{n^\pm}$ form two cis and one trans.	

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
$\text{Ma}_3\text{b}_2\text{c}$	3	0	3
Ma_3bcd	5	1	4
$\text{Ma}_2\text{b}_2\text{c}_2$	6	1	5
$\text{Ma}_2\text{b}_2\text{cd}$	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

Transiton elements are those d-block elements which has partially 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

$$ns^{0-2} (n-1)d^{1-10}$$

Exceptions $\left\{ \begin{array}{l} Cr = 4s^1 3d^5 \\ Cu = 4s^1 3d^{10}, Pd = 5s^0 4d^{10} \end{array} \right.$

TRANSITION SERIES

1 st	3d series	$Sc_{21} - Zn_{30}$	$9 + 1 = 10$
2 nd	4d series	$Y_{39} - Cd_{48}$	$9 + 1 = 10$
3 rd	5d series	$La_{57}, Hf_{72} - Hg_{80}$	$9 + 1 = 10$
4 th	6d series	$Ac_{89}, Unq_{104} - Uub_{112}$	$9 + 1 = 10$

ATOMIC RADIUS

3d series $Sc > Ti > V > Cr > Mn \geq Fe \approx CO \approx Ni \leq Cu < Zn$

In a group 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f electron.
(Lanthanide contraction)

$$3d < 4d \approx 5d$$

e.g.: $Ti < Zr \approx Hf$ Smallest radius – Ni
Largest radius – La

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 Fully filled d^{10}
 ∵ weak metallic bond ∵ weak metallic bond
 Melting point $Zn > Cd > Hg$
 $Cu > Ag \leq Au$ (data based)

E.N. Exception $Zn < Cd < Hg$

Density : s-block metals < d-block metals.

3d series

$Sc < Ti < V < Cr < Mn < Fe < Co \leq Ni < Cu > Zn$

Density in a Group

$$3d < 4d \ll 5d$$

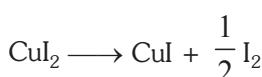
Metallic character : They are solid, hard, ductile, malleable, good conductor of heat and electricity and exhibit metallic lusture, high tensile strength. Hg is liquid

Electrical conductor $Ag > Cu > Au > \underbrace{Al}_{d\text{-block}}$

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 stabilized 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.
e.g. 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.
- ⇒ Beyond Mn trihalide are not observed 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 basic CrO_3 acidic
- ⇒ MnO basic MnO_2 basic Mn_2O_7 acidic
- ⇒ CuI_2 basic CuO basic Cu_2O basic
- ⇒ CuI_2 does not exist



- ⇒ In aqueous Cu^+ disproportionated 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.
e.g. 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	$\mu = 1.73 \text{ BM}$	n is 2	$\mu = 2.84 \text{ BM}$	n is 3	$\mu = 3.87 \text{ BM}$
n is 4	$\mu = 4.90 \text{ BM}$	n is 5	$\mu = 5.92 \text{ BM}$		

Substances that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block element and ions having d⁰ and d¹⁰ 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 – Sc³⁺, Ti⁴⁺, Zn²⁺ etc

Coloured – Fe³⁺ yellow, Fe²⁺ green, Cu²⁺ blue, Co³⁺ blue etc

ALLOYS

Solid mixture of metals in a definite 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, Mn₄N, Fe₃H 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 process = V₂O₅

Ostwald process = Pt/Rh

Haber process = Fe₂O₃ + Al₂O₃ + K₂O

Zeigler Natta = TiCl₄ + (C₂H₅)₃ Al

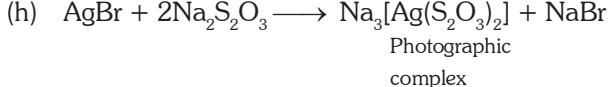
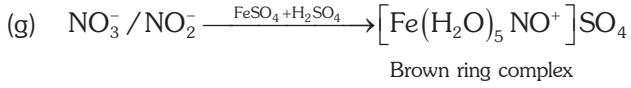
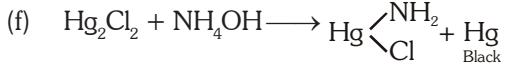
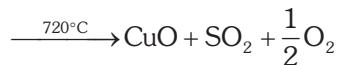
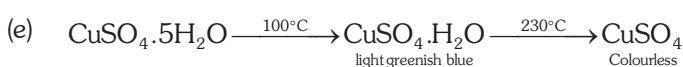
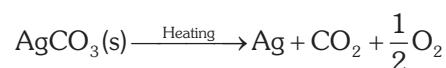
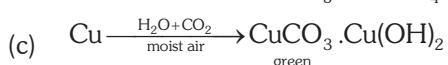
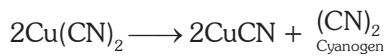
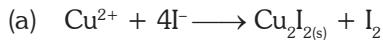
Phenton reagent = FeSO₄ + H₂O₂

Hydrogenation of Alkene = Ni/Pd

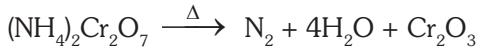
Decomposition of KClO₃ = MnO₂

Wilkinson catalyst = RhCl + PPh₃

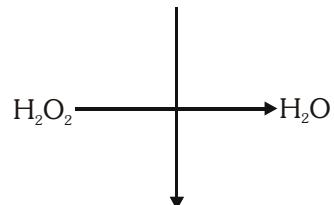
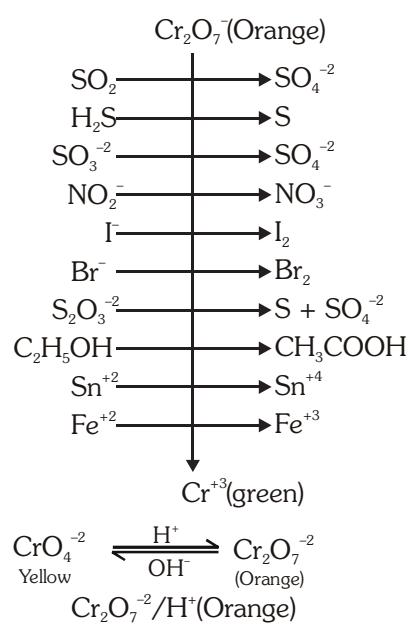
Important reactions of d-block elements



(i) **Chemical volcano :**

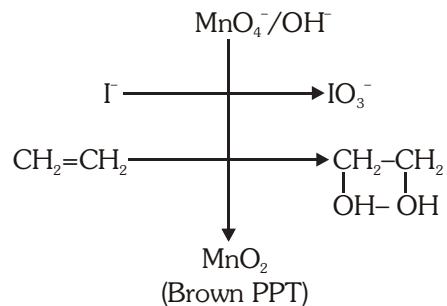
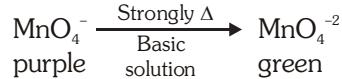
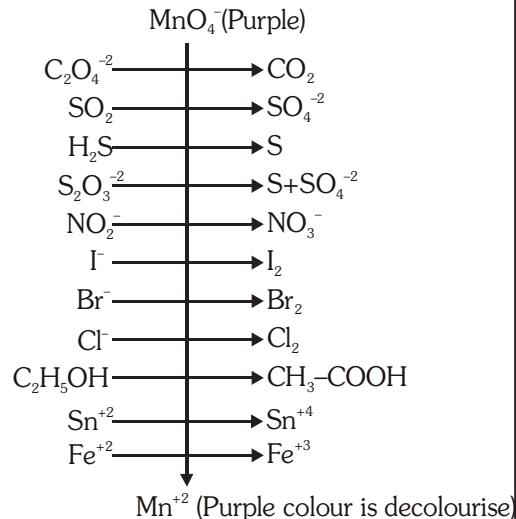


Reactions of Cr₂O₇⁻²:



(Stabilize in the presence of organic solvent such as pyridine etc.)

Reaction of MnO₄⁻

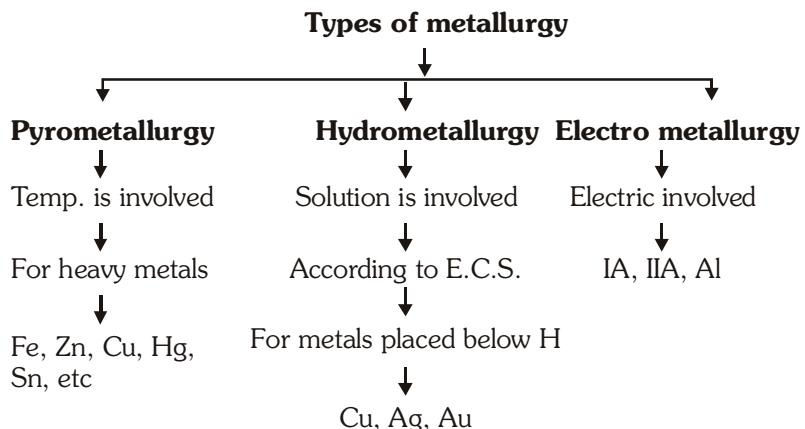


IMPORTANT NOTES

METALLURGY

- Bunch of process to extract metal from their respective ore

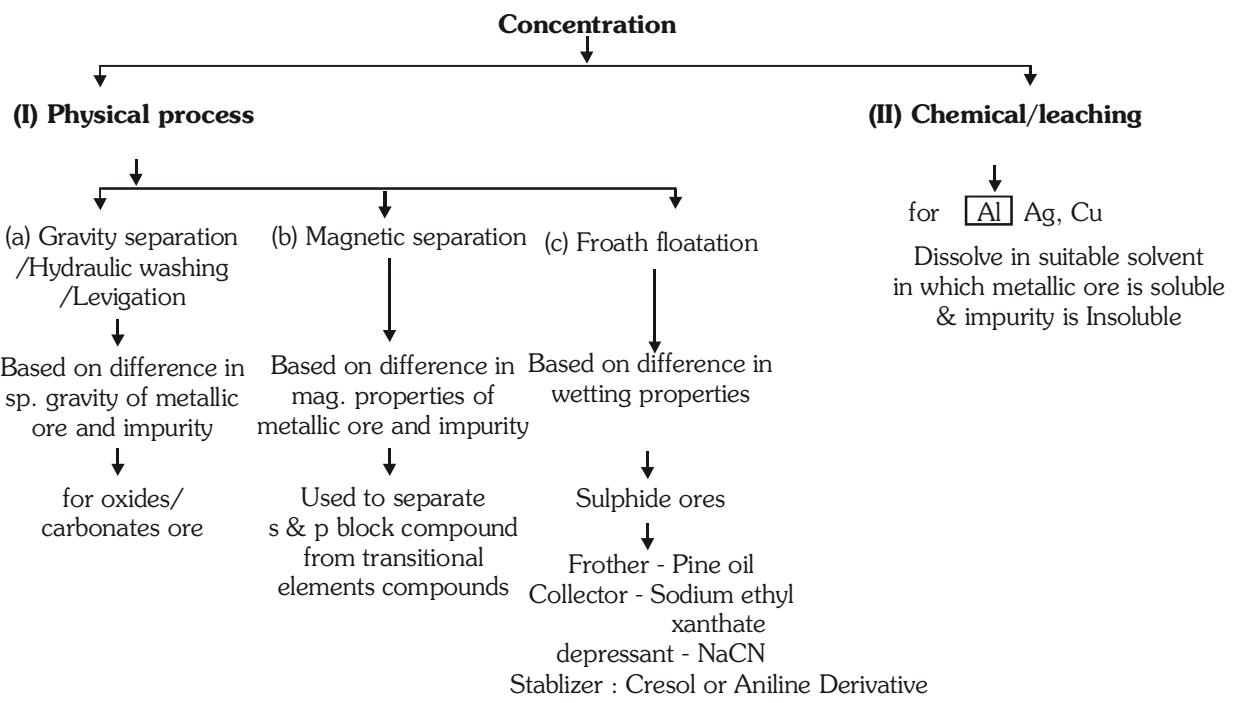
Ore : Minerals from which metal can be extracted economically :



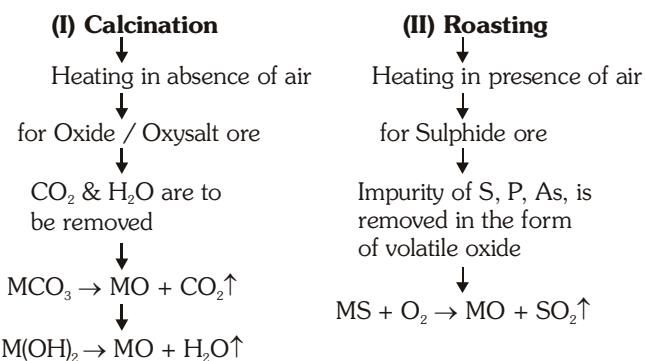
Metallurgical process :

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 concentration of ore particle in ore sample.



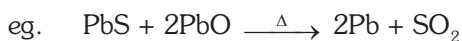
4.

Calcination & Roasting

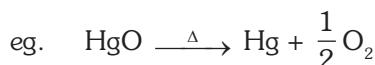
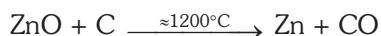
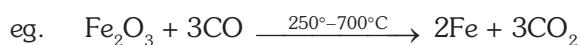
5. Reduction : To obtain metal (95 to 98%) from oxidized metallic ore.

Self reduction :

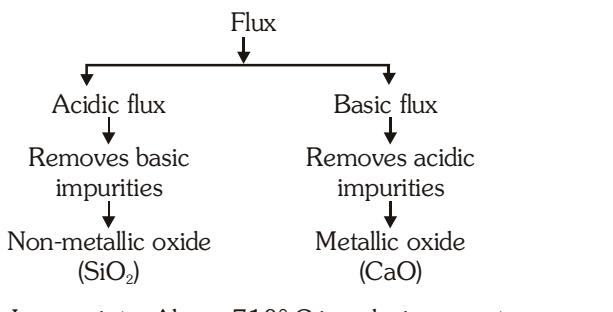
⇒ Sulphide ore itself act as reducing agent.



⇒ Thermal decomposition

**Carbon reduction (Smelting) :** Reducing agent C/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



Thermite mixture mass ratio : $\text{Cr}_2\text{O}_3 : \text{Al} = 3 : 1$

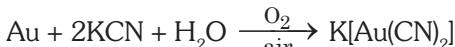
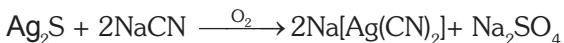
METAL DISPLACEMENT REDUCTION

⇒ Metal placed below H. in E.C.S.

⇒ Ag, Au, Cu

Example of extraction of :

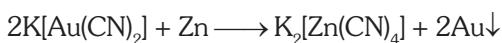
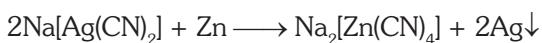
(i) Cyanidation (Leaching Process)



NaCN / KCN → Leaching agent

O₂ → oxidizing agent

(ii) Recovery of Ag/Au (Metal displacement Reactions)



Zn → reducing agent

ELECTROLYTIC REDUCTION

⇒ For IA, IIA, Al

⇒ Electrolysis of molten solution

Example :-

(i) Extraction of Al (Hall-Herault)

– Al can be extracted from Al₂O₃

– Na₃AlF₆ & CaF₂ act as auxiliary electrolyte increase the conductivity & to reduce the fusion temp. of mixture

(ii) At cathode impure Al is collected and at anode O₂, CO, CO₂ is released.

(iii) Extraction of Na (Down cell process)

– Na can be extracted from NaCl

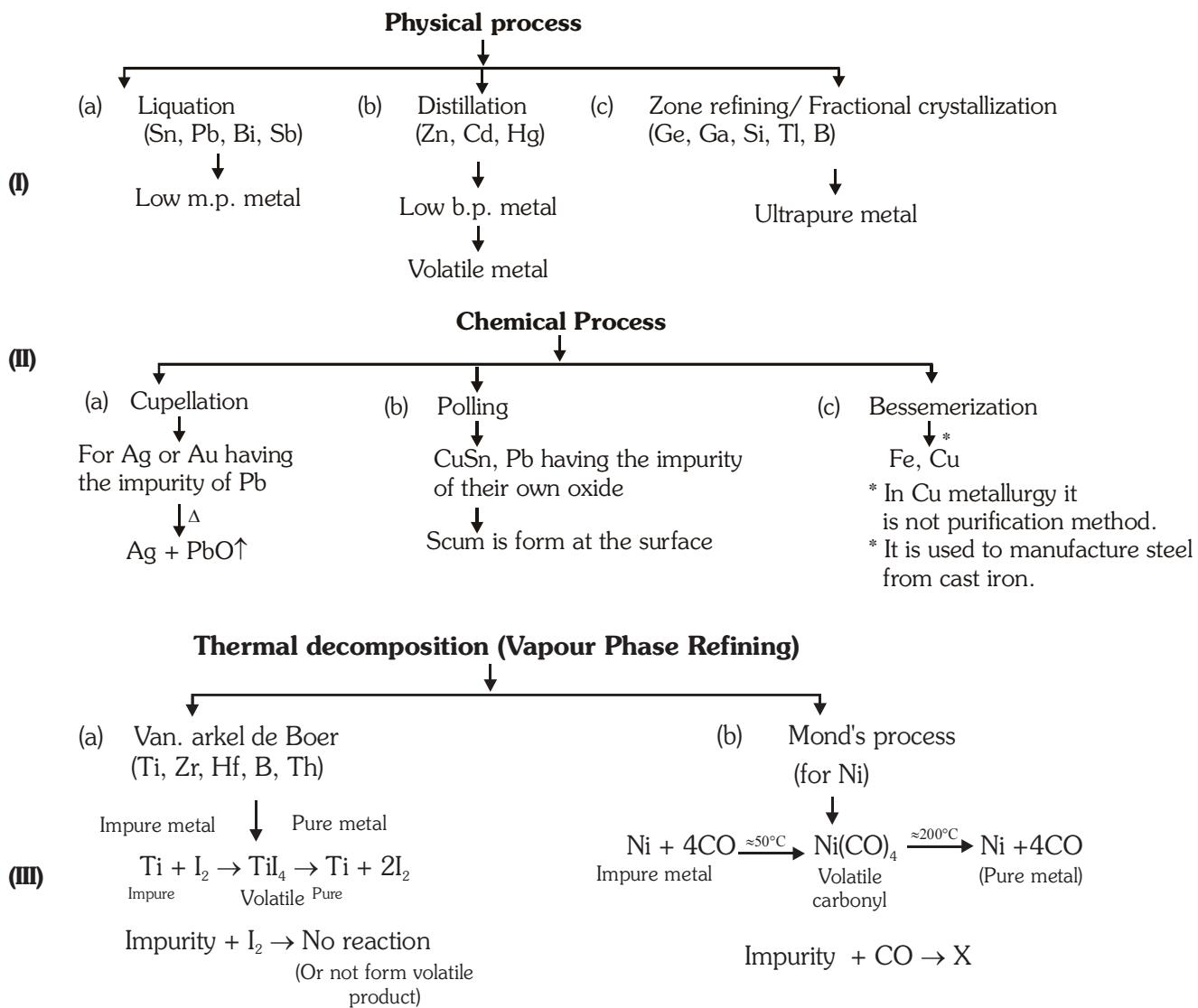
– Down Process Neutral flux (CaCl₂) to be added to decrease the fusion temp. of NaCl

– Neutral flux - substance used to increase the conductivity of NaCl

Auxiliary 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%)



THERMODYNAMICS PRINCIPLE OF METALLURGY

- The graphical representation of Gibbs energy was first used by H.I.T. Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram. Such diagram helps us in predicting the feasibility of thermal reduction of an ore.
 - The criteria of feasibility is that at a given temperature, Gibbs energy of reaction must be negative.
 - At high temperature 'C' is the best reducing agent.
 - At low temperature 'CO' is the best reducing agent.
 - In blast furnace reduction takes place at low temperature i.e. why CO is the reducing agent (For Fe).

A summary of the occurrence and Extraction of some Metals is presented in the following table :

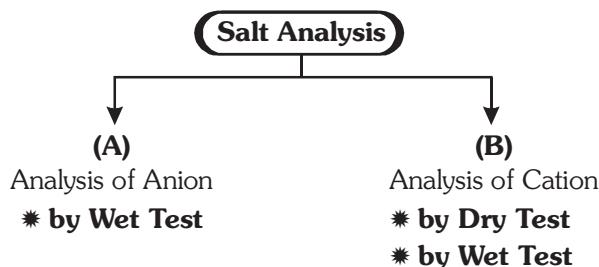
Metal	Occurrence	Common method of extraction	Refining	Remarks
Aluminium $E^\circ = -1.66$	1. Bauxite, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten $\text{Na}_3\text{AlF}_6 + \text{CaF}_2$	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required
Iron $E^\circ = -0.44$	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 3. Limonite, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ 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 $E^\circ = -0.34$	1. Copper pyrites, CuFeS_2 2. Copper glance, Cu_2S 3. Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ 4. Cuprite, Cu_2O 5. Azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	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 $E^\circ = -0.76$	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 purified by fractional distillation	For ZnO , carbon is better reducing agent then CO and Zn is obtain in vapours form $\text{ZnO} + \text{C} \xrightarrow{1673\text{K}} \text{Zn} + \text{CO}$
Mg $E^\circ = -2.36$	1. Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 2. Magnesite, MgCO_3	Electrolysis of fused MgCl_2 with KCl	-	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is heated in the excess current of dry HCl gas to produce anhydrous MgCl_2
Sn $E^\circ = -0.14$	1. Cassiterite, SnO_2 (Tin stone)	Reduction of the SnO_2 with carbon. $\text{SnO}_2 + 2\text{C} \rightarrow \text{Sn} + 2\text{CO}$	Polling and Liquidation	Ore contain impurity of wolframite, $\text{FeWO}_4 + \text{MnWO}_4$ (magnetic separation)
Pb $E^\circ = -0.13$	1. Galena, PbS	Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon $\text{PbS} + 2\text{PbO} \rightarrow 3\text{Pb} + \text{SO}_2$ $\text{PbO} + \text{C} \rightarrow \text{Pb} + \text{CO}$	Liquidation & electrolytic method.	-
Ag $E^\circ = 0.80$	1. Argentite- Ag_2S , native Silver	Hydro metallurgy $\text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{NaAg}(\text{CN})_2 + \text{N}_2\text{S}$ $2\text{NaAg}(\text{CN})_2 + \text{Zn} \rightarrow \text{Na}_2\text{Zn}(\text{CN})_4 + 2\text{Ag}$	Cupelation & electrolytic method	In hydro metallurgy Ag obtain in the form of dark amorphous ppt.
Au $E^\circ = 1.40$	Native ore	1. Amalgamation. 2.Cynide process	Cupelation & electrolysis method.	In hydro metallurgy 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 substance 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.



ANALYSIS OF ACIDIC RADICAL

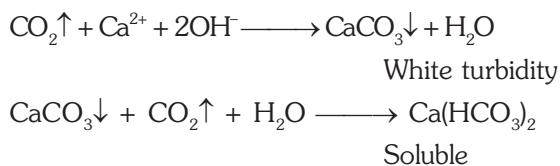
Classification of acidic radical

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 effervescence, 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 barya 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.

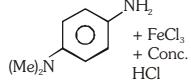
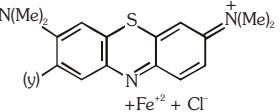
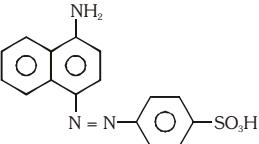
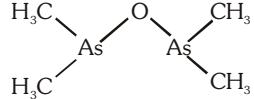
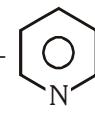


Note : SO_2 also gives similar observation.

Acidic Radical Table

	dil. H_2SO_4	Conc. H_2SO_4	CaCl_2	BaCl_2	HgCl_2	AgNO_3	Pb(OAc)_2	$\text{MnO}_4^- / \text{H}^+$
CO_3^{2-}	$\text{CO}_2 \uparrow$	$\text{CO}_2 \uparrow$	$\text{CaCO}_3 \downarrow$ white	$\text{BaCO}_3 \downarrow$ white	$\text{HgCO}_3 \downarrow$ Reddish brown	$\text{Ag}_2\text{CO}_3 \downarrow$	$\text{PbCO}_3 \downarrow$ $2\text{Pb(OH)}_2 \downarrow$	—
$\Delta + \text{HCO}_3^-$	$\text{CO}_2 \uparrow$	$\text{CO}_2 \uparrow$	$\text{CaCO}_3 \downarrow$	$\text{BaCO}_3 \downarrow$	$\text{HgCO}_3 \downarrow$ Reddish brown	$\text{Ag}_2\text{CO}_3 \downarrow$	$\text{PbCO}_3 \downarrow$ $2\text{Pb(OH)}_2 \downarrow$	—
SO_3^{2-}	$\text{SO}_2 \uparrow$	$\text{SO}_2 \uparrow$	$\text{CaSO}_3 \downarrow$ white	$\text{BaSO}_3 \downarrow$ white	—	$\text{Ag}_2\text{SO}_3 \downarrow$ white	$\text{PbSO}_3 \downarrow$ white	SO_4^{2-}
$\text{S}_2\text{O}_3^{2-}$	$\text{SO}_2 \uparrow + \text{S} \downarrow$	$\text{SO}_2 \uparrow$	—	$\text{BaS}_2\text{O}_3 \downarrow$ white	$\text{HgS}_2\text{O}_3 \downarrow$ white	$\text{Ag}_2\text{S}_2\text{O}_3 \downarrow$ white	$\text{PbS}_2\text{O}_3 \downarrow$ white	$\text{SO}_4^{2-} + \text{S} \downarrow$
S^{2-}	$\text{H}_2\text{S} \uparrow$	$\text{S} \downarrow + \text{SO}_2 \uparrow$	—	$\text{BaS} \downarrow$ black	$\text{HgS} \downarrow$ black	$\text{Ag}_2\text{S} \downarrow$ black	$\text{PbS} \downarrow$ black	$\text{S} \downarrow$
NO_2^-	$\text{NO}_2 \uparrow$	$\text{NO}_2 \uparrow$	—	—	—	$\text{AgNO}_2 \downarrow$	—	NO_3^-
CH_3COO^-	$\text{CH}_3\text{COOH} \uparrow$	$\text{CH}_3\text{COOH} + \text{SO}_2 \uparrow$	—	—	—	—	—	—
Γ		$\text{I}_2 \uparrow$ violet	—	—	$\text{HgI}_2 \downarrow$ scarlet red	$\text{AgI} \downarrow$ yellow	$\text{PbI}_2 \downarrow$ dark yellow	$\text{I}_2 \uparrow$
Cl^-		$\text{HCl} \uparrow$	—	—	—	$\text{AgCl} \downarrow$ white	$\text{PbCl}_2 \downarrow$ white	$\text{Cl}_2 \uparrow$
Br^-		$\text{Br}_2 \uparrow$ brown	—	—	—	$\text{AgBr} \downarrow$ pale yellow	$\text{PbBr}_2 \downarrow$ white	$\text{Br}_2 \uparrow$
$\text{C}_2\text{O}_4^{2-}$	—	$\text{CO}_2 \uparrow + \text{CO} \uparrow$	$\text{CaC}_2\text{O}_4 \downarrow$ white	$\text{BaC}_2\text{O}_4 \downarrow$ white	—	$\text{Ag}_2\text{C}_2\text{O}_4 \downarrow$ white	—	$\text{CO}_2 \uparrow$
BO_2^-	—	$\text{H}_3\text{BO}_3 \uparrow$	$\text{Ca(BO}_2\text{)}_2 \downarrow$ white	$\text{Ba(BO}_2\text{)}_2 \downarrow$ white	—	$\text{AgBO}_2 \downarrow$ white	—	—
NO_3^-	—	$\text{NO}_2 \uparrow$	—	—	—	—	—	—
SO_4^{2-}	—	—	$\text{CaSO}_4 \downarrow$ white	$\text{BaSO}_4 \downarrow$ curdy white ppt	$\text{HgSO}_4 \downarrow$ $2\text{HgO} \downarrow$ yellow	—	$\text{PbSO}_4 \downarrow$ white	—
PO_4^{3-}	—	—	$\text{CaHPO}_4 \downarrow$ white	$\text{BaHPO}_4 \downarrow$ white	—	$\text{Ag}_3\text{PO}_4 \downarrow$ yellow	—	—
CrO_4^{2-}	—	—	—	$\text{BaCrO}_4 \downarrow$ yellow	—	$\text{Ag}_2\text{CrO}_4 \downarrow$ brick red	$\text{PbCrO}_4 \downarrow$ 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, naphthyl 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	$FeCl_3 + H_2O \xrightarrow{\text{boil}}$	$[Fe_3(OH)_2(CH_3OO)_6]^{+}$ ↓ 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
$C_2O_4^{2-}$	$Mn^{+2} + NaOH$	$NaOH + Mn^{+2} \xrightarrow[\text{air}]{\Delta}$	$[Mn(C_2O_4)_3]^{3-}$	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	$Conc. H_2SO_4 + R OH + \Delta(\text{Flame})$	$B(OR)_3$	Green edge flame
BO_3^{3-}	Modified Green Flame Test	$CaF_2 + Conc. H_2SO_4 + \Delta$	$BF_3 \uparrow + Ca(HSO_4)_2$	Green flame
PO_4^{3-}	Ammonium molybdate	$(NH_4)_2MoO_4 + dil. HNO_3 + 30 - 40^\circ C$	$(NH_4)_3PO_4 \cdot 12MoO_3$	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. $\text{Co}(\text{NO}_3)_2$ and heat.

Zn^{+2}	$\text{ZnO} \cdot \text{CoO}$	Rinmann's Green
Al^{+3}	Al_2O_3	Thenard Blue
Mg^{+2}	$\text{MgO} \cdot \text{CoO}$	Pink residue
Sn^{+2}	$\text{SnO} \cdot \text{CoO}$	Bluish residue

Classification of Basic Radical

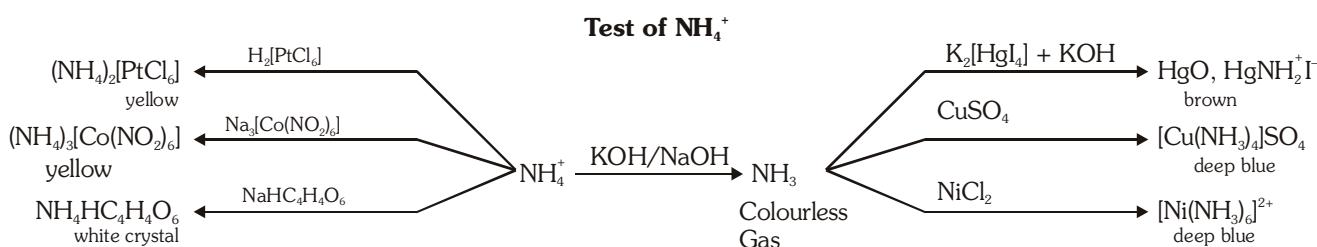
Group	Basic Radical	Reagent used	Precipitate form
Group-I	Pb^{+2} , Hg_2^{+2}	dil HCl	AgCl PbCl_2 Hg_2Cl_2 white ppt.
Group-II	Cu^{+2} , Pb^{+2} , Hg^{+2} , Cd^{+2} , Bi^{+3} Sn^{+2} , Sn^{+4} , As^{+3} , As^{+5} , Sb^{+3} , Sb^{+5}	H_2S +dil. HCl	Cu_2S , PbS , HgS , CdS , Bi_2S_3 black SnS brown SnS_2 As_2S_3 As_2S_5 Sb_2S_3 Sb_2S_5 yellow orange
Group-III	Cr^{+3} , Al^{+3} , Fe^{+3}	$\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$	$\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$ gelatinous reddish green white brown
Group-IV	Zn^{+2} , Mn^{+2} , Ni^{+2} , Co^{+2}	$\text{H}_2\text{S} + \text{NH}_4\text{OH}$	ZnS white MnS buff NiS CoS black
Group-V	Ca^{+2} , Sr^{+2} , Ba^{+2}	$(\text{NH}_4)_2\text{CO}_3 + \text{NH}_4\text{OH}$	CaCO_3 , SrCO_3 , BaCO_3 white

Test of Basic Radical

	Ag⁺	Hg₂²⁺	Pb²⁺	Cu²⁺	Hg⁺²	Cu⁺₂	Pb³⁺	Al³⁺	Cr³⁺	Fe⁺³	Fe⁺²	Zn⁺²	Mn⁺²	Ni⁺²	Co⁺²
KI	AgI Yellow	Hg ₂ ¹²⁻ Green	PbI ₂ Yellow	CuI + I ₃ ⁻ White solution	HgI ₂ Scarlet Red	—	—	—	—	FeI ₂ + I ₃ ⁻ yellowish brown sol.	—	—	—	—	—
ex KI	—	Hg + [Hg] ₄ ²⁻ Black	[PbI] ₂₋ soluble complex	—	[Hg] ₄ ²⁻ Solution	—	—	—	—	—	—	—	—	—	—
KCN	AgCN White	Hg + Hg(CN) ₂ Black	Pb(CN) ₂ White	CuCN + [CN] ₂ ↑ 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	[Co(CN) ₆] ⁴⁻ Brown Solution	
ex KCN	[Ag(CN) ₂] ⁻	—	K ₃ [Cu(CN) ₄] ₂ 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(OHCl) ₆] ⁴⁻ Blue	
NaOH	Ag ₂ O Brown	Hg ₂ O Black	Pb(OH) ₂ White	Cu ₂ (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	Zn(OH) ₂ White	Mn(OH) ₂ Pink	Ni(OH) ₂ Green	Co(OHCl) ₆ Blue	—	
ex NaOH	—	—	Na ₂ [Pb(OH) ₄] ₂ soluble complex	—	—	—	Na[Al(OH) ₄] soluble complex	Na[Cr(OH) ₄] Yellow	—	—	—	—	—	Co(OH) ₂ pink	
NH₄OH	Ag ₂ O Brown	Hg + HgO, HgNH ₂ ⁺ NO ₃ ⁻ black	Pb(OH) ₂ White	Cu(OH) ₂ Pale Blue	HgO, HgNH ₂ ⁺ CT White	Cd(OH) ₂ White	Al(OH) ₃ Gelatinous white	Cr(OH) ₃ Green	Fe(OH) ₃ Reddish Brown ppt	Zn(OH) ₂ White	Mn(OH) ₂ Pink	Ni(OH) ₂ Green	Co(OHCl) ₆ Blue	—	
ex NH₄OH	[Ag(NH ₃) ₂] ⁺	—	—	[Cu(NH ₃) ₄] ²⁺ Deep blue.	—	[Cd(NH ₃) ₄] ²⁺	—	[Cr(NH ₃) ₄] ³⁺ Phn/violet	—	[Zn(NH ₃) ₄] ²⁺ White	—	Ni[(NH ₃) ₆] ²⁺ Deep blue	[Co(NH ₃) ₆] ²⁺ Yellow		
H₂S₂(*NH₃)₂S	Ag ₂ S Black	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	
K₂CrO₄	Ag ₂ CrO ₄ Red	Hg ₂ CrO ₄ Red	PbCrO ₄ Yellow	—	—	—	—	—	—	—	—	—	—	—	—
Na₂S₂O₃	Ag ₂ S ₂ O ₃ White	—	PbS ₂ O ₃ White	Cu ₂ S ₂ O ₃ White	HgS ₂ O ₃ White	—	—	—	—	Fe ⁺² Green solution	—	—	—	—	
K₄[Fe(CN)₆]	Ag ₂ [Fe(CN) ₆] White	—	Cu ₂ [Fe(CN) ₆] Brown	—	Cd ₂ [Fe(CN) ₆] —	—	—	Fe ₂ [Fe(CN) ₆] ₃ Prussian blue	K ₂ Fe[Fe(CN) ₆] White	Mn ₂ [Fe(CN) ₆] White	Ni ₂ [Fe(CN) ₆] Light green	Co ₂ [Fe(CN) ₆] Green	—		
K₃[Fe(CN)₆]	—	—	Cu ₃ [Fe(CN) ₆] Green	—	—	—	—	Fe ₃ [Fe(CN) ₆] Turnball's blue	—	—	—	—	—	—	

Other important reaction of basic radical

Basic radical	Reagent	Product	Observation
Fe ⁺³	SCN ⁻	[Fe(H ₂ O) 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

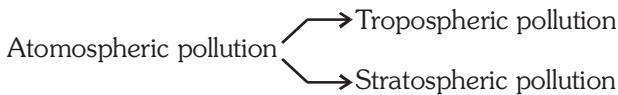


IMPORTANT NOTES

ENVIRONMENT POLLUTION

Pollutant :

Substance which cause pollution is known as pollutant.



⇒ Tropospheric pollution occurs due to presence of undesirable solid or gaseous particles in air.

Gaseous pollutant :
SO₂ :

- * Cause respiratory diseases of anthma, bronchitis emphysema etc & irritatling to eyes.

NO₂ :

- * Form by fossil fuel burn, Damage lungs.
- * Higer concentration of NO₂ damage the leaves of plant and retard rate of photosynthesis.

Hydrocarbon :

- * Form by incomplete combustion of fuel of automobile, Carcogenic.

Oxide of carbon :
CO :

- * Blocks the delivery of oxygen to organs and tissues.
- * Carboxy hemoglobin is 300 times more stable than oxy hemoglobin about 3-4% of carboxy hemoglobin the oxygen carrying capacity is highly reduced.

CO₂ :

- * Main source is respiration, burning of fossil fuels, demposition of lime stone in cement industry.
- * Increase of CO₂ cause global warming.

Global warming and Green House Effect :

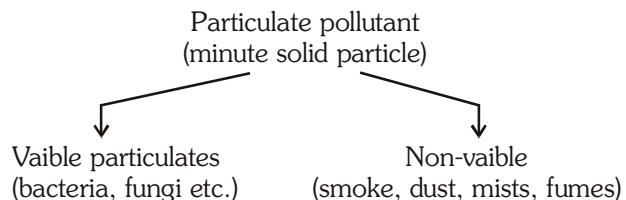
Some of the gases such as CO₂, CH₄, O₃, CFC(s) and water vapour tapped the heat and does not radiates back to the atomosphere. This cause global warming.

Acid Rain :

- * Normally the pH rain water is 5.6 due to the reaction between rain water and CO₂.
- * When pH less then 5.6 then it is called acid rain.
- * Source : burning of fuel (contain N & S) form SO₂ & NO₂.

- * 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.

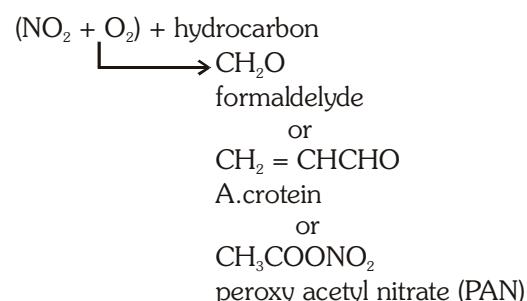
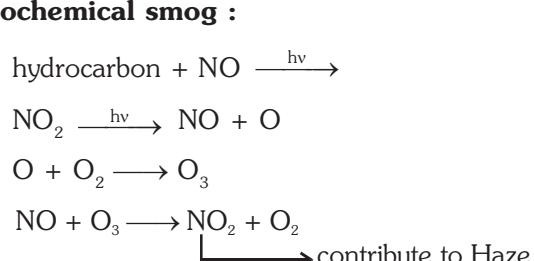
Mist :

Mist are produced by particle of spray liquid condensation of vapours, eg. herbiciaes mist etc.

Note : Pb is major air pollutant.

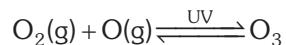
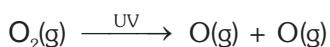
Smog (Smoke + fog) :

(Smoke + fog + SO₂) also called reducing smog

Photochemical smog :


Stratospheric pollution :

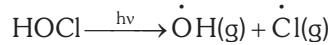
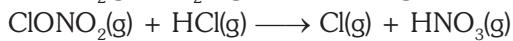
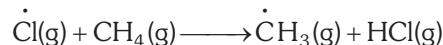
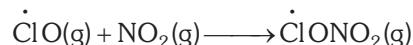
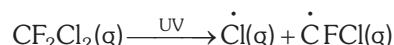
Formation & decomposition of oxone.



Ozone is thermodynamically 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 freons)

Reaction of ozone depletion :**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 would have BOD value of less than 5 ppm whereas 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	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	Carboxy	-oic acid
Sulphonic acid	$-\text{SO}_3\text{H}$	Sulpho	sulphonic acid
Anhydride	$\begin{array}{c} \text{O} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{O} \end{array}$	x	oic-anhydride
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR} \end{array}$	Alkoxy carbonyl or Carbalkoxy	alkyl...oate
Acid chloride	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{Cl} \end{array}$	Chloroformyl or Chlorocarbonyl	-oyl chloride
Acid amide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \end{array}$	Carbamoyl/ Amido	-amide
Carbonitrile/Cyanide	$-\text{C} \equiv \text{N}$	Cyano	nitrile
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	Formyl or Oxo	-al
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	Keto or oxo	-one
Alcohol	$-\text{OH}$	Hydroxy	-ol
Thio alcohol	$-\text{SH}$	Mercapto	thiol
Amine	$-\text{NH}_2$	Amino	amine
Ether	$-\text{O}-\text{R}$	Alkoxy	-
Oxirane	$\begin{array}{c} \text{---C} \\ \diagdown \\ \text{---C} \\ \diagup \\ \text{O} \end{array}$	Epoxy	-
Nitro derivative	$-\text{NO}_2$	Nitro	-
Nitroso derivative	$-\text{NO}$	Nitroso	-
Halide	$-\text{X}$	Halo	-
Double bond	$\text{C} = \text{C}$	-	ene
Triple bond	$\text{C} \equiv \text{C}$	-	yne

IMPORTANT NOTES



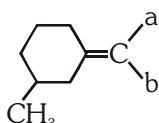
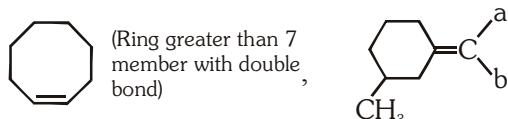
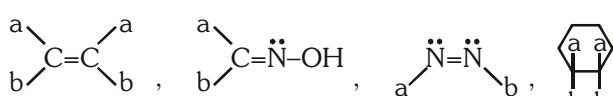
(B) STEREOISOMERISM

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.

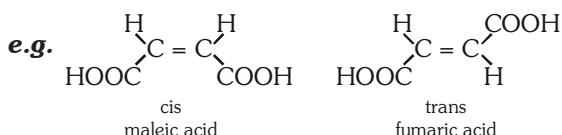
TYPES OF STEREOISOMERISM

GEOMETRICAL ISOMERISM

It is due to restricted rotation and is observed in following systems



- 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.



- 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.

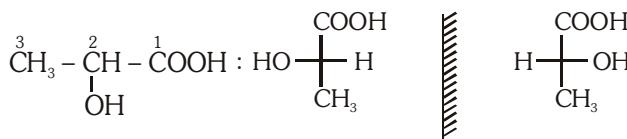
OPTICAL ISOMERISM

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	(2) Optically inactive
• dextrorotatory (d)	• meso
• laevorotatory (l)	
- 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.

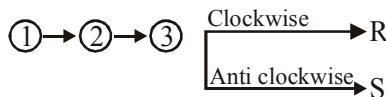
Fischer projection representation of lactic acid
(2-hydroxypropanoic acid)



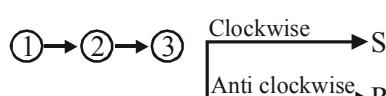
- Configuration of optical isomer :**
 - Absolute configuration (R/S system)
 - Relative configuration (D/L system)
- Determination of R/S configuration :**

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

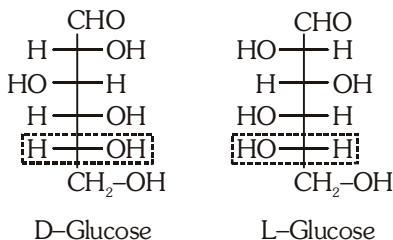


Rule-3 If lowest priority ④ is bonded to horizontal line then moving



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 \rightarrow D
If OH group on LHS \rightarrow L

**CIP SEQUENCE RULE :**

The following rules are followed for deciding the precedence order of the atoms or groups :-

- Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
- In case of isotopes, isotopes having higher atomic mass is given priority.
- 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.
- 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 necessary condition.

Calculation of number of optical isomers

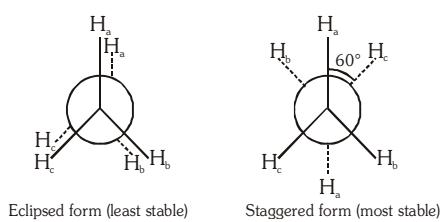
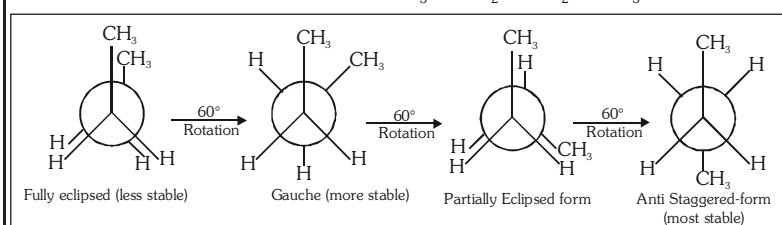
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2^n	Zero
Symmetrical If n = even	$2^{(n-1)}$	$2^{\frac{n}{2}-1}$
Symmetrical If n = odd	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

* 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.

**Conformations of butane :** ${}^4\text{CH}_3 - {}^3\text{CH}_2 - {}^2\text{CH}_2 - {}^1\text{CH}_3$ 

- 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.

e.g. H^+ , R^+ , NO_2^+ , X^+ , PCl_3 , PCl_5

(NH_4^+ and H_3O^+ are not electrophile)

Nucleophiles are electron rich species.

e.g. Cl^- , CH_3^- , OH^- , RO^- , CN^- , NH_3 , $\ddot{\text{O}}\text{H}$, $\text{CH}_2=\text{CH}_2$, $\text{CH}\equiv\text{CH}$

Relative electron withdrawing order (-I order)

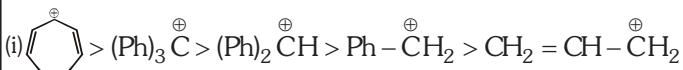
$-\text{NF}_3 > -\text{NR}_3 > -\text{NH}_3 > -\text{NO}_2 > -\text{CN} > -\text{COOH} > -\text{X} > -\text{OR} > -\text{OH} > -\text{C}\equiv\text{CH} > -\text{NH}_2 > -\text{C}_6\text{H}_5 > -\text{CH} = \text{CH}_2$

Relative electron releasing order (+I order)

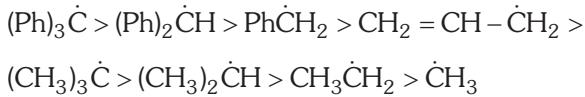
$-\text{NH} > -\ddot{\text{O}}^- > -\text{COO}^- > 3^\circ \text{ alkyl} > 2^\circ \text{ alkyl} > 1^\circ \text{ alkyl} > -\text{CH}_3$

RELATIVE STABILITY ORDER

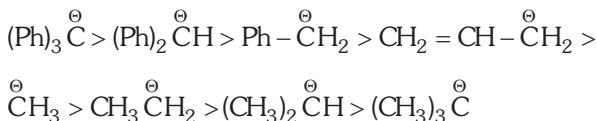
(A) Stability of carbocation



(B) Stability of free radical



(C) Stability of Carbanion



$$\text{BASIC STRENGTH} \propto K_b \propto \frac{1}{pK_b}$$

- Basic strength of amine :-**

In aqueous medium

$\text{R} \Rightarrow -\text{CH}_3 \quad 2^\circ > 1^\circ > 3^\circ > \text{NH}_3^-$

$\text{R} \Rightarrow -\text{CH}_2\text{CH}_3 \quad 2^\circ > 3^\circ > 1^\circ > \text{NH}_3^-$

In gaseous medium

$\text{R} \Rightarrow -\text{CH}_3 \quad 3^\circ > 2^\circ > 1^\circ > \text{NH}_3^-$

$\text{R} \Rightarrow -\text{CH}_2\text{CH}_3 \quad 3^\circ > 2^\circ > 1^\circ > \text{NH}_3^-$

- Reactivity towards nucleophile (NAR)**

(1) $\text{HCHO} > \text{CH}_3\text{CHO} > (\text{CH}_3)_2\text{CO}$

(2) $\text{CCl}_3\text{CHO} > \text{CHCl}_2\text{CHO} > \text{CH}_2\text{ClCHO}$

- 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**

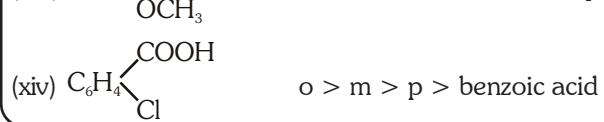
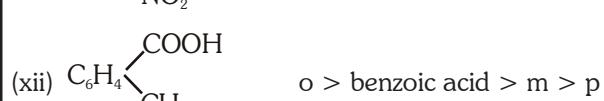
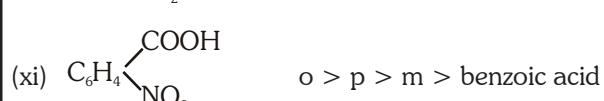
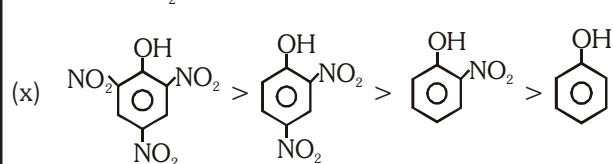
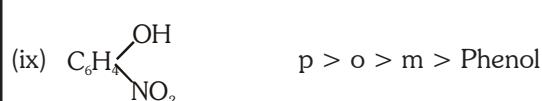
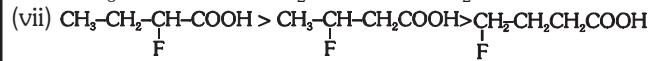
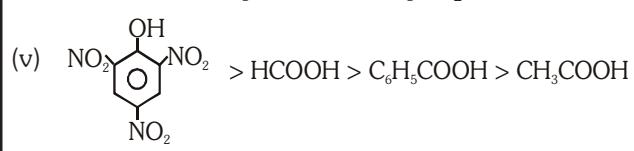
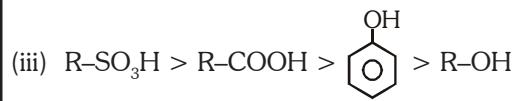
$\text{R}_2\text{C}=\text{CR}_2 > \text{R}_2\text{C}=\text{CHR} > \text{R}_2\text{C}=\text{CH}_2 > \underset{\text{trans form}}{\text{RCH}=\text{CHR}} > \underset{\text{cis form}}{\text{RCH}=\text{CHR}}$

$\text{RCH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2$

- Heat of hydrogenation \propto $\frac{1}{\text{Stability of alkene}}$**

ACIDIC STRENGTH \propto Stability of conjugate base

$$\propto K_a \propto \frac{1}{pK_a}$$



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
- (iv) Bromo Benzene
- (vi) o-Nitrophenol
- (iii) Nitro Benzene
- (v) Naphthalene

$$\begin{array}{l} P = P_1 + P_2 \\ \text{Vapour pressure of Organic liquid} \quad \text{Vapour pressure of water} \\ \text{Organic liquid} \end{array}$$

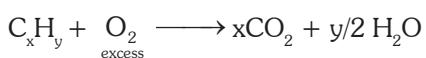
LASSAIGNE'S METHOD (detection of elements)

Element	Sodium extract	Confirmed test
Nitrogen	$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$	$(\text{NaCN} + \text{FeSO}_4 + \text{NaOH})$ boil and cool $+ \text{FeCl}_3 + \text{conc. HCl} \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ Prussian blue colour
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$	(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ sodium nitrosopruiside $\rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}_2]$ a deep violet colour (ii) $\text{Na}_2\text{S} + \text{CH}_3\text{COOH} + (\text{CH}_3\text{COO})_2\text{Pb} \rightarrow$ A black ppt. (PbS_3)
Halogen	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$	(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	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaCNS}$ 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



$$\% \text{ of C} = \frac{12}{44} \times \frac{\text{wt. of CO}_2}{\text{wt. of org. compd}} \times 100$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{\text{wt. of H}_2\text{O}}{\text{wt. of org compd}} \times 100$$

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 ($-\text{N} = \text{N}-$) and nitrogen in the ring (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

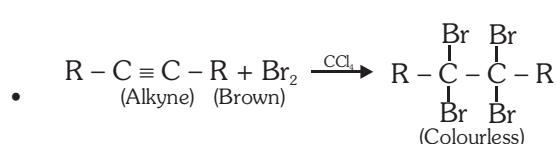
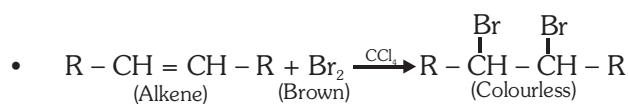
IMPORTANT NOTES



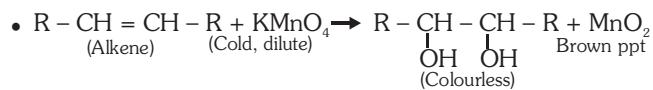
DISTINCTION BETWEEN PAIRS OF COMPOUNDS

UNSATURATION TEST

- (a) Double/Triple bonded Compounds ($C=C$)/($C\equiv C$) + Br_2 in CCl_4 (Brown colour) → Colourless compound



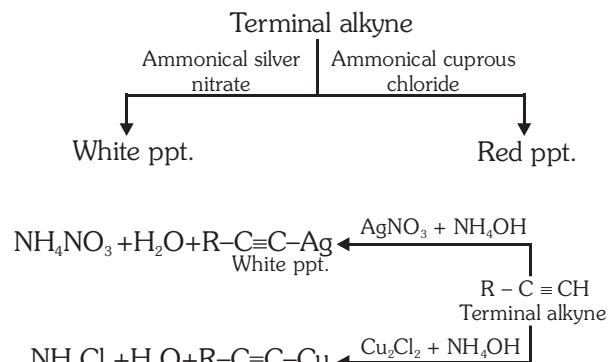
- (b) Double/Triple bonded Compounds + Baeyer's reagent (Pink colour) → Brown precipitate



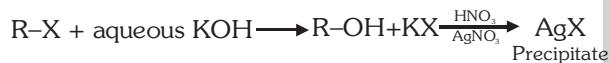
Baeyer's reagent is cold, dilute $KMnO_4$ solution having pink colour.

Note : The above test are not given by Benzene. Although it has unsaturation.

TEST FOR TERMINAL ALKyne

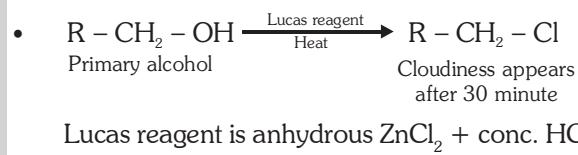
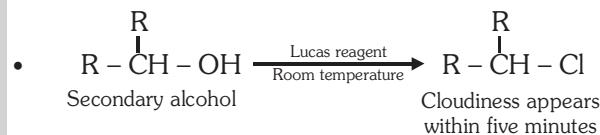
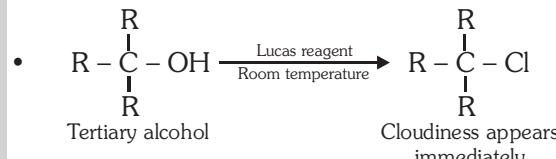


NATURE OF X-GROUP IN C-X BOND



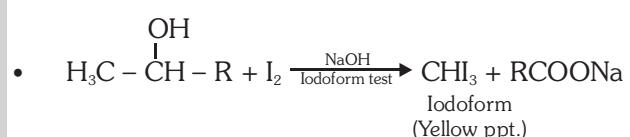
If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOLS



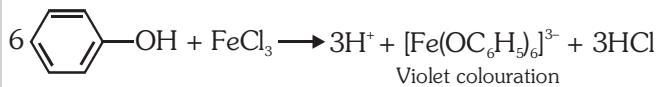
Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl.

$H_3C-\overset{OH}{C}-R$ type of alcohols give iodoform test.



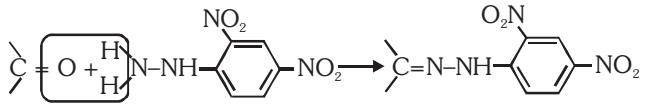
PHENOL

Phenol + ferric chloride → Violet colouration (neutral)

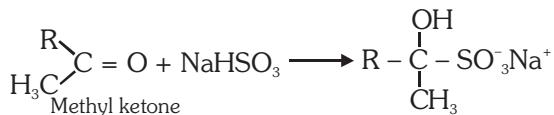
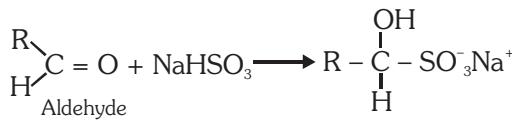


CARBONYL GROUP

- Carbonyl compound + 2, 4-Dinitrophenylhydrazine → Yellow/orange crystal (Brady's reagent)



- All aldehydes and only aliphatic methyl ketones + $NaHSO_3$ → White crystalline bisulphite.

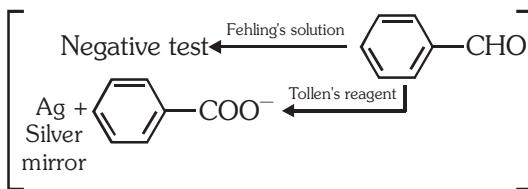


ALDEHYDE GROUP

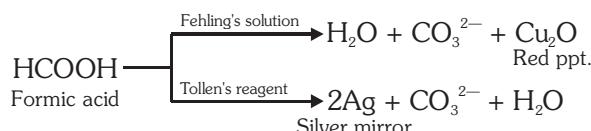
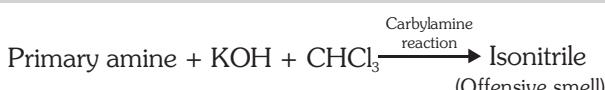
- Aldehyde + Tollen's reagent → Silver mirror
 $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{H} + 3\text{OH}^\ominus + 2[\text{Ag}(\text{NH}_3)_2]^\ddagger \rightarrow \text{RCOO}^\ominus + 2\text{H}_2\text{O} + 4\text{NH}_3 + 2\text{Ag} \downarrow$
(silver mirror)
- Aldehyde + Fehling's solution → Reddish brown precipitate
 $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{H} + 2\text{Cu}^{2+} + 5\text{OH}^- \rightarrow \text{RCOO}^\ominus + 3\text{H}_2\text{O} + \text{Cu}_2\text{O}$
(Reddish brown ppt.)
- $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-$ group also give iodoform test
 $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{R} + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{CHI}_3 + \text{RCOONa}$
Iodoform (Yellow ppt.)

AROMATIC ALDEHYDE GROUP

- Aromatic aldehyde + Tollen's reagent → Silver mirror
- Aromatic aldehyde + Fehling's solution → Negative test

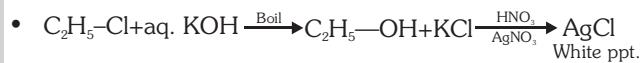
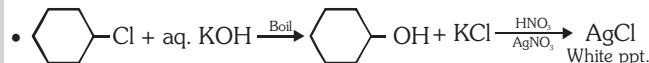
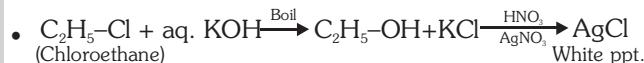
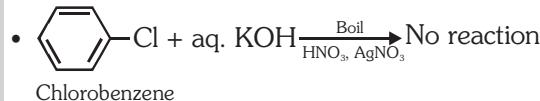
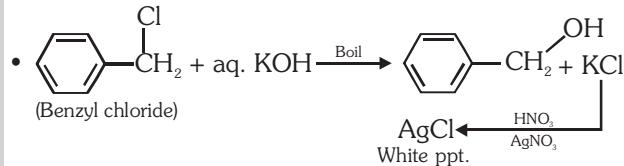
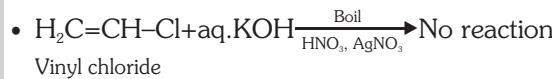
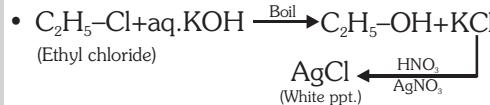
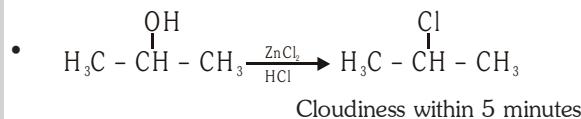
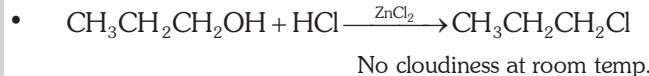
**CARBOXYLIC GROUP**

Carboxylic acid + Sodium bicarbonate → effervescence
 $\text{RCOOH} + \text{NaHCO}_3 \rightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$

FORMIC ACID**AMINES (1°)****Amines (1°, 2° & 3°) (Hinsberg's test)**

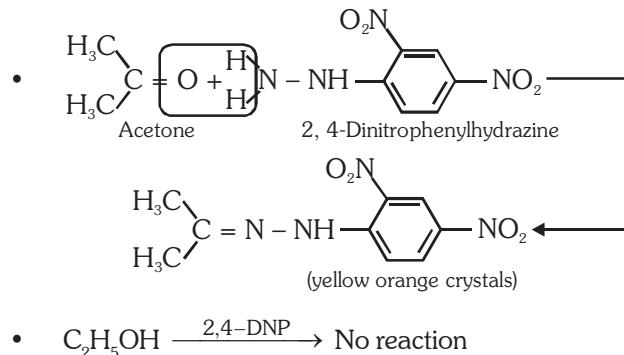
- Primary amine + Benzenesulphonyl chloride
 \rightarrow Precipitate $\xrightarrow{\text{KOH}}$ soluble
- Secondary amine + Benzenesulphonyl chloride
 \rightarrow Precipitate $\xrightarrow{\text{KOH}}$ insoluble
- Tertiary amine + Benzenesulphonyl chloride → No reaction

Note : Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and chlorobenzene**Chlorocyclohexane and chlorobenzene****Chloroethane and bromoethane****Benzyl chloride and chlorobenzene****Ethyl chloride and vinyl chloride****n-Propyl alcohol and iso-propyl alcohol**

Ethyl alcohol and methyl alcohol (Iodoform test)

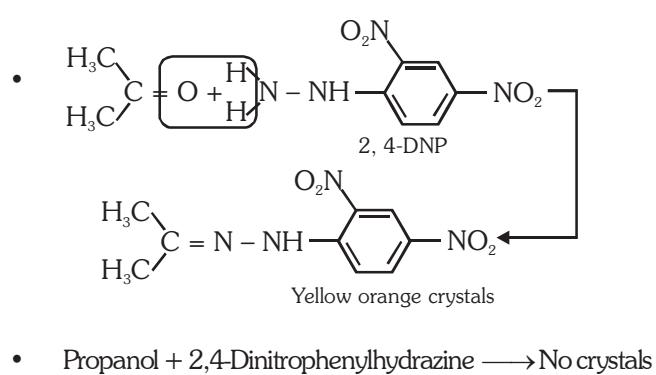
- $\text{CH}_3\text{CH}_2\text{OH} + 4\text{I}_2 + 6\text{NaOH} \rightarrow \text{CHI}_3 + \text{HCOONa}$
Yellow ppt.
- $\text{CH}_3\text{OH} + 4\text{I}_2 + 6\text{NaOH} \rightarrow$ No yellow ppt.

Ethyl alcohol and acetone (2, 4 - DNP)**Phenol and ethyl alcohol (Neutral FeCl_3)**

- Phenol + Neutral ferric chloride \rightarrow Violet colouration
- $6 \text{C}_6\text{H}_5\text{OH} + \text{FeCl}_3 \rightarrow 3\text{H}^+ + [\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-} + 3\text{HCl}$
Violet colouration
- $\text{CH}_3\text{CH}_2\text{OH} + \text{Neutral ferric chloride} \rightarrow$ No violet colouration

Benzoic acid and phenol (NaHCO_3)

- Benzoic acid + Sodium bicarbonate \rightarrow effervescence
 $\text{C}_6\text{H}_5\text{COOH} + \text{NaHCO}_3 \rightarrow \text{C}_6\text{H}_5\text{COONa} + \text{CO}_2 \uparrow + \text{H}_2\text{O}$
- Phenol + Sodium bicarbonate \rightarrow No effervescence
(Phenol is less acidic than benzoic acid)

Propanone and propanol (2, 4 - DNP)**Ethanal and propanal (Iodoform test)**

- $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{H} + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{CHI}_3 + \text{HCOONa}$
Iodoform
(Yellow ppt.)
Ethanal
- $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H} + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$
Propanal

Propanal and propanone (Tollen's and Fehling reagent)

- Propanal + Tollen's reagent \longrightarrow Silver mirror
- $$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H} + 3\text{OH}^- + 2[\text{Ag}(\text{NH}_3)_2]^+ \longrightarrow \text{CH}_3\text{CH}_2\text{COO}^- + 2\text{H}_2\text{O} + 4\text{NH}_3 + 2\text{Ag} \downarrow$$

(Silver mirror)
- Propanal + Fehling's solution \rightarrow Reddish brown precipitate
- $$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{CH}_3\text{CH}_2\text{COO}^- + 3\text{H}_2\text{O} + \text{Cu}_2\text{O}$$

(Reddish brown ppt.)
- Propanone $\xrightarrow{\text{Fehling's solution}}$ Negative test
- Propanone $\xrightarrow{\text{Tollen's reagent}}$ Negative test

Pentan-2-one and pentan-3-one (Iodoform test)

- $$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3 + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{CHI}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$$

Iodoform
(Yellow ppt.)
- $$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{CH}_3 + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$$

Pentan-3-one

Propanal and benzaldehyde (Fehling solution)

- Propanal + Fehling's solution \rightarrow Reddish brown precipitate
- $$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{CH}_3\text{CH}_2\text{COO}^- + 3\text{H}_2\text{O} + \text{Cu}_2\text{O}$$

Fehling's solution
- Benzaldehyde + Fehling's solution \rightarrow No precipitate
- $$\text{C}_6\text{H}_5\text{CHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{No reaction}$$

Methanoic acid and ethanoic acid**(Tollen's & Fehling solution)**

- $$\text{HCOOH} \xrightarrow{\text{Fehling's solution}} \text{H}_2\text{O} + \text{CO}_3^{2-} + \text{Cu}_2\text{O}$$
- $$\text{HCOOH} \xrightarrow{\text{Tollen's reagent}} 2\text{Ag} \downarrow + \text{CO}_3^{2-} + \text{H}_2\text{O}$$
- $$\text{HCOOH} \xrightarrow{\text{Fehling's solution}} \text{No brown ppt.}$$
- $$\text{HCOOH} \xrightarrow{\text{Tollen's reagent}} \text{No silver mirror}$$

Ethanal and methanal (Iodoform test)

- $\text{CH}_3\text{CHO} + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{CHI}_3 + \text{HCOONa}$
Ethanal Iodoform (Yellow ppt.)
- $\text{HCHO} + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$
Methanal

Acetophenone and benzophenone (Iodoform test)

- $\text{C}_6\text{H}_5\text{COCH}_3 + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{CHI}_3 + \text{C}_6\text{H}_5\text{COONa}$
(Acetophenone) (Yellow ppt.)
- $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{C}_6\text{H}_5 + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}} \text{No ppt.}$
(Benzophenone)

Benzoic acid and ethylbenzoate

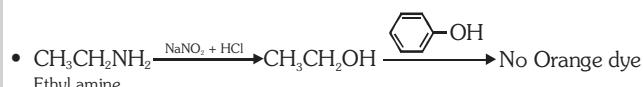
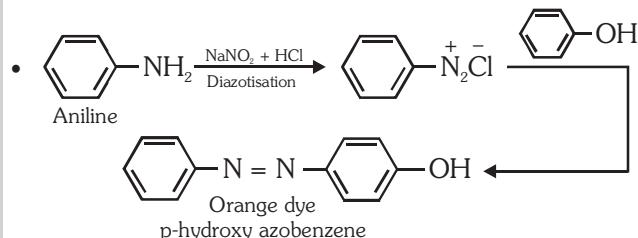
- $\text{C}_6\text{H}_5\text{COOH} + \text{NaHCO}_3 \rightarrow \text{C}_6\text{H}_5\text{COONa} + \text{CO}_2 \uparrow + \text{H}_2\text{O}$
effervescence
- Ethyl benzoate + Sodium bicarbonate \rightarrow No effervescence

Benzaldehyde and acetophenone (Tollen's test)

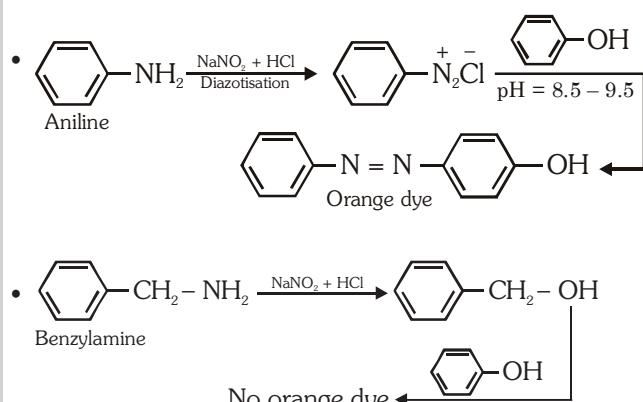
- Benzaldehyde + Tollen's reagent \rightarrow Silver mirror
- $\text{C}_6\text{H}_5\text{CHO} + 3\text{OH}^- + 2[\text{Ag}(\text{NH}_3)_2]^+ \xrightarrow{\text{(Tollen's reagent)}}$
 $\text{C}_6\text{H}_5\text{COO}^- + 2\text{H}_2\text{O} + 4\text{NH}_3 + 2\text{Ag} \downarrow$
- Acetophenone + Tollen's reagent \rightarrow No silver mirror

Methyl amine and dimethyl amine (Isocyanide test)

- $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{CH}_3\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$
Methyl amine (alc.) Methyl isocyanide (Offensive smell)
- $\text{H}_3\text{C}-\text{NH}-\text{CH}_3 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{(alc.)}} \text{No offensive smell}$
Di-methyl amine

Aniline and ethyl amine (Diazotisation)Aniline and N-methylaniline (Isocyanide test)

- $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{(alc.)}} \text{C}_6\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$
Aniline Phenyl isocyanide (Offensive smell)
- $\text{C}_6\text{H}_5\text{NH}-\text{CH}_3 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{(alc.)}} \text{No offensive smell}$
N-Methylaniline

Aniline and Benzylamine (Diazotisation + phenol)Glucose and fructose

- Glucose + $\text{Br}_2 + \text{H}_2\text{O} \rightarrow$ Gluconic acid + 2HBr
(Brown colour) (Colourless)
- Fructose + $\text{Br}_2 + \text{H}_2\text{O} \rightarrow$ Brown colour
(Brown colour) (no change in colour)

Glucose and sucrose

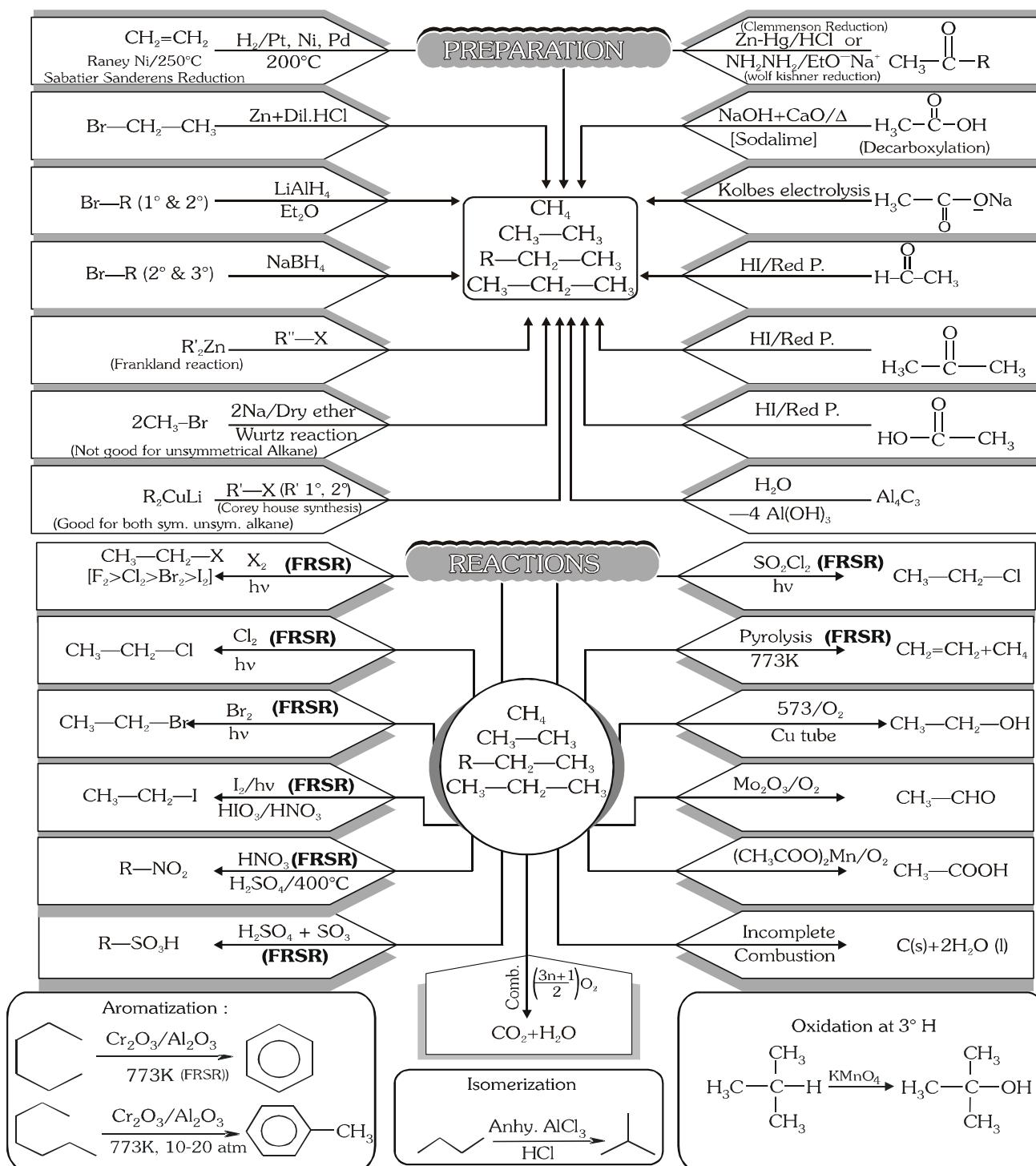
- Glucose + Tollen's reagent \rightarrow Silver mirror
- Sucrose + Tollen's reagent \rightarrow No silver mirror

Glucose and starch

- Glucose + Fehling's solution \rightarrow Red ppt.
- Starch + Fehling's solution \rightarrow No red ppt.
OR
- Glucose + I_2 solution \rightarrow No blue colour
- Starch + I_2 solution \rightarrow Blue colour

IMPORTANT NOTES

HYDROCARBON - ALKANE



- Reactivity of alkane towards free radical halogenation is \propto stability of free radical
 $\text{C}_6\text{H}_5-\text{CH}_3 > \text{CH}_2=\text{CH}-\text{CH}_3 > (\text{CH}_3)_3\text{CH} > \text{CH}_3-\text{CH}_2-\text{CH}_3 > \text{CH}_3-\text{CH}_3 > \text{CH}_4$
- Reactivity of halogen towards free radical substitution
 $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Knocking tendency of petroleum as fuel decrease with increase in side chain. Straight chain > Branched chain

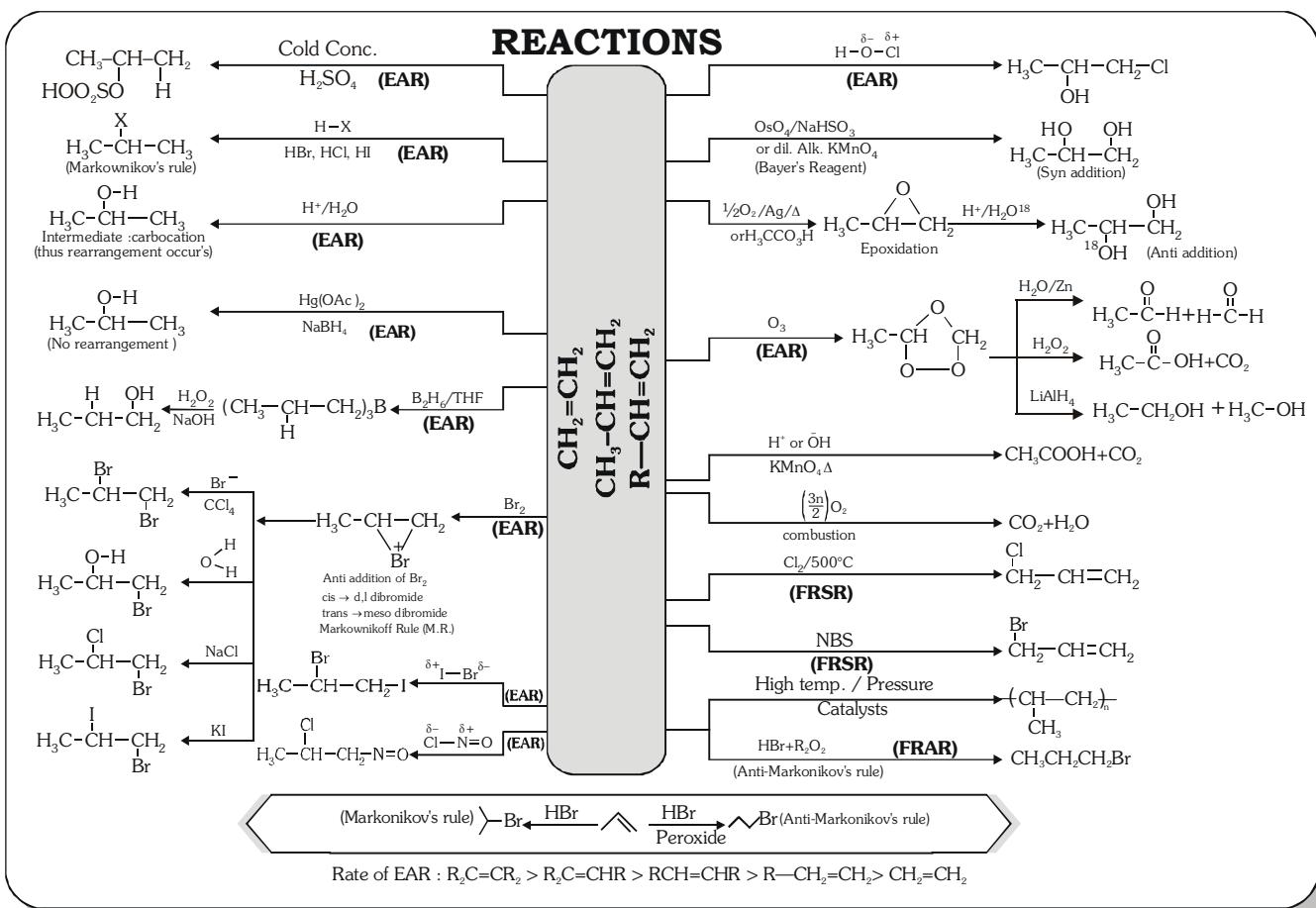
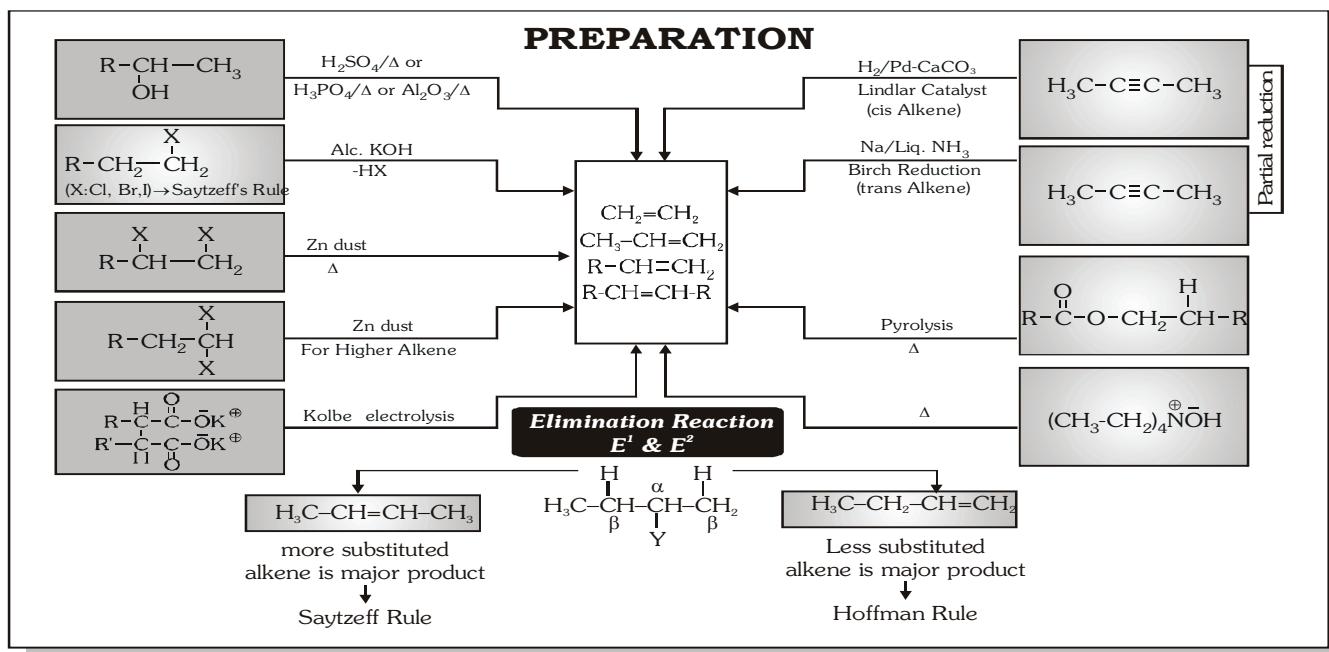
Knocking tendency is in the order

Olefin > cycloalkane > aromatic

- Boiling point decrease with increase in number of side chain.

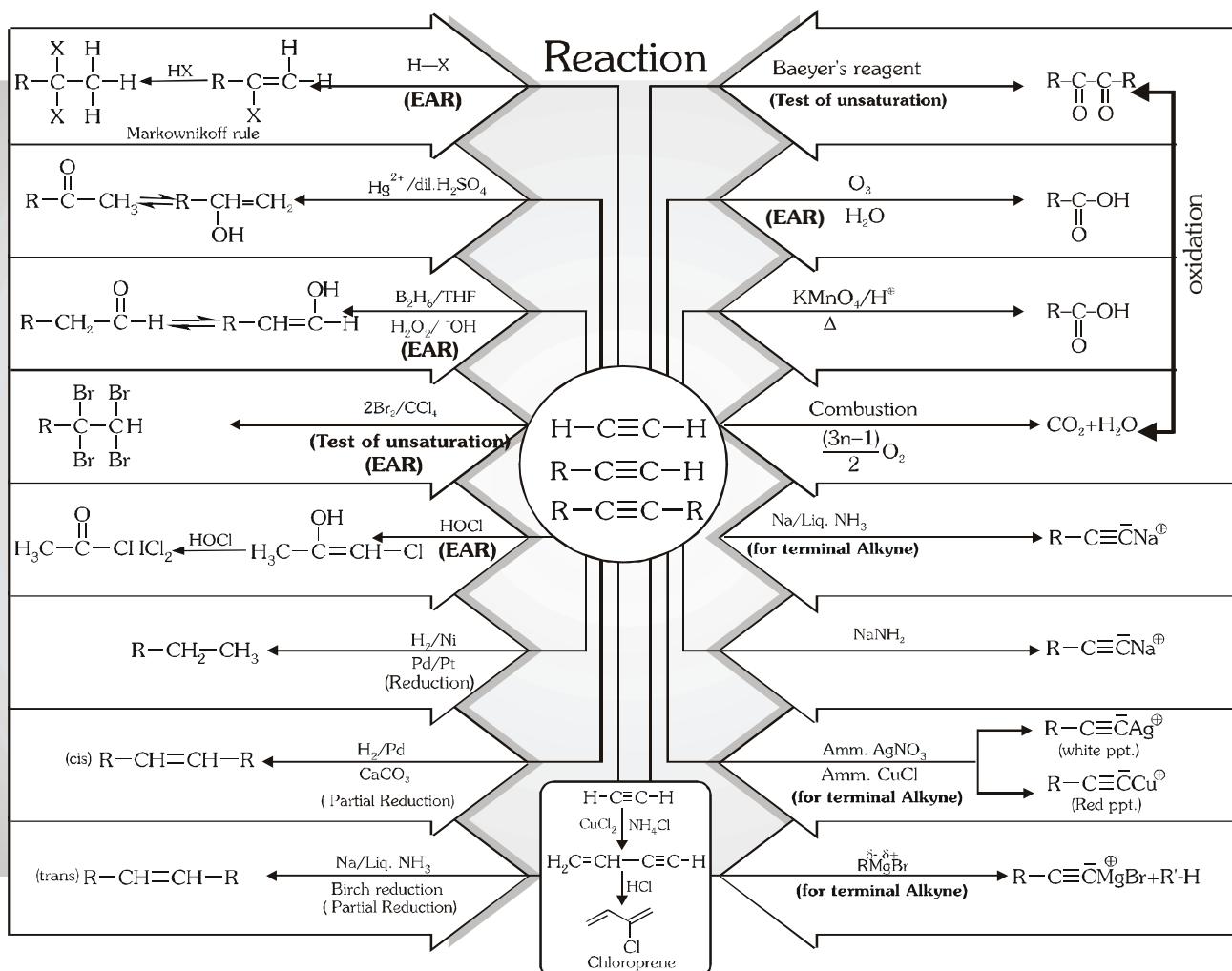
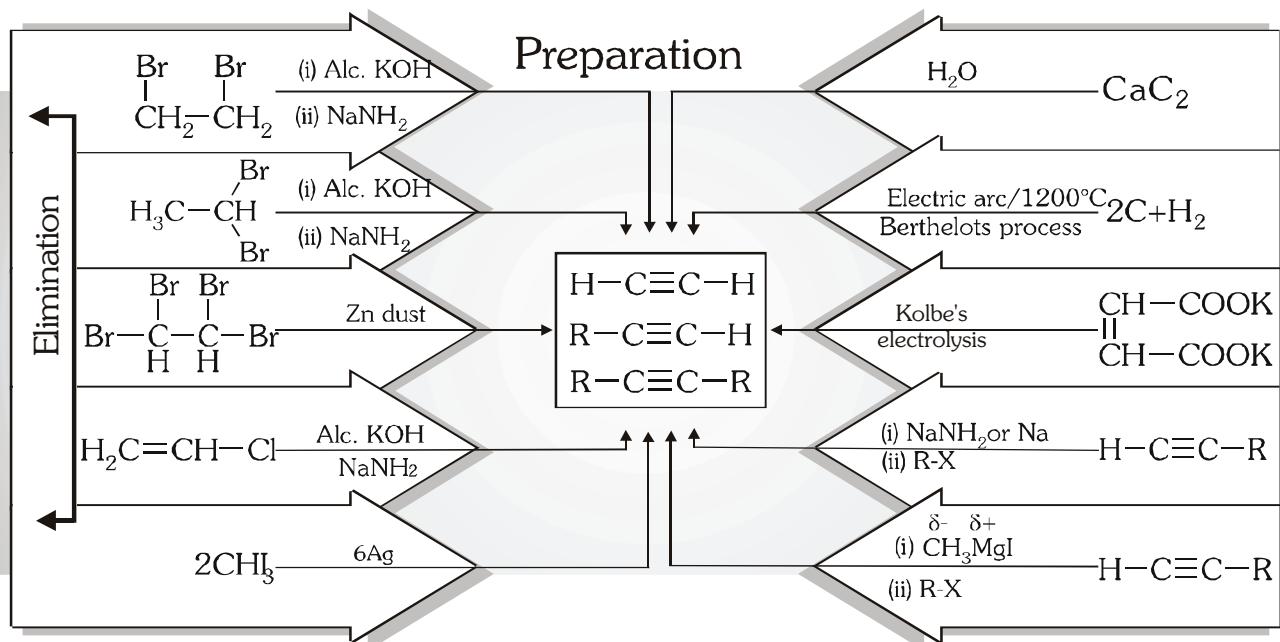
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 > \text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3 > \text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$
 normal iso neo

HYDROCARBON - ALKENE



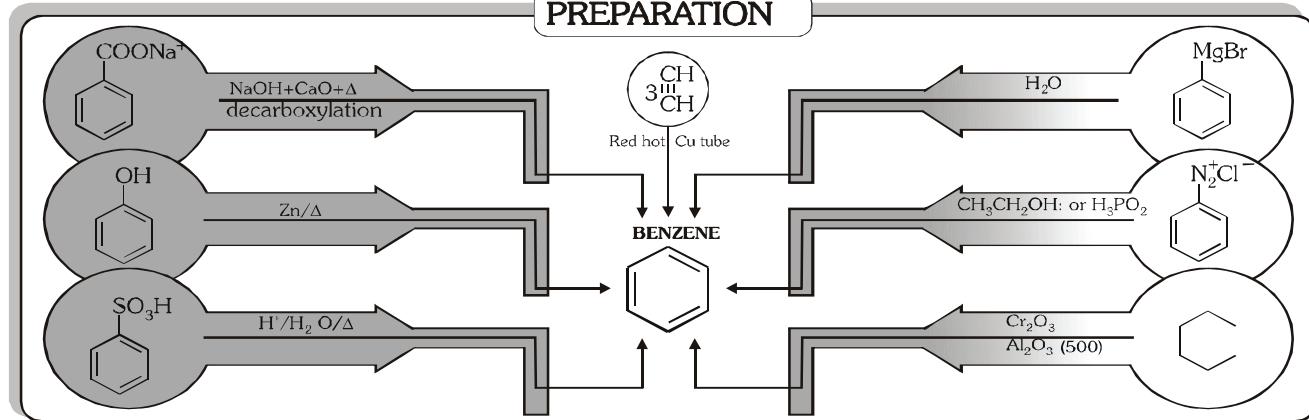
- Order of reactivity of olefins for hydrogenation $\text{CH}_2=\text{CH}_2 > \text{R}-\text{CH}=\text{CH}_2$ (Reverse of stability)
- Order of reactivity of alkene towards hydration $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}=\text{CH}_2 > \text{CH}_3-\text{CH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2$

HYDROCARBON - ALKYNE



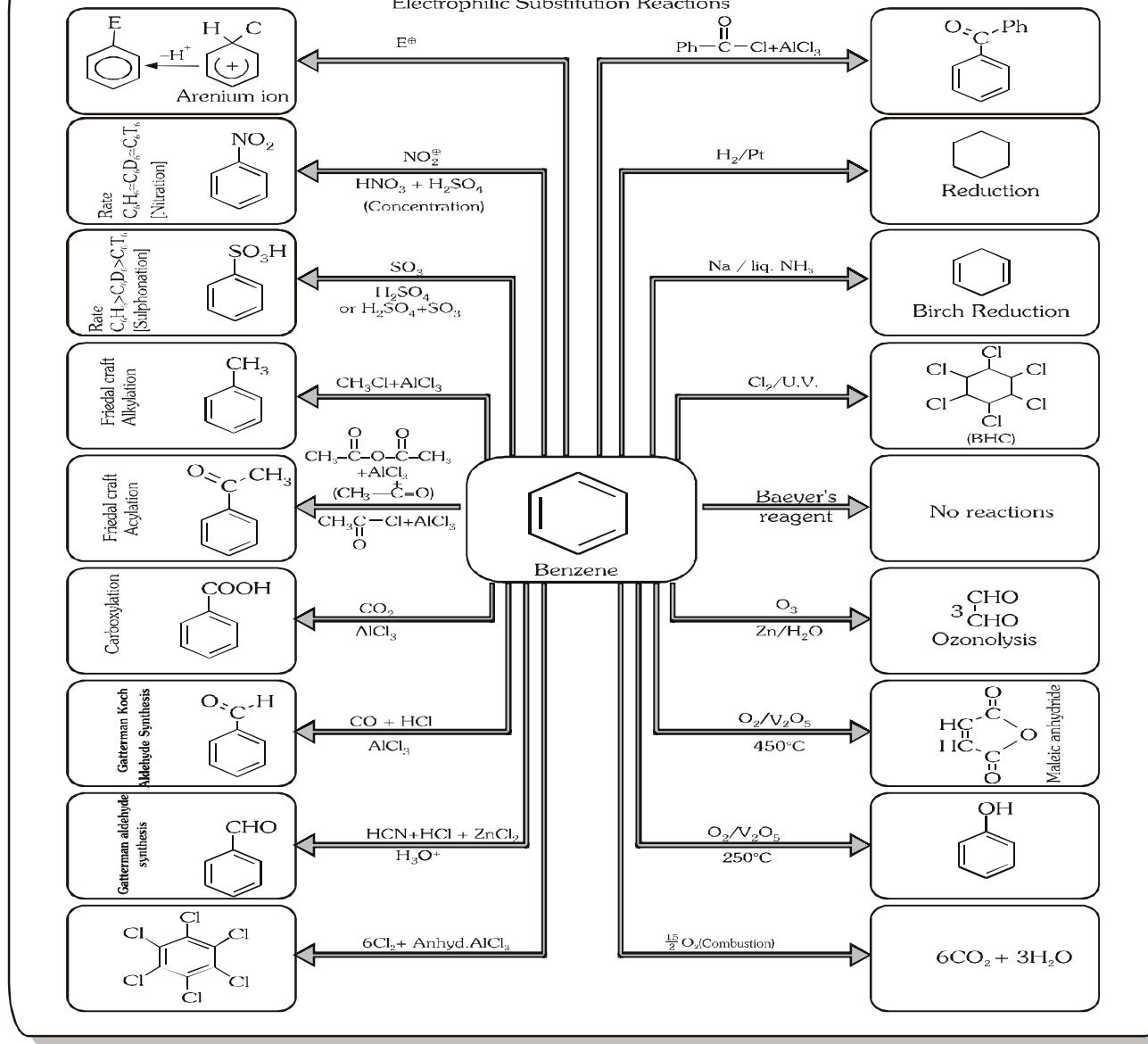
HYDROCARBON - BENZENE

PREPARATION



REACTIONS

Electrophilic Substitution Reactions

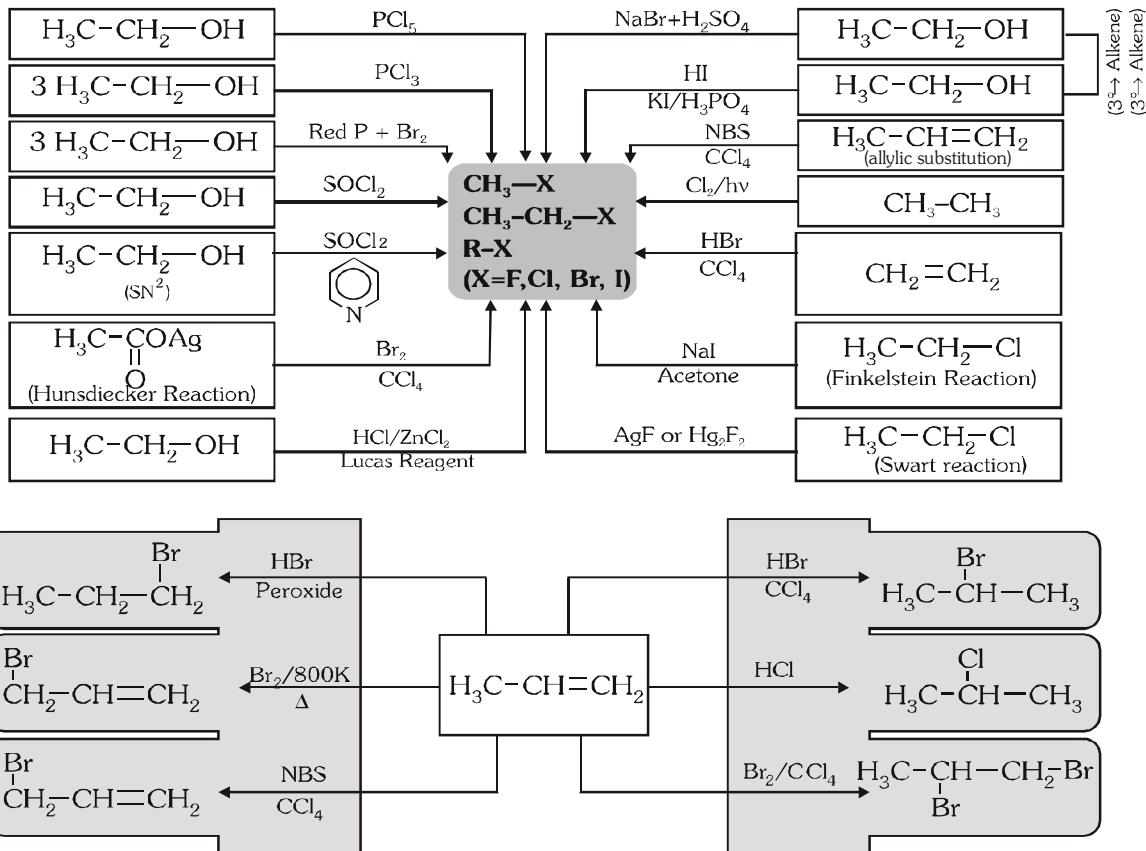


IMPORTANT NOTES

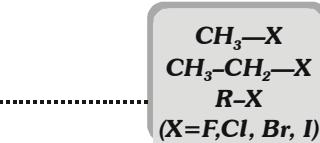
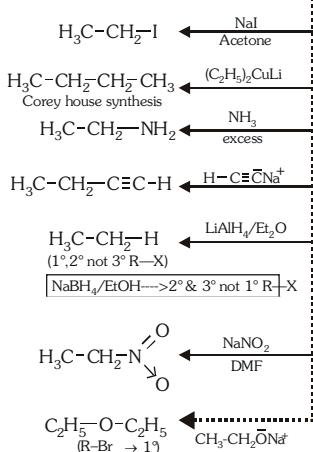


HALOALKANE

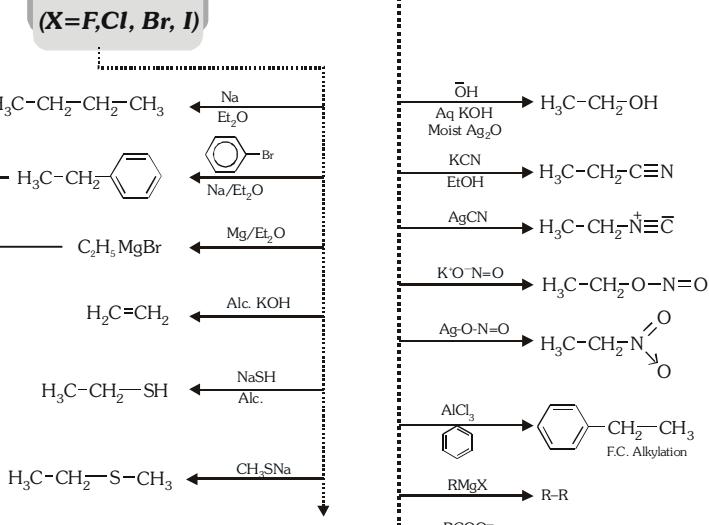
PREPARATION



REACTIONS



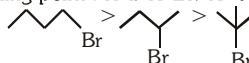
(Reactivity order)
 $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$
 Ambident Nucleophile: - $\ddot{\text{C}}\text{N}$, $\ddot{\text{O}}-\text{N=O}$



PHYSICAL PROPERTIES

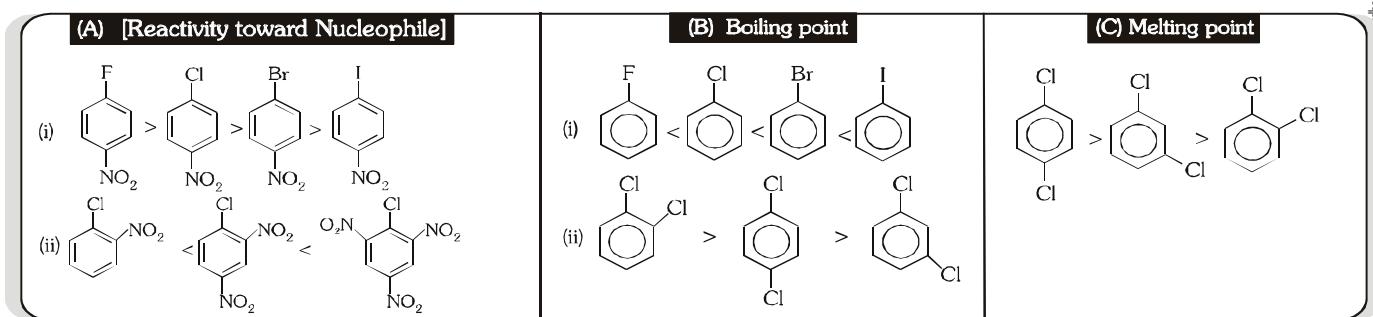
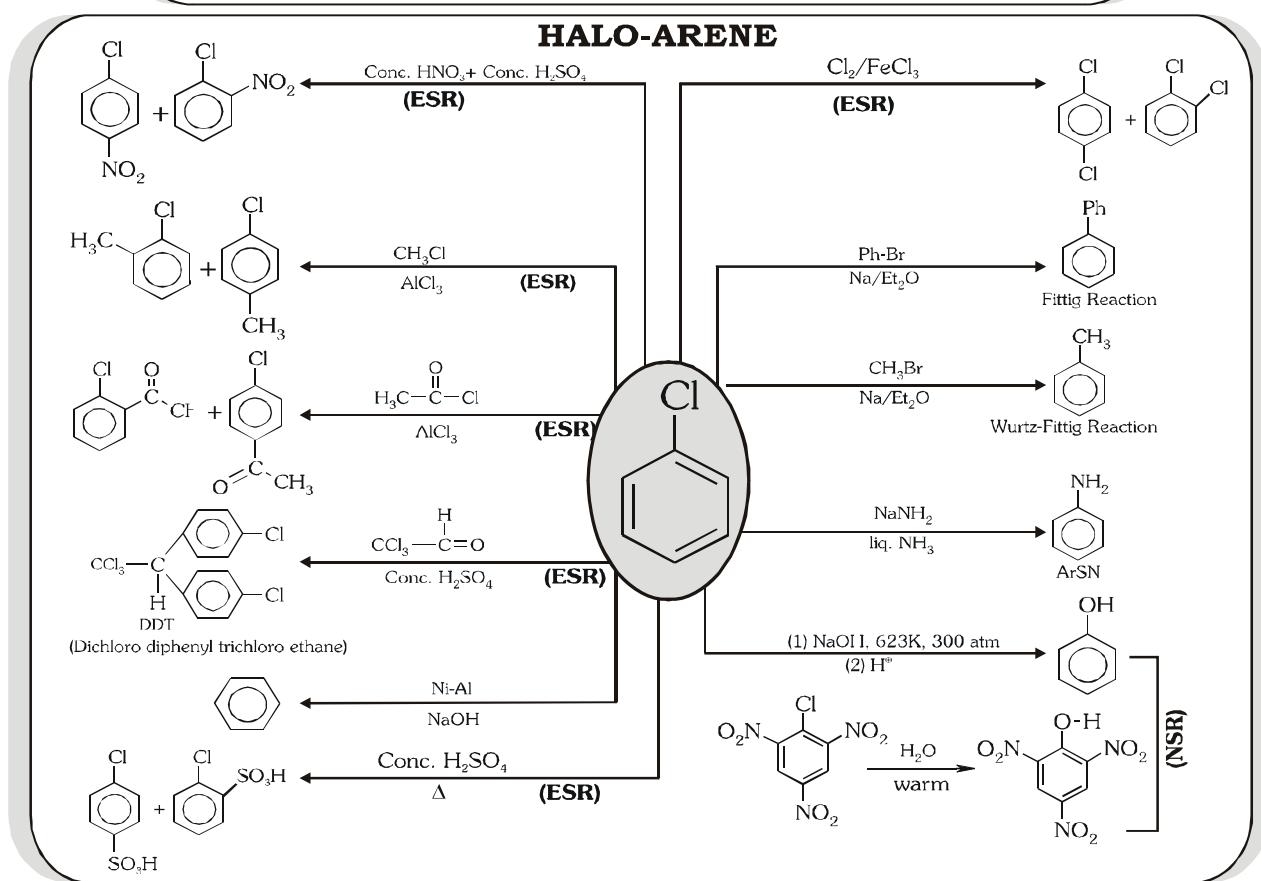
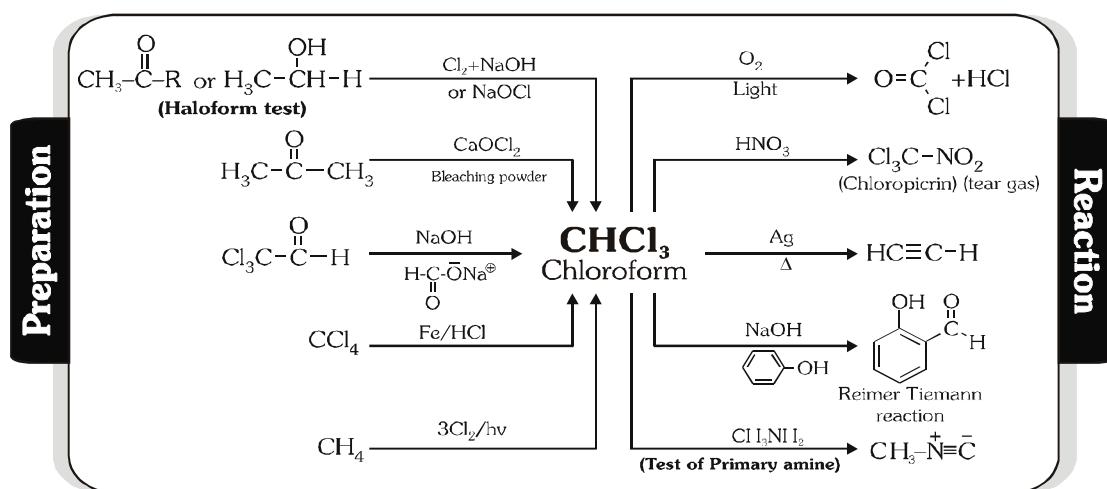
- (1) Dipole moment : $\text{CH}_3\text{-Cl} > \text{CH}_3\text{-F} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$
 (2) Bond enthalpies : $\text{CH}_3\text{-F} > \text{CH}_3\text{-Cl} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$

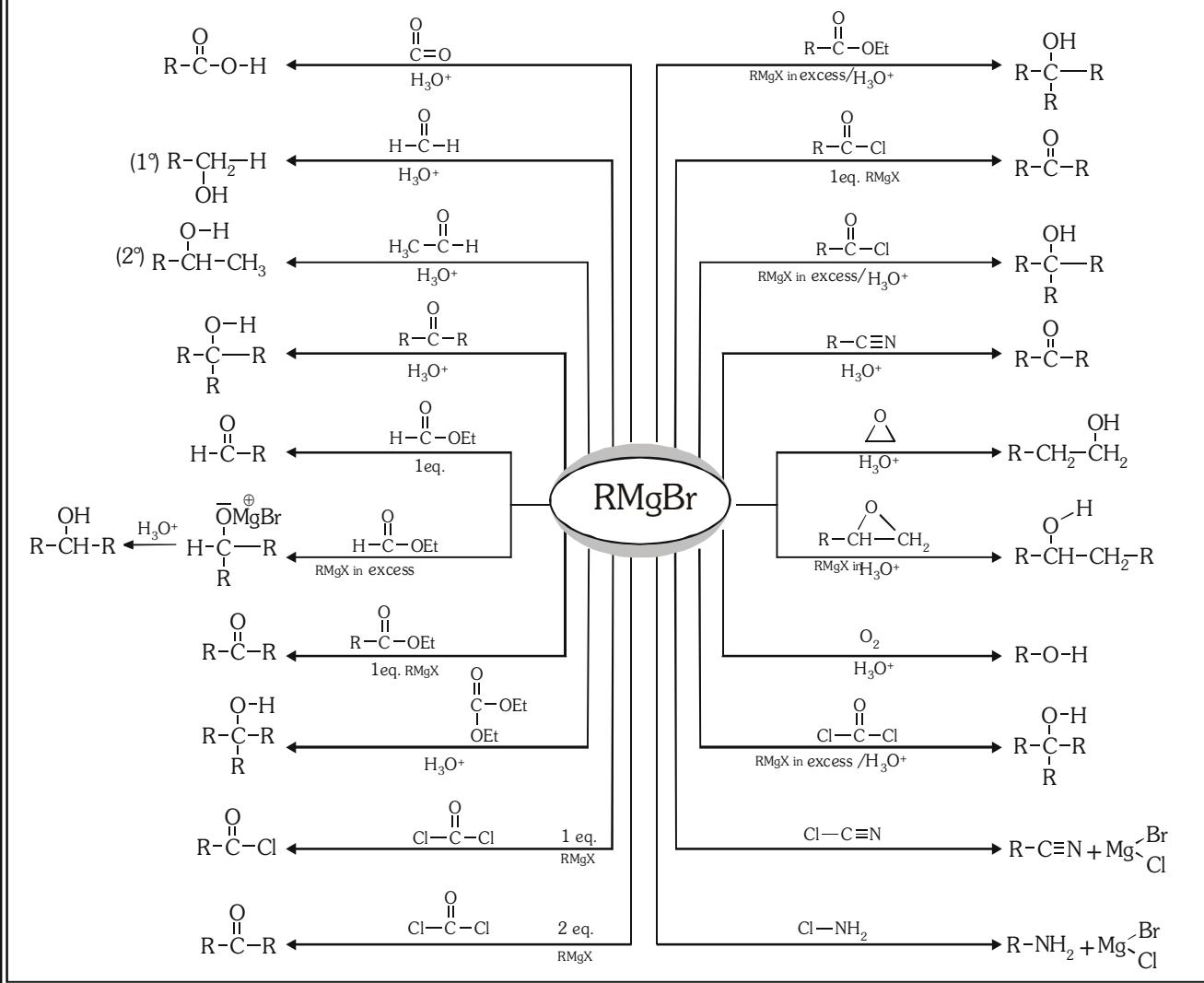
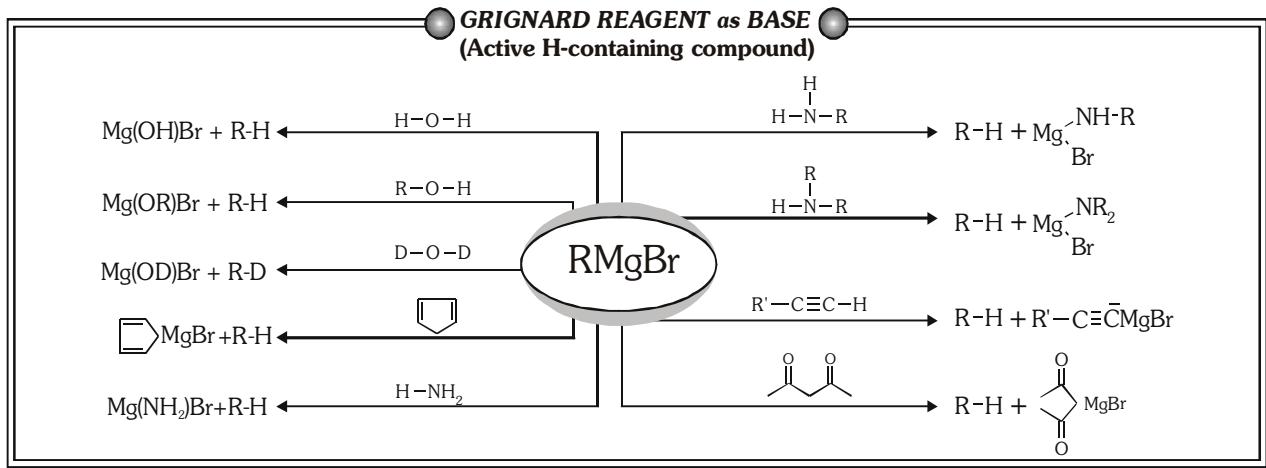
(3) Boiling point : R-I > R-Br > R-Cl > R-F



(4) Density : $n\text{-C}_3\text{H}_7\text{Cl} < n\text{-C}_3\text{H}_7\text{Br} < n\text{-C}_3\text{H}_7\text{I}$

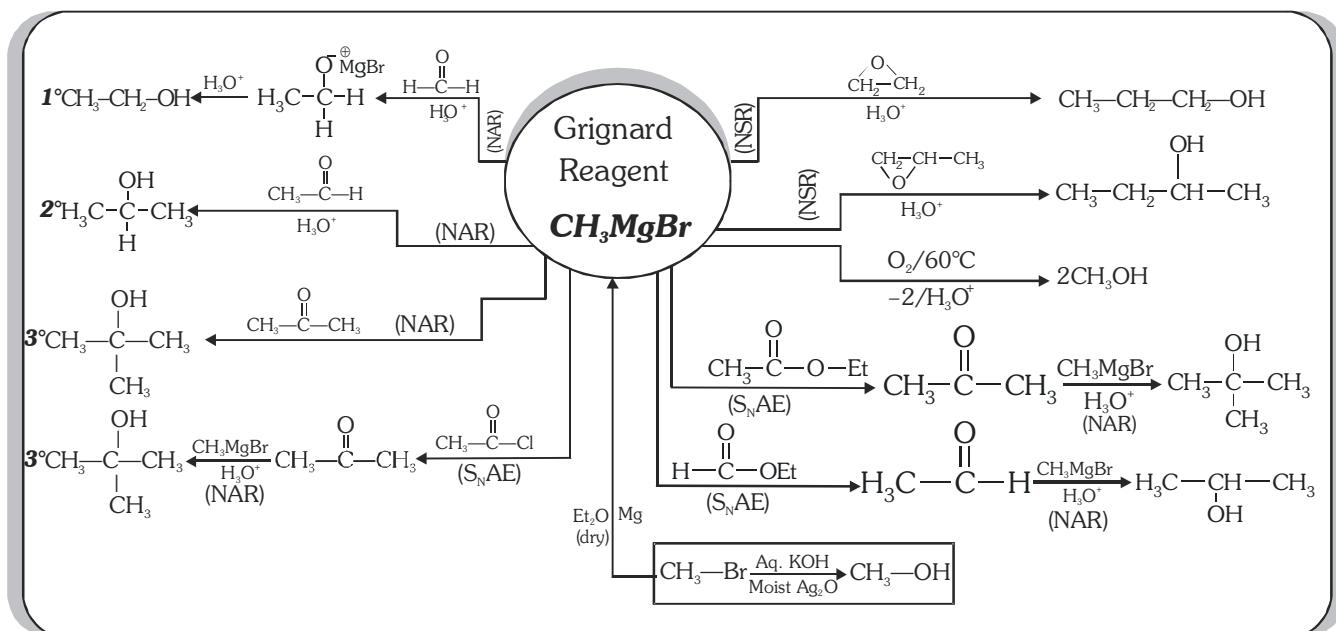
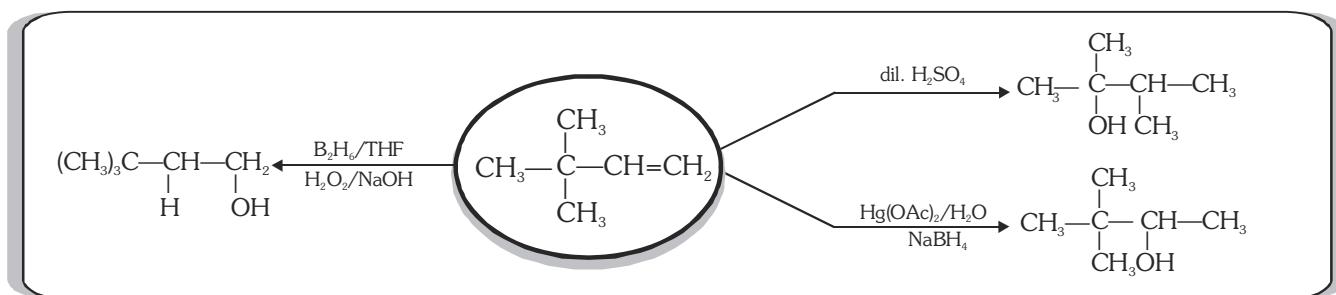
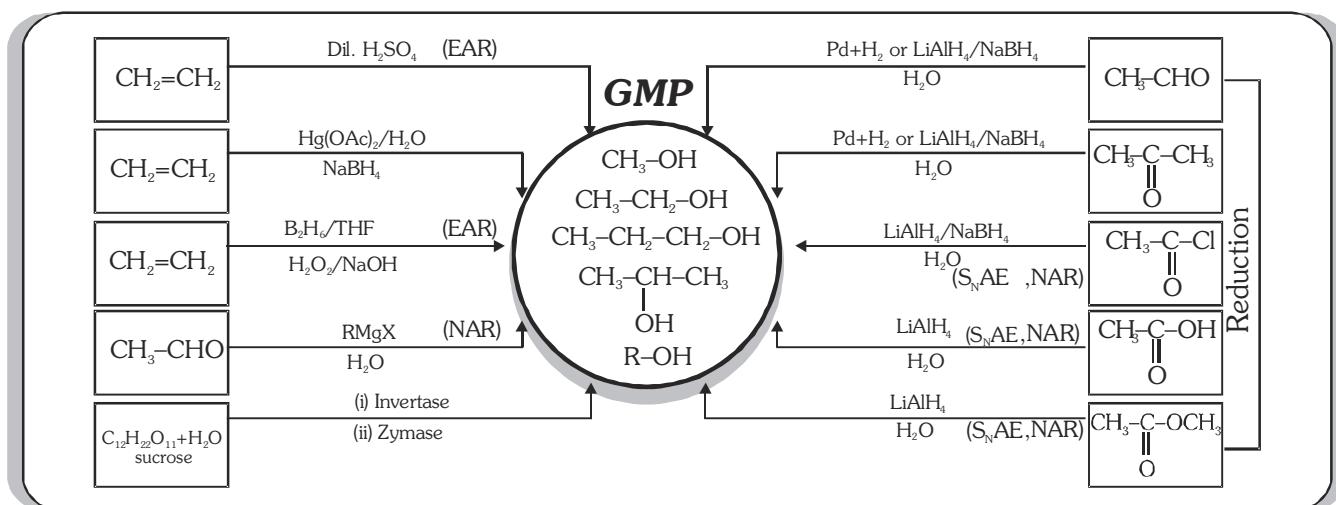
(5) Solubility → slightly soluble in water

TRI-HALO ALKANE

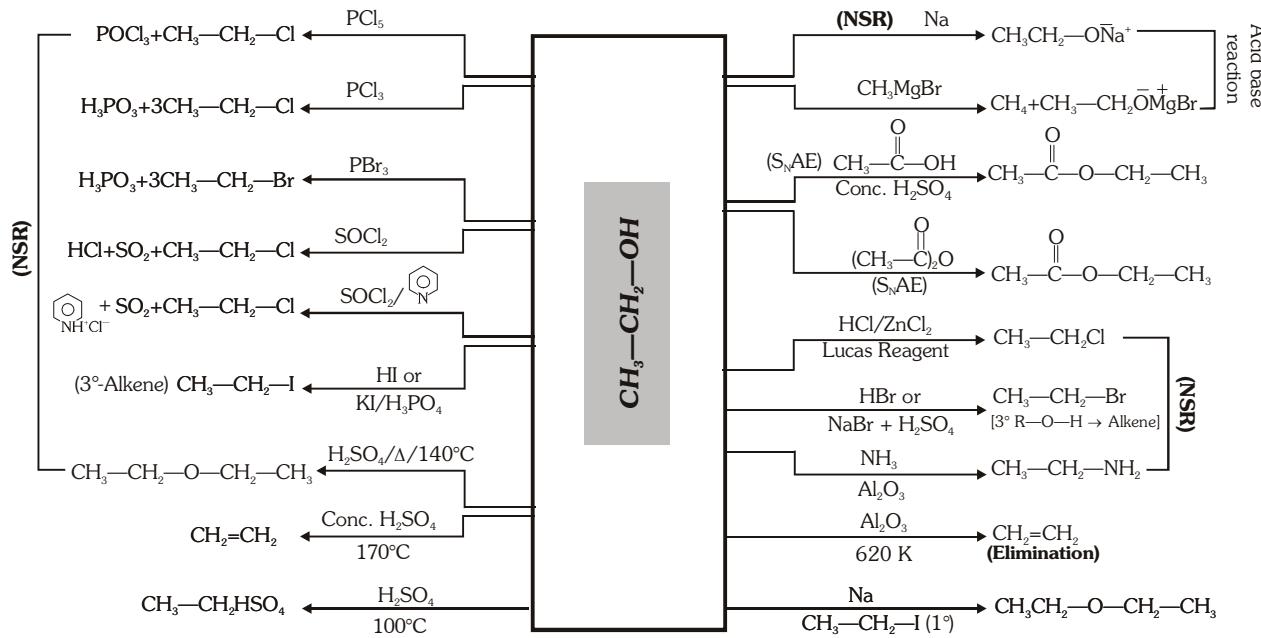
GRIGNARD REAGENT**REACTION****GRIGNARD REAGENT as Nucleophile****GRIGNARD REAGENT as BASE
(Active H-containing compound)**

IMPORTANT NOTES



ALCOHOL

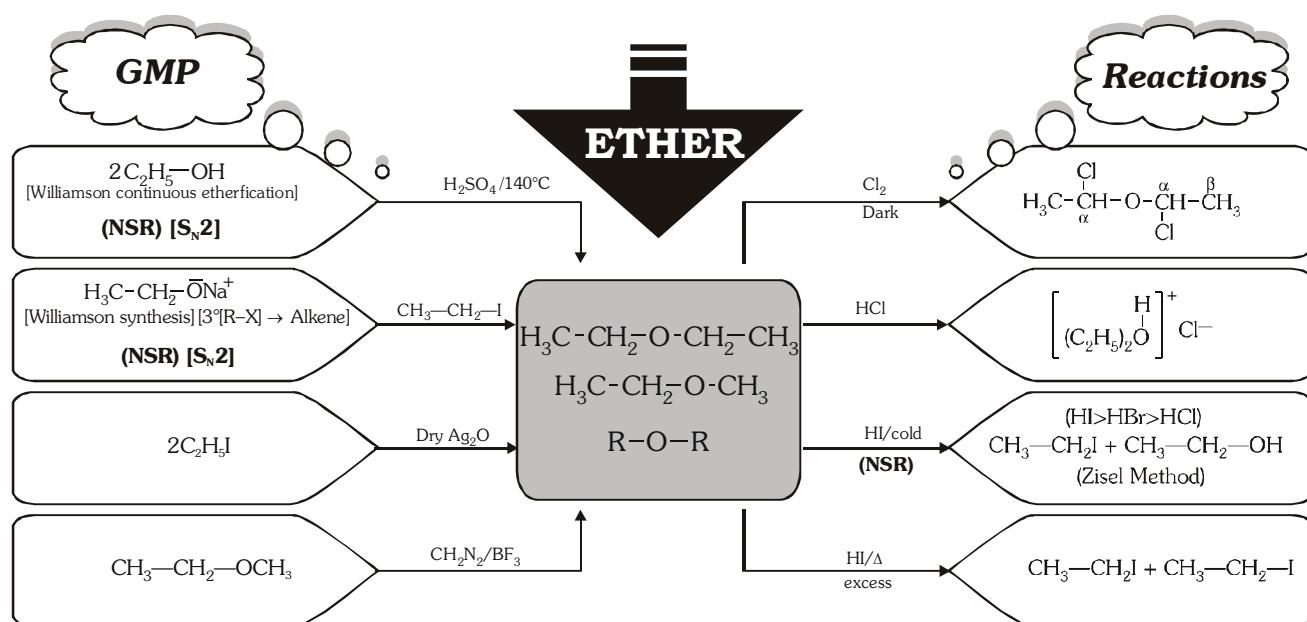
- Solubility of alcohol increase with increase in branching $n < \text{iso} < \text{neo}$ (isomeric)
- Relative order of reactivity
 - (i) $1^\circ > 2^\circ > 3^\circ$ (O-H bond fission)
 - (ii) $3^\circ > 2^\circ > 1^\circ$ (C-O bond fission)
 - (iii) $3^\circ > 2^\circ > 1^\circ$ (Dehydration)

ALCOHOL**DEHYDROGENATIONS**

Reagent	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$ 1° Alcohol	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{CH}-\text{CH}_3$ 2° Alcohol	$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OH}$ 3° Alcohol
PCC/PDC Anhy. CrO_3	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{H}$	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{CH}_3$	No reaction
$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^\oplus$ $\text{KMnO}_4/\text{H}^\oplus/\text{OH}^-/\Delta$ Jones Reagent	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{OH}$	$\text{H}_3\text{C}-\overset{\text{O}}{\text{C}}-\text{OH} + \text{CH}_3-\overset{\text{O}}{\text{C}}-\text{OH}$	No reaction
$\text{Cu}/500^\circ\text{C}$	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{H}$	$\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{CH}_3$	$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}=\text{CH}_2$
Lucas Reagent HCl/ZnCl_2	Cloudiness appear upon heating after 30 mins.	within five min.	Immediately

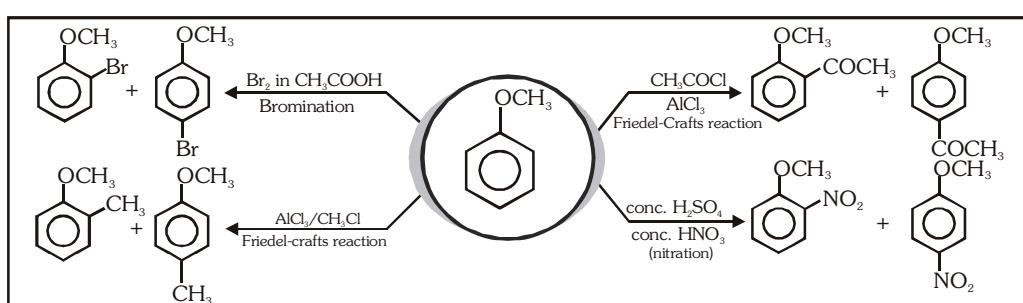
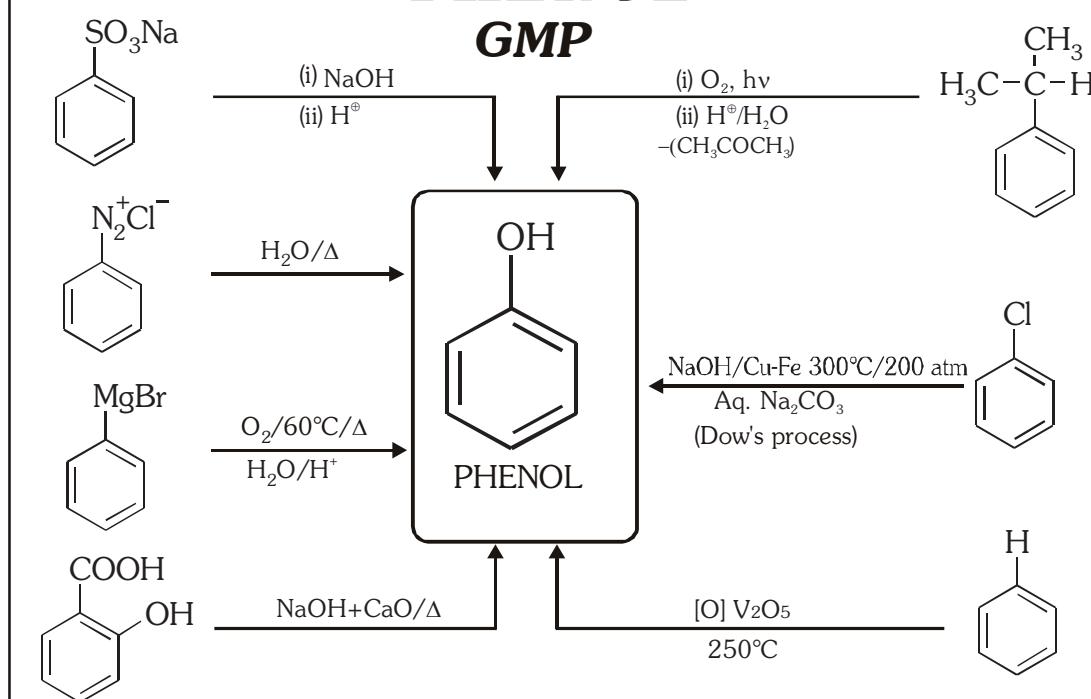
VICTOR MAYER'S TEST

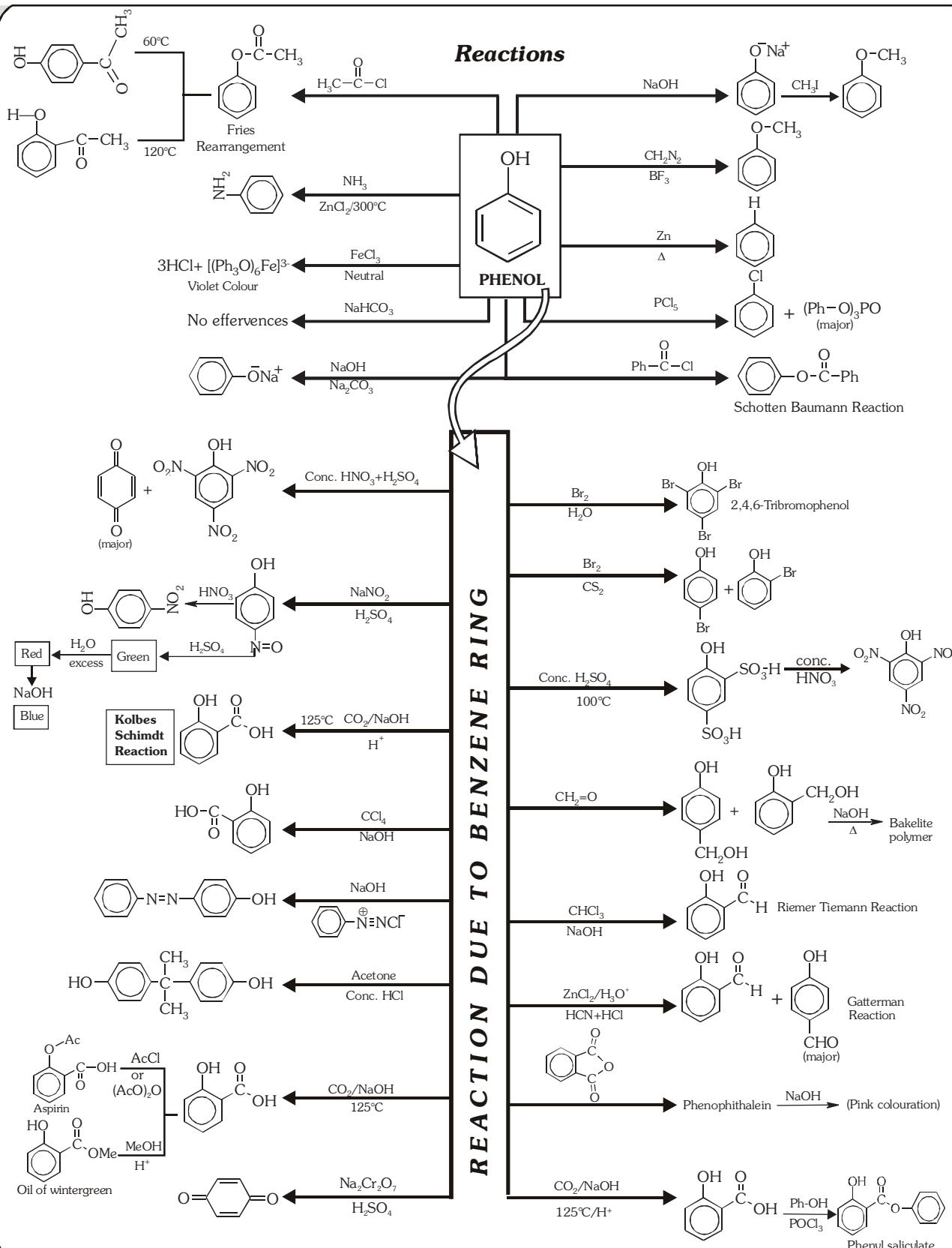
P/I_2	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I}$	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{I}}{\text{C}}}-\text{I}$	$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{I}$
AgNO_2	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NO}_2$	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{NO}_2}{\text{C}}}-\text{NO}_2$	$(\text{CH}_3)_3\text{C}-\text{NO}_2$
HNO_2	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{N}=\text{O}}{\underset{\text{OH}}{\text{C}}}-\text{NO}_2$ Nitrolic acid	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{N}=\text{O}}{\text{C}}}-\text{NO}_2$ Blue colour	No reaction : Colourless
NaOH	Red Color	No reaction	



PHENOL

GMP



PHENOL

Comparision of S_N1 and S_N2

REACTIONS		S_N1	S_N2
A	Kinetics	1 st order	2 nd order
B	Rate	$k[RX]$	$k[RX][Nu:]^{\ominus}$
C	Stereochemistry	Racemisation	Inversion
D	Substrate (reactivity)	$3^\circ > 2^\circ > 1^\circ > MeX$	$MeX > 1^\circ > 2^\circ > 3^\circ$
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	1 st order	2 nd order
B	Rate	$k[RX]$	$k[RX][B:^-]$
C	Stereochemistry	No special geometry	Anti-periplanar
D	Substrate	$3^\circ > 2^\circ >>> 1^\circ$	$3^\circ > 2^\circ > 1^\circ$
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, E₁ and E₂ Reactions

Order of reactivity of

RX	Mechanism	Nu/B	Solvent	Temp.
1°	$\text{S}_{\text{N}}2$	Better $\text{OH}, \text{C}_2\text{H}_5\text{O}$	Polar aprotic	Low
	E2	Strong & bulky base $(\text{CH}_3)_3\text{CO}$		High
2°	$\text{S}_{\text{N}}2$	$\text{HO}; \text{C}_2\text{H}_5\text{O}$	Polar aprotic	Low
	E2	$(\text{CH}_3)_3\text{CO}$		High
	($\text{S}_{\text{N}}1$)	(Solvent)	Polar aprotic	(Low)
	(E1)	(Solvent)		(High)
3°	$\text{S}_{\text{N}}1$	Solvent	Protic	Low
	E1	Solvent	Protic	High

S.1 \propto Benzylic > Allylic > 3° > 2° > 1°

S. 1 & Stability of carbocation

S 2 \times 1° \geq 2° \geq 3°

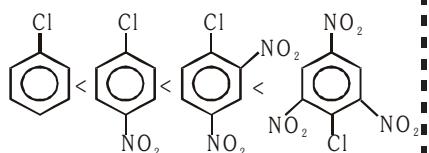
$$C \frac{1}{\text{Steric hindrance}}$$

Reactivity order towards

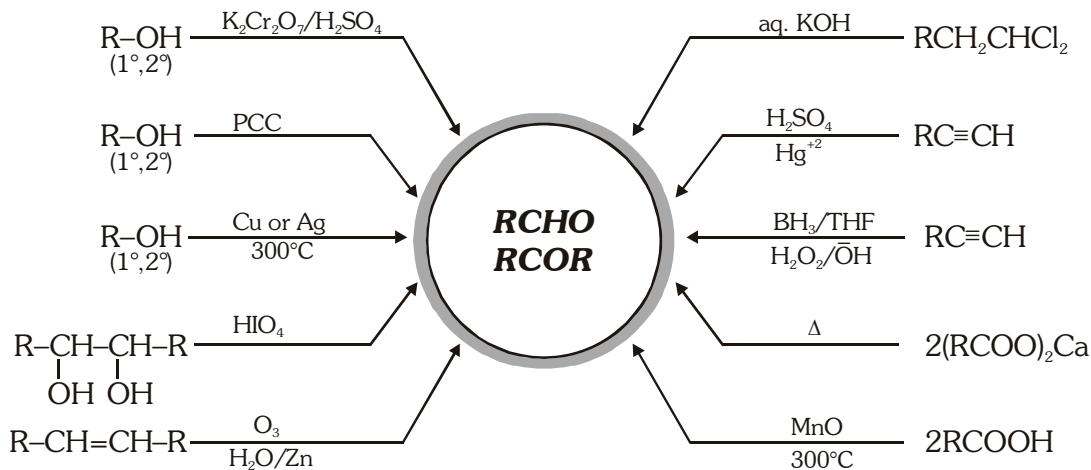
S₁ or **S₂** and **E₁** or **E₂**

$$R-I > R-Br > R-Cl > R-F$$

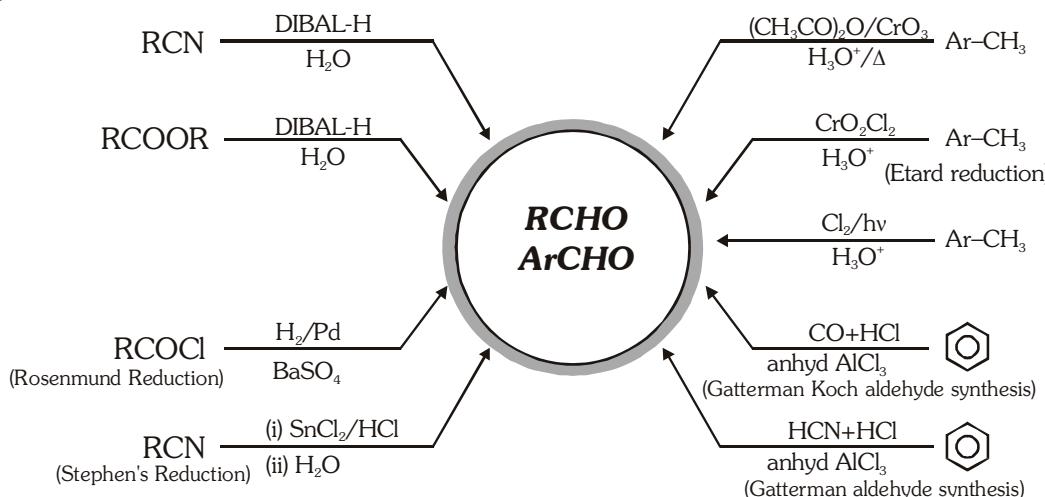
With increase in number of strong electron withdrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitution increases.



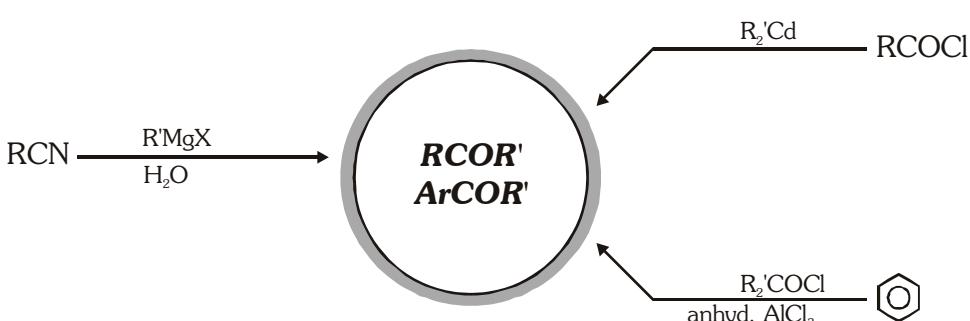
Preparation of Aldehyde & Ketone both



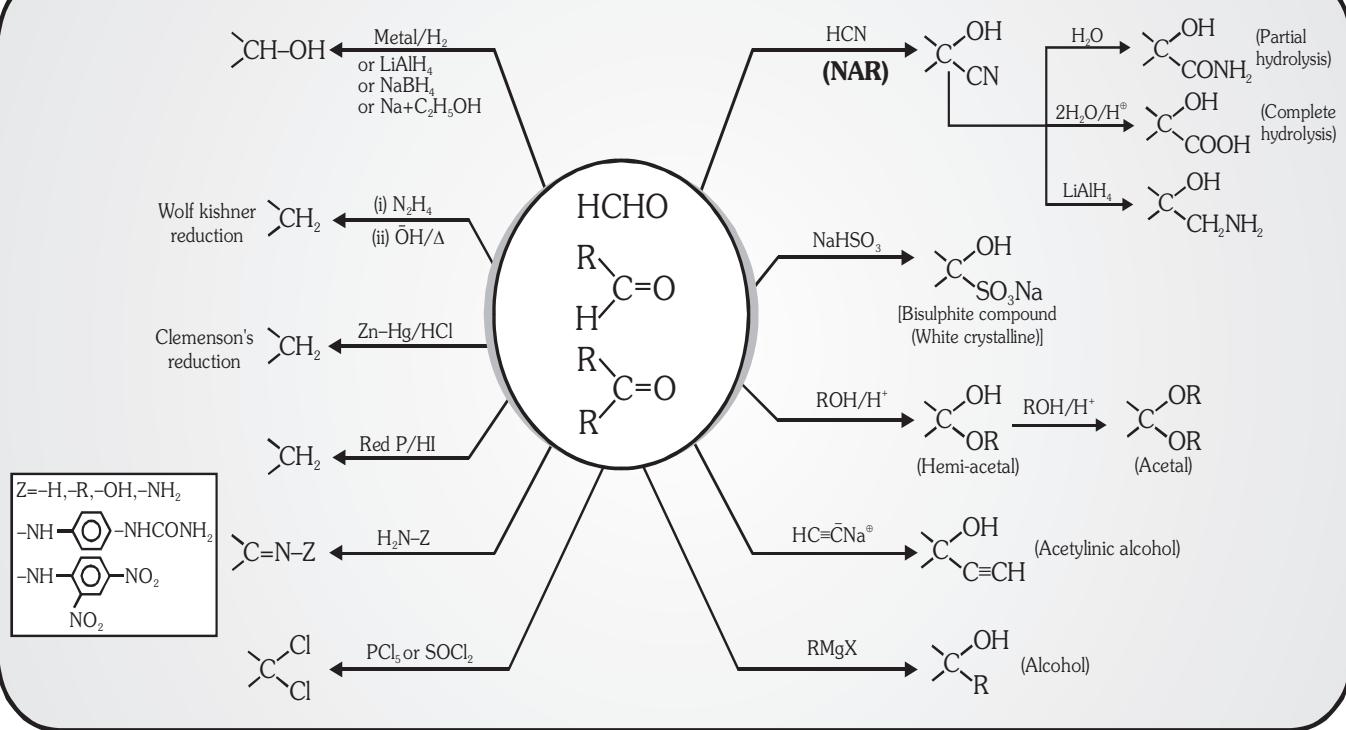
Preparation of Aldehyde only



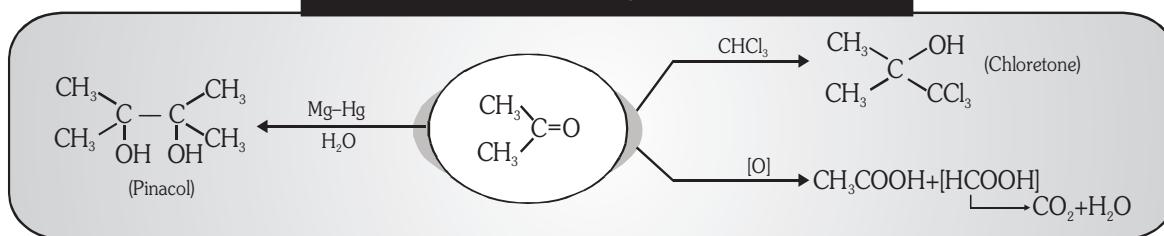
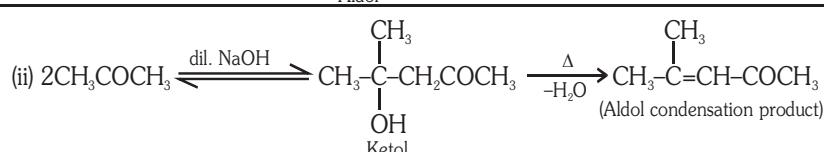
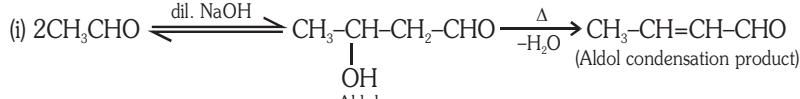
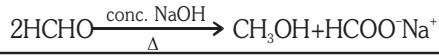
Preparation of Ketone only



Reaction of Aldehyde & Ketone

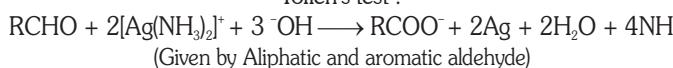


Reaction of only Ketone

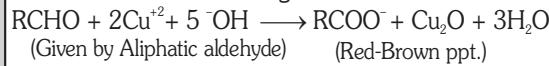
Aldol Reaction (Aldehyde or ketone with α H)Cannizzaro reaction (Aldehyde with no α H)

TESTS

Tollen's test :-



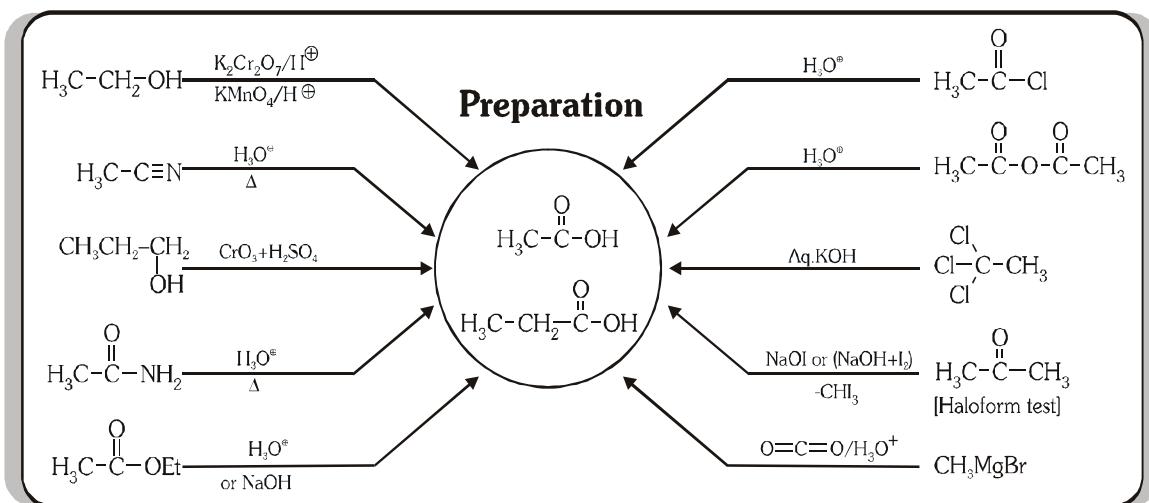
Fehling's test



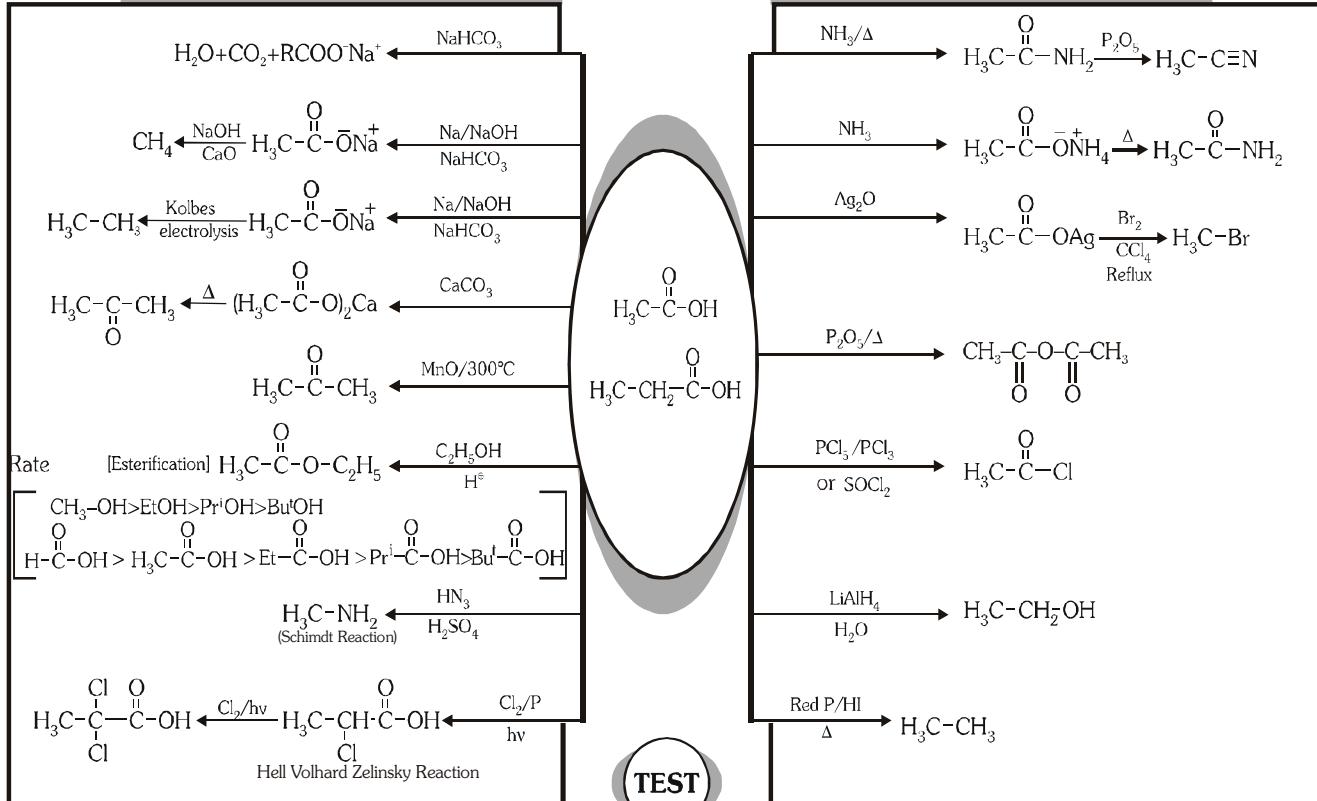
IMPORTANT NOTES



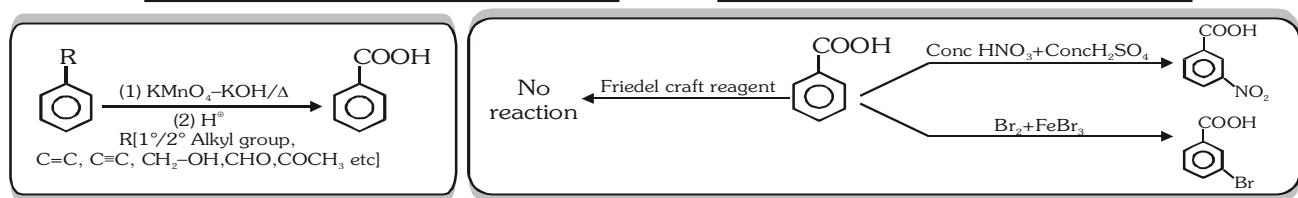
CARBOXYLIC ACID

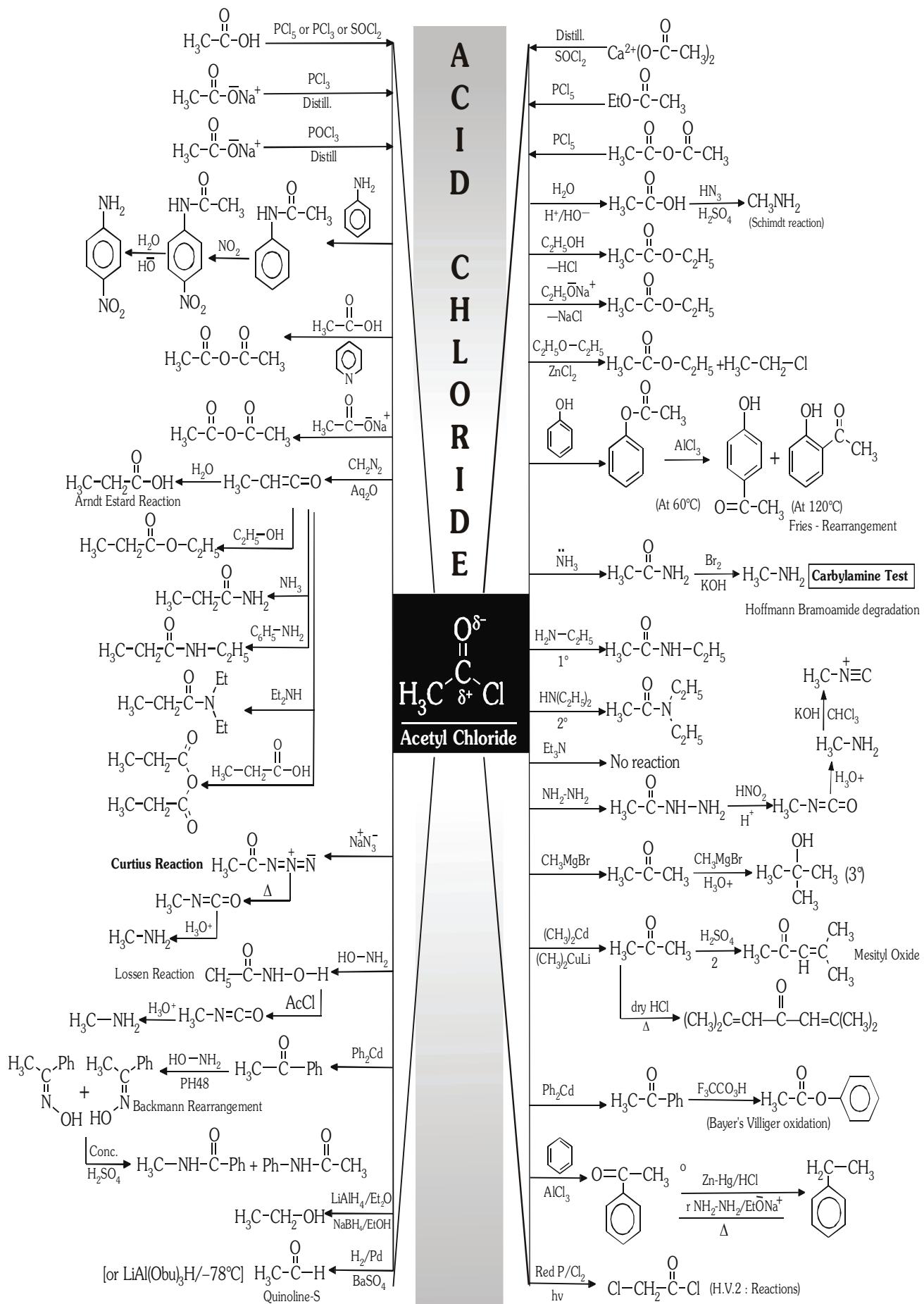


Reactions

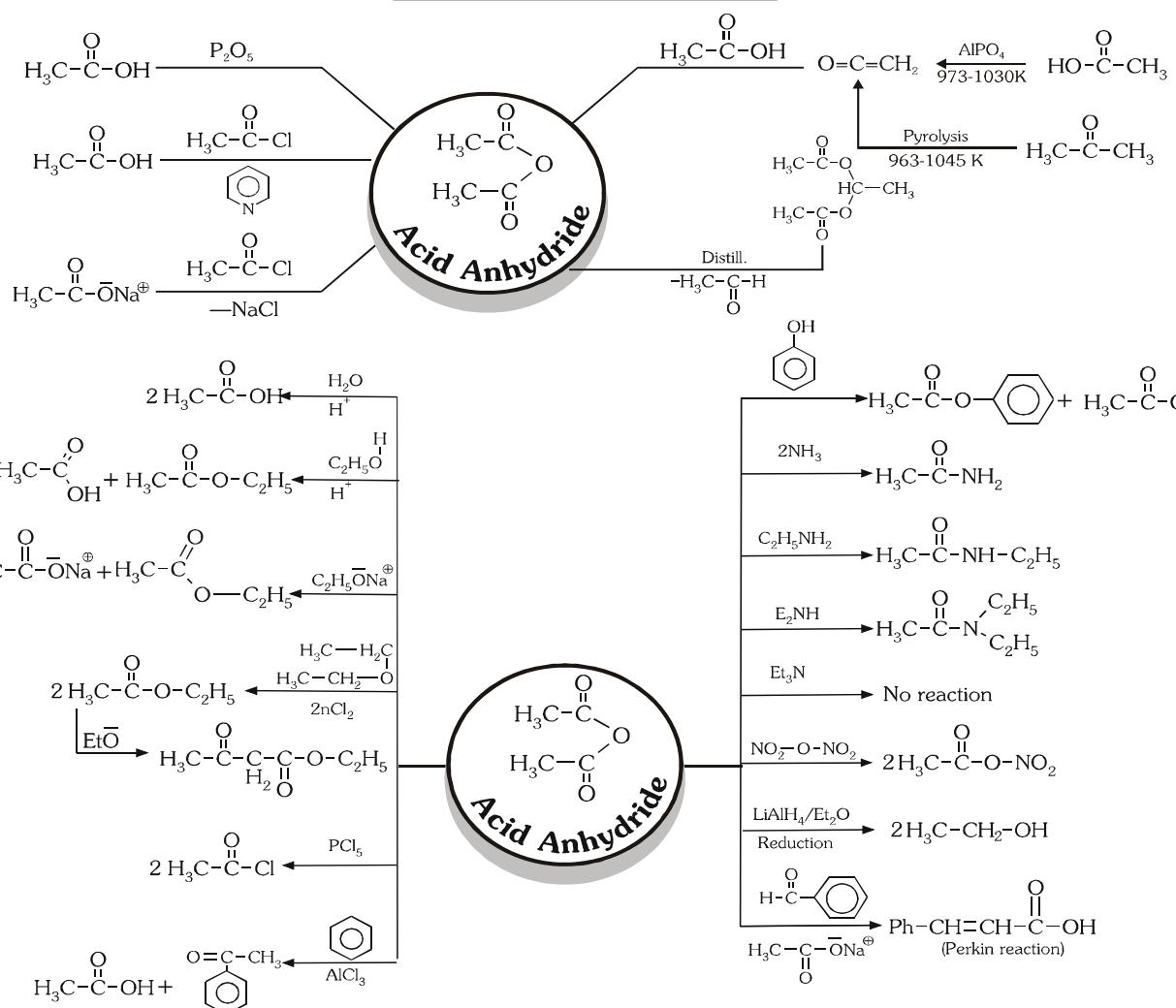


TEST

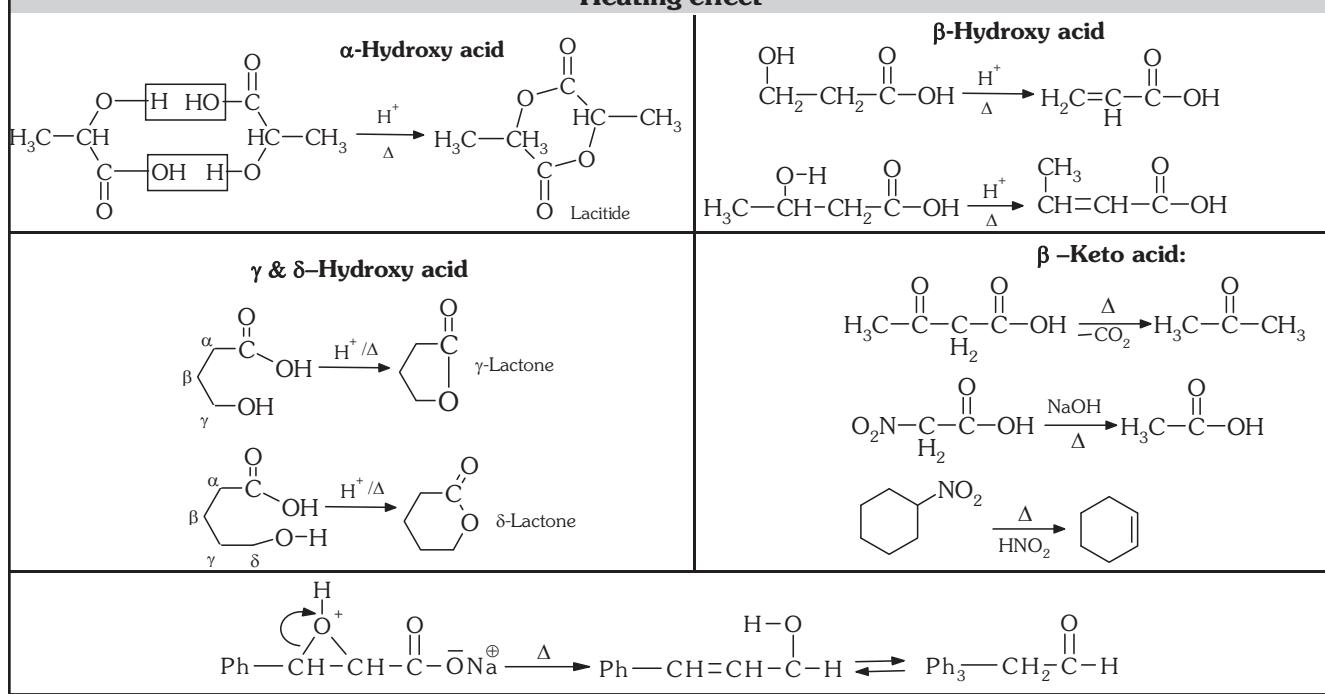




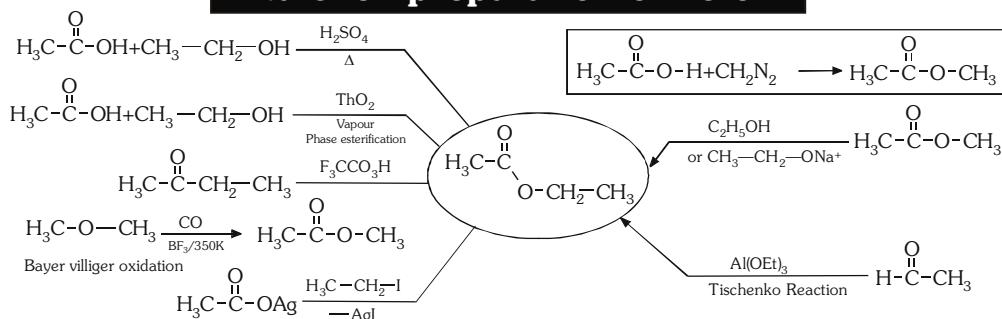
ACID anhydride



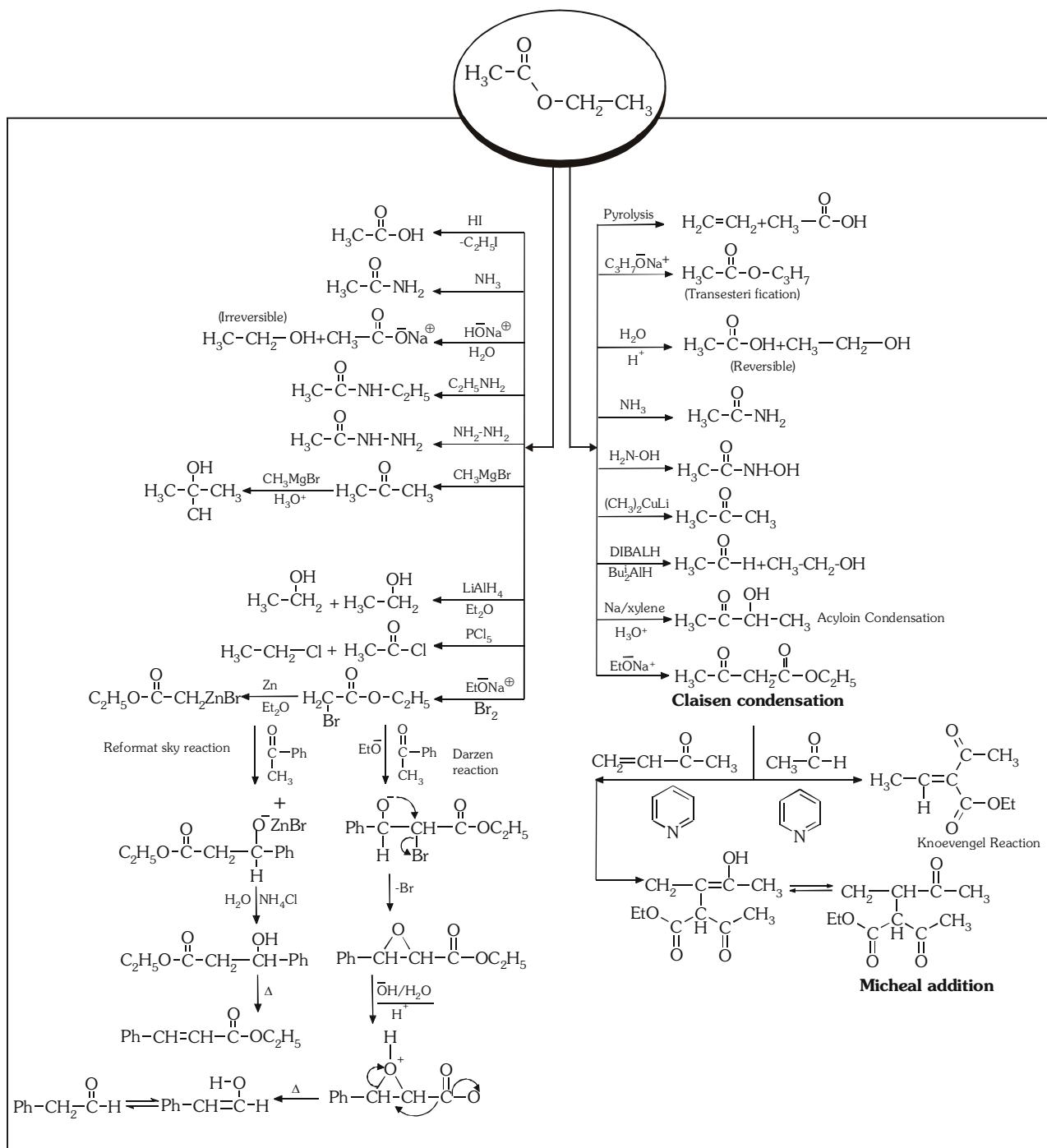
Heating effect



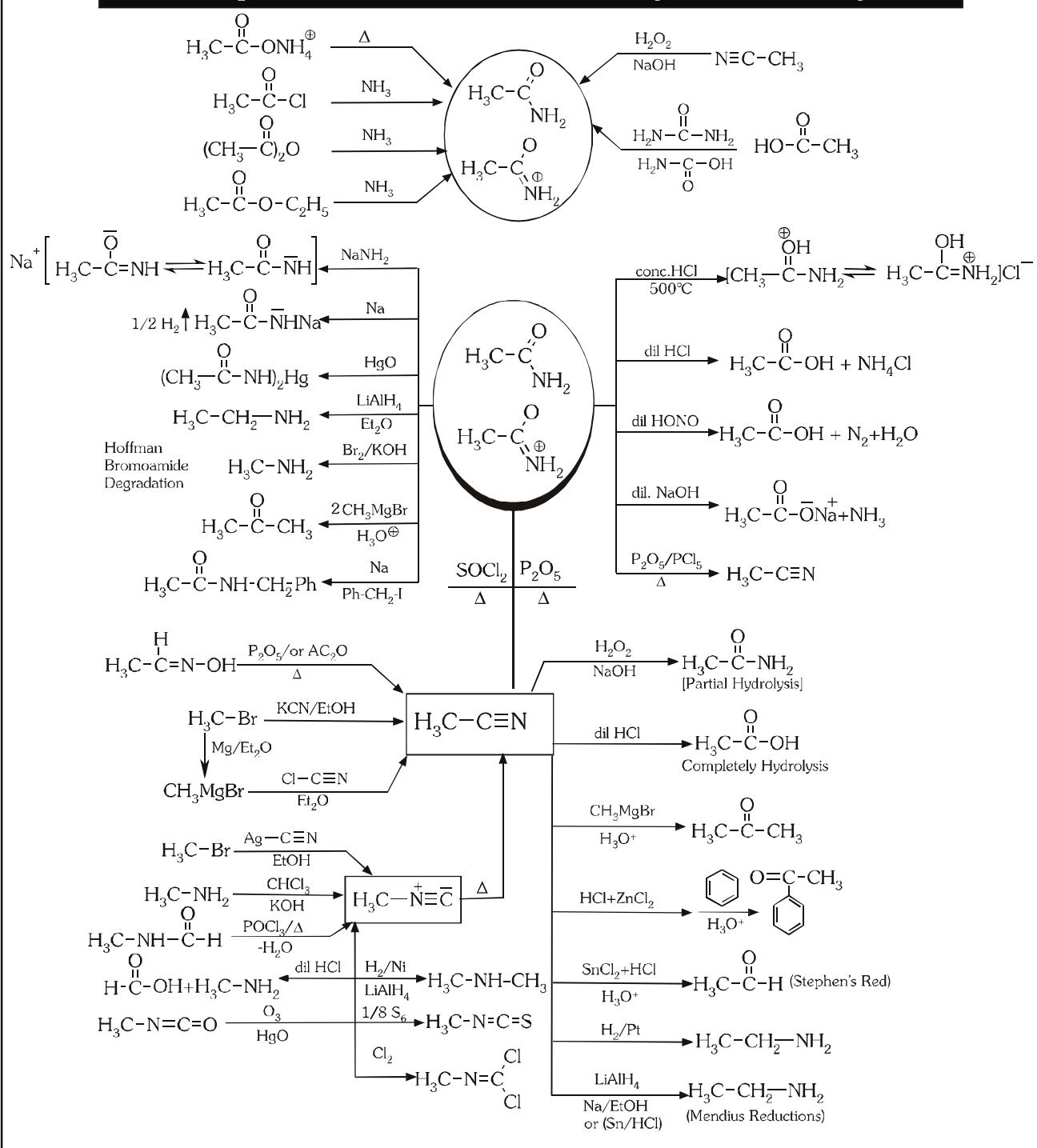
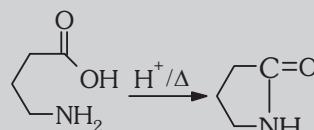
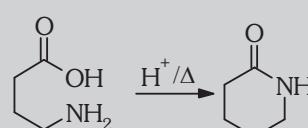
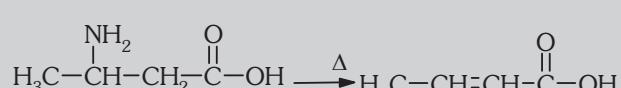
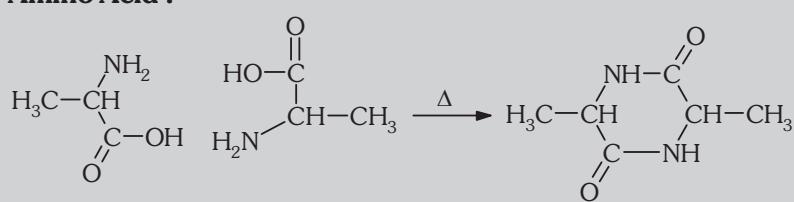
Nutshell preparation of Ester



Nutshell chemical properties of Ester

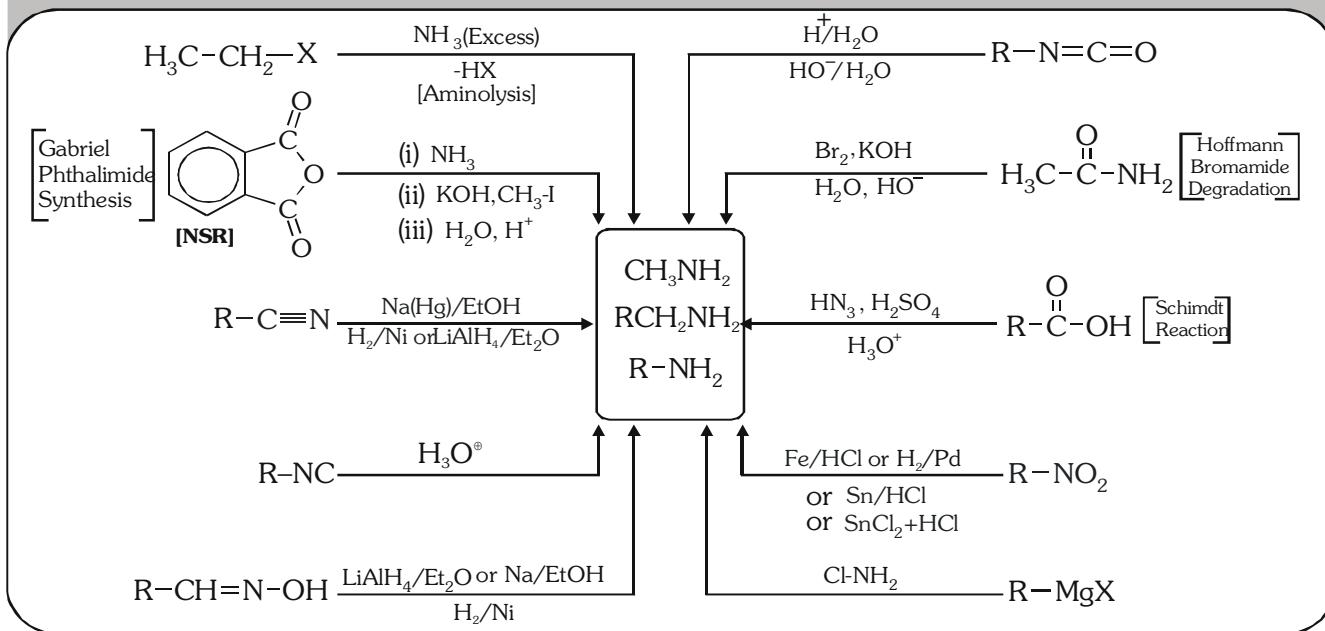
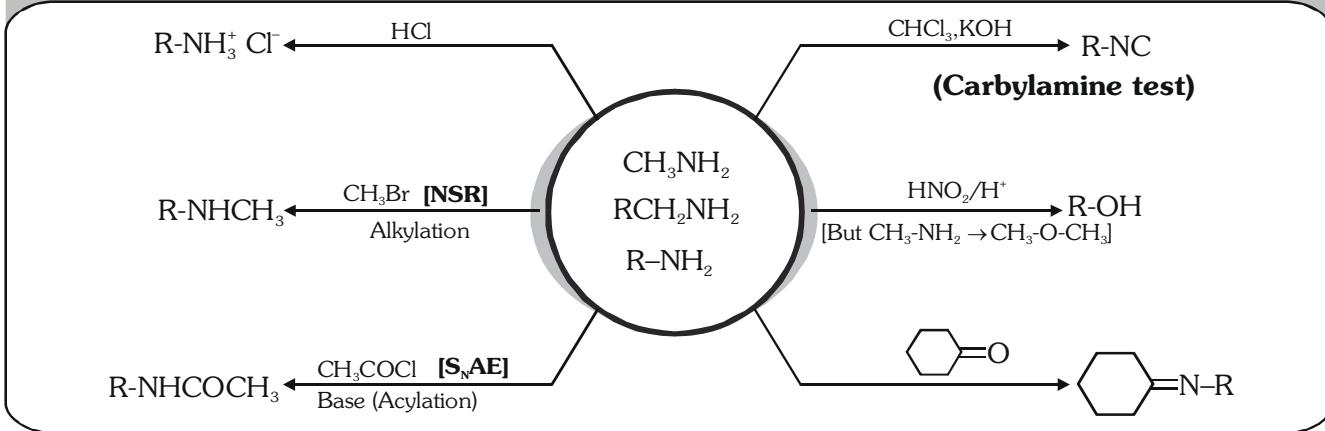


Nutshell preview and review of Amide, Cyanide and Isocyanide

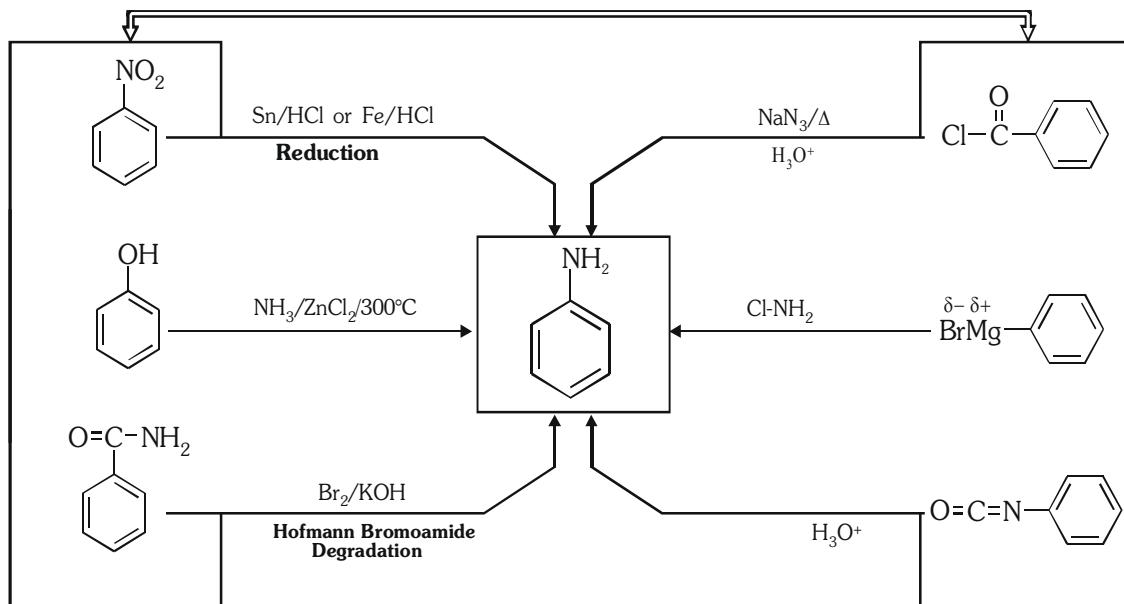
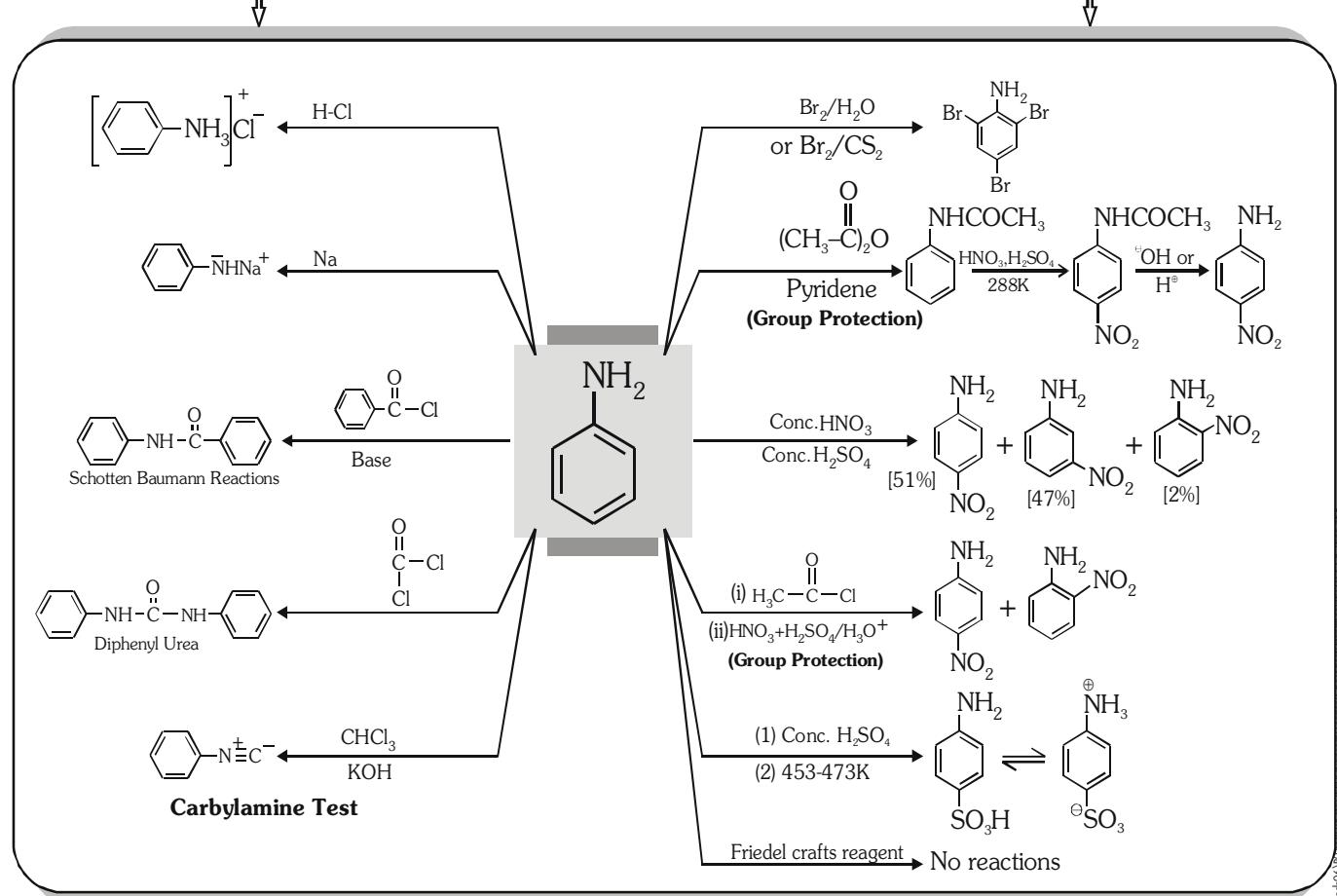
**Amino Acid :**

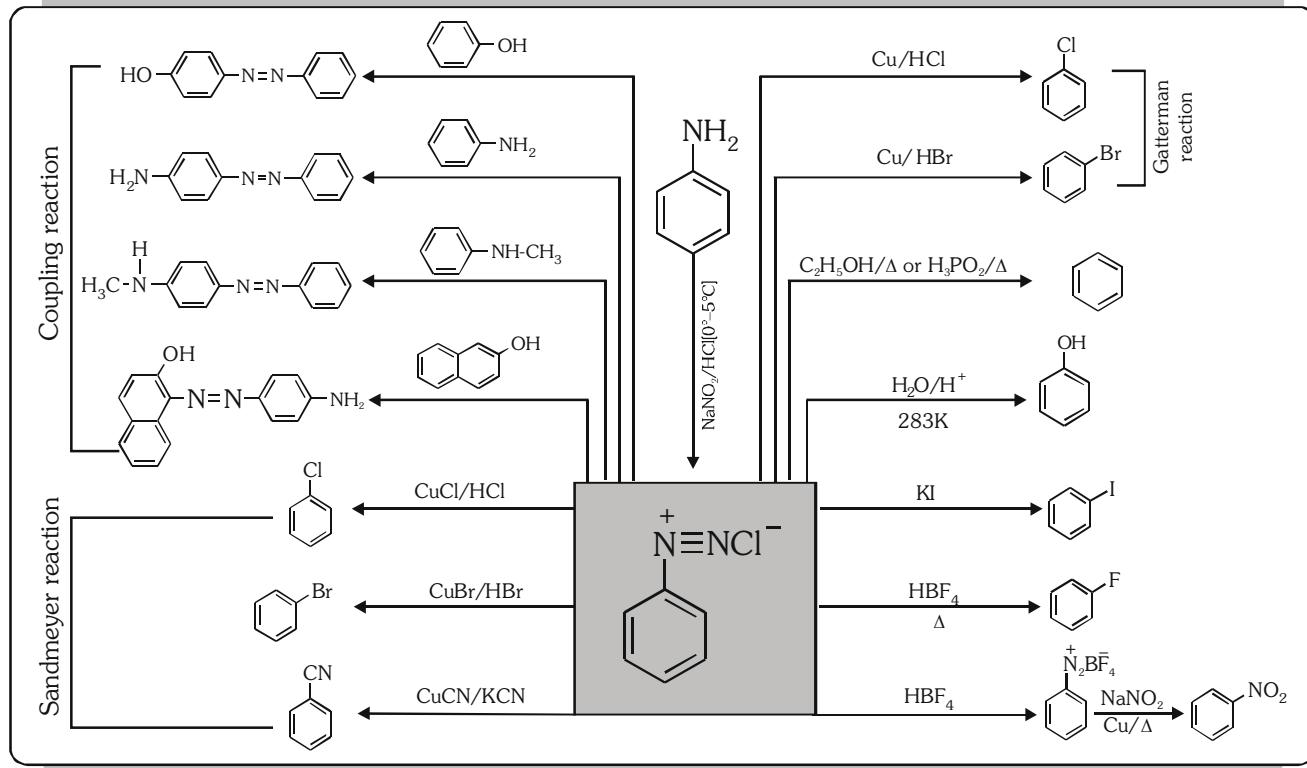
IMPORTANT NOTES



AMINES**PREPARATION****REACTION****TEST**

Reagent	$\text{R}-\ddot{\text{N}}\text{H}_2$ (1°)	$\text{R}_2\ddot{\text{N}}\text{H}$ (2°)	$\text{R}_3\ddot{\text{N}}$ (3°)	
$\text{Ph-SO}_2\text{Cl}$ (Hinsberg reagent)	$\text{R}-\overset{\text{H}}{\underset{\downarrow}{\text{N}}}-\text{SO}_2-\text{Ph}$ soluble $\downarrow \text{NaOH}$ $[\text{R}-\text{N}-\text{SO}_2-\text{Ph}]\text{Na}^+$	$\text{R}_2\overset{\text{O}}{\underset{\downarrow}{\text{N}}}-\text{S}-\text{Ph}$ $\downarrow \text{NaOH}$ Insoluble	No reaction	
$\text{S}\equiv\text{C=S}$ Δ/HgCl_2 Mustard oil test	$\text{R}-\text{NH}-\overset{\text{S}}{\underset{\Delta}{\text{C}}}-\text{SH}$ $\text{HgCl}_2 \Delta$ $\text{R}-\text{N}=\text{C=S}+\text{HgS}$	$\text{R}_2\overset{\text{S}}{\underset{\Delta}{\text{N}}}-\text{C}-\text{SH}$ $\text{HgCl}_2 \Delta$ No reaction	No reaction	$\text{KOH} \rightarrow \text{Ph}-\text{N}=\text{C=S}+\text{HgS}$

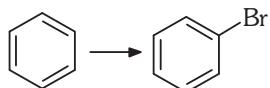
ANILINE**PREPARATION****REACTION**

BENZENE DIAZONIUM CHLORIDE**REACTION**

FrSR	Free Radical Substitution reaction
ESR	Electrophilic Substitution reaction
NSR	Nucleophilic Substitution reaction
S _N AE	Substitution Nucleophilic (addition elimination)
FrAR	Free radical addition reaction
NAR	Nucleophilic addition reaction
EAR	Electrophilic addition reaction
FrER	Free Radical Elimination reaction

IMPORTANT NOTES



18. $\text{Fe} + \text{Br}_2/\text{FeBr}_3$ **19. Fehling solution**

used to identify $-\text{CH}=\text{O}$ group.

PhCHO gives -ve test

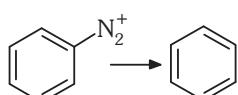
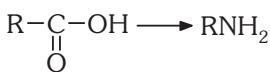
Observation: red ppt of Cu_2O formed

20. Grignard Reagent

Follows (i) Acid base reaction (ii) NAR (iii) NSR

21. $\text{H}_2(\text{Pd}/\text{CaCO}_3)$ Quinoline (Lindlar catalyst)

$\text{R}-\text{C}\equiv\text{C}-\text{R} \rightarrow \text{R}-\text{CH}=\text{CH}-\text{R}$ (cis)

22. H_3PO_2 **23. $\text{HN}_3 + \text{H}_2\text{SO}_4$** 

(Schmidt Reaction)

24. $\text{H}_3\text{PO}_4/\Delta$

$\text{H}_3\text{PO}_4 \Rightarrow$ Same as $\text{H}_2\text{SO}_4/\Delta$

25. $\text{H}_2\text{SO}_4/\Delta$ 

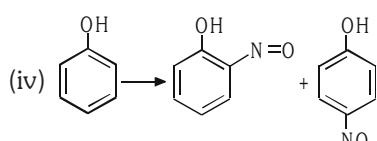
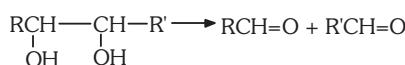
Saytzeff product; C^+ mechanism;
Rearranged alkene can be formed

26. HNO_2 ($\text{NaNO}_2 + \text{HCl}$)

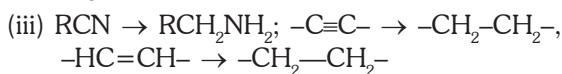
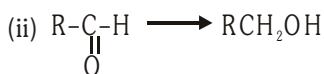
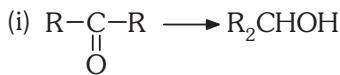
(i) $\text{RNH}_2 \rightarrow \text{R}-\text{OH}$;

(ii) $\text{PhNH}_2 \rightarrow \text{PhN}_2^+$ ($0 - 5^\circ\text{C}$)

(iii) $\text{PhNH}_2 \rightarrow \text{PhOH}$ (high temperature)

**27. HIO_4 (Periodic acid)**

Oxidative cleavage of diol

28. $\text{H}_2(\text{Ni})$ can reduce**29. $\text{H}_2(\text{Pd}/\text{BaSO}_4)$**

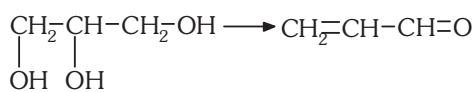
Quinoline



O (Rosenmund reduction)

30. Jones Reagent ($\text{CrO}_3 + \text{dil. H}_2\text{SO}_4 + \text{acetone}$)

(i) $\text{RCH}_2\text{OH} \rightarrow \text{RCH}=\text{O}$; (ii) $\text{R}_2\text{CHOH} \rightarrow \text{R}_2\text{C}=\text{O}$

31. KHSO_4 Dehydrating Reagent**32. $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$**

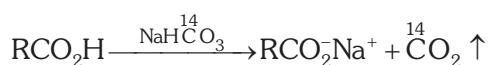
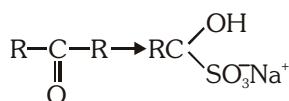
(i) $\text{RCH}_2\text{OH} \rightarrow \text{RCO}_2\text{H}$; (ii) $\text{R}_2\text{CHOH} \rightarrow \text{R}_2\text{C}=\text{O}$

33. MnO_2

(i) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{OH} \rightarrow \text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{O}$

(ii) $\text{PhCH}_2\text{OH} \rightarrow \text{PhCH}=\text{O}$

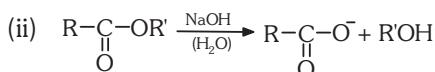
To oxidise allylic / benzylic hydroxyl group into corresponding carbonyl.

34. NaHCO_3 **35. NaHSO_3** 

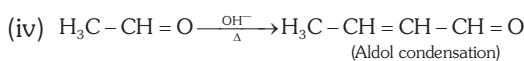
[White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]

36. NaOH(aq)

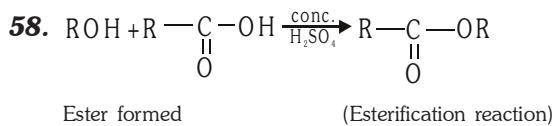
(i) $\text{R}-\text{X} \rightarrow \text{R}-\text{OH}$



Basic hydrolysis of ester



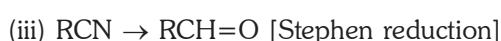
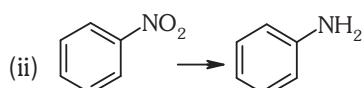
(Aldol condensation)



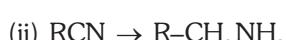
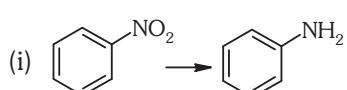
59. $\text{SnCl}_3 + \text{HCl}$

(Esterification reaction)

59. $SnCl_4 + HCl$



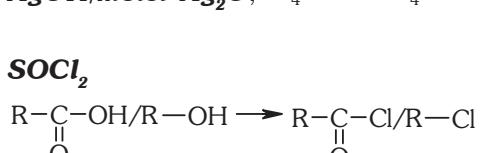
60. Sn + HCl



61. Silver salt $RCOOAg$ (Hunsdiecker reaction)



62. AgOH



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

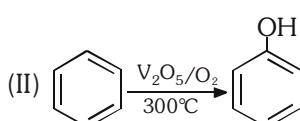
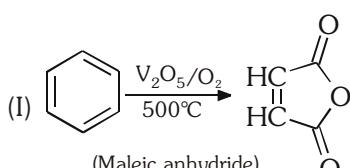
65. Benzene sulphonyl chloride

It is used to distinguish and separate (Hinsberg reagent) 1°, 2° and 3° amines.

66. Tetra ethyl lead (TEL)

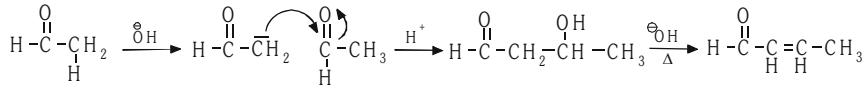
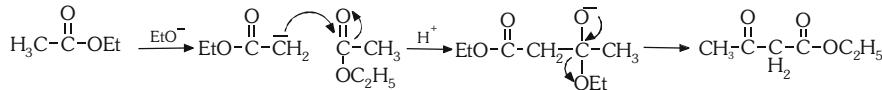
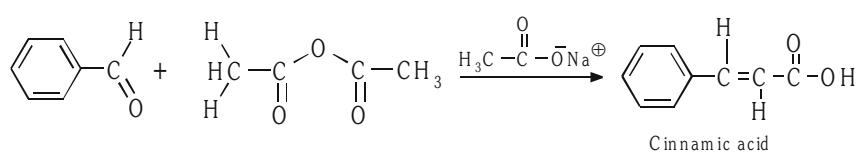
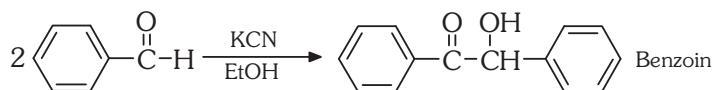
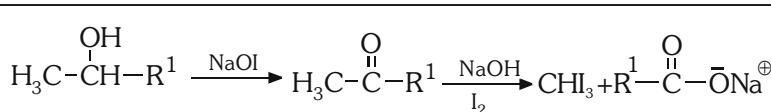
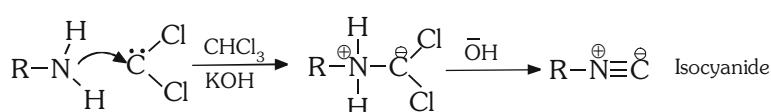
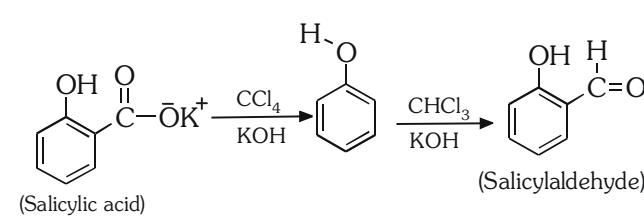
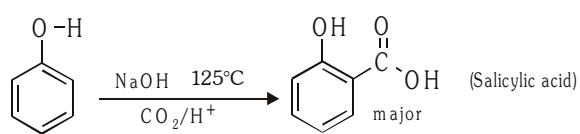
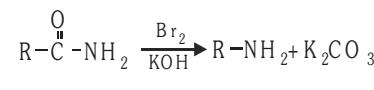
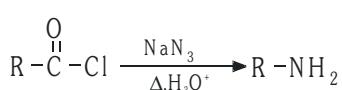
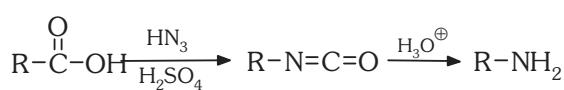
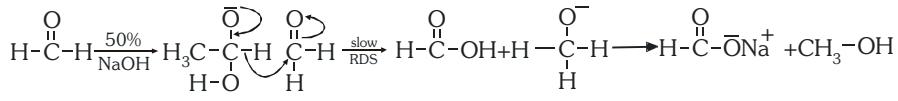
Used as antiknock compound

67. V_2O_5

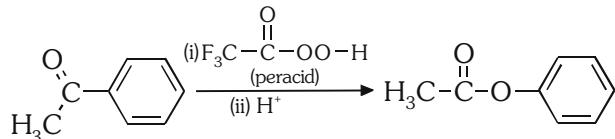


IMPORTANT NOTES

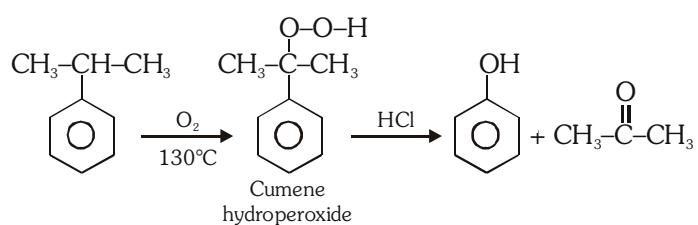
Nutshell review & preview of ORGANIC NAME REACTIONS

• Aldol Condensation	
• Claisen Condensation	
• Perkin Condensation	
• Benzoin Condensation	
• Haloform Reaction	
• Carbylamine Test	
• Reimer Tiemann Reaction	
• Kolbe's Schmidt Reaction	
• Hoffmann Bromamide Degradation	
• Curtius Reaction	
• Schmidt Reaction	
• Cannizzaro reaction	

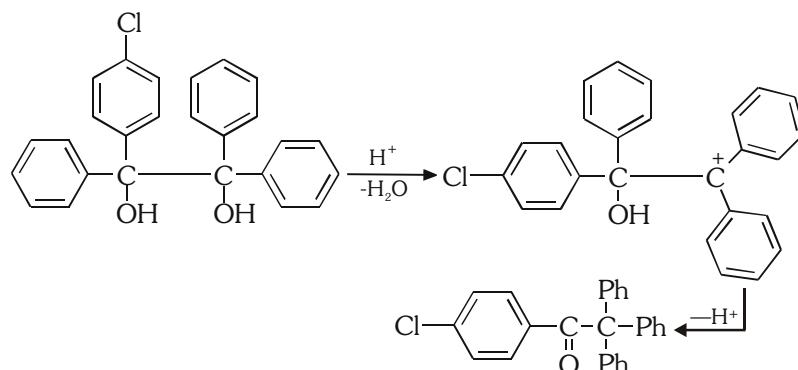
• **Bayer villiger oxidation**



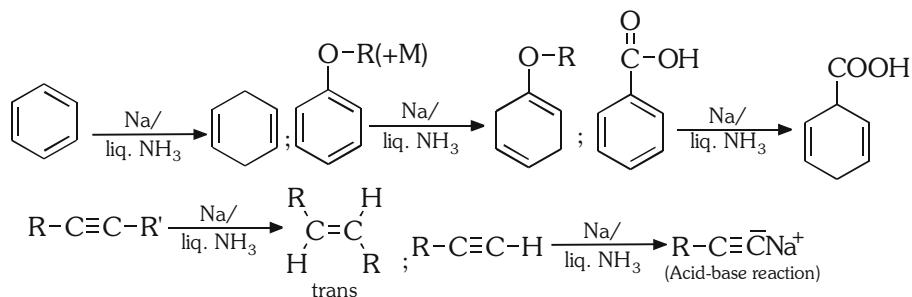
• **Cumene**



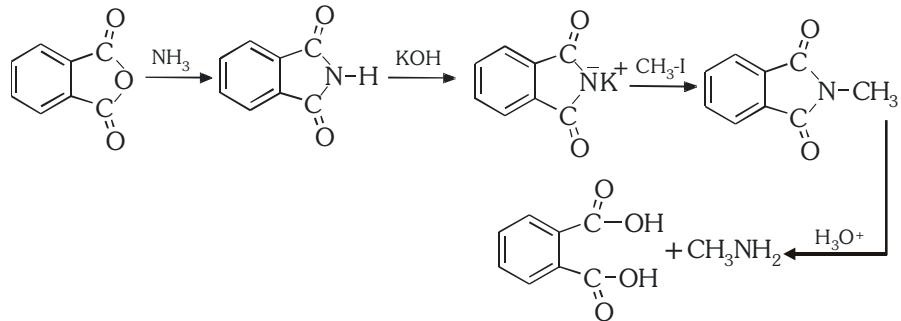
• **Pinacol-Pincolone rearrangement**



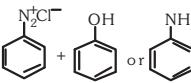
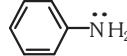
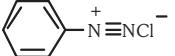
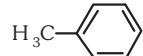
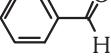
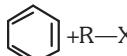
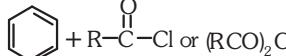
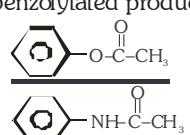
• **Birch Reduction**



• **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 ₂ Cl ₂ /CS ₂	 (Benzaldehyde)
Fittig Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation		Anhydrous AlCl ₃	Alkyl Benzene
Friedel Craft acylation		Anhydrous AlCl ₃	Acyl Benzene
Gattermann aldehyde synthesis	C ₆ H ₆	HCN + HCl / ZnCl ₂ /H ₃ O ⁺	Benzaldehyde
Gattermann-Koch reaction	C ₆ H 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 /Δ	CH ₃ CH 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 ₂ H ₅ OH	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 ₆ H ₅ N ₂ ⁺ Cl ⁻	CuCl/HCl or CuBr/HBr or CuCN/KCN, heat	Halo or cyanobenzene
Gattermann Reaction	C ₆ H ₅ N ₂ ⁺ Cl ⁻	Cu/HX(HBr/HCl)	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	NaOH + C ₆ H ₅ COCl	benzoylated product 
Stephen reaction	alkyl cyanide	(i) SnCl ₂ /HCl (ii) H ₂ O	Aldehyde
Williamson synthesis	alkyl halide	sodium alkoxide or sodium phenoxide	Ether
Wurtz-Fittig reaction	alkyl halide + aryl halide	Na/dry ether	alkyl benzene

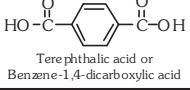
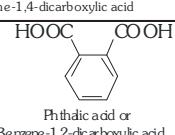
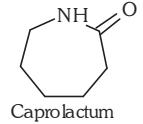
IMPORTANT NOTES

POLYMERS

ADDITION POLYMERS

S.No	Name of Polymer	Starting Materials	Nature of Polymer
I. Polyolefins			
1.	Polyethylene or Polyethene	$\text{CH}_2=\text{CH}_2$	Low density homopolymer (branched chain growth)
2.	Polypropylene or Polypropene	$\text{CH}_3\text{CH}=\text{CH}_2$	Homopolymer, linear, chain growth
3.	Polystyrene	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	Homopolymer, linear, chain growth
II. Polydienes			
1.	Neoprene	$\text{CH}_2=\text{CH}-\overset{\text{Cl}}{\underset{\text{C}}{\text{C}}}-\text{CH}_2$ Chloroprene or 2-Chloro-1,3-butadiene	Homopolymer, chain growth
2	Buna S (Styrene-Butadiene, Rubber) SBR or GRS	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (and) $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ 1,3-butadiene Styrene	Copolymer, chain growth
III. Polyacrylates			
1.	Polymethylmethacrylate (Flexiglass) Lucite, Acrylite or Perspex PMMA	$\text{CH}_3\text{C}(\text{CH}_3)=\text{C}-\text{COOCH}_3$	Homopolymer
2.	Polyethylacrylate	$\text{H}_2\text{C}=\text{CH}-\text{COOC}_2\text{H}_5$	Homopolymer
3.	Polyacrylonitrile or Orlon PAN	$\text{CH}_2=\text{CH}-\text{CN}$	Homopolymer
IV. Polyhalofins			
1.	Polyvinyl chloride PVC	$\text{CH}_2=\text{CH}-\text{Cl}$	Homopolymer, chain growth
2.	Polytetrafluoroethylene or Teflon PTFE	$\text{F}_2\text{C}=\text{CF}_2$	Homopolymer
3.	Polymonochlorotrifluoro-ethylene PCTFE	$\text{ClFC}=\text{CF}_2$	Homopolymer

CONDENSATION POLYMERS

S.No	Name of Polymer	Starting Materials	Nature of Polymer
I. Polyesters			
1.	Terylene or Dacron	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ 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	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ (and) Ethylene glycol  Phthalic acid or Benzene-1,2-dicarboxylic acid	Copolymer, linear step growth
II. Polyamides			
1.	Nylon-6,6	$\text{HO}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}(\text{CH}_2)_4-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{OH}$ (and) $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ Adipic acid Hexamethylenediamine	Copolymer, linear, step growth
2	Nylon-6,10	$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ (and) $\text{HOOC}(\text{CH}_2)_8\text{COOH}$ Hexamethylene diamine Sebacic acid	Copolymer, linear, step growth
3.	Nylon-6		Homopolymer, linear
Formaldehyde resins			
1.	Phenolformaldehyde resin or Bakelite	Phenol and formaldehyde	Copolymer, step growth
2.	Melamine formaldehyde resin	Melamine and formaldehyde	Copolymer, step growth

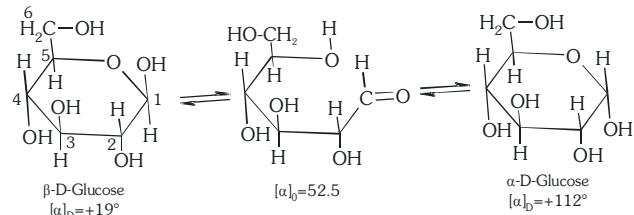
IMPORTANT NOTES

CARBOHYDRATES

- Carbohydrates 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 glycosidic 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.

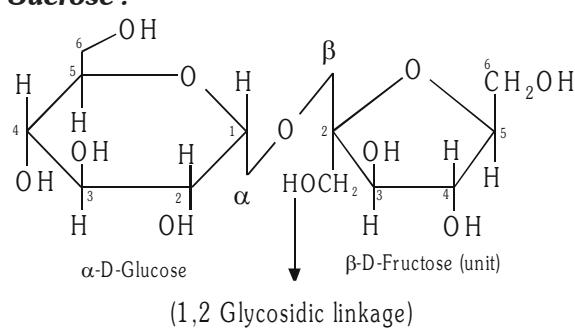
TYPE OF SUGAR		
Give Test	Reducing	Non Reducing
Tollen's Reagent	+ve test	-ve test
Fehling Reagent	+ve test	-ve test
Benedict Test	+ve test	-ve test
Mutarotation	Yes	No
Functional Unit	$\begin{array}{c} \text{---}\overset{\alpha}{\underset{\text{OH}}{\text{C}}}=\text{O} / \text{---}\overset{\text{O}}{\underset{\text{OH}}{\text{C}}}-\text{C}\text{---}$ 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 ($\pm 52.5^\circ$) is reached.

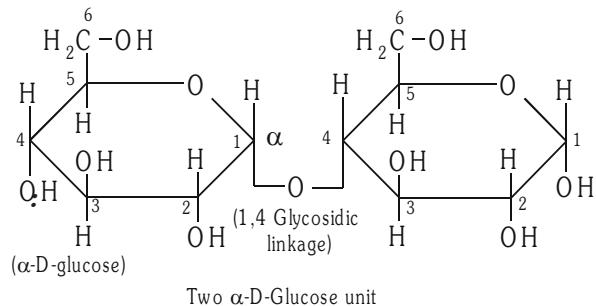


- Anomer's :** Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new-asymmetric carbon is referred to as Anomeric carbon.
- Epimer's :** Diastereomer's which differ in conformation at any one chiral carbon
 eg. D-Glucose & D-mannose
 D-Glucose & D-Galactose

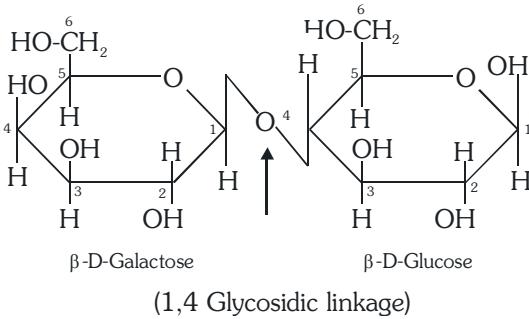
Sucrose :



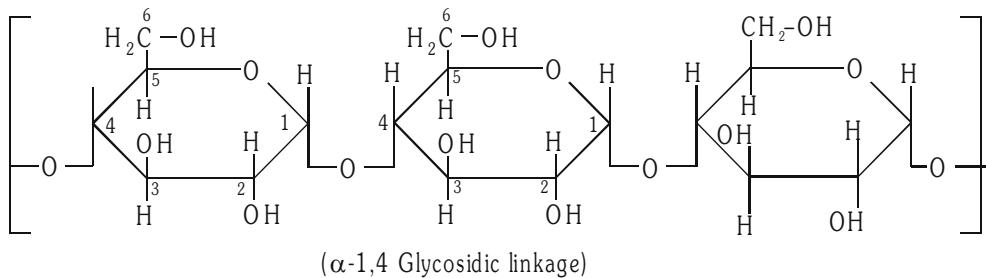
Maltose :



Lactose :

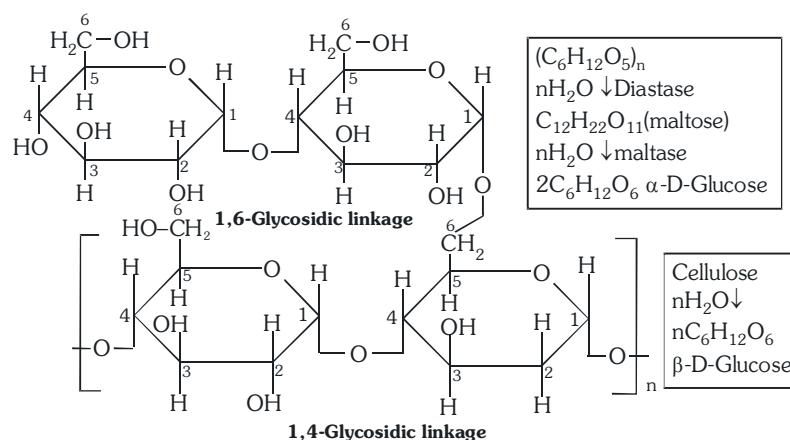


- **Starch** : (Amylose & Amylopectin)
- **Amylose** : (Straight Chain) :



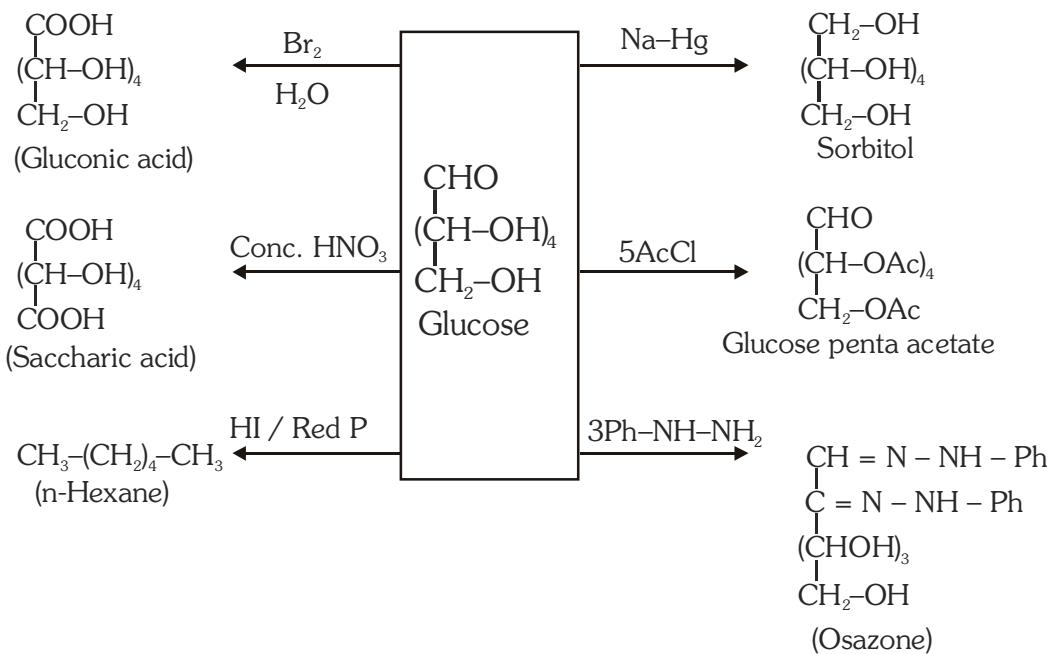
(i) Soluble in H_2O & gives blue colour with I_2

- **Amylopectin (Branch chain) : $(C_6H_{12}O_5)_n$**



REACTION OF GLUCOSE (OPEN CHAIN STRUCTURE)

* Fructose doesn't react with Br_2/H_2O



IMPORTANT NOTES

