CHAPTER

Some Basic Concepts of Chemistry

SOME USEFUL CONVERSION FACTORS

$$1 \text{ Å} = 10^{-10} \text{m}, 1 \text{nm} = 10^{-9} \text{ m}$$

$$1 \text{ pm} = 10^{-12} \text{m}$$

1 litre =
$$10^{-3}$$
 m³ = 1 dm³

1 atm = 760 mm or torr

$$= 101325 \text{ Pa or Nm}^{-2}$$

$$1 \text{ bar} = 10^5 \text{ Nm}^{-2} = 10^5 \text{ Pa}$$

1 electron volt(eV) = 1.6022×10^{-19} J

$$(1 J = 10^7 \text{ ergs})$$

$$(1 \text{ cal} > 1 \text{ J} > 1 \text{ erg} > 1 \text{ eV})$$

ATOMIC MASS OR MOLECULAR MASS

Mass of one atom or molecule in a.m.u.

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

$$NH_3 \rightarrow 17 amu$$

Actual Mass

Mass of one atom or molecule in grams

$$C \rightarrow 12 \times 1.6 \times 10^{-24} \text{ g}$$

$$CH_4 \to 16 \times 1.6 \times 10^{-24} \text{ g}$$

Relative Atomic Mass or Relative Molecular Mass

Mass of one atom or molecule w.r.t. 1/12th of ¹²C atom

$$C \rightarrow 12$$

$$CH_4 \rightarrow 16$$

It is unitless

GRAM ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one mole of atom or molecule

$$C \rightarrow 12 g$$

$$CO_2 \rightarrow 44 g$$

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

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

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

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

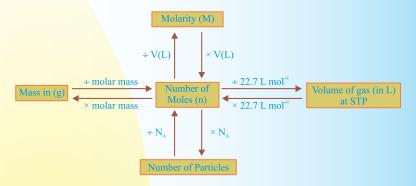
For Ionic Compounds

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

VAPOUR DENSITY

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

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



STOICHIOMETRY BASED CONCEPT

$$aA + bB \rightarrow cC + dD$$

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

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

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 Purity

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

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

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



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

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

For determination of atomic mass:

Dulong's & Petit's Law:

Atomic weight of metal × specific heat capacity (cal/gm- $^{\circ}$ 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.

CONCENTRATION TERMS

Concentration Type	Mathematical Formula	Concept
Percentage by mass	$\% \left(\frac{w}{w}\right) = \frac{\text{Mass of solute} \times \frac{100}{\text{Mass of solution}}$	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 cm³) present in 100 cm³ 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	$ppm = \frac{Mass of solute \times 10^6}{Mass of solution}$	Parts by mass of solute per million parts by mass of the solution



Concentration Type	Mathematical Formula	Concept
Mole fraction	$X_{A} = \frac{\text{Mole of A}}{\text{Mole of A + Mole of B + Mole of C +}}$ $X_{B} = \frac{\text{Mole of B}}{\text{Mole of A + Mole of B + Mole of C +}}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M = \frac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$	Moles of solute in one liter of solution.
Molality	$m = \frac{\text{Mole of solute}}{\text{Mass of solvent (Kg)}}$	Moles of solute in one kg of solvent

MIXING OF SOLUTIONS

It is based on law of conservation of moles.

(i) Two solutions having same solute:

Final molarity =
$$\frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

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

Volume Strenght of H₂O₂ Solutions

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

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

• Volume Strenght of H_2O_2 solution = 11.35 × molarity

PERCENTAGE LABELLING OF OLEUM

Labelled as '% oleum' means maximum amount of H₂SO₄ that can be obtained from 100 gm of such oleum (mixture of H₂SO₄ and SO₃) by adding sufficient water. For example, 109% oleum sample means, with the addition of sufficient water to 100 gm oleum sample 109 gm H₂SO₄ is obtained.

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

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

• % of free SO₃ in oleum =
$$\left(\frac{40}{9} \times x\right)$$
%



EUDIOMETRY

Some basic assumptions related with calculations are:

 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.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

1 vol. 3 vol. 2 vol.

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

The stoichiometric coefficients of a balacned 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.

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

2 mole 1 mole 2 mole
2 vol. 1 vol. 0 vol.

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

Solvent	Gases absorb
КОН	CO ₂ , SO ₂ , Cl ₂
Ammonical Cu ₂ Cl ₂	СО
Turpentine oil	O_3
Alkaline pyrogallol	O_2
water	NH ₃ , HCl
CuSO ₄ /CaCl ₂	H_2O





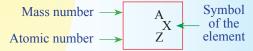


Atomic Structure

IMPORTANT DEFINITIONS

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

REPRESENTATION OF AN ELEMENT



Terms associated with elements:

- Atomic Number (Z): = No. of protons Electron = Z ± C (charge on atom)
- Mass number (A) = Total number of neutron and proton present
 A = Number of proton + Number of Neutrons
- Isotopes: Same atomic number but different mass number Example: ${}_{6}C^{12}$, ${}_{6}C^{13}$, ${}_{6}C^{14}$
- Isobars: Same mass number but different atomic number Example: 1H³, 2He³
- **Isodiaphers:** Same difference of number of Neutrons & protons **Example:** ${}_{5}B^{11}$, ${}_{6}C^{13}$

• Isotones: Having same number of neutron

Example: 1H³, 2He⁴

• **Isosters:** They are the molecules which have the same number of atoms & electrons

Example: CO₂, N₂O

• Isoelectronic: Species having same no. of electrons

Example: Cl⁻, Ar

ATOMIC MODELS

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

Electron is revolving around the nucleus in circular path.

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

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

SIZE OF NUCLEUS

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

ELECTROMAGNETIC SPECTRUM

- RW→MW→IR→Visible→UV→X-ryas→CR (Radiowaves→
 Microwaves → Infrared rays→Visible rays → Ultraviolet rays →
 X-rays → Cosmic rays)
- Wavelength decreases →
- Frequency increases →

•
$$c = v\lambda$$
 $\lambda = \frac{c}{v}$ $\frac{-}{v} = \frac{1}{\lambda} = \frac{v}{c}$

$$T = \frac{1}{v}$$
 $E = \frac{hc}{\lambda} = hv, h = 6.626 \times 10^{-34} \text{ Js}$

$$E(ev) = \frac{12400}{\lambda(\Lambda)}$$

• Total amount of energy transmitted $E = nhv = \frac{nhc}{\lambda}$

BOHR'S ATOMIC MODEL

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

$$\frac{K(Ze)(e)}{r^2} = \frac{mv^2}{r}$$

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) = Total energy =
$$-13.6 \times \frac{Z^2}{n^2}$$
 eV/atom

•
$$TE = -\frac{KZe^2}{2r}$$
, $PE = \frac{-KZe^2}{r}$, $KE = \frac{KZe^2}{2r}$
 $PE = -2KE$, $KE = -TE$, $PE = 2TE$

• Revolutions per sec =
$$\frac{v}{2\pi r}$$

• Time for one revolution =
$$\frac{2\pi r}{v}$$

• Energy difference between n₁ and n₂ energy level

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

where IE = ionization energy of single electron species.

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

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

E = 21.8 × 10⁻¹²
$$\frac{z^2}{n^2}$$
 erg per atom
= -21.8 × 10⁻¹⁹ $\frac{z^2}{n^2}$ per atom
= -13.6 $\frac{z^2}{n^2}$ eV/atom
1 eV = 3.8 3 × 10⁻²³ kcal

$$1 \text{ eV} = 3.8 \ 3 \times 10^{-23} \text{ kca}$$

$$1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$E = -313.6 \frac{z^2}{n^2} \text{ kcal/mole (1 cal = 4.18 J)}$$

$$V = \frac{2\pi kze^2}{nh}$$

$$r = \frac{n^2h^2}{4\pi^2mkze^2}$$

$$E = \frac{2\pi^2mz^2e^4k^2}{n^2h^2}$$

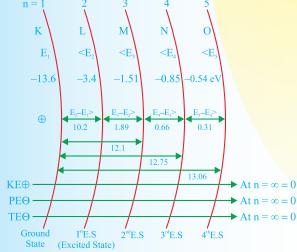
HYDROGEN SPECTRUM

• Rydberg's Equation:

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

 $R_{\rm H} \cong 109700 \text{ cm}^{-1} = \text{Rydberg constant}$

- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_{α} line means $n_2 = n + 1$; also known as line of longest λ , shortest ν , least E
- Similarly H_{β} line means $n_2 = n_1 + 2$
- When electron de-excite from higher energy level (n) to ground state in atomic sample, then number of spectral lines observed in the spectrum = $\frac{n(n-1)}{2}$
- When electrons de-excite from higher energy level (n_2) to lower energy level (n_1) in atomic sample, then number of spectral line observed in the spectrum = $\frac{(n_2 n_1)(n_2 n_1 + 1)}{2}$
- No. of spectral lines in a particular series $= n_2 n_1$.



DE-BROGLIE HYPOTHESIS

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

Number of waves = n = principal quantum number

- Wavelength of electron (λ) $\cong \sqrt{\frac{150}{V(\text{vols})}}$ Å
- $\lambda = \frac{h}{\sqrt{2mKE}}$

HEISENBERG UNCERTAINTY

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

If one of them is measured with greater accuracy, the other becomes less accurate.

•
$$\Delta x.\Delta p \ge \frac{h}{4\pi}$$
 or $(\Delta x)(\Delta v) \ge \frac{h}{4\pi m}$

where $\Delta x = Unc$ ertainty in position

 $\Delta p = Uncertainty in momentum$

 $\Delta v = Un$ certainty in velocity

m = mass of microscopic particle

Heisenberg replaced the concept of orbit by that of orbital.

QUANTUM NUMBER

- Principal Quantum number (By Bohr)
 - \Rightarrow Indicates = Size and energy of the orbit, distance of e⁻ from nucleus
 - \Rightarrow Values n = 1, 2, 3, 4, 5 ...
 - \Rightarrow Angular momentum = $n \times \frac{h}{2\pi}$
 - \Rightarrow Total number of e s in an orbit = $2n^2$
 - \Rightarrow Total number of orbitals in an orbit = n^2
 - \Rightarrow Total number of subshell in an orbit = n

Azimuthal/Secondary/Subsidiary/Angular momentum quantum number (l)

- \Rightarrow Given by = Sommerfeld
- ⇒ Indicates = Sub shells/sub orbit/sub level
- \Rightarrow Values $\Rightarrow 0, 1 \dots (n-1)$
- ⇒ Indicates shape of orbital/Sub shell

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

- \Rightarrow Total no. of e s in a suborbit = 2(21 + 1)
- \Rightarrow Total no. of orbital in a suborbit = (21 + 1)
- ⇒ Orbital angular momentum = $\sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \frac{h}{l}$ h = Planck's constant
- ⇒ For H & H like species all the subshells of a shell have same energy.

.e
$$2s = 2p$$
 $3s = 3p = 3d$

Magnetic Quantum number (m)

- ⇒ Given by Lande
- ⇒ Indicates orientation of orbital i.e. direction of electron density.
- \Rightarrow Value of m = -l0....+l
- \Rightarrow Maximum no of e's in an orbital = 2 (with opposite spin)

m for p sub shell =
$$p_x$$
 p_y p_z 0

m for d sub shell =

• Spin Quantum Number (m, 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

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



RULES FOR FILLING OF ORBITALS

• **Aufbau principle:** The electrons are filled up in increasing order of the energy in subshells.

 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$

- (n + l) rule: The subshell with lowest (n + l) value is filled up first, but when two or more subshells have same (n + l) value then the subshell with lowest value of n is filled up first.
- Pauli exclusion principle: Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.
- Hund's rule of maximum multiplicity: Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.



Gaseous State

GAS LAW

Boyle's law:

$$V \propto \frac{1}{P}(n, T = const) P_1 V_1 = P_2 V_2$$

Charle's law:

$$V \propto T(n, P = const) \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

Gay lussac's law:

$$P \propto T(n, V = const) \frac{P_2}{P_1} = \frac{T_2}{T_1}$$

Avogadro's law:

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

Ideal gas equation PV = nRT

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

 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ or } 8.314, \text{ N} \times \text{m K}^{-1} \text{ mol}^{-1}$

 $R = 2 \text{ cal } \text{K}^{-1} \text{ mol}^{-1}, R = 8.314 \times 10^7 \text{ erg } \text{K}^{-1} \text{ mol}^{-1}$

GRAHAM'S DIFFUSION LAW

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}; \, r \propto \frac{1}{\sqrt{VD}}; \, r \propto \frac{1}{\sqrt{M_{_{\rm W}}}}(P, T = constant)$$

$$VD = \frac{d_{gas}}{d_{H_2}} = \frac{M_w}{2}$$

Rate of diffusion

$$r = \frac{\mathit{l}_{diffused\,gas}}{t_{time\,taken}}; r = \frac{V_{diffused\,gas}}{t_{time\,taken}}; r = \frac{n_{diffused\,gas}}{t_{time\,taken}}$$

(When, l =distance traveled by diffused gas)

Kinetic Gas Equation : $PV = 1/3 \text{ mN V}_{rms}^2$		
Kinetic Gas Equatio		
Dalton's Law of Partial Pressure	Average Kinetic Energy (KE _{av})	
$P_{\text{mixture}} = P_1 + P_2 + P_3(T & V \text{ const.})$	$KE_{av} = \frac{3}{2} nRT $ (n moles)	
Partial pressure	$KE_{av} = \frac{3}{2}RT$ (1 mol or N_A molecules)	
$P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapours}}$	$KE_{av} = \frac{3}{2}KT$ (1 molecule)	
It is applicable for non reacting gases.	$K = 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$	
Methods of determination of partial pressure	K is called Boltzman's constant	
(P _A & P _B are partial pressure)	$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_n^2}{N}}$	
From ideal gas equation	$v_{av} = \frac{v_1 + v_2 + v_3 v_n}{N}$	
$P_AV = n_A RT \& P_BV = n_B RT$ • In the form of mole fraction.	$v_{rms} = \sqrt{\frac{3RT}{Mw}} v_{av} = \sqrt{\frac{8}{\pi} \frac{RT}{Mw}} v_{mp} = \sqrt{\frac{2RT}{Mw}}$	
$P_{A} = X_{A}P_{T} = \frac{n_{A}}{n_{t}}P_{T};$ $P_{B} = X_{B}P_{T} = \frac{n_{B}}{n_{t}}P_{T}$ $[X_{A} + X_{B} = 1]$	$v_{rms} = \sqrt{\frac{3PV}{Mw}} \ v_{av} = \sqrt{\frac{8}{\pi} \frac{PV}{Mw}} \ v_{mp} = \sqrt{\frac{2PV}{Mw}}$	
P_T = sum of partial pressure of all gases	$v_{rms} = \sqrt{\frac{3P}{d}} v_{av} = \sqrt{\frac{8}{\pi}} \frac{P}{d} v_{mp} = \sqrt{\frac{2P}{d}}$	
• In the form of volume fraction.	v_{rms} : v_{av} : $v_{\text{mp}} = \sqrt{3} : \sqrt{\frac{8}{\pi}}$: $\sqrt{2}$	
$P_{A} = \frac{V_{A}}{V} P_{T} & P_{B} = \frac{V_{B}}{V} P_{T}$	=1 : 0.92 : 0.82	
• If individual pressure and individual	$v_{\rm mp}$: $v_{\rm av}$: $v_{\rm rms} = \sqrt{2}$: $\sqrt{\frac{8}{\pi}}$: $\sqrt{3}$	
volume are given	=1 : 1.128 : 1.224	
V	Compressibility factor	
$P_A = \frac{V_A}{V} P_1$ and $P_B = \frac{V_B}{V} P_2$	$(z) = \frac{(V_{\rm m})obs}{V_{\rm l}} = \frac{P(V_{\rm m})obs}{RT}$	
P_1 , P_2 = pressure of gases before mixing	IF $z = 1$, the gas show ideal gas behaviour.	
P_A , P_B = pressure of gases after mixing	IF $z > 1$, the gas show positive deviation. IF $z < 1$, the gas show negative deviation.	

VANDERWAAL'S EQUATION

Vanderwaal's Equation

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

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

a↑ force of attraction↑

liquification >;

b↑ effective size of molecule↑, imcompressible vol.↑,

compressible vol. ↓

• At high pressure, Vanderwaal's eqⁿ is

$$PV_m - Pb = RT$$

• At low pressure or Moderate pressure vanderwaal's eqⁿ is

$$PV_{m} + \frac{a}{V_{m}} = RT$$

• At very low pressure, high temp. Vanderwaal's Equation is

$$VP = nRT$$

Ideal gas behaviour.

Gases having \(\gamma \) alue of a; will have \(\gamma \)_C; \(\gamma \) rate of liquefaction.



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: Divide system & surrounding

SYSTEM

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

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

THERMODYNAMIC PROPERTIES

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

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

PROCESSES

	horic Isobai const. P = cor		Cyclic Initial & final state of system are same
--	--------------------------------	--	---

Reversible process	Irreversible process
 Slow process 	Fast process
 At any time system and surrounding 	 No equilibrium between system
are in equilibrium.	and surro <mark>unding</mark>
$\bullet P_{\rm sys} = P_{\rm surr} \pm dP$	$\bullet \ P_{sys} = P_{surr} \pm \Delta P$

HEAT (q)

Energy exchange due to temperature difference:

$$q = C\Delta T$$
,

$$q = nC_m \Delta T$$
,

$$q = ms\Delta T$$

C = heat capacity

 C_m = molar heat capacity

s = specific heat capacity

m = Amount of substance



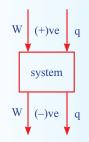
General values of C_V & C_P for an ideal gas can be taken as follows.

						(Zv.	C	P	γ	
Ato	omicity	n _{tr}	n _{Rot}	$n_{ m Vib}$	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	
N	Mono	3	0	0	$\frac{3}{2}$ R	$\frac{3}{2}$ R	$\frac{5}{2}$ R	$\frac{5}{2}$ R	$\frac{5}{3}$	$\frac{5}{3}$	
	Di	3	2	1	$\frac{5}{2}$ R	$\frac{7}{2}$ R	$\frac{7}{2}$ R	$\frac{9}{2}$ R	$\frac{7}{5}$	$\frac{9}{7}$	
Tri	Linear	3	2	4	$\frac{5}{2}$ R	$\frac{13}{2}$ R	$\frac{7}{2}$ R	$\frac{15}{2}$ R	$\frac{7}{5}$	$\frac{15}{13}$	
111	Non Linear	3	3	3	3R	6R	4R	7R	$\frac{4}{3}$	$\frac{7}{6}$	

WORK (W)

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

SIGN CONVENTION



INTERNAL ENERGY (E & U)

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

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

FIRST LAW OF THERMODYNAMICS

Law of conservation of energy

$$\Delta U = q + W$$

19





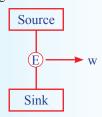
ENTHALPY

$$H = U + PV$$
, $\Delta H = \Delta U + (\Delta n_g) RT$

Process	Expression for w	Expression for q	Work on PV-graph
Reversible isothermal	1	$q = nRT \ln \left(\frac{V_2}{V_1}\right)$ $q = nRT \ln \left(\frac{P_1}{P_2}\right)$	P-(atm)-A
Reversible adiabatic process	$w = nC_{V}(T_{2}-T_{1})$ $= \frac{P_{2}V_{2} - P_{1}V_{1}}{\gamma - 1}$	$q = 0$ $PV^{\gamma} = constant$ $TV^{\gamma-1} = constant$ $TP^{1-\gamma/\gamma} = constant$	P ₁ ————————————————————————————————————

STATEMENTS OF SECOND LAW OF THERMODYNAMICS

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



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

$$\Delta S_{syt} + \Delta S_{sur} = 0$$
 for rev. process $\Delta S_{syt} + \Delta S_{sur} > 0$ for irrev. process $\Delta S_{syt} + \Delta S_{surr} \ge 0$ (In general)

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

THIRD LAW OF THERMODYNAMICS

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

VARIATION OF AS, 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

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1)$$

{Kirchhoff'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)

SOME FACTS TO BE REMEMBERED:

- (a) Standard condition
 - For gases/solid/liquid

$$P = 1 bar$$

• For ion/substance in solution

$$Concentration = 1M$$

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

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

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

(All above equation will be derived in thermochemistry)





THERMOCHEMISTRY

BOND ENTHALPY

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

 $\Delta_r H = (Sum \text{ of bond enthalpy of gaseous reactant}) - (Sum \text{ of bond enthalpy of gaseous product})$

RESONANCE ENERGY

$$\Delta H_{\text{resonance}}^{\circ} = \Delta_{r} H^{\circ} \text{ (experimental)} - \Delta_{r} H^{\circ} \text{ (calculated)}$$

= $\Delta_{c} H^{\circ} \text{ (calculated)} - \Delta_{c} H^{\circ} \text{ (experimental)}$

ENTHALPY OF NEUTRALIZATION (AHneut)

(Always exothermic)

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

SA + SB
$$\rightarrow$$
 salt + water; ΔH_{neut}^{+}
 $H_{(aq)}^{+} + OH_{(aq)}^{-} \rightarrow H_{2}O_{(l)}; \Delta H = -13.7 \text{ kCal eq}^{-1} = 57.3 \text{ kJ eq}^{-1}$

In case of weak acid/base or both $|\Delta H_N^{\circ}| < 13.7 \, \text{Kcal/eq}^{-1}$ and the difference is enthalpy of ionisation of ionisation of weak species except in case of HF when $|\Delta H_N| > 13.7 \, \text{Kcal/eq}^{-1}$ due to hydration of F⁻.



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

$$\Delta_{\rm r}H = \sum (\Delta H_{\rm C})_{\rm reactant} - \sum (\Delta H_{\rm C})_{\rm product}$$

(b) For heat of formation

$$\Delta_{\rm r} H = \sum (\Delta H_{\rm f})_{\rm product} - \sum (\Delta H_{\rm f})_{\rm reactant}$$



Chemical Equilibrium

Consider a reversible reaction,

$$aA + bB \stackrel{r_f}{\rightleftharpoons} cC + dD$$

AT EQUILIBRIUM STATE

Rate of forward reaction (r_f) = rate of backward reaction (r_b) So, at equilibrium,

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

$$K_{p} = \frac{[P_{C}]^{c}[P_{D}]^{d}}{[P_{C}]^{a}[P_{D}]^{b}}$$

$$K_{X} = \frac{[X_{C}]^{C}[X_{D}]^{d}}{[X_{C}]^{a}[X_{C}]^{b}}$$

$$[A_A][A_B]$$

$$K_P = K_C (RT)^{\Delta n_g}$$

In terms of active mass

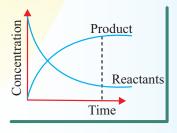
In terms of partial pressure

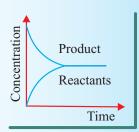
In terms of mole fraction

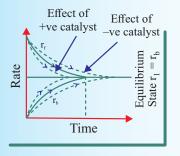
While determining Δn_g take only gaseous species.

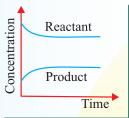
The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

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 increase.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

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

In general for the reversible reaction:

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

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

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

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

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

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

Degree of dissociation (α) No. of moles of reactant dissociated
No. of mole of reactant present initially

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

Effect due to change in		$\Delta \mathbf{n}_{\mathbf{g}} = 0$ $\mathbf{A} \stackrel{\sim}{\rightleftharpoons} \mathbf{B}$	$\begin{array}{c} \Delta n_{g} > 0 \\ A \rightleftharpoons 2B \end{array}$	$\begin{array}{c} \Delta n_{g} < 0 \\ 2A \rightleftharpoons B \end{array}$
Concentration	(i) ↑ [A] (ii) ↓ [A]	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
Pressure	(i) ↑ in pressure (ii) ↓ in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
Temperature	(i) ↑ in Endothermic(ii) ↑ in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
Dissociation	(i) ↑ in pressure(ii) ↑ in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Increases	Dissociation Increases Dissociation Decreases
Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Increases Unchanged	Dissociation Decreases Unchanged

Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G

 $\Delta G = \Delta G^{\circ} + RT \ln Q$...(i) where, $\Delta G^{\circ} = Standard$ free energy difference between the products and reactant, T = Absolute temperature in kelvin, R = Universal gas constant.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, then equation (i) becomes

$$0 = \Delta G^{\circ} + RT \ln K_{c}$$
 or $\Delta G^{\circ} = -RT \ln K_{c}$ or $\ln K_{c} = (-\Delta G^{\circ}/RT)$

Case I: If $\Delta G^{\circ} < 0$, then $(-\Delta G^{\circ}/RT)$ is positive, i.e., $e^{(-\Delta G^{\circ}/RT)} > 1$ hence $K_c > 1$, which implies a spontaneous reaction, i.e., the reaction proceeds in the forward reaction.

Case II: If $\Delta G^{\circ} > 0$, then $(-\Delta G^{\circ}/RT)$ is negative, i.e., $e^{(-\Delta G^{\circ}/RT)} < 1$, hence $K_c < 1$, which implies a non-spontaneous reaction or the reaction proceeds in the forward direction to a very small extent i.e., only a very small quantity of product is formed.



Ionic Equilibrium

	ACID		
Strong		Weak	
▼	₩		—
HClO ₄	HClO ₃		H_2CO_3
HI	HClO ₂		HNO_2
HBr	HClO		H_2SO_3
H_2SO_4	H_3PO_4		HCN
HC1	H_3PO_2		H_3BO_3
HNO_3	H_3PO_2		HF
	H_2S		Almost all organic acid
		Like:	acetic acid oxalic acid

BASE	
Strong	Weak
Strong	Veak
Group-1 hydroxide	All other bases
except-LiOH	like
NaOH	NH₄OH
KOH	Zn(OH) ₂
RbOH	\ /2
Group-2 hydroxide	$Al(OH)_3$
except Be(OH) ₂	$Fe(OH)_3$
and Mg(OH) ₂	$Cu(OH)_2$
**Ca(OH) ₂	etc.
Sr(OH) ₂	
Ba(OH) ₂	

ACID BASE THEORII	ES (Arrhenius Concept)
Acid	Base
Which produce H ⁺ ion in aqueous	Which produce OH ion in aqueous
solution. e.g. HCl, H ₂ SO ₄ , HClO ₄ ,	solution. e.g. NaOH, Mg(OH) ₂ , Ba(OH) ₂
H ₃ PO ₄ , CH ₃ COOH but H ₃ BO ₃ is not a	
Arrhenius acid.	
Major Limitation: Defined only in	
water solvent.	

Bronsted - Lowry Concept Acid: Which gives H⁺ in any solvent. To find conjugate base any $Acid \rightarrow Remove one H^+$ Base: Which accepts H⁺ in any solvent • To find conjugate acid Base \rightarrow add one H⁺ $HCl + NH_3 \rightleftharpoons Cl^- + NH_4^+$ Conjugate Water is Amphiprotic solvent (can accept as well as lose H⁺) Major Limitation: Does not explain $H_2O \rightleftharpoons H^+ + OH^- \qquad H_2O + H^+ \rightleftharpoons H_2O^+$ acidic behaviour of aprotic acids e.g. SO₂, CO₂, AlCl₃, SiCl₄

	LEWIS	THEORY
	ACID	BASE
	TYPES OF LEWIS ACID	TYPES OF LEWIS BASE
Le	wis acid is an electron pair acceptor.	Lewis base is an electron pair donor.
1.	Having Incomplete octet: BF ₃ , BCl ₃ , B(OH) ₃ , AlCl ₃ etc.	1. Neutral molecule having lone pair $\ddot{N}H_3$, $R - \ddot{N}H_2$, $R_2 - \ddot{N}H$,
2.	Having vacant d-orbitals: SF ₄ , SF ₆ , SnCl ₂ , SnCl ₄ etc.	$H - \ddot{O} - H, R - \ddot{O} - R$ etc.
3.	Having multiple bonds between atoms of different EN: CO, SO ₂ , SO ₃ etc.	O ²⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , CΓ, Br ⁻ , Γ, CH ₃ COO ⁻ etc.
4.	Cations Ag ⁺ , Li ⁺ , Al ⁺³ , Mg ²⁺ False cations (which cannot act as Lewis acid):] NH ₄ ⁺ , H ₃ O ⁺ , PH ₄ ⁺ etc.	 All the Lewis bases are Bronsted bases but all the Lewis acids are not Bronsted acids. All Arrhenius acids are Bronsted acid but it is not so for bases.

OSTWALD'S DILUTION LAW

OSTWALD'S DILUTION LAW

(Only for weak electrolytes)

 $\alpha \propto \sqrt{\text{dilution}} \text{ dilution } \uparrow \Rightarrow \alpha \uparrow$

EXPLANATION OF WATER

 $H_2O \rightleftharpoons H^+ + OH^-$

 $K_w = Ionic product of water$

 $pK_w = pH + pOH$

K = dissociation constant of water

$$K = \frac{K_w}{[H_2O]} [::[H_2O] = 55.5]$$

FOR PURE WATER

- 1. $[H^{+}] = [OH^{-}]$
- 2. pH = pOH
- 3. $(pH)_{pure water} = \frac{pK_w}{2}$
 - pH of an acidic solution is always less than pH of pure water.
 - pH of an basic solution is always greater than pH of pure water.

HYDROLYSIS OF SALTS

Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K _h)	Degree of hydrolysis (h)	рН
Weak acid and Strong base	Anionic	Alkaline pH > 7	$ m k_w/k_a$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$





Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K _h)	Degree of hydrolysis (h)	рН
Strong acid and Weak base	Cationic	Acidic pH < 7	$k_{\rm w}/k_{\rm b}$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$
Weak acid and Weak base	Anionic and Cationic both	Neutral, pH = 7 (If K_a $= K_b$)	$k_{\rm w}/\left(k_{\rm a} \cdot k_{\rm b}\right)$	$h = \sqrt{K_h}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

Buffer Solutions

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called **buffer solutions**.

Buffers are classified into two categories:

- Simple buffers: These are the solutions of salts of weak acid and weak base. For example, CH₃COONH₄ (ammonium acetate).
- Mixed buffers: These are the mixtures of two solutions. These are further of two types:
- Acidic buffers: These are the solutions of mixtures of weak acid and salt of this weak acid with strong base.
 For example, CH₃COOH + CH₃COONa. They have pH value lesser than 7.
- Basic buffers: These are the solutions of mixtures of weak base and salt of this weak base with strong acid. For example, NH₄OH + NH₄Cl. They have the pH value more than 7.
- pH of an acidic buffer:

$$pH = pK_a + log \frac{[Salt]}{[Acid]} = pK_a + log \frac{[Conjugate base]}{[Acid]}$$
(Henderson - Hasselbalch equation)

pH of an basic buffer:

$$pOH = pK_b + log \frac{[Salt]}{[Base]} = pK_b + log \frac{[Conjugate acid]}{[Base]}$$

Buffer capacity = No. of moles of acid or base added per litre of buffer Change in pH

The range of pH over which the buffer solutions remain effective is called buffer range.

•	
Buffer	Buffer range in pH
Acidic	$pK_a \pm 1$
Basic	$(pK_w - pK_b) \pm 1$
→ HAN	D BOOK (CHEMISTRY)

SOLUBILITY (s) & SOLUBILITY PRODUCT (K_{sp})

Solubility

The maximum amount of solute that can be dissolved in a particular amount of solvent at a given temperature is called solubility(s). It is generally expressed in molarity.

$$AgCl(s) \rightleftharpoons AgCl(aq) \rightarrow Ag^{+} + Cl^{-}$$
dissolution dissociation

Solubility Product (K_{sp})

$$AgCl \rightleftharpoons Ag^{+} + Cl^{-}$$

$$K_{sp} = [Ag^{+}] [Cl^{-}]$$

depends only on temperature.

Expressions of
$$K_{sp}: A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

General form
$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

In terms of 'S': $K_{sp} = (xS)^x (yS)^y$

Ionic Product [Q_{sp}]

$$A_x B_y \rightleftharpoons x A^{y^+} + y B^{x^-}; Q_{sp} [A^{y^+}]^x [B^{x^-}]^y$$

In Q_{sp} the concentration taken are at any time but in K_{sp} the concentration are at equilibrium time/saturation time.

Application

- 1. If $Q_{sp} \le K_{sp}$ [unsaturated]
- 2. If $Q_{sp} = K_{sp}$ [saturated]
- 3. If $Q_{sp} > K_{sp}$ [super saturated/ppt. will form]

Effect of Common Ion

Presence of common ion decreases the solubility but has no effect on K_{sp} as it depends only on temperature.

Effect of Odd Ion

Presence of odd ion increases the solubility but has no effect on K_{sp}.

ACID-BASE TITRATION						
Type of titration pH range of titration		Suitable indicators				
SA/SB.	3-11	All indicators (MeOH, HPh etc.)				
SA/WB	3-7	Methyl orange (MeOH) and methyl red				
WA/SB	7-11	Phenolphthalein (HPh)				
WA/WB	6.5-7.5	Phenol red				

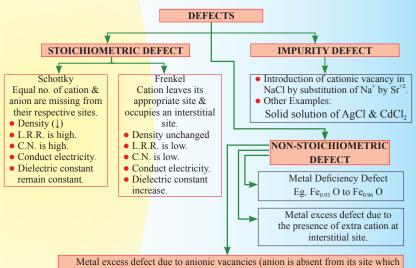
KEY TIPS

- Buffer capacity = $\frac{\text{No. of moles of acid/base added per litre}}{\text{change in pH of buffer solution}}$
- Maximum buffer action when [salt] = [acid]
- pH of Amphiprotic species: (NaHPO₄, NaHCO₃) which can donate as well as accept H^+ pH = $\frac{pK_{a_1} + pK_{a_2}}{2}$





Solid State



is occupied by an electron). This site is called F-centre.

$d = \frac{Z \times M}{N_A \times a^3}$						
CONTRIBUTION	CORNERS	8				
AT CORNER 1/8	FACES	6				
AT FACE 1/2	EDGES	12				
AT EDGE 1/4	BODY CENTRE	1				
AT BODY CNETRE 1	BODY DIAGONAL	4				
	FACE DIAGONAL	12				
	FACE CENTRES	6				
	EDGE CENTRES	12				

Limiting Radius Ratio	Coordination No. of Cation	Geometry of Void	Void found in	Location of void	No. of void per atom	Example
0.155 ≤ r/R < 0.225	3	Plane Trigonal	_	_	_	Boron oxide (B ₂ O ₃)
0.225 ≤ r/R < 0.414	4	Tetrahedral	FCC,HCP	On body diagonal at √3a/4 distance from corner of the unit cell	2	ZnS, SiO ₂ , Na ₂ O, CaF ₂
0.414 ≤ r/R< 0.732	6	Octahedral	FCC, HCP	Body centre & edge centre	1	NaCl, MgO
$0.732 \le r/R < 1.000$	8	Cubical	SCC	Body centre	1	CsCl

Classification of solid on the basis of nature of order of arrangement of constitutent particles.

CRYSTALLINE				
These solids have definite characteristic				
shape				
Definite melting point & heat of fusion				
Cleavage surfaces are smooth				
Anisotropic in nature.				
Long range order.				

Ex.: NaCl, Quartz, Metal, Diamond etc.

AMORPHOUS					
These s	solids have irregular shape.				
Indefinite	Indefinite melting point & heat of fusion.				
Cleav	Cleavage surface are irregular.				
	Isotropic in nature.				
Short range order.					
Ex. Glass, Quartz Glass, Rubber,					
	Plastics etc.				

Name of system	Axial	Axial angle	Bravais Lattices	
1. Cubic	a=b=c	$\alpha = \beta = \gamma = 90^{\circ}$	SCC, BCC, FCC	
2. Tetragonal	a=b≠c	$\alpha = \beta = \gamma = 90^{\circ}$	SCC, BCC	
3. Orthorhombic or Rhombic	a≠b≠c	$\alpha = \beta = \gamma = 90^{\circ}$	SCC, BCC, FCC, ECC	
4. Monoclinic	a≠b≠c	$\alpha = \gamma = 90^{\circ}, \beta \neq 90^{\circ}$	SCC,ECC	
5. Triclinic	a≠b≠c	$\alpha = \beta \neq \gamma \neq 90^{\circ}$	SCC	
6. Rhombohedral or Trigonal	a=b=c	$\alpha = \beta = \gamma \neq 90^{\circ}$	SCC	
7. Hexagonal	a=b≠c	$\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$	SCC	

S. No.	Type of Ionic Crystal	Geometry	Coordination Number	No. of formula per U.C.	Examples
1.	NaCl (1:1) (Rock salt Type)	CCP CCP Na [†] : At Every OHV	6:6	4Na ⁺ + 4Cl ⁻ 4NaCl (4)	Halides of (Li, Na, K, Rb); Oxides & sulphides of Alkaline earth metals; (some exception) AgF, AgCl, AgBr, NH ₄ X
2.	CsCl Type (1:1)	CIT: At Every Corner BCC Type Cs*: At Body centre	8:8	1Cs ⁺ + 1Cl [−] 1CsCl (1)	● Halides of 'Cs' ● TICl, TIBr, CaS



S. No.	Type of Ionic Crystal	Geometry	Coordination Number	No. of formula per U.C.	Examples
3.	ZnS Type (1:1) (Zinc Blende Type) (Sphalerite)	S ⁻² : Every element of CCP CCP Zn ⁻² : At 50% of THV or At Alternate THV	4 : 4	$4Zn^{+2} + 4S^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI CuCl, CuBr, Cul
4.	CaF ₂ Type (1:2) (Fluorite Type)	Ca*2: Every element of CCP CCP F: At every THV	4Ca ⁺² 8F ⁻ 8 : 4	$4Ca^{+2} + 8F^{-1}$ $4CaF_2$ (4)	BaCl ₂ , BaF ₂ , SrCl ₂ , SrF ₂ , CaCl ₂ , CaF ₂
5.	Na ₂ O Type (2:1) (Antifluorite Type)	Na*: At every THV CCP O ⁻² : Every element of CCP	8Na ⁺ 4O ⁻² 4 : 8	$8Na^{+} + 4O^{-2}$ $4Na_{2}O$ (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) another geometry of ZnS	S ⁻² : Every Element of HCP HCP Zn ⁻² : 50% of THV or at alternate THV	4 : 4	$6Zn^{+2} + 6S^{-2}$ $6ZnS$ (6)	Same as Sphalerite

S. No.	Contents	SCC	BCC FCC/CCP		НСР	
1.	Geometry					
2.	Arrangement	AAAA Packing but not close packing	ABAB Packing but not close packing	ABCABC Close Packing or CCP packing	ABAB Close Packing	
3.	No. of atoms/UC	1	2	4	6	
4.	Coordination No.	6	8	12	12	
5.	a & r relation	r = a/2	$r = \sqrt{3a/4}$	$r = \sqrt{2a/4}$	_	
6.	Packing Efficiency	π/6 or 52.4%	√3π/8 or 68%	π/3√2 or 74%	π/3√2 or 74%	
7.	Example	Mn	IA ; Group: V&Cr Ba, Fe	Ca, Sr, Al, Group : Co, Ni, Cu All inert gases except He	Remaining d-block elements, Be & Mg	

MAGNETIC PROPERTIES

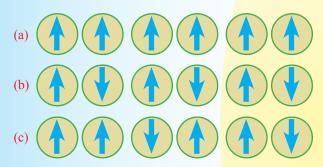
The magnetic properties of different materials are studied in terms of their magnetic moments which arise due to orbital motion and spinning motion of the electrons.

Classification of substances on the basis of magnetic properties:

- Paramagnetic substances are weakly attracted by a magnetic field. They have one or more unpaired electrons and lose their magnetism in the absence of magnetic field, e.g., O₂, Cu²⁺, Fe³⁺, Cr³⁺.
- Diamagnetic substances are weakly repelled by a magnetic field. They have no unpaired electrons and hence have zero magnetic moment, e.g., $\rm H_2O$, NaCl and $\rm C_6H_6$.



- Ferromagnetic substances are those which show permanent magnetism even in the absence of magnetic field, as when placed in magnetic field, their unpaired electrons (or magnetic domains) get permanently oriented in one direction, e.g., Fe, Ni, Co, Gd, CrO₂, etc.
- Antiferromagnetic substances are those which are expected to possess paramagnetism or ferromagnetism but actually have zero net magnetic moment due to equal number of domains in opposite directions, e.g., MnO.
- Ferrimagnetic substances are those expected to have large magnetism but actually have small net magnetic moment due to unequal number of domains in opposite, e.g., magnetite (Fe₃O₄), ferrites like MgFe₂O₄ and ZnFe₂O₄. These substances lose ferrimagnetism on heating and become paramagnetic.



Schematic alignment of magnetic moments in

(a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic





Solutions

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
$$\begin{cases} B = \text{Non volatile solid} \\ P_{p} = 0 \end{cases}$$

$$P_{A} = P_{A}^{\circ} X_{A}$$

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

No. of particle of Non volatile solute Properties

(1) Relative lowering of V.P.:

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

where $n_{\rm B}$ = mole of Non-volatile solute.

i = Vant Hoff's factor.

(2) Elevation in B.P.:

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

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

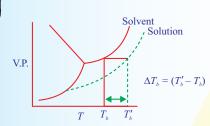
where $T_b = B.P.$ of pure solvent.

l = Latent heat of vapourization per gm

 K_b = molal elevation constant

M = Molar mass

where
$$l_{\rm v} = \left(\frac{\Delta H_{\rm vap}}{M}\right)$$



(3) Depression in FP.
$$\Delta T_f = T_f - T_f' = i \ k_f \times m$$
 where $k_f = \frac{RT_f^2}{1000 \times \ell_f}$
$$T_f = \text{f.p. of pure solvent}$$
 $k_f = \text{molal depression constant}$ $\ell_f = \text{latent heat of fusion per gm.}$

(4) Osmotic pressure:

$$\pi \propto (P_{A}^{\circ} - P_{A})$$

 $\pi = iC. S.T.$

where $\pi = \text{osmotic pressure}$

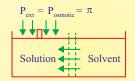
C = molarity (mole/lit)

S = R = const. for solution.

If
$$\pi_1 = \pi_2$$
 Isotonic

If
$$\pi_1 > \pi_2$$

$$\begin{cases} sol^n(1) \text{ hypertonic} \\ sol^n(2) \text{ hypotonic} \end{cases}$$



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

Solute	Example	Ionisation/ association (x degree)	y*	Van't Hoff factor	Abnormal mol. wt. (m_1')
Non- electrolyte	urea-glucose, sucrose etc.	none	1	1	normal mol.wt.
Ternary electrolyte	K ₂ SO ₄ , BaCl ₂	$A_2 B 2A^+ + B_x^{2-}$	3	(1+2x)	$\frac{m_1}{(1+2x)}$

Solute	Example	Ionisation/ association (x degree)	y *	Van't Hoff factor	Abnormal mol. wt. (m ₁ ')
Electrolyte	K ₃ [Fe(CN) ₆],	$A_2 B A_x^{3+} + 3 B^-$ _{1-x}	4	(1+3x)	$\frac{m_1}{(1+3x)}$
A_2B, AB_3	FeCl ₃				
Associated Solute	benzoic acid in benzene	$2A \Longrightarrow A_2$	$\frac{1}{2}$		$\frac{2m_1}{(2-x)}$
	forming dimer	$\underset{(1-x)}{A} \frac{1}{2} \underset{x/2}{A_2}$			
	any solute	$nA \rightleftharpoons A_n$	$\frac{1}{n}$	$\left[1 + \left(\frac{1}{n} - 1\right)x\right]$	$\left[\frac{m_1}{1 + \left(\frac{1}{n} - 1\right)x}\right]$
	forming polymer A _n	$A \longrightarrow \frac{1}{n} A_n$ $(1-x) \longrightarrow \frac{1}{n} A_n$			
General	one mole of solute giving y mol of products	$A \Longrightarrow yB$	у	[1 + (y -1) x]	$\frac{m_1}{[1+(y-1)x]}$

* number of products form one mole solute

Raoult's Law

(1) Volatile binary liquid mix:

Volatile liq.

В

Mole fraction

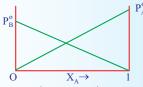
 $X_A / Y_A \qquad X_B / Y_B \Rightarrow \text{liq/vapour}$

V.P. of pure liq.

 P_{A}°

 $P_{\rm B}^{\circ}$

Binary liquid solution:



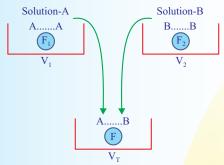
By Raoult's law
$$\Rightarrow P_T = P_A^{\circ} X_A + P_B^{\circ} X_B = P_A + P_B \qquad(i)$$

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

$$P_B = Y_B P_T \qquad(iii)$$



Ideal and Non-Ideal Solution



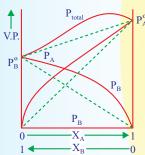
Ideal solution :
$$\begin{cases} F_1 \simeq F_2 \simeq F \\ V_T = V_1 + V_2 \end{cases} \Rightarrow \Delta \mathbf{H}_{\text{solution}} = 0$$

Non-Ideal Solution

(1) Solution showing +ve deviation:

$$F < F_1 \& F_2$$

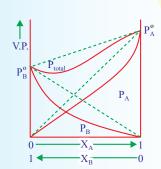
 $V_T > V_1 + V_2 \Delta H_{\text{solution}} > 0$



(2) Solution showing -ve deviation:

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

\Rightarrow V_T < (V_1 + V_2)
\Rightarrow \Delta H_{solution} < 0



Deviation from Raoult's Law

	Positive deviation (∆H = +ve)	Negative deviation (∆H = – ve)	Zero deviation (∆H = 0)
(i)	ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(ii)	acetone + carbon disulphide n-hexane + n-heptane +	benzene + chlorform	
(iii)	acetone + benzene	nitric acid + chloroform	ethyl bromide + ethyl iodide
(iv)	ethanol + acetone	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 soluton 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 HNO₃ (68%) + water (32%) mixture boils at 393.5 K.





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.



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

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

REPRESENTATION OF A CELL (IUPAC CONVENTIONS)

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

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

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

- (ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.
- (iii) EMF (electromotive force) may be written on the right hand side of the cell.
- (iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

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

(v) Inert electrodes are represented in the bracket

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

RELATIONSHIP BETWEEN AG AND ELECTRODE POTENTIAL

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

Work done = Charge \times 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.

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

- (i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from eq. (i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- (ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.

Reactions	$\Delta \mathbf{G}$	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 eq. (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 R.P of anode

NERNST EQUATION

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

$$\Delta G = \Delta G^{\circ} + RT \ln Q \qquad ...(A)$$





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

∴
$$-\Delta G = nFE$$
 and $-\Delta G^{\circ} = nFE^{\circ}$

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

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

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

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

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

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

.. From Eq. (i), we have

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

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

$$-\Delta G = nFE$$
 (i)

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

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_{p}$$
 (ii)

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

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

$$\therefore \Delta \mathbf{H} = -\mathbf{n} \mathbf{F} \mathbf{E} + \mathbf{n} \mathbf{F} \mathbf{T} \left[\frac{\partial \mathbf{E}}{\partial \mathbf{T}} \right]_{\mathbf{P}}$$

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

where ΔG = Free energy change; ΔH = Enthalpy change and ΔS = entropy change. According to Gibbs Helmoholtz equation,



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

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

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

or
$$\Delta S = nF \left[\frac{\partial E}{\partial T} \right]_{P}$$

CONCENTRATION CELL

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

(i) Electrode Gas concentration cell:

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

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

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

$$\frac{H^{+}(c) + e^{-} \rightarrow 1/2H_{2}(p_{2})}{1/2H_{2}(p_{1}) \rightleftharpoons 1/2H_{2}(p_{2})} \quad \therefore \quad E = -\frac{2.303RT}{F} log \left[\frac{p_{2}}{p_{1}}\right]^{1/2}$$

or
$$E = \left[\frac{2.303RT}{2F}\right] log \left[\frac{p_2}{p_1}\right]$$
, $At25^{\circ}C$, $E = \frac{0.059}{2F} log \left[\frac{p_1}{p_2}\right]$

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

(ii) Electrolyte concentration cells:

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

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

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

$$\frac{\operatorname{Zn}^{2+}(\operatorname{C}_2) + 2\operatorname{e}^{-} \to \operatorname{Zn}(\operatorname{s})}{\operatorname{Zn}^{2+}(\operatorname{C}_2) \rightleftharpoons \operatorname{Zn}^{2+}(\operatorname{C}_1)}$$
 (Over all process)

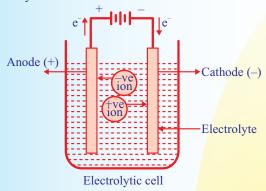
:. From Nernst equation, we have

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

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

ELECTROLYSIS

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



ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy.

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

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	Positive
		or oxidatio <mark>n takes</mark>	current enters
		place	
Cathode	Negative	Gain of electron	Current
		or reduction takes	leaves
		place	

FARADAY'S LAWS OF ELECTROLYSIS:

when Q = 1 coulomb, then w = Z

(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.

(utilized) through the solution.
$$w \propto Q$$

$$W = weight \ liberated, \ Q = charge \ in \ columb$$

$$w = ZQ$$

$$Z = electrochemical \ equivalent$$







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.

$$Z = \frac{Eq. \text{ wt. of the substance}}{96500}$$

(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.

$$R \propto \frac{l}{A}$$
 or $R = \rho \frac{l}{A}$ (ρ = 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.

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

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

Mho and siemens are other units of conductance

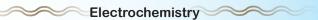
$$K = \frac{l}{A}C$$

Specific conductance = Cell constant – Conductance

Specific conductance is conductance of 1 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 .

$$\Lambda = K \times V$$

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

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

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 liter. It is denoted by Λ_m .

$$\Lambda_{\rm m} = K V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole electrolyte per liter.

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

Hence,
$$\Lambda_{\rm m} = K \times \frac{1000}{M}$$

Relation between Λ and Λ_m :

Application of Kohlrausch's Law

(A) Determination of Λ_m^0 of a weak electrolyte:

In order to calculate Λ_m^0 of a weak electrolyte say CH₃COOH, we determine experimentally Λ_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 CH₃COONa.
- (c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

 $\Lambda_{\rm m}^0$ of CH₃COOH is then given as:

$$\Lambda_{\rm m}^0$$
 of (CH₃COOH) = $\Lambda_{\rm m}^0$ (HCl) + $\Lambda_{\rm m}^0$ (CH₃COONa) - $\Lambda_{\rm m}^0$ (NaCl)



Proof:

$$\Lambda_{\rm m}^{0}$$
 (HCl) = $\chi_{\rm H}^{0} + \lambda_{\rm Cl}^{0}$...(i)

$$\Lambda_{\rm m}^{0} \left(\text{CH}_{3}\text{COONa} \right) = \lambda_{\text{CH}_{3}\text{COO}^{-}}^{0} + \lambda_{\text{Na}^{+}}^{0} \qquad \qquad \dots \text{(ii)}$$

$$\Lambda_{\rm m}^{0} ({\rm NaCl}) = \lambda_{{\rm Na}^{+}}^{0} + \lambda_{{\rm Cl}^{-}}^{0}$$
 ...(iii)

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

$$\Lambda_{\rm m}^0$$
 (HCl) + $\Lambda_{\rm (CH,COON_a)}^0$ - $\Lambda_{\rm (NaCl)}^0$ = $\chi_{\rm (H)^+}^0$ + $\chi_{\rm (CH,COO^-)}^0$ = $\Lambda_{\rm (CH,COOH)}^0$

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

$$\alpha = \frac{\text{Number of molecules ionised}}{\text{total number of molecules dissovled}} = \frac{\Lambda_{\text{m}}}{\Lambda_{\text{m}}^{0}}$$

(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).

$$\Lambda_{\rm m}^0 = \frac{1000 \rm K}{C}$$

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



10

Chemical Kinetics

- Rate of reaction (ROR) = Rate of disappearance of reactant (appearance of products)

 Stoichiometric coefficient of reactant (products)
- For a reaction:

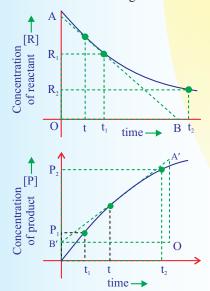
$$aA + bB \rightarrow cC + dD$$

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

⇒ Graphical method for determining rate:



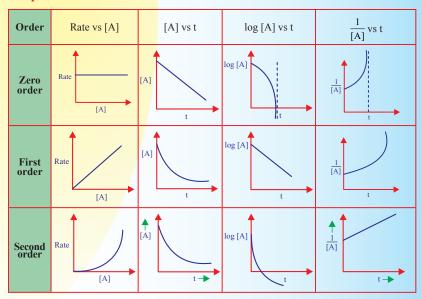
Avg. Rate =
$$-\left(\frac{[R]_2 - [R]_1}{t_2 - t_1}\right) = \frac{([P]_2 - [P_1])}{t_2 - t_1}$$

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

Important kinetic expression for reaction of type A \rightarrow **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	$[A_0]-[A] = kt$	$kt = \ln \frac{[A]_0}{[A]}$	$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$	$kt = \frac{1}{(n-l)} \left[\frac{1}{[A]^{n-l}} - \frac{1}{[A]^{n-l}_0} \right]$
Half life (t _{1/2})	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$	$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{[A_0]^{n-1}} \right]$
t _{3/4}	$t_{3/4} = 1.5 t_{1/2}$	$t_{3/4} = 2 t_{1/2}$	$t_{3/4} = 3 t_{1/2}$	$t_{3/4} = (2^{n-1}+1)t_{1/2}$

Graphs of Various Order



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.

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

Example: (For Monitoring Kinetics Experimentally

(i) Inversion of cane sugar:

$$k = \frac{2.303}{t} log \left(\frac{r_{\infty} - r_{0}}{r_{\infty} - r_{t}} \right)$$

 r_0 = rotation at time, t = 0

 r_t = rotation at time, t = t

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

(ii) Acidic hydrolysis of ethyl acetate:

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

$$k = \frac{2.303}{t} log \left(\frac{V_{\infty} - V_{0}}{V_{\infty} - V_{t}} \right)$$

 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 = ∞



Here NaOH acts as a reagent. Acetic acid is one of the product the amount of which can be found be 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.

$$t = 0 \qquad \qquad t = t \qquad \qquad t = 2t \qquad t =$$

 a_0

Reactant conc.

 a_0x

 $a_0 x^2$ $a_0 x^3$

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

- Graph of In [A] vs t is straight line with slope = $\frac{k}{2.303}$
- Graph of [A] vs t is exponentially decreasing.

Zero order

- t₁₀ of zero order is directly proportional to initial concentration.
- In equal time interval, reaction finishes by equal amount.

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

• Graph of [A] vs t is straight line.

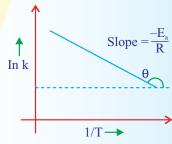
A zero order reaction finishes in $t = \frac{[A]_0}{k}$

Temperature dependence

- Arrhenious equation : $k = A.e^{-E_a/RT}$
- $E_a = minimum energy$ over and above the average 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 then E_a .
- A and E_a are constant i.e. do not vary with temperature

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

Graph: Graphical determination of E_a.

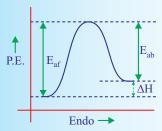


Temperature coefficient = $\frac{\mathbf{k}_{T+10}}{\mathbf{k}}$

By default T = 298K

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:





$$\Delta \mathbf{H} = \mathbf{E}_{af} - \mathbf{E}_{ab}$$

Parallel reaction:



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

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

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

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

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

Pseudo-order reaction:

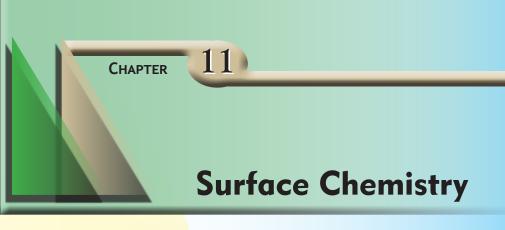
Rate law \rightarrow rate = k [A]^m [B]ⁿ

Pseudo rate law:

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

[B] assumed constant in two cases:

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



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 (suspensoid)
1.	Preparation	Can be easily prepared by shaking or warming the substance with solvent	Can not be prepared easily special methods are required
2.	Stability	are more stable	are less stable
3.	Reversibility	are reversible	are irreversible
4.	Viscosity	Viscosity is much higher than that of solvent	Viscosity is nearly same as that of the solvent
5.	Surface tension	Surface tension is usually low	Surface tension is almost same as that of solvent
6.	Hydration or solvation	These are highly solvated as the particles have great affinity for solvent	These are less solvated as the particles have less affinity for the solvent
7.	Charge	The particles have little charge or no charge at all	The particles carry a characteristic charge either positive or negative
8.	Visibility	Particles can not be seen under microscope	Particles can be seen under microscope

	Property	Lyophilic sol (Emulsoid)	Lyophobic sol (suspensoid)
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 or organic nature Ex. Gelatin, Starch, Gum, Albumin & Cellulose Solution	Mostly of Inorganic nature Ex. Transiton metal salt in water like Gold, As etc.

PEPTIZATION

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

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

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

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

$$[Fe(CN)_6]^{3-} > SO_4^{2-} > C1^{-}$$

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.

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

GOLD NUMBER

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

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

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





Gelatin and startch have the maximum & minimum protective power.

Protection Capacity $\alpha \frac{}{\text{Protection Number}}$ (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 polymer 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)	Ex. → Starch, Cellulose,	Ex. → Soap & Detergent
Sulphur sol (S ₈)	Protein etc.	

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. (20–40) KJ/mol	Heat of adsorption is high. (80–240 KJ/mol)
5.	No appreciable activation is energy is involved.	High activation energy involved.
6.	If forms multimolecular layers on adsorbent surface.	If forms unimolecular layer under high pressure.

Critical temperature increases Ease of liquification increases

Extent of adsorption increases (true for physisorption)

GENERAL CHARACTERISTICS OF CATALYSTS

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







- (ii) Only a very small amount of catalyst is sufficient to catalyse a reaction.
- (iii) A catalyst does not initiate a reaction.
- (iv) Solid catalyst is more efficient when used in finely divided form.
- (v) generally catalyst does not change the nature of products.
- (vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time.
- (vii) The catalyst are generally specific in nature.
- (viii) Changes rate constant of reaction.
 - (ix) Does not change free energy of reaction.
 - (x) Participates in mechanism or reaction.

Charge on colloidal particles: Colloidal particles always carry an electric charge. The nature of this charge is same on all the particles in a given colloidal solution and may be either positive or negative. The charge is due to preferential adsorption of ions from solution.

Origin of charge on colloidal sol particles:

- Colloidal sol particles carry charge. Charge on sol particles may arise due to any of the following reasons: by friction, ionisation and adsorption.
- Colloidal sol particles adsorb their own ions from the solution and become charged, e.g., when KI is added to AgNO₃ solution, silver iodide, AgI is formed which adsorbs silver ions, Ag⁺ and becomes positively charged.

AgI/I^{+}

 However when AgNO₃ is added to potassium iodide solution, silver iodide is precipitated which adsorbs iodide ions from the solution and becomes negatively charged.

AgI / I

Positively Charged Sols	Negatively Charged Sols
Hydrated metallic oxides. e.g., Al ₂ O ₃ . xH ₂ O, Fe ₂ O ₃ . xH ₂ O, metal hydroxides, Fe(OH) ₃ , Al(OH) ₃ , basic dye stuff like Prussian blue, haemoglobin (blood).	Metals, e.g., Cu, Ag, Au, Metallic sulphides – e.g., As ₂ S ₃ , CdS, acidic dyes like eosin, congo red, etc., sols of gelatin, gum, starch, etc.









Organic Chemistry Some Basic Principles and Techniques

Electrophiles are electron deficient species.

(NH₄ and H₃O[⊕] are not electrophile)

Nucleophiles are electron rich species.

Relative electron withdrawing order (-I order)

$$-NF_3 > -NR_3 > -NH_3 > -NO_2 > -CN > -COOH > -X > -OR > -OH > -C=CH > -NH_2 > -C_6H_5 > -CH = CH_2$$

Relative electron releasing order (+I order)

$$-NH > -O^{\ominus} > -COO^{\ominus} > 3^{\circ}$$
 alkyl $> 2^{\circ}$ alkyl $> 1^{\circ}$ alkyl $> -CH_3$

RELATIVE STABILITY ORDER

(A) Stability of carbocation

$$(CH_3)_2 \xrightarrow{\oplus} (Ph)_3 \xrightarrow{\oplus} (Ph)_2 \xrightarrow{\oplus} Ph - CH_2 > CH_2 = CH - CH_2 > (CH_3)_3 \xrightarrow{\oplus} C$$

$$(CH_3)_2 \xrightarrow{\oplus} CH > CH_3 \xrightarrow{\oplus} CH_2 > CH_3 > CH_2 = CH > CH \equiv C$$

(B) Stability of free radical

$$(Ph)_3$$
C > $(Ph)_2$ CH > Ph CH₂ > CH_2 = $CH - CH_2$ > $(CH_3)_3$ C > $(CH_3)_2$ CH > CH_3 CH₂ > CH_3

(C) Stability of carbanion

$$(Ph)_3 \overset{\Theta}{C} > (Ph)_2 \overset{\Theta}{CH} > Ph - \overset{\Theta}{CH}_2 > CH_2 = CH - \overset{\Theta}{CH}_2 > \overset{\Theta}{CH}_3 > CH_3 \overset{\Theta}{CH}_2$$

$$> (CH_3)_2 \overset{\Theta}{CH} > (CH_3)_3 \overset{\Theta}{C}$$

$\textbf{BASIC STRENGTH} \ \, ^{ \text{\tiny α}} \, K_{_b} \propto \frac{1}{pK_{_b}}$

• Basic strength of amine:

In aqueous medium

$$R \Rightarrow -CH_3 2^{\circ} > 1^{\circ} > 3^{\circ} NH_3$$

$$R \Rightarrow -CH_2 CH_3 2^{\circ} > 3^{\circ} > 1^{\circ} NH_3$$

In gaseous medium

$$R \Rightarrow -CH_3 3^{\circ} > 2^{\circ} > 1^{\circ} NH_3$$

$$R \Rightarrow -CH_2CH_3 3^{\circ} > 2^{\circ} > 1^{\circ} NH_3$$

- Reactivity towards nucleophile (NAR)
 - (1) HCHO > $CH_3CHO > (CH_3)_2CO$
 - (2) CCl₃CHO > CHCl₂CHO > CH₂ClCHO
- Reactivity order towards acyl nucleophilic substitution reaction
 Acid chloride > anhydride > ester > amide
- Order of electronic effect
 Mesomeric > Hyperconjugation > Inductive effect
- Stability of alkene ∞ no. of α-hydrogen

$$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > \frac{RCH=CHR}{RCH=CHR} > RCH=CHR$$

cis form

trans form

$$RCH=CH_2 > CH_2=CH_2$$

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

ACIDIC STRENGTH ∞ **STABILITY OF CONJUGATE BASE**

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

- (i) $H_2O > CH \equiv CH > NH_3$
- (ii) $CH = CH > CH_2 = CH_2 > CH_3 CH_3$

(iii)
$$RSO_3H > R-COOH > \bigcirc > R-OH$$

(iv) HCOOH > CH₃COOH > CH₃CH₂COOH

(v)
$$NO_2$$
 OH NO_2 NO_2 > HCOOH > C_6H_5COOH > CH_3COOH NO_2

(vi) CCl₃COOH > CHCl₂COOH > CH₂ClCOOH

$$(viii) C_6H_4 Phenol > m > p > o$$

(ix)
$$C_6H_4$$
 OH $p > 0 > m > Phenol$

$$(x) \begin{array}{c} OH \\ NO_2 \\ \hline \\ NO_2 \end{array} > \begin{array}{c} OH \\ OH \\ NO_2 \\ \hline \\ NO_2 \end{array} > \begin{array}{c} OH \\ OH \\ \hline \\ \\ \\ \\ \end{array} > \begin{array}{c} OH \\ OH \\ \hline \\ \\ \\ \\ \\ \end{array}$$

(xi)
$$C_6H_4$$
 COOH $O > p > m > benzoic acid$

(xiii)
$$C_6H_4$$
 COOH CH_3 $0 > benzoic acid > m > p$

(xiv)
$$C_6H_4$$
 COOH $O > m > p > benzoic acid$

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 = 475K)







- (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.

Examples

- (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.

P	=	P_1 +	P_2
Vapour		Vapour	Vapour
pressure		pressure	pressure
		of Organic liquid	of water

Examples

- (i) Aniline is separated from water
- (ii) Turpentine oil
- (iii) Nitro Benzene
- (iv) Bromo Benzene
- (v) Naphthalene
- (vi) O-Nitrophenol

LASSAIGNE'S METHOD

(detection of elements)

Element	Sodium extract	Confirmed test
Nitrogen	Na+C+N ∆↓ NaCN	(NaCN+FeSO ₄ +NaOH) boil and cool +FeCl ₃ +conc. HCl→Fe ₄ [Fe(CN) ₆] ₃ Prussian blue colour
Sulphur	2Na+S ∆↓ Na ₂ S	(i) Na ₂ S+Na ₂ [Fe(CN) ₅ NO] sodium nitrosorpuside →Na ₄ [Fe(CN) ₅ NOS] a deep violet colour (ii) Na ₂ S+CH ₃ COOH+(CH ₃ COO) ₂ Pb→ A black ppt. (PbS↓)
Halogen	Na+X ∆↓ NaX	NaX+HNO ₃ +AgNO ₃ (i) White ppt. soluble in aq. NH ₃ confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH ₃ confirms Br. (iii) Yellow ppt. insoluble in aq. NH ₃ confirms I.
Nitrogen and sulphur together	Na+C+N+S	As in test for nitrogen; insted of green or blue colour, blood red colouration confirms presence of N and S both

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Extimation of carbon and hydrogen-Leebig's method

$$C_x H_y + O_2 \rightarrow xCO_2 + y/2 H_2O$$

$$\text{excess}$$
% of $C = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of org. compd}} \times 100$
% of $H = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of org. compd}} \times 100$



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 CO₂ gas. The mixture of gases is collected over potassium hydroxide solution in which CO₂ is absorbed and volume of nitrogen gas is determined.

% of N =
$$\frac{28}{22400} \times \begin{pmatrix} \text{Vol.of N}_2 \\ \text{collected} \\ \text{at N.T.P.} \\ \text{Wt.of} \\ \text{organic} \\ \text{compound} \end{pmatrix} \times 100$$



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. H₂SO₄ 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

% of N =
$$\frac{1.4 \times \text{voume of acid (ml)}}{\text{wt. of organic compound}}$$



This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuff, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (-N=N-) and nitrogen in the rign (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.



Isomerism

DEFINITION

Compounds having same molecular formula but differ in atleast one physical or chemical or biological properties are called isomers and this phenomena is known as isomerism.

Types of Isomerism: (A) Structural isomerism (B) Stereo isomerism

(A) STRUCTURAL ISOMERISM

Structural isomerism is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

Types of Structural Isomerism

Chain isomerism: This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

Key points: Parent carbon chain or side chain should be different.

e.g.
$$C_5H_{12}$$
: $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
n-pentane

 CH_3
 $H_3C - CH - CH_2 - CH_3$, $H_3C - C - CH_3$
 CH_3
iso-pentane

 CH_3
neo-pentane

Positional isomerism: It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

Key points: Parent carbon chain remain same and substituent, multiple bond and functional group changes its position.

Functional isomerism: It occurs when compounds have the same molecular formula but different functional groups.

e.g.
$$C_3H_9N$$
: $CH_3-CH_2-CH_2-NH_2$, 1-propanamine $CH_3-CH_2-NH-CH_3$, N-methylethanamine CH_3 CH_3 CH_3-N-CH_3 N, N-dimethylmethanamine

Metamerism: This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

e.g.
$$C_4H_{10}O$$
: $CH_3 - O - CH_2 - CH_2 - CH_3$

n-propyl methylether

 $CH_3 - CH_2 - O - CH_2 - CH_3$

diethyl ether

Ring-Chain isomerism: In this type of isomerism, one isomer is open chain but another is cyclic.

e.g.
$$C_3H_6$$
: $CH_3 - CH = CH_2$
propene $H_2C - CH_2$
cyclopropane

- For chain, positional and metamerism, functional group must be same.
- Metameris may also show chain and position isomeris but priority is given to metamerism.

Tautomerism: This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

Conditions:

(ii) Presence of at least one α -H atom which is attached to a saturated C-atom.

e.g. Acetoacetic ester.
$$CH_3$$
– C – $CH_2COOC_2H_5$ \rightleftharpoons CH_3 – C = $CHCOOC_2H_5$ enol form

Enol content enhance by:

- Acidity of α-H of keto form
- Intra molecular H-Bonding in enol form
- Resonance in enol form
- Aromatisation in enol form



(B) STEREOISOMERISM

Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms of 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

a
$$C = C$$
 a $C = N - OH$ $N = N$ $A =$

• 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 isomers:

Unsymmetrical	2 ⁿ	
Symmetrical	$2^{n-1} + 2^{m-1}$	
	$m = \frac{n}{2}$ (If	n is even)
	$m = \frac{n+1}{2}$ (If	n is odd)

• Where n = number of sites where GI is possible.

Optical isomerism: Compounds having similar molecular and structural formula but differing in the stereo chemical formula and behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomersim.







Types of optical isomers

- (1) Optically active
 - dextrorotatory (d)
 - laevorotatory (l)
- (2) Optically inactive
 - meso
 - Condition Molecule should be asymmetric or chiral i.e. symmetry elements (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)

$$\begin{array}{c}
\text{COOH} \\
\text{CH}_3 - \text{CH} - \text{COOH} : \text{HO} + \text{H} \\
\text{CH}_3
\end{array}$$

- Configuration of optical isomer
 - (a) Absolute configuration (R/S system)
 - (b) Relative configuration (D/L system)
- Determination of R/S configuration
 - Rule-1 Assign the priority to the four groups attached to the chiral carbon according to priority rule.
 - Rule-2 If lowest priority 4 is bonded to vertical line then moving

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

$$\begin{array}{c}
\text{Clockwise} \\
\text{S} \\
\text{Anti clockwise} \\
\text{R}
\end{array}$$

DETERMINATION OF D/L SYSTEM

- Reference molecule glyceraldehyde
- It is used to assign configuration in carbohydrate amino acid and similar compounds.

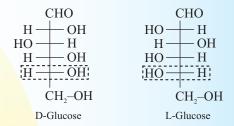
Rule: Arrange parent carbon chain the vertical line

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:-

- (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
- (ii) In case of isotopes, isotopes having higher atomic mass is given priority.
- (iii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2nd atom or subsequent atoms in group.
- (iv) If there is a double bond or triple bond, both atoms are considered to the duplicated for 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 d*l* 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

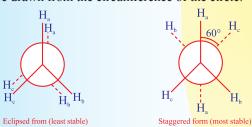
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2 ⁿ	Zero
Symmetrical If n = even	2 ⁽ⁿ⁻¹⁾	$2^{\frac{n}{2}-1}$
Symmetrical If n = odd	$2^{(n-1)} - 2^{(n-1)/2}$	2 ^{(n-1)/2}

* Where n = no, of chiral carbon

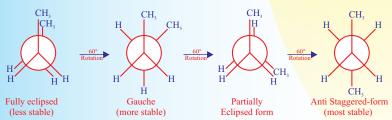
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomers.

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.

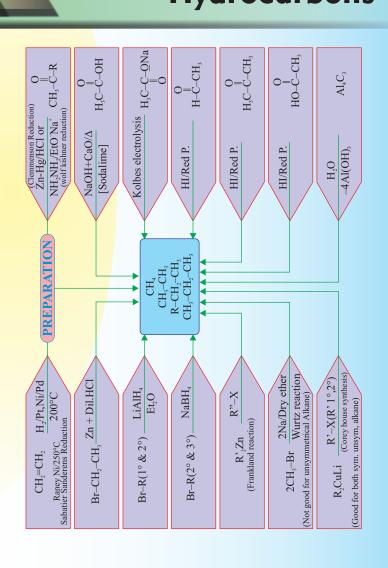


• Conformations of butane: ${}^{4}_{C}H_{3} - {}^{3}_{C}H_{2} - {}^{2}_{C}H_{2} - {}^{2}_{C}H_{3}$

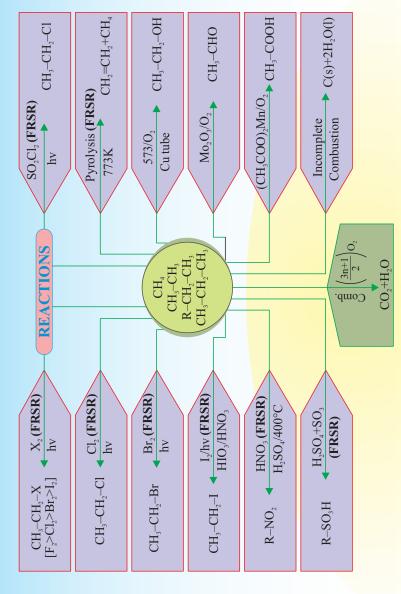


- The order of stability of conformations of n-butane.
 Anti staggered > Gauche > Partially eclipsed > Fully eclipsed.
- Relative stability of various conformation of cyclohexane is Chair > twist boat > boat > half chair

ALKANE



HYDROCABON OF ALKANE



Aromatization

$$\frac{\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3}{773\text{K (FRSR)}}$$

$$\frac{\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3}{773\text{K, 10-20 atm}}$$

$$-\text{CH}_3$$

Isomerization

Oxidation at 3°H

$$\begin{array}{cccc} & CH_3 & CH_3 \\ CH_3 - C - H & \xrightarrow{KMnO_4} & H_3C - C - OH \\ CH_3 & CH_3 & CH_3 \end{array}$$

• Reactivity of alkane towards free radical halogenation is ∝ stability of free radical

Reactivity of halogen towards free radical substitution

 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

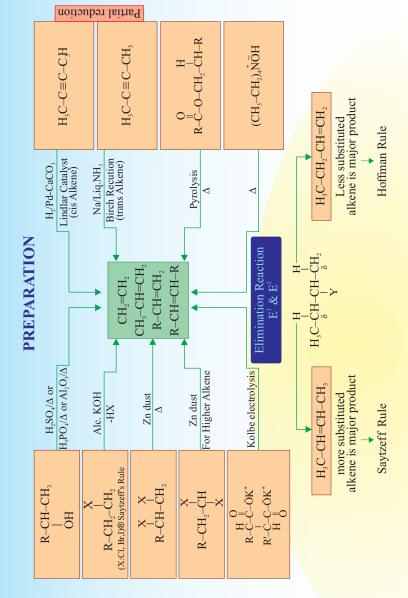
• Boiling point decrease with increase in number of side chain.

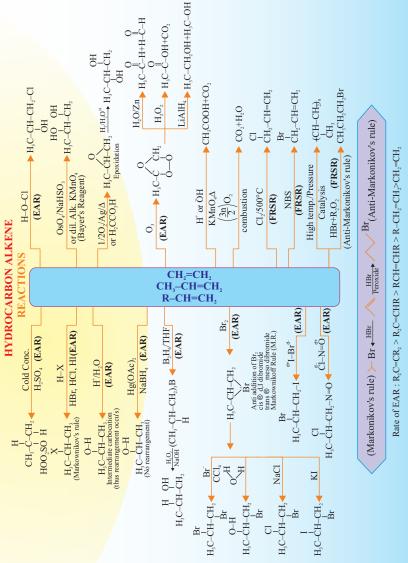
71

Hydrocarbons



HYDROCARBON-ALKENE

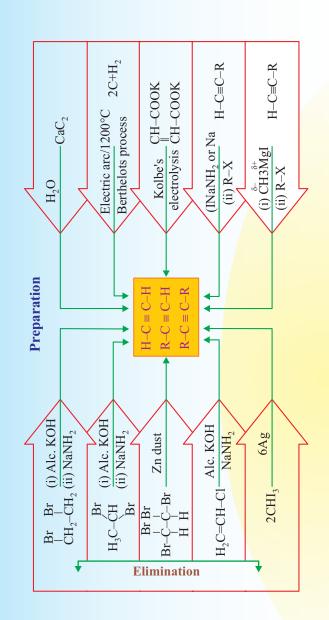


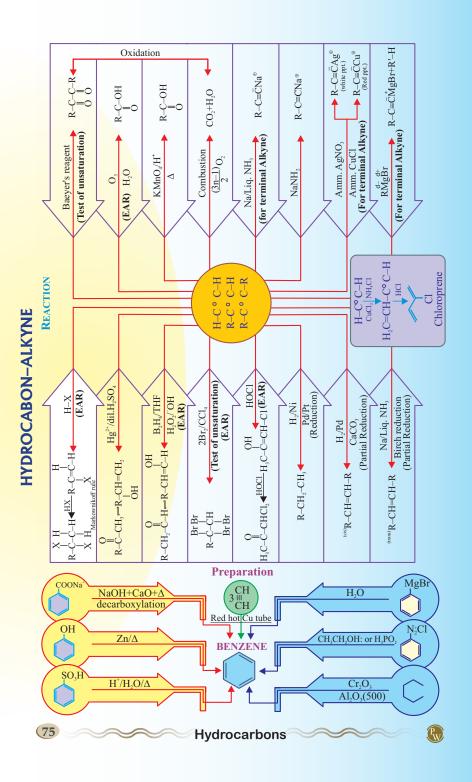


- Order of reactivity of olefins for hydrogenation CH₂ = CH₂ > R-CH=CH₂ (Reverse of stability)
- Order of reactivity of alkene towards hydration

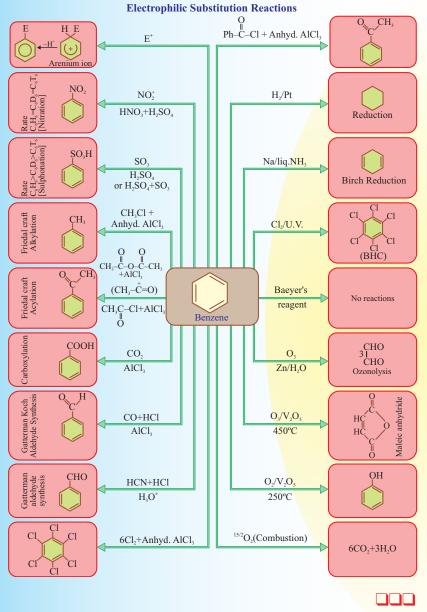
$$CH_3-C=CH_2 > CH_3-CH = CH_2 > CH_2 = CH_2$$

 CH_3













POLLUTANT

Substance which cause pollution is known as pollutant.



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

Gaseous Pollutant

SO₂: Cause respiratory diseases of anthma, bronchitis emphysema etc & irrataling 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, Carcogonic.

Oxide of Carbon

CO: Blocks the delivery of oxygen to organs and tissues.

Carboxy hemoglobine 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.

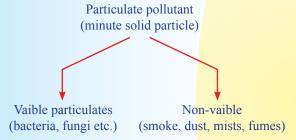
Global WWarming and Green House Effect

Some of the gases such as CO₂, CH₄,O₃ CFC(s) and water vapour tapped the heat and does not radiates back to the atmosphere. 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 than 5.6 then it is called acid rain.
- Source: burning of fuel (contain N & S) form SO₂ & NO₂.
- Harmful to agriculture, tree and plants.
- Taj Mahal affect by acid rain.

Particulate 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.



Pb is major air pollutant.

Smog (Smoke + Fog)

Classical smog: (Smoke + fog + CO₂) also called reducing smog

Photochemical smog:

hydrocarbon: NO
$$\xrightarrow{hv}$$
 NO₂ \xrightarrow{hv} NO + O



$$O + O_2 \xrightarrow{hv} O_3$$
 $NO + O_3 \rightarrow NO_2 + O_2$
 \longrightarrow contribute of Haze

 $(NO_2 + O_2) + \text{hydrocarbon}$
 \longrightarrow CH_2O
formaldelyde
or
 $CH_2 = CHCHO$
A.crotein
or
 CH_3COONO_2
peroxy acetyl nitrate (PAN)

Stratospheric Pollution

Formation & decomposition of ozone.

$$O_2(g) \xrightarrow{UV} O(g) + O(g)$$

$$O_3(g) + O(g) \xrightarrow{UV} O_3$$

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 freous).

Reaction of Ozone Depletion

$$\begin{array}{c} CF_2Cl_2(g) \xrightarrow{UV} \dot{C}l(g) + \dot{C}F_2Cl(g) \\ \dot{C}l(g) + O_3(g) \longrightarrow \dot{C}lO(g) + O_2(g) \\ \dot{C}lO(g) + NO_2(g) \longrightarrow \dot{C}lONO_2(g) \\ \dot{C}l(g) + CH_4(g) \longrightarrow \dot{C}H_3(g) + HCl(g) \\ ClONO_2(g) + H_2O(g) \longrightarrow HOCl(g) + HNO_3(g) \\ ClONO_2(g) + HCl(g) \longrightarrow Cl(g) + HNO_3(g) \\ HOCl \xrightarrow{hv} \dot{O}H(g) + \dot{C}l(g) \\ Cl_2(g) \longrightarrow 2\dot{C}l(g) \end{array}$$

WATER POLLUTION

Cause of Water Pollution

- (i) Pathogen
- (ii) Organic waste
- (iii) Organic waster

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 where as highly polluted water could have a BOD value of 17 ppm or more.

Fluoride: Soluble fluoride is often added to drinking waler 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 ppm. 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

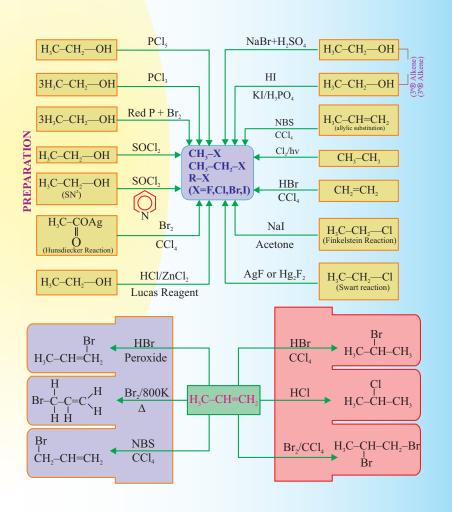
Metal	Maximum concentration (ppm or mg dm ⁻³)
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

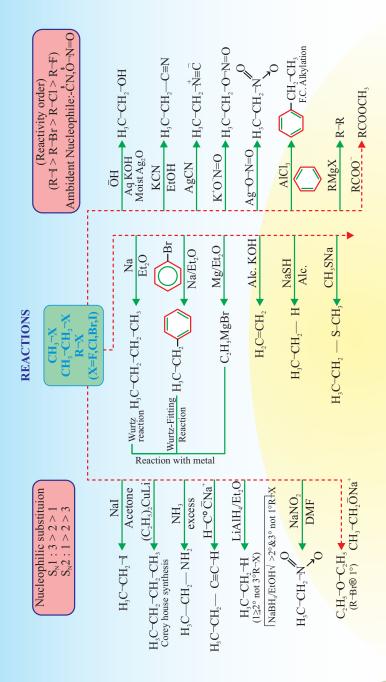






Haloalkane and Haloarene

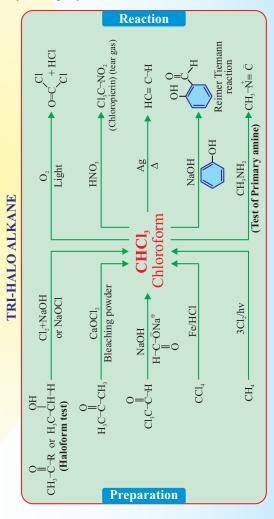


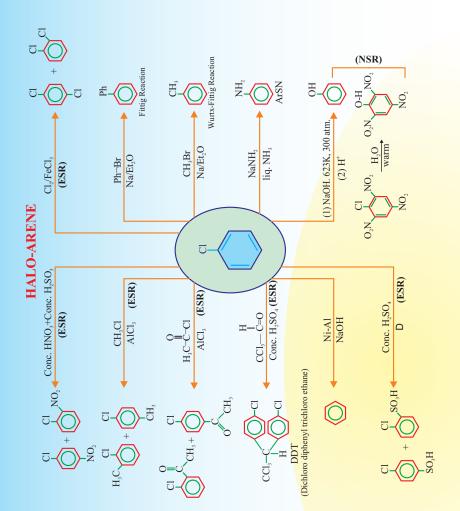


Physical Properties

- (1) Dipole moment: $CH_3-Cl > CH_3-F > CH_3-Br > CH_3-I$
- (2) Bond enthalpies: $CH_3-F > CH_3-Cl > CH_3-Br > CH_3-I$
- (3) Boiling point: R-I > R-Br > R-Cl > R-F

- (4) Density: $n-C_3H_7Cl < n-C_3H_7Br < n-C_3H_7I$
- (5) Solubility \rightarrow slightly soluble in water





(A) [Reactivity toward Nucleophile]

(i)
$$\begin{array}{c} F \\ Older \\$$

(B) Boiling point

$$(i) \qquad F \qquad Cl \qquad Br \qquad I \qquad \\ (i) \qquad < \bigcirc \qquad < \bigcirc \qquad < \bigcirc$$

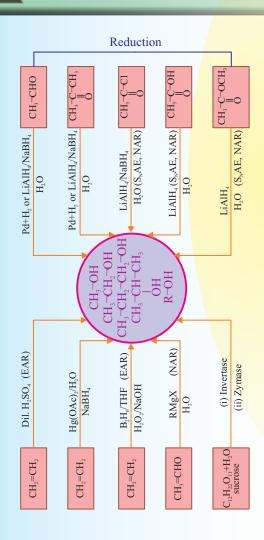
(C) Melting point

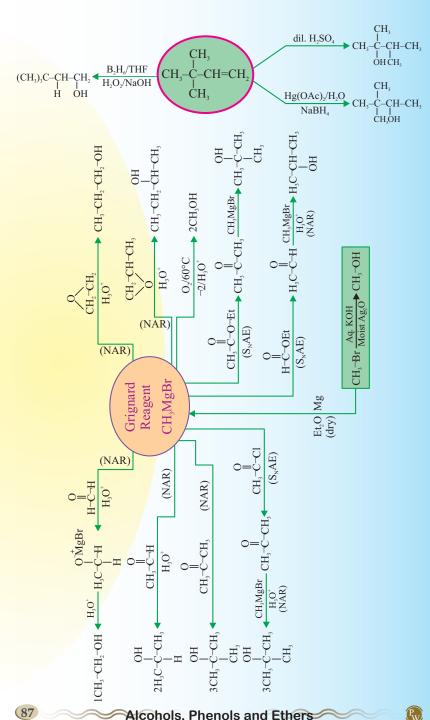
$$(i) \bigcirc Cl > \bigcirc Cl > \bigcirc Cl$$





Alcohols, Phenols and Ethers

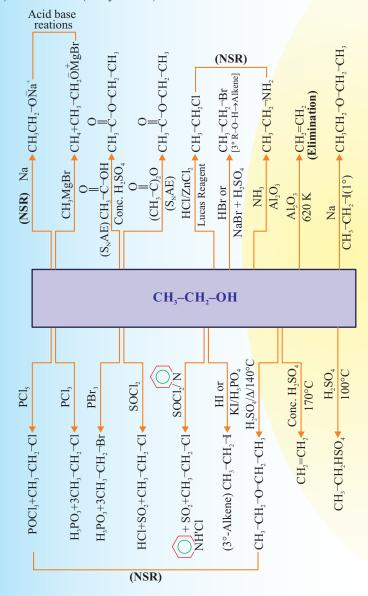




Solubility of alcohol increase in branching $n \le iso \le neo$ (Isomeric).

Relative order of reactivity

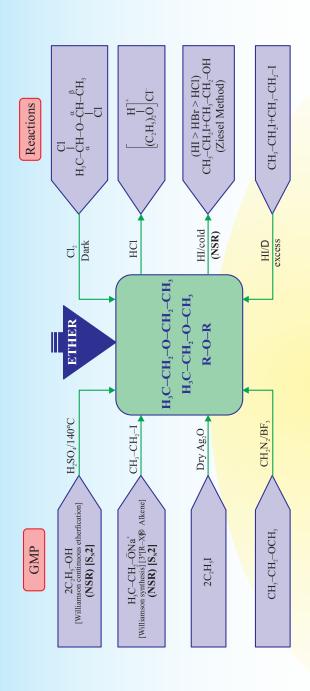
- (i) $1^{\circ} > 2^{\circ} > 3^{\circ}$ (O–H bond fission)
- (ii) $3^{\circ} > 2^{\circ} > 1^{\circ} > (C-O \text{ bond fission})$
- (iii) $3^{\circ} > 2^{\circ} > 1^{\circ}$ (Dehydration)

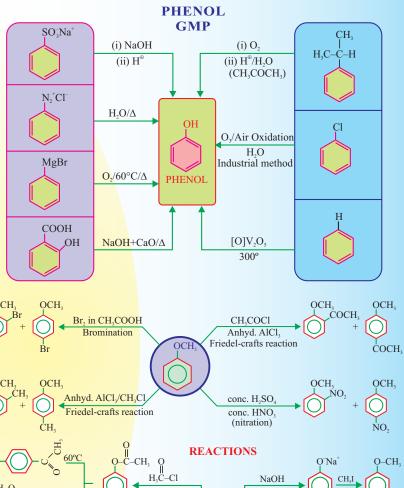


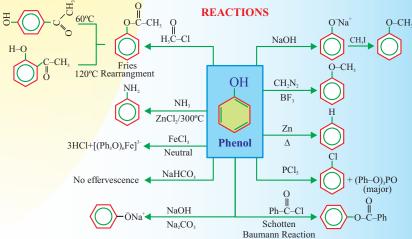


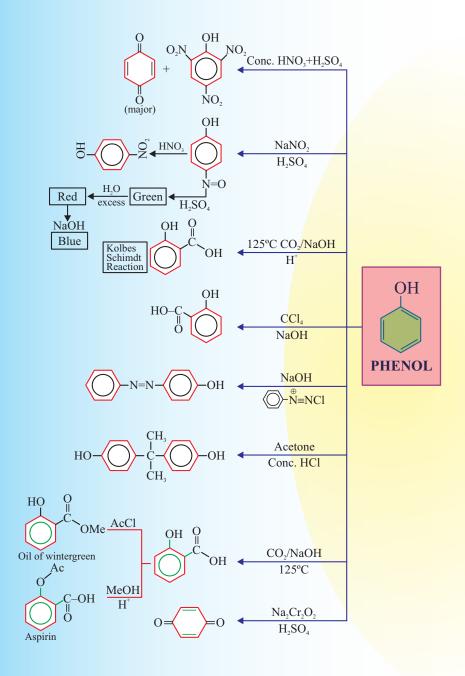
	DEHYDROGENATIONS				
Reagent	OH H ₃ C-CH ₂ -CH ₂ -CH ₂ 1° Alcohol		OH H ₃ C-CH ₂ -CH-CH ₃ 2°Alcohol	CH ₃ H ₃ C-C-OH CH ₃ 3° Alcohol	
PCC/PDC Anhy. CrO ₃	O H ₃ C-CH ₂ -CH ₂ -C-H		O H ₃ C-CH ₂ -C-CH ₃	No reaction	
$K_2Cr_2O_7/H^{\oplus}$ $KMnO_4/H^{\dagger}/$ OH/Δ Jones Reagent	H ₃ C-CH ₂ -C	O H ₂ –C–OH	O O H ₃ C–C–OH+CH ₃ –C–OH	No reaction	
Cu/500°C	H ₃ C–CH ₂ –C	O CH ₂ –C–H	O CH ₃ –CH ₂ –C–CH ₃	CH ₃ H ₃ C-C=CH ₂	
Lucas Reagent HCl/ZnCl ₂	Cloudiness ap heating after		within five min.	Immediately	

VICTOR MEYER'S TEST			
$\mathrm{P/I}_2$	CH ₃ -CH ₂ -CH ₂ -CH ₂ -I	CH ₃ H ₃ C–CH ₂ –CH–I	CH ₃ H ₃ C-C-I CH ₃
${\sf AgNO}_2$	CH ₃ -CH ₂ -CH ₂ -NO ₂	CH ₃ H ₃ C-CH ₂ -CH-NO ₂	(CH ₃) ₃ C–NO ₂
HNO ₂	H ₃ C–CH ₂ –C–NO ₂ N–OH Nitrolic acid	CH ₃ H ₃ C-CH ₂ -C-NO ₂ N=O Blue colour	No reaction: Colourless
NaOH	Red Colour	No reaction	









	Comparison of $\mathrm{S_{N}1}$ and $\mathrm{S_{N}2}$				
Reactions		$S_N 1$	S _N 2		
A	Kinetics	1 st order	2 nd order		
В	Rate	k[RX]	k[RX] [Nu: ^Θ]		
С	Stereochemistry	Racemisation	Inversion		
D	Substrate (reactivity)	$3^{\circ} > 2^{\circ} > 1^{\circ} > MeX$	$MeX > 1^{\circ} > 2^{\circ} > 3^{\circ}$		
Е	Nucleophile	Rate Independent	Needs Strong Nu		
F Solvent Good ionizing Faster in aprotic		Faster in aprotic			
G	Leaving Group	Needs Good LG	Needs Good LG		
Н	Rearrangement	Possible	Not Possible		

	Comparison of $\mathbf{E_1}$ and $\mathbf{E_2}$				
Reactions		\mathbf{E}_1		\mathbb{E}_2	
A	Kinetics	1 st order		2 nd order	
В	Rate	k[RX]		k[RX] [B:]	
С	Stereochemistry	No special geometry		Anti-periplanar	
D	Substrate	3° > 2° >>> 1°		3° > 2° > 1°	
Е	Base Strength	Rate Independent		Needs Strong bases	
F	Solvent	Good ionizing		Polarity not import	
G	Leaving Group	Needs Good LG		Needs Good LG	
Н	Rearrangement	Possible		Not Possible	

Summary of $S_N 1$, $S_N 2$, E_1 and E_2 Reactions				
RX	Mechanism	Θ Θ Nu/B	Solvent	Temp.
10	$S_N 2$	$_{\Theta}^{}$ Better $_{\Theta}^{}$ OH,C $_{2}$ H $_{5}$ O	D.I.	Low
1°	E_2	Strong & bulky base (CH ₃) ₃ CO	Polar aprotic	High
	$S_N 2$	^Θ HO;C ₂ H ₅ O	Dalamannatia	Low
2°	E_2	(CH₃)₃CO	Polar aprotic	High
	(S _N 1)	(Solvent)	Dolor protio	(Low)
	(E ₁)	(Solvent)	Polar protic	(High)
3°	$S_N 1$	Solvent	Protic	Low
3°	E_1	Solvent	Protic	High



	Primary (1°)	Secondary (2°)	Tertiary (3°)
Strong nucleophile	S _N 2>>E ₂	$S_{N}2+E_{2}$ (if weak base, $S_{N}2$ favored)	E_2
Weak nucleophile weak base	Mostly S _N 2	Mostly S _N 2/S _N 1	Mostly S _N 1 at low T mostly E ₁ at high T
Weak nucleophile strong base	Mostly E ₂	Mostly E ₂	E_2

Order of reactivity of Allylic Halide towards

$$S_N 1 \propto Benzylic > Allylic > 3^\circ > 2^\circ > 1^\circ$$

$$S_N 1 \propto Stability of carbocation$$

$$S_N 2 \propto 1^o > 2^o > 3^o$$

$$S_N 2 \propto \frac{1}{\text{Steric hindrance}}$$

Reactivity order towards $S_N 1$ or $S_N 2$ and E_1 or E_2

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

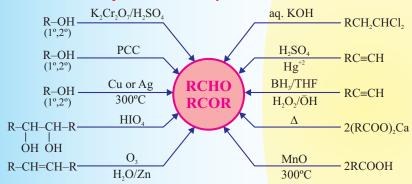
With increase in number of strong electron withdrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitution increases.

$$Cl$$
 Cl NO_2 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2

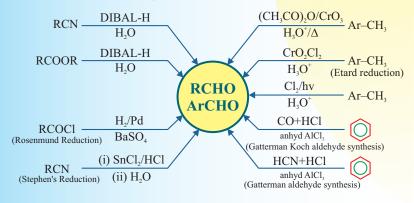


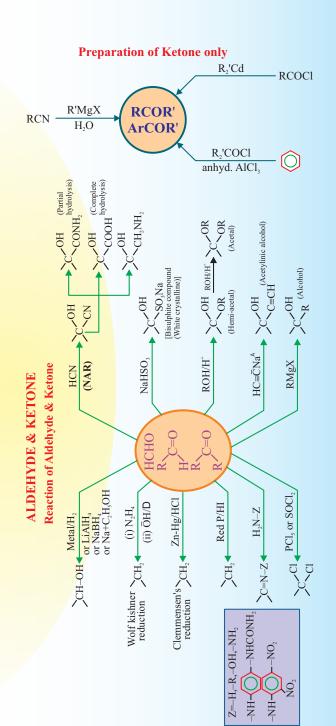
Aldehydes, Ketones and Carboxylic Acids

Preparation of Aldehyde & Ketone both



Preparation of Aldehyde only





$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\$$

Aldol Reaction (Aldehyde or ketone with αH)

(i)
$$2CH_3CHO \stackrel{\text{dil.NaOH}}{\longleftarrow} CH_3$$
— CH — CH_2 — $CHO \stackrel{\Delta}{\longrightarrow} CH_3$ — CH = CH — CHO

OH

Aldol (Aldol condensation product)

Cannizzaro reaction (Aldehyde with no αH)

2HCHO $\xrightarrow{\text{conc. NaOH}}$ CH₃OH+HCOO Na⁺

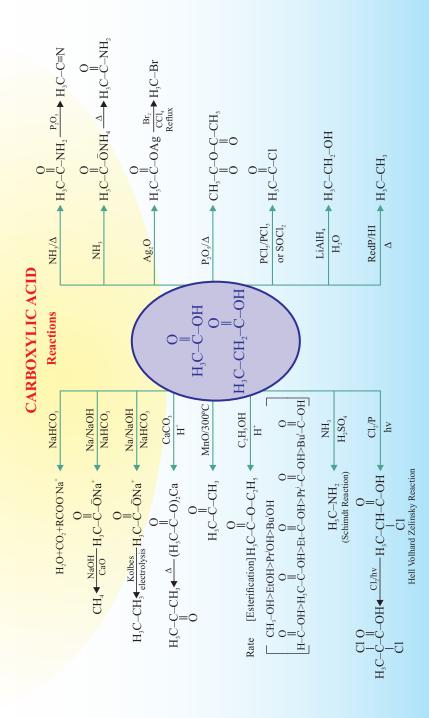
Tollen's test $RCHO+2[Ag(NH_3)_2]^++3^-OH \rightarrow RCOO^-+2Ag+2H_2O+4NH_3$ (Given by Aliphatic and aromatic aldehyde)

Fehling's test

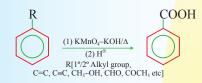
RCHO+2Cu⁺²+5 $^{-}$ OH \rightarrow RCOO $^{-}$ +Cu₂O+3H₂O

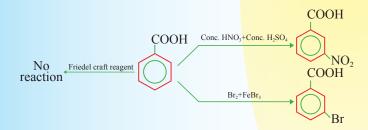
(Given by Aliphatic aldehyde) (Red-Brown ppt.)





TEST			
Tollen's Reagent Fehling solution			
$O \\ H-C-OH \longrightarrow Ag \downarrow +CO_2 \uparrow +H_2O$	$ \begin{array}{c} O \\ H-C-OH \xrightarrow{2CuO} Cu_2O\downarrow +CO_2+H_2O \end{array} $		

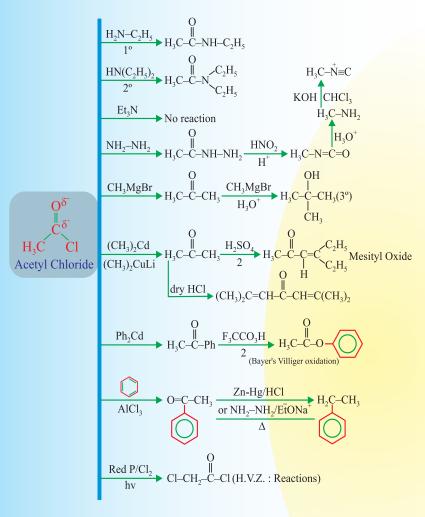


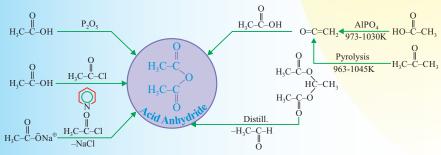




Curtius Reaction
$$H_3C-C-N=N=N=N$$
 $H_3C-N=C=O$
 $H_3C-N=C=O$
 H_3C-NH_2
 H_3O^+
 H_3C-NH_2
 H_3O^+
 H_3C-NH_2
 H_3O^+
 $H_3C-N=C=O$
 H_3C-NH_2
 $H_3C-N+C=O$
 H_3C-C-O
 H_3C-C-O
 H_3C-O
 H_3C-O

$$O^{\delta}$$
 C^{δ^+}
 C^{δ^+}
 C^{δ^+}
 C^{δ^+}
Acetyl Chloride





Heating Effect

O—H HO—C H

O—H HO—C H

C—CH₃
$$\xrightarrow{H^{\dagger}}$$
 H₃C—CH₃ HC—CH₃

C—O

Lacitide

γ & α-Hydroxy acid

$$\beta \stackrel{\text{Q}}{\longleftarrow} OH \stackrel{\text{H}^+/\Delta}{\longrightarrow} OH \stackrel{\text{C}}{\longrightarrow} OH \stackrel{\text{H}^+/\Delta}{\longrightarrow} OH \stackrel{\text{C}}{\longrightarrow} OH \stackrel{\text{H}^+/\Delta}{\longrightarrow} OH$$

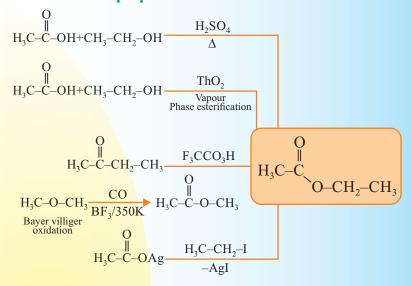
β-Hydroxy acid

β-Keto acid

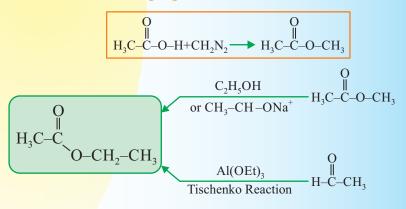
$$\begin{array}{c|c} O & H & O & O \\ \parallel & \parallel & \parallel & \parallel \\ H_3C-C-C-C-C-OH \xrightarrow{\Delta} H_3C-C-CH_3 \end{array}$$

$$\begin{array}{c|c}
 & NO_2 \\
 & \underline{\Lambda} \\
 & \overline{HNO_2}
\end{array}$$

Nutshell preparation of Ester

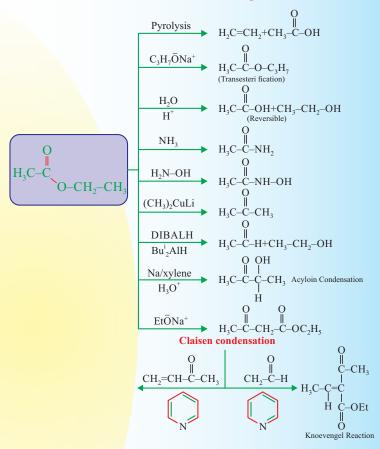


Nutshell preparation of Ester

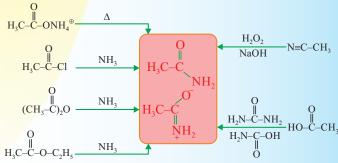


Nutshell Chemical Properties of Ester

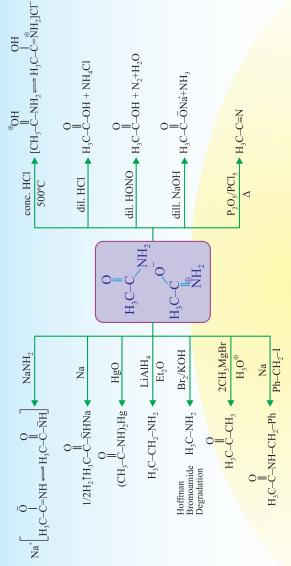
Nutshell Chemical Properties of Ester



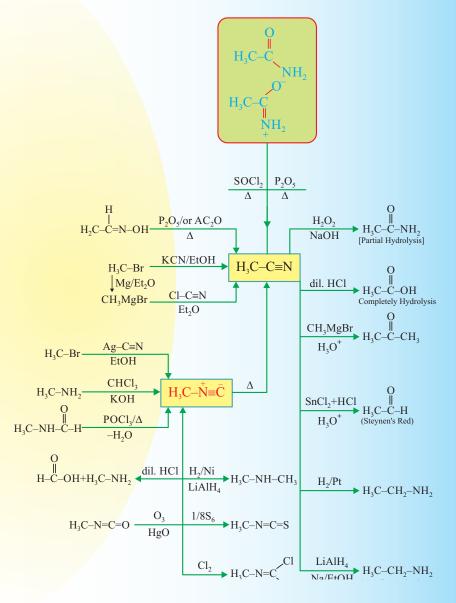
Nutshell preview and review of Amide, Cyanide and Isocyanide



Nutshell preview and review of Amide, Cyanide and Isocyanide

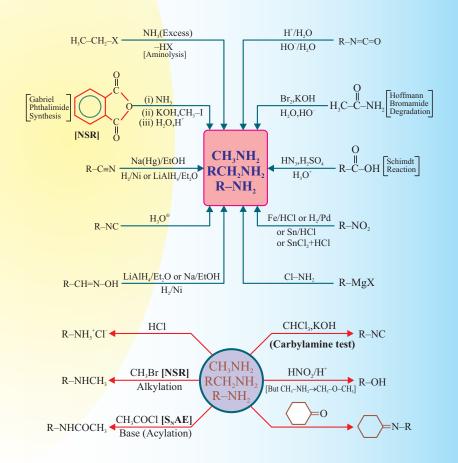


Nutshell preview and review of Amide, Cyanide and Isocyanide

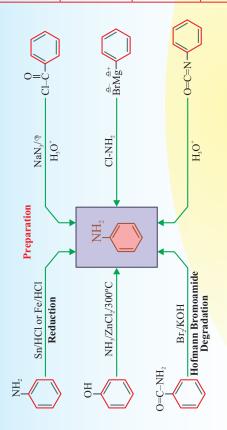


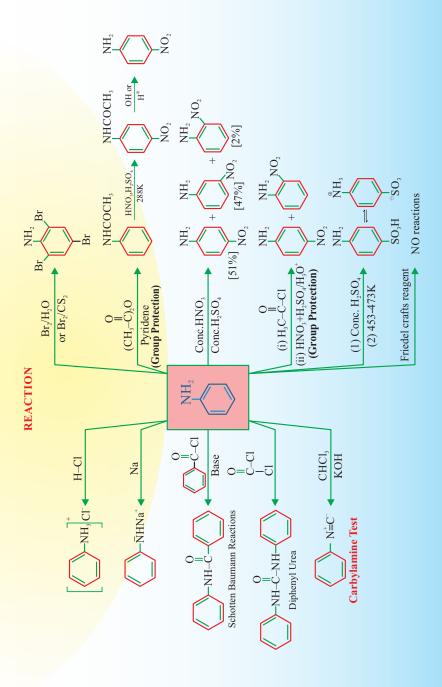
Amino Acid:

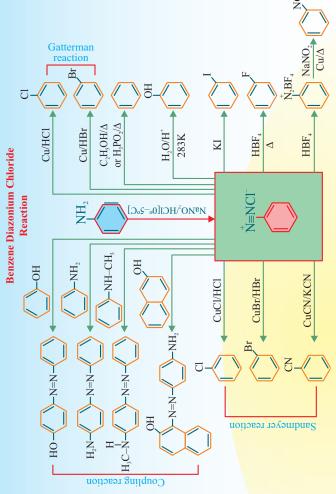
Amines



Test				
Reagent	R-NH ₂ (1°)	R ₂ NH(2°)	R ₃ N(3°)	√NH ₂
Ph-SO ₂ Cl (Hinsberg reagent)	$\begin{array}{c} R-N-SO_2-Ph \\ H & soluble \\ H & NaOH \\ [R-N-SO_2-Ph]Na^+ \end{array}$	$\begin{matrix} O \\ \parallel \\ R_2N-S-Ph \\ \downarrow \\ O \end{matrix} \upharpoonright NaOH \\ Insoluble \end{matrix}$	No reaction	NH-SO ₂ -Ph
S C=S \(\Delta/\text{HgCl}_2\) Mustard oil test	S $R-NH-C-SH$ $HgCl_2 \downarrow \Delta$ $R-N=C=S+HgS$	$\begin{array}{c} S \\ \parallel \\ R_2N-C-SH \\ HgCl_2 \downarrow \Delta \\ No \ reaction \end{array}$	No reaction	KOH→Ph−N=C=S+HgS





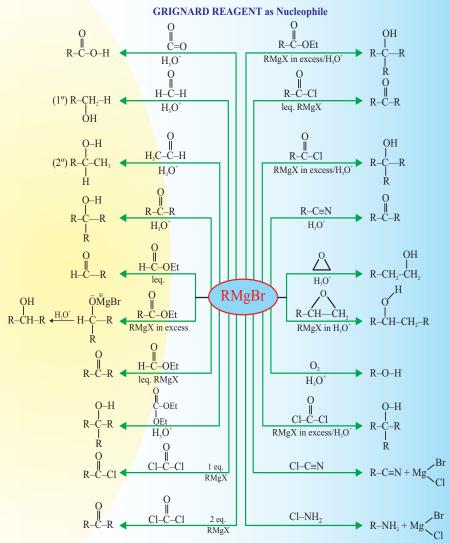


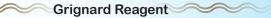
FrSR	Free Radical Substitution reaction
ESR	Electrophilic Substitution reaction
NSR	Nucleophilic Substitution reaction
S _N AE	Substitution Nucleophilic (addition elimination)
FrAR	Free radical addition reaction
NAR	Nucleophilic addition reaction
EAR	Electrophilic addition reaction
FrER	Free Radical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



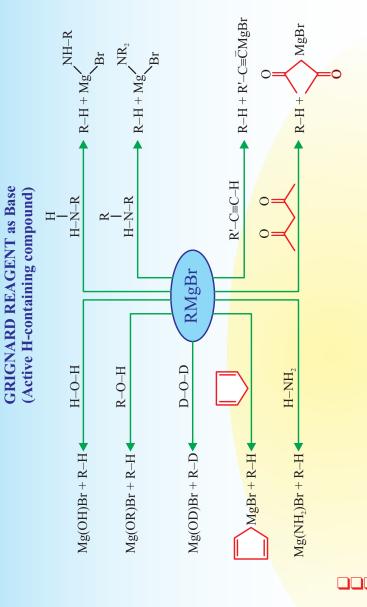
GRIGNARD REAGENT

REACTION









Polymers

ADDITION POLYMERS				
S.No	Name of Polymer	Starting Materials	Nature of Polymer	
	I. Polyolefins			
1.	Polyethylene or Polyethene	CH ₂ =CH ₂	Low density homopolymer (branched chain growth)	
2.	Polypropylene or Polypropene	CH₃CH=CH₂	Homopolymer, linear, chain growth	
3.	Polystyrene	C ₆ H ₅ CH=CH ₂	Homopolymer, linear, chain growth	
	II. Polydiences			
1.	Neoprene	Cl CH ₂ =CH-C=CH ₂ Chloroprene or 1-Chloro-1,3-butadiene	Homopolymer, chain growth	
2.	Buna S (Styrene-Butadiene, Rubber SBR or GRS)	CH ₂ =CH-CH=CH ₂ and 1,3-butadiene C ₆ H ₅ CH=CH ₂ Styrene	Copolymer, chain growth	
III. Polyacrylates				
1.	Polymethylmethacrylate (Flexiglss Lucite, Acrylite or Perspex PMMA)	CH ₃ I H ₂ C=C-COOCH ₃	Homopolymer	
2.	Polyethylacrylate	H ₂ C=CH-COOC ₂ H ₅	Homopolymer	
3.	Polyacrylonitrile or Orlon PAN	CH ₂ =CH–CN	Homopolymer	

IV. Polyhalofins			
1.	Polyvinyl chloride PVC	CH ₂ =CH–Cl	Homopolymer, chain growth
2.	Polytetrafluoroethylene or Teflon PTFE	F ₂ C=CF ₂	Homopolymer
3.	Polymonochlorotrifluoro- ethylene PCTFE	CIFC=CF ₂	Homopolymer

CONDENSATION POLYMERS				
S.No	Name of Polymer	Starting Materials	Nature of Polymer	
		I. Polyesters		
1.	Terylene or Dacron	HO-CH ₂ -CH ₂ -OH Ethylene glycol or Ethane-1,2-diol and O HO-C Terephthalic acid or Benzene-1,4-dicarboxylic acid	Copolymer, step growth, linear	
2.	Glyptal or Alkyl resin	HO-CH ₂ -CH ₂ -OH Ethylene glycol and HOOC COOH Phthalic acid or Benzene-1,2-dicarboxylic acid	Copolymer, linear step growth	
	II. Polyamides			
1.	Nylon-6,6	O O O O O O O O O O	Copolymer, linear, step growth	
2.	Nylon-6,10	H ₂ N(CH ₂) ₆ NH ₂ Hexamethylene diamine and HOOC(CH ₂) ₈ COOH Sebacic acid	Copolymer, linear, step growth	
3.	Nylon-6	H N O Caprolactum	Homopolymer, linear	
Formaldehyde resins				
1.	Phenolformaldehye resin or Bakelite	Phenol and formaldehyde	Copolymer, step growth	
2.	Melamine formaldehyde resin	Melamine and formaldehyde	Copolymer, step growth	





Biomolecules

- 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
$$\xrightarrow{\text{H}_3\text{O}^+}$$
 α -D. Glucose + β -D. Fructose;

Maltose
$$\xrightarrow{\text{H}_3\text{O}^+}$$
 2 α –D. Glucose unit

Lactose
$$\xrightarrow{H_3O^+} \beta$$
-D. Glucose + β -D. Galactose.

• Polysaccharide: Contain more than ten monosaccharide units. (C₆H₁₀O₅)_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	OH CC-C=O / -C-C-C- OH OH OH Hemiacetal OR OH Hemiketal	O H OR Acetal O R OR Ketal	

TYPE OF SUGAR		
Example	All monosaccharides Glucose Fructose Mannose Galactose Disaccharide Maltose Lactose	Disaccharide Sucrose Polysaccharide Starch Cellulose

• Mutarotation: When either form of D-glucose is placed in aq. solution it slowly form the other via open chain aldehyde and gradual change in specific rotation until specific rotation (± 52.5°) is reached.

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

eg. D-Glucose & D-mannose D-Glucose & D-Galactose

• Sucrose:

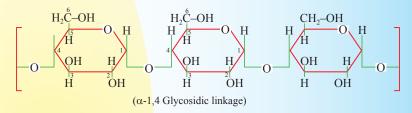
Maltose:

• Lactose

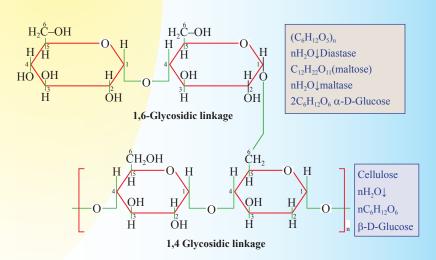
(1,4 Glycosidic linkage)

Starch: (Amylose & Amylopectin)

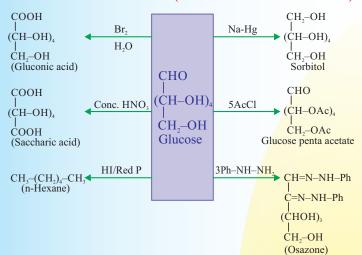
• Amylose (Straight Chain)



- (i) Soluble in H₂O & gives blue colour with I₂
- Amylopectin (Branch chain): (C₆H₁₂O₅)_n



REACTION OF GLUCOSE (OPEN CHAIN STRUCTURE)





Distinction between Pairs of Compounds

UNSATURATION TEST

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

•
$$R - CH = CH - R + Br_2$$

(Brown)

 CCl_4
 $R - CH - CH - R$

(Colourless)

•
$$R-C \equiv C-R+Br_2$$
(Alkene) (Brown)

 CCl_4
 $R-C-C-R$
 Br
 Br
 $CC-R$
 Br
 Br
 $CC-R$
 Br
 Br
 $CC-R$
 Br
 Br
 Br
 Br
 Br
 Br
 Br

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

•
$$R - CH = CH - R + KMnO_4 \rightarrow R - CH - CH - R + MnO_2$$
(Cold, dilute)

(Cold, dilute)

(Colourless)

(Colourless)

•
$$R - C \equiv C - R' + KMnO_4 \rightarrow MnO_2 + RCOOH R'COOH$$
(Hot, dilute) Brown ppt.

•
$$R - C \equiv C - H + KMnO_4 \rightarrow MnO_2 + RCOOH + CO_2 + H_2O$$
(Alkyne) (Hot, dilute) Brown ppt. (Colourless)

Baeyer's reagent is cold, dilute KMnO₄ solution having pink colour.



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

TEST FOR TERMINAL ALKYNE

Terminal alkyne



$$NH_4NO_3 + H_2O + R - C \equiv C - Ag$$

$$White ppt.$$

$$R - C \equiv CH$$

$$Terminal alkyne$$

$$CuCl_2 + NH_4OH$$

$$CuCl_2 + NH_4OH$$

$$CuCl_2 + NH_4OH$$

NATURE OF X-GROUP IN C-X BOND

$$R-X$$
 + aqueous KOH \rightarrow $R-OH + KX $\xrightarrow{\text{HNO}_3}$ $\xrightarrow{\text{AgX}}$ $\xrightarrow{\text{(Precipitate)}}$$

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

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOL

$$\begin{array}{c|cccc} R & & & R \\ \hline \bullet & R - \overset{\textstyle I \\ \textstyle C} - OH & & \underline{ & Lucas \ reagent \\ \textstyle H & & \\ \hline Secondary \ alcohol & & \\ \hline \end{array} \begin{array}{c} R & & R \\ \hline R - \overset{\textstyle I \\ \textstyle C} - C1 \\ \hline H & & \\ \hline Cloudiness \ appears \\ within \ five \ minutes \end{array}$$

Lucas reagent is anhydrous ZnCl₂ + conc. HCl.

OH
$$H_{3}C - CH - R + I_{2} \xrightarrow{\text{NaOH} \atop \text{Iodoform}} CHI_{3} + RCOONa$$

$$\xrightarrow{\text{Iodoform} \atop \text{(Yellow ppt.)}}$$

PHENOL

Phenol + ferric chloride → Violet colouration (neutral)

6 OH + FeCl₃
$$\rightarrow$$
 3H⁺ + [Fe(OC₆H₅)₆]³⁻ + 3HCl Violet colouration

CARBONYL GROUP

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

$$\begin{array}{c|c}
 & \text{NO}_2 \\
\hline
 & \text{NO}_2 \\$$

All aldehydes and only aliphatic methyl ketones
 + NaHSO₃ → White crystalline bisulphite.

$$\begin{array}{c|c} R & OH \\ H & C = O + NaHSO_3 \rightarrow R - C - SO_3^-Na^+ \\ H & OH \\ H_3C & Methyl ketone \end{array}$$

ALDEHYDE GROUP

Aldehyde + Tollen's reagent → Silver mirror

$$\begin{array}{c}
O \\
R-C-H+3OH^{\Theta}+2[Ag(NH_3)_2]^{+}\rightarrow RCOO^{\Theta}+2H_2O+4NH_3+2Ag\downarrow\\
\text{(silver mirror)}
\end{array}$$

Aldehyde + Fehling's solution → Reddish brown precipitate

$$\begin{array}{c} O \\ R-C-H+2Cu^{2^+} + 5OH^- \rightarrow RCOO^{\Theta} + 3H_2O + Cu_2O \\ \text{(Reddish brown ppt)} \end{array}$$

• H₃C – C – group also give iodoform test

$$O$$
 \parallel
 $H_3C - C - R + I_2 + NaOH \xrightarrow{Iodoform test} CHI_3 + RCOONa \xrightarrow{Iodoform} (Yellow ppt.)$

AROMATIC ALDEHYDE GROUP

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

CARBOXYLIC GROUP

Carboxylic acid + Sodium bicarbonate → effervescence RCOOH + NaHCO₃ → RCOONa + H₂O + CO₂↑

FORMIC ACID

HCOOH
Formic acid

Fehling's solution

$$H_2O + \frac{CO_3^{2-} + Cu_2O}{Red ppt.}$$
 $2Ag + \frac{CO_3^{2-} + H_2O}{Red ppt.}$

Silver mirror

AMINES (1°)

Amines (1°, 2°& 3°) (Hinsberg's test)

- Primary amine + Benzenesulphonyl chloride → Precipitate KOH Soluble
- Secondary amine + Benzenesulphonyl chloride → Precipitate KOH insoluble
- Tertiary amine + Benzenesulphonyl chloride → No reaction.



Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and Chlorobenzene

•
$$C_2H_5$$
-Cl + aq KOH \xrightarrow{Boil} C_2H_5 -OH + KCl $\xrightarrow{HNO_3}$ AgCl White ppt

• Cl + aq. KOH
$$\xrightarrow{\text{Boil}}$$
 No reaction $\xrightarrow{\text{HNO}_3}$



HAND BOOK (CHEMISTRY)



Chlorocyclohexane and chlorobenzene

• Cl + aq. KOH
$$\xrightarrow{\text{Boil}}$$
 OH + KCl $\xrightarrow{\text{HNO}_3}$ AgCl $\xrightarrow{\text{HNO}_3}$ White ppt.

Cl + aq. KOH
$$\xrightarrow{\text{Boil}}$$
 No reaction $\underset{\text{HNO}_3}{\text{No reaction}}$

Chlorocyclohexane and bromoethane

•
$$C_2H_5$$
-Cl + aq. KOH $\xrightarrow{\text{Boil}}$ C_2H_5 -OH+KCl $\xrightarrow{\text{HNO}_3}$ AgCl (Chloroethane)

•
$$C_2H_5$$
-Br + aq. KOH $\xrightarrow{\text{Boil}}$ C_2H_5 -OH+KBr $\xrightarrow{\text{HNO}_3}$ AgBr (Bromoethane)

Benzyl chloride and chlorobenzene

$$Cl$$
 $CH_2 + aq$
 $CH_2 + aq$
 $CH_2 + aq$
 $CH_2 + kCl$
 $AgCl$
 $AgNO_3$
 $AgNO_3$

• Cl + aq. KOH
$$\frac{\text{Boil}}{\text{HNO}_3, \text{AgNO}_3}$$
 No reaction

Ethyl chloride and vinyl chloride

•
$$C_2H_5$$
-Cl+aq. KOH \xrightarrow{Boil} C_2H_5 -OH+KCl (Ethyl chloride)

AgCl $\xrightarrow{HNO_3}$ $\xrightarrow{AgNO_3}$

•
$$H_2C = CH - CI + aq$$
. KOH \xrightarrow{Boil} No reaction Vinyl chloride

n-Propyl alcohol and iso-propyl alcohol

• CH₃CH₂CH₂OH + HCl ZnCl₂ → CH₃CH₂CH₂Cl No cloudiness at room temp.

OH Cl

$$H_3C - CH - CH_3 \xrightarrow{Z_{DCl_2}} H_3C - CH - CH_3$$

Cloudiness within 5 minutes

Ethyl alcohol and methyl alcohol (lodoform test)

- $CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow CHI_3 + HCOONa$ Yellow ppt.
- $CH_3OH + 4I_2 + 6NaOH \rightarrow No \text{ yellow ppt.}$

Ethyl alcohol and acetone (2,4 - DNP)

$$H_3C$$
 $C = O + H$
 $N - NH$
 NO_2
 O_2N
 O_2N

• $C_2H_5OH \xrightarrow{2,4-DNP}$ No reaction

Phenol and ethyl alcohol (Neutral FeCl₃)

Phenol + Neutral ferric chloride → Violet colouration

6 OH + FeCl₃
$$\rightarrow$$
 3H⁺ + [Fe(OC₆H₅)₆]³⁻ + 3HCl
Violet colouration

CH₃CH₂OH + Neutral ferric chloride → No violet colouration

Benzoic acid and phenol (NaHCO₃)

- Benzoic acid + Sodium bicarbonate → effervescence
 C₆H₅COOH + NaHCO₃ → C₆H₅COONa + CO₂↑ + H₂O
- Phenol + Sodium bicarbonate → No effervescence (Phenol is less acidic than benzoic acid)

Propanone and propanol (2,4 - DNP)

$$\begin{array}{c} H_3C \\ H_3C \\ \end{array} C = \begin{array}{c} O_2N \\ \\ H_3C \\ \end{array} N - NH \\ \begin{array}{c} O_2N \\ \\ \end{array} NO_2 \\ \end{array}$$

$$\begin{array}{c} O_2N \\ \\ O_2N \\ \\ \end{array} NO_2$$

$$\begin{array}{c} O_2N \\ \\ \end{array} NO_2$$

• Propanol + 2,4–Dinitrophenylhydrazine \rightarrow No crystals



Ethanal and propanal (lodoform test)

•
$$H_3C - CH_2 - C - H + I_2 + NaOH \xrightarrow{Iodoform \text{ test}}$$
 No yellow ppt.

Propanal and propanone (Tollen's and Fehling reagent)

Propanal + Tollen's reagent → Silver mirror

Propanal + Fehling's solution → Reddish brown precipitate

• Propanone Propanone Negative test

Negative test

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

• H₃C-CH₂-C-CH₂-CH₃+I₂+NaOH - No yellow ppt.

Propanal and benzaldehyde (Fehling solution)

Propanal + Fehling's solution → Reddish brown precipitate

$$\begin{array}{c} O \\ \parallel \\ H_3C-CH_2-C-H+2Cu^{2+} + 5OH^- \rightarrow CH_3CH_2COO^- + 3H_2O+Cu_2O \\ & \text{Fehling's} \\ & \text{solution} \end{array}$$

• Benzaldehyde + Fehling's solution → No precipitate

CHO+2Cu²⁺+5OH
$$^-$$
 No reaction

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

• HCOOH

Methanoic acid

Fehling's solution

$$H_2O + CO_3^{2-} + Cu_2O$$
 $2Ag \downarrow + CO_3^{2-} + H_2O$

Fehling's solution

No brown ppt.

Tollen's reagent

No silver mirror

Ethanal and methanal (lodoform test)

- CH₃CHO+I₂+NaOH lodoform test → CHI₃+HCOONa lodoform (Yellow ppt.)
- HCHO+I₂+NaOH Iodoform test
 No yellow ppt.

 Methanal

Acetophenone and benzophenone (lodoform test)

O
$$C-CH_3 + I_2 + NaOH \xrightarrow{Iodoform \ test}$$

$$CHI_3 + (Yellow \ ppt.)$$

$$COONa \leftarrow +I_2 + NaOH \xrightarrow{Iodoform \ test} No \ ppt.$$

$$(Benzophenone)$$

Benzoic acid and ethylbenzoate

effervescence

Ethyl benzoate + Sodium bicarbonate → No effervescence

Benzaldehyde and acetophenone (Tollen's test)

Benzaldehyde + Tollen's reagent → Silver mirror

Acetophenone + Tollen's reagent → No silver mirror



Methyl amine and dimethyl amine (Isocyanide test)

• $CH_3NH_2 + CHCl_3 + 3KOH \rightarrow CH_3NC + 3KCl + 3H_2O$ Methyl amine (alc.) Methyl isocyanide (Offensive smell)

CH₃

H₃C-NH+CHCl₃+3KOH(alc.) → No offensive smell
 Di-methyl amine

Aniline and ethyl amine (Diazotisation)

$$NH_{2} \xrightarrow{\text{NaNO}_{2} + \text{HCl}} \longrightarrow N_{2}Cl$$

$$N = N \longrightarrow OH$$
Orange dye
p-hydroxy azobenzene

Aniline and N-methylaniline (Isocyanide Test)

Aniline and Benzylamine (Diazotisation + phenol)

NH₂ NaNO₂+HCl
$$N_2$$
Cl N_2 Cl $N_$

Glucose and fructose

- Glucose + Br₂ + H₂O → Gluconic acid + 2HBr

 (Brown colour) (Colourless)
- Fructose + Br_2 + H_2O \rightarrow Brown colour (Brown colour) (no change in colour)

Glucose and sucrose

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

Glucose and starch

- Glucose + Fehling's solution → Red ppt.
- Starch + Fehling's solution → No red ppt.

OR

- Glucose + I_2 solution \rightarrow No blue colour
- Starch + I₂ solution → Blue colour



Organic Reagents

1. Alcoholic KOH

 $R-X \rightarrow Alkene$; Elimination

2. Aluminium Ethoxide

$$\begin{array}{ccc}
R-C-H=O \rightarrow R-C-O-CH_2R \text{ (Tischenko Reaction)} \\
O & O \\
\text{(Aldehyde)} & \text{(Ester)}
\end{array}$$

3. Aqueous KOH/NaOH

$$R-X \rightarrow ROH$$

Nucleophilic substitution reaction also used for Cannizzaro reaction with aldehyde.

4. Baeyer's Reagent (Alkaline cold dilute KMnO₄)

RCH = CHR'
$$\rightarrow$$
 RCH-CHR'
OH OH
(Syn)

alkene \rightarrow 1, 2 diol
(used to detect unsaturation)

5. Bromine water

(i) Used to detect unsaturation;

$$\begin{array}{c|c} & NH_2 & OH & OH \\ Br & Br_{2(aq.)} & Br & Br_{3(aq.)} & Br & Br \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ &$$

6. Benedict's solution

Used to detect aldehyde group RCHO \rightarrow RCO₂ [ketone gives –ve test]

7. $Cu_2Cl_2 + NH_4OH$

Used to Detect Terminal Alkyne Red Precipitate observed

8. CrO₂Cl₂

Etard reaction

9. CrO₃

- (i) $RCH_2OH \rightarrow RCHO$,
- (ii) $R_2CHOH \rightarrow R_2C=O$
- (iii) R₃COH → no reaction

10. CCl₄ + O H (Reimer Tiemann)

$$\begin{array}{ccc}
OH & OH \\
CO_{2}^{-} \\
+ p-Product
\end{array}$$

11. CO + HCl + AlCl₃

Gatterman koch reaction

12. HCN + HCl + AlCl₃

Gatterman Aldehyde Synthesis

13. CHCl₃ + KOH

$$(i) \begin{picture}(60,0) \put(0,0){\ovalpha} \put(0,0){\oval$$

Reimer Tiemann reaction

(ii) RNH₂ → RNC (*Carbyl amine reaction*) (used to detect 1° amine) (Isocyanide test)

14. $CO_2 + OH^-$ (high temp. + Pressure)

$$OH \qquad OH \qquad CO_2^- + p\text{-Product}$$

Kolbe's reaction

15. Cu/Δ

(i)
$$RCH_2OH \rightarrow RCHO$$
,

(ii)
$$R_2CHOH \rightarrow R_2C=O$$

 CH_3
(iii) $H_3C-C-OH \rightarrow H_2C=C$
 CH_3

16. 2,4 - D.N.P.

Used to detect carbonyl group (orange ppt. observed)

17. DMSO

Polar aprotic solvent: favour S_N2 mechanism.

18. $Fe + Br_2/FeBr_3$

19. Fehling solution

Used to identify –C–H group.

PhCHO gives –ve test

Observation: red ppt. of Cu₂O formed

20. Grignard Reagent

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

21. H₂(Pd/CaCO₃) Quinoline (Lindlar catalyst)

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

22. H₃PO₂

$$N_2^+$$

23. $HN_3 + H_2SO_4$

$$\begin{array}{c}
R-C - OH \longrightarrow RNH_2 \\
O
\end{array}$$

(Schmidt Reaction)

24. H₃PO₄/∆

 $H_3PO_4 \Rightarrow Same as H_2SO_4/\Delta$

25. H₂SO₄/Δ

$$\begin{array}{c} RCH-CH_3 \longrightarrow RCH = CH_2 \\ OH \end{array}$$

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

26. HNO_2 (NaNO₂ + HCl)

- (i) $RNH_2 \rightarrow R OH$;
- (ii) $PhNH_2 \rightarrow PhN_2^+ (0 5^{\circ}C)$
- (iii) $PhNH_2 \rightarrow PhOH$ (high temperature)

$$(iv) \longrightarrow OH OH OH N=O + NO$$

27. HIO₄ (Periodic acid)

28. H₂(Ni) can reduce

(i)
$$R-C-R \longrightarrow R_2CHOH$$

O

(ii)
$$R-C-H \longrightarrow RCH_2OH$$

O

(iii) RCN
$$\rightarrow$$
 RCH₂NH₂; $-C \equiv C - \rightarrow -CH_2 - CH_2 -$

$$-HC = CH - \rightarrow -CH_2 - CH_2 -$$

29. H₂(Pd/BaSO₄)

Quinoline

$$\begin{array}{c}
R-C-Cl \longrightarrow RCH=O \\
\downarrow \\
O \\
(Rosenmund reduction)
\end{array}$$

30. Jones Reagent (CrO₃ + dil. H₂SO₄ + acetone)

(i)
$$RCH_2OH \rightarrow RCHO$$
; (ii) $R_2CHOH \rightarrow R_2C = O$

$$\begin{array}{c} \mathrm{CH_2\text{-}CH\text{-}CH_2\text{-}OH} \longrightarrow \mathrm{CH_2\text{-}CH\text{-}CH\text{-}O} \\ \mathrm{OH} \quad \mathrm{OH} \end{array}$$

32. K₂Cr₂O₇/H⁺

(i) RCH₂OH
$$\rightarrow$$
 RCO₂H; (ii) R₂CHOH \rightarrow R₂C = O

33. MnO₂

(i)
$$CH_3$$
- $CH = CH$ - CH_2 - $OH \rightarrow CH_3$ - $CH = CH$ - $CH = O$

(ii)
$$PhCH_2OH \rightarrow PhCH = O$$

To oxidise allylic/benzylic hydroxyl group into corresponding carbonyl.

34. NaHCO₃

$$RCO_2H \xrightarrow{NaHCO_3} RCO_2Na^+ + CO_2\uparrow$$

35. NaHSO₃

$$\begin{array}{c}
\text{OH} \\
\text{R-C-R} \longrightarrow \text{RC} \\
\text{SO}_{3}^{-}\text{Na}^{+}
\end{array}$$

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

36. NaOH(aq)

(i)
$$R-X \rightarrow R-OH$$

(ii)
$$R$$
- C - OR' \xrightarrow{NaOH} R - C - O ⁻ + R'OH O

(iii) HCHO OH HCO₂ + CH₃OH (cannizaro)

(iv)
$$H_3C$$
-CH = $O \xrightarrow{OH} H_3C$ -CH = CH-CH = O
(Aldol condensation)

37. Ninhydrin

Detection of amino acid

$$\begin{array}{c} O \\ C \\ O \\ O \\ O \\ \end{array}$$

$$\begin{array}{c} O \\ C \\ O \\ \end{array}$$

Observation: Purple coloured ion

Yellow orange product

38. NaOR

Strong base:

(i)
$$RCH-CH_2-R \longrightarrow RCH=CH-R$$

 X
(Saytzeff Product : E_2 elimination)

(ii)
$$H_3C-C-OEt \longrightarrow H_3C-C-CH_2-C-OEt$$

 $O O O$
(claisen condensation) $(\beta \text{ keto ester})$

39. NaOH + X, or NaOX

(ii)
$$R-C-NH_2 \longrightarrow RNH_2$$
 (Hoffman Degradation)

$$RCO_2H \rightarrow RH$$

41. MnO / 300°C Used for –CO₂ & –H₂O in carboxylic acid.

42. NBS

43.
$$NaNO_2 + HCl$$

 $RNH_2 \rightarrow R-OH$

44. NaNH₂ in paraffin

Non-terminal Alkyne \rightarrow Terminal Alkyne (2-Butyne \rightarrow 1-Butyne)

45. Na/EtOH

Reduce all except c/c double & triple bond

46. Zn(Hg) + HCl [Clemmensen's reduction]

$$R-C-R \longrightarrow R-CH_2-R$$



47. NH₂ –NH₂/OH⁻ [Wolf Kishner reduction]

$$\begin{array}{c}
O\\
R-C-R \rightarrow R-CH_2-R
\end{array}$$

48. Na in Liq. NH₃ [Birch reduction]

$$R-C \equiv CR \longrightarrow R$$
 $C=C \setminus R$
 $(trans alkene)$

49. $OsO_4 + H_2O$

50. O₃: R-CH=CH-R H_{2O/Zn} R-CHO+R-CHO (Ozonolysis process)

51. Oxirane followed by H⁺ RMgX → RCH₂-CH₂-OH

- **52. PCC**
 - (i) RCH₂OH → RCHO,
 - (ii) $R_2CHOH \rightarrow R_2C=O$
 - (iii) R₃COH → no reaction

(Mild oxidizing reagent)

53. $P(red) + Br_2$

(i)
$$CH_3CO_2H \rightarrow H_2C - CO_2H$$
 (HVZ reaction)

Br

- (ii) $ROH \rightarrow R-Br$
- 54. P (red) + HI

$$CH_3CO_2H \rightarrow CH_3-CH_3$$

$$CH_3CH = O \rightarrow CH_3-CH_3$$

$$CH_3CH_2OH \rightarrow CH_3-CH_3$$

(strong reducing agent can reduce any oxygen or halogen containing compound to alkane)

55. Perbenzoic acid [Baeyer Villiger Oxidation]

$$\begin{array}{c}
R-C-R' \longrightarrow R-C-OR' \\
0 & 0
\end{array}$$

R' having more migrating tendency than R

56. RCl + AlCl₃ [Friedel craft alkylation]

$$\bigcap \rightarrow \bigcap^{R}$$

57. RCOCl + **AlCl**₃ [Friedel craft acylation]

$$\bigcap \longrightarrow \bigcap_{O} \bigcap_{O} \bigcap$$

58. ROH+R-C-OH $\xrightarrow{\text{Conc.}}$ R-C-OR $\xrightarrow{\text{H}_2\text{SO}_4}$ R = C OR $\xrightarrow{\text{U}}$ (Esterification reaction)

59. SnCl₂ + HCl

(i)
$$R-N=N-R' \rightarrow RNH_2 + R'NH_2$$

(ii)
$$NO_2$$
 NH_2

(iii) RCN \rightarrow R-CH₂NH₂

60. Sn + HCl

(ii) RCN \rightarrow R-CH₂NH₂

61. Silver salt RCOOAg (Hunsdiecker reaction) $Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

62. AgOH/moist Ag₂O; $R_4NX \rightarrow R_4NOH$ $Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

$$\begin{array}{c} R-C-OH/R-OH \longrightarrow R-C-CI/R-CI \\ \parallel & O \end{array}$$

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. V₂O₅

(i)
$$V_2O_3/O_2$$
 HC O HC O HC O O (Maleic anhydride)



Organic Name Reactions

Aldol Condensation

$$\begin{array}{c} O \\ H - C - CH_2 \\ \hline H \\ \end{array} \begin{array}{c} O \\ H - C - \overline{C}H_2 \\ \hline H \\ \end{array} \begin{array}{c} O \\ H - \overline{C} \\ \overline{C} \\ \end{array} \begin{array}{c} O \\ H \\ \overline{C} \\ \end{array} \begin{array}{c} O \\ \overline{C} \\ \overline{C} \\ \overline{C} \\ \end{array} \begin{array}{c} O \\ \overline{C} \\ \overline{C} \\ \overline{C} \\ \end{array} \begin{array}{c} O \\ \overline{C} \\ \overline{C} \\ \overline{C} \\ \overline{C} \\ \overline{C} \\ \overline{C} \\ \end{array} \begin{array}{c} O \\ \overline{C} \\ \overline{C}$$

Claisen Condensation

Perkin Condensation

Benzoin Condensation

Haloform Reaction

$$\begin{matrix} OH & O & O \\ \parallel & \parallel & \parallel \\ H_3C-CH-R^1 & \xrightarrow{NaOI} & H_3C-C-R^1 & \xrightarrow{NaOH} & CHI_3+R^1-C-\overline{O}Na^{\oplus} \end{matrix}$$

Carbylamine Test

$$R-N \overset{H}{\longleftarrow} \ddot{C} \overset{Cl}{\longleftarrow} \overset{CHCl_1}{\underset{KOH}{\longleftarrow}} R \overset{H}{\longrightarrow} \overset{H}{\underset{N-C}{\longleftarrow}} \overset{Cl}{\longleftarrow} \overset{\bar{O}H}{\underset{Cl}{\longleftarrow}} R \overset{\oplus}{\longrightarrow} \overset{\ominus}{\underset{R-N=C}{\longleftarrow}} \operatorname{Isocyanide}$$

Reimer Tiemman Reaction

Kolbe's Schimdt Reaction

Hoffmann Bromamide Degradation

$$\begin{array}{c} O \\ R-C-NH_2 \xrightarrow{Br_2} R-NH_2+K_2CO_3 \end{array}$$

Curtius Reaction

$$\begin{array}{c}
O \\
\parallel \\
R-C-Cl \xrightarrow{NaN_3} R-NH_2
\end{array}$$

Schimdt Reaction

$$\begin{array}{c} O \\ \parallel \\ R-C - OH \xrightarrow{HN_3} R-N=C=O \xrightarrow{H_3O^{\oplus}} R-NH_2 \end{array}$$

Cannizzaro Reaction

Bayer villiger oxidation

Cumene

$$\begin{array}{c|c} O-O-H \\ CH_3-CH-CH_3 & CH_3-C-CH_3 & OH \\ \hline \\ O_2 & \hline \\ 130^{\circ}C & \hline \\ Cumene \\ hydroperoxide \\ \end{array} + CH_3-C-CH_3$$

Pinacol-Pincolone rearrangement

$$\begin{array}{c} Cl \\ Cl \\ CH \\ OH \\ OH \end{array}$$

$$\begin{array}{c} H' \\ -H_2O \end{array}$$

$$Cl \\ Cl \\ -C \\ -C \\ -Ph \\ -H' \\ O \\ -Ph \\ O \\ -Ph \\ -H' \\ O \\ -Ph \\ -H' \\ -H'$$

Birch Reduction

$$\begin{array}{c|c} & & & & & & & & & & & & & & & & \\ \hline & N_{a'} & & & & & & & & & & \\ \hline & N_{a'} & & & & & & & & \\ \hline & N_{a'} & & & & & & & \\ \hline & N_{a'} & & & & & & & \\ \hline & N_{a'} & & & & & & \\ \hline & N_{a'} & & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & & & \\ \hline & N_{a'} & & & \\ \hline & N_{a'} & & & & \\ \hline & N_{a'} & & & \\$$

Gabriel Synthesis

Name	Reactant	Reagent	Product
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl	Alkane
Coupling Reaction	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Azo Dye (Detectionof OH or NH ₂ gr)
Diazotization	-ÑH ₂	NaNO ₂ + HCl (0° – 5°C)	
Etard reaction	H ₃ C-	CrO ₂ Cl ₂ /CS ₂	O H (Benzalde hyde)
Fitting Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation	+ R-X	Anhydrous AlCl ₃	Alkyl Benzene
Friedel Craft acylation	O + R-C-Cl or (RCO) ₂ O	Anhydrous AlCl ₃	Acyl Benzene
Gattermann aldehyde synthesis	$\mathrm{C_6H_6}$	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/C₂H₅OH	primary amine

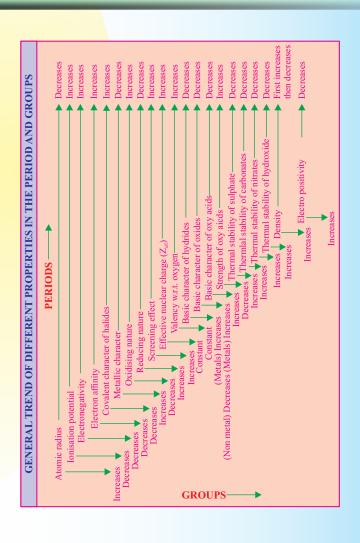
Name	Reactant	Reagent	Product
Rosenmund reduction	acid chloride	H ₂ ,Pd/BaSO ₄ boiling xylene	aldehyde
Sabatier- Senderens reaction	Unsaturated hydrocarbon	Ranye Ni/H ₂ , 200–300°C	Alkane
Sandmeyer reaction	$C_6^{}H_5^{}N_2^{}C\bar{\Gamma}$	CuCl/HCl or CuBr/ HBr or CuCN/KCN, heat	Halo or cyanobenzene
Gattermann Reaction	$\mathrm{C_6H_5N_2^+Cl^-}$	Cu/HX(HBr/H <mark>Cl)</mark>	Halobenzene
Schotten- Baumann reaction	(phenol or aniline or alcohol)	NaOH + C ₆ H <mark>₅COCl</mark>	benzolytated product O O O O O O O O O O O O O
Stephen reaction	alkyl cyanide	(i) SnCl ₂ /HCl (ii) H ₂ O	Aldehyde
Williamson synthesis	alkyl halide	sodium alko <mark>xide or</mark> sodium phe <mark>noxide</mark>	Ether
Wurtz-Fitting reaction	alkyl halide + aryl halide	Na/dry et <mark>her</mark>	alkyl benzene







Periodic Properties



PERIODICITY

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

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

ATOMIC RADIUS

Distance between centre of nucleus to outermost electron.

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

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

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

Vander wall radius mainly used for noble gases.

Factors Affecting atomic radius:

- (1) AR ∝ Number of shells
- (2) 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.



Atomic radius of Al > Ga : Due to poor sheilding of 3d subshell electron. Atomic radius of 4d \approx 5d series element due lanthanide construction.

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



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

Ionic Radius:

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

Factors Affecting Ionic Radius

- (+) charge ↑ ionic radius ↓
 (-) charge ↑ ionic radius ↑ $Z_{\text{eff}} \uparrow ionic radius ↓$ $n \uparrow ionic radius ↑$
 - ⇒ In isoelectronic species (+) charge ↑ lonic radius ↓
 (-) charge ↑ tonic radius ↑

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

 $K^{+} > Li^{+} > Mg^{2+} > Al^{3+}$

IONIZATION ENERGY

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

Successive I.E.

I.E₁, I.E₂, combined ly termed as successive I.E.

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

$$IE_1 \le IE_2 \le IE_2 \dots$$

Factors Affecting

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

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

(2) IE
$$\propto$$
 (+) charge,

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

- (5) half filled and full filled configration (allected 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.





upto 4th period (lonization Energy)

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



after 4th period (lonization Energy)

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

Al < Ga (Poor sheilding of 3d sutshell e⁻)

 $T1 > ln \atop Pb > Sn \begin{cases} due \ to \ lanthanide \ contraction \end{cases}$

Periodic Trend (d-block)

- (1) Generally increases on moving down the group
- (2) Generally increase when moving left to right in the period. Sc > Y > La, Ag < Cu < Au, Cd < Zn < Hg

Application of Ionization Energy

IE↑ Metallic Character ↓

IE↑ Electropositive Character ↓

IE↑ Reducing Property ↓



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

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

Highest jump between IE₃ & IE₄ therefore Ve⁻ is 3

Electron Affinity & Electron Gain Enthalpy

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



Successive Electron Affinity

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

EA₁ is generally exothermic except N, Be, Mg and Noble gas EA₂, EA₃ always endothemic

Factors Affecting

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

- (2) EA $\propto \frac{1}{\text{size}}$
- (3) Nature of subshell
- (4) hall and full filled

Periodic Trend

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



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

$$O < Te < Se < S$$
,



$$|IE_A| = |EA_A|$$
 and $|EA_A| = |IE_A|$

Electronegativity

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

Factors Affecting

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

- (2) EN $\propto \frac{1}{\text{size}}$
- (3) $EN \propto \frac{1}{(-) \text{ charge}}$
- (4) EN \propto (+) charge,
- (5) EN ∞% 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) Mg²⁺, Na⁺, F⁻, O²⁻. N³⁻

(Hint: Isoelectronic series)

- (ii) Ca²⁺, Ar, Cl⁻, S²⁻
- (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) Ba²⁺, Sr²⁺, Ca²⁺, Mg²⁺, Be²⁺
- (*ii*) Cs⁺, Rb⁺, K⁺, Na⁺, Li⁺
- (iii) Na⁺, Mg²⁺, Al³⁺

7. Tonic Radii in water

- (i) Cs⁺, Rb⁺, K⁺, Na⁺, Li⁺ (ii) Li⁺, Be²⁺
- (iii) Na⁺, Mg²⁺, Al³⁺

8. Molar Conductivity in Water

Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺

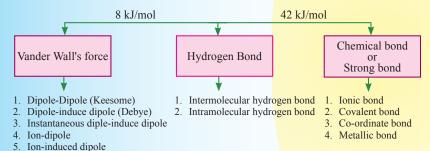


Chemical Bonding

CHEMICAL BOND

The force of attraction which hold together atom, molecule or ions with in chemical species.

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.

COVALENT BOND

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

$$H_2$$
 molecule \ddot{O} \ddot{O}

COORDINATE BOND (DATIVE BOND)

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

EXCEPTION OF OCTET RULE				
(a) electron deficient Central atom: No. of electron < 8 BeH ₂ BF ₃ , BCl ₃ , BBr ₃ , BI ₃ AlCl ₃ , AlBr ₃ , AlI ₃	(b) electron rich Central atom: No. of electron > 8 PCl ₅ , IF ₇ SF ₆ , XeF ₂	(c) odd electron species central atom: has odd electron NO, NO ₂ , ClO ₂ , ClO ₃		

CO-ORDINATE BOND (DATIVE BOND)

In this type of bond, shared pair of electron donates by one species but shared by both.

- For this type of sharing.
- One species must have lone pair act as donar known as Lewis base - acquire +ve charge.
- Another species must have 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.

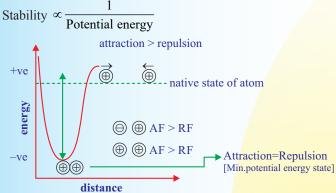




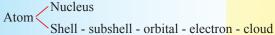


1. Valence Bond Theory

Proposed by Heitler & London as per VBT bonding takes place for attaining stability.



- Bond formation is an exothermic process.
- During this process some extent of electron cloud merge into each other; this part is known as overlapped known as overlapping.



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. $H \rightarrow 1s^1$ $Cl \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5$

- Opposite spin
- 1. Nature of Orbitals
 - (a) No. of shell: lower the number of shell higher overlapping.

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

• Exception:
$$Cl_2 > Br_2 > F_2 > I_2$$
 due to $O - O < S - S$ lp-lp $N - N < P - P$ repulsion

(b) Type of Sub-shell

Valence shell contain subshell s & p

s-non-directional Directional orbital has higher extent of overlapping

Possibler Combination & Strength of Overlapping

$$s-s < s-p < p-p$$

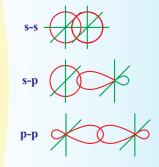
This factor is applicable when number of shell is same otherwise shell factor prominent.

$$2s - 2s < 2s - 2p < 2p - 2p$$
 sub-shell factor $1s - 1s > 1s - 2s > 1s - 3s$ shell factor

2. Pattern of Overlapping

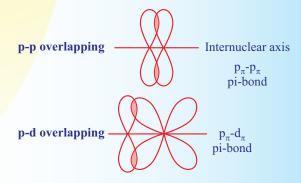
(a) Axial overlapping:

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



(b) Co-lateral overlapping

Side wise overlapping has less extent of overlapping for π -bond. Weak bond



HYBRIDISATION

S.No.	Type or 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	Triangula <mark>r</mark> bipyrami <mark>dal</mark>	PCl ₅
5.	one s + three p + two d	6 ; sp^3d^2	Octahe <mark>dral</mark>	SF ₆
6.	one s + three p + three d	$7; sp^3d^3$	Penta <mark>gonal</mark> bipyr <mark>amidal</mark>	IF ₇

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

• 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	3	-	Trigonal planar	BF ₃ , AlCl ₃ , BeF ₃
(b) sp ² -hybridisation	2	1	V-shape, Angul <mark>ar</mark>	NO_2 , SO_2 , O_3
3. (a) sp ³ -hybridisation	4	0	Tetrahedral	CH ₄ , CCl ₄ , PCl ₄ ⁺ , ClO ₄ ⁻ , NH ₄ ⁺ , BF ₄ ⁻¹ , SO ₄ ⁻² , AlCl ₄ ⁻ ,
(b) sp ³ -hybridisation	3	1	Pyramidal	NH ₃ , PF ₃ , ClO ₃ , H ₃ O ⁺ , PCl ₃ , XeO ₃ , N(CH ₃) ₃ , CH ₃
(c) sp ³ -hybridisation	2	2	V-shape Angular	H ₂ O, H ₂ S, NH ₂ , OF ₂ , Cl ₂ O ₂ , SF ₂ , I ₃ ⁺
4. (a) sp ³ d-hybridisation	5	_	Trigonal bipyramidal	PCl ₅ , SOF ₄ , AsF ₅
(b) sp ³ d-hybridisation	4	1	See-Saw,	SF ₄ , PF ₄ , AsF ₄
			folded square distorted tetrahedral	SbF ₄ , XeO ₂ F ₂
(c) sp ³ d-hybridisation	3	2	almost T-shape	ClF ₃ , ICl ₃
(d) sp ³ d-hybridisation	2	3	Linear	I ₃ , Br ₃ , ICl ₂ , XeF ₂
5. (a) sp ³ d ² -hybridisation	6	-	Square bipyramidal/ octahedral	PCl ₆ , SF ₆
(b) sp ³ d ² -hybridisation	5	1	Square pyramidal/ distorted octahedral	XeOF ₄ , ClF ₅ , SF ₅ ,
(c) sp ³ d ² -hybridisation	4	2	Square planar	XeF ₅ , XeF ₄

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Examples
6. (a) sp ³ d ³ -hybridisation	7	-	Pentagonal bipyramidal	IF ₇
(b) sp ³ d ³ -hybridisation	6	1	Pentagonal pyramidal/ distorted octahedral/ capped octahedral	XeF ₆
(c) sp ³ d ³ -hybridisation	5	2	Pentagonal planar	XeF ₅

DIPOLE MOMENT

Measurement of Polarity in a molecule

$$\frac{\vec{\mu} = q \times d}{1D = 10^{-18}} = \text{esu-cm}$$

(A) Identification of polar or Non-polar molecule.

Molecule: Symmetrical distribution of electron cloud-Non-polar.

Molecule: Unsymmetrical distribution of electron cloud-Polar.

Diatomic Molecule

(a) Homoatomic
$$\Delta EN = 0 \rightarrow \vec{\mu} = 0 \rightarrow Non-polar$$
.

$$H_2$$
, F_2 , Cl_2 , N_2 etc.

(b) Heteroatomic
$$\Delta EN \neq 0 \rightarrow \vec{\mu}_{net} \neq 0 \rightarrow polar$$

Polyatomic Molecule:

$$\mu_R \rightarrow \text{vector sum of bond moment}$$

$$\mu_{\rm R} \to \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

Important Order

$$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$$

$$NH_3 > SbH_3 > AsH_3 > PH_3$$

$$H_2O > H_2S$$

$$CH_3Cl > CH_3F > CH_3Br > CH_3I$$

$$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$$

Applications

Predict shape and polarity of molecule

Symmetrical geometry $\rightarrow \mu = 0 \rightarrow \text{non-polar}$

Unsymmetrical geometry $\rightarrow \mu \neq 0 \rightarrow polar$

Distinguish between cis & transform

Dipole moment in Aromatic Compounds

$$\begin{array}{c|c} Cl & Cl \\ \hline \\ Orthodichloro \\ benzene \end{array} > \begin{array}{c|c} Cl \\ \hline \\ Cl \\ \hline \\ Paradichloro \\ benzene \end{array}$$

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 → between the molecules
 Intramolecular hydrogen bond → the molecules
- Intromolecular H-bonding takes places mainly in ortho derivatives only.



- 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 (densile nature)	∞	H-bond
Melting Point (mp)	∞	H-bond
Boiling Point (bp)	∞	H-bond
Viscosity	∞	H-bond
Surface Tension	∞	H-bond
Volatility	∞	1/H-bond
Vapour Pressure	œ	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 **antibonding 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:

163

Linear Combination of Atomic Orbitals (LCAO)

Case I: When two waves are in same phase (constructive interference) the wave adds up and amplitude of new wave is the sum of wave functions of individual atomic orbitals.

$$\psi_{MO} = \psi_A + \psi_B$$
 (Bonding M.O.)

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

$$\psi_{MO}^* = \psi_A - \psi_B$$
 (Antibonding M.O.)





Condition for Combination Atomic Orbitals

- The combining atomic orbitals must have the same or nearly the same energy.
- 2. The combining atomic orbitals must have the same symmetry about the molecular axis.
- 3. The combining atomic orbitals must overlap to the maximum extent. Energy level diagram from MOs:

Molecular orbital energy diagram for up to N_2 (molecule having \leq 14 electrons)

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

Molecular orbital energy diagram for O₂ and F₂ (molecule having > 14 electrons)

$$\sigma_{1s} < \sigma_{1s}^*$$
; $< \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^* = \sigma_{2p_y}^* < \sigma_{2p_z}^*$
 σ^* , σ^* = 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 filed), e.g.,

- 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. O₂ molecule. Otherwise diamagnetic (e.g.: N₂)

Fractional bond order it will be always paramagnetic

7.					
S.No.	No. of electrons in molecules	N_b	N_a	B.O.	Paramagnetic/ diamagnetic
1.	1	1	0	1/2	paramagnetic
2.	2	2	0	1	diamagnetic
3.	3	2	1	0.5	paramagnetic
4.	4	2	2	0	does not exist
5.	5	3	2	1/2	paramagnetic
6.	6	4	2	1	diamagnetic
7.	7	4	3	1/2	paramagnetic
8.	8	4	4	0	does not exist
9.	9	5	4	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	does not exist



In case of same bond order, stability depends upon No. of anti-bonding electrons

Stabiligy
$$\propto \frac{1}{\text{No. of anti-bonding e}^-}$$

BONDING PARAMETER

1. Bond length: Internuclear distance

Factor affecting Bond length

- (i) Atomic size: bond length ∝ size```` [No. of shell]
- (ii) Δ EN, Bond length $\propto \frac{1}{\Delta$ EN

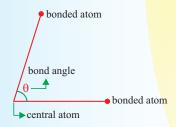
$$d_{A-B} = r_A + r_B - 0.09 \times \Delta EN \, \text{Å}$$

$$\propto \frac{1}{\text{B.O.}}$$

- (iii) Bond order: Bond length
- (iv) Hybridisation: Bond length $\propto \frac{1}{\% \text{age of s character}}$

Bond Angle

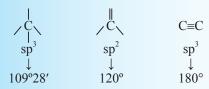
Angle between two adjacent bond is known as bond angle.



FACTORS AFFECTING BOND ANGLE

(i) Hybridisation

Bond angle ∝ % age of s-character



(ii) No. of lp/bp

[when hybridisation is same]

Bond angle
$$\propto \frac{1}{lp}$$
 Eg.: $CH_4 > \ddot{N}H_3 > H_2\ddot{O}$:

(iii) Type of Central atom: Applicable when:

- hybridisation same
- No. of lp/bp same

Bond angle ∝ EN of central atom.

Eg.
$$NH_3 > PH_3 > AsH_3 > SbH_3$$

(iv) Type of bonded atom: Applicable when:

- hybridisation same
- No. of lp/bp same
- Central atom same

Bond angle ∝ size of bonded species

$$Eg. OF_2 < OCl_2 < OBr_2 < OI_2$$



Regular geometry / same hybridisation / bond angle same $BF_3 = BCl_3 = BBr_3 = BI_3$

Ionic Bond

Extreme polar covalent bond is an Ionic Bond.

Therefore Ionic Bond \triangle EN - 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.

$$\underbrace{\text{Metal (M)}}_{\text{Solid}}\underbrace{\frac{\text{Sublimation}}{\Delta H = + ve}}_{\text{S.E.}} \text{M(g)} \underbrace{\frac{\text{Ionisation}}{\Delta H = + ve}}_{\text{I.E.}} \text{M(g)}; X_2 \underbrace{\frac{\text{Dissociation}}{\Delta H = + ve}}_{\text{Non metal molecule}}$$

$$X \xrightarrow{+e^{-}} X_{(g)}^{-} \qquad M_{(g)}^{+} + X_{(g)}^{-} \xrightarrow{\Delta H = -ve} MX_{(solid)}$$
electron gain enthalpy

$$\Delta H_{\text{formation}} = \text{S.E.} + \text{I.E.} + \frac{1}{2}\text{BDE} + \Delta H_{\text{eg}} + \text{U}$$

bond formation is always an exothermic process.

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

S.E.: 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

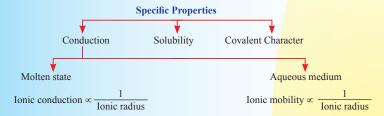
General Properties

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



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

Ionic Radius: Li⁺ <<< Cs⁺

Conductance: CsCl < RbCl < KCl < NaCl < LiCl

Hyd. radius: $Cs^+ <<< Li^+(aq)$

conductance: LiCl < NaCl < KCl < RbCl, CsCl

COVALENT CHARACTER / FAJAN'S RULE

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

Polarisibility of anion ∞ size of anion ∞ charge of anion

Smaller cation Large anion Condition of polarisation Higher charge

FACTORS AFFECTING POLARISATION

(1) Polarisation ∝ charge of cation or anion

Eg. (i)
$$\overset{+2}{\text{Cr}}O < \overset{+3}{\text{Cr}}_2O_3 < \overset{+6}{\text{Cr}}O_3$$
 Covalen (ii) $\overset{+2}{\text{SF}}_2 < \overset{+4}{\text{SF}}_4 < \overset{+6}{\text{SF}}_6$ Covalen (iii) $\overset{-1}{\text{Li}}F < \overset{-2}{\text{Li}}_2O < \overset{-3}{\text{Li}}_3N$ Covalen

(ii)
$$SF_2 < SF_4 < SF_6$$

i)
$$\text{LiF}^{-1} < \text{Li}_2 \overset{-2}{\text{O}} < \text{Li}_3 \overset{-3}{\text{N}}$$

Covalent character ↑

Covalent character \

Covalent character ↑ (anion charge↑)



- (2) Polarisation $\propto \frac{\text{size of anion}}{\text{size of cation}}$
 - **Eg.** (i) LiF < LiCl < LiBr < LiI anion size ↑ polarisability ↑

covalent character ↑

(ii) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ cation size \uparrow

polarisation ↓ covalent character ↑

SOLUBILITY

For s-block

Same group cation

Lattice Energy / Hydration Energy

- (i) BaCO₃, SrCO₃, CaCO₃, MgCO₃, BeCO₃
- (ii) Be(OH)₂, Sr(OH)₂, Mg(OH)₂, Ca(OH)₂, Ba(OH)₂
- (iii) BaSO₄, SrSO₄, CaSO₄, MgSO₄, BeSO₄
- (iv) Li₂CO₃, Na₂CO₃, K₂CO₃, Rb₂CO₃, Cs₂CO₃
- (v) LiOH, NaOH, KOH, RbOH, CsOH
- (vi) LiF, LiCl, LiBr, LiI
- (vii) LiF, NaF, KF, RbF, CsF
- (viii) BaF₂, SrF₂, MgF₂, CaF₂, BeF₂
 - (ix) CaF₂, CaCl₂, CaBr₂, Cal₂
 - (x) AgI, AgBr, AgCl, AgF (xi) PbO₂, CdI₂, RbI solubility $\propto \frac{1}{\text{covalent char.}}$

For all solubility ∞ 1 covalent char.

solubility in org. solvent ∞ cov. char ∞ ionic char.

[CCl4, benzene, ether, alcohol, acetone]

- Eg. (i) $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$ (Anion size \uparrow , cov. char. \uparrow , solubility \downarrow)
 - (ii) $Fe^{+2}(OH)_2 > Fe^{+3}(OH)_3$ (+) charge \(\gamma\), $PP\uparrow$, $CC\uparrow$, solubility \(\begin{array}{c}\)
 - (iii) $ZnCl_2 > CdCl_2 > HgCl_2$ $Z_{eff} \uparrow$, $PP \uparrow$, $CC \uparrow$, solubility \downarrow
 - (iv) Na₂SO₄ > MgSO₄ (+) charge↑, PP↑, CC↑, solubility ↓
 - (v) $ZnCl_2 > CdCl_2 > HgCl_2$ $Z_{eff} \uparrow, PP \uparrow, CC \uparrow, solubility \downarrow$

(vi) NaCl > CuCl PP↑, CC↑, solubility↓

(vii) AgF > AgCl > AgBr > AgI Anionic Size↑, PP↑, CC↑, solubility ↓

HYBRIDISATION OF FOLLOWING SPECIES IN SPECIFIED STATE					
Species	Cationic part	Anionic part			
PCl ₅	$PCl_4^+(sp^3)$	$PCl_6^-(sp^3d^2)$			
PBr ₅	$PBr_4^+(sp^3)$	Br ⁻			
XeF ₆	$XeF_5^+(sp^3d^2)$	F ⁻			
N_2O_5	$NO_2^+(sp)$	$NO_3^-(sp^2)$			
I ₂ Cl ₆ (liquid)	$ICl_2^+(sp^3)$	$ICl_4^-(sp^3d^2)$			
Cl ₂ O ₆	$ClO_2^+(sp^2)$	$ClO_4^-(sp^3)$			
I ₂ (molten state)	$I_3^+ (sp^3)$	$I_3^-(sp^3d)$			

SILICATES					
Silicates	Sharing of O-atom/Basic Tetrahedral unit Contribution of O-atom/Basic Tetrahedral unit		General formula		
Ortho	0	4	SiO ₄ ⁴⁻		
Pyro	1	3.5	Si ₂ O ₇ ⁶⁻		
Cyclic	2	3	$(SiO_3)_n^{2n-}$		
Simple chain (pyroxene)	2	3	$(SiO_3)_n^{2n-}$		
Double chain (Amphibole)	(3,2) avg. = 2.5	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(Si_4O_{11})_n^{6n-}$		
2D or (Sheet)	3	2.5	$(Si_2O_5)_n^{2n-}$		
3D	4	2	(SiO ₂) _n		

HYDROLYSIS

Hydro - Water

lysis - break down

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

• It is nucleophilic substitution reaction.

•
$$H\ddot{O}H + MX \rightarrow H - \ddot{O} - M - X \rightarrow M - OH + HX$$

H

molecule Intermediate Product



Extent of Hydrolysis ∞ **Covalent Character**

$$BeCl_2 + 2HOH \rightarrow Be(OH)_2 + 2HCl$$

$$BCl_3 + 3HOH \rightarrow B(OH)_3 + 3HCl$$

$$AlCl_3 + 3HOH \rightarrow Al(OH)_3 + 3HCl$$

$$SiCl_4 + 4HOH \rightarrow Si(OH)_4 + 4HCl$$

 $SF_6 + H_2O \rightarrow No$ hydrolysis due to crowding

$$BF_3 + 3HOH \rightarrow B(OH)_3 + 3HF$$

$$3BF_3 + 3HF \rightarrow 3H^+ [BF_4]^-$$

$$4BF_3 + 3H_2O \rightarrow 3H[BF_4]$$
(partially hydrolysis)

Similarly

$$SiF_4 + 4HOH \rightarrow Si(OH)_4 + 4HF$$

$$2SiF_4 + 4HF \rightarrow H_2^+ [SiF_6]^{2-}$$

hydrolysis followed by Lewis acid-base reaction.

15th Group Halides

NF ₃ + HOH	ordinary conditions	No hydrolysis
NCl ₃ + HOH	\rightarrow	$NH_3 + 3HOC1$
$PCl_3 + HOH$	\rightarrow	$H_3PO_3 + 3HC1$
$AsCl_3 + HOH$	\rightarrow	$As(OH)_3 + 3HC1$
SbCl ₃ + HOH	\rightarrow	SbOCl + 2HCl (partial hydrolysis)
BiCl ₃ + HOH	\rightarrow	BiOCl + 2HCl (partial hydrolysis)
PCl ₅ + HOH	\rightarrow	$POCl_3 \rightarrow H_3PO_4$ partial completely

Hydrolysis of Higher Covalent Character Containing Salt

$$Al_4C_3 + 12HOH \rightarrow 4Al(OH)_3 + 3CH_4$$

$$Mg_3N_2 + 6HOH$$
 \rightarrow $3Mg(OH)_2 + 2NH_3$
 $AIN + 3HOH$ \rightarrow $AI(OH)_3 + NH_3$

$$Ca_3P_2 + 6HOH \rightarrow 3Ca(OH)_2 + 2PH_3$$

$$LiH + HOH \rightarrow LiOH + H_2$$

$$CaH_2 + 2HOH \rightarrow Ca(OH)_2 + H_2$$

Hydrolysis of Interhalogen Compounds

$$AX + HOH \rightarrow HX + HOA$$

$$AX_3 + HOH \rightarrow 3HX + HAO_2$$

$$AX_5 + HOH \rightarrow 5HX + HAO_3$$

$$AX_7 + HOH \rightarrow 7HX + HAO_4$$

HX Hydrohalic acid

HOA, HAO₂, HAO₃, HAO₄ oxyacid of halogen

Some Specific Hydrolysis

$$XeF_2 \xrightarrow{HOH} Xe + 2HF + O_2$$

$$6XeF_4 \xrightarrow{HOH} 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 \xrightarrow{HOH} 2HF + XeOF_4 \xrightarrow{HOH} 2HF + XeO_2F_2 \xrightarrow{HOH} 2HF + XeO_3$$
partial partial complete

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.
- (ii) And another atoms must have vacant orbital.

Type of Back Bond:

- (i) $(p\pi p\pi)$ type of back bond, eg. BF₃, BCl₃, CF₂, CCl₂
- (ii) $(p\pi d\pi)$ type of back bond eg. CCl_3^- , $O(SiH_3)$, $N(SiH_3)_2$, SiH_5O^- , etc.

Application of Back Bonding

Lewis acid character:

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

 $BeF_2 < BeCl_2 < BeBr_2 < BeI_2$
 $SiF_4 > SiCl_4 > SiBr_4 > SiI_4$



Lewis basic character:

$$N(CH_3)_3 > N(SiH_3)_3$$

 $O(CH_3)_3 > O(SiH_3)_3$

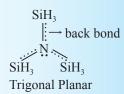


Due to back bonding $\underline{B}_3N_3H_6$, $(\underline{B}O_2)_3^{3-}$, $\underline{N}(SiH_3)_3$ is planar around under lined atom.

Few more examples of Back Bonding

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

No back bonding due to no vacant orbital in carbon.



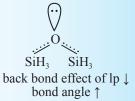
2. Lewis base strength

$$\ddot{N}(CH_3)_3 > \ddot{N}(SiH_3)_3$$
Ip involve in back bonding

3. Bond angle of (CH₃)₂O is very less than (SiH₃)₂O



No back bonding C: No vacant orbital



Chemical Species having Multicentered Bond

(3c-2e) bond is also termed as banana bond. Bridge bond is stronger than terminal bond. Bridge bond is longer than terminal bond.







	Bridge bond	Hybridisation of central atom
Be ₂ Cl ₄	(3c-4e)	sp ²
(BeCl ₂) _n	(3c-4e)	sp ³
Al ₂ Cl ₆	(3c-4e)	sp ³
I_2Cl_6	(3c-4e)	sp^3d^2
B_2H_6	(3c-2e)	sp ³
Be_2H_4	(3c-2e)	sp^2
(BeH ₂) _n	(3c-2e)	sp ³
(AlH ₃) _n	(3c-2e)	sp^3d^2
Al ₂ (CH ₃) ₆	(3c-2e)	sp ³

Odd e species: Total number of electron or valence 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	Pyramida <mark>l</mark>	Para
*CH ₃	sp^2	Trigonal pla <mark>nar</mark>	Para
°CH ₃ /°CHF ₂ /CH ₂ F	sp ³	Pyramidal	Para

OXY-ACIDS

- Mainly oxy-acids are hydroxide of Non-metal oxides.
- No. of H⁺ ion furnish by an oxy-acid is known as their basicity.

 Oxy-acid obtained by dissolving non-metal oxide in water.

Eg. $CO_2 + HOH \rightarrow H_2CO_3$ or $OC(OH)_2$

Here: $CO_2 \rightarrow Non \text{ metal oxide - Anhydride of carbonic acid } OC(OH)_2 \rightarrow Oxyacid$

- NO₂ → Mixed anhydride
- it gives → HNO₂ & HNO₃

Oxide Acid

- N_2O_3 \rightarrow HNO_2 Nitrous acid
- N_2O_5 \rightarrow HNO₃ Nitric acid



- Phosphoric acid • $P_4O_{10} \rightarrow H_3PO_4$ \rightarrow H₂SO₃ - \bullet SO₂ Sulphurous acid Sulphuric acid • SO₃ \rightarrow H₂SO₄ -• Cl₂O₇ HClO₁ Perchloric acid
- Oxyacids of different elements

Order of acidic strength

 $H_3PO_2 > H_3PO_3 > H_3PO_4$

Reducing nature

 $H_3PO_2 > H_3PO_3 > H_3PO_4$

Element	Oxide	Oxyacid	Basicity
Boron	B_2O_3	B(OH) ₃ boric acid	Not protonic acid monobasic Lewis acid
Carbon	CO_2	H ₂ CO ₃ carbonic acid	Two
Nitrogen		H ₂ N ₂ O ₂ Hyponitrous aicd HNO ₂ Nitrous acid HNO ₃ Nitric acid HNO ₄ Pernitric acid	
Phosphorus		H ₃ PO ₂ Hypophosphorus acid H ₃ PO ₃ Phosphorus acid H ₃ PO ₄ Ortho phosphoric acid HPO ₃ Meta phosphoric acid H ₄ P ₂ O ₅ Pyrophosphorus acid H ₄ P ₂ O ₇ Pyrophosphoric acid H ₄ P ₂ O ₆ Hypophosphoric acid	

OXYACIDS OF SULPHUR

- 1. Sulphurous acid H₂SO₃
- 2. Sulphuric acid H₂SO₄
- 3. Thiosulphuric acid H₂S₂O₃
- 4. Peroxymonosulphuric (Caro's acid) H₂SO₅ (Peroxide bond)







- 5. Peroxydisulphuric acid (Marshal's acid) H₂S₂O₈ (Peroxide bond)
- 6. Pyrosulphurous acid H₂S₂O₅ (S-S linkage)
- 7. Pyrosulphuric acid H₂S₂O₇ (S-O-S linkage)
- 8. Thionus acid H₂S₂O₄
- 9. Thionic acid H₂S₂O₆
- 10. Polythionus acid H₂(S)_nO₄ (S-S linkage)
- 11. Polythionic acid H₂(S)_nO₆ (S-S- linkage)

OXYACIDS OF HALOGEN (CI)

- 1. Hypochlorous acid HClO
- 2. Chlorous acid HClO₂
- 3. Chloric acid HClO₃
- 4. Perchloric acid HClO₄

Order of acidic strength: HClO < HClO₂ < HClO₃ < HClO₄

Oxidising nature: HClO > HClO₂ > HClO₃ > HClO₄

ALLOTROPY

- Those substance which are made up of same elements but having different bonding arrangement are known as allotropes & this phenomenon known as allotropy.
- Those elements which exhibit higher tendency of catenation exhibit higher tendency of allotropy.
- Therefore carbon, phosphorus & sulphur exhibit maximum allotropy.

ALLOTROPES OF CARBON		
Diamond	Graphite	Fullerene
C-sp³, tetrahedral structure C-C bond length 1.54Å Compact 3 dimensional structure Hardest substance Very high mp (~ 3400°C) Very high density Non conductor Very high refractive index Exhibit total internal reflection Shines bright in light	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.	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 of MP or density \rightarrow white < red < black

$$\begin{array}{ccc} & & & 803K \\ & & & \text{high P} \end{array} & \alpha\text{-Black Phosphorous} \\ & & & \text{inert} \\ & & & \text{medium} \end{array}$$

$$\begin{array}{c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array} & \begin{array}{c} & & & \\ & & \\ & & \\ \end{array} & \begin{array}{c} & & \\ \end{array} & \begin{array}{c} & & \\ & & \\ \end{array} & \begin{array}{c} & & \\ & & \\ \end{array} & \begin{array}{c} & & \\ & & \\ \end{array} & \begin{array}{c} & & \\ & \\ \end{array} & \begin{array}{c} & \\ & \\ \end{array} & \begin{array}{c} & & \\ & \\ \end{array} & \begin{array}{c} & & \\ & \\ \end{array} & \begin{array}{c} & \\ & \\$$

ALLOTROPES OF SULPHUR			
Crystalline	Amorphous		
Rhombic sulphur (α -S) most stable form Monoclinic sulphur (β -S) α -S $\stackrel{>95.6^{\circ}\text{C}}{<95^{\circ},6^{\circ}\text{C}}$ β -S 95.6°C = transition Temperature both are soluble in CS ₂ but insoluble in water	Milk of sulphur Plastic sulphur (γ -S) Colloidal sulphur H ₂ S + 2HNO ₃ Redox S + 2NO ₂ + 2H ₂ O		

- (a) Density of $\alpha S > \beta S$.
- (b) Both are puckered crown shape having S₈ units.
- (c) S_2 is paramagnetic sulphur which exist in vapour form at high temperature.
- (d) S_6 is chair form of S.

Effect of Temperature

$$S_{8(\alpha)} \xrightarrow{95.5^{\circ}C} S_{8(\beta)} \xrightarrow{130-200^{\circ}C} Viscosity of liquid increase \xrightarrow{>200^{\circ}C} Viscosity decrease$$



Chemical Bonding



SOME IMPORTANT INCREASING ORDER

1. Acidic property

- (i) SiO₂, CO₂, N₂O₅, SO₃
- (ii) MgO, Al₂O₃, SiO₂, P₄O₁₀
- (iii) HClO, HClO₂, HClO₃, HClO₄
- (iv) CH₄, NH₃, H₂O, HF
- (v) SiH₄, PH₃, H₂S, HCl
- (vi) H₂O, H₂S, H₂Se, H₂Te
- (vii) HF, HCl, HBr, HI
- (viii) lnCl₃, GaCl₃, AlCl₃
 - (ix) BF₃, BCl₃, BBr₃, BI₃

2. Bond Angle

- (i) CH₄, C₂H₄, C₂H₂
- (ii) H₂O, NH₃, CH₄, CO₂
- (iii) H₂O, NH₃, CH₄, BH₃
- (iv) NO₂, NO₂, NO₂
- (v) H_2Se , H_2S , H_2O
- (vi) AsH₃, PH₃, NH₃
- (vii) PF₃, PCl₃, PBr₃, PI₃
- (viii) NF₃, NCl₃
 - (ix) NF₃, NH₃, NCl₃
 - (x) OF_2 , OH_2 , Cl_2O

3. Basic Character

- (i) LiOH, NaOH, KOH, RbOH, CsOH
- (ii) Be(OH)₂, Mg(OH)₂, Ca(OH)₂, Ba(OH)₂
- (iii) BeO, MgO, CaO, SrO
- (iv) NiO, MgO, SrO, K₂O, Cs₂O
- (v) CO₂, B₂O₃, BeO, Li₂O
- (vi) SiO₂, Al₂O₃, MgO, Na₂O
- (vii) SbH₃, AsH₃, PH₃, NH₃
- (viii) F, OH, NH, CH,

4. Thermal Stability

- (i) Li₂CO₃, Na₂CO₃, K₂CO₃, Rb₂CO₃, Cs₂CO₃
- (ii) BeCO₃, MgCO₃, CaCO₃, BaCO₃



- (iii) Be(OH)₂, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂ Polarisation
- (iv) LiOH, NaOH, KOH, RbOH, CsOH
- (v) BeSO₄, MgSO₄, CaSO₄
- (vi) CsH, RbH, KH, NaH, LiH
- (vii) SbH₃, AsH₃, PH₃, NH₃
- (viii) H₂Te, H₂Se, H₂S, H₂O
 - (ix) HI, HBr, HCl, HF

5. Ionic Character

- (i) LiBr, NaBr, KBr, RbBr, CsBr
- (ii) LiF, NaF, KF, RbF, CsF
- (iii) BeCl₂, MgCl₂, CaCl₂, SrCl₂, BaCl₂
- (iv) BCl₃, AlCl₃, GaCl₃
- (v) VCl₄, VCl₃, VCl₂
- (vi) AlF₃, Al₂O₃, AlF₃
- (vii) AlN, Al₂O₃, AlF₃
- (viii) HI, HBr, HCl, HF
 - (ix) CuCN, AgCN
 - (x) AgCl, KCl

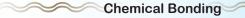
6. Oxidizing Power

- (i) $Cr_2O_7^{2-}$, MnO_4^{-}
- (ii) MnO_4^{2-} , MnO_4^{-}
- (iii) WO₃, MoO₃, CrO₃
- (iv) GeCl₄, SnCl₄, PbCl₄
- (v) I₂, Br₂, Cl₂, F₂
- (vi) Zn⁺², Fe⁺², Pb²⁺, Cu²⁺, Ag⁺

7. Melting Point

- (i) Cs, Rb, K, Na, Li
- (ii) Mg, Ba, Sr, Ca, Be
- (iii) CaI₂, CaBr₂, CaCl₂, CaF₂
- (iv) BeCl₂, MgCl₂, CaCl₂, SrCl₂, BaCl₂
- (v) NaI, NaBr, NaCl, NaF
- (vi) CsCl, RbCl, KCl, NaCl
- (vii) AlCl₃, MgCl₂, 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) PH₃, AsH₃, NH₃, SbH₃
- (ii) H₂S, H₂Se, H₂O
- (iii) HCl, HBr, HI, HF
- (iv) NH₃, HF, H₂O
- (v) He, Ne, Ar, Kr
- (vi) H₂O, D₂O
- (vii) H₂, Cl₂, Br₂

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) CCl₄, MgCl₂, AlCl₃, SiCl₄, PCl₅
- (ii) BiCl₃, SbCl₃, AsCl₃, PCl₃, NCl₃

13. Bond Strength

(i) HI, HBr, HCl, HF

(ii)
$$-C - I$$
, $-C - Br$, $-C - Cl$, $-C - F$

- (iii) N N, N = N, $N \equiv N$
- (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 CsCl, RbCl, KCl, NaCl

NaI, NaBr, NaCl, NaF BaO, SrO, CaO, MgO

(vii) F₂, H₂, O₂, N₂

- (viii) NO, NO, NO
 - (ix) I_2 , F_2 , Br_2 , Cl_2
 - (x) O O, S S
 - (xi) F F, O O, N N, C C, H H

14. Reducing Power

- (i) PbCl₂, SnCl₂, GeCl₂
- (ii) HF, HCl, HBr, HI
- (iii) Ag, Cu, Pb, Fe, Zn
- (iv) HNO₃, H₂SO₃, H₂S
- (v) H₃PO₄, H₃PO₃, H₃PO₂

15. Covalent Character

- (i) LiCl, BeCl₂, BCl₃, CCl₄
- (ii) SrCl₂, CaCl₂, MgCl₂
- (iii) TiCl₂, TiCl₃, TiCl₄
- (iv) LiCl, LiBr, LiI
- (v) Na₂O, Na₂S
- (vi) AlF₃, Al₂O₃, 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,
$$C = O, -C - O - O$$

- (iv) NO⁺, NO, NO⁻
- $(v) O_2, O_3, H_2O_2 (O O bond length)$

- (vi) CO, CO₂, CO₃⁻²
- (vii) N_2, N_2^-, N_2^{-2}
- (viii) O_2^{+2} , O_2 , O_2^- , O_2^{-2}
 - (ix) HF, HCl, HBr, HI

20. Dipole moments

- (i) CCl₄, CHCl₃, CH₂Cl₂, CH₃Cl
- (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
 - $(x) H_2O, H_2O_2$

Group 15	Bond angle	Group 16	Bond angle
NH ₃	107°48′	H ₂ O	104°28′
PH_3	93°36′	H_2S	92°
AsH ₃	91°48′	H ₂ Se	91°
SbH ₃	91°18′	H₂ <mark>Te</mark>	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 example, Tl is more stable in oxidation state + 1 than the oxidation state +3.

In p-block elements the stability of the lower oxidation state increases on descending the group.

Group 13	Group 14
B (+3)	C (+4)
Al (+3)	Si (+4)
Ga (+3), (+1)	Ge (+4), (+2)
In (+3), (+1)	Sn (+4), (+2)
T1 (+3), (+1)	Pb (+4), (+2)



Order of stability

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

Order of stability

 $Pb^{+2} > Sn^{+2} > Ge^{+2}$ (due to inert pair effect)

Molecules that do not Exist

- (1) SF₄, SF₆ & PF₅ exist while. OF₄, OF₆, NF₅ do not exist.
- (2) (a) PI₅(vap) & SCl₆ do not exist.
 - (b) SCl₆ does not exist while TeCl₆ exist.
 - (c) PI₅ (Solid) exist
- (3) SF₆, PF₅, XeF₆, XeF₄ & XeF₂ exist while SH₆, PH₅, XeH₆, XeH₄, XeH₂ do not exist.

ALLOTROPIC FORM OF SO₇

 SO_3 have three allotropic form α - SO_3 , β - SO_3 and γ - SO_3 .

Polymeric chain structure β-SO₃



s-Block Elements

ALKALI METALS

Physical Properties

General electronic configuration ns¹.

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

Molten
$$Li < Na < K < Rb < Cs$$

$$aqueous Li > K \approx Rb > Cs > Na$$

Chemical Properties

With O₂: Lithium forms normal oxide [Li₂O]

Sodium forms peroxide (Na₂O₂)

K, Rb, Cs forms superoxide KO₂, RbO₂, CsO₂

 $M_2O \xrightarrow{H_2O} M(OH)$

$$\begin{aligned} &M_2O_2 \xrightarrow{\quad H_2O\quad} M(OH) + H_2O_2 \\ &MO_2 \xrightarrow{\quad H_2O\quad} M(OH) + H_2O_2 + O_2 \end{aligned}$$

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

With Air

Moist air
$$O_2$$
 $M_2O \xrightarrow{H_2O} MOH \xrightarrow{CO_2} M_2CO_3$

$$M_2O + M_3N$$
only Li gives nitride

With NH₃

$$M + (X + Y) NH_3 \rightarrow [Na(NH_3)_x]^+ + [e(NH_3)_y]^-$$
ammoniated e

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

on standing

Li + NH₃
$$\rightarrow$$
 Li₂NH (Lithmide) + H₂
M(Na/K/Rb/Cs) + NH₃ \rightarrow MNH₂(amide) + H₂

With Halides

$$M + X_2 \rightarrow MX$$

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

SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM

- (a) Both lithium and magnesium are harder and lighter than other elements in the respective groups.
- (b) Lithium and magnesium react slowly with cold water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, Li₃N and Mg₃N₂.
- (c) The oxides, Li₂O 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 CO₂. Solid bicarbonates are not formed by lithium and magnesium.
- (e) Both LiCl and MgCl₂ are soluble in ethanol.
- (f) Both LiCl and MgCl₂ are deliquescent and crystallise from aqueous solution as hydrates,

LiCl.2H₂O and MgCl₂.8H₂O.







Carbonates

Only Li_2CO_3 decomposes $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{CO}_2$

Nitrates

LiNO₃
$$\stackrel{\Delta}{\longrightarrow}$$
 Li₂O + NO₂ + O₂
MNO₃ $\stackrel{\Delta}{\longrightarrow}$ MNO₂ + O₂ (M = Na/K/Rb/Cs)
Na₂CO₃.10H₂O (Washing Soda)

• In Solvay's process, CO₂ gas is passed through saturated brine (NaCl) solution when sparingly soluble NaHCO₃ separates out.

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$$

 $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 \downarrow + NH_4Cl$

The NaHCO₃ formed above is calcined to form Na₂CO₃

$$2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + CO_2 + H_2O$$

- The reactions taking place at different stages during the manufacture of Na₂CO₃ by Solvay process are given as under:
 - (a) $2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2 CO_3$ $(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$ $2NaCl + 2NH_4HCO_3 \rightarrow 2NaHCO_3 + 2NH_4Cl$
 - (b) Ammonia recovery tower

$$NH_4HCO_3 \xrightarrow{\Delta} NH_3 + CO_2 + H_2O$$

 $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$

(c) Calcination of NaHCO₃2NaHCO₃ → Na₂CO₃ + CO₂ + H₂O

(i) Efflorescence: Na₂CO₃.10H₂O when exposed to air it gives out nine out of ten H₂O molecules.

$$Na_2CO_3.10H_2O \rightarrow Na_2CO_3.H_2O + 9H_2O$$

(Monohydrate)

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

(ii) **Hydrolysis:** Aqueous solution of Na₂CO₃ is alkaline in nature due to anionic hydrolysis.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{-2}$$
 and $CO_3^{-2} + H_2O \rightleftharpoons H_2CO_3 + 2OH^-$ (Carbonic acid)

 Na₂CO₃ does not impart any colour to the flame but NaCl does because the thermal ionization of Na₂CO₃ does not take place at the temperature of flame of the burner.



Reaction of NaOH

(i) NaOH is strong base.

NaOH
$$\longrightarrow$$
 Na₂SiO₃ + H₂O \longrightarrow 2NaAIO₂ + H₂O

(ii) Reaction with non metals: no reaction with H₂, N₂ and C



(iii) Reaction with Metal:



ALKALINE EARTH METALS

Physical properties: General electronic configuration ns².

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 energy.

Ca - Brick red

Sr - Crimson red

Ba - Apple green

Basic nature increases down to the group

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

$$Be^{+2} \le Mg^{+2} \le Ca^{+2} \le Sr^{+2} \le Ba^{+2}$$

CHEMICAL PROPERTIES

With O₂

$$M \xrightarrow{O_2} MO \xrightarrow{O_2} MO_2$$

(Be, Mg, Ca, Sr, Ba, oxide) (Ca, Sr, Ba, peroxide)

With Water

$$M + 2H_2O \rightarrow M(OH)_2 + H_2$$

With Air

In moist air, except Be oxide 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 BeCO₃, all the carbonates are stable towards heat

$$BeCO_3 \xrightarrow{\Delta} BeO + CO_2$$

(ii) Order of decreasing stability

$$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$$

Nitrates

- (i) Alkaline earth metals forms M(NO₃)₂ type nitrates. (M -Alkaline earth metal).
- (ii) All alkaline metals nitrates on heating gives oxides and $NO_2 + O_2$ $M(NO_3)_2 \xrightarrow{\Delta} Oxides + NO_2 + O_2$

DIAGONAL SIMILARITY BETWEEN BERYLLIUM AND ALUMINIUM

In many of its properties, beryllium resembles Aluminium. Thus

- (a) The two elements have same electronegativity and their charge/ radius ratios.
- (b) Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalies to form soluble complexes, beryllates [Be(OH)₄]²⁻ and aluminates, [Al(OH)₄].



(c) The chlorides of both beryllium and aluminium

have bridged chloride structures in vapour phase.

- (d) Salts of these metals form hydrated ions, Ex. $[Be(OH_2)_4]^{2^+}$ and $[AI(OH_2)_6]^{3^+}$ in aqueous solution. Due to similar charges/radius rations 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 $AIF_6^{3^-}$ and $[AI(C_2O_4)_3]^{3^-}$.
 - Be₂C on treatment with H₂O forms CH₄ while CaC₂ forms C₂H₂.

$$Be_2C + 2H_2O \rightarrow 2 BeO + CH_4$$
Methane

$$\frac{\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}}{\text{Acetylene}} \text{Acetylene}$$

CHLORIDE OF ALKALINE EARTH METAL

- BeCl₂ in the vapour phase above 900°C is monomeric; below 900°C in the vapour exists as a mixture of monomer BeCl₂ and dimer Be₂Cl₄, in the solid state, has a polymeric structure and when dissolved in a coordinating solvent it exits as a monomer.
- Anhydrous MgCl₂ cannot be prepared by the simple heating of hydrated magnesium chloride MgCl₂, 6H₂O, as it gets hydrolysed to magnesium oxide.

$$MgCl_2.6H_2O \xrightarrow{Heat} MgO + 2HCl + 2H_2O$$

 Out of the oxides of group 2 elements only BeO is extremely hard, non volatile, has high melting point and it is amphoteric.

ANALYTICAL DETECTION OF Mg

- (i) Charcoal cavity test. On heating on a charcoal cavity with one drop of Co(NO₃)₂, a pink colour is imparted to the residue CoO.MgO.
- (ii) The salt solution when mixed with NH₄Cl and NH₄OH and finally treated with soluble phosphates forms a with precipitate of magnesium ammonium phosphate.

$$\begin{split} MgSO_4 + Na_2HPO_4 + NH_4OH \rightarrow Mg(NH_4)PO_4 + Na_2SO_4 + H_2O \\ white ppt. \end{split}$$







CALCIUM CYANAMIDE

Calcium cyanamide (CaCN₂) is prepared by heating a mixute of CaC₂ in an atmosphere of N₂ at 1270-1370K with CaF₂.

$$CaC_2 + N_2 \xrightarrow{CaF_2} CaCN_2 + C$$

It trade name is Nitrolim.

- Calcium cyanamide (CaCN₂) is a slow acting manure and is preferred to soluble compounds like NaNO₃ or (NH₄)₂ SO₄ since it confers fertility of a permanent nature. It is a nitrogenous fertiliser and undergoes a series of changes giving cyanamide, urea, NH₃ and finally the nitrates which are assimilable by plants.
- $CaCN_2 + H_2O + CO_2 \rightarrow CaCO_3 + H_2NCN$
- $H_2NCN + H_2O \rightarrow H_2NCONH_2$

Urea

• $H_2NCONH_2 + H_2O \rightarrow CO_2 + 2NH_3$

OXIDE OF CALCIUM

Ouick lime (CaO) is obtained when limestone is heated at about 1000°C. On adding water, quick lime gives a hissing sound and forms calcium hydroxide, known as slaked lime. The paste of lime in water is called milk of lime while the filtered and clear solution is known as lime water. Chemically both are Ca(OH)₂.

Quick lime is used for making caustic soda, bleaching powder, 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 (CaSO₄.2H₂O) 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 (CaSO₄. 1/2 H₂O) known as plaster of Paris.
- Plaster of Paris has the property of setting to a hard mass CaSO₄. 2H₂O, 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 his no setting property.







Cement

Cement is an important building material. The average composition of portland cement is: CaO 61.5%, SiO₂ 22.5%, Al₂O₃ 7.5%. Cement consists of:

Tricalcium silicate 3CaO.SiO₂

Dicalcium silicate 2CaO.SiO₂

Tricalcium aluminate 3CaO.Al₂O₃

Tetracalcium alumino - ferrite 4CaO. Al₂O₃. Fe₂O₃

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, Ca₉(PO₄)₆. Ca(OH)₂ is the main component of tooth enamel. Cavities are formed when acids decompose this enamel. This can be prevented by converting the hydroxyapatite to more resistant enamel-fluorapatite, Ca₉(PO₄)₆.CaF₂.

HYDROLITH

Hydrolith (CaH₂) is calcium hydride & on hydrolysis for calcium hydroxied & librate hydrogen.









p-Block

13th-GROUP

- Some important ores of Boron are given as under.
 - (i) Boric acid, H₃BO₃
 - (ii) Borax, Na₂B₄O₇.10H₂O
 - (iii) Colemanite, Ca₂B₆O₁₁.5H₂O
- Some important minerals of aluminium are given as under.
 - (i) Corundum, Al₂O₃
 - (ii) Bauxite, Al₂O₃.2H₂O
 - (iii) Cryolite, Na₃AlF₆
 - (iv) Feldspar, KAlSi₃O₈

$$Na_{2}[B_{4}O_{5}(OH)_{4}].8H_{2}O$$

Properties

- (i) It is a white crystalline solid of formula Na₂B₄O₇.10H₂O. In fact it contain the tetranuclear units [B₄O₅(OH)₄]²⁻ and correct formula; therefore, is Na₂[B₄O₅(OH)₄].8H₂O.
- (ii) Hydrolysis

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

(iii) Heating

(iv) When borax is heated in a Bunen burner flame with CoO on a loop of platinum wire, a blue coloured CO(BO₂)₂ bead is formed.

DIBORANE, B2H6

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 $3(\text{BF}_3)$

- (ii) Laboratory method $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$
- (iii) Industrial scale

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Properties

- (i) Diborane is a colourless, highly toxic gas with a boiling point of 180 K.
- (ii) Diborane catches fire spontaneously upon exposure to air.
- (iii) Reaction with oxygen:

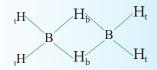
$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$
; $\Delta_cH^\circ = -1976 \text{ kJ mol}^{-1}$

(iv) Hydrolysis:

$$B_2H_6(g) + 6H_2O(ℓ)$$
 (Cold is enough) → $2B(OH)_3(aq) + 6H_2(g)$
 $B_2H_6 + HCl (dry)$ anh $AlCl_1 > B_2H_5Cl + H_2$

- (v) Reaction with Lewis Bases
 - (a) $B_2H_3 + 2NMe_3 \rightarrow 2BH_3.NMe_3$
 - (b) $B_2H_6 + 2CO \rightarrow 2BH_3.CO$
 - (c) $3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\text{Heat}} > 2B_3N_3H_6 + 12H_2$
- (vi) Reaction with ROH:

$$B_2H_6 + 6ROH \rightarrow 2B(OR)_3 + 6H_2O$$



dimer due to formation of 3 centre-2e-bond inorganic benzene.

193

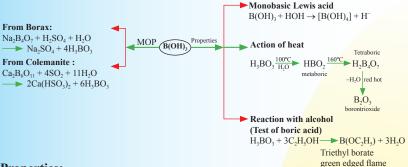








ORTHOBORIC ACID [H₃BO₃ OR B(OH)₃]



Properties:

Boric acid is a weak monobasic acid
 B(OH)₃ + 2H₂O ⇔ H₃O[⊕] + [B(OH)₄]⁻
 pKa = 9.25

• It is difficult to titrate boric acid against NaOH solutions and the end point cannot be located correctly However, it can be successfully titrated in the presence of polhydroxy alcohols (e.g. Glycerol, mannitol, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.

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

EXTRACTION OF ALUMINIUM

Al is usually extracted from Bauxite, Al₂O₃.2H₂O. First, bauxite is purified from the impurities (Red bauxite contains Fe₂O₃) 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 Fe₂O₃ and then digested at 423K with conc. NaOH solution for a few hours when Al₂O₃ gets dissolved to give a solutions of [Al(OH)₄]⁻¹ The basic oxide impurities such as Fe₂O₃ are not affected.

$$Al_3O_3 + 2OH^{-1} + 3H_2O + 2[Al(OH)_4]^{-1}$$



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

$$[Al(OH)_4]^{-1} + H^+ \rightarrow Al(OH)_3 + H_2O$$
(White ppt.)

The Al(OH)₃ precipitate is removed by filtration and ignited to get alumina, Al₂O₃.

• Hall's process involves the fusion of the ore with Na₂CO₃ when soluble sodium meta aluminate, NaAlO₂ is produced. This is extracted with water when Fe₂O₃ is left as a residue.

$$\begin{array}{l} Al_2O_3 + Na_2CO_3 {\:\longrightarrow\:} 2NaAlO_2 + CO_2 \\ \text{Sodium meta aluminate} \end{array}$$

The water extract is heated upto 333K and CO_2 is passed through it. $Al(OH)_3$ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_3 .

$$2\text{NaAlO}_2 + 3\text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{Al(OH)}_3 + \text{Na}_2\text{CO}_3$$

Serpeck's process involves the heating of bauxite with coke in a current of N₂ at 2075K. The SiO₂ present in the ore is reduced to silicon which volatilizes off and alumina gives aluminium nitride. This can be hydrolysed to Al(OH)₃ which on fusion gives alumina.

$$SiO_2 + 2C \rightarrow Si \uparrow + 2CO \uparrow$$

 $Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$
 $AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$
Aluminium nitride

Electrolysis of Al₂O₃ to form aluminium. Pure alumina is dissolved in fused cryolite, Na₃AlF₆ at 1225 K by current of 100 amp eres and 6-7 voltstoget Al. The Alobtain edispurified by Hoope's process.

ALUMINIUM TRIFLUORIDE

• Aluminium trifluride (AlF₃) is different from other trihalides of Al in being insoluble and nonvolatile in nature. In AlF₃ 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 octahedral

ALUMINIUM CHLORIDE

- Aluminium chloride (AlCl₃) in the pure and anhydrous state is a
 white solid but commercial samples are yellowish due to the impurity
 of FeCl₃.
- Anhydrous AlCl₃, in the crystalline state possesses a closely pakced layer structure with six coordinated aluminium octahedral arrangement.

195





Anhydrous AlCl₃ has a very high affinity for water. On treating AlCl₃ with water, the Cl⁻ ions go outside the coordination sphere to form [Al(H₂O)₀]Cl₃ with enthalpy of solution −300 KJ mol⁻¹. Due to this strong Al − O linkage hydrate connot be dehydrated on heating to form AlCl₃.

$$2[Al(H_2O)_6]Cl_3 \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$$

- Aluminium chloride, is a polymeric solid which exists as a dimer Al₂Cl₆ between 200–400°C and then monomer up to 800°C.
- Thermite welding, Aluminium has got a very high affinity for oxygen.

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

$$\Delta H = -3230 \text{ KJ mol}^{-1}$$

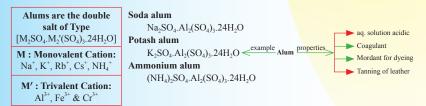
It, therefore, displaces metals less electropositive than itself from oxides. The large amount of heat produced is used in welding rails or heavy machinery without removing them from their position. This is called thermite welding or Gold Schmidt's aluminothermic process. In this process, a mixture of Ferric oxide (3 parts) and aluminium powder (1 part) called thermite is used.

- Boron nitride (BN), has a structure similar to that of graphite.
- Green edged flame test for borate (BO₃³⁻) ion. A mixture of C₂H₅OH and BO₃³⁻ salt with conc. H₂SO₄ burns with green edge flame due to the formation of ethyl borate.

$$H_3BO_3 + 3C_2H_5OH \rightarrow B (OC_2H_5)_3 + 3H_2O$$
Ethyl borate

 Charcoal cavity test for aluminium. On heating with Na₂CO₃ and a drop of cobalt nitrate solution a blue coloured residue to cobalt metaaluminate (Thenard's blue) is obtained.

ALUMS $[M_2SO_4.M_2'(SO_4)_3.24H_2O]$



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

(i) MnSO₄.
$$Al_2(SO_4)_2.24H_2O$$
 (ii) FeSO₄. $Al_2(SO_4)_2.24H_2O$ They are not isomorphous with true alums.



14th-GROUP ELEMENTS

- 1. The common oxidation 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 $C >> Si > Ge \approx Sn$. 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:

	С–С	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 an CO is neutral
 - ⇒ Among 14th group element only Sn reacts with steam to produce H₂ gas.
 - \Rightarrow Tetrahalide of 14th group elements are covalent except SnF₄ and PbF₄.

Stability of oxidationstate

- \Rightarrow $C^{+4} \rightarrow Pb^{+4}$ (Stability)
- \Rightarrow $C^{+2} \rightarrow Pb^{+2}$ (Stability)
- ⇒ Pb⁺⁴ compounds are strong oxidizing agent.
- \Rightarrow 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: $(R_2SiO)_n$. Where $R = -CH_3$, $-\frac{C_2H_5}{C_6H_5}$

(i)
$$R_2SiCl_2 + 2H_2O \xrightarrow{-2HCl} R_2Si(OH)_2 \xrightarrow{\Delta}$$

Linear Silicones/Cyclic Silicones

(ii)
$$R_3SiCl + H_2O \xrightarrow{HCl} R_3Si(OH)_2 \xrightarrow{A \longrightarrow Dimer Silicones}$$

(iii)
$$RSiCl_3 + 3H_2O \xrightarrow{-3HCl} RSi(OH)_3 \xrightarrow{\Lambda \atop -H_2O}$$

Crossed Linked Silicones

CARBON SUBOXIDE

Carbon suboxide (C₃O₂) is an foul smellting gas which can be prepared by the dehydration of malonic acid with P₄O₁₀.

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

$$C_3O_2 \xrightarrow{200^{\circ}C} CO_2 + 2C$$

The molecule is throught to have a linear structure.

$$O = C = C = C = O$$

OXIDE OF LEAD

- Read lead (Pb₃O₄) is considered to be mixture of lead monoxide and lead dioxide and it is written as (PbO₂· 2PbO).
- Lead dioxide (PbO₂). It is a brown powder obtained by the treatment of red lead with HNO₃.

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O$$

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



REACTION OF LEAD OXIDES

Oxide	ex NaOH	НСІ	H ₂ SO ₄	HNO ₃
PbO	Na ₂ PbO ₂	PbCl ₂	PbSO ₄	Pb(NO ₃) ₂
PbO ₂	Na ₂ PbO ₃	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	Pb(NO ₃) ₂
Pb ₂ O ₃	Na ₂ PbO ₂ + NaPbO ₃	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$
Pb ₃ O ₄	$Na_2PbO_2 + Na_2PbO_3$	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$

Tin and Its Compound

- Action of conc. HNO3 on tin
 - (a) Dilute HNO₃

$$4\text{Sn} + 10\text{HNO}_3 \rightarrow 4\text{ Sn(NO}_3)_2 + \text{HN}_4\text{NO}_3 + 3\text{H}_2\text{O}$$

(b) Hot conc. HNO₃

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$$

Metastannic acid

Action of conc. NaOH on tin

$$\Rightarrow$$
 Sn + 2NaOH + H₂O \rightarrow Na₂SnO₃ + 2H₂ \uparrow

SnCl₂

- SnCl₂· 2H₂O on heating undergoes to form it's basic chloride Sn(OH).Cl. The anhydrous salt, therefore, be obtained by heating the hydrated salt in the presence of HCl vapour.
- Stannous chloride reduces mercuric chloride (HgCl₂) to a white precipitate of mercurous chloride (Hg₂Cl₂)

$$2Hg^{2^{+}} + 3Cl^{-} + Sn^{2^{+}} \rightarrow Hg_{2}Cl_{2} + Sn^{+4}$$
Mercurous chloride

which finally turns to metallic mercury (dark grey or black)

$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg_2 \downarrow + SnCl_4$$

 Mosaic gold (SnS₂): 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 NH₄Cl in a retort.

$$Sn + 4NH_4Cl \rightarrow (NH_4)_2SnCl_4 + H_2 + 2NH_3$$

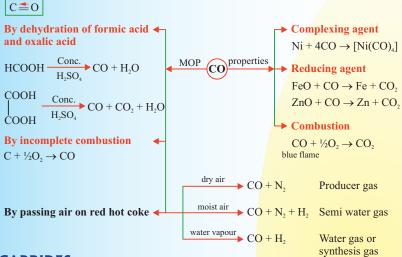
 $2(NH_4)_2SnCl_4 + 2S \rightarrow SnS_2 + (NH_4)_2SnCl_6 + 2NH_4Cl$



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

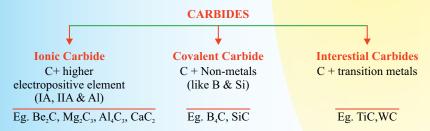
CARBON MONOXIDE [CO]

Colorless odourless, tasteless, neutral, poisionous gas



CARBIDES

Binary compounds of carbon with other elements (except hydrogen) are known as carbides



15th-GROUP ELEMENTS

Nitrogen Family

- 1. Nitrogen and phosphorus are non-metals, arsenic and antinomy 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 characterissed Bi (V) compound is BiF₅.



5. In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. for example,

(i)
$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

- **6.** In case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.
- 7. The oxides of the type E₂O₃ of nitrogen and phosphorus are purely acidic, that of arsenic and antinomy amphoteric and those of bismuth predominantly basic.
- **8.** In case of nitrogen, only NF, is known to be stable.
- 9. Trihalides except BiF₃ are predominantly covalent in nature.
 - \Rightarrow The only well characterised Bi (V) compound in BiF₅.
 - ⇒ All the oxidation states from +1 to +4 tend to disproportionate in acidic solution :

exp:
$$3HNO_2 \rightarrow HNO_3 + 2NO$$

 \Rightarrow All the intermediate oxidation states disproportionate into +5 and -3

$$\begin{array}{ccc}
4H_3PO_3 & \xrightarrow{\Delta} & 3H_3PO_4 + PH_3 \\
H_3PO_2 & \xrightarrow{\Delta} & H_3PO_4 + PH_3
\end{array}$$

⇒ Hybride of 15th group elements:

$$NH_3 > PH_3 > A_5H_3 > SbH_3 \ge BiH_3$$
 Basic character

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

$$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$$
 Boiling Point $PH_3 < AsH_3 < SbH_3 < NH_3$ Melting Point

$$NH_3 > PH_3 > AsH_3 > SbH_3$$
 Bond Energy

- \Rightarrow Penta oxide of 15th group element is acidic. N₂O₃, P₂O₃ are acidic, As₂O₃, Sb₂O₃ are amphoteric with Bi₂O₃ is basic.
- ⇒ Trihalide of 15th group elements are covalent except BiF₃

Structure of Oxides of Nitrogen and Phosphorus Nitrogen

Oxide of Nitrogen	Oxide State	Physical Appearance	Structure
N ₂ O nitrous oxide	+1	Colourless gas	$N \equiv N \rightarrow O$
NO Nitric oxide	2	Colourless gas	N = O





Oxide of Nitrogen	Oxide State	Physical Appearance	Structure
N ₂ O ₃ Dinitrogen trioxide	+3	Blue colour solid	$\vec{O} = \vec{N} - N \vec{Q}$
N ₂ O ₄ Dinitrogen tetraoxide	+4	Colourless solid	O N - N O
NO ₂ Nitrogen dioxide	+4	Brown gas	o v
N ₂ O ₅ Dinitrogen pentaoxide	+5	Colourless solid	0 0 0 0 N N O

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	$ \begin{array}{c} NH_4NO_3 \xrightarrow{Heat} \\ N_2O + 2H_2O \end{array} $	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2\text{NaNO}_2 + \frac{2\text{FeSO}_4 +}{3\text{H}_2\text{SO}_4 \rightarrow \frac{\text{Fe}_2(\text{SO}_4)_3}{4 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O}}}$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$ \begin{array}{c} 2NO + N_2O_4 \\ \xrightarrow{250 \text{ K}} & 2N_2O_3 \end{array} $	Blue solid, acid blue liquid (-30°C)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO ₂	+4	$ \begin{array}{c} 2\text{Pb}(\text{NO}_3)_2 \\ \xrightarrow{673 \text{ K}} & 4\text{NO}_2 + \\ 2\text{PbO} + \text{O}_2 \end{array} $	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	$ m N_2O_4$	+4	$\begin{array}{c} 2NO_2 \xrightarrow{Cool} \\ N_2O_4 \end{array}$	Colourless solid/ liquid, acidic



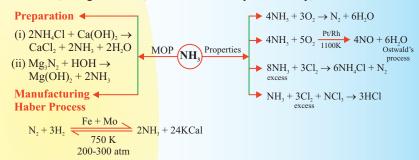


Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen pentaoxide [Nitrogen (V) oxide]	N ₂ O ₅	+5	$4HNO_3 + P_4O_{10} \rightarrow$ $4HPO_3 + 2N_2O_5$	Colourless solid, acidic

COMPOUNDS OF NITROGEN FAMILY

Ammonia (NH₃)

Colorless, Pungent Smell, basic in nature liquified easily, uses as coolant



Nitric Acid (NHO₃)

Preparation

Ostwald's process

(i)
$$4NH_3(g) \xrightarrow{Pt/Rh - guage \text{ catalyst}} 4NO(g) + 6H_2O(g)$$

(ii)
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

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

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

$$FeSO_4 + 8HNO_3 \rightarrow Fe_2(SO_4)_3 + 2NO + 4H_2O$$

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

$$3\text{Cu} + 8 \text{ HNO}_3 \text{ (dilute)} \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$$

 $\text{Cu} + 4\text{HNO}_3 \text{ (conc.)} \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
 $4\text{Zn} + 10\text{HNO}_3 \text{ (dilute)} \rightarrow 4\text{Zn}(\text{NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}$
 $\text{Zn} + 4\text{HNO}_3 \text{ (conc.)} \rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2$

Concentration of nitric acid	Metal	Main products	
	Mg, Mn	H ₂ + metal nitrate	
Very Dilute HNO ₃	Fe, Zn, Sn	NH ₄ NO ₃ + metal nitrate	
	Cu, Ag, Hg	No reaction	
Diluto HNO	Fe, Zn	N ₂ O + metal nitrate	
Dilute HNO ₃	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 (PH₃)

Preparation

(i)
$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

(ii)
$$PH_4I + NaOH \rightarrow NaI + H_2O + PH_3$$

Laboratory preparation

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

Uses

As Holme's signals in deep seas and oceans.

For the production of smoke screens.

Physical properties

Colourless gas having smell of garlic or rotten fish, slightly soluble in water and slightly heavier than air.

Chemical properties

(i)
$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$$



(ii)
$$4PH_3 \xrightarrow{713 \text{ K}} P_4 + 6H_2$$

(iii)
$$PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$$

Oxoacids of Phosphorus

Name	Formula	Oxidation state of nitrogen	Characteristic bonds and their number	Preparation
Hypophosphorus (Phosphinic)	H ₃ PO ₂	+ 1	One P — OH	white P ₄ + alkali
Orthophosphorous (Phosphonic)	H ₃ PO ₃	+ 3	Two P — OH One P — H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P — OH Two P — H Two P = O	PCl ₃ + H ₃ PO ₃
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P — OH Two P = O One P — P	red P ₄ + alkali
Orthophosphoric	H ₃ PO ₄	+ 5	Three P — OH One P = O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P — OH Two P = O One P — O — P	heat phosporic acid
Metaphosphoric*	(HPO ₃) _n	+5	Three P — OH Three P = O Three P — O — P	phosphorous acid + Br ₂ , heat in a sealed tube

- Acidity of oxides and the solubility of 15 group oxides decreases from N to Bi. For example, N₂O₃, N₂O₅, P₄O₆, P₄O₁₀, As₄O₁₀ are acidic and dissolve water forming acids. Sb₄O₆ and Sb₄O₁₀ are weakly acidic and insoluble in water Bi₂O₃ is a basic oxide and is insoluble in water.
- On heating, phosphorus acid, H₃PO₃ decomposes into phosphine (PH₃) and phosphoric acid (H₃PO₄).

$$4H_{3}PO_{3} \xrightarrow{\text{Heat}} 3H_{3}PO_{4} + PH_{3}$$

$$2H_{3}PO_{2} \xrightarrow{\text{Heat}} H_{3}PO_{4} + PH_{3}$$









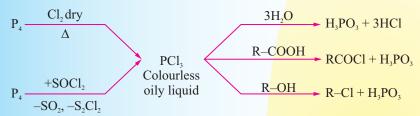
• Holme's signals: A mixture of Ca₃P₂ and CaC₂ on treatment with H₂O forms PH₃ and P₂H₄ along with C₂H₂. The mixture burns with a bright

$$Ca_3P_2 + 6H_2O + 3Ca(OH)_2 + 2PH_3$$

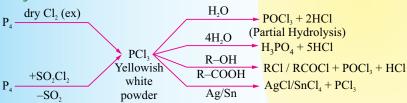
 $CaC_2 + H_2P \rightarrow Ca(OH)_2 + C_2H_2$

- Smoke screens, involve the use of calcium phosphide, Ca₃P₂. The PH₃ gas obtained from Ca₃P₂ 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.

PCI₃



PCI₅



16th-GROUP ELEMENTS

Oxygen Family

- 1. Oxygen is the most abundant of all the elements on earth crust.
- 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 SO₂ to TeO₂, SO₂ is reducing while TeO₂ is an oxidising agent.
- 5. Sulphur hexafluoride, SF₆ is exceptionally stable for steric reasons.
- 6. The well known monohalides are dimeric in nature. Examples are S₂F₂, S₂Cl₂, S₂Br₂, Se₂Cl₂ and Se₂Br₂. These dimeric halides undergo disproportionation as given below: 2Se₂Cl₂ → SeCl₄ + 3Se

- The weakening of M–H bond with the increase in the size of M (not the electronegativity) explains the increasing acidic character of hydrides down the group.
- **Halides:** All these elements form a number of halides. The halides of oxygen are not very stable. Selenium does not form dihalides. e.g. OF₂, Cl₂O₆, I₂O₅, etc.

SODIUM THIOSULPHATE Na₂S₂O₃·5H₂O

- **Preparation**
 - (a) $Na_2SO_3 + S \xrightarrow{Boil} Na_2S_2O_3$

(b)
$$4S + 6NaOH \xrightarrow{Boil} Na_2S_2O_3 + 2Na_2S + 3H_2O$$

- (c) $2Na_2S + 3SO_2 \xrightarrow{Boil} 2Na_2S_2O_3 + SO_2$
- (d) Spring's reaction

$$Na_2S + Na_2SO_3 + I_2 \xrightarrow{Heat} Na_2S_2O_3 + 2NaI$$

Concentrated Na₂S₂O₃ does not give a white ppt. with AgNO₃. This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.

$$3S_2O_3^{2-} + Ag_2S_2O_3 \rightarrow 2[Ag(S_2O_3)_2]^{3-}$$

Reaction with oxidizing agent

- (i) $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$
- (ii) $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI_{Sodium tetrathionate}$

This reaction forms the basis of iodometric estimation of Cr₂O₇²⁻ and Cu²⁺ salts.

(iii) $3S_2O_3^{2^-} + 2Fe^{3^+} \Leftrightarrow [Fe(S_2O_3)_2]^{-1}$ The violet colour disappear quickly due to the reduction of ferric chloride by S₂O₃² ions,

$$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{+2} + S_4O_6^{2-}$$

- (iv) $2CuCl_2 + 2Na_2S_2O_3 \rightarrow 2CuCl + Na_2S_4O_6 + 2NaCl$
- (v) $\text{AuCl}_3 + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{AuCl} + \text{S}_4\text{O}_6^{2-} + 2\text{Cl}^{-}$ $AuCl + 2S_2O_2^{2-} \rightarrow [Au(S_2O_2)_2]^{3-} + Cl^{-}$
 - Sulphur trioxides (SO₃) is a white crystalline solid with melting point 290 K and boiling point 318 K.
 - SO₃ is prepared by the direct oxidation of SO₂ with atmospheric oxygen in presence of finally divided Pt or V₂O₅ at a pressure of 2 bar and temperature 720 K.



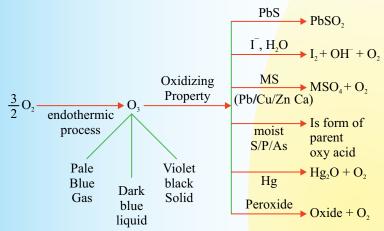
 SO₃ reacts with water to produce H₂SO₄ and large amount of heat is evolved.

$$SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

SO₃ reacts with water to produce H₂SO₄ and large amount of heat is evolved.

$$SO_3 + H_2O \rightarrow H_2SO_4 + heat$$

OZONE



* Fishy odour, Highly toxic.

Gases	Absorbent		
O_3	Turpentine Oil/ <mark>Oil of cinnamon.</mark>		
NO	FeSO ₄		
SO_2	NaO <mark>H</mark>		
СО	Cu ₂ Cl 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)

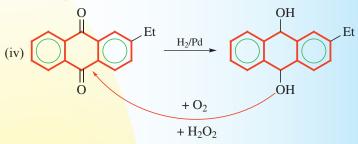


(iii)
$$2H_2SO_4 \rightarrow 2H^+ + 2HSO_4^-$$

Anode:
$$2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$$

Cathode:
$$2H^+ + e^- \rightarrow H_2$$

$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$$



Properties

Oxidizing Property

(i)
$$H_2O_2 \xrightarrow{PbS} PbSO_4$$

(ii)
$$H_2O_2 \xrightarrow{BaSO_3} BaSO_4 + H_2O_4$$

(iii)
$$H_2O_2 \xrightarrow{H_2S/HI} S/I_2 + H_2O$$

(iv)
$$H_2O_2 \xrightarrow{F^{+2}/H^-} Fe^{+3} + H_2O$$

(iv)
$$H_2O_2 \xrightarrow{Cr^{+3}/OH^-} Cr^{+6} + H_2O$$

Reducing Property

(i)
$$H_2O_2 \xrightarrow{Fe^{+3}/OH^-} Fe^{+2} + O_2$$

(ii)
$$H_2O_2 \xrightarrow{Pb^+ Grids} PbO$$

(iii)
$$H_2O_2 \xrightarrow{Cl_2/Br_2} PbO$$

(iv)
$$H_2O_2 \xrightarrow{MnO_4^*/OH^-} HX \downarrow + O_2$$

(v)
$$H_2O_2 \xrightarrow{MnO_4^-/H^+} Mn^{+2} + O_2$$

(vi)
$$H_2O_2 \xrightarrow{Cr_2O_7^{2-}/H^+} Cr^{+2} + O_2$$

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

$$2Hg + O_3 \rightarrow Hg_2O + O_2$$

As a result of it, mercury looses it's meniscus and starts sticking to the glass.

• The bleaching action of Ozone and H₂O₂ is permanent and is due to oxidation while that of SO₂ is temporary and is due to reduction.



• H₂O₂ is used to resture the colour of old lead paintings which have been blackened due to the formation of PbS by the action of H₂S present in the air.

$$PbS_{Black} + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

- Antichlor action H₂O₂ is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl.
 - \Rightarrow NH₂ · NH₂ + H₂O₂ as rocket propellant.
 - ⇒ Storage:

SULPHURIC ACID (H₂SO₄)

It is also known as oil of vitriol and king of chemicals.

Manufacture of sulphuric acid

Lead chamber process

The various steps involved are:

(a) Production of SO₂: By burning S or iron pyrites.

$$S + O_2 \xrightarrow{\Delta} SO_2$$

 $4FeS_2 + 11O_2 \xrightarrow{} 2Fe_2O_3 + 8SO_2$

(b) Production of catalyst: Oxides of nitrogen.

$$2\text{NaNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_3$$

$$2\text{HNO}_3 \stackrel{\Delta}{\longrightarrow} \text{H}_2\text{O} + \text{NO} + \text{NO}_2 + \text{O}_2$$

(c) Reaction in lead chamber

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

 $SO_3 + H_2O \longrightarrow H_2SO_4$
 $2NO + O_2 \longrightarrow 2NO_2$ (used again)

Contact process

The steps involved are:

- (a) Production of SO₂: It is produced by burning sulphur or iron pyrites and purified by treating with steam to remove dust particles.
- (b) Conversion of SO₂ to SO₃: It is done in container or catalyst chamber after being pre-heated to 450°C.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + x \text{ cal}$$

Catalyst: Formerly, platinised asbestos was used which is costly and easily poisoned. These days V₂O₅ is used.

(c) SO₃ is absorbed by conc. H₂SO₄ and then water is added to produce the acid of desired concentration.



$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

 $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Properties: Its specific gravity is 1.8 and it is 98% by weight.

It is strong dibasic acid.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$Metal above$$

$$H_2$$

$$In reactivity$$

$$Series$$

$$Class A$$

$$Sub gp - I$$

$$acidic radical$$

$$Volatile Product$$



Uses:

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

17th-GROUP 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 $F_2 > Cl_2 > Br_2 > I_2$.









4. In general, a halogen oxidises halide ions of higher atomic number.

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

 $Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 (X = Br \text{ or } I)$
 $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

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)
 $4\Gamma^- (aq) + 4H^+ (aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(l)$

- **6.** Halogens form many oxides with oxygen but most of them are unstable.
- 7. Flourine forms two oxides OF₂ and O₂F₂. However, only OF₂ is thermally stable at 298 K.

These oxides are essentially oxygen fluoride because of the higher electronegativity of fluorine the oxygen. Both are strong fluorinating agents.

- **8.** O₂F₂ oxidises plutonium to PuF₆ and the reaction is issued in removing plutonium as PuF₆ from spent nuclear fuel.
- 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: CIF, BrF, BrCl, ICl, IBr AB₃ type: CIF₃, 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 ↑.

 Bond strength is inversely, proportional to bond length i.e., larger the bond length, lower the bond strength is

• Higher the bond dissociation energy greater will be thermal stability. Thus, thermal stability follows the order.

REDUCING CHARACTER

The reducing character of hydrogen halides increases down the group as

$$2HX \rightarrow H_2 + X_2$$

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

ACIDIC STRENGTH

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

Since H–I bond is weakest, it can be easily dissociated into H $^+$ and Γ ions while HF with greater bond dissociation energy can be dissociated with maximum difficulty.

HYDROCHLORIC ACID, (HCI)

Preparation: By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

By the direct combination of hydrogen and chlorine.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Sunlight}} 2HCl_{(g)}$$

Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.

Properties : Hydrogen chloride is a covalent compound but when dissolved in water it ionizes to form hydrogen ions and chloride ions.

$$\mathrm{HCl}_{(aq)} \to \mathrm{H}^{\scriptscriptstyle +}_{(aq)} + \mathrm{Cl}^{\scriptscriptstyle -}_{(aq)}$$

Thus anhydrous HCl does not show acidic properties. Only aqueous HCl or in pressure of moisture, HCl behaves as an acid.

Metal + Hydrochloric → Metal chloride + Hydrogen

$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$$

It react with bases and basic oxides or hydroxides to form their respective chlorides and water.









$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

It reacts with metal carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites, etc, to form their respective chlorides.

$$AgNO_3 + HCl \rightarrow HNO_3 + AgCl \downarrow$$

Reducing property: HCl is a strong reducing agent.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

Uses

In the production of dyes, paints, photographic chemicals, etc. Used in the preparation of chlorides, chlorine, aquaregia, etc.

Used as a laboratory reagent.

PSEUDO HALIDES

Pseudo halides are uninegative group which show certain characteristics of halide ions. For example Cyanide (CN), Cyanate (OCN), Thiocyanate (SCN), Selencyanate (SeCN), Azide (N₃), Aziothnio carbonate (SCSN₃) and isocyanate (ONC).

CHLORINE (CI₂)

Preparation: By oxidation of conc. HCl.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$$

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture:

Weldon's process: By heating pyrolusite with conc. HCl.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

Deacon process:
$$2HCl + O_2 \xrightarrow{CuCl_2} Cl_2 + H_2O$$

Properties: It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate Cl₂·8H₂O.

Bleaching action and oxidising property

(i)
$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$HOCl \rightarrow HCl + [O]$$

Coloured matter + nascent : $[O] \rightarrow Colourless$ matter

The bleaching action of chlorine is permanent and is due to its oxidising nature.

(ii)
$$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

Action of hydrogen:

$$H_2 + Cl_2 \xrightarrow{U.V. \text{ light}} 2HCl$$



Displacement reactions:

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

 $2KI + Cl_2 \rightarrow 2KCl + I_2$

Action of NaOH:

$$\underset{(\text{cold \& dil.})}{2NaOH} + \underset{dry}{Cl_2^0} \rightarrow NaCl^{-1} + \underset{sodium\ hypochloride}{NaOCl^{+1}} + \underset{l}{H_2O}$$

Addition reactions:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

 $CO + Cl_2 \rightarrow COCl_2$

- Test for chlorine :
 - (a) It is a greenish yellow gas with irritating smell.
 - (b) It turns starch iodide paper blue.
 - (c) It bleaches litmus paper and indigo solution.



 Action of silica and glass: Strong solution of HF attacks readily forming silicon fluoride which gives complex fluosilicic acid, H₂SiF₆ with excess HF.

$$SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O$$

$$SiF_4 + H_2F_2 \rightarrow H_2SiF_6$$

This is called etching of glass.

• Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI=3.

$$KI + I_2 \rightarrow KI_3$$

The solution behaves as a simple mixture of KI and I₂.

OXY-ACID

 The acidic strength of the oxoacids of halogen decreases in the following order.

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

The chlorine oxyanion in which the central atoms has highest oxidation number will have maximum number of oxygen atoms











for participation in the extension of the π -bond. Thereby the charge on the ion is delocalized which greatly stabilizes the ion and thus decreases its tendency to accept a proton i.e., causes the ion to be very weak base with the result that the strength of the acid increases.

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

18th-GROUP ELEMENTS

1. Relative Abundance:

2. Melting and Boiling point:

- 3. He has the lowest boiling point among all element.
- 4. Noble gases are monoatomic, colourless, odourless, spraingly soluble in water and diffusing through most commonly used laboratry materials.
- **5.** $O_2[PtF_6]$ is the first noble gas compound.
- 6. Ar, Kr and Xe from clathrate compound when pass in ice with high pressure.

$$A \cdot 6H_2O (A = Ar/Kr/Xe)$$

Preparation of Xe-Fluoride



Properties

Fluoride donor : Eg.
$$XeF_2 + MF_5 \longrightarrow [XeF_4]^+ [MF_6]^-$$

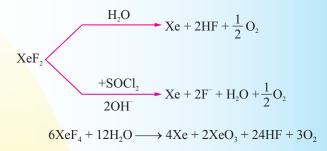
Fluoride acceptor : Eg.
$$XeF_6 + MF_{(M=Na/K/Rb/Cs)} \longrightarrow M^+ [XeF_7]^-$$

Fluoride agents : Eg.
$$XeF_4 \xrightarrow{SF_4/Pt} PtF_4/SF_6 + Xe$$

Reaction with SiO₂: Eg.
$$2XeF_6 + SiO_2 \rightarrow SiF_4 + XeOF_4$$

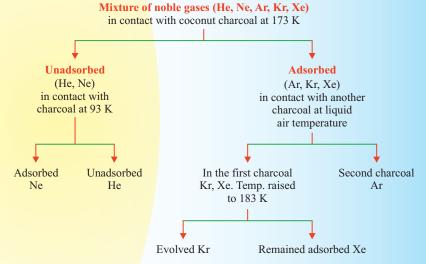


Hydrolysis



NOBLE GAS

In Dewar's method, the separation of noble gases is summerized below:



The viscosity of He is extremely low, about 1/100th of hydrogen gas.









d-Block Transition Elements

DEFINITION

Transition 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
$$\begin{cases} Cr = 4s^{1}3d^{5} \\ Cu = 4s^{1}3d^{10}, Pd = 5s^{0}4d^{10} \end{cases}$$

TRANSITION SERIES

1^{st}	3d series	Se_{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 $Sc > Ti > V > Cr > Mn \ge Fe \simeq Co \simeq Ni \le Cu \le Zn$

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

$$3d < 4d \simeq 5d$$

e.g:
$$Ti < Zr \simeq Hf$$
 | Smallest radius - Ni | Largest radius - La

Melting point: s-block metals < d-block metals

In a series on increasing number of unpaired e⁻ melting point increases upto Cr then decreases.

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

$$\downarrow \qquad \qquad \downarrow$$

Half filled d5

Fully filled d¹⁰

∴ weak metallic bond

.. weak metallic bond

E.N. Exception Zn < Cd < Hg

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

3d series

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

Density in a Group: 3d < 4d << 5d

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

Electrical conductor

$$Ag > Cu > Au > Al$$
 $block$

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 oxidation state of metals is zero due to synergic effects.
- Their higher oxidation states are more stable in fluoride and oxides.
- Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.
 eg. stable fluoride in higher oxidation state of Mn is MnF₄ while oxide is Mn₂O₇

- ⇒ Mn show maximum number of oxidation state (+2 to +7) among 3d series.
- \Rightarrow Beyond Mn, trihalide are not observe except FeX₃ (X = Cl/Br/I) & CoF₃
- $\Rightarrow V_2O_3$ V_2O_4 basic basic amphoteric ⇒ CrO Cr₂O₃ CrO₃ basic amphoteric acidic ⇒ MnO MnO_2 Mn_2O_7 basic amphoteric acidic
- $\Rightarrow \operatorname{CuI}_2 \text{ does not exist}$ $\operatorname{CuI}_2 \longrightarrow \operatorname{CuI} + \frac{1}{2} \operatorname{I}_2$
- ⇒ In aqueous, Cu⁺ disproportinated into Cu & Cu⁺². In p-block lower oxidation states of heavier elements are more stable while in d-block higher oxidation state of heavier elements are more stable.

eg. In VIB gp Mo(+6) & W(+6) are more stable than Cr(+6)

MAGNETIC PROPERTY

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using formula $\mu = \sqrt{n(n+2)}$ Bohr magneton. (n is number of unpaired e.)

If n is 1 μ = 1.73 BM n is 2 μ = 2.84 BM n is 3 μ = 3.87 BM n is 4 μ = 4.90 BM n is 5 μ = 5.92 BM

Substances that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block element and ions having 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 definate ratio (15% difference in metallic radius) They are hard and have high melting point.

Hg when mix with other metals from semisolid amalgam except Fe, Co, Ni, Pt.

Interstitial compound

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 =
$$V_2O_5$$

Haber process =
$$Fe_2O_3 + Al_2O_3 + K_2O$$

Fenton's reagent =
$$FeSO_4 + H_2O_2$$

Decomposition of
$$KClO_3 = MnO_2$$

Zeigler Natta =
$$TiCl_4 + (C_2H_5)_3 Al$$

(a)
$$Cu^{2+} + 4\Gamma \longrightarrow Cu_2I_{2(s)} + I_2$$

(b)
$$CuSO_4 + KCN \longrightarrow K_2SO_4 + Cu(CN)_2$$

$$2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$$

$$Cyanogen$$
Unstable
$$Cyanogen$$
Unstable

$$CuCN + 3KCN \longrightarrow K_3[Cu(CN)_4]$$

(c)
$$Cu \xrightarrow{\text{H}_2O + \text{CO}_2} \text{Poist air} \text{CuCO}_3.\text{Cu(OH)}_2$$

$$Au \xrightarrow{\text{Aqua regia}} \text{H[AuCl}_4] + \text{NOCl} + \text{H}_2\text{O}$$

(d) AgNO₃(s)
$$\xrightarrow{\text{Heating}}$$
 Ag + NO₂ + $\frac{1}{2}$ O₂
AgCO₃(s) $\xrightarrow{\text{Heating}}$ Ag + CO₂ + $\frac{1}{2}$ O₂

(e)
$$CuSO_4.5H_2O \xrightarrow{100^{\circ}C} > CuSO_4.H_2O \xrightarrow{720^{\circ}C} > CuSO_4$$
light greenish blue
$$\begin{array}{c} CuSO_4.5H_2O \xrightarrow{230^{\circ}C} > CuO + SO_2 + \frac{1}{2}O_2 \end{array}$$

(f)
$$Hg_2Cl_2 + NH_4OH \longrightarrow Hg \stackrel{NH_2}{\longrightarrow} Hg$$

(g)
$$NO_3^-/NO_2^- \xrightarrow{FeSO_4 + H_2SO_4} = [Fe(H_2O)_5 NO^+]SO_4$$
Brown ring complex

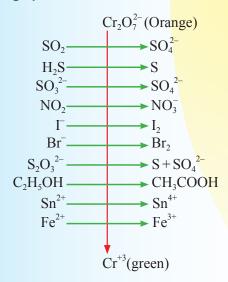
(h)
$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Photographic complex

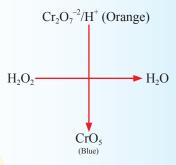
(i) Chemical volcano:

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

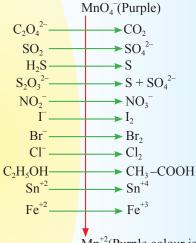
Reactions of Cr₂O₇²⁻



$$\begin{array}{c} CrO_4^{2-} \xrightarrow[\overline{OH}]{H^+} Cr_2O_7^{2-} \\ \text{Yellow} & \text{(Orange)} \end{array}$$



Reaction of MnO₄



Mn⁺²(Purple colour is decolourise)

$$\begin{array}{c|c} MnO_4 & \xrightarrow{Strongly \Delta} & MnO_4^{2-} \\ \hline & Basic \\ purple & solution & green \\ \hline & MnO_4^{-}/OH^{-} \\ \hline & I & & IO_3^{-} \\ \hline & CH_2 = CH_2 & & CH_2 - CH_2 \\ \hline & OH & OH \\ \hline & MnO_2 \\ \hline & & & OH \\ \hline & & & OH \\ \hline \end{array}$$





Coordination Chemistry

Addition compound

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



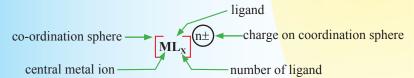
Double salt

* Loose their identity in aqueous solution eg. KCl.MgCl₂.6H₂O carnalite salt K₂SO₄Al₂(SO₄)₃.24H₂O potash alum

Co-ordination compound

* Retain their indentity in aqueous solution eg. K₄[Fe(CN)₆] Potassium hexacyanidoferrate (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 on the Basis of Denticity

(Denticity: –Number of electron pair donated by central metal atom or ion)

Monodentate (denticity = 1):

eg. H, X, Py, N₂, N³⁻, N₂H₄ etc.

Bidentate (denticity = 2):

eg. en, pn, bn, ox²⁻, acac⁻¹, gly⁻¹, dmg⁻¹

Polydentate (denticity = 2):

eg. dien, trien, EDTA⁴

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

eg.: (CN⁻, NC⁻), (NO₂⁻, ONO⁻), (SCN⁻, NCS⁻), (OCN⁻, NCO⁻), (S₂O₃²⁻, SO₂S²⁻)

Flexidentate ligand: Show more than one type of denticity.

eg.: CO₃²⁻, SO₄²⁻, CH₃COO⁻



Bidentate and Polydentate are also called chelating ligand.

Classification on the basis of electron donating and accepting tendency

Classical ligand: H₂O, NH₃ etc.

 $\alpha = \Gamma U(CO) 1$

Non-classical ligand: CN⁻, NO⁺, NO, CO, PPh₃

 π – donor ligand \Rightarrow C₂H₄, C₂H₂ etc.

BONDING IN COORDINATION COMPOUND

Effective atomic number & Sidgwick rule

Total number of electron present on central metal atom or ion after accepting the electron pair from ligand.

$$K_4[Fe(CN)_6]$$

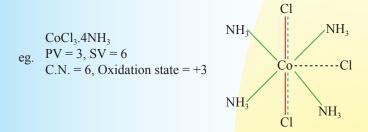
EAN = 26 - (+2) + 6(2) = 36

- If EAN value is equal to atomic number of Noble gas then complex follow sidgwick rule of EAN.
- In carbonyl complex, if EAN value = Atomic number of Noble gas then carbonyl complex is more stable.

	eg. [V(CO) ₆]	$[Cr(CO)_6]$	$[Mn(CO)_6]$
	act as oxidising	stable	act as reducing
	agent	complex	agent
•	Brown ring complex	37	
	Sodium nitroprusside	36	
	Zeise's Salt	84	
	$Mn_2(CO)_{10}$	36	
	$Fe_2(CO)_9$	36	
	$Co_2(CO)_8$	36	

WERNER'S CO-ORDINATION THEORY

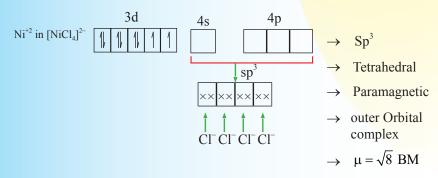
- Metals possesses two types of valencies PV & SV.
- PV is non-directional, represent by (doted line) is satisfied by negative charge species.
- SV is directional, represent by _____ (solid line) and satisfied by negative or neutral species.
- Now a days primary valency and secondary valency is consider as oxidation & co-ordination number respectively.

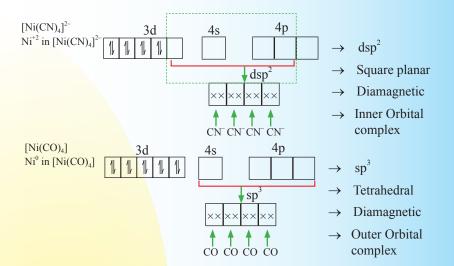


VBT

- Metal provoide 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.

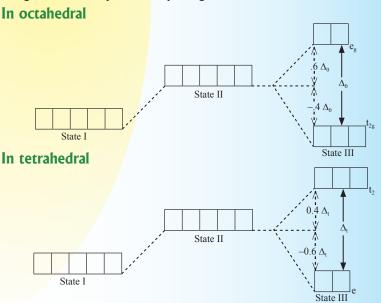
eg.
$$CN = 4$$
; $[NiCl_4]^{2-}$





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.



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 $^-$ < C $_2$ O $_4$ ²⁻ < H $_2$ O < NCS $^-$ < edta $^{4-}$ < NH $_3$ < en < CN $^-$ < CO(strongest)

Crystal Field Stabilisation Energy (CFSE)

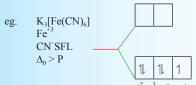
- (i) For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{eg})] \Delta_0$ + Paring energy (P.E.) × xWhere $n_{t_{2g}}$ = number of electron in t_{2g} orbitals n_{eg} = number of electron in eg orbitals x = number of electron pair
- (ii) For tetrahedral CFSE

=
$$[-0.6(n_e) + 0.4 (n_{t_2}) \Delta_t + \text{Paring energy (P.E.)} \times x]$$

tere n_{t_2} = number of electron in t_2 orbitals n_e = number of electron in e orbitals x = number of electron pair

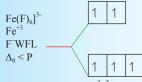
⇒ Follow Hund's Pauli & Aufbau rule.

CN-6



d²sp³, Octahedral low spin complex, inner orbital complex, paramagnetic

$$\mu = \sqrt{3} BM$$



sp³d², Octahedral high spin complex, outer orbital complex, paramagnetic

$$\mu = \sqrt{35} \, \text{BM}$$



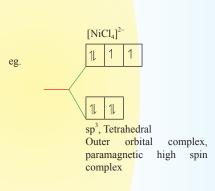
d²sp³, Octahedral low spin complex, inner orbital complex, paramagnetic

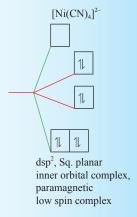


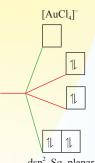
Exception

$\left[\text{Co(OX)}_3\right]^{3-}$	d^2sp^3	diamagnetic
$[Co(H_2O)_6]^{3+}$	d^2sp^3	diamagnetic
$[NiF_6]^{2-}$	d^2sp^3	diamagnetic
$[Cr(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[Mn(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
[Fe(NH ₃) ₆] ²⁺	sp^3d^2	paramagnetic
$\left[\text{CoL}_{6}\right]^{4-}\left(\text{L}=\text{NO}_{2}^{-}/\text{CN}\right)$	d^2sp^3	paramagnetic

CN-4







dsp², Sq. planar inner orbital complex, paramagnetic low spin complex,

Exception

• d³s hybridisation, Td, diamagnetic, inner orbital complex eg.

$$MnO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}, CrO_2Cl_2, CrO_2F_2, VO_4^{3-}$$

• Transference of electron

(where
$$L = NO_2^- / CN^- / NH_3$$
 etc.)

Factor affecting splitting

- (i) Strength of ligand
- (ii) Oxidation state of central metal ion
- (iii) Transition series (d-series)
- (iv) Geometry (number of ligands)
- (v) Chelation

Colour of complexes

Colour

d-d transition

- \rightarrow d¹-d⁹ complex can show colour.
- → Complementry colour of absorb colour is observe.
- eg.: $[Ti(H_2O_6)]^{3+}$, $[Ni_1(H_2O)_6]^{2+}$ $[Cu(NH)_4]^{2+}$

Charge transfer

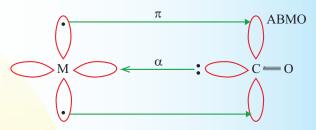
- → Metal-metal charge transfers or metal ligand charge transfers
- → MnO₄, brown ring complex sodium nitroprusside purssian blue, turnbull's blue

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.
 R-Mg-X, (CH₃-CH₂)₂ 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. Ni(CO)₄, Fe(CO)₅ etc.





IUPAC nomenclature of complex compounds

• For anionic complex (like K₄[Fe(CN)₆])

Common name of normal cation (without numeral prefix) + name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + oxidation state (in roman number).

eg.: Potassium hexacyanoferrate (II)

For cationic complex like [Cu(NH₃)₄]SO₄

Name of ligands (with numeral prefix) + Common name of CMI + oxidation state (In roman number) + Name of anion (without numeral prefix)

eg.: Tetraammine copper (II) sulphate.

• For neutral complex (like [Fe(CO)₅])

Name of ligands (with numeral prefix)

+ Common name of CMI + oxidation state (In roman number)

eg.: Pentacarbonyl iron (O)

• Rule same just apply alphabetical order when write the name of ligands e.g. [Pt(NH₃)₂Cl₂]

Diamminedichloroplatinum (II)

STRUCTURAL ISOMERISM

• Ionisation isomerism: Counter ion as a ligand & ligand act as counter ion.

 $[Co(H_2O)_5Cl]SO_4 \rightarrow [Co(H_2O)_5SO_4]Cl$

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

 $[\operatorname{Cr}(H_2O)_6]\operatorname{Cl}_3 \leftrightarrow [\operatorname{Cr}(H_2O)_5\operatorname{Cl}]\operatorname{Cl}_2.H_2O \leftrightarrow [\operatorname{Cr}(H_2O)_4\operatorname{Cl}_2]\operatorname{Cl}.2H_2O$

• Linkage: Exihibit when ambidentate ligand is present in co-ordination sphere.

 $[NC \to Ag \leftarrow CN]^{-} \leftrightarrow [NC \to Ag \leftarrow NC]^{-} \leftrightarrow [CN \to Ag \leftarrow NC]^{-}$

• Co-ordination isomerism: Exihibit when both are cationic & anionic complex

 $[Pt(NH_3)_4] [PtCl_4] \leftrightarrow [Pt(NH_3)_3Cl] [Pt(NH_3)Cl_3]$



STEREO ISOMERISM

Stereo Isomerism in Co-ordination Compound

CN-4

- Square planar complex does not show optical isomerism.
- Square planar complex show optical activity if the cooridinated ligand having chiral center.
- Square planar complex
 [Ma₂b₂]^{n±}, [Ma₂bc]^{n±}, [Mabcd]^{n±}, [M(AB)cd]^{n±}
 [M(AB)(CD)]^{n±} show geometrical isomerism
- [Mabcd]^{n±} form two cis and one trans.
- Tetrahedral com plex [Mabcd]^{n±}, [M(AB)cd]^{n±} [M(AB)(CD)] n± show optical isomerism
- Tetrahdral complex does not show geometrical isomerism.

Numbe	CN er of Possible Isom	N-6 ers for Specific Cor	nplexes
Formula	Number of stereoisomers	Pairs of Enantiomers	Number of G.I.
Ma_4b_2	2	0	2
Ma_3b_3	2	0	2
Ma ₄ bc	2	0	2
Ma ₃ b ₂ c	3	0	3
Ma ₃ bcd	5	1	4
$Ma_2b_2c_2$	6	1	5
Ma ₂ b ₂ cd	8	2	6
Ma ₂ bcde	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



Uppercase letter represent chelating ligands and lowercase letter represent monodentate ligands.





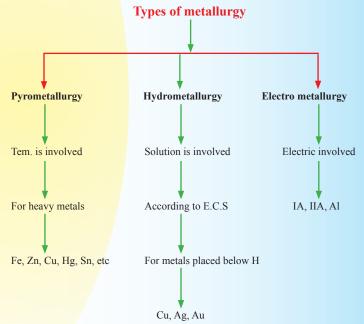




Metallurgy

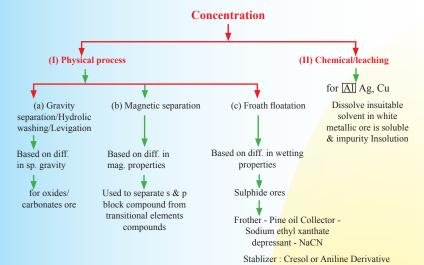
Bunch of Process to Extract Metal from their Respective Ore

Ore: Minerals from which metal can be extracted economically:

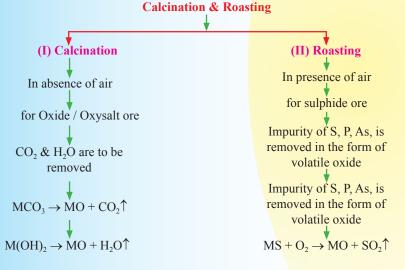


Metallurgical process:

- 1. Mining: Ore obtain in big lumps (less reactive)
- 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.



Ag, Au, are concentrated by cyanide process.



Reduction: To obtains metal (95 to 98%) from metal oxide.

Self reduction

• Sulphide ore itself act as reducing agent.

eg. PbS + 2PbO
$$\xrightarrow{\Delta}$$
 2Pb + SO₂

• Thermal decomposition

eg. HgO
$$\xrightarrow{\Delta}$$
 Hg + $\frac{1}{2}$ O₂

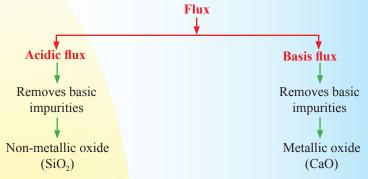


Carbon reduction (Smelting): Reducing agent C/CO

• eg.
$$Fe_2O_3 + 3CO \xrightarrow{250^{\circ} - 700^{\circ}C} > 2Fe + 3CO_2$$

$$ZnO + C \xrightarrow{\approx 1200^{\circ}C} > Zn + CO$$

Flux - substance to convert non-fusible impurities to fusible one.



Imp. point – Above 710° C is reducing agent.

Below 710°C CO is better reducing agent.

Aluminum reduction method: (Thermite process)

Al act as reducing agent

eg.
$$Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$$

Thermite mixture mass ratio: Cr_2O_3 : Al = 3:1

METAL DISPLACEMENT REDUCTION

- Metal placed below H. in E.C.S.
- Ag, Au, Cu

Example of extraction of

(i) Cynidation (Leaching Process)

$$\begin{array}{ccc} Ag_2S + 2NaCN & \xrightarrow{O_2} & 2Na[Ag(CN)_2] + Na_2SO_4 \\ Au + 2KCN + H_2O & \longrightarrow & K[Au(CN)_2] \end{array}$$

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

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN_4)] + 2Ag \downarrow$$

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN_4)] + 2Au \downarrow$$

ELECTROLYTIC REDUCTION

- For IA, IIA, Al
- Electolysis of molten solution





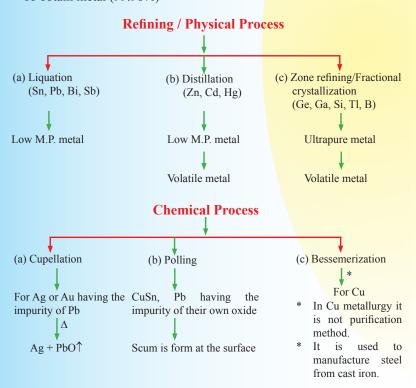




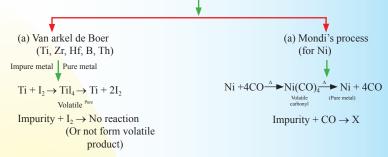
Example:-

- (i) Extraction of Al(Hall-Herault)
 - Al can be extracted from Al₂O₃
 - To decrease fusion temp. of Al₂O₃, Na₃ AlF₆ & CaF₂ is to added as auxilary electrolytes.
 - -Na₃ AlF₆ & CaF₂ increase the conductivity & reduce the fusion temp.
- (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.

 To obtain metal (99.98%)







(I) Electrolytic refining

Anode-made up of impure metal

Cathode-pure metal

impurity deposited below anode as anode mud or goes to electrolytic solution pure metal deposited at cathod.

THERMODYNAMICS PRINCIPLE OF METALLURGY

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

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

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Aluminium E° = -1.66	1. Bauxite, Al ₂ O ₃ .xH ₂ O 2. Cryolite, Na ₃ AlF ₆	Electrolysis of Al ₂ O ₃ dissolved in molten Na ₃ AlF ₆ + CaF ₂	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required









Metal	Occurrence	Common method of extraction	Reffining	Remarks
Iron E° = -0.44	1. Haematite, Fe ₂ O ₃ 2. Magnetite, Fe ₃ O ₄ 3. Limonite, Fe ₂ O ₃ .3H ₂ 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° = -0.34	1. Copper pyrites, CuFeS ₂ 2. Copper glance, Cu ₂ S 3. Malachite, CuCO ₃ .Cu(OH) ₂ 4. Cuprite, Cu ₂ O 5. Azurite, 2CuCO ₃ . Cu(OH) ₂	Roasting of sulphide partially and reduction	(i) Polling (ii) Electrolytic method	It is self reduction in a specially designed converted. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc E° = -0.76	Zinc blende or Sphalerite, ZnS Calamine, ZnCO ₃ Zincite, ZnO	Roasting of sulphide ore or calcination of ZnCO ₃ followed by reduction with coke	The metal may be purifed by fractional distillation	For ZnO, carbon is better reducing agent then CO and Zn is obtain is vapours form ZnO+C is The CO
Mg E° = -2.36	1. Carnallite, KCl.Mg Cl ₂ .6H ₂ O 2. Magnesite, MgCO ₃	Electrolysis of fused MgCl ₂ with KCl		MgCl ₂ .6H ₂ O is heated in the excess current of dry HCl gas to produce anhydrous MgCl ₂
Sn E° = -0.14	1. Cassiterite, SnO ₂ (Tin stone)	Reduction of the SnO_2 with carbon. SnO_2 + $2C \rightarrow Sn + 2CO$	Polling and Liquidation	Ore contain impurity of wolframite, FeWO ₄ + MnWO ₄ (magnetic sepration)



Metal	Occurrence	Common method of extraction	Reffining	Remarks
Pb E° = -0.13	1. Galena, Pbs	Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon PbS+2PbO→ 3Pb+SO ₂ PbO+C → Pb+CO	Liquadation & electrolytic method.	
Ag E° = 0.80	1. Argentite- Ag ₂ S, native Silver	$\begin{aligned} & \text{Hydro metallurgy} \\ & \text{Ag,S} + 4 \text{NaCN} \\ & 2 \text{NaAg(CN)}_2 \\ & + \text{N_2S} \\ & 2 \text{NaAg(CN)}_2 \\ & + \text{Zn} \rightarrow \\ & \text{Na_2Zn(CN)}_4 \\ & + 2 \text{Ag} \end{aligned}$	Cupelation & electrolytic method	In hydro mettallurgy Ag obtain in the form of dark amorphous ppt.
Au E° = 1.40	Native ore	Amalgamation. Cynide process	Cupelation & electrolysis method.	In hydro mettallurgy Au obtain in the form of dark amorphous ppt.







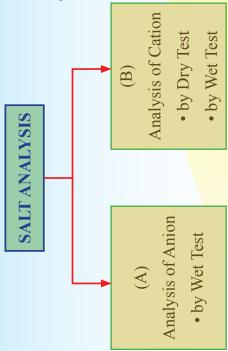


DEFINITION

The branch of chemical analysis which aims to find out the constituents of a mixture of compound is known as Qualitative Analysis.

Salt Analysis

The Identification of a substances usually involves its conversion into a new substance possessing characteristic properties with the help of one or more substance of known composition. The Substance which is used to bring about such change is called a Reagent.



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	Sub group-I
(Form volatile product with dil. HCl/dil. H ₂ SO ₄) CO ₃ ²⁻ , HCO ₃ ⁻ , SO ₃ ²⁻ , HSO ₃ ⁻ , S ₂ O ₃ ²⁻ , S ²⁻ , CH ₃ COO ⁻ , NO ₂ ²⁻	(Detected by precipitation reaction) SO_4^{2-} , PO_4^{3-} , AsO_3^{3-} , AsO_4^{3-}
Sub group-II	Sub group-II
(Form volatile product with conc. H ₂ SO ₄) F ⁻ , Cl ⁻ , Br ⁻ , l ⁻ , NO ₃ ⁻ , BO ₃ ³⁻ , C ₂ O ₄ ²⁻ + sub group-I	(Detected by redox reaction) CrO_4^{2-} , $Cr_2O_7^{2-}$, MnO_4^{-} , MnO_4^{-2}

- CO₂ is colourless, odourless gas evolved with brisk effevescence, Detected by lime water test.
- So₂ is colourless, Suffocating gas with burning sulphur odour. Detected by lime water test or by passing in $Cr_2O_7^{2-}/H^+$ solution.
- H₂S is a colourless gas having rotten egg odour.
- CH₃COOH has colourless fumes having vinegar odour.
- NO₂/Br₂ is brown gas.
- I₂ is violet gas.

LIME WATER / BARYTA WATER TEST

When CO₂ is passed in lime water or baryta water then white turbidity (milky appearance) is formed due to the formation of soluble carbonate but when excess of CO₂ is passed then white turbidity disappeared due to formation of soluble bicarbonate.

$$CO_2$$
↑ + Ca^{2+} + $2OH^-$ → $CaCO_3$ ↓ + H_2O
White turbidity
 $CaCO_3$ ↓ + CO_2 ↑ + H_2O → $Ca(HCO_3)_2$
Soluble



SO₂ also gives similar observation.







ACIDIC RADICAL TABLE

	dil. H ₂ SO ₄	Conc. H ₂ SO ₄	Cacl ₂	BaCl ₂	HgCl ₂	$AgNO_3$	Pb(OAc) ₂	$\mathrm{MnO}_4^-/\mathrm{H}^+$
CO_3^{2-}	CO ₂ ↑	CO₂↑	CaCO₃↓ white	BaCO₃↓ white	HgCO₃. 3HgO↓ Reddish brown	${ m Ag}_2{ m CO}_3{f \downarrow}$	PbCO ₃ . 2Pb(OH) ₂ ↓	I
$HCO_3^- + \Delta$	CO ₂ ↑	CO ₂ ↑	CaCO₃↓	BaCO₃↓	HgCO₃. 3HgO↓ Reddish brown	Ag ₂ CO₃↓	PbCO ₃ . 2Pb(OH) ₂ ↓	I
SO_3^{2-}	$\mathrm{SO}_2 \!\! \uparrow$	$SO_2\!$	CaSO₃↓ white	$BaSO_3 \downarrow$ white	I	${ m Ag_2SO_3} \downarrow$ white	PbSO₃↓ white	SO_4^{2-}
$\mathrm{S_2O_3^{2-}}$	$SO_2\uparrow + S\downarrow$	$\mathrm{SO}_2\!\!\!\uparrow$	I	$BaS_2O_3 \downarrow$ white	${ m HgS_2O_2} \downarrow$ white	$Ag_2S_2O_3 \downarrow$ white	$PbS_2O_3 \downarrow$ white	$SO_4^{2-} + S \downarrow$
S^{2-}	$_2^{\rm S}$	\$\dagge\ \ \SO_2\	-	BaS↓ black	HgS↓ <mark>black</mark>	Ag₂S↓ black	PbS↓ black	S
NO_2^-	NO₂↑	NO₂↑	I	I	I	$AgNO_2 \downarrow$	1	NO_3^-
CH3COO	СН₃СООН↑	CH₃COOH + SO₂↑	I	I	I	I	ı	ı
		${ m I}_2^{\uparrow}$ violet	I	I	Hgl₂↓ scarlet red	AgI↓ yellow	PbCl₂↓ dark yellow	$I_2 \uparrow$

$Pb(OAc)_2 MnO_4^-/H^+$	PbCl ₂ \downarrow Cl ₂ \uparrow white	PbBr ₂ \downarrow Br ₂ \uparrow white	_ CO ₂ ↑		1		→ ₄ • • •	
AgNO ₃ P	AgCl↓ Jwhite	W	$Ag_2C_2O_4 \downarrow$ white	$AgBO_2 \downarrow$	white	white -	white —	white $ Ag_3PO_4 \checkmark$ yellow
HgCl,	I	ı		I		I	– HgSO₄.2HgO↓ yellow	– HgSO ₄ .2HgO↓ yellow
BaCl ₂	I	ı	BaC₂O₄↓ white	Ba(BO ₂)↓ white		_	_ BaSO₄↓ curdy white ppt	BaSO ₄ ↓ curdy white ppt BaHPO ₄ ↓
Cacl ₂	I	ı	CaC ₂ O ₄ ↓ white	$Ca(BO_2)$ \$\depsilon\$ white		ı	– CaSO₄↓ white	– CaSO ₄ ↓ white CaHPO ₄ ↓
Conc. H ₂ SO ₄	НСІ↑	$\mathrm{Br}_2 \!\! \uparrow$ brown	$CO_2\uparrow + CO\uparrow$	H₃BO₃↑		NO₂↑	NO ₂ ↑	NO ₂ ↑
dil. H ₂ SO ₄			I	I		ı	1 1	1 1 1
	CI_	Br ⁻	$C_2O_4^{2-}$	BO_2^-		NO_3^-	$NO_3^ SO_4^{2-}$	NO ₃ ⁻ SO ₄ ⁻ PO ₄ ³⁻

SPECIFIC REACTION OF ACIDIC RADICAL

Sodium Nitro Prusside So²- Prusside So²- Methylene blu	the late of the same of the same of			
	Reaction Miliae /with	Reagent	Product	Observation
	Nitro	Na ₂ [Fe(CN) ₅ NO]	Na ₄ [Fe(CN) ₃ NOS]	Purple Complex
	Methylene blue Test	(Me) ₂ N HCI	$N(Me)_2$ (y) $+Fe+C1$	Methylene Blue
NO ⁷ Gries III	Gries Illosavay Test	(i) Sulphanilic acid (ii) 1, Methyl Amine	NH_2 $N = N$ $N = N$ $N = N$	Red Azo dye
NO_2^- Brown]	Brown Ring Test	$FeSO_4 + dil.H_2SO_4$	[Fe(H ₂ O) ₅ NO]SO ₄	Brown Ring
CH ₃ COO Cacodyl Test		$\mathrm{As}_2\mathrm{O}_3$	H ₃ C O CH ₃ AS AS H ₃ C CH ₃	Nauseating odour
CH3COO FeCl3 Sol"		$FeCl_3 + H_2O \xrightarrow{boil}$	[Fe ₃ (HO) ₂ (CH ₃ OO) ₆] ⁺	Blood Red solution \$\sqrt{\text{Boiling}}\$ Reddish Brown ppt.

Anion	Reaction Nmae /with	Reagent	Product	Observation
NO_3^-	Brown Ring test	FeSO ₄ + Conc. H_2SO_4	$[\mathrm{Fe}(\mathrm{H}_2\mathrm{O})_5\mathrm{NO}]\mathrm{SO}_4$	Brown Ring
$C_2O_4^{2-}$	Mn ⁺² + NaOH	NaOH + Mn^{+2} \longrightarrow	$[Mn(C_2O_4)_3]^{3-}$	Red Complex
Br^{-}	Layer Test	Cl ₂ Water + CCl ₄	$Br_2 + CCl_4$	Red layer
I	Layer Test	Cl ₂ Water + CCl ₄	$I_2 + CCI_4$	Violet Layer
I	HgCl_2	HgCl ₂	Hgl ₂	Red/yellow
CI_	Chromyl Chloride Test	(i) K ₂ Cr ₂ O ₇ (s) + conc. H ₂ SO ₄ (ii) NaOH	CrO ₂ Cl ₂ CrO ₄ ²⁻	Reddish brown Vapour Yellow Solution
		(iii) Pb(CH ₃ COO) ₂ + CH ₃ COOH	$PbCrO_4$	↓ Yellow PPt.
BO_3^{3-}	Green Flame Test	Conc. $H_2SO_4 + ROH + \Delta(Flame)$	B(OR) ₃	Green edge flame
BO_3^{3-}	Modified Green Flame Test	CaF ₂ + Conc. H ₂ SO ₄	$BF_3 \uparrow + Ca(HSO_4)_2 + \Delta$	Green flame
PO_4^{3-}	Ammonium molybdate	$ \begin{array}{l} (NH_4)_2 MoO_4 + dil \; HNO_3 \\ + 30 - 40^{\circ} C \end{array} \begin{array}{l} Na_3 MoO_4.12 MoO_3 \end{array} $	Na ₃ MoO ₄ .12MoO ₃	Canary yellow ppt.
$\frac{{ m Cr}\ { m O}_4^{2-}}{{ m Cr}_2{ m O}_7}$	Acidic Solution of H ₂ O ₂ + pyridine	$H_2O_2 + H^+ + \bigcirc$	${ m CrO}_{ m s}$	Blue Solution

BASIC RADICAL ANALYSIS

Dry Text 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	Crimosn Red	Apple green	Green flame
Cobalt glass:		flame disappear	crimson red	Green	Purple	Bluish green	Green flame

Borax Bead Text

- Used for cloured cation (d-block cation)
- Given salt heated on borax bead than metal metaborate are form.
- Metal metaborate on heating show characteristic bead colour.

	Oxidizing fl	ame	Redu	icing flame
	Hot	Cold	Hot	Cold
Mn	Violet	Amethyst	Colourless	Colourless
Cr	Yellow	Yellow	Green	Green
Fe	Yellowish brown	Green	Green	Green
Co	Blue	Blue	Blue	Blue
Ni	Violet	Brown	Grey	Grey
Cu	Green	Blue	Colourless	Opaque red

Charcol Cavity Text

Heat salt with Na₂CO₃ in charcoal cavity

Zn⁺² In hot yellow and in cold white residue.

Pb⁺² Yellow residue in hot and grey metal in cold.

As⁺³ White residue with garlic odour.

Cd⁺² Brown residue.



If white residue is obtain then add. Co(No₃)₂ and heat.

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

CLASSIFICATION OF BASIC RADICAL

Group	Basic Radical	Reagent used	Precipitate form
Group-I	Pb ⁺² , Hg ₂ ⁺²	dil HCl	AgCl PbCl ₂ Hg ₂ Cl ₂ white ppt.
Group-II	Cu ⁺² , Pb ⁺² , Hg ⁺² , Cd ⁺² , Bi ⁺³	H ₂ S+dil. HCl	Cu ₂ S, PbS, HgS, CdS, Bi ₂ S ₃ yellow black
	Sn ⁺² , Sn ⁺⁴ , As ⁺³ , As ⁺⁵ , Sb ⁺³ , Sb ⁺⁵		SnS SnS ₂ As ₂ S ₃ As ₂ S ₅ Sb ₂ S ₃ Sb ₂ S ₅ Brown Brown yellow Gray
Group-III	Cr ⁺³ , Al ⁺³ , Fe ⁺³	NH ₄ OH + NH ₄ Cl	Al(OH) ₃₊ Fe(OH) ₃ , Cr(OH) ₃ gelatinous reddish green white brown
Group-IV	Zn ⁺² , Mn ⁺² , Ni ⁺² , Co ⁺²	$H_2S + NH_4OH$	ZnS MnS NiS CoS white buff black
Group-V	Ca ⁺² , Sr ⁺² , Ba ⁺²	(NH ₄) ₂ CO ₃ + NH ₄ OH	CaCO ₃ , SrCO ₃ , BaCO ₃ white

TEST OF BASIC RADICAL

Agi Agi Yellow	Hg. ^{2*} Hg. ¹ , Green Hg + [Hgl4] ^{2*}	Pb ²⁺ Pbl ₂ Yellow [Pbl ₄] ²⁻	Cul + I ₃ White solution	Hg ⁺² Hgl ₂ Scarlet Red [Hgl ₄] ²⁻	Cd ² 2	Al ³
AgCN White	Black Hg + Hg(CN) ₂	soluble complex Pb(CN) ₂ White	CuCN + [CN]₂↑	Red solution	Cd(CN) ₂	1
[Ag(CN) ₂]	I	I	K ₃ [Cu(CN) ₄] soluble complex	I	[Cd(CN) ₄] ²	I
Ag ₂ O Brown	Hg ₂ O Black	Pb(OH) ₂ White	Cu(OH) ₂ Pale Blue	HgO yellow	Cd(OH) ₂ White	Al(OH) ₃ Gelatinous white
I	l	Na ₂ [Pb(OH) ₄] soluble complex	I	1	ı	Na[Al(OH),] soluble complex



Al ⁺³	Al(OH) ₃ Gelatinous white	I	Al(OH) ₃ Gelatinous white	I	I	I	I
Cd ⁺²	Cd(OH) ₂ White	[Cd(NH ₃),] ^{2*}	CdS Yellow	l	l	l	I
${ m Hg}^{+2}$	HgO. HgNH ₂ CI White	_	HgS Black	l	${ m HgS}_2{ m O}_3$ white	_	I
Cu+2	Cu(OH) ₂ Pale Blue	[Cu(NH ₃₎₄] ²⁺ Deep blue	CuS Black	-	Cu ₂ S ₂ O ₃ White	Cu ₂ [Fe(CN) ₆] Brown	Cu ₃ [Fe(CN) ₆] Green
Pb ²⁺	Pb(OH) ₂ White	I	PbS Back	PbCrO ₄ Yellow	PbS ₂ O ₃ White	I	I
${ m Hg}_2^{2+}$	Hg + HgO. HgNH²NO3	I	Hg + HgS black	${ m Hg_2CrO_4}$ Red	l	I	I
$\mathrm{Ag}^{\scriptscriptstyle{+}}$	Ag ₂ O Brown	[Ag(NH _{3),]} *	Ag ₂ S Black	Ag,CrO ₄ Red	Ag ₂ S ₂ O ₃ White	Ag ₄ [Fe(CN) ₆] White	I
	HO³HN	ех NН4ОН	H ₂ S/*(NH ₄) ₂ S	$ m K_2CrO_4$	Na ₂ S ₂ O ₃	K ₄ [Fe(CN) ₆]	K ₃ [Fe(CN) ₆]

TEST OF BASIC RADICAL

					3		
	${ m Cr}^{+3}$	Fe ⁺³	Fe ⁺²	Zn ⁺²	Mn ⁺²	Ni ⁺²	C0 ⁺²
KI	l	Fel ₂ + I ₃ yellowish brown sol.	I	I	I	I	I
ex KI	I	l	I	Zn(CN) ₂ White	-	I	I
KCN	l	Fe(CN) ₃ Brown	Fe(CN) ₂ yellowish brown	I	Mn(CN) ₂ , Mn(OH) ₂ Pink	$Ni(CN)_2$ green	Co(CN) ₂ Reddish Brown
ex KCN	I	K ₃ [Fe(CN) _o] Yellow	K4[Fe(CN) ₆] Pale yellow	l	l	K ₂ [Ni(CN) ₄] Soluble Complex	[Co(CN)6]⁴ Brown Solution
NaOH	Cr(OH) ₃ Green	Fe(OH) ₃ Reddish Brown ppt	Fe(OH) ₂ Dirty Green	Zn(OH) ₂ White	Mn(OH) ₂ Pink	Ni(OH) ₂ Green	Co(OH)Cl Blue
ex NaOH	Na[(AIOH)4] Yellow	ı	I	Na ₂ [Zn(OH) ₄]	I	-	(CoOH) ₂ pink
HO [†] HN	Cr(OH) ₃ Green	Fe(OH) ₃ Reddish Brown ppt	Fe(OH) ₂ Dirty Green	Zn(OH)2	ı	Ni(OH) ₂ Green	Co(OH)CI

C0 ⁺²	[Co(NH ₃) ₆] ²⁺ Yellow	CoS Black	l		Co ₂ [Fe(CN) ₆] Green	l
Ni^{+2}	Ni[(NH _{3)6,]²⁺ Deep blue}	NiS Black	I		Ni ₂ [Fe(CN) ₆] Light green	l
Mn ⁺²	-	MnS Pink			Mn ₂ [Fe(CN) ₆] White	I
$\mathrm{Zn}^{\scriptscriptstyle +2}$	$[\mathrm{Zn}(\mathrm{NH}_3)_4]^{2+}$	ZnS White	I		K ₂ Zn ₃ [Fe(CN) ₆] White	I
Fe ⁺²	l	FeS Black			$\mathrm{K}_2\mathrm{Fe}[\mathrm{Fe}(\mathrm{CN})_6]$	Fe ₃ [Fe(CN ₆)] ₂ Turnbull's blue
Fe ⁺³		FeS + S Black yellow		Fe ⁺² Green solution	Fe ₄ [Fe(CN ₆)] ₃ Prussian blue	Fe[Fe(CN ₆)] Brown
Cr ⁺³	[Cr(NH ₃) ₆] ³⁺ Pink/vollet	Cr(OH) ₃ Green	I	l	I	l
	ex NH ₄ OH	$\mathrm{H}_2\mathrm{S}/st(\mathrm{NH}_4)_2\mathrm{S}$	$ m K_2CrO_4$	Na ₂ S ₂ O ₃	K ₄ [Fe(CN),]	K ₃ [Fe(CN) ₆]

OTHER IMPORTANT REACTION OF BASIC RADICAL

Basic radical	Reagent	Product	Observation
Fe ⁺³	SCN ⁻	Fe(SCN) ₃	Blood red colcuration
Ni ⁺²	dmg / NH4 ⁺	[Ni(dmg) ₂]	Rosy red complex
Co ⁺²	KNO ₂	K ₃ [Co(NO ₂) ₆]	Yellow ppt
Hg ⁺²	SnCl ₂ (ex)	Нg	Grey / black
K ⁺	HClO ₄	KClO ₄	White ppt

