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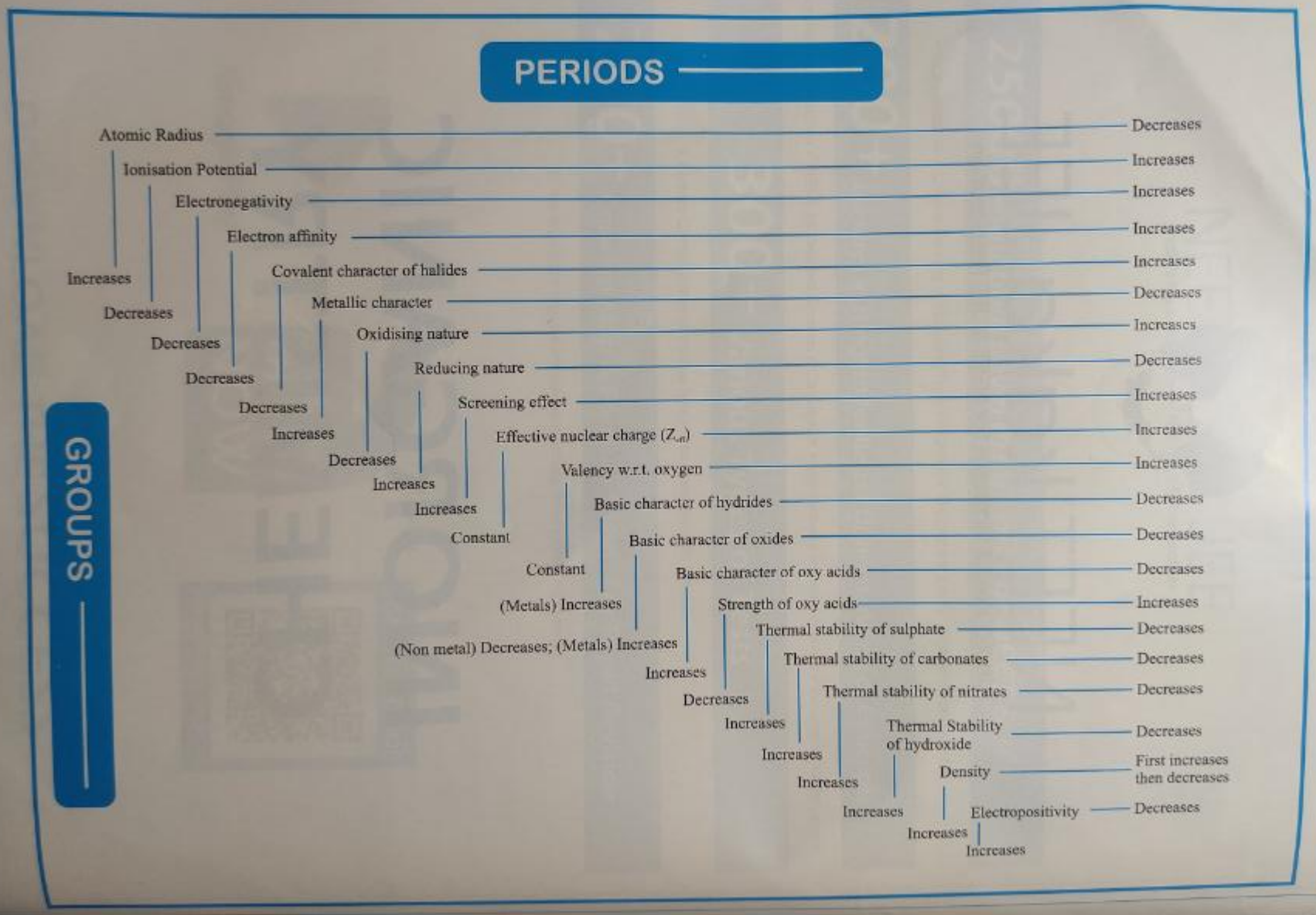
GENERAL TREND OF DIFFERENT PROPERTIES IN THE PERIODS AND GROUPS



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Long Forms of Periodic Table

PERIODIC TABLE OF ELEMENTS

s-block

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium																
11 Na Sodium	12 Mg Magnesium																
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Caesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson

d-block

p-block

f-block

58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Hydrogen | Alkali Earth Metals | Lanthanides | F block Non-Metals & Metals | Noble Gases

Alkali Metals | d block Metals | Actinides | Metalloids

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Periodic Table

Position of Element in Periodic table

- **Period :** Highest number of shell, which contain electron (1-7)
- **Group No. :** (1-18)
- **Block :** Highest energy sub-shell which contain electron. (s, p, d, f)
  - s-block : number of ns electrons
  - p-block : number of np electrons + 12
  - d-block : number of ns + (n -1)d electrons
  - f-block : III / IIIB group

Screening Effect / Shielding Effect

Repulsive force applied by inner electron on a particular electron/last electron/ tested electron.

Calculation of screening (σ) by

Slater's Rules

- σ by test electron = 0.00
- σ by rest of valence electron = 0.35
- σ by (n-1) s, p = 0.85
- σ by (n-2) or inner electron = 1.0

Varation of σ : along the period & down the group increases.

Order of σ : s > p > d > f

Bohr classification

Normal/representative elements

s & p block **(except inert gas)** :

$ns^{1-2} np^{1-5}$; use of electrons in valence shell only during chemical combination

Transition elements

d- block : use electrons of n shell as well as (n – 1) shell during chemical combination.

Zn, Cd & Hg are not transition elements

Inner transition elements

f-block: Use electrons of n shell (n-1) shell and (n-2) shell

Inert gases:

18 group He, Ne, Ar, Kr, Xe,Rn

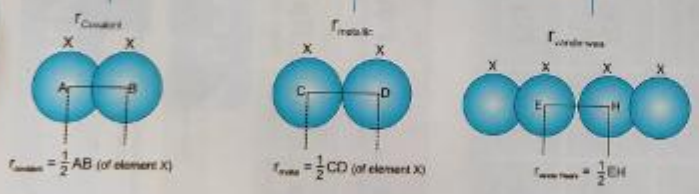
Do not use any electron during chemical combination **(exception Xe)**

Effective Nuclear Charge (Z_{eff})

$$Z_{eff} = Z - \sigma$$

Effective attraction felt by outermost shell electron.

Atomic Radius (r)



Order of Atomic Radii of same atom

$$r_{covalent} < r_{metallic} < r_{vanderwaal}$$

Order of Atomic Size

$N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+}$

Li < Na < K < Rb < Cs

Be < Mg < Ca < Sr < Ba

Li > Be > B > C > N > O > F

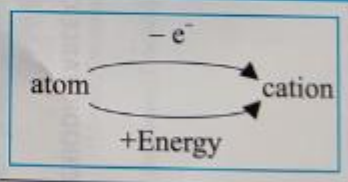
Na > Mg > Al > Si > P > S > Cl

Al ≈ Ga (Transition Contraction)

4d ≈ 5d (Lanthanide Contraction)

Isoelectric species size ∝ 1/No. of Protons

Ionisation Energy (I.E.)



$$M_{(g)} \xrightarrow{-e^-} M^+_{(g)} \qquad \Delta H = +ve$$

Always an endothermic process

Successive Ionisation Energy

$$M_{(g)} \xrightarrow[IE_1]{-e^-} \overset{I}{M^+_{(g)}} \xrightarrow[IE_2]{-e^-} \overset{II}{M^{2+}_{(g)}} \xrightarrow[IE_3]{-e^-} \overset{III}{M^{3+}_{(g)}}$$

Order of successive I.E.:

$IE_1 < IE_2 < IE_3$ always

Total energy required for the formation of M^{n+} ion = $IE_1 + IE_2 + IE_3 \ldots\ldots IE_n$

Order of $I.E_1$.

Li < Be > B < C < N > O < F < Ne

Na < Mg > Al < Si < P > S < Cl < Ar

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Important Points to remember

- Order of Ionization Energy in a shell s > p > d > f.
- $I.E._1$ Be > $I.E._1$ B
  (Since 2s is more closer to nucleus than 2p)
- $I.E._1$ N > $I.E._1$ O but $I.E._2$ O > $I.E._2$ N.
- Reason : half filled stable configuration
- The reason for stability of half filled & full filled configurations- Spherical symmetry and higher exchange energy.
- $E.A._1$ Li > $E.A._1$ Be.
- (Since 2s is more closer to nucleus than 2p)
- $E.A._1$ C > $E.A._1$ N.
- Reason : It is difficult to add electron in stable half filled configuration of N.
- $E.A._1$ Cl > $E.A._1$ F, $E.A._1$ S > $E.A._1$ O, $E.A._1$ P > $E.A._1$ N.
- Reason : due to large size of Cl, S, P repulsion is less pronounced.

Valency

- Total Number of bonds around central atom.
- The valency of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and / or equal to eight minus the number of outermost electrons as shown below.

Group	1	2	13	14	15	16	17	18
No. of valence e^-.	1	2	3	4	5	6	7	8
Valancy	1	2	3	4	3,5	2,6	1,7	0,8

Nature of Oxides

- Neutral Oxides:- N_2O, NO, H_2O, CO.
- Amphoteric Oxides :- BeO, Al_2O_3, Ga_2O_3, As_2O_3, Sb_2O_3, ZnO.
- Acidic oxide :- Cl_2O_7, P_2O_5.
- Basic oxide :- Na_2O, MgO.

Applications of electronegativity

- Electronegativity of hybridized orbitals - $sp > sp^2 > sp^3$.
- Reason : smaller is the size of orbital more is the electronegativity.
- Nature of bond in A-B molecule - [X = Electronegativity]

$X_A \sim X_B = 0$	The bond A-B is 100% covalent or non polar bond.
$X_A \sim X_B = 1.7$	The bond A-B is 50% covalent and 50% ionic.
$X_A - X_B > 1.7$	The bond A - B is more ionic less covalent
$X_A \sim X_B < 1.7$	The bond A - B is less ionic more covalent

Eg:

Compound	F_2	HF	LiF
ΔEN	0	1.8	3
Type of bond	Non polar covalent	Polar covalent	Ionic

Electron Gain Enthalpy/ Electron Affinity

$$\text{atom} \xrightarrow{+e^-} \text{anion}$$

– Energy

$$X_{(g)} + e^- \longrightarrow X^-_{(g)} \qquad \Delta H = -ve$$

Generally exothermic

Successive Electron Affinity

$$X_{(g)} \xrightarrow[EA_1]{+e^-} X^-_{(g)} \xrightarrow[EA_2]{+e^-} X^{2-}_{(g)} \xrightarrow[EA_3]{+e^-} X^{3-}_{(g)}$$

(I, II, III)

Order of E.A. (in a period)

Li > Be < B < C > N < O < F > Ne

Na > Mg < Al < Si > P < S < Cl > Ar

Order of E.A. (up to down)

B < Al C < Si N < P

O < S F < Cl

In P-block - EA of 2nd period < 3rd period
Maximum EA 'Cl'

Electronegativity

Tendency of an atom to attract shared pair of electrons toward itself in bonded state is known as electronegativity

Properties

Relative Phenomenon

Unitless property

For Nobel gas we consider EN = Zero

Periodicity

Order of E.N. (in a period)

Li < Be < B < C < N < O < F

Na < Mg < Al < Si < P < S < Cl

Nature of Oxides and hydroxides	Bond length	Percentage ionic character
Acidic character $\propto$ EN	Schumaker stevenson formula	Hanny-Smith formula
Basic character $\propto \frac{1}{EN}$	$d_{A-B} = r_A + r_B - 0.09 \times \Delta EN$	$16 \times \Delta EN + 3.5(\Delta EN)^2$

Order of E.N.

B > Al < Ga < In < Tl

C > Si = Ge = Sn < Pb

ΔEN↑ → Bond Polarity↑
↓
Bond length↓
↓
Bond strength↑
↓
Ionic character↑

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Early Classification

- **Dobereiner's Law of Triads**
  He arranged the elements in groups of three, called triads such that atomic weight of middle element is average of first and third element. These elements resembled in their properties.
- **Newlands Law of Octaves**
  He arranged the elements in increasing order of their atomic weights and found that any given element has similar properties to the eighth element that followed it. The relationship was same as that existing between musical note and its octave.
- **Lothar Mayer**
  Lothar Mayer plotted a graph between atomic weight and atomic volume (i.e., atomic weight in solid state/density). Elements with similar properties of the element occupied the similar positions on the graph.

Mendeleev's Periodic Table

The physical and chemical properties of the elements are the periodic functions of their **atomic masses.**

Merits of Mendeleev's Periodic Table

- Correction of atomic Masses.
- Prediction of New elements which justify the basis of the blank spaces given in its periodic table.
- Eka boron - Scandium
- Eka aluminium - Gallium
- Eka silicon - Germaniuma

Demerits of Mendeleev's Periodic Table

- Position of H could not be explained.
- In certain pairs of elements, increasing order of atomic masses was not followed.
- Position of isotopes could not be explained.
- Anomalous positions of lanthanides and actinides in periodic table.
- Similar elements were placed in different groups.

Development of Modren Periodic Table

- Moseley x-ray experiment $Z \propto \sqrt{v}$
- The physical and chemical properties of elements are periodic functions of their **atomic numbers.**
- Introduced zero group for Nobel gases.

Periodicity

The repetition of the properties of elements after regular intervals when the elements are arranged in the order of increasing atomic number is called periodicity.

Cause of Periodicity :

- The periodic repetition of the properties of the elements is due to the recurrence of similar valence shell electronic configurations after certain regular intervals.
- The modern periodic table consists of horizontal rows (periods) and vertical column (groups).
- **Atomic radius, ionization enthalpy, electron gain enthalpy, electronegativity, valency, oxidizing and reducing nature are periodic properties.**

Block	Last e^- enters	Electronic Configuration	Group No.	Metal/Non Metals
s-block	*ns* orbital	ns^{1-2}	1 and 2	Metal
p-block	*np* orbital	ns^2np^{1-6}	13 and 18	Few are metals and metalloids but most of them are non-metals
d-block	*(n-1)d* orbital	$(n-1)d^{1-10}ns^{0-2}$	3 and 12	Transition metals
f-block	*(n-2)f* orbital	$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$	Related to group 3	Inner transition metals

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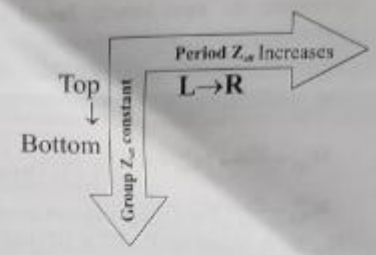
Screening Effect

- Repulsive force applied by inner electron or a particular electron/last electron/tested electron.
- Calculation of screening (σ) by Slater's Rules
  - σ by test electron = 0.00
  - σ by rest of valence electron = 0.35
  - σ by (n-1) s, p = 0.85
  - σ by (n-2) or inner electron = 1.0
- Variation of σ along the period & down the group increases.
- Order of σ : s > p > d > f

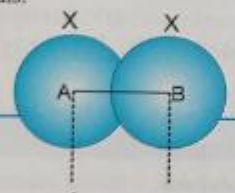
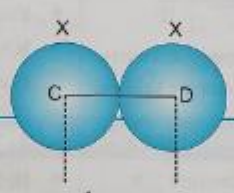
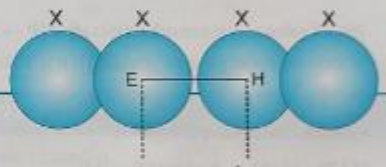
Effective nuclear charge

- Due to screening effect the valence electrons experiences less attraction towards nucleus. This brings decrease in the nuclear charge (Z) actually present on the nucleus. The final nuclear charge experienced is termed **effective nuclear charge**
- $Z_{eff} = (Z - \sigma)$
- Z = actual nuclear charge / atomic no. of the element.
- σ = screening or shielding constant
- **Periodic Trend**



Atomic Radius

- The distance between the nucleus and outermost orbit is called radius of an atom.

Covalent Radius	Metallic Radius	Van der Waals Radius
• It is half of the distance between the centres of two nuclei (of like atoms) bonded by a single covalent bond • Covalent radius is generally use for non metals.	• It is half of the distance between the nuclei of two adjacent metal atoms in the metallic crystal lattice.	• It is half of the internuclear distance between two adjacent atoms in two nearest neighbouring molecules of the substance in solid state
		
$r_{covalent} = \frac{1}{2}AB$ (of element X)	$r_{crystal} = \frac{1}{2}CD$ (of element X)	$r_{van\ der\ Waals} = \frac{1}{2}EH$

Some Important Orders of Radius

- $r_{covalent} < r_{metallic} < r_{van\ der\ Waals}$
- Upto down atomic radius increases (Li < Na < K < Rb < Cs)
- Left to right atomic radius decreases (Na > Mg > Al > Si > P > S > Cl)
- Diagonally radius remain same (Li = Mg)
- Ionic radius $\propto \frac{-ve\ charge}{+ve\ charge}$ $(Al^{3+} < Mg^{2+} < Na^{+} < F^{-} < O^{2-} < N^{3-})$
- Order of size : $A^{+} < A < A^{-}$
- On moving left to right radius decreases but $Zn_{(s)} > Cu_{(s)}$ (due to d-d electron repulsion)
- On moving up to down radius increases but Zr ≈ Hf and Nb ≈ Ta (due to poor screening of f electrons)
- 4d series radius ≈ 5d series radius (due to Lanthanide Contraction, also know as poor screening of f electrons)
- On moving up to down radius increases but Al > Ga (due to poor screening of d electrons)
- Introduction of d and f electrons is more impulsive on initial group elements for example : 3rd and 13th group

Diagonal Relationship

2nd period Li Be B C

3rd period Na Mg Al Si

Diagonal relationship arises because of ;

- On descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases. Thus on moving diagonally, the size remains nearly the same. (Li = 1.23 Å & Mg = 1.36 Å ; Li^{+} = 0.76 Å & Mg^{2+} = 0.72 Å)
- When we move diagonally we are moving left to right and up to down simultaneously.
- It is sometimes stated that the diagonal relationship arises because of diagonal similarity in electronegativity values. (Li = 1.0 & Mg = 1.2 ; Be = 1.5 & Al = 1.5 ; B = 2.0 & Si = 1.8)

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Ionization Energy

- Ionisation energy (IE) is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a cation.
- Always an endothermic process (ΔH = Positive)

$$M_{(g)} \xrightarrow{(IE_1)} M^+_{(g)} + e^-$$

$$M^+_{(g)} \xrightarrow{(IE_2)} M^{2+}_{(g)} + e^-$$

$$M^{2+}_{(g)} \xrightarrow{IE_3} M^{3+}_{(g)} + e^-$$

$(IE)_1 < (IE)_2 < (IE)_3 < .....$
Order of successive IE

- IE_1, IE_2 & IE_3 are the Ist, IInd & IIIrd ionization energies to remove electron from a neutral atom, monovalent and divalent cations respectively.

Variation of Ionization Energy

- **In Period**
  I.E. Increase
- **In Group**
  I.E. Decrease

Factors affecting I.E.

- **Size of Atom.** - I.E. decreases with increase in atomic size
- **Nuclear charge** - The I.E. increases with increase in the nuclear charge.
- **Shielding or screening effect** - The larger the number of electron in the inner shells, greater is the screening effect and smaller the force of attraction and thus I.E. decrease.
- **Penetration effect of the electron** - Penetration effect of the electrons follows the orders **s > p > d > f** for, the same energy level. Higher the penetration of electron higher will be the ionisation energy.
- **Electronic configuration** - If an atom has exactly half-filled or completely filled orbitals, then such an arrangement has extra stability.

Factor 4 & 5 applicable upto 4th period only
Be > B Sb > Te N > O

Application of IE

- Metallic character $\propto \frac{1}{IE}$
- Reactivity of metal $\propto \frac{1}{IE}$
- Electro +ve character $\propto \frac{1}{IE}$
- Reducing nature $\propto \frac{1}{IE}$
- No. of valence e^- = consider successive IP → highest jump in successive IP indicate nobel gas configuration if it is 'b' then no. of valence e Valence e^- = b – 1
- Consider Successive IP :
- If Δ IP = 11 eV → higher O.S. stable
- If ΔIP = 16 eV → lower O.S. stable

Exceptions of IE

- Exceptions of I.E. in a period
- N > O • Be > B • P > S • Mg > Al • Hg > Tl • Pd > Ag • Cd > In
  Exceptions of I.E. in a group
- Ga > Al • Pb > Sn • Cl > P • Tl > In • Zr > Hf • Nb > Ta
- 5d > 4d series
- He has highest I.E. in the periodic table.

Electron Affinity

- The energy released when an extra electron is taken up by a neutral gaseous atom to form an anion is called its electron affinity.

$$X_{(g)} + e^- \longrightarrow X^-_{(g)} + \text{energy}$$

- Always an exothermic process (ΔH = Negative)
- When an atom gains more than one e^-; these electrons are known as successive electrons and their energy is known as successive electron affinity

$$X_{(g)} + e^- \xrightarrow[\text{energy}]{\text{I}} X^-_{(g)} \xrightarrow[\text{energy}]{\text{II}\ +e^-} X^{2-}_{(g)}$$

$$\downarrow \qquad\qquad \downarrow$$

$$EA_1 \qquad\qquad EA_2$$

- **EA_2 is always endothermic due to repulsion between anion & incoming electron**
- Group 17 elements (halogens) have very high negative electron gain enthalpies (i.e. high electron affinity) because they can attain stable noble gas electronic configuration by picking up an electron.
- Noble gases have large positive electron gain enthalpies because the electron has to enter the next higher energy level leading to a very unstable electronic configuration.
- Negative electron gain enthalpy of O or F is less than S or Cl.

Factors Affecting Electron Affinity

- Electron Affinity $\propto \frac{1}{\text{Atomic size}}$
- Electron affinity $\propto$ Effective nuclear charge (Z_{eff})
- Electron Affinity $\propto \frac{1}{\text{Screening effect}}$
- Electron Affinity $\propto \frac{1}{\text{Stable electronic configuration}}$

Variation of Electron Affinity

- **In Period**
  EA ↑; ΔH_{eg} – ve ↑
- **In Group**
  EA ↓; ΔH_{eg} – ve ↓
- II period F > O > C > B > Li > N > Be > Ne
- III period Cl > S > Al > P > Na > Mg > Ar

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Super Note:
Electron gain enthalpy is usually negative except for N (+31) Be (+66) Mg (+67) Ne (+112) and all the noble gases

Electronegativity

- Electronegativity is a measure of the tendency of an element to attract shared electrons towards itself in a covalently bonded molecules.
- Electronegativity cannot be defined for isolated gaseous atom.
- In a period, electronegativity increases from left to right.
- In a group, electronegativity decreases from top to bottom.

Factors affecting E.N.

- $EN \propto Z_{eff}$
- $EN \propto 1/\text{atomic size}$
- $EN \propto +ve\ O.S.$
- $EN \propto$ percentage of s-character
- $EN \propto$ percentage of s-character [for eg. $sp > sp^2 > sp^3$]

Scales of E.N.

- Pauling's scale

$$\chi_A - \chi_B = 0.208\sqrt{\Delta E}$$

ΔE = acutal bond energy $= \sqrt{E_{A-A} \times E_{B-B}}$

E_{A-B} = Bond enthalpy/ Bond energy of A – B bond.

E_{A-A} = Bond energy of A – A bond

E_{B-B} = Bond energy of B – B bond

- At Mulliken's scale

$$\chi_M = \frac{IE + EA}{2}$$

IE - Ionization Enthalpy
EA - Electron Affinity

- $E.N._{pauling} = \frac{E.N._{mulliken}}{2.8}$ (Trick : mulliken has more letters so we divide)

Some Important values of E.N.

- Up to down EN decreases except : Ga > Al Pb > Sn Tl > In
- Elements with same value of EN : C = S = I = 2.5 Cs = Fr = 0.7 Be = Al = 1.5 N = Cl = 3

Application of Electronegativity

- $\frac{\text{Metallic nature}}{\text{Non-metallic nature}} \propto \frac{1}{E.N.}$
- $B.L. = r_A + r_B - 0.09\ (\Delta E.N.)$
- $\Delta E.N.$ increases, bond length decreases
- $\frac{\text{Covalent characters}}{\text{Ionic characters}} \propto \frac{1}{\Delta E.N.}$
- While writing the formula of inorganic compound lesser electronegative elements are written first.
- $\frac{\text{Basic nature of oxides}}{\text{Acidic nature of oxides}} \propto \frac{1}{\Delta E.N. \text{ of element}}$
- Percentage of ionic character
  $= 16(X_A - X_B) + 3.5(X_A - X_B)^2$
  $= 16\Delta + 3.5\Delta^2$
  $= (0.16\Delta + 0.035\Delta^2) \times 100$
  X_A is electronegativity of element A (Higher)
  X_B is electronegativity of element B (Lower)
  $\Delta = X_A - X_B$

Difference between Electronegativity and Electron gain Enthalpy

Electronegativity	Electron gain Enthalpy
It is defined in combined state	It is defined for isolated gaseous atom
It cannot be calculated experimentally	It can be calculated experimentally
It is relative	It has own experimental value
It is unit less	Its unit is kJ/mol
It is tendency to attract electrons in combined state	It is tendency to attract electrons in isolated state
Maximum for fluorine	Maximum for chlorine

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Chapter – 2 Chemical Bonding

Atoms → highly unstable → due to their electronic configuration & high amount of energy → In the process to decrease their energy and to attain the stability

Start from here

↓

Atoms undergo bond formation

↓

Which leads to formation of chemicals

known as

1 Chemical Bond

ΔH = –ve (Always exothermic)

Based on Octet Rule (in general)

Can be of two types mainly

2

If Octet of Central atom incomplete then there will be ADAPTATIONS for survival

*Mainly in the compounds of B, Be, Al.

Back Bonding

- Presence of Vacant orbital on Central/Peripheral atom.
- Lone pair on Central/Peripheral atom.
- Eg. BF_3, BCl_3, BBr_3, BI_3, & Boric Acid
  (L.P. on Peripheral atom, Peripheral to center back bonding).
- Eg. $O(SiH_3)_2$, $N(SiH_3)_3$, OCl_2, CCl_2
  (L.P. on Central atom, center to peripheral back bonding).

Bridge Bonding

- Size of central atom should be Large than B.
- Size of Be & Al > B.
- Due to large size lesser Steric Hindrance.
- Be & Al can Arrange 4 Peripheral atom.
- Eg. : $BeCl_2$ (Dimer), $BeCl_2$ (Polymer), $AlCl_3$ (Dimer), $AlCl_3$ (Polymer)

Banana Bonding

- Peripheral atom must be Hydrogen.
- 3 C - 2 e^- bond.
- Eg. Diborane (B_2H_6), BeH_2 (Dimer).

3 Primary Bond

- **Required for the existence of molecules & Compounds.**
- **Involvement of electrons occurs in the formation of primary bond**
- **Bond energy = 200 - 400 kJ/mol^{-1}**
- **Secondary bonds cannot exist without primary bonds**

Can be of four types

Ionic Bond

- Transfer of electron/s.
- In between metal and non-metal.
- Formation of Ionic Bond, via Electrostatic force of attraction.
- Non directional in nature.

Covalent Bond

- Sharing of electron/s.
- In between non-metal and non-metal.
- Nuclear-electron attraction is more than nuclear-nuclear and electron-electron repulsion.
- Directional in nature.

Co-ordinate Bond

- First transfer then sharing of electron/s.
- Formed between lewis base and lewis acid.
- Also known as Co-ionic, semi-polar or Dative bond.
- Both electrons come from single atom/molecule.

Metallic Bond

- Metal ions are dipped in sea of electrons.
- In between metal and metal.
- **Exception: Mercurous ion [Hg_2^{2+}], has covalent bond in between [Hg^+–Hg^+].**
- Metallic bonds have free electrons which conduct electricity.
- Strength ∝ no. of unpaired electrons in metal atom.

***Zn, Cd, Hg are volatile due to lack of unpaired electron**

Scan this QR code for the Better understanding this Concept Map

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Representation of Hydrogen bonding in various molecules

Zig-zag H-bonding in HF molecule

Linear H-bonding in NH_3 molecule

3D H-bonding in H_2O molecule

4 Secondary Bond

- Cannot exist without the formation of Primary Bond.
- Secondary bonds lack the involvement of Electrons.
- Based on Electrostatic force of attraction
- Bond energy = 2 - 40 kJ/mol^{-1}

14366

Trick to remember distance dependence of molecular forces

Hydrogen Bond

- Hydrogen must be connected with F/O/N.
- It is stronger version of dipole-dipole interaction.
- **Strength of hydrogen bond** $\propto \frac{\text{E.N. of atom}}{\text{Size of atom}}$

Mainly of two types

Intra-molecular hydrogen bonding

- Hydrogen bond within molecule.
- Found in Ortho substituted, Phenols, Aldehydes, Amines & Carboxylic Acids by OH, NO_2, F etc. groups.
- B.P. ↓, V.P. ↑, Viscosity ↓, Solubility ↓

Inter-molecular hydrogen bonding

- Hydrogen bond in between molecule.
- Found in HF, H_2O, NH_3, and Para substituted Phenols, Aldehydes, Amines & Carboxylic Acids by OH, NO_2, F etc. groups.
- B.P. ↑, V.P. ↓, Viscosity ↑, Solubility ↑

- H_2S is gas but H_2O is liquid due to hydrogen bonding.
- B.P. of H_2O is greater than HF due to more no. of hydrogen bonds in H_2O.

Examples

H_2O is liquid while H_2S is gas.
HF is liquid while HCl is gas.
Viscosity
&
Surface tension ⟹ Glycerol > Ethylene glycol > Methanol

Molecular Forces

Non Vanderwaal's forces

- **Ion dipole.** $\propto \frac{1}{r}$
  Responsible for solubility of ionic compound in water.
  Responsible for the hydrated radius of the ions.
- **Ion induced dipole.** $\propto \frac{1}{r^4}$

Vanderwaal's forces

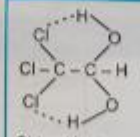
- **dipole-dipole** $\propto \frac{1}{r^3}$
- **dipole induced dipole** $\propto \frac{1}{r^6}$
- **London force of attraction** $\propto \frac{1}{r^6}$

London force of attraction $\propto \frac{\text{molecular mass}}{\text{branching}}$
Responsible for physical adsorption.
Determining the B.P. of molecules and nobel gases.

Strength of molecular forces :

- **Ion dipole > dipole-dipole > ion-induced dipole > dipole - induced dipole > london forces**

Special type of Hydrogen Bonding



Chloral hydrate

Chloral hydrate is stable only on account of intramolecular hydrogen bonding.

KHF_2 is possible but not $KHCl_2$ it is due to $K^+ [F \cdots H — F]^-$
Ion type H-bond

Order of Boiling Point

HF > HI > HBr > HCl
$H_2O > H_2Te > H_2Se > H_2S$
$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

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Covalent Bond

first time explained by

1 Lewis dot structures

Electron of outermost shell are shared to complete octet of central atom to achieve noble gas like configuration.

Lewis dot structures are based on Octet Rule.

Formal charge is the by-product of octet rule in which specific charge is assigned to Lewis dot structure to complete the octet.

Lewis dot structures Failed to Explain

- Existence of molecules having incomplete octet of central atom.
  No. of electron < 8
  BeH_2, BF_3, BCl_3, BBr_3, BI_3, $AlCl_3$, $AlBr_3$, AlI_3
- Existence of molecules having super octet / expanded octet of central atom.
  No. of electron > 8
  PCl_5, IF_7, XF_6, XeF_2, SF_4
- Species having odd electron.
  Central atom: Has odd electron
  NO, NO_2, ClO_2, ClO_3, O_2^-

Lewis theory was not able to explain the process of sharing of electrons between two atoms

2 V.B.T. (Valence Bond Theory)

How Electron are shared was explained by V.B.T.

Electrons are shared via orbital overlapping.

Requirement of Orbital Overlapping according to V.B.T.

- Orbitals of outermost shell participate in overlapping.
- Orbitals undergoing overlapping must be half-filled.
- If electron in the orbitals undergoing overlapping are paired then promotional energy is used to unpair
- Insufficient promotional energy causes inert pair effect in heavy p block elements

Factors affecting overlapping

Strength of covalent bond ∝ extent of overlapping

- **Shape of Orbitals** **(p-p > s-p > s-s)**
  Directional orbitals form stronger bond
- **Size of Orbitals** **(2p-2p > 2p - 3p > 2p- 4p > 2p - 5p)**
  Same size better fitting for overlapping
- **l.p. - l.p. repulsion** $-\underset{|}{C}-\underset{|}{C}- > :\underset{|}{N}-\underset{|}{N}: > :\underset{\cdot\cdot}{O}-\underset{\cdot\cdot}{O}: > :\underset{\cdot\cdot}{\ddot{F}}-\underset{\cdot\cdot}{\ddot{F}}:$
  Presence of l.p. decreases overlapping
- **Hybrid orbital undergoes stronger overlapping than pure atomic orbitals**

Scan this QR code for the better understanding of σ and π bond

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Overlapping can be of two types

Based on electron density

- Positive Overlapping
  - Head to Head
  - Tail to Tail
- Negative Overlapping
  - Head to Tail
  - Tail to Head
- Zero No Overlapping

Angle of approach

- $\theta = 180°$ — **Axial overlapping** σ bond formation
  - s-s overlapping
  - s-p overlapping
  - p-p overlapping
- $\theta = 0°$ — **Partial / parallel overlapping** π bond / δ bond formation
  - p-p overlapping — Internuclear axis — pπ-pπ pi-bond
  - p-d overlapping — pπ-dπ pi-bond
  - d-d overlapping — dπ-dπ pi-bond — also known as δ bond

V.B.T. Fails to Explain

- V.B.T. Could not explain the shape of molecule

  Explained by

  Valence shell e⁻ pair repulsion theory (V.S.E.P.R.T)

- In CH_4 molecule 3 bonds are formed by s-p overlapping while one by p-p overlapping. Besides these bonds have same bond energy however it couldn't be explained by V.B.T.

  Explained by

  Hybridization (mixing of atomic orbitals)

- V.B.T. Could not explain magnetic behavior of molecule
- V.B.T. Could not explain existence and non-existence of various molecules and bond order as well.

  Explained by

  Molecular Orbital Theory M.O.T.

Hybridization (Mixing of Atomic Orbitals)

Salient features of hybridization : The main features of hybridization are as under :

- In CH_4 molecule 3 bonds are formed by s-p overlapping while one by p-p overlapping. Besides these bonds have same bond energy however it couldn't be explained by V.B.T.
- The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- The hybridized orbitals are always equivalent in energy and shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridization indicates the geometry of the molecules.

Important conditions for hybridization :

- The orbitals present in the valence shell of the atom are hybridized.
- The orbitals undergoing hybridization should have almost equal energy.
- Promotion of electron is not essential condition prior to hybridization.
- It is the orbital that undergoes hybridization and not the electrons.

Hybridization involving d-orbital	Type of 'd' orbital involved
sp^3d	d_{z^2}
sp^3d^2	$d_{x^2-y^2}$ & d_{z^2}
sp^3d^3	$d_{x^2-y^2}$, d_{z^2} & d_{xy}
dsp^2	$d_{x^2-y^2}$

S.No.	Type of Orbital	No. of hybrid orbital	Geometry	Example
1.	One s + one p	2 ; sp	Linear	BeH_2, $BeCl_2$
2.	One s + two p	3 ; sp^2	Triangular	BCl_3, BF_3
3.	One s + three p	4 ; sp^3	Tetrahedral	CH_4, CCl_4
4.	One s + three p + one d	5 ; sp^3d	Triangular bipyramidal	PCl_5
5.	One s + three p + two d	6 ; sp^3d^2	Octahedral	SF_6
6.	One s + three p + three d	7 ; sp^3d^3	Pentagonal bipyramidal	IF_7

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Valence Shell Electron Pair Repulsion Theory

- The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair in VSEPR.
- lone pair - lone pair > lone pair - bond pair > bond pair - bond pair (order of repulsion)

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Example
• sp-hybridisation	2	-	Linear	$BeF_2, CO_2, CS_2, BeCl_2, HgCl_2$
• (a) sp^2 hybridisation	3	-	Trigonal planar	BF_3, $AlCl_3$ BeF_3^-
(b) sp^2 hybridisation	2	1	V-shape, Angular	NO_2^-, SO_2, O_3
• (a) sp^3 hybridisation	4	0	Tetrahedral	$CH_4, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-1}, SO_4^{-2}, AlCl_4^-$
(b) sp^3 hybridisation	3	1	Pyramidal	$NH_3, PF_3, ClO_3^-, H_3O^+, PCl_3, XeO_3, N(CH_3)_3, CH_3^-$
(c) sp^3 hybridisation	2	2	V Shape	H_2O, H_2S, NH_2^-
			Angular	OF_2, Cl_2O, SF_2, I_3^+
• (a) sp^3d-hybridisation	5	-	Trigonal bipyramidal	PCl_5, SOF_4, AsF_5
(b) sp^3d-hybridisation	4	1	See Saw	SF_4, PF_4^-, XeO_2F_2
(c) sp^3d-hybridisation	3	2	Almost T shape	ClF_3, ICl_3
(d) sp^3d-hybridisation	2	3	Linear	$I_3^-, Br_3^-, ICl_2^-, XeF_2$
• (a) sp^3d^2 hybridisation	6	-	Square bipyramidal/octahedral	PCl_6^-, SF_6
(b) $sp_3^3d_2^2$ hybridisation	5	1	Square pyramidal	$XeOF_4, ClF_5, SF_5^-, XeF_5^+$
(c) sp d hybridisation	4	2	Square planar	XeF_4
• (a) $sp_3^3d_3^3$ hybridisation	7	-	Pentagonal bipyramidal	IF_7
(b) sp d hybridisation	6	1	distortedoctahedral	XeF_6

Super Note : In finding geometry both l.p. and b.p. are added but to find shape only b.p. are considered.

$NH_3 = \left[\begin{array}{l}\text{Geometry} \Rightarrow \text{Tetrahedral}\\ \text{Shape} \Rightarrow \text{Pyramidal}\end{array}\right]$ $SF_4 = \left[\begin{array}{l}\text{Geometry} \Rightarrow \text{Triangular bipyramidal}\\ \text{Shape} \Rightarrow \text{seesaw shape}\end{array}\right]$ $XeF_4 = \left[\begin{array}{l}\text{Geometry} \Rightarrow \text{Octahedral}\\ \text{Shape} \Rightarrow \text{Square Planar}\end{array}\right]$

Bonding Parameter (bond length, bond angle & factors affecting)

Bond Length

1. **Bond length :** Internuclear distance

Factor affecting Bond length

- Atomic size ; bond length $\propto$ size [No. of shell]
- ΔEN, Bond length $\propto 1/\Delta EN$

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

- Bond order : Bond length $\propto \frac{1}{B.O.}$
- Hybridisation :

$$\text{Bond length} \propto \frac{1}{\text{\%age of s-character}}$$

Note:
Regular geometry/same hybridization/ Bond angle same
$BF_3 = BCl_3 = BBr_3 = BI_3$

$$B.A. \propto \frac{1}{E.N. \text{ of size atoms}}$$

$$B.E \propto \Delta EN \propto B.O. \propto \frac{1}{\text{size of atoms}}$$

Bond Angle

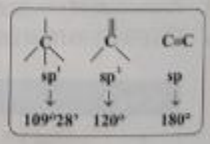
2. **Bond Angle:**

Angle between two adjacent Bonds is known as bond angle.

Factor Affecting Bond Angle

- **Hybridisation**

Bond angle $\propto$ %age of s-character



- **No. of lp/bp**

[when hybridization is same]

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

- **Type of central atom,** Apply when:

* hybridization same * No. of lp/bp same

Bond angle $\propto$ EN of central atom

Eg. $NH_3 > PH_3 > AsH_3 > SbH_3$

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Molecular Orbital Theory (MOT)

- M.O.T. explained existence and non-existence of various molecules, ions their bond order and magnetic behaviour.

Super Note : According to M.O.T. electrons are considered in wave form

Atomic orbitals → electron waves → interference
- → Constructive interference → Bonding Molecular Orbital (BMO)
- → Destructive interference → Anti-Bonding Molecular Orbital (ABMO)

- Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.
- Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- 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.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called bonding molecular orbital and anti-bonding molecular orbital are formed.
- The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital , the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli's Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**. But the filling order of these molecular orbitals is always **experimentally decided**, there is no rule like (n + l) rule in case of atomic orbitals.

Super Note : Same orbitals under go LCAO or interference according to M.O.T., s with s and p with p orbital there is no mixing of orbitals according to M.O.T. like hybridisation.

Super Note : If two molecules or ions have same bond order then molecule or ion with more electrons in A.B.M.O. is lesser stable for example N_2^- and H_2^- are lesser stable then N_2^+ and H_2^+ respectively.

Internuclear axis = Z

Energy level of molecular orbitals	$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (\pi 2p_x - \pi 2p_y) < \sigma 2p_z < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$	Total Electrons < 14
	$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$	Total Electrons > 14

Bond Order and Magnetic Behaviour

Bond order : No. of bonds present between two atoms.

$$B.O. = \frac{N_b - N_a}{2}$$

- Stability of molecules ∝ B.O.
- Bond Strength ∝ B.O.
- Bond length ∝ 1/B.O.

- Bonding electron (N_b) → No. of electrons present in BMO
- Anti-bonding electron (N_a) → No. of electrons present in ABMO

Magnetic Nature:

- Species with 12, 14, 18, 20 electrons are dimegnetic
- Species with 11, 13, 15, 16, 17, 19 electrons are paramegnetic

Isoelectronic species (CN^-, NO^-, C_2, O_2^-)

- Same bond order → same magnetic properties

- In case of same bond order, stability depends upon no. of anti-bonding electron/s
- Stability $\propto \frac{1}{\text{no. of anti bonding } e^-}$
- Stability order = $N_2 > N_2^+ > N_2^-$, $H_2 > H_2^+ > H_2^-$
- The bond order CO^+ is 3.5 which is an exception.
- **In C_2 molecule both the bonds are π and it is diamagnetic.**

Scan this QR code for Trick to solve MOT

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Bond Order and Magnetic Behaviour

S.No.	No. of electron in molecule	N_b	N_a	B.O.	Paramagnetic/diamagnetic
1	1	1	0	0.5	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	0.5	Paramagnetic
6	6	4	2	1	Diamagnetic
7	7	4	3	0.5	Paramagnetic
8	8	4	4	0	Does not exist
9	9	5	4	0.5	Paramagnetic
10	10	6	4	1	Paramagnetic
11	11	7	4	1.5	Paramagnetic
12	12	8	4	2	Diamagnetic
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

Dipole Moment

- It is vector quantity and is defined as the product of the magnitude of charge on any of the atom and the distance between the atoms. It is represented by .
- Magnitude of dipole moment $|\mu| = \underset{\text{(charge in esu)}}{q} \times \underset{\text{(Distance in Å)}}{r}$
- The direction of dipole moment is from positive to negative end.
- Dipole moment is usually expressed in Debye units (D). 1 Debye = 1×10^{-18} e.s.u. cm.
- $1\ D = 3.33564 \times 10^{-30}$ Cm, where C is coulomb and m is meter.
- Calculation of m for Polyatomic Molecule:

$\boxed{\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}}$ $\mu_R \rightarrow$ Vector sum of bond moment

Important Orders of Dipole Moment

(1) $NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$ (2) $CH_3Cl > CH_3F > CH_3Br > CH_3I$ (3) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

(4) $H_2O > H_2S$ (5) $CD_3Cl > CH_3Cl$ (6) $SO_2 > CO_2$

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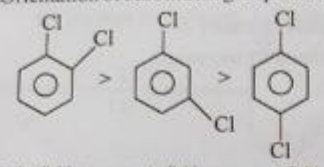
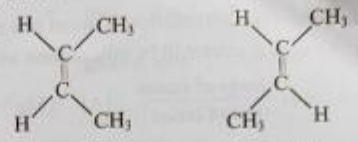
Application of Dipole Moment

- % Ionic character of a covalent bond = $\frac{\text{Experimental dipole moment}}{\text{Theoretical dipole moment assuming 100\% ionic character}} \times 100$
- Orientation of substituent groups on benzene ring



Orthodichloro benzene > metadichloro benzene > paradichloro benzene

- Differentiation between cis and trans alkenes.



$\mu \neq 0$ $\mu = 0$

- Predict shape and polarity of molecule
- Identification of Polar or Non-polar molecule
- Non-polar molecule: Symmetrical distribution of electron cloud H_2, F_2, Cl_2, N_2 etc.
- Polar molecule : Unsymmetrical distribution of electron cloud HF > HCl > HBr > HI
- $\mu \propto \frac{\Delta E.N.}{\text{bond angle}}$
- Molecules with regular geometry and same peripheral atoms have zero dipole moment.
  For example : CO_2, BF_3, CCl_4, PCl_5, SF_6, IF_7 (regular geometry = l.p. absent on central atom)
- In general molecule with lone-pair on central atom have non-zero dipole moment.
  For example : NH_3, H_2O, SO_2, SF_4
- Some molecules even with lone-pair on central atom have zero dipole moment.
  For example : XeF_4, XeF_2
- Molecule with higher dipole moment have greater critical temperature and surface tension.
- A symmetrical molecule is non-polar even though it contains polar bonds.
  For example, carbon dioxide, methane and carbon tetrachloride, being symmetrical molecules, have zero dipole moments.

Super Note :
Critical temperature and surface tension represent attraction between the molecules

Super Note :
Bond moment - It defines polarity in a bond.
Dipole moment it defines polarity (ionic character) in a molecule

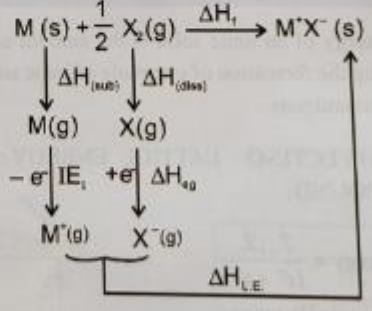
Ionic Bond

- Transfer of electron/s.
- In other words extreme polar covalent bond is an ionic bond.
- In between metal and non-metal.
- Formation of Ionic Bond, via Electrostatic force of attraction.
- Non directional in nature.
- Eg. NaCl , KF

Properties of Ionic Salt

- Hard, Solid, Brittle (Strong electrostatic force of attraction between ions)
- Non directional nature (ionic compound do not exhibit stereoisomerism)
- Higher Melting Point /Boiling Point
- Isomorphism : $MgSO_4.7H_2O$; $ZnSO_4.7H_2O$; $FeSO_4.7H_2O$

Energetics of Ionic Bond



ΔH_f = heat of formation of M^+X^- $\Delta H_{(sub)}$ = heat of sublimation of M

IE_1 = ionisation energy of M $\Delta H_{(diss)}$ = heat of dissociation of X_2

ΔH_{eg} = electron gain enthalpy of X U = Lattice energy of M^+X^-.

So according to Hess' law.

$\Delta H_f = \Delta H_{sub} + IE_1 + \Delta H_{diss} + \Delta H_{eg} + U_L$

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Fajan's Rule

- Fajan's Rule explained covalent character in ionic compound.
- According to Fajan's rule no compound is 100% ionic.
- Even most ionic compound CsF has 9% covalent characters.
- Fajans pointed out that greater the polarization of anion in a molecule, greater is the covalent character in it.
- Greater the distortion of anion, greater will be polarisation as a result of which covalent character increases.
- Polorizing power of cation(ϕ) $\frac{\text{charge of cation}}{\text{size of cation}}$ $(Al^{+3} > Mg^{+2} > Li^{+} > Na^{+})$
- Polarisability of anion $\propto$ size of anion $\propto$ charge of anion $(F^{-} < Cl^{-} < Br^{-} < I^{-})$, $(F^{-} < O^{-2} > N^{-3})$

Factors Affecting Polarisation

- Polarisation $\propto$ charge of cation or anion
- $\overset{+2}{Cr}O < \overset{+3}{Cr_2}O_3 < \overset{+6}{Cr}O_3$ Covalent character↑
- $\overset{+2}{S}F_2 < \overset{+4}{S}F_4 < \overset{+6}{S}F_6$ Covalent character↑
- $\overset{-1}{Li}F < Li_2\overset{-2}{O} < Li_3\overset{-3}{N}$ Covalent character↑ (anion charge↑)
- Polarisation $\propto \frac{\text{size of anion}}{\text{size of cation}}$
- $LiF > LiCl > LiBr > LiI$ — Anion size↑, Polarisability of anion↑, Covalent character↑
- $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ — Cation size↑, Polarization by cation↓, Covalent character↓

Application of Fajan's Rule

- Variation of M.P. [M.P. of covalent < M.P. of ionic] $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$
- Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.
- Solubility order $Na_2S > ZnS > CuS$ ($Zn^{2+}_{(s)} > Cu^{+2}_{(s)}$), polarizing power of Cu^{2+} is greater than Zn^{2+}.
- $Fe(OH)_3$ easily form precipitate in water than $Fe(OH)_2$.
- The colour of some compound can be explained on the basis of polarization of their bigger negative ions.
- For example: AgCl is colour less but AgBr and AgI are yellow due to large size of Br^{-} and I^{-}.

Concept of Solubility

- Solubility of S-block salts is determined on the basis of hydration enthalpy and lattice enthalpy.
- Solubility of p & d-block salts is determined on the basis of Fajan's rule.

Lattice Energy (U)

- The lattice energy of an ionic solid is the amount of energy released during the formation of one mole of ionic solid from gaseous constituent ions.
- FACTORS AFFECTING LATTICE ENERGY OF AN IONIC COMPOUND :
- $\text{Lattice energy} \propto \frac{Z_+, Z_-}{(r^{+} + r^{-})}$
- $(r^{+} + r^{-})$ = Inter-ionic Distance.
- Z_+/Z_- ⇒ charge on cation and anion respectively.
- Lattice energy $\propto$ coordination number (C.N.)
- Lattice energy should be less than hydration energy for solubility of ionic compound.
- Lattice energy decides solubility of s-block salts having small common ion.

Hydration Energy

- Hydration enthalpy is the amount of energy released when one mole of gaseous ions combine with water to form hydrated ions.
- Hydration $\propto \phi \propto \frac{\text{charge}}{(\text{size})^2}$
- More the hydration more is hydrated radius.
- More the hydrated radius lesser the ionic mobility.
- $Li^{+}_{(aq)} > Na^{+}_{(aq)} > K^{+}_{(aq)} > Rb^{+}_{(aq)} > Cs^{+}_{(aq)}$ (hydrated radius)
- $Li^{+}_{(aq)} < Na^{+}_{(aq)} < K^{+}_{(aq)} < Rb^{+}_{(aq)} < Cs^{+}_{(aq)}$ (Ionic mobility)
- Lithium is strongest reducing agent due to high hydration enthalpy.
- Fluorine is strongest oxidizing agent also due to high hydration enthalpy.
- Hydration Energy determines solubility of s-block for large common Anions.

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Trick to find Solubility

Solubility of s-block salts depends on lattice and hydration enthalpy

- If common ion smaller, L.E. decides solubility

$$\text{Solubility} \propto \frac{1}{LE} \propto \text{size} \begin{cases} \xrightarrow{IA} O^{-2}, OH^-, F^-, SO_4^{-2}, CO_3^{-2} \\ \xrightarrow{IIA} O^{-2}, OH^-, F^- \end{cases}$$

- If common ion is larger, H.E. decides solubility

$$\text{solubility} \propto HE \begin{cases} \xrightarrow{IA} Br^-, I^-, ClO_4^- \\ \xrightarrow{IIA} CO_3^{-2}, SO_4^{-2}, NO_3^-, Br^-, I^-, S^{-2}, Cl^- \end{cases}$$

- $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- Common ion smaller (CO_3^{-2}), solubility $\propto \frac{1}{LE}$

  $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

  Common ion larger (CO_3^{-2}), solubility $\propto$ HE
- $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

  Common ion (SO_4^{-2}), larger solubility $\propto$ HE

Solubility of p & d-block salts depends on Fajan's Rule

- $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$

  (Anion size ↑, cov. Char. ↑, solubility↓)
- $Fe(OH)_3 > Fe(OH)_2$

  (+) charge ↑, PP↑, CC↑, solubility↓
- $ZnCl_2 > CdCl_2 > HgCl_2$

  Z_{eff} ↑, PP↑, CC↑, solubility↓
- $AgF > AgCl > AgBr > AgI$

  Anionic size↑, PP↑, CC↑, solubility↓
- $NaCl > CuCl$

  PP ↑, CC↑, solubility↓

Co-ordinate Bond (Dative Bond)

- First transfer then sharing of electron/s.
- In ionic bond electrons are transferred, in covalent bond electrons are shared, but in coordinate bond electrons first transfer then shared
- Also known as Co-ionic, semi-polar or Dative bond.
- Both electrons come from single atom/molecule.
- Example : NH_4^+, O_3, H_2SO_4, HNO_3, H_3O^+, N_2O, $[Cu(NH_3)_4]^{2+}$
- Formed between lewis base and lewis acid.

Scan this QR code to understand the concept of solubility

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S – Block

Physical Properties

	I A	II A
Order of metallic or Ionic radii	Cs > Rb > K > Na > Li	Ba > Sr > Ca > Mg > Be
Reason	**up to down size increases**	**up to down size increases**
Order of density	Cs > Rb > [Na > K] > Li	Ba > Sr > [Be] > [Mg > Ca]
Reason	**due to empty d orbitals in K density of K < Na**	**due to empty d orbitals density of Ca < Mg and due to small size of Be density of Be > Mg**
Order of MP & BP	Li > Na > K > Rb > Cs	Be > Ca > Sr > Ba > Mg
Reason	**On increasing size packing efficiency decreases**	
Order of hydration in cation	$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	$Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$
Reason	**up to down size increases and charge density decreases hydration ∝ charge density**	
Order of conductivity of cations in polar solvent like water	$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$	$Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2} > Be^{+2}$
Reason	**up to down size of hydrated ion decreases**	
Order of conductivity in non-polar solvent	$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	$Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$
Reason	**up to down size of hydrated ion Increases**	

TYPE OF HYDRIDE

Ionic/salt like/ saline

* form ionic bond * give H^- in H_2O

Eg. s, p – block metal

BeH_2 and LiH are more covalent

Covalent/molecular

Form covalent bond give H^+ in H_2O

Eg. p-block non-metal

Interstitial hydride

Do not form strong bond, do not give H^+ and H^- in H_2O

Eg. : d and f block metal

Ammonia-Soda process or Solvay's process.

$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$

$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

Solvay's process cannot be employed for the manufacture of K_2CO_3 because $KHCO_3$ is fairly soluble in water.

Abnormal properties of Lithium

- **due to its small size and high charge density (atom and ion.)**

(i) LiOH, Li_2CO_3, $LiNO_3$ behave differently than other alkali corresponding salts towards heating

$2LiOH \rightarrow Li_2O + H_2O$;

$Li_2CO_3 \rightarrow Li_2O + CO_2$;

$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

Hydroxides and carbonates of other alkali metals are stable. The nitrates of other metals decompose given only oxygen.

(ii) Lithium directly combines with nitrogen.

$6Li + N_2 \rightarrow 2Li_3N$

(iii) $LiHCO_3$ is known only in solution but not in solid state.

(iv) Li_2SO_4 does not form double salt

(v) LiF, Li_3PO_4, $Li_2C_2O_4$, Li_2CO_3 are sparingly soluble in water

Abnormal properties of Beryllium

- **due to its small size and high charge density (atom and ion.)**

(1) Be is lightest alkaline earth metal.

(2) Be possesses higher m.pt. and b.pt than other group members.

(3) BeO is amphoteric in nature whereas oxides of other group members are strong base.

(4) It is not easily effected by dry air and does not decompose water at ordinary temperature.

(5) $BeSO_4$ is soluble in water.

(6) Be and Mg carbonates are not precipitated by $(NH_4)_2CO_3$ in presence of NH_4Cl.

(7) Be and Mg salts do not impart colour to flame.

(8) Be does not form peroxide like other alkaline earth metals.

(9) It salts can never have more than four molecules of water of crystallization as it has only four available orbitals in its valence shell.

(10) Beryllium carbide reacts with water to give methane whereas magnesium carbide and calcium carbide give propyne and acetylene respectively.

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Chemical Properties

	I A	II A
Reactivity towards moist air	$M \xrightarrow{O_2} M_2O \xrightarrow{H_2O} MOH \xrightarrow{CO_2} M_2CO_3$	$M \xrightarrow{O_2} MO \xrightarrow{H_2O} M(OH)_2 \xrightarrow{CO_2} MCO_3$
Exception	**Li when heated in air it also forms nitride**	**Be when heated in air it also forms nitride**
Reactivity towards Oxygen	Li – Normal oxide, Na – peroxide , K – Super oxide, Rb – Super oxide, Cs – Super oxide	Be – Normal oxide, Mg – Normal oxide Ca – Peroxide, Sr – Peroxide, Ba - Peroxide
Reason	**Up to down size increases so affinity towards oxygen increases.**	
Reactivity towards H_2O	$Li < Na < K < Rb < Cs$	$Be < Ca < Sr < Ba < Mg$
Reducing Power	**Li is strongest reducing agent due to high heat of hydration.**	**Be is weakest reducing agent due to high heat of Atomization**
Affinity towards H_2	$2M + H_2 \rightarrow 2MH$	$M + H_2 \rightarrow MH_2$
Stability of Hydride	**LiH > NaH > KH > RbH > CsH**	**$BeH_2 > MgH_2 > CaH_2 > SrH_2 > BaH_2$**
Reaction with liquid NH_3	$M + (X+Y)NH_3 \rightarrow M^+(NH_3)_X + e^-(NH_3)_Y$ (Ammoniated electrons)	$M + (X+Y)NH_3 \rightarrow M^{2+}(NH_3)_X + 2e^-(NH_3)_Y$ (Ammoniated electrons)

Due to these ammoniated electrons solution become deep blue and with respect to time this blue color fades due to formation of metal amide

Diagonal Relationship

Li shows resemblance with Mg, an element of group 2nd.

Be shows resemblance with Al, an element of group 13th

Group 1st	Group 2nd	Group 13th
Li	Be	B
Na	Mg	Al

Reason for Diagonal Relationship :- Approx same size, Comparable electronegativity , High polarization power

Order of Thermal Stability

- $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- $LiH > NaH > KH > RbH > CsH$
- $BeH_2 > MgH_2 > CaH_2 > SrH_2 > BaH_2$
- $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
- $BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4$
- Instability of $BeCO_3$ & $BeSO_4$ is due to small size of Be^{2+} ion which is unable to stabilize the bigger CO_3^{2-} & SO_4^{2-}.

Order of Solubility

- $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- $LiOH < NaOH < KOH < RbOH < CsOH$
- $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
- $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
- For carbonates and sulphates of IIA increase in lattice energy down the group which predominates over hydration energy so that solubility decreases down the group..

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General Characteristics of The Compounds of The Alkali Metal

Oxides and hydroxides

- The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour and paramagnetic due to presence of unpaired electron in superoxide ion.

  Eg: KO_2 Orange

  RbO_2 Brown

- Sodium peroxide is used as oxidising agent in purifying air because it release oxygen when reacts with carbon dioxide.

  $$2Na_2O_2 + 2CO_2 \rightarrow 2Na_2CO_3 + O_2$$

- The oxides are easily hydrolysed by water to form the hydroxides

  $$M_2O + H_2O \rightarrow 2MOH$$

  $$M_2O_2 + 2H_2O \rightarrow 2MOH + H_2O_2$$

  $$2MO_2 + 2H_2O \rightarrow 2MOH + H_2O_2 + O_2$$

- The alkali metal hydroxides are strongest of all bases and dissolve in water with evolution of heat due to high enthalpy of hydration.

Salt of Oxo-acids

- The alkali metals are highly electropositive, therefore their hydroxides are very strong bases and thus they form salts with all oxoacids and hydracids.
- They are generally soluble in water and stable towards heat. The carbonates (M_2CO_3) of alkali metals are remarkably stable upto 1273K, above which they first melt and then eventually decompose to form oxides.
- Li_2CO_3, however is considerably less stable and decomposes readily.

  $$Li_2CO_3 \rightarrow Li_2O + CO_2$$

- This is due to large size difference between Li^+ and CO_3^{2-} which makes the crystal lattice unstable.
- The stability of the carbonates increases in the order:-

  $$\mathbf{Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3}$$

- Being strongly basic, alkali metals also form solid bicarbonates.
- Lithium, however does not form solid bicarbonates though it exist in solution.
- Aqueous solutions of carbonates and bicarbonates are basic in nature due to anionic hydrolysis

Some Important Compounds of Sodium

Sodium Carbonate (Washing soda), $Na_2CO_3.10H_2O$

- Sodium carbonate is generally prepared by **Solvay Process** and **Leblanc process.**
- Due to low solubility of sodium hydrogen carbonate, it gets precipitated in the reaction of sodium chloride with ammonium hydrogen carbonate. (NH_4HCO_3)

  $$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$

  $$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4^+ + 2HCO_3^-$$

  $$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

- In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$. **Calcium chloride is obtained as a by-product.**

  $$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$$

Super Note :

- Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties

- This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate.
- Above 373 K, the anhydrous and monohydrate changes to becomes a white powder called soda ash.

$$Na_2CO_3 \cdot 10H_2O \xrightarrow{375K} Na_2CO_3.H_2O + 9H_2O$$

$$Na_2CO_3 \cdot H_2O \xrightarrow{\text{above } 373K} Na_2CO_3 + H_2O$$

Sodium Hydroxide (Caustic Soda), NaOH

$$NaCl \rightarrow Na^+ + Cl^-$$

$$Na^+ + e^- + Hg \rightarrow Na - Hg$$

$$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$

- The amalgam is treated with water to give sodium hydroxide and hydrogen gas

  $$2NaHg + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

Uses:

- It is used in the manufacture of soap, paper, artificial silk and a number of chemicals,
- Sodium hydrogencarbonate (Baking Soda), $NaHCO_3$

  $$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

- It is mild antiseptic for skin infections

Biological Importance Sodium and Potassium

- Na^+ and K^+ are present in sodium Pump
- This process is responsible for maintaing large excess of Na^+ outside the cell and large excess of K^+ ions the inside of cell.

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General Characteristics of The Compounds of The Alkaline Earth Metal

Oxides and hydroxides

- The alkaline earth metal oxides, MO are prepared either by heating the metals in oxygen

$$2Ca + O_2 \xrightarrow{heat} 2CaO$$

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

- Except BeO, all the alkaline earth oxides are ionic in which doubly charged ions are packed in a NaCl type of lattice (6 : 6) leading to their high crystal lattice energy and thus high stability.
- However beryllium oxide is covalent due to small size and relatively large charge on the beryllium ion.

$$MO + H_2O \rightarrow M(OH)_2 + Heat;$$

- The solubility of hydroxides of alkaline earth metals in water increases on moving down the group. The increasing solubility of the hydroxides on moving down the group is evident from their solubility products.
- Due to the small size, high electronegativity and high ionisation energy of beryllium, the oxides and hydroxides of beryllium are more covalent than ionic and thus are amphoteric.

$$Be(OH)_2 + 2HCl \rightarrow BeCl_2 + 2H_2O$$

$$Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

- On the other hand, the oxides and hydroxides of the other metals are basic in character, and their basicity increases on moving down the group.

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

Salt of Oxo-acids

(i) Carbonates

The carbonates dissolve in water in the presence of carbon dioxide to give bicarbonates.

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

Calcium Carbonate — Calcium Bicarbonate

(ii) Sulphates

These can be prepared by dissolving the metal oxide in H_2SO_4.

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$

(iii) Nitrates

Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt.

This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy.

All of them decompose on heating to give the respective oxide.

$$2M(NO_3)_2 \rightarrow 2MO + 4MNO_2 + O_2$$

(M = Be, Mg, Ca, Sr, Ba)

Halides

$$M + 2HX \rightarrow MX_2 + H_2$$

$$M(OH)_2 + 2HX \rightarrow MX_2 + H_2O$$

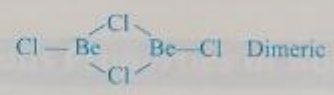
$$MCO_3 + 2HX \rightarrow MX_2 + CO_2 + H_2O$$

- Beryllium halides are covalent compounds due to small size and relatively high charge on Be^{2+} ion causing high polarising power.
- Due to covalent bonding, beryllium chloride, a typical member of beryllium halides, shows following anomalous characteristics,
- It does not conduct electricity in the fused state.
- Beryllium chloride reacts with lithium aluminium hydride to form the following products.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + AlCl_3 + LiCl$$

- Hygroscopic nature of beryllium halides is due to the fact that Be^{2+} ion has high value of hydration energy and therefore has a strong tendency to form hydrates.
- It is electron-deficient and behaves as Lewis acid. Beryllium chloride exhibits different structure in the vapour and in the solid states, as shown below:

Cl - Be - Cl monomeric



Dimeric

Some Important Compounds of Calcium

Calcium Oxide, CaO

- CaO is known as quick lime.
- On calcination of lime stone ($CaCO_3$), CaO is formed.

$$CaCO_3 \xrightarrow[\Delta]{1070K} CaO + CO_2 \uparrow$$

- Reverse reaction is suppressed by removing CO_2 in lime kilns by calcining lime stone in an open vessel.
- $CaC_2 + N_2 \rightarrow CaCN_2 + C$
- $CaCN_2 + C$ - **Nitrolium**
- As limestone contains clay as impurity it reacts at high temperature with CaO to form a fusible slag ($CaSiO_3$).

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

Calcium Hydroxide (Slaked lime), $Ca(OH)_2$

- Calcium hydroxide is prepared by adding water to quick lime, CaO.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

- The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime.
- CO_2 is passed through lime water and forms calcium carbonate (White ppt.)

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

- Milk of lime reacts with chlorine to form bleaching powder $Ca(OCl)_2$

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$$

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Calcium Sulphate

- Calcium sulphate is formed when lime stone ($CaCO_3$) is treated with dilute H_2SO_4

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

- On concentrating and crystallising calcium sulphate dihydrate ($CaSO_4.2H_2O$) separates out.

Super Note :

- $CaSO_4.2H_2O$ is called as **gypsum.**
- $CaSO_4.2H_2O$, is heated to 393 K, to form **plaster of paris**
- $2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4)H_2O + 3H_2O$
- Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as **'dead burnt plaster'.**
- Plaster of paris is $CaSO_4.\frac{1}{2}H_2O$ (or) $2CaSO_4.H_2O$
- Plaster of paris is thus hemihydrate (or) semihydrate of calcium sulphate.
- It is prepared by heating gypsum at 1200 – 1300°C

$$CaSO_4 \cdot 2H_2O \xrightarrow{390\,K} CaSO_4\,\frac{1}{2}H_2O + \frac{3}{2}H_2O$$

Cement

- It is important building material. It was introduced by Joseph Aspdin. It resembles with natural limestone so it is also called as power plant cement.
- Cement is a dirty greyish heavy powder containing calcium aluminates and silicates.
- The composition of the portland cement:

CaO	50-60%
SiO_2	20-50%
Al_2O_3	5-10%
MgO	2-3%
Fe_2O_3	1-2%
SO_3	1-2%

- Portland cement contains the important ingredients as

  Dicalcium silicate (Ca_2SiO_4) 26%

  Tricalcium silicate (Ca_3SiO_5) 51%

  Tricalcium aluminate ($Ca_3Al_2O_6$) 11%

Biological Importance of Mg^{2+} and Ca^{2+}

Mg^{2+} in Biology

Enzymes like phosphohydryase and phosphotransferase contain Mg^{2+} ions. These enzymes participate in ATP reactions and release energy. Mg^{2+} is complexed with ATP.

- Mg^{2+} is a constituent of chlorophyll, the green pigment in plants.

Ca^{2+} in Biology

- Ca^{2+} ions are necessary for blood clotting.
- Ca^{2+} ions are necessary to maintain heart beating.
- Ca^{2+} ions are necessary for muscles contraction.

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BORON FAMILY

Occurence and Physical Properties of Boron Family

Occurence

Boron → H_3BO_3 = Orthoboric acid
$Na_2B_4O_7.10H_2O$ = Borax - Puga valley (Ladakh)
$Na_2B_4O_7.4H_2O$ = Kernite

Aluminium → Most abundant metal in earth crust
$Al_2O_3.2H_2O$ = Bauxite
Na_3AlF_6 = Cryolite

Physical Properties

Boron → Hard and black coloured (has allotropes)

- Due to very highly stable crystalline lattice, boron has high melting point.
- Gallium has low melting point and high boiling point so used has liquid lubricant in thermal plants.

Chemical Properties of Boron Family

Atomic Radius : Tl > In > Al > Ga > B
I.E. : B > Tl > Ga > Al > In
E.N. : B > Tl > In > Ga > Al

Oxidation State and Reactivity

- Boron has high I.E. so forms covalent compound mainly.
- Aluminium : +3 is the most common state
- Indium, Gallium, Thallium has +1 and +3 but +1 is more stable due to inert pair effect.
- Stability of +1 Tl > In > Ga > Al

Tendency to behave as Lewis acids

- As we go upto down tendency of their halides to behave as Lewis acid decreases.
- $AlCl_3$ achieves stability by forming a dimer through bridge bonding.

Hydrolysis

$MCl_3 + H_2O \longrightarrow [M(OH)_4]^-$ Tetrahedral

$AlCl_3 + H_2O \xrightarrow{H^+} [Al(OH)_6]^{-3}$ Octahedral

Reactivity towards Air

- Boron is unreactive in crystalline form and crystalline aluminium forms thin oxide layer.
- However amorphous boron and aluminium react with air.

B_2O_3	Acidic
Al_2O_3 , Ga_2O_3	Amphoteric
In and Tl oxides	Basic

Reactivity towards acids & alkalies

- Boron does not react with acids or alkalies
- Aluminium reacts with both but conc. HNO_3 renders Al passive due to oxide layer

$Al + HCl \rightarrow AlCl_3 + H_2$

$Al + NaOH + H_2O \rightarrow Na[Al(OH)_4] + H_2$

Reactivity towards Halogens

$E + X_2 \rightarrow EX_3$

TlI_3 does not exist

Important Trends and Anomalous Properties of Boron

- The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water.
- Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, (except in boron) exist in aqueous medium.
- It is due to the absence of d orbitals that the maximum covalence of boron is 4.
- Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium.
- Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.
- $F_3B + :NH_3 \rightarrow F_3B \leftarrow NH_3$
- All boron trihalides , except BF3, are hydrolysed to boric acid
- $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$
- The increasing order of Lew is acid character is

  $BBr_3 > BCl_3 > BF_3$.
- BF_3 is **expected** to behave as a stronger lewis acid than BCl_3 and BBr_3 because of more electronegativity of fluorine. But practically BF_3 is less acidic.
- BF_3 has delocalised dative π bond from fluorine to Boron which is called **"Back Bonding"**.
- Back bonding ability is more with fluorine atoms as B- F bond involves the overlap of almost equal orbitals (2p - 2p)

POCO
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Some Important Compounds of Boron

Borax ($Na_2B_4O_7.10H_2O$)

Preparaties

- Borax is a white powder, less soluble in cold water more soluble in hot water.
- Super Note : Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH.

$$Na_2B_4O_7 + 7H_2O \rightarrow 4H_3BO_3 + 2NaOH$$

Action of heat:

- When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O\uparrow$$

$$Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2 + B_2O_3 \text{(borax bead)}$$

- Super Note : Correct formula of borax is $Na_2[B_4O_5(OH)_4].8H_2O$. It contains boron in both planar BO_3 ad tetrahedral BO_4 units. It contains five B—O—B linkage.

Borax-bead rest

- Borax reacts with certain metal salts such as, Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740°C} \underbrace{2HBO_2 + B_2O_3}_{\text{glassy mass}};$$

$$CuO + B_2O_3 \xrightarrow{\Delta} Cu(BO_2)_2 \text{(blue bead)}$$

$$CoO + B_2O_3 \xrightarrow{\Delta} Co(BO_2)_2 \text{ (blue bead)}$$

Uses : It is used :

- In borax bead test
- In production of glass.

Orthoboric acid (H_3BO_3)

Preparaties

- $Na_2B_4O_7 + 2HCl/H_2SO_4 + 5H_2O \rightarrow 2NaCl/Na_2SO_4 + 4H_3BO_3\downarrow$
- Super Note : It is a weak monobasis acid soluble in water and in aqueous solution the boron atom completes its octet by acceptin OH^- from water molecules :

$$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq)$$

$$pK_a = 9.25$$

- It, therefore, functions as a Lewis acid and not as a proton donor like most acids.
- Since $B(OH)_3$ only partially reacts with water to form H_3O^+ and $[B(OH)_4]^-$, it behaves as a weak.
- In the solid state, the $B(OH)_3$ units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry.

Uses :

- It is an antiseptic and its water solution is used as an eyewash.
- It is also used in glass, enamel and pottery industry.

Diborane (B_2H_6)

- Binary compounds of B with H are called boron hydrides or boranes. These compounds form following two types of series:

$$B_nH_{n+4} - B_2H_6, B_5H_9, B_6H_{10}, B_{10}H_{14}$$

$$B_nH_{n+6} + B_4H_{10}, B_5H_{11}, B_6H_{12}, B_9H_{15}$$

Preparaties

$$4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3Li[AlF_4]$$

- Laboratory method : It involves the oxidation of sodium borohydride with iodine.

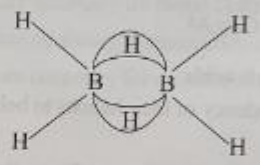
$$2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$$

Properties

- It catches fire spontaneously in air and explodes with O_2. Reaction with oxygen is extremely exothermic.

Structure

- In diborane the four terminal hydrogen atoms and the two boron atoms lie in same plane but two bridging hydrogen atoms lie above and below this plane.
- The four B-H bonds are regular two centre-two electrons bonds whereas the two bridging B-H bonds are three centre-two electrons bonds which are called as **banana bonds.**



Uses of Boron and Aluminium

Boron

- Borax is used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as consituent of medicinal soaps.

Aluminium

- Al is used for manufacture of cooking and household utensils.
- Al_2O_3 is used for making artificial gems.

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CARBON FAMILY

Chemical Properties of Carbon Family

Oxidation state and trends in chemical reactivity

- The common oxidation states exhibited by these elements are +4 and +2.
- Carbon also exhibits negative oxidation state.
- Since the sum of the first four ionization enthalpies is very high, compound in +4 oxidation state are generally covalent in nature.
- Super Note : In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding (inert pair effect).
- The relative stabilities of these two oxidation states vary down the group.
- Other element of the group can exceed its covalency beyond, 4. It is because of the presence of d orbital in them.
- Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like SiF_6^{2-}, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ and $[Pb(OH)_6]^{2-}$ exist in solutions as covalently bonded complex ions.

Anomalous Behaviour of Carbon

Catenation

- This is because C–C bonds are very strong.
- Down the group the size increase tendency to show catenation decreases.
- The order of catenation is C >> Si > Ge ≈ Sn.
- **Lead does not show catenation.** Due to the property of catenation and pπ-pπ bonds formation, carbon is able to show allotropic forms.

Allotropes of Carbon

- Carbon exhibits many allotropic forms; both crystalline as well as amorphous.
- Diamond and graphite are two well-known crystalline forms of carbon.
- Third form of carbon known as **fullerences.** It contain 20 six membered rings and 12 five membered rings.

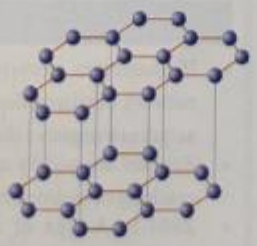
Diamond

C-sp^3, tetrahedral structure
C-C bond length 1.54 Å
Compact 3 dimensional structure
Hardest substance
Very high m.pt. (~3400°C)
Very high density
Non conductor
Very high refractive index
Exhibit total internal reflection
Shines brightly in light

Graphite

Hexagonal layer structure

- All sp^2 hybrid carbon
- Unhybridised orbital electrons form π bond. This π bond exhibit resonance there is mobility of electrons and it becomes conductor of electricity.
- Graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively.



Fullerene

Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds.

- Fullerene are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminster fullerene.**
- It contains twenty six -membered rings and twelve five membered rings.
- A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.
- All the carbon atoms are equal and they undergo sp^2 hybridisation.
- Each carbon atom forms three sigma bonds with other three carbon atoms.
- The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule.

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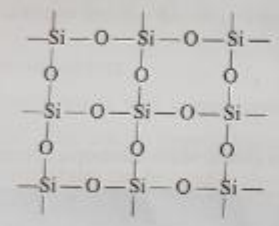
Some Important Compounds of Carbon and Silicon

Carbon Monoxide

- On small scale pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K.
- The mixture of CO and H_2 is known as water gas or synthesis gas.
- When air is used instead of steam, a mixture of CO and N_2 is produced, which is called producer gas.
- Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat, so very important industrial fuels

Silicon Dioxide, SiO_2

- SiO_2 is covalent in nature
- Silica in its normal form is almost non-reactive because of very high Si–O bond enthalpy.



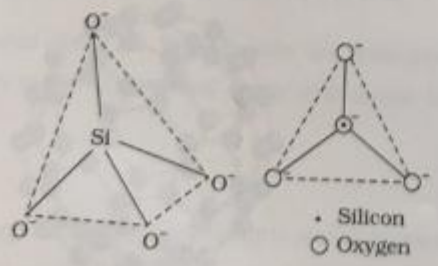
- SiO_2 has eight membered ring.
- It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures.
- However, it is attacked by HF and NaOH.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Silicates

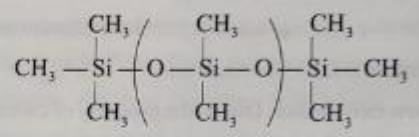
- Binary compounds of silicon with oxygen are called silicates but they contain other metals also in their structures. Basic unit is SiO_4^{4-}
- Some of the examples are feldspar, zeolites, mica and asbestos.
- The basic structural unit of silicates is SiO_4^{4-}.
- Pyro silicate - share one oxygen atom, Cyclic and Chain silicates - shares two oxygen atoms, sheet silicate - shares three oxygen atoms, Three Dimensional Silicates - shares four oxygen atoms.
- Two important man-made silicates are glass and cement



Silicones

- Silicones are synthetic organosilicon compounds having repeated R_2SiO units held by Si–O–Si linkages.
- These compounds have the general formula (R_2SiO), where R- alkyl or aryl group.
- The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes (R_nSiCl_{4-n}) and their subsequent polymerisation.
- Silicones can be prepared from the following types of compounds onnly.

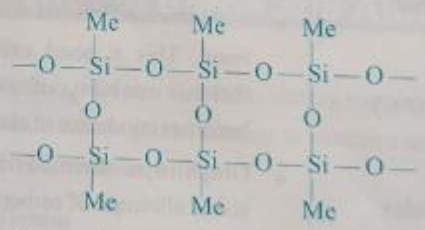
  (i) R_3SiCl (ii) R_2SiCl_2 (iii) $RSiCl_3$
- Silicons from the hydrolysis of a mixture of $(CH_3)_3SiCl$ & $(CH_3)_2SiCl_2$.
- The dichloro derivative will form a long chain polymer as usual. But the growth of this polymer can be blocked at any stage by the hydrolysis product of mono-chloro derivative.



- **The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the** ends.

Super Note :

- Silicones from the hydrolysis of trichloro derivative.
- When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three place as



- Silicones being surrounded by non-polar alkyl groups are water repelling in nature.
- They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals.

Zeolites

- If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge.
- Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation,
- ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline.
- Hydrated zeolites are used as ion exchangers in softening of "hard" water.

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NITROGEN FAMILY

Occurence and Physical properties of Pnicogens

- $NaNO_3 \rightarrow$ Chile salt petre
- $KNO_3 \rightarrow$ Indian salt petre
- $Ca_5(PO_4)_6.CaX_2 \rightarrow$ Apetite family (phosphate rocks) (X = F, Cl, OH)
- As, Sb, Bi are found as sulphide minerals

Physical properties :

- Nitrogen occurs as gas while all others are solid
- Except nitrogen all other show allotropy

Chemical Properties of Pnicogens

(A) Oxidation State : –3, + 3, +5

- Tendency to form –3 decreases up to down (metallic character increase)
- Tendency to form +5 decreases up to down (Inert pair effect) (+5 of bismuth occurs only in BiF_5
- Oxidation states of nitrogen from +1 to +4 disproportionate in acidic solution $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$
- Oxidation states of P disproportionate in to +5 and –3 in acid and alkali
- +3 states of As, Sb, Bi do not disproportionate

(B) Anamolous properties of nitrogen due to its small size, high EN, high IE and unavailability of d-orbitals

- Heavier members do not form pπ- pπ bonds as their atomic orbitals are large and diffuse
- Single N-N bond is weaker than P-P bond due to lp-lp repulsion
- N cannot form pπ-dπ bond

(C) Reaction with hydrogen

- Stability $\rightarrow NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
- Reducing $\rightarrow NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
- Basicity $\rightarrow NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
- Boiling Point $\rightarrow BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$

Reaction with oxygen

N_2O_3, P_2O_3 — Acidic

As_2O_3, Sb_2O_3 — Amphoteric

$Bi_2O_3 \rightarrow$ Basic

Reaction with Halogen

- Nitrogen trihalides are not stable except NF_3
- Trihalides except BiF_3 are covalent

Compounds of Nitrogen

Dinitrogen

Preparation :

- Produced **commercially** by the liquefaction and fractional distillation - Liquid dinitrogen distils out first.
- Laboratory method :

  $NH_4Cl + NaNO_2 \rightarrow N_2(g) + 2H_2O(l) + NaCl$

  Inpurity of NO and HNO_3 removed via H_2SO_4 and $K_2Cr_2O_7$
- $(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$
- Very pure nitrogen : $Ba(N_3)_2 \rightarrow Ba + 3N_2$

Properties :

- Colourless, odourless, tasteless
- With metals $\rightarrow$ Ionic nitrides
- With non-metals $\rightarrow$ Covalent nitrides

  $6Li + N_2 \xrightarrow{Heat} 2Li_3N \qquad 3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$
- Haber's process : $N_2 + 3H_2 \xrightarrow{773K} 2NH_3$

  $N_2 + O_2 \xrightarrow{2000K} 2NO$

Uses :

- Manufacture NH_3 and calcium cynamide
- For inert atmosphere (iron steel industries)
- As refrigerant

Ammonia

Preparation :

$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$

- Small scale :

  $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$

  $(NH_4)_2SO_2 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$
- Large scale : Haber's process (high pressure and temperature needed) catalyst iron oxide + $K_2O + Al_2O_3$ earlier used - Fe

Properties :

- Colourless, pungent odour
- Precipitates hydroxide of metals from salts

  $ZnSO_4 + 2NH_4OH \rightarrow \underset{\text{(white ppt)}}{Zn(OH)_2} + (NH_4)_2SO_4$

  $FeCl_3 + NH_4OH \rightarrow \underset{\text{(brown ppt)}}{Fe_2O_3.xH_2O} + NH_4Cl$
- Detection of compounds or elements by complex formation

  $[Cu(NH_3)_4]^{2+}$ (deep blue)

  AgCl (white ppt)

  $[Ag(NH_3)_2]Cl$ (colour less)

Uses :

- To make nitrogenus fertilizer - nitrate, urea
- Manufacture HNO_3a

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Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

Acids of Nitrogen (Nitric acid)

$H_2N_2O_2$ (hypronitrous acid) HNO_2 (nitrous acid) HNO_3 (nitric acid)

Preparation

- Laboratory : $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$
- Large scale - ostwald's process : Catalytic oxidation of NH, by atmospheric O_2

$$4NH_3 + 5O_2 \rightarrow 4NO \underset{}{\overset{\frac{1}{2}O_2}{\rightleftharpoons}} 4NO_2 \xrightarrow{H_2O} 2HNO_3 + NO$$

Uses

- To make ammonium nitrate
- Explosives and pyrotechniques
- Nitroglycerine and tri-nitrotoluene

Properties

- Strong oxidizing agent so attacks all metals except gold and platinum
- Product of oxidation depends on concentration of acid, nature of compound and temperature

$3Cu + 8HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
$Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
$4Zn + 10HNO_3(dilute) \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$
$Zn + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

- Chromium and Al do not react with HNO_3 due to passive oxide film
- Brown ring test : Used to detect nitrates

$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$
$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$

Compounds of Phosphorus

Name	Formula	Oxidation state of phosphorus	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	phosphorus acid + Br_2, heat in a sealed tube

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Compound of Phosphorus

Allotropes of P

White Phosphorus

- Translucent white waxy solid
- Poisonous - soluble in CS_2 insoluble in water
- Has chemiluminescense

  $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + NaH_2PO_2$
- Less stable more reactive
- Catches fire forms demse white fumes of P_4O_{10}

Red Phosphorus

- White phosphorus $\xrightarrow[\text{Several days}]{573K\ \Delta}$ red P
- Iron gray lusture
- Non-poisonous insoluble in CS_2 and water
- No chemiluminescense less reactive

Black Phosphorus

α-form

- Red phosphorus $\xrightarrow[\text{inert atm}]{\Delta 803K}$ α-black P
- Sublime in air
- Opaque monoclinic and rhombohedral
- does not oxidised

β-form

- White phosphorus $\xrightarrow{473K}$ β-black phosphorus
- Does not burn upto 673 K

Phosphine

$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$

Laboratory preparation

$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + NaH_2PO_2$

- When pure it is non-inflammable
- Becomes inflammable due to P_2H_4 or P_4 impurities
- For purification absorb PH_3 on HI
- $PH_4I + KOH \rightarrow KI + H_2O + PH_3$

Properties

- Explodes in HNO_3, Cl_2, Br_2 vapours
- $PH_3 + H_2O \rightarrow$ red $P + H_2$
- $CuSO_4 + PH_3 \rightarrow Cu_3P_2 + H_2SO_4$
- $HgCl_2 + PH_3 \rightarrow Hg_3P_2 + HCl$
- $PH_3 + HBr \rightarrow PH_4Br$

Uses :

- Combustiomn of phosphine is used in holme's signal
- Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- It is also used in smoke screens.

Phosphorus Halides

PI_5 does not exist

A : Trihalides

Preperation :

- $P_4(\text{white}) + 6Cl_2 \rightarrow 4PCl_3$
- $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

Properties

- Colourless oily liquid
- $PCl_3 + H_2O \rightarrow H_3PO_3 + HCl$
- Direct halogenating agent

B : Pentahalides

- Yellowish white powder

$PCl_5 \xrightarrow{\text{moist air}} POCl_3 + HCl$

$POCl_3 \xrightarrow{H_2O} H_3PO_4 + HCl$

$Ag + PCl_5 \longrightarrow AgCl + PCl_3$

$Sn + PCl_5 \longrightarrow SnCl_4 + PCl_3$

- Direct chlorinating agent
- In solid phase exist as PCl_4^+ and PCl_6^-
- In gaseous phase exist as PCl_5(axial bond longer than equatirial bond)

POCO
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OXYGEN FAMILY

Occurence and Physical Properties of Chalcogens

Occurence :

- Elements of oxygen family are called chalcogens (greek word for brass)
- Denotes association of sulphur and its congeners with copper
- Oxygen is most abundant element on earth
- Sulphur occurs as sulphate and sulphide
  - Gypsum : $CaSO_4.2H_2O$
  - Epson salt $MgSO_4.7H_2O$
  - Baryte $BaSO_4$
  - Zinc blende ZnS
  - Galena PbS
  - Copper pyrites $CuFeS_2$

Physical Properties :

- All elements show allotrophy
- Oxygen have minimum electron gain enthalpy in 16th group
- Electron gain enthalpy - S > Se > Te > Po > O
- Large difference in melting and boiling point of sulphur and oxygen because oxygen occurs as O_2 and sulphur and S_8
- Always remember boiling point is function of mass, more mass more boiling point

Chemical Properties of Chalcogens

Oxidation States :

- Oxygen show – 2 except fluorides (OF_2)
- Sulphur and other show +2, +4 and +6 (+4 with oxygen and +6 with fluorine)

Anamolous behaviour of oxygen :

- It is due to small size and high EN
- So H_2O shows hydrogen bonding where as H_2S does not
- Maximum covalency = 4 usually it is 2

Reaction with Hydrogen

- Acidic strength : $H_2Te > H_2Se > H_2S > H_2O$
- Thermal Stability : $H_2Te < H_2Se < H_2S < H_2O$
- Reducing nature : $H_2Te > H_2Se > H_2S$ **(H_2O is not reducing)**

Reaction with Oxygen

- Oxides of type EO_2 and EO_3 exist
- O_3 and SO_2 - Gases SeO_2 solid
- Reducing nature $SO_2 > SeO_2 > TeO_2$ **(SO_2 - reducing TeO_2 - oxidising)**

Reaction with Halogens

- Stability : F > Cl > Br > I
- Monohalide are all dimeric in nature and all disproportionate
- All except Se form dihalides
- Tetrahalides : SF_4 - Gas SeF_4 - Liquid TeF_4 - Solid
- All hexahalides are gaseous and octahedraral

Compounds of Sulphur

Sulphuric Acid (H_2SO_4)

Preparation :

Contact Process

- The steps involved are :

(i) Burning of sulphur (or) sulphide ores (like ironpyrites) in air to get SO_2

$$S + O_2 \rightarrow SO_2$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(ii) Conversion of SO_2 to SO_3 catalytically

$$2SO_2 + O_2 \xrightarrow[\Delta]{V_2O_5} 2SO_3$$

(iii) SO_3 is absorbed in 98% H_2SO_4 to get oleum

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

- Oleum is diluted with water to get sulphuric acid of desired concentration

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

- The key step in the process is catalytic oxidation of SO_2 with O_2 to give SO_3 in presence of catalyst
- The process is reversible

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{\text{Catalyst}} 2SO_{3(g)};\ \Delta H = -189\,kJ$$

- Forward reaction is : Exothermic and $\Delta n = -ve$
- According to Le chatlier's principle to favour forward process the following conditions are to be maintained i.e., high pressure and low temperature.

Properties

- High boiling point and high viscosity of H_2SO_4 is due to the fact that H_2SO_4 molecules are associated together by H-bonding.
-

Chemical Properties

- Strong affinity for water.
- Ability to act as oxidising agent
- It is very good dehydrating agent.

Uses

- Industrial process : To make fertilizers like $(NH_4)_2SO_4$ & superphosphate
- Petroleum refining
- To make pigments, paints, dyestuffs

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Allotropes

- Number of allotropes exist

(a) Rhombic Sulphur (α)

- More dense and less Bp
- Stable at room temperature
- Insoluble in water, slightly soluble in organic solvent, readily soluble in CS_2
- Prepared by evaporating solution of roll sulphur on CS_2

(b) Monoclinic sulphur (β)

- Less specific gravity and more Bp
- Stable above 369 K
- Prepared by melting α-sulphur in a dish and cooled - cryust formed, holes are made in cryust and liquid poured out
- Super Note : 369 K is called transition temperature where both type of sulphur exist

(c) Other synthetic sulphur

- 6-20 member rings
- S6-chain form bond angle less and bond length more than S8

Sulphur dioxide

Preparation

$S(s) + O_2(g) \rightarrow SO_2(g)$

$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$

$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$

Properties

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

- In it reaction with water and alkalies, the behaivour of sulphur dioxide is very similar to that of carbon dioxide
- **Bleaching action:** $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$
  coloured matters $\underset{\text{air oxidation}}{\overset{H^+}{\rightleftharpoons}}$ colourless matter
- Bleaching is through reduction but it is temporary. It is a more powerful reducing agent in alkaline medium than in acidic medium.

Structure of SO_2

- In SO_2, sulphur atom is sp^2 hybridised. It is an angular molecule with a lone pair on 'S' atom SO_2 molecule has two resonance structures.

Super Note :

- SO_2 acts as reducing agent in most of the reaction
- Bleaching action of SO_2 is due to it reducing behaviour while reducing behaviour of chlorine is due to oxidising nature

Compounds of Oxygen

Dioxygen

Preparation

- Laboratory : Heating salts like nitrate, chlorate etc.
  $KClO_3 \xrightarrow[\Delta]{MnO_2} KCl + O_2$
- Thermal decomposition of less reactive metal
  $Ag_2O \longrightarrow Ag + O_2$
  $HgO \longrightarrow Hg + O_2$
- Decomposition of H_2O_2
- Large scale : Electrolysis of water
- Industries : From air

Properties

- Paramagnetic
- Combines with all element except Au, Pt and noble gases
- Combustion is exothermic but needs ignition
- **Contact process :** $SO_2 + O_2 \xrightarrow{V_2O_5} SO_3$
- **Decon's process :** $HCl + O_2 \xrightarrow{CuCl_2} Cl_2 + H_2O$

Uses :

- Oxyacetylene welding
- Steel manufacture
- Thrust in rocket

Ozone

Preparation

- Slow stream of O_2 on silent electric discharge - 10% O_3 obtained
- Silent discharge is to prevent decomposition
- Greater than 10% concentration - battery of ozonizers is used. O_3 is condence in vessel surrounded by liquid oxygen

Properties

- Pale blue in gas, dark blue in liquid, violet black in solid
- Thermodynamically unstable
- Powerful oxidising agent
- Quantitative estimation of O_3 is done with help of KI and borate buffer (pH = 9.2). I_2 evolved is tritated against sodium thiosulphate
- Depletion of ozone layer is because of NO released by supersonic Jets

Uses :

- Bleaching oil, ivory, flour etc.
- Disinfectant, germicide, water sterlizer

Oxides

- Binary compound of oxygen with other elements
- Simple oxide = MgO, Al_2O_3
  mixed oxide = Fe_3O_4, Pb_3O_4
- Acidic oxide = $SO_2, Cl_2O_7, CO_2, N_2O_5, Mn_2O_7, CrO_3, V_2O_5$
- Basic oxide = Na_2O, CaO, BaO
- Amphoteric = Al_2O_3
- Neutral = CO, NO, N_2O

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HALOGEN FAMILY

Chemical Properties of Halogen Family

Order of electronegativity : F > Cl > Br > I > At

Order of Electron Affinity: Cl > F > Br > I

Colour: F_2 is light yellow, Cl_2 is greenish yellow, Br_2 is reddish brown and I_2 is deep violet.

Bond dissociation energy : $Cl_2 > Br_2 > F_2 > I_2$

Bond length : $F_2 < Cl_2 < Br_2 < I_2$

Oxidising power : $F_2 > Cl_2 > Br_2 > I_2$

Heat of hydration : $F^- > Cl^- > Br^- > I^-$

Reaction with H_2O :

$$2H_2O + 2F_2 \rightarrow 4HF + \underset{\text{Oxygen}}{O_2}$$

$$Cl_2 + H_2O \rightarrow HCl + \underset{\text{Hypochlorous acid}}{HClO}$$

$$Br_2 + H_2O \rightarrow HBr + \underset{\text{Hypobromous acid}}{HBrO}$$

Acidic strength in aqueous solution : $HI > HBr > HCl < HF$

Reducing character of hydrides : $HI > HBr > HCl > HF$

Boiling point : $HF > HI > HBr > HCl$

Thermal stability : $H-F > H-Cl > H-Br > H-I$

Oxidising Power

- As number of covalent bonds increases covalent nature increases.
- Fluorine is the strongest oxidising agent even though chlorine has maximum electron affinity.

Chemical Reactivity

- Halogens are highly reactive elements they can react with metals as well as non-metal and other substances. The order of reactivity of Halogens is $\mathbf{F_2 > Cl_2 > Br_2 > I_2}$.

Anomalous Behaviour of Fluorine

- The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell.
- It forms only one oxoacid while other halogens form a number of oxoacids.
- **Super Note :** Hydrogen fluoride is liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

(i) Reactivity towards oxygen (Oxides of Halogens)

- Fluorine forms two oxides OF_2 and O_2F_2.
- These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen.
- The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides. (middle row anomaly)

(ii) Reaction with Hydrogen (Hydrides or Hydrogen Halides)

- All the Halogens directly combine with Hydrogen to form Hydrides.
- The reactivity of Halogens with Hydrogen decreases from F_2 to I_2.

(iii) Reaction with Metals

- The order of the ionic character of the halides MF > MCl > MBr > MI where M is a monovalent metal. Halides in higher oxidation state will be more covalent than the one in lower oxidation state.

Some Important Compounds

Chlorine

Preparation

- Deacon's process : $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Properties

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3;\ S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$

- Reaction with NaOH :

$$\underset{\text{(cold \& dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaClO + H_2O$$

$$\underset{\text{(hot \& conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

- Reaction with dry slaked lime, $Ca(OH)_2$:

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

- Bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$
- **Oxidising & bleaching properties :**
- Chlorine dissolves in water (Cl_2 water is yellow) giving HCl (colourless) and HOCl (colourless). Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.
- It is a powerful bleaching agent; bleaching action is due to oxidation.
- Coloured substance + O → Colourless substance

Oxoacids of Halogens

- Flourine forms only one oxoacid HOF known as fluoric (I) acid or hypofluorous acid.
- All other forms oxy acids of the type HOX, HXO_2, HXO_3 and HXO_4 as shown below.

Oxidation state	Chlorine	Bromine	Iodine	Thermal stability and acid strength	Oxidising power
+1	HClO	HBrO	HIO	Increase	Decrease
+3	$HClO_2$	–	–		
+5	$HClO_3$	$HBrO_3$	HIO_3		
+7	$HClO_4$	$HBrO_4$	HIO_4		
	Acidity decrease →				

Order of Acidic Strength : $HClO < HClO_2 < HClO_3 < HClO_4$

Order of Basic Strength : $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$

Order of Oxidising Power: $BrO_4^- > IO_4^- > ClO_4^-$

- Cl – O bond length decreases from OCl^- to ClO_4^-
- Cl – O bond energy increases from OCl^- to ClO_4^- except for ClO_3^-

Super Note : Some poisonous gases of chlorine :
Phosgene ($COCl_2$), tear gas (CCl_3NO_2),
Mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$)

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Interhalogen Compounds

- Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called **interhalogen compounds.** These are of four types.

Preparation

$Cl_2 + F_2$ (equal volumes) $\xrightarrow{473K} 2ClF$;

$Cl_2 + 3F_2$ (excess) $\xrightarrow{573K} 2ClF_3$;

$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$;

Diluted with water : $Br_2(g) + 3F_2 \longrightarrow 2BrF_3$

F_2 is diluted with N_2 : $I_2 + 3F_2 \xrightarrow{-78°C} 2IF_3$

F_2 is taken in freon : $Br_2 + 5F_2$ (excess) $\longrightarrow 2BrF_5$

Properties

- Gases : ClF, BrF, ClF_3, IF_7
- Liquids : BrF_3, BrF_5
- Solids : ICl, IBr, IF_5, ICl_3
- Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2.

Uses

- Non aqueous solution
- Direct fluorinating agent
- ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$

Hydrogen Chloride

Preparation

- Glauber prepared this acid in 1648. Davy in 1810 showed that it is compound of hydrogen and chlorine.

$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$

$NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$

- HCl gas can be dried by passing through concentrated sulphuric acid.

Properties

- It reacts with NH_3 and gives white fumes of NH_4Cl

$NH_3 + HCl \rightarrow NH_4Cl$

- When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$

$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

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

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$

Uses

- In the manufacture of chlorine, NH_4Cl and glucose (from corn starch)
- For extracting glue from bones and purifying bone black
- In medicine and as a laboratory reagent

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NOBLE GASES

Chemical Properties of Noble Gases

In general, nnoble gases are least reactive. Their inertness to chemical reactivity is because they have high ionisation enthalpy and more positive electron gain enthalpy.

Xenon-Fluorine Compounds

Xenon difluoride

$$Xe + F_2 \xrightarrow[\text{sealed nickel tube}]{673\ K,\ 1\ bar} XeF_2$$

- The solution which have pungent smell due to XeF_2 are powerful oxidizing agents.

$$XeF_2 + 2H^+ + 2e^- \longrightarrow Xe + 2HF;\ E^\circ = +2.64V$$

$$XeF_2 + H_2 \longrightarrow 2HF + Xe$$

- Hydrolysis is slow in water due to dissolution of XeF_2 in HF formed, but is rapid in basic solution.

$$2XeF_2 + 2H_2O(l) \longrightarrow 2Xe + 4HF + O_2$$

$$XeF_2 + 2OH^- \longrightarrow Xe + \frac{1}{2}O_2 + 2F^- + H_2O$$

Xenon tetrafluoride

$$Xe + 2F_2 \xrightarrow[\text{sealed nickel tube}]{873\ K,\ 7\ bar} XeF_4$$

- XeF_4 reacts violently with water, giving dangerously explosive XeO_3.

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

Xenon hexafluoride

$$\underset{(1:20\ \text{mixture})}{Xe + 3F_2} \xrightarrow[\text{sealed nickel tube}]{573\ K,\ 60\text{-}70\ bar} XeF_6(s)$$

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

- XeF_6 reacts violently with water but slow hydrolysis with atmospheric moisture giving XeO_3.

$$XeF_6 + 6H_2O \longrightarrow XeO_3 + 6HF\ (\text{complete hydrolysis})$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

Xenon-Oxygen Compounds

- Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3

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

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

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

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeOF_2 + 4HF$$

Summary of Stable Compounds of Xe

Compound	Oxidation State of Xe	Hybridisation	No. of lone pair(s) of electrons	Shape
XeF_2	+2	sp^3d	3	Linear
XeF_4	+4	sp^3d^2	2	Square planar
XeF_6	+6	sp^3d^3	1	Distorted pentagonal bipyramidal
$XeOF_2$	+4	sp^3d	2	T-shaped
XeO_2F_2	+6	sp^3d	1	Distorted trigonal bipyramidal
$XeOF_4$	+6	sp^3d^2	1	Square pyramidal
XeO_3	+6	sp^3	1	Pyramidal

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d-Block Elements (Transition Elements)

- **Incomplete n and n-1 shell in atomic or in ionic state – Transition Element**
- *** Zn, Cd & Hg – are d-block nontransition element**

General Electronic Configuration

- $ns^{0-2}\,(n-1)\,d^{1-10}$
- Exceptions $\begin{cases} Cr = 4s^1\ 3d^5 \\ Cu = 4s^1\ 3d^{10} \end{cases}$, $Pd = 5s^0\,4d^{10}$

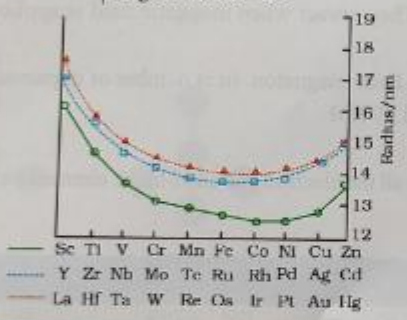
Atomic Radius

- **Left to Right**

  3d series Sc > Ti > V > Cr > Mn > Fe = Co ≃ Ni < Cu < Zn

  The end of each period, there is slight increase in the atomic radii

- **In a Group:** 3d to 4d series increase but 4d and 5d series nearly same due to poor shielding of f electron. **(Lanthanide contraction)**
- $\boxed{3d < 4d \simeq 5d}$
- Eg.: Ti < Zr = Hf | Smallest radius – Ni; Largest radius – La



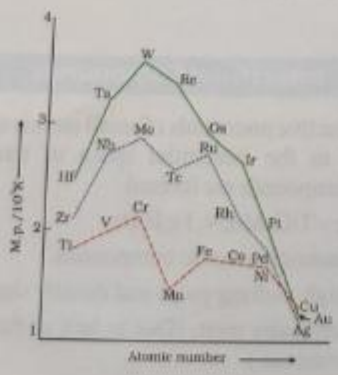
Melting Point : s - block metals < d-block metals

In a series on increasing number of unpaired e^- M.pt. increases upto Cr then decreases.

- Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn

  Cr ↓ Half filled d^5 ∴ weak metallic bond; Zn ↓ fully filled d^{10} ∴ weak metallic bond

- Melting Point | Zn > Cd > Hg; Cu > Ag ≤ Au (data based)



Oxidation State

- Transition element exhibit variable oxidation state due to small energy difference of ns and (n-1) d electrons.
- Sc (+3) and Zn(+2) → only one oxidation state.
- Common oxidation state is +2.
- 3d series → +7 (Mn) (high oxidation state).
- In d – block → [highest oxidation state is +8 (Os, Ru)].
- In carbonyl compound oxidation state of metals is zero due to Synergic effect/ back bonding.
- Their higher oxidation states are more stable in fluorides and oxides.
- Higher oxidation state in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.

Super Note : Most stable oxidation state of Mn is +2 while for Cr, it is + 3.

- In + 3 Oxidation state Mn acts as oxidizing agent, while Cr in +2 acts as reducing agent.

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, (+4), (+5), +6
Mn	$3d^5 4s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^7 4s^2$	+2, +3, (+4)
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

Transition Series

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

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Density

- s-block metals< d-block metals
- **Density in a period**
- Sc < Ti < V < Cr < Mn < Fe < Co ≤ Ni < Cu > Zn
- The density vary inversely with the atomic radii. As we move in a period, the density increases (as the radii decreases). The density increases while descending a group.
- **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

** Greater the number of unpaired of *d*- electron, greater is the number of bonds and therefore greater is the strength of these bonds, so hardness and enthalpy of atomization increases with increase in number of unpaired electron.

Ionisation Potentials

- **First Ionization Potentials:** 1st I.P. values for the first four 3d block elements (Sc, Ti, V and Cr) differ only slightly from one another. The value of 1st I.P. for Zn is considerably higher. This is due to the extra-stability of $3d^{10}$ level which is completely filled in Zn-atom.
- **Second ionisation potentials:** The value of 2nd IP for Cr and Cu are higher than those of their neighbours. This is due to the fact that the electronic configurations of Cr+ and Cu+ ions have extra stable $3d^5$ and $3d^{10}$ levels.There is a sudden fall in the values of ionisation potentials in going from II B (Zn-group elements) to IIIA sub-group

Magnetic Property

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using formula $\mu = \sqrt{n(n+2)}$ Bohr magneton. (n is number of unpaired e^-)

If n is 1, $\mu = 1.73$ BM n is 2, $\mu = 2.84$ BM n is 3, $\mu = 3.87$ BM

n is 4, $\mu = 4.90$ BM n is 5, $\mu = 5.92$ BM

Substance that are not attracted by applied magnetic field are diamagnetic, they have all the electron paired. d-block element and ions having d^0 and d^{10} configuration are diamagnetic.

Colour

- Colour in transition metal ions is associated with d-d transition of unpaired electron from t_{2g} to e_g set of energies.
- This is achieved by absorption of light in the visible spectrum, rest of the light is not longer white.
- Colourless – Sc^{3+}, Ti^{4+}, Zn^{2+} etc
- Coloured – Fe^{3+} yellow, Fe^{2+} green, Cu^{2+} blue, Co^{2+} blue etc.

Alloys

- Solid mixture of metals in a definite ratio.
- (15% difference in metallic radius)
- They are hard and having high melting point.
- Eg. Brass (Cu + Zn)
- Bronze (Cu + Sn) etc.
- Hg when mix with other metals form semisolid amalgam except Fe, Co, Ni, Li

Catalyst

- **Transition metals & their compounds act as catalyst due to -**
  - Variable oxidation state
  - Tendency to form complex
- Eg. V_2O_5 – Contact process
- Fe – Haber process
- Ni – Catalytic hydrogenation

Complex Formation

- Transition elements show tendency to form complex compounds due to. Small size and high effective nuclear charge.
- **Availability** of low lying vacant d–orbitals which can accept lone pair of electrons donated by a ligand.
- Complex forming tendency ∝ charge on metal / size of metal

Interstitial Compounds

- When less reactive nonmetals of small atomic size eg. H, B, N, C, Trapped in the interstitial space of transition metals, interstitial compounds are formed
- For example :- TiC, Mn_4N, Fe_4H etc.
- They are nonstoichiometric compounds.
- They have high melting point and density than pure metals.
- They are chemically inert, (Due to lack of free space for electron movement.)

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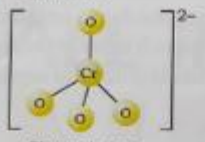
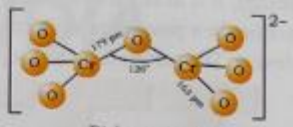
Potassium Dichromate ($K_2Cr_2O_7$)

Properties

- **Physical :**



Chromate ion



Dichromate ion

- Super Note : $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric estimation because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not

- **Chemical :**

$$2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$$

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O \text{ (colour change in basic med.)}$$

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O \text{ (colour change in acidic med.)}$$

- CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium and are interconvertable by **altering the pH** of solution

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

- It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Potassium permanganate ($KMnO_4$)

Preparation

- Commercially it is prepared by fusion of MnO_2 with KOH followed by electrolytic oxidation of manganate.

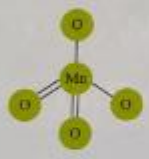
$$MnO_4^{2-}\text{(green)} \longrightarrow MnO_4^-\text{(purple)} + e$$

- Laboratory :

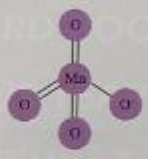
$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^-$$

Properties

(a) Physical :



Tetrahedal manganate (green) ion



Tetrahedal permanganate (purple) ion

(b) Chemical :

- **Effect of heating** $2KMnO_4 \xrightarrow{751K} K_2MnO_4 + MnO_2 + O_2$
- **In alkaline & neutral medium :**

$$2KMnO_4 + \underset{\text{(conc.)}}{2KOH} \longrightarrow \underset{\text{manganate}}{2K_2MnO_4} + H_2O + [O]$$

If solution is dilute

$$2K_2MnO_4 + 2H_2O \longrightarrow 2MNO_2 + \underset{\text{(Brown ppt)}}{4KOH} + 2[O]$$

- This type of behaviour is shown by $KMnO_4$ itself in neutral medium

$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$$

- Inn alkaline or neutral medium $KMnO_4$ shows **oxidising properties.**
- **In acidic medium (in presence of dilute H_2SO_4) :**

$$MnO_4^- + \underset{\text{Green}}{5Fe^{2+}} + 8H^+ \longrightarrow \underset{\text{Yellow}}{5Fe^{3+}} + Mn^{2+} + 4H_2O$$

$$2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$$

Some Important Reagents and Catalyst

- Ziegler Natta catalyst : $TiCl_4 + (C_2H_5)_3Al$
- Lindlar's catalyst : Pd / $BaSO_4$
- Wilkinson's catalyst : $(Ph_3P)_3RhCl$
- Adam's catalyst : Pt / PtO
- Brown's catalyst or P-2 catalyst: Nickel boride

- Baeyer's reagent Dilute alkaline $KMnO_4$ used to test the presence of unsaturation.
- Tollen's reagent Ammoniacal solution of $AgNO_3$, i.e., $[Ag(NH_3)_2]OH$. used to test the aldehyde group.
- Nessler's reagent Alkaline solution of K_2HgI_4 (g) and NH_3: .
- Benedict's solution $CuSO_4$ solution + sodium citrate + Na_2CO_3, used to test the aldehyde group
- Lucas reagent HCl (cone.) + anhydrous $ZnCl_2$, used to distinguish between 1°, 2° and 3° alcohols.

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f-Block Element

Inner Transition Elements

The f-block elements are known as inner transition elements because they involve the filling for inner sub-shells (4f or 5f)

(a) Lanthanides

It consists of elements that follows lanthanum and involve the filling of 4 subshell

Electronic Configuration : [Xe] $4f^{0+1}$ $5d^{0}6s^{2}$ or [Xe] $4f^{n}$ $5d^{1}$ $6s^{2}$

Oxidation State: +3, +2 and +4.

- **Colouration**

Many of the lanthanides ions are coloured in solid state as well as in solutions. The colour is due to the f-f transition since they have partly filled f-orbitals.

- **Lanthanide Contraction**

The steady decrease in the size of lanthanide ions (M^{3+}) with the increase in atomic no. is called lanthanide contraction.

- **Causes**

As we move from left to right in a lanthanide series, the atomic no. increases and for every proton in the nucleus the extra electron goes to 4f orbital. The 4f orbital is too diffused to shield the nucleus effectively, thus there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Consequently , the attraction of the nucleus for the electrons in the outermost shell increases with the increase of atomic number, thus size decreases.

- **Consequence of Lanthanide Contraction**

Separation of Lanthanides: Due to the similar sizes of the lanthanides, it is difficult to separate them but due to lanthanide contraction their properties slightly vary (such as ability to form complexes). The variation in the properties is utilized to separate them.

- **Basic Strength of Hydroxide**

Due to the lanthanide contraction, size of M^{3+} ions decreases and there is increase in covalent character in M–OH and hence basic character decreases.

- **Similarity of second and third transition series**

The atomic radii of second row transition elements are almost similar to those of the third row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to the lanthanide contraction.

(b) Actinides

It consists of elements that follow Actinium and involve the filling of 5f subshell. These are radioactive substances.

$7s^{2}$ is stable configuration for actinides.

Show +3, +4, +5, +6 & +7 oxidation state.

Difference between Lanthanides and Actinides

Lanthanides	Actinides
1. In lanthanide the filling of 4f orbitals take place	1. In actinide the filling of 5f orbitals take place
2. This series includes atomic number 57 to 71.	2. This series includes atomic number 89 to 103.
3. These elements are non-radioactive except promethium.	3. All the elements of this series are radioactive.
4. Binding energy of 4f orbitals is higher.	4. Binding energy of 5f orbitals is higher.
5. Besides +3 oxidation number it also shows + 2 and +4 oxidation state in few compounds.	5. Besides +3 oxidation number it also shows +4, +5 and +7 oxidation state in few compounds.
6. Lanthanides have a bright and silvery appearance.	6. Most of the actinides ions are deeply coloured.
7. Lanthanides have less tandency towards complex formation.	7. Actinides have stronger tandency towards complex formation.
8. Oxides and hydroxides of lanthanides are less basic.	8. Oxides and hydroxides of actinides are more basic.

Mischmetall

- It is a well-known alloy which consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al.
- A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.

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Chapter – 6 Coordination Compounds

ADDITION OF COMPOUNDS
(Two or more simple salts are mixed)

DOUBLE SALTS
Lose their identity in solutions
$FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's Salt)

Coordination Compounds

The concept of co-ordination compounds arises from the complex formation tendency of transition elements.

Retain their identity (i.e. doesn't lose their identity) in solution
$K_4[Fe(CN)_6]$, $K[Ag(CN)_2]$

1

Central Metal Atom

Accept l.p./πe^- from ligands to form co-ordinate πe^- bond.

Oxidation Number

$K_4[\underline{Fe}(CN)_6]$
$+4 + x + 6(-1) = 0$
$+4 + x - 6 = 0$
$x = +2$

Co-ordination No.

Coordination no. = No. of ligand × denticity

Ligand

The atom/ group of atom which donates *l.P.* to C.M.A. in order to form co-ordinate bond.

On the basis of charge
- **Neutral** (Ex. H_2O, NH_3)
- **Anionic** (Ex. I^-, CN^-, OH^-)
- **Cationic** (Ex. NO^+, $NH_2-\overset{\oplus}{N}H_3$)

On the basis of denticity
- **Monodentate** (Ex. F^-, NH_3)
- **Bidentate** (Ex. DMG, Gly)
- **Polydentate** (Ex. EDTA)
- **Flexidentate** (Ex. EDTA] It can be hexadentate, pentadentate
- **Ambidentate** (Ex. CN^-, NO_2^-)

On the basis of l.p. donation/accepting e⁻s
- **Classical** ligands with *l.p.*
- **Non-classical**
  - **πe^- Donating ligand**
  - **π acid ligand**

2 Werner's Theory

It gives an idea about the structures of complex compounds.

Postulates of Werner's Theory

- A central metal atom is bonded to ligands through [I] primary valence (1° valence) [II] secondary valence (2° valence).
- Attempted to explain reactions & structures of coordination compounds.
- Primary valence (ionisable) = oxidation no.
- Secondary valence (non ionisable) = coordination no. of CMA.
- For eg: $CoCl_3.6NH_3$. 2° valence, 1° valence
- It gives 3 mol AgCl on adding excess $AgNO_3$ solution in cold.

Limitation of Werner's Theory

- **Werner's theory could not explain.**
- The complex forming property of only certain elements.
- Directional characteristic of bonds.
- Characteristic magnetic and optical properties of complex

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3 Valence Bond Theory (V.B.T.)

Postulates of V.B.T.

- The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number which hybridise together.
- The vacant hybrid ortibals form coordinate bond with ligands. These bonds are of equal strength and directional in nature.

Hybridization and geometry of complexes

C.N.	Type of hybridization	Geometry of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

Limitation of V.B.T.

- It could not explain why the pairing of electron occurs in the presence of strong ligands.
- It could not explain the color and electronic spectra of complexes.
- It could not explain the structure of $[Cu(NH_3)_4]^{2+}$ ion.
- It does not distinguish between weak and strong ligands.

4 Crystal Field Theory (C.F.T.)

According to CFT, under the influence of ligand field, degeneracy of d-orbitals is destroyed and they split into two or more energy levels.

The extent of splitting depends upon the strength of ligand.

Degenerated Orbitals - When all orbitals are of same energy level.

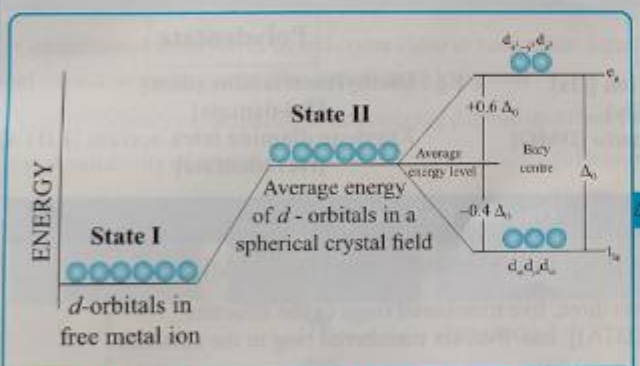
Explain

Spectrochemical Series

Arrangement of ligands in the order of increasing field strength.

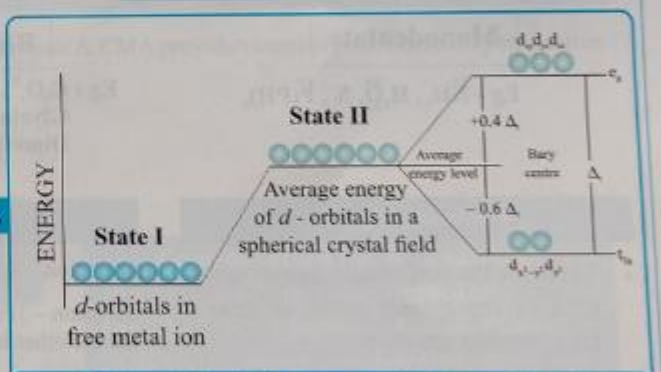
$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$.

* C and N donar acts as SFL except N_3^-.
* If $\Delta_o < P$, then complex is high spin. (no pairing)
* If $\Delta_o > p$, then complex is low spin. (pairing occur)



Splitting of *d*-orbitals in an octahedral crystal field

$\Delta_t = (4/9)\Delta_o$



Splitting of *d*-orbitals in an tetrahedral crystal field

Isomerism

Structural isomerism
- Ionisation isomerism
- Hydrate or solvate isomerism
- Coordination isomerism
- Linkage isomerism

Stereoisomerism
- Geometrical isomerism
- Optical isomerism

5 Jahn-Teller Distortion

- Only for octahedral complexes.
- If the d-orbitals are asymmetrically filled, they will repel some ligands in the complex more than the others. This results in distortion of octahedral complexes.
- Distortion caused by asymmetric filled of t_{2g} is too small to measure.
- d^4 (high spin), d^7 (low spin) and d^9 configuration show Jahn Teller distortion.

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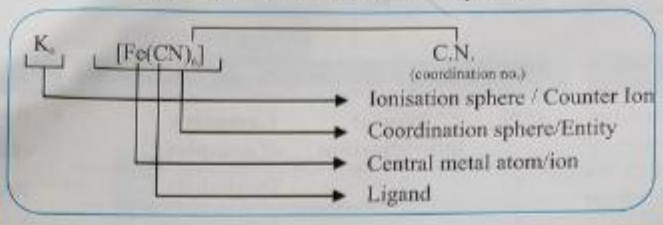
Complex Compound

Representation of coordination compound



Ligand

Other type

Ambidentate

They can change there donar atom but not denticity.

Eg : SCN^-, NO_2^-, CN^-, NCO^-

Flexidentate

Variable Denticity.

Eg : EDTA, SO_4^{2-}

π acid ligand

Eg : CO

O.T.B. of charge

Cation Ligand

Eg : $N = O^+$, NH_2-NH_3^+

Natural Ligand

Eg : H_2O, NH_3, Pyridine, CO, NO

Anionic Ligand

Eg : X^-, OH^-, NH_2^-

O.T.B. of Denticity

Monodentate

Eg - $\ddot{N}H_3$, $H_2\ddot{\underset{..}{O}}$, X^-, $\ddot{P}(PH)_3$

Bidentate

Eg : $C_2O_4^{2-}$, [Oxalate ion [Ox]
Glycinate ion (Gly)
Dimethylglyoximato [DMG]

Polydentate

Eg : Diethylenetriamine (dien) [Tri-dentate]
Ethylene diamine tetra acetato [EDTA] [Hexadentate]

Chelating Ligand

- These are the polydentate ligands which bind to the central metal to form a puckered ring structure.
- Chelation leads to extra stability.

For Eg : All bidentate or polydentate ligand

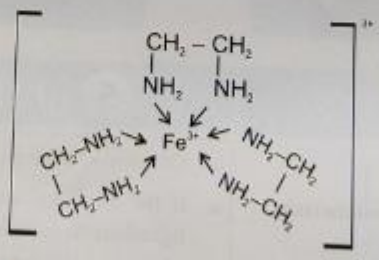
Except : Hydrazine (NH_2NH_2)

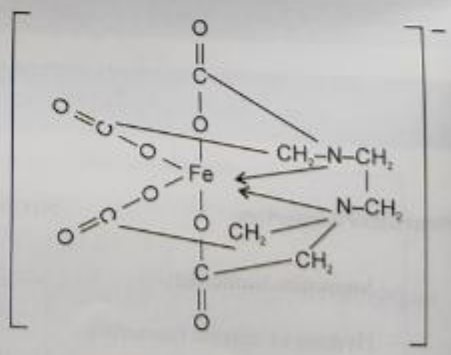
Due to formation of three membered ring angle strain is there.

Question for Concept

Question – Explain why $[Fe(en)_3]^{3+}$ is less stable than $[Fe(EDTA)]^-$?

Solution – $[Fe(en)_3]^{3+}$ has three, five membered rings in the structure. On the other hand $[Fe(EDTA)]^-$ has five, six membered ring in the structure.





EFFECTIVE ATOMIC NUMBER RULE GIVEN BY SIDGWICK :

Effective Atomic Number (EAN) = No. of electron present on the metal atom/ion + No. of electrons donated by ligands to it.

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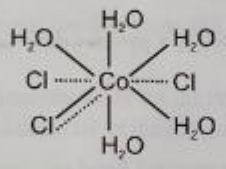
Bonding

Werner Theory

Metal in a complex shows two type of valences – Primary & Secondary

Primary Valency	Secondary Valency
It is oxidation no. of metal	It is coordination number
It is variable	It is non variable
Satisfied by anions (present in coordination or ionisable sphere).	Satisfied by ligands (present in coordination sphere)
Ionisable.	Non - ionisable
Ionic : nondirectional	Directional : Decide geometry of complex ion.
Represented by dotted line in Werner structure	Represented by solid lines in Werner Structure

$CoCl_3.5H_2O$, $[CoCl(H_2O)_5]Cl_2$



3 dotted lines shows – Primary Valence
6 solid line shows – Secondary Valence

Valence Bond Theory

Central metal atom/ion & ligand come close to each other, ligand donate lone pair & CMA provide vacant orbital. There is hybridization of atomic orbitals provided by central atom to ligands.

Type of Orbitals participating in intermixing depend upon two factors.

(a) Availability of orbitals (b) Nature of ligand

Coordination Number of metal	Type of hybridisation	Shape of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planer
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral (High Spin)
6	d^2sp^3	Octahedral (Low Spin)

Co-ordination no. 4 - Example

$[NiCl_4]^{2-}$ sp^3 ----- Tetrahedral
$[Ni(CN)_4]^{2-}$ dsp^2 ------- Square Planar
$[Ni(CO)_4]$ sp^3 ----- Tetrahedral
$[Zn(NH_3)_4]^{2+}$ sp^3 ----- Tetrahedral
$[Cu(NH_3)_4]^{2+}$ dsp^2 ----- Square Planar

Coordination No. 6 : Example

$[Fe(CN)_6]^{4-}$ d^2sp^3
$[Fe(CN)_6]^{3-}$ d^2sp^3
$[Co(NH_3)_6]^{3+}$ d^2sp^3
$[Ni(H_2O)_6]^{2+}$ sp^3d^2

- If the complex is formed by the use of inner d-orbitals for hybridization (d^2sp^3), it is called inner orbital complex.
- If the complex is formed by the use of outer d-orbital for hybridization (sp^3d^2), it is called an outer orbital compelx. Such complex is also called as high spin complex e.g. $[CoF_6]^{3-}$.
- Unpaired electron present ⇒ high spin complex.
- Unpaired electron absent ⇒ low spin complex.

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Magnetic Moment ⇒ $\mu = \sqrt{n(n+2)}$ (n = no. of unpaired electron)

Limitation of V.B.T.

- It couldn't explain why pairing occurs in S.F.L. and no pairing in W.F.L.
- It couldn't explain color of compound.
- It doesn't distinguish between strong and weak ligands.

Crystal Field Theory

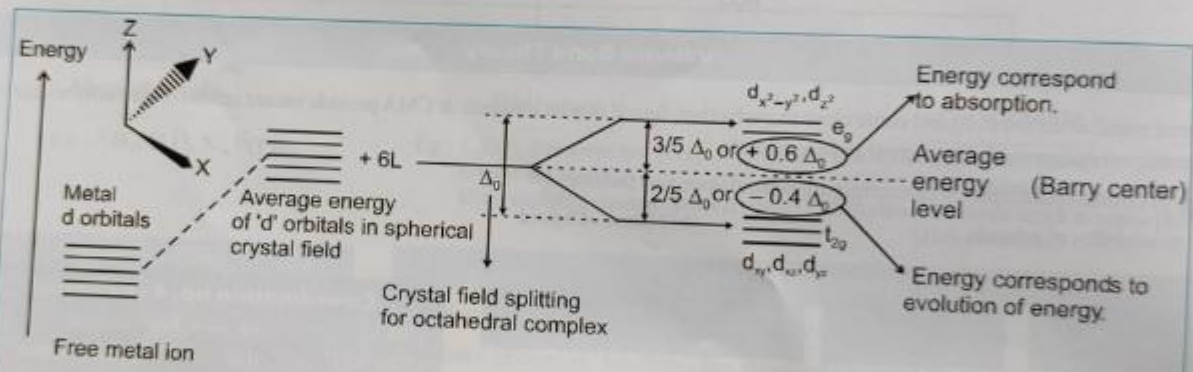
- The splitting of five degenerate d-orbitals of the metal into different sets of orbitals having different energies in the presence of electrostatic field of ligands is called crystal field splitting.

  e_g set –: $dx^2 - y^2$, dz^2 $\qquad$ t_{2g} set –: dxy, dyz, dxz
- Crystal field splitting energy, (Δ_0 for octahedral structure and $\Delta_t = 4/9\Delta_0$ tetrahedral structure) is the difference between the various sets of energy level formed by crystal field splitting.
- Weak field ligands which cause a small degree of crystal field splitting

  e.g. I^-, Br^-, Cl^-, F^-, OH^-, $C_2O_4^{2-}$, H_2O etc.
- Strong field ligands are those ligands which cause a high degree of splitting e.g. CO, CN, NO. etc.
- Spectrochemical series

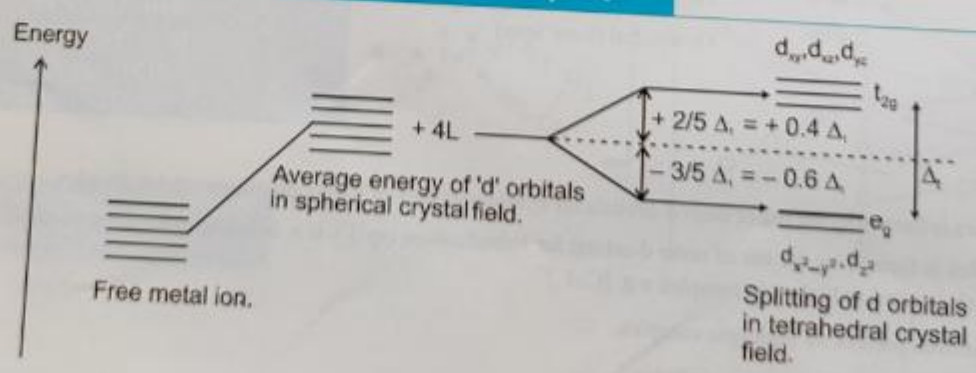
  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < N_3^- < F^- < OH^- < ox^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 <$ py–en < dipy < o-phen < $N_2^- < CN^- < CO$.

  (O) and N donar act as SFL except N_3^-)



Crystal field splitting in octahedral complex.

$$\Delta_t = (4/9)\Delta_0$$



CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COMPLEX.

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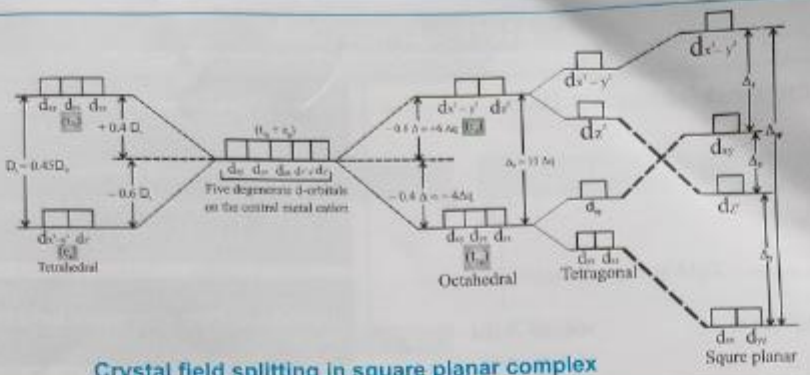


Crystal field splitting in square planar complex

$\Delta_{sp} = 1.3\ \Delta_o$.

COLOUR IN COORDINATION COMPOUNDS :

According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths.

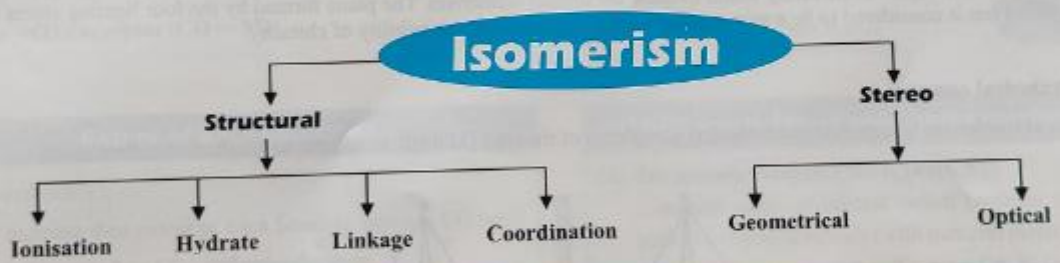
Limitations of crystal field theory

(1) It considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals (such as s, p_x, p_y and p_z orbitals).

(2) It is unable to account satisfactorily for the relative strengths of ligands. For example it gives no explanation as to why H_2O is a stronger ligand than OH^- in the spectrochemical series.

(3) According to this theory, the bond between the metal and ligands are purely ionic. It gives no account on the partly covalent nature of the metal ligand bonds.

(4) The CFT cannot account for the π-bonding in complexes.



Structural

(a) Ionisation isomerism

same molecular formula but gives different ionisable species. (only anionic)

Eg: $Co(NH_3)_5BrSO_4$ → $[Co(NH_3)_5Br]SO_4$; $[Co(NH_3)_5SO_4]Br$

(b) Linkage isomerism

Ligand should be ambidentate

Eg:

(NO_2^-, CSN^-, CN^-, CNO^- etc)

$[Co(ONO)(NH_3)_5]\ Cl_2$ & $[Co(NO_2)(NH_3)_5]\ Cl_2$

(c) Hydrate/solvent isomerism

same molecular formula but different number of water molecules associated with central metal.

Eg: $CrCl_3.6H_2O$ → (a) $[Cr(H_2O)_6]Cl_3$; (b) $[Cr(H_2O)_5Cl]Cl_2.H_2O$; (b) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

(d) Coordination isomerism

Isomers having both anion and cation as complex entity. Can inter change position of ligands as well as metal.

$[Co(NH_3)_6][Cr(SCN)_6]$ and $[Cr(NH_3)_6(SCN)_3][Co(NH_3)_2(SCN)_4]$

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Stereoisomerism

Geometrical Isomerism (GI)

- CN = 4
  - **Tetrahedral** ⇒ cannot show G.I. because all 4 position are equivalent in tetrahedral geometry
  - **Square planar** ⇒
    - Ma_4 – NO GI
    - Ma_3b – NO GI
    - Ma_2b_2 – 2GI (cis & trans)
    - Ma_2bc – 2GI (cis & trans)
    - Mabcd – 3 GI
- CN = 6
  - Mabcdef – 15 GI
  - Ma_2bcde – 9 GI
  - Ma_2b_2cd – 6 GI
  - $Ma_2b_2c_2$ – 5 GI
  - Ma_2bcd – 4 G
  - Ma_2b_2c – 3 GI
  - Ma_2b_3 – 2(Fac-Mer)
  - Ma_2bc – 2 (cis-trans)
  - Ma_2b_2 – 2(cis-trans)
  - Ma_2b – NO GI
  - Ma_6 – NO GI

Square Planar complex with symmetrical bidentate ligand Eg. No GI

Octahedral $[M(AA)a_4]$ and $[M(AA)_3]$ Type of complex can not exhibit G.I.

$[M(AA)_2a_2]$ type of complex have two GI (Cis & trans)

* $[M(AA)_2a_2]$ type of complex gives three stereo isomer:
  (1) cis (2) trans (3) mirror image of cis

Compounds containing bidentate ligand and unidentate ligands

(I) $M(AA)a_2b$ – Two geometrical isomers are possible

(II) $M(AA)a_2b_2$ – Three geometrical isomers are possible.

(iii) $M(AA)_2a_2$ – Two geometrical isomers are possible.

Optical Isomerism

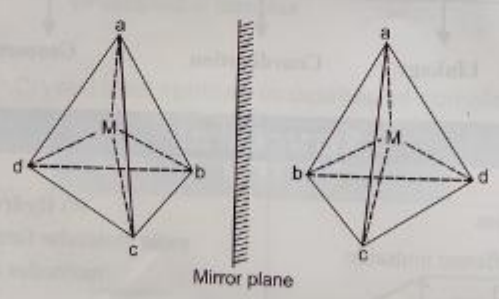
A coordination compound which can rotate the plane of polarized light is set to be optically active.

(I) Square planar complex

Square planar complexes are rarely found to show the optical isomerism. The plane formed by the four ligating atoms and the metal ion is considered to be a mirror plane and thus prevents the possibility of chirality.

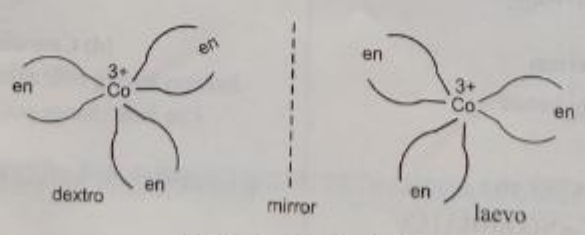
(II) Tetrahedral complex

Optical isomerism is expected in tetrahedral complexes of the type [Mabcd] analogous to tetrahedral carbon atom.



(III) Octahedral complex

Optical isomerism is common in octahedral complexes involving bidentate ligands. For example, $[Co(en)_3]^{3+}$ has d and *l* forms as given below.



d and *l* of $[Co(en)_3]^{3+}$

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Organometallic Compounds

Metal Carbonyl

Metal with CO as a ligand

Monomeric

Contain only one metal atom per molecule.

Eg:

$[Ni(CO)_4]$, $[Fe(CO)_5]$

Polymeric

Contain two or more than two metal atoms per molecule. They have Metal-Metal bond.

Eg:

$Mn_2(CO)_{10}$, $CO_2(CO)_8$

Sigma (σ) bonded

Eg:

1) Grigard Reagent R-MgX
2) $(CH_3)_4Sn$
3) $(C_2H_5)_4Pb$
4) $Al_2(CH_3)_6$
5) $Al_2(C_2H_5)_6$

pie (π) bonded

Metal with alkenes, alkynes, Benzene ring and other rings.

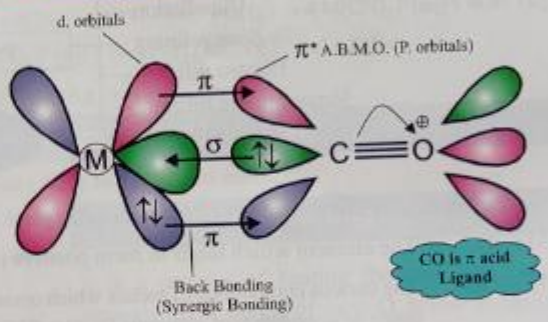
Eg:

1) Zeise's Salt
   $K[PtCl_3(\eta^2\text{-}C_2H_4)]$
2) Ferroscene
   $[Fe(\eta^5\text{-}C_5H_5)_2]$
3) Bis(Benzene) chromium
   $[Cr(\eta^6\text{-}C_6H_6)_2]$

Back Bonding

- M-C π bond - Donation of l.p. of e^- from metal to vacant * A.B.M.O. of CO.

  CO acts as a
- (1) σ donar (CO → M)
- (2) π acceptor (CO ← M)



Extent of Back Bonding

No of d-orbitals'e^-.

- If e^- increase then extent of back bonding increase CO bond length decrease then CO bond order decrease.

If No. of d orbitals e^- are same then Back Bonding depends on charge of Metal ion.

+Ve charge

Extent of B.B. decrease because metal ion will not give e^-

–Ve charge

Extent of B.B. increase because metal ion will give e^- easily.

Due to back bonding the carbon oxygen bond length is increase by 0.01Å - 0.1 Å.

IUPAC nomenclature of complex compounds

(A) For anionic complex (like $K_4[Fe(CN)_6]$

Common name of normal cation (without numeral prefix) + Name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + Ox. St (in roman number.)

Eg. Potassiumhexacyanoferrate (II)

(B) For cationic complex like $[Cu(NH_3)_4]SO_4$

Name of ligands (with numeral prefix) + common name of CMI + Ox. St (In roman number) + Name of anion (without numeral prefix)

Eg. Tetraammine copper (II) sulphate.

(C) For neutral complex like $[Fe(CO)_5]$

Name of ligands (with numeral prefix) + common name of CMI + Ox. St.

(in roman number)

Eg. Pentacarbonyliron

(D) Rule same just apply alphabatical order when write the name of ligands

Eg. $[Pt(NH_3)_2Cl_2]$

Diamminedichloroplatinum (II)

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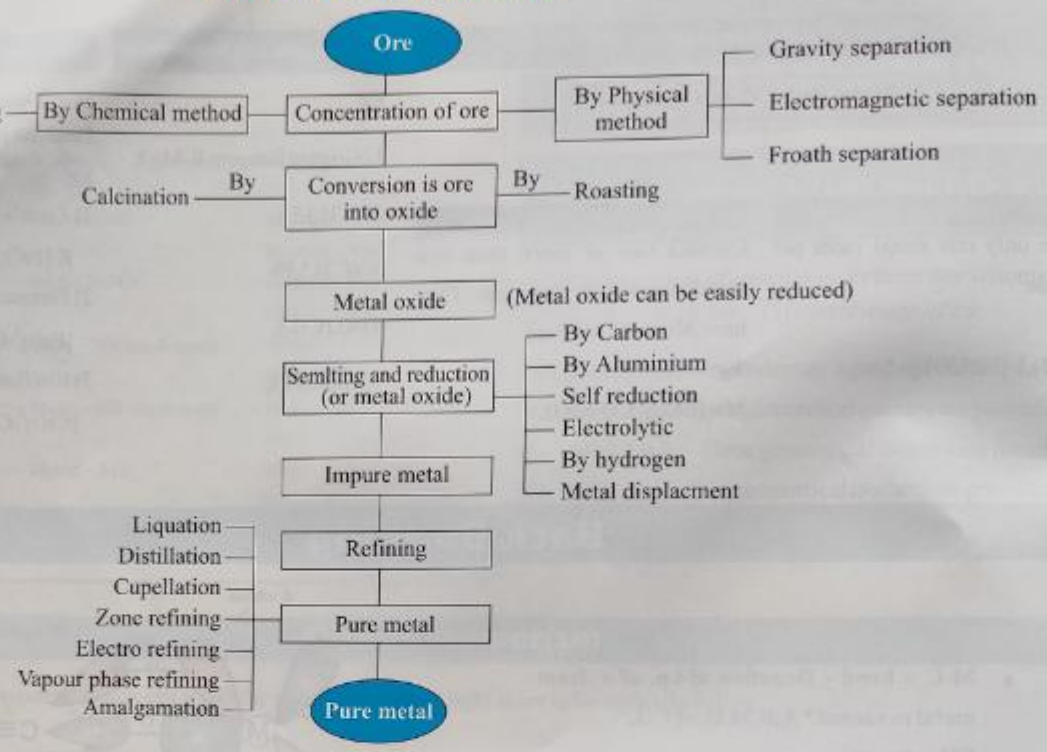
GENERAL METALLURGY



Super Note : The ultimate target of every metallurgical step is to increase the concentration of metal.

Metal : The element which tends to form positive ion is called a metal.

Minerals : The various compounds of metals which occur in the earth's crust and are obtained by mining are called minerals. In earth crust order of abundance of elements is. O > Si > Al > Fe

A mineral may be single compound or a mixture.

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

Type of Ores

(I) **Combined Ore :** Metals placed above H in electrochemical series are generally reactive i.e. why they generally found in combined state.

(a) **Halide ore / Sulphate ore / Oxy ore :** Metals are highly reactive (Li → Mg)

(b) **Oxide ore :** Reactive metal (Al to Sn)

(c) **Sulphide ore :** Metal placed near H or below H. (Pb, Hg, Cu, Ag)

(II) **Native Ore :** Metal placed below H in electrochemical series are generally found in native state. (Ag, Au, Cu, Pt etc.)

Gangue or matrix : The undesirable impurities present in an ore are called gangue.

Type of Metallurgy

Pyrometallurgy	Hydrometallurgy	Electro metallurgy
Temp. is involved	Solution is involved	Electricity involved
For heavy metals	According to E.C.S.	IA, IIA, Al
Fe, Zn, Cu, Hg, Sn etc	For metals placed below H	
	Cu, Ag, Au	

Metallurgical Process

1. **Mining** : Ore obtain in big lumps (less reactive
2. **Crushing/grinding/pulverization:** Big lumps convert into powder (more reactive)
3. **Concentration**: To remove matrix/ gangue (major impurities) from ore to increase the concentration of ore particle in ore sample.

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Concentration

Physical Process

(a) Gravity separation/ Hydraulic washing/ Levigation

- Based on difference in the densities of the gangue and ore particles.
- Generally use the concentration of oxide carbonate ores and native ores

(b) Electromagnetic Separation

- Based on differences in magnetic properties of the ore components
- Chromite ore($FeO.Cr_2O_3$) is separated from non–magnetic silicious impurities and Cassiterite ore(SnO_2) is separated from magnetic Wolframite ($FeWO_4 + MnWO_4$).

(c) Froath floatation

- Based on the fact that gangue and ore particles have different degree of wettability with water and pine oil;
- The gangue particles are preferentially wetted by water while the ore particles are wetted by oil.
- Generally used for concentration of Sulphide ore.
- Frother – Pine oil, Floating agent – Sodium ethyl xanthate depressant - NaCN, Froth stabilisers – cresol, aniline etc.

Chemical Process

Leaching

- Leaching is often used if the ore is soluble in some suitable solvent
- E.g. acids, bases and suitable chemical reagents.
- Baeyer's process, Hall's process and Cyanide process are example of leaching

(a) Alumina from Bauxite : $Al_2O_3.2H_2O + Fe_2O_3$ (Major impurity)

(i) Baeyer's process : NaOH is used.

$$Al_2O_3 + NaOH \rightarrow NaAlO_2 \xrightarrow[H_2O]{excess} Al(OH)_3 + NaOH$$

$$FeO\ (Basic) + NaOH \rightarrow insoluble$$

(ii) Hall's process : Na_2CO_3 is used.

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 \xrightarrow[CO_2]{HOH} Al(OH)_3 + Na_2CO_3$$

(b) Cyanide Process

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)$$

$$2[M(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s)$$

where (M = Ag or Au)

Extraction of crude metal from concentration ore

Conversion to Oxide (Oxides are easy to reduce to metal)

Calcination

In the absence of air

For carbonate/ Hydroxide/ Oxide ore

i) The carbonate ore gets decomposed to form the oxide of the metal

$$MCO_3 \rightarrow MO + CO_2 \uparrow$$

ii) Water of crystallisation present in the hydrated oxide ore gets lost as moisture $M(OH)_2 \rightarrow MO + H_2O \uparrow$

iii) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed

Roasting

It is a process of heating the concentrated ore strongly in the excess of air or O_2 below its melting point.

For sulphides ore

Impurity of S, P, As, SO_2 to be removed

$$MS + O_2 \rightarrow MO + SO_2 \uparrow$$

Reduction of Oxides to Metal

I. Chemical reduction

(a) by C (smelting)

$$MO + C + Flux \rightarrow M + CO_2 \uparrow + Slag$$

(b) by Al

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$

$$Mn_2O_3 + 2Al \rightarrow Al_2O_3 + 2Mn$$

Flux - Substance to convert non-fusible impurities to fusible one.

Flux

- Acidic Flux → Remove basic impurities → Non metallic oxide (SiO_2)
- Basic Flux → Remove acidic impurities → Metallic oxide (CaO)

Imp. Point – At high temp. C is reducing agent
– At low temp. CO is reducing agent

II. Self reduction

Compounds of certain metals are reduced to metal without using any additional reducing agent. ores of Cu, Pb, Hg etc

Their sulphide ores are partially roasted to give some oxide. This oxide is now reduced to the metal by the remaining sulphide ore at elevated temperatures in the absence of air. The process is known as self reduction.

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

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

III. Metal displacement reduction

Metal placed below H. In E.C.S.

$\boxed{Ag, Au,}$ Cu

(i) Cyano complex or Mac Arthur process

$$4Au(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

(ii) Reduction to free metal

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

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au \downarrow$$

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IV. Electrolytic Reduction

In aqueous solution : Electrolysis can be carried out conveniently and cheaply in aqueous solution that the products do not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulphates.

In other solvents : Electrolysis can be carried out in solvents other than water.
Fluorine reacts violently with water and it is produced by electrolysis of KHF_2 dissolved in anhydrous HF.

In fused melts : Elements that react with water are often extracted from fused melts of their ionic salts.
Aluminum is obtained by electrolysis of a fused mixture of Al_2O_3 and cryolite $Na_3[AlF_6]$.
Both sodium and chlorine are obtained from the electrolysis of fused NaCl.

Hall heroult process :

This process is used for extraction of Al from alumina. The extraction of Al from Al_2O_3 is quite difficult because

(i) Fusion temperature of Alumina is quite high (2050°C). Even more than boilling point of Al (1150°C).

(ii) It is a bad conductor of electricity. To overcome these difficulties we mix some amount of neutral flux $[Na_3AlF_6 + CaF_2]$. Neutral flux provides free ions to the solution which decreases the fusion temperature of Alumina from 2050°C to 950°C.

(i) **From cryolite :** $AlF_3 \longrightarrow Al^{+3} + 3F^-$

At cathode : $Al^{+3} + 3e^- \rightarrow Al$ (reduction)

At anode : $2F^- - 3e^- \rightarrow \frac{3}{2}F_2$

F_2 reacts with Al_2O_3 $3F_2 + Al_2O_3 \rightarrow 2AlF_3 + \frac{3}{2}O_2$

So at anode O_2 gas is liberated which on reaction with graphite anode convert into CO_2 & destroy the anode $C + O_2 \longrightarrow CO_2 \uparrow$

(ii) **From Al_2O_3**

At cathode : $Al^{+3} + 3e^- \rightarrow Al$ (reduction)

At anode : $C(s) + 2O^{-2} \rightarrow CO_2(g) + 4e^-$

The main drawback of this process it that anode should be changed frequently.

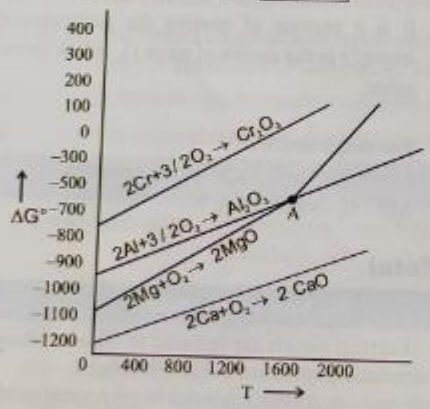
Thermodynamics Of Extraction : Ellingham Diagram of A Metal

It is explanation of the feasibility of pyrometallurgical process by using gibbs equation $\boxed{\Delta G = \Delta H - T\Delta S}$

If $\Delta G = -$ ve Process is stable or Spontaneous

$\Delta G = +$ ve or Less – ve then process is Unstable or non-Spontaneous

When pyrometallurgical process contains more than one type of reaction then stability of reaction can be explain by Ellingham diagram. Ellingham diagram contains plot $\boxed{\Delta G \text{ vs } T}$.



$\Delta G = -Ve$

Ca + | MgO | Al_2O_3 | Cr_2O_3 | $\longrightarrow$ CaO + | Mg | Al | Cr |

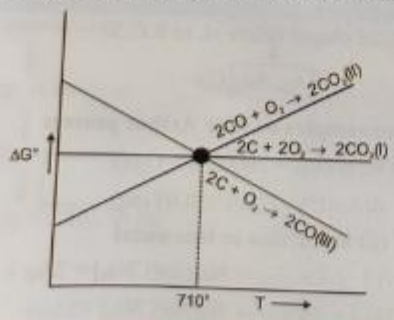
$\Delta G = +Ve$

Cr + | CaO | MgO | Al_2O_3 | $\longrightarrow$ Cr_2O_3 + | Al | Mg | Ca |

According to Ellingham diagram, the metal below can reduce the oxide of metal above it in the curve, as affinity of metal below for oxygen is more.

Example Al Metal can reduce Cr_2O_3 but can not reduce MgO & CaO.

At very high T after 'A' Point Al' metal can reduce MgO because Formation of MgO contains less – ve DG.



Super Note :

According to diagram at high T(710° OR above 710°C) Oxidation of C contains more –ve ΔG so at high T 'C' is good Reducing agent.

At Low T (below 710°C) Oxidation of CO contains more –ve ΔG so at Low T, CO is good Reducing agent.

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Refining : To obtain metal (99.98%)

(I) Physical Process

- (a) Liquation → Low M.P. metal Sn, Pb, As, Sb
- (b) Distillation → Low M.P. metal → Volatile metal (Zn, Cd, Hg)
- (c) Zone refining/ Fractional crystallization → Ultrapure metal → Volatile metal (Ge, Ga, Si)

(II) Chemical Process

- (a) Cupellation → For Ag having the imp. of Pb → Impure metal + O_2 → Pure metal + O_2 → x ; Imp + O_2 → volatile oxide
- (b) Polling → Cu, Pb having imp. of their own oxide → $CuO + C \rightarrow Cu + CO\uparrow$, $CuO + H_2 \rightarrow Cu + H_2O\uparrow$
- (c) Bessemerization → For Cu, Pb

(III) Thermal decomposition

- Van. Arkel - process For Ti, Zr, Hf → Impure metal $Ti + 2I_2 \rightarrow TiI_4 \rightarrow Ti + 2I_2$ (Volatile; pure metal)
  - Impurity + I_2 → No reaction
- Monds – Process Ni, Pd → $Ni + 4CO \xrightarrow{\Delta} Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO$ (Impure metal; Volatile carbonyl; Pure metal)
  - Impurity + CO → No reaction

IV. Electrolytic refining

- Anode – made up of impure metal
- Cathode – made up of pure metal (pure metal deposit)
- Impurity deposited below anode as anode mud

Important Ores

Oxide Ore	$Al_2O_3.2H_2O$ Fe_2O_3 ZnO (Philosopher's Wool) SnO_2	Bauxite Haematite Zincite Cassiterite (Tin stone)
CarbonatOre	$CaCO_3$ $MgCO_3.CaCO_3$ $ZnCO_3$ (Smithosonite) $PbCO_3$ $FeCO_3$ $CuCO_3 . Cu(OH)_2$ $2CuCO_3 .Cu(OH)_2$	Lime stone Dolomite Calamine Cerrusite Siderite Malachite Azurite
SulphateOre	$MgSO_4.7H_2O$	Epsomite Or Epsom salt
SulphideOre	ZnS HgS PbS FeS_2 $CuFeS_2$, CuS.FeS Cu_2S (Copper glance)	Zinc Blende (Sphalerite) Cinnabar Galena Iron pyrites (Fool's gold) Copper pyrites (Chalcopyrities) Chalcocite
Halide Ore	AgCl CaF_2 $AlF_3.3NaF$ $KCl.MgCl_2.6H_2O$	Horn Silver Flourspar Cryolite Carnelite

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Chapter – 8 Hydrogen

General Introduction

- First lighter element (non-metal) in the periodic table.
- It exists as diatomic gas (H_2) at STP.
- Most abundant element in the humen body as it is the main constitute of water.
- It resembles both alkali metal and halogen.
- It is the only element that exist without neutrons.

Isotopes of Hydrogen

- Hydrogen (Protium) : $_1H^1$ or H ($e=1, p=1, n=0$)
- Deuterium (Heavy hydrogen) : $_1H^2$ or D ($e=1, p=1, n=1$)
- Tritium : $_1H^3$ or T ($e=1, p=1, n=2$)
- The three isotopes of hydrogen have almost same chemical properties but differ in their rates of reactions mainly due to their different enthalpy of bond dissociation.

Preparation of Hydrogen

(A) Laboratory preparation of dihydrogen :

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \uparrow$$

$$Zn + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2 \uparrow$$

(B) Commercial preparation of dihydrogen :

$$2H_2O_{(l)} \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$$

- **By electrolysis of brine solution :**

$$2Na^+_{(aq)} + 2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2Na^+_{(aq)} + 2OH^-_{(aq)}$$

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270K} nCO + (2n+1)H_2$$

- **Coal gasification :**

$$C_{(s)} + H_2O_{(g)} \xrightarrow{1270K} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas or Syn gas}}$$

The production of H_2 can be increased by **water-gas shift reaction.**

$$CO_{(g)} + H_2O_{(g)} \xrightarrow[\text{Iron chromate catalyst}]{673\ K} CO_{2(g)} + H_{2(g)}$$

High purity (> 99.95%) dihydrogen is obtained by electrolysis of warm aqueous solution of $Ba(OH)_2$ between Ni electrodes.

- **Note :** Dihydrogen is a **colourless, odourless, tasteless and combustible gas.** The **H—H bond dissociation enthalpy** is the highest for a single bond between two atoms of any element, hence it is **inert** at room temperature.

Chemical Properties of Hydrogen

- $\underset{\text{Dihydrogen}}{H_{2(g)}} \xrightarrow[95.5\%]{5000K} \underset{\text{Atomic Hydrogen}}{2H_{(g)}}$
- Ethene / Acetylene + H_2 $\xrightarrow[473K]{Ni/Pt/Pd}$ Ethane
- Aldehyde + H_2 $\xrightarrow{Ni}$ Alcohol
- Vegetable oil (Liquid) + H_2 $\xrightarrow{Ni,\ 473\ K}$ Vegetable fat (solid)
- $H_{2(g)} + X_{2(g)} \rightarrow 2HX_{(g)}$ (X = F, Cl, Br, I)
- $2H_{2(g)} + O_{2(g)} \xrightarrow{\text{catalyst or } \Delta} 2H_2O_{(l)}$
- $3H_{2(g)} + N_{2(g)} \xrightarrow[Fe]{673\ K,\ 200\ atm} 2NH_{3(g)}$
- $H_{2(g)} + 2M_{(g)} \rightarrow 2MH_{(s)}$ where M is an alkali metal.
- $yH_{2(g)} + M_xO_{y(s)} \rightarrow xM_{(s)} + nH_2O_{(l)}$

Hydrides (MHX)

Ionic/ Saline / Salt Like

- Formed by s-block elements. Except Be and Mg → forms covalent hydrides.
- High b.p. & m.p., heats of formation and density.
- Powerful reducing agents.
- Always stoichiometric.

Molecular/ Covalent

- Formed by p-block and some s-block elements
- low b.p., m.p.
- Hydrides of

  Group 13 : called electron deficient (BH_3, AlH_3)

  Group 14 : called electron exact (CH_4, SiH_4)

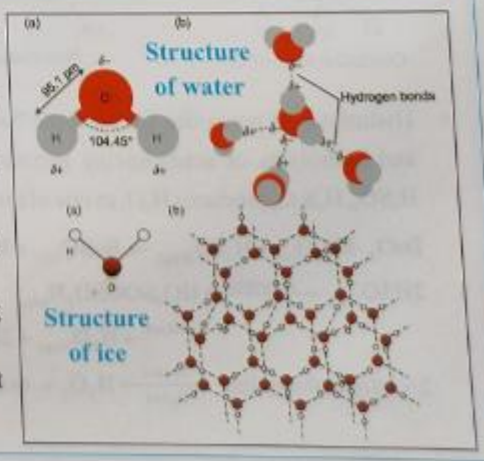
  Group 15 : called electron rich (NH_3, PH_3)

Metallic / Inter-interstitial

- Formed by d and f block element.
- Non-stoichiometery ($LaH_{2.87}$, $TiH_{1.5-1.8}$)
- Due Interstitial hydrides, metals adsorb large volume of hydrogen (occlusion)
- Order is Pd > Pt > Au > Ni.

Water H_2O

- Water is a **bent molecule** with a **bond angle** of 104.5° and **O—H bond length** of 95.7 pm.
- Water has high freezing point, high boiling point, high heat of vaporisation and high heat of fusion due to presence of **extensive hydrogen bonding** between water molecules.
- Water has high specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant as compared to other liquids.
- The crystalline form of water is **ice** which has an **open cage like structure** with wide holes and hence its density is less than that of water.
- Water has amphoteric character, undergoes redox reactions, has very strong hydrating tendency due to high dielectric constant and form hydrates.
- Water is said to be **soft** if it produces sufficient lather with soap. **Hard water** does not form lather readily with soap as it forms an insoluble scum/precipitate with soap.



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Hardness of Water

Pure Water

Mixing of Ca, Mg salt via.
Naturally, industrial activity

Hard Water (Forms scum with soap)

Hardness of Water

- **Temporary hardness**

  Due to the presence of bicarbonates of calcium and magnesium.

  $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

- **Hardness removal method**

  (a) Temporary hardness in water is easily removed by boiling.

  $Ca(HCO_3)_2 \xrightarrow{Boil} CaCO_3 \downarrow + H_2O + CO_2$

  $Mg(HCO_3)_2 \xrightarrow{Boil} MgCO_3 \downarrow + H_2O + CO_2$

  (b) Clark's method : Involves the addition of slaked lime, Ca(OH)$_2$

  $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3 \downarrow + 2H_2O$

- **Permanent hardness**

  Due to sulphates or chlorides of calcium and magnesium.

  Permanent hardness cannot be removed by boiling or by the addition of slaked lime.

- **Hardness removal method**

  (a) Washing soda method

  $MgSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + MgCO_3 \downarrow$

  $CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3 \downarrow$

  (b) Calgon Process $Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$ (M = Mg, Ca)

  $M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$

  (c) Permutit process : $Na_2Z + CaCl_2 \rightarrow 2NaCl + CaZ$

  (d) Ion exchange resin :

  (i) Cation exchange resin : This resin contains granular insoluble organic acid having giant molecules with $RCOO^-H^+$ group.

  $2RCOO^-H^+ + CaCl_2 \rightarrow (RCOO)_2Ca + 2H^+ + 2Cl^-$

  $2RCOO^-H^+ + MgSO_4 \rightarrow (RCOO)_2Mg + 2H^+ + SO_4^{-2}$

  (ii) Anion exchange resin : This resin contain giant organic molecules with basic groups derived from amines with $RNH_3^+OH^-$

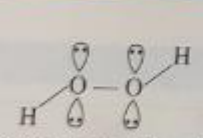
  $RNH_3^+OH^- + H^+ + Cl^- \rightarrow RNH_3^+Cl^- + H^+OH$

Heavy Water (D_2O)

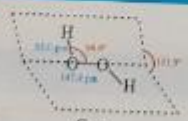
- Like ordinary water, it is also colourless, odourless and tasteless.
- Why it is used as a moderator in nuclear reactors?

  Ans : Heavy water is used as a moderator in nuclear reactor because it slows down neutrons effectively and also has a low probability of absorption of neutrons.

Hydrogen Peroxide

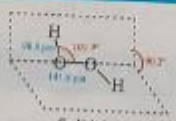


Oxidation state of O = –1



Gas

Non-planar (Open book like)



Solid (crystal)

H_2O_2 (Oxidation state of O = –1) → O.A. → H_2O Oxidation state of O = –2

H_2O_2 (Oxidation state of O = –1) → R.A. → O_2 Oxidation state of O = 0

- Hydrolysis of peroxides for example Na_2O_2, BaO_2, SrO_2, K_2O_2 and hydrolysis of acids having peroxy linkage for example H_2SO_5, $H_2S_2O_8$ produces H_2O_2 as one of the product.

$$BaO_2 \cdot 8H_2O_{(s)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + H_2O_{2(aq)} + 8H_2O_{(l)}$$

$$2HSO_{4(aq)}^- \xrightarrow{Electrolysis} HO_3SOOSO_3H_{(aq)} \quad (H_2S_2O_8)$$

$$\xrightarrow{Hydrolysis} H_2O_{2(aq)} + 2H_{(aq)}^+ + 2HSO_{4(aq)}^-$$

$$2-\text{ethylanthraquinol} \xrightarrow[H_2/Pd]{O_2\,(air)} H_2O_2 + \text{oxidised product}$$

- H_2O_2 acts as an **oxidising agent** as well as a **reducing agent** both in the acidic as well as in the basic medium.
- Due to l.p. – l.p. repulsion between oxygen lone pair, it releases nascent oxygen and acts as a **bleaching agent.**

  $H_2O_2 \rightarrow H_2O + [O]$

- **Storage of H_2O_2 :** It is stored in wax-lined glass or plastic vessels in dark as it decomposes slowly on exposure to light and the presence of metal surface or traces of alkali (present in glass containers), catalyse the decomposition reaction.

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Chapter – 9 Some Important Increasing Order

1 Acidic Property

(i) SiO_2, CO_2, N_2O, SO_3

(ii) MgO, Al_2O_3, SiO_2, P_4O_{10}

(iii) $HClO$, $HClO_2$, $HClO_3$, $HClO_4$

(iv) CH_4, NH_3, H_2O, HF

(v) SiH_4, PH_3, H_2S, HCl

(vi) H_2O, H_2S, H_2Se, H_2Te

(vii) HF, HCl, HBr, HI

(viii) $InCl_3$, $GaCl_3$, $AlCl_3$

(ix) BF_3, BCl_3, BBr_3, BI_3

2 Bond Angle

(i) CH_4, C_2H_4, C_2H_2

(ii) H_2O, NH_3, CH_4, CO_2

(iii) H_2O, NH_3, CH_4, BH_3

(iv) NO_2^-, NO_2, NO_2^+

(v) H_2Se, H_2S, H_2O

(vi) AsH_3, PH_3, NH_3

(vii) PF_3, PCl_3, PBr_3, PI_3

(viii) NF_3, NH_3, NCl_3

(ix) OF_2, H_2O, Cl_2O

3 Basic Character

(i) $LiOH$, $NaOH$, KOH, $RbOH$, $CsOH$

(ii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$

(iii) BeO, MgO, CaO, SrO

(iv) NiO, MgO, SrO, K_2O, Cs_2O

(v) CO_2, B_2O_3, BeO, Li_2O

(vi) SiO_2, Al_2O_3, MgO, Na_2O

(vii) SbH_3, AsH_3, PH_3, NH_3

(viii) F^-, OH^-, NH_2^-, CH_3^-

4 Thermal Stability

(i) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3

(ii) $BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$

(iii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
Polarisation

(iv) $LiOH$, $NaOH$, KOH, $RbOH$, $CsOH$

(v) $BeSO_4$, $MgSO_4$, $CaSO_4$

(vi) SbH_3, AsH_3, PH_3, NH_3

(vii) H_2Te, H_2Se, H_2S, H_2O

(viii) HI, HBr, HCl, HF

5 Solubility

(i) $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $BeCO_3$

(ii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$

(iii) $BaSO_4$, $SrSO_4$, $CaSO_4$, $MgSO_4$, $BeSO_4$

(iv) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3

(v) LiF, $LiCl$, $LiBr$, LiI

(vi) LiF, NaF, KF, RbF, CsF

(vii) BaF_2, SrF_2, MgF_2, CaF_2, BeF_2

(viii) CaF_2, $CaCl_2$, $CaBr_2$, CaI_2

(ix) AgI, $AgBr$, $AgCl$, AgF

(x) PbO_2, CdI_2, RbI

$$\text{solubility} \propto \frac{1}{\text{covalent char.}}$$

6 Ionic Character

(i) $LiBr$, $NaBr$, KBr, $RbBr$, $CsBr$

(ii) LiF, NaF, KF, RbF, CsF

(iii) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

(iv) BCl_3, $AlCl_3$, $GaCl_3$

(v) VCl_4, VCl_3, VCl_2

(vi) AlF_3, MgF_2, NaF

(vii) AlN, Al_2O_3, AlF_3

(viii) HI, HBr, HCl, HF

(ix) $CuCN$, $AgCN$

(x) $AgCl$, KCl

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7 Atomic/Ionic Size

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

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

(iii) O, C, S, Se

(iv) B, Be, Li, Na

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

8 Oxidizing Power

(i) $Cr_2O_7^{2-}$, MnO_4^{-}

(ii) MnO_2^{2-}, MnO_4^{-}

(iii) WO_3, MoO_3, CrO_3

(iv) $GeCl_4$, $SnCl_4$, $PbCl_4$

(v) I_2, Br_2, Cl_2, F_2

(vi) Zn^{+2}, Fe^{+2}, Pb^{+2}, Cu^{2+}, Ag^{+}

9 Ionization Energy

(i) Na, Al, Mg, Si

(ii) Li, B, Be, C, O, N, F, Ne, He (I^{st} I.P.)

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

10 Melting Point

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

(ii) Mg, Ba, Sr, Ca, Be

(iii) CaI_2, $CaBr_2$, $CaCl_2$, CaF_2

(iv) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

(v) NaI, NaBr, NaCl, NaF

(vi) CsCl, RbCl, KCl, NaCl

(vii) $AlCl_3$, $MgCl_2$, NaCl

11 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

12 Boiling Point

(i) PH_3, AsH_3, NH_3, SbH_3

(ii) H_2S, H_2Se, H_2O

(iii) HCl, HBr, HI, HF

(iv) NH_3, HF, H_2O

(v) He, Ne, Ar, Kr

(vi) H_2O, D_2O

(vii) H_2, Cl_2, Br_2

13 Electric conductivity

Cr, Pt, Fe, Al, Au, Cu, Ag

14 Reactivity with water

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

(ii) Be, Mg, Ca, Sr, Ba

15 Extent of Hydrolysis

(i) CCl_4, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5

(ii) $BiCl_3$, $SbCl_3$, $AsCl_3$, PCl_3, NCl_3

16 Bond Strength

(i) HI, HBr, HCl, HF

(ii) $-\overset{\backslash}{\underset{/}{C}}-I$, $-\overset{\backslash}{\underset{/}{C}}-Br$, $-\overset{\backslash}{\underset{/}{C}}-Cl$, $-\overset{\backslash}{\underset{/}{C}}-F$

(iii) N – N, N = N, N ≡ N

(iv) As – H, Sb – H, P – H, N – H

(v) N_2^{2-}, N_2^{-}, N_2^{+}, N_2

(vi) O_2^{2-}, O_2^{-}, O_2, O_2^{+}, O_2^{2+}

(vii) LiI, LiBr, LiCl, LiF

(viii) NaI, NaBr, NaCl, NaF

(ix) CsCl, RbCl, KCl, NaCl

(x) BaO, SrO, CaO, MgO

(xi) F_2, H_2, O_2, N_2

(xii) NO^{-}, NO, NO^{+}

(xiii) I_2, F_2, Br_2, Cl_2

(xiv) O – O, S – S

(xv) F – F, O – O, N – N, C – C, H – H

17 Reducing Power

(i) $PbCl_2$, $SnCl_2$, $GeCl_2$

(ii) HF, HCl, HBr, HI

(iii) Ag, Cu, Pb, Fe, Zn

(iv) HNO_3, H_2SO_3, H_2S

(v) H_3PO_4, H_3PO_3, H_3PO_2

18 Covalent character

(i) LiCl, $BeCl_2$, BCl_3, CCl_4

(ii) $SrCl_2$, $CaCl_2$, $MgCl_2$

(iii) $TiCl_2$, $TiCl_3$, $TiCl_4$

(iv) LiCl, LiBr, LiI

(v) Na_2O, Na_2S

(vi) AlF_3, Al_2O_3, AlN

(vii) HF, HCl, HBr, HI

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19 Strength of Hydrogen bonding (X... H – X)

(i) S, Cl, N, O, F

(ii) NH_3, H_2O, HF

20 Ionic Radii in Water

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

(ii) Li^+, Be^{+2}

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

21 Molar Conductivity in Water

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

22 Reactivity with Hydrogen

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

(ii) Ba, Sr, Ca, Mg, Be

23 Reactivity Towards Air

Be, Mg, Cs, Sr, Ba

24 Hydration of Ion/Hydration Energy

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

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

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

25 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

26 Electronegativity

(i) As, P, S, Cl

(ii) I, Br, Cl, F

(iii) C, N, O, F

27 Bond Length

(i) N_2, O_2, F_2, Cl_2

(ii) N ≡ N, C = N, C ≡ C

(iii) CO, C = O, –C–O–

(iv) NO^+, NO, NO^-

(v) O_2, O_3, H_2O_2 (O-O bond length)

(vi) CO, CO_2, CO_3^{2-}

(vii) N_2, N_2^-, N_2^{-2}

(viii) O_2^{+2}, O_2, O_2^-, O_2^{-2}

(ix) HF, HCl, HBr, HI

28 Dipole Moments

(i) CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl

(ii) NF_3, NH_3, H_2O, HF

(iii) Cis-chloropropene, Trans-chloropropene

(iv) p, m, o-dichlorobenzene

(v) CH_3I, CH_3Br, CH_3F, CH_3Cl

(vi) NH_3, SO_2, H_2O, HF

(vii) H_2S, H_2O

(viii) HI, HBr, HCl, HF

(ix) PH_3, AsH_3, SbH_3, NH_3

(x) H_2O, H_2O_2

29 Abundance of Element

(i) Element of earth crust - Fe, Al, Si, O

(ii) Metals on earth crust - Ca, Fe, Al

(iii) Non – Metals - Si, O

(iv) In atmosphere - O, N

(v) In universe - He, Si, H

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Chapter – 1 Table for IUPAC Nomenclature

The order of priority of functional group used in IUPAC nomenclature of organic compounds. (Up to down)

Functional Group	Structure	Prefix	Suffix
Carboxylic Acid	$-\overset{O}{\overset{\|\|}{C}}-OH$	Carboxy	-oic acid
Sulphonic acid	$-SO_3H$	Sulpho	-sulphonic acid
Anhydride	$-\overset{O}{\overset{\|\|}{C}}-O-\overset{O}{\overset{\|\|}{C}}-$	×	-oic-anhydride
Ester	$-\overset{O}{\overset{\|\|}{C}}-OR$	Alkoxycarbonyl or carbalkoxy	–alkanoate
Acid chloride	$-\overset{O}{\overset{\|\|}{C}}-Cl$	Chloroformyl or Chlorocarbonyl	–oyl chloride
Acid amide	$-\overset{O}{\overset{\|\|}{C}}-NH_2$	Carbamoyl/ Amido	-amide
Carbonitrile/Cyanide	$-C\equiv N$	Cyano	–nitrile
Aldehyde	$-\overset{O}{\overset{\|\|}{C}}-H$	Formyl or Oxo	–al
Ketone	$-\overset{O}{\overset{\|\|}{C}}-$	Keto or oxo	–one
Alcohol	$-OH$	Hydroxy	– ol
Thio alcohol	$-SH$	Mercapto	– thiol
Amine	$-NH_2$	Amino	– amine
Ether	$-O-\mathbf{R}$	Alkoxy	–
Oxirane	$-C-C-$ (O)	Epoxy	–
Nitro derivative	$-NO_2$	Nitro	–
Nitroso derivative	$-NO$	Nitroso	–
Halide	$-X$	Halo	–
Double bond	$C=C$	–	–ene
Triple bond	$C\equiv C$	–	– yne

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Isomerism

Defination

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

- Isomerism
  - Structural (Constitutional) isomerism
    - Chain isomerism
    - Position isomerism
    - Functional group isomerism
    - Metamerism
    - Tautomerism
  - Stereo (Configurational) isomerism

Structural Isomerism

Chain Isomerism

Same molecular formula but differ in the order in which carbon atoms are bonded to each other.

Condition

I. Size of main chain or side chain or both should be different.

II. Nature of functional group, multiple bond or substituent should not change.

e.g. C_5H_{12} $\boxed{CH_3-CH_2-CH_2-CH_2-CH_3}$

n – pentane

$\boxed{H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3}$, $\boxed{H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$

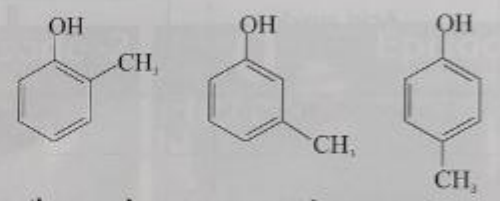
iso - pentane neo - pentane

Position Isomerism

Same molecular formula but they differ in the position of the functional group or the substituent

Condition

I. Same size of main chain or side chain but different position of group or substituents or functional group.



ortho-cresol **meta-cresol** **para-cresol**

Functional Group Isomerism

Same molecular formula but different functional groups in their molecules show functional group isomerism.

Condition:

Functional group should be different, chain and position isomerism are not considered.

e.g. C_3H_9N ⇒

$CH_3-CH_2-CH_2-NH_2$, $CH_3-CH_2-NH-CH_3$, $CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$,

1-propanamine N-methylethanamine N,N-dimethylmethanamine

Metamerism

Metamerism is due to the difference in the nature of alkyl groups attached to the polyvalent atom or functional group. Metamers belong to the same homologous series.

Condition:

I. Functional group should be polyvalent, heteroatomic.

II. Nature of functional group should not change

III. Chain and position isomerism is not considered

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

Methyl n-propyl ether

$CH_3-CH_2-O-CH_2-CH_3$

diethyl ether

Tautomerism

Tautomerism is the phenomenon in which two structural isomers differ in the relative positions of their atoms and are spontaneously interconvertible and can exist in dynamic equilibrium.

In tautomerism two compounds have different functional groups due to shifting of H-atom.

Structural Requirement for tautomerism

(I) Compound should have electron withdrawing groups such as $-CO$, $-NO_2$ and $-CN$.

(ii) Compound should have atleast one acidic hydrogen on α–carbon of the molecule.

e.g.

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{O}{||}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{||}}{C}-CH_3$$

keto form **enol form**

Enol Content Enhancedby:

- Acidic α–H of keto form
- Aromatisation in enol form
- Resonance in enol form
- Intra–molecular H-bonding in enol form.

Ring Chain Isomerism

One isomer is open chain but another is cyclic

Ex. : Propene and cyclopropane

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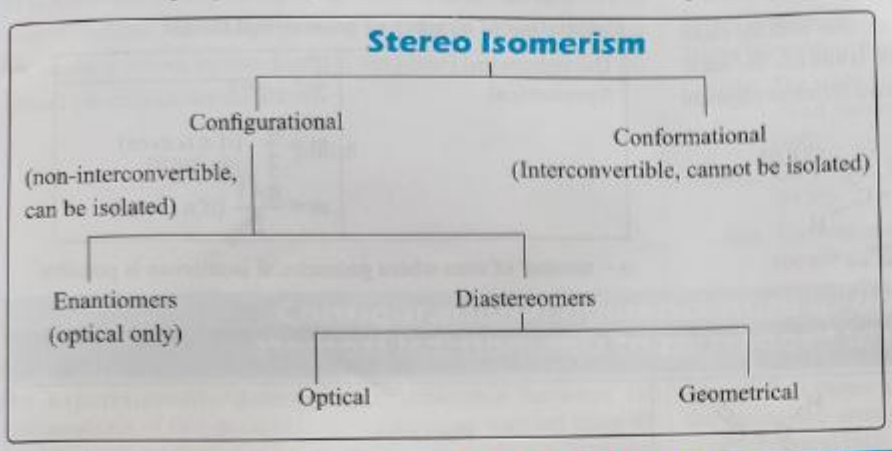
Stereo Isomerism

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**.

(Spatial - arrangement in space)



Configurational Isomerism

(i) These isomers differ in the configuration (The spatial arrangement of atoms that characterises a particular stereoisomer is called its configuration).

(II) Configurational isomerism arises due to non-interconvertibility at room temperature. Since they are non-interconvertible they can be separated by physical or chemical methods.

Geometrical Isomerism

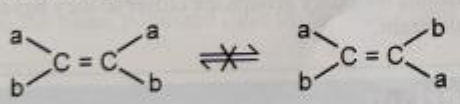
Isomers which possess the same **molecular and structural formula** but differ in the arrangement of atoms or groups in space due to **restricted rotation** are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

Conditions of geometrical isomerism :

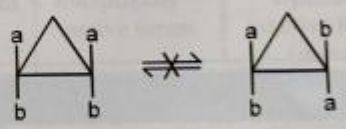
Geometrical isomerism arises due to the presence of a double bond or a ring structure

(i.e. $>C=C<$, $>C=N-$, $-N=N-$ or ring structure)

Due to the rigidity of double bond or the ring structure to rotate at the room temperature the molecules exist in two or more orientations. This **rigidity to rotation** is described as restricted rotation / hindered rotation / no rotation.

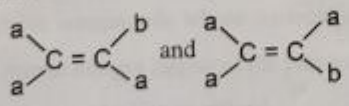


(Restricted Rotation)



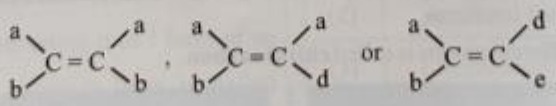
(Restricted Rotation)

Different groups should be attached at each doubly bonded atom. For example



are identical but not geometrical isomers

On the other hand, following types of compounds can exist as geometrical isomers :



Sequence rules : (Cahn - Ingold - Prelog Sequence Rules) (CIP)

For deciding the seniority of groups following rules are applied :

Rule I : The group with the first atom having higher atomic number is senior. According to this rule the seniority of atoms is :

$$I > Br > Cl > S > F > O > N > C > H$$

Rule II : The higher mass isotope is senior.

Thus (a) $-T > -D > -H$. (b) $-C^{14}H_3 > -C^{13}H_3$

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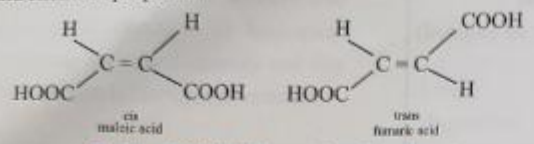
Rule III : If the first atom of group is identical then second atom is observed for seniority.

Rule IV : Groups containing double or triple bonds are assigned seniority as if both atoms were duplicated or triplicated.

Rule V : Bond pair is senior to lone pair.

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



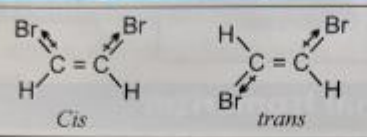
Trick : FRUIT (Fumaric acid - Trans)

Calculation of number of geometrical isomer

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

n = number of sites where geometrical isomerism is possible.

Physical Properties of Geometrical Isomers

Physical Properties		Remarks
Dipole Moment	*Cis* > *trans*	cis-isomer has resultant of dipoles while in trans isomer dipole moments cancel out.
Boiling Point	*Cis* > *trans*	Molecules having higher dipole moment have higher boiling point due to larger intermolecular force of attraction.
Solubility (in H_2O)	*Cis* > *trans*	More polar molecules are more soluble in H_2O
Melting point	*trans* > *Cis*	More symmetric isomers have higher melting points due to better packing in crystalline lattice & trans isomers are more symmetric than cis.
Stability	*trans* > *Cis*	The molecule having more vander waal strain are less stable. In cis isomer the bulky groups are closer so they have larger vander waals strain.

Optical Isomerism

Compounds having similar molecular and structural formula but differing in the stereo chemical formula and behavior towards plane polarized light are called optical isomers. Isomers and this phenomenon is called optical isomerism

- **Types of optical isomers**

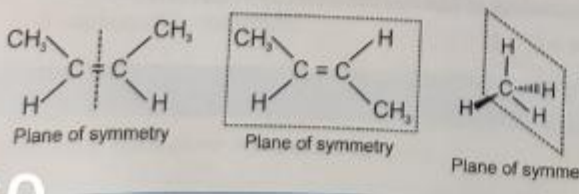
  (1) Optically active
  * dextrorotatory (d)
  * laevorotatory (*l*)

  (2) Optically inactive
  *meso

- **Condition:**
- Molecule should be asymmetric or chiral i.e. symmetry element (POS & COS) should be absent. : [POS – Plane of symmetry, COS – Centre of Symmetry]
- The carbon atom linked to four different groups is called **chiral carbon**.

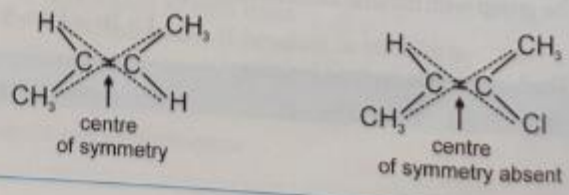
Plane of symmetry

It is an imaginary plane which bisects the molecule in two equal halves in such a way that each half of the molecule is the mirror image of the other half.



Centre of symmetry

The centre of symmetry is defined as the point in a molecule through which if a straight line is drawn from any part of the molecule this line encounters identical groups at equal distances in opposite direction.



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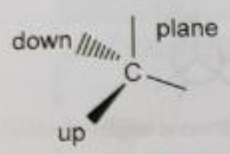
Projection formula in optical isomerism

(i) Wedge-dash projection formula

It is a convenient way of depicting three dimensional structure in two dimension. In this projection four bonds of a tetrahedral molecule is shown by two lines (in the plane) one wedge (up the plane) one dash (down the plane)



(II) Fischer projection formula

It is also a convenient way of depicting three dimensional structure in two dimension.

Rules for writing Fischer projection formula :

(i) The molecule is drawn in the form of cross (+) with the chiral carbon at the intersection of horizontal & vertical lines.

(ii) On vertical line, main chain is taken with first carbon at the top.

(iii) The horizontal lines represent the bonds directed towards the viewer and vertical lines away from the viewer

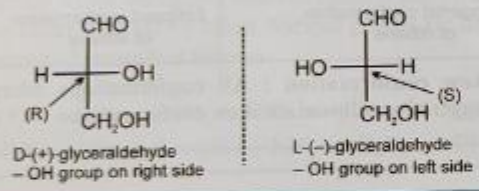
Configurational nomenclature in optical isomers

Relative configuration

The experimentally determined relationship between the configurations of two molecules, even though we may not know the absolute configuration of either. Relative configuration is expressed by D-L system.

D - L System

This method is used to relate the configuration of sugars and amino acids by the help of enantiomers of glyceraldehyde. The configuration of (+)-glyceraldehyde has been assigned as D and the compounds with the same relative configuration are also assigned as D, & those with (-) glyceraldehyde are assigned as L.



Absolute configuration

The detailed stereochemical picture of a molecule, including how the atoms are arranged in space. Alternatively the (R) or (S) configuration at each chirality centre.

R and S configurations in Fischer projection

Rule I : The priorities of groups which are attached with the asymmetric C-atom are assigned by sequence rule.

Rule II : The lowest priority group is brought to the bottom of Fischer projection by two or even simultaneous exchanges.

Rule III : Then an arrow is drawn from first priority group to second priority group to third priority group. If the arrow is clockwise the configuration assigned to the projection is **R** & If it is anticlockwise the configuration assigned is **S**.

- Non-superimposable mirror images are called **enantiomers** which rotate the plane polarized 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. **(internal compensation)**
- 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. (External compensation)**
- The process by which d,*l* mixture is separated into d and *l* form 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 isomerism only 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

	Properties of optical isomers	Remarks
(1)	Molecular Formula	Same
(2)	Structural formula	Different
(3)	Stereochemical formula (str. formula with orientation)	Same
(4)	Dipole Moment (m.p., b.p., density, solubility, refractive index etc.)	Same
(5)	Chemical properties	
	(a) with optically inactive compound	Same
	(b) with optically active compound	Different

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Conformational isomerism

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

Conformations

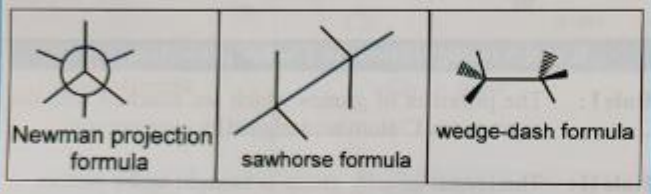
Different arrangements of atoms that can be converted into one another by rotation about single bonds are called conformations.

Conformational isomers

There are infinite arrangement (conformations) which arise due free rotation around carbon-carbon σ bond, different conformations corresponding to energy minima are called conformational isomers. The conformational isomerism arises due to free rotation along a bond.

Newman projection

For conformational analysis, a special type of structural formula is convenient to use which is called Newman projection formula and another type is a Sawhorse formula.



To write Newman projection formula we imagine ourselves taking a view from one carbon atom directly along the selected bond axis to the next atom. The front carbon and its other bonds are represented as and those of the back carbon

Dihedral angle :

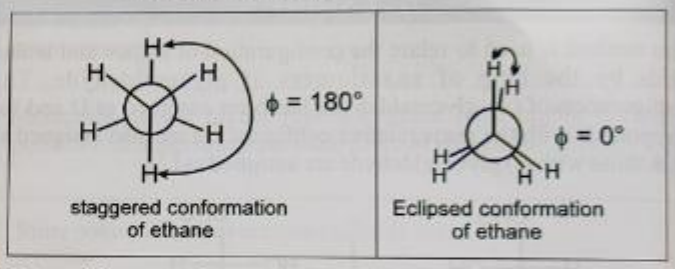
The angle between C – X and C – Y in X – C – C – Y when it is visualised along C – C bond.

ϕ = dihedral angle

Staggered, eclipsed and skew conformations :

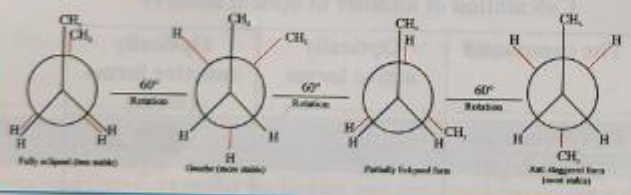
(I) The staggered conformation of a molecule is that conformation where the dihedral angle between the bonds at each atom of carbon-carbon bond is 180°.

(II) In eclipsed conformation the atoms bonded to carbons at each end of carbon-carbon bond are directly opposite to one another. The dihedral angle between them is 0°.



(III) Skew conformation : All conformations other than staggered or eclipsed are skew conformations.

Conformation of butane : $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_3$



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 > twisted boat > boat > half chair

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ELECTRONIC EFFECTS

The effect which appears due to electronic distribution is called electronic effect.

Electron Displacement Effects

- **(Permanent)**
  - **Polarisation Effects**
    - **Inductive effect (±I)**
    - **Mesomeric effect (±M) or Resonance effect**
    - **Hyperconjugation**
- **(Temporary)**
  - **Electromeric effect (±E)**

Electrophiles are electron deficient species.

e.g. $H^{\oplus}, R^{\oplus}, NO_2^{\oplus}, X^{\oplus}, PCl_3, PCl_5$

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

Nucleophiles are electron rich species.

e.g. $Cl^{\ominus}, \overset{\ominus}{C}H_3, \overset{\ominus}{O}H, RO^{\ominus}, \overset{\ominus}{C}N, \ddot{N}H_3, R\ddot{\underset{..}{O}}H, CH_2=CH_2, CH\equiv CH$

Inductive Effect

Inductive effect may be defined as a permanent shifting of σ bond pair electrons due to difference in Electronegativity. (Polar bond)

– I Effect

The group which withdraws electron cloud is known as – I group and its effect is called – I effect. Various groups are listed in their decreasing – I strength as follows

$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH > -X > -OR > -OH > -C\equiv CH > -NH_2 > -C_6H_5 > -CH=CH_2$

+ I Effect

The group which releases electron cloud is known as + I group and effect is + I effect.

$-\overset{\ominus}{N}-H > -O^{\ominus} > -COO^{\ominus} > 3°alkyl > 2°alkyl > 1°alkyl > -CH_3$

Super Note :
The hydrogen atom is reference for + I and – I series. The inductive effect of hydrogen is assumed to be zero.

Application of Inductive Effect

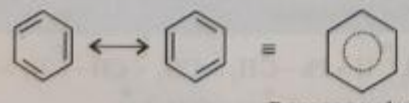
- Acidic strength / K_a / stability of conjugate base / $\frac{1}{pK_a} \propto \frac{-I}{+I}$
- Basic strength / K_b / stability of conjugate acid / $\frac{1}{pK_b} \propto \frac{+I}{-I}$
- Stability of carbocation/ carbene / nitrene / free radical $\propto \frac{+I}{-I}$
- Stability of Carbanion/ Benzene $\propto \frac{-I}{+I}$

Resonance & Mesomeric effect

- Resonance is the phenomenon in which two or more structures involving identical position of atom, can be written for a particular species, all those possible structures are known as resonating structures or canonical structure.
- The ultimate target of resonance is to find the real structure of molecule or ion.

Resonance Hybrid

It is the actual structure of the species without violating the rules of **covalence maxima** for the atoms.



Resonance hybrid

Resonance Energy

The difference in energy between the hybrid and the most stable canonical structure is referred to as the resonance energy

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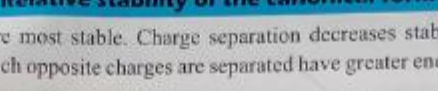
Relative stability of the canonical form

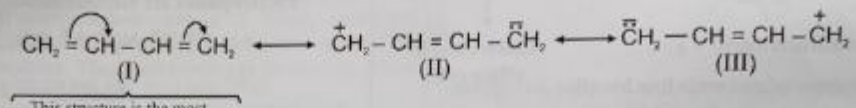
- Nonpolar (uncharged) structure are most stable. Charge separation decreases stability. Separating opposite charges requires energy. Therefore, structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation.



(I) (II)

- Structures in which all of the atoms have a complete valence shell of electrons (i.e., the noble gas electronic configuration) are especially stable and make large contributions to the hybrid.

- Structures with more covalent bonds are more stable than other structures



(I) (II) (III)

This structure is the most stable because it contains the most covalent bonds.

- Structure that carries negative charge on a more electronegative atom and positive charge on less electronegative atom are comparatively more stable.

Super Notes -
- The structure with incomplete octet is least stable among all , and charge separation decreases stability.
- Charge separation is endothermic process , which increases energy and decreases stability of R.S.

– M Effect

When the group withdraws electron from the conjugated system, it shows – m effect

$-NO_2 > -C\equiv N > -SO_3H > -CHO > -\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C}-OH$

+ M Effect

When the group donates electron to the conjugated system it shows + m effect.

$O^{\ominus} > -NH_2 > -NHR > -NR_2 > -OH > -OR > -NH-\underset{\underset{O}{\|}}{C}-R$

$> -O-\underset{\underset{O}{\|}}{C}-R > -Ph > -CH=CH_2 > -F > -Cl > -Br > -I$

Hyperconjugation

It is delocalisation of sigma electron with p-orbital. Also known as $\sigma-\pi$ conjugation or no bond resonance. It may take place in alkene, alkynes, carbocation, free radical, benzene nucleus.

Super Note : Presence of at least one α-hydrogen in Alkenes, Alkynes, carbocations, free-radical and benzene nucleus is necessary for operation of hyperconjugation.

Types of hyperconjugation
- Isovalent - Present in C^+, $C^{\bullet}$ intermediates.
- Sacrificial - Present in unsaturated / aromatic hydrocarbon

Applications of hyperconjugation

(a) Stability of Alkenes :- "More alkylated alkenes are more stable" Stability of alkenes $\propto$ no. of hyperconjugative structures.

(b) Heat of hydrogenation : Stability of alkenes $\propto$ no. of hyperconjugative structures $\propto \dfrac{1}{\Delta H_{Hydrogenation}}$

(c) Bond Length

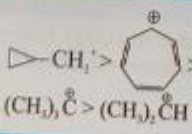
(d) Dipole moment

(e) Stability of carbocation

(f) Stability of free radical

Relative Stability Order

(A) Stability of carbocation



$\triangleright CH_2^{\oplus} > \text{[ring]}^{\oplus} > (Ph)_3C^{\oplus} > (Ph)_2CH^{\oplus} > Ph-CH_2^{\oplus} > CH_2=CH-CH_2^{\oplus} >$

$(CH_3)_3C^{\oplus} > (CH_3)_2CH^{\oplus} > CH_3CH_2^{\oplus} > CH_3^{\oplus} > CH_2=CH^{\oplus} > CH\equiv C^{\oplus}$

(B) Stability of free radical

$(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2=CH-\dot{C}H_2 >$

$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

(C) Stability of Carbanion

$(Ph)_3C^{\ominus} > (Ph)_2CH^{\ominus} > Ph-CH_2^{\ominus} > CH_2=CH-CH_2^{\ominus} >$

$CH_3^{\ominus} > CH_3CH_2^{\ominus} > (CH_3)_2CH^{\ominus} > (CH_3)_3C^{\ominus}$

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Some important orders in organic chemistry

- **Basic strength of amine:-**

  In aqueous medium

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

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

  In gaseous medium

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

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

- **Reactivity towards nucleophile (NAR)**

  (1) $HCHO > CH_3CHO > (CH_3)_2CO$

  (2) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$

- **Reactivity order towards acyl nucleophilic substitution reaction**

  Acid chloride > anhydride > ester > amide

- **Order of electronic effect**

  Mesomeric > Hyperconjugation > Inductive effect

- **Stability of alkene $\propto$ no. of α hydrogen**

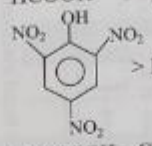
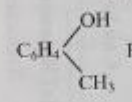
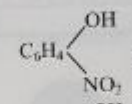
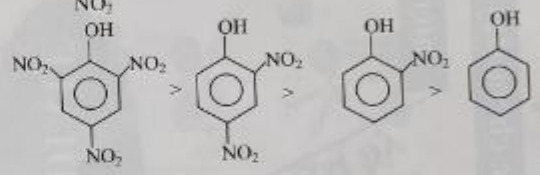
  $R_2C{=}CR_2 > R_2C = CHR > R_2C{=}CH_2 >$

  $\underset{\text{Trans form}}{RCH = CHR} > \underset{\text{cis form}}{RCH - CHR}$

  $RCH = CH_2 > CH_2 = CH_2$

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

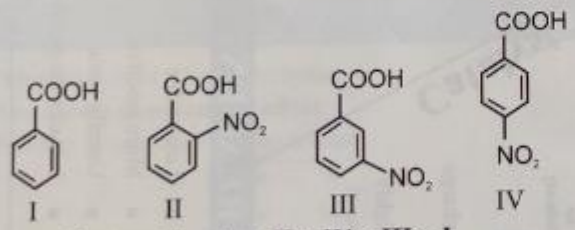
Some important order of acidic strength.

- $H_2O > CH \equiv CH > NH_3$
- $CH \equiv CH > CH_2 - CH_2 > CH_3 - CH_3$
- $R - SO_3H > R - COOH >$ $> R - OH$
- $HCOOH > CH_3COOH > CH_3CH_2COOH$
-  $> HCOOH > C_6H_5COOH > CH_3COOH$
- $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$
- $CH_3 - CH_2 - \underset{F}{CH} - COOH > CH_3 - \underset{F}{CH} - CH_2 - COOH > CH_3 - \underset{F}{CH_2}CH_2COOH$
-  Phenol > m > p > o
-  p > o > m > Phenol
- 

Ortho Effect

Acidic Strength

- It is common observation that generally ortho substituted benzoic acids are highly acidic as compared to their isomers and benzoic acids itself.

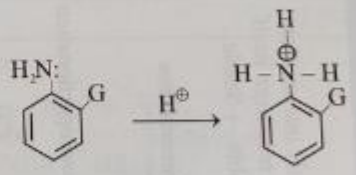


I II III IV

acid strength order : II > IV > III > I

Basic Strength

- Ortho-substituted anilines are mostly weaker bases than aniline itself.
- Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).



Carbenes

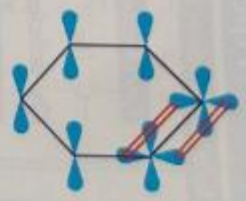
There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon compounds are called carbenes.

Nitrenes

There is a group of intermediates in which nitrogen forms only one bond. These neutral Monovalent nitrogen compounds are called nitrenes.

Benzyne

The benzene ring has one extra C – C π bond in benzyne



All carbon are sp^2 hybridised

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Concept Map

Script of organic chemistry

INTERMEDIATE

- High energy
- Less stability
- Formed for a very short period of time
- Only one type of intermediate is formed in a reaction but their degree can be different
- **Rate of reaction ∝ stability of intermediates**

Types of Intermediate

Electron Deficient intermediate

Carbocation — $C^{\oplus}$ is the only intermediate which can rearrange itself from Unstable → Stable.

$-\overset{+}{C}$ [6e⁻] (2e⁻ deficient)

Free radical — Undergoes → Dimerisation, Disproportionation

$-\dot{C}$ [7e⁻] (1e⁻ deficient)

Carbene

$>C:$ [6e⁻] (2e⁻ deficient)

Types:

- Singlet: $H-\overset{..}{C}-H$ — Bent, sp^2 diamagnetic
- Triplet: $H-\overset{\cdot}{C}-H$ — Linear, sp paramagnetic

Nitrene

$-\ddot{N}:$ 6e⁻ (2e⁻ deficient)

Singlet — Triplet

Electron rich intermediate

Carbanion — $-C^{\ominus}$ 8e⁻ with -ve charge

Benzyne — (8e⁻) Unstable Highly reactive π bond electrons.

Triple bonded carbon is also sp^2 hybridised

Stabilised by

Intermediates are stabilised by electronic movements

(a) Inductive effect :
Shifting of σ electrons due to ΔEN
Parmanent effect
It is of two types — [+ I (electron releasing) / – I (electron withdrawing)]

(b) Hyperconjugation:
Transfer of σ electrons of a C-H bond of a sp^3 hybridized carbon.
Can be of two types — [isovalent / sacrificial]

(c) Resonance :
Delocalisation of π bond electrons.
Can be of two types — [+ R/+M / – R/–M]

(d) Dancing resonance :
Transfer of C–C σ bond electron.
Due to high angle strain.
Observed in Cyclo-propyl methyl cation [CPM]

(e) Electromeric effect :
Temporary transfer of π bond e⁻ in the presence of $E^{\oplus}/Nu^{\ominus}$.

Catalyst

SUBSTRATE	+	REAGENT
More stable		Less stable
Less reactive		More reactive
Usually covalent		Usually ionic
Never initiates the reaction		Initiates the reaction

PRODUCT

Major Product

- Formed by more stable intermediate.
- More than 50% in amount.
- Have greater stability via resonance, hyper conjugation or lesser dipole moment.

Minor Product

- Formed by less stable intermediate.
- Less than 50% in amount.

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Methods to stabilize Intermediate

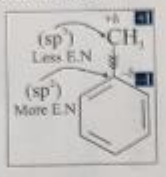
Intermediates are stabilised by movement of electrons.

Electronic movement is of two types

- **Permanent electron movement**
  - Inductive Effect
- **Temporary electron Movement**
  - Hyper-Conjugation
  - Resonance
  - Electromeric effect
    - Temporary transfer of π bond e^- in the presence of $E^{\oplus}/Nu^{\ominus}$.

Inductive Effect

- Shifting of σ electrons due to ΔEN.



- It is of two types.

  1) + I Effect ⇒

  Eg. $-NH^- > -O^- > -COO^- > -3°R >$
  $-2°R > -1°R > -CH_3$.

  2) – I Effect ⇒

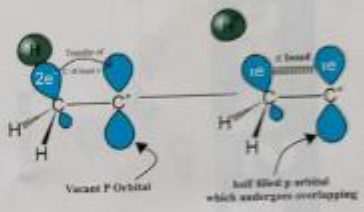
  Eg. $NF_3^+ > NR_3^+ > NH_3^+ > NO_2 > CN >$
  $F > Cl > Br > I > OH > OR > H$.

- Inductive effect is defined with respect to hydrogen.
- Inductive effect of protium is zero while deuterium has +I effect.
- Negatively charged groups have very high tendency to release electrons.

Hyper-Conjugation

- Transfer of σ electrons of a C-H bond of a sp^3 hybridized carbon.
- Also called **"no bond resonance", Baker Nathan effect.**
- Can be of two types.

  1) isovalent 2) sacrificial



Hyper-conjugation can explain

- Stability of alkenes.
- Stability of carbocation & free radical.
- Activation of benzene ring by alkyl group, methyl is most activating while tertiary butyl being least activating.

  [Sacrificial Hyperconjugation]

Resonance

- Delocalisation of π bond electrons.
- Also known as **mesomeric effect.**
- Presence of conjugate system is must.

Conjugated system →

= – =
= – l.p.
= – F.R.
= – +ve
= – -ve.

Super Note :

$-F > -Cl > -Br > -I$
$-OH > -OR$
$-NH_2 > -NHR > -NR_2$
} Order of +M

negatively charged groups are highly e^- releasing.

- It is of two types.

  1) +R / + M ⇒ e.g. : $-\overset{\oplus}{C}H_2 > -\overset{\oplus}{N}H > -\overset{\oplus}{O} > -NH_2 > -NHR > -NR_2 > -OH > -OR > NH-\overset{O}{\overset{\|}{C}}-CH_3 > -O-\overset{O}{\overset{\|}{C}}-CH_3$

  2) –R / – M ⇒ e.g.: $-NO_2 > -C \equiv N > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-CH_3 > -\overset{O}{\overset{\|}{C}}-OR > -\overset{O}{\overset{\|}{C}}-OH > -\overset{O}{\overset{\|}{C}}-NH_2$

Effectiveness of various effects : Dancing resonance > Resonance > Hyper conjugation > Inductive effect

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Attacking Species

Electrophile ($E^{\oplus}$)

Charged

+vely charged species except cation of IA & IIA group elements

eg: Cl^-, CH_3^+, R^+, Fe^{+3}, NO_2^+, H^+, Cr^{+3}

Neutral

Incomplete octet
eg : BX_3, B_2H_6, Dry $AlCl_3$, CO_2

$\boxed{R} \rightarrow X$
$E^{\oplus}$

Expanded octet
Eg. $SiCl_4$, PCl_5
Vacant d-orbital

Multiple bonded carbon with more E.N. element

$-\overset{O}{\overset{\|}{C}}-$

$-C \equiv N$

$-CS_2$

$-CO_2$

$CH \equiv CH$

Nucleophile (Nu^-)

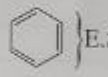
Charged

-ve charged & σ-bonded oragno metallic compound

Eg: R^- (from RMgX or R_2Cd), H^-, OR^-, X^-, HX^-

Multiple bonded carbon with similar E.N. element

Eg. $CH_3 - C \equiv CH$, $CH_3 - CH = CH_2$ } E.A.R.

 } E.S.R.

Neutral

NH_3

$R-NH_2$

H_2O

Presence of l.p. of e^-

* All positively charged species are E^+ except NH_4^+/ cation of IA & IIA/ Al^{+3}
* Neither E^+ nor Nu^- are electron precise compounds with complete octet

Eg: C_2H_6, CH_4 (Alkanes)

H_2, NH_4^+, Na^+, K^+

These species are having complete octet

Electrophile as well as Nu^-

Eg :- PH_3, ester, Acetone, Acetamide, X_2

Organic Reaction

Addition Reaction

EAR - Electrophilic Addition Reaction

- π bond electrons are mobile in nature and donated to electrophile.
- In first step addition of electrophile takes place, that's why known as EAR.
- Compound with multiple bond between similar atoms.

Eg. : Alkene, Alkyne

NAR – Nucleophilic Addition Reaction

- Multiple bonds are present in b/w different atoms having difference in E.N.
- In first step addition of nucleophile takes place.

Eg. : Addition Reaction of aldehyde, ketone and Cyanides.

FRAR – Free Radical Add. Reaction

- Metal adsorb hydrogen on its surface and converts molecular H_2 into atomic H. ($H_2 \rightarrow H^{\bullet} + H^{\bullet}$)

Eg.1: Reduction by H_2 in the presence of metal (Ni, Pd, Pt),

Eg.2: Alkene + HBr in presence of peroxide.

Follow anti-markonikov's rule (HBr + Peroxide).

Substitution Reaction

ESR – Electrophilic Substitution Reaction

- Characteristic Reaction of benzene and its derivatives to maintain aromaticity.
- Substituted E^+ is always H^+.
- Protonic acids like HCl, HF etc does not directly react with benzene.

Eg. : Friedel craft Alkylation and Friedel craft Acylation (Anhy. $AlCl_3$ Produces electrophile), and other reaction of benzene and its derivatives.

FRSR – Free Radical Substitution Reaction

- Free radical substituted by other free radical.
- Generally in alkanes.
- **$3^\circ H > 2^\circ H > 1^\circ H$ (Reactivity order)**

Eg. : Halogenation of alkanes {$X^{\bullet}$ replaces $H^{\bullet}$}

NSR – Nucleophilic Substitution Reaction

- Nucleophile is substituted by another nucleophile.
- $S_N^1 \Rightarrow 3^\circ$ R-X > 2° R-X > 1° R-X.
- $S_N^2 \Rightarrow 1^\circ$ R-X > 2° R-X > 3° R-X.
- Ar SN $\Rightarrow$ Ph–X.
- S_NAE $\Rightarrow$ Acid derivatives.

Elimination Reaction

E_1 - Elimination Reaction

- I.M. is Carbocation and can undergo rearrangement.
- 1st Order Reaction.
- R.O.R. $\propto$ [Substrate]
- $3^\circ > 2^\circ > 1^\circ$.
- Polar protic solvent and high temperature is required.

Eg : - Dehydration of alcohols.

E_2 - Elimination Reaction

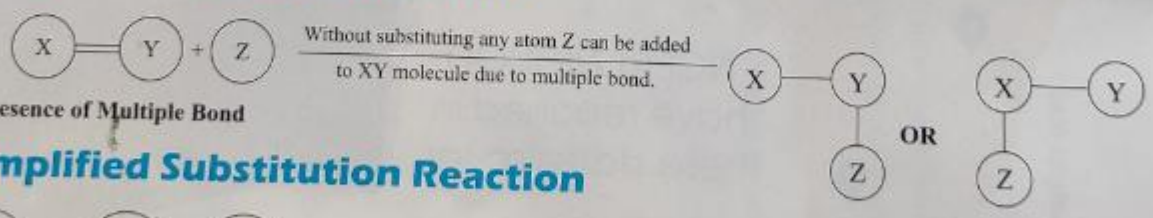
- No carbocation is formed.
- 2nd order reaction.
- R.O.R. $\propto$ [Substrate] [Nu^-]
- $1^\circ > 2^\circ > 3^\circ$.
- In presence of strong Nu^-.
- Substrate should be sterically crowded.

Eg. : Dehydrohalogenation.

Elimination unimolecular conjugate base reaction E^1 - CB

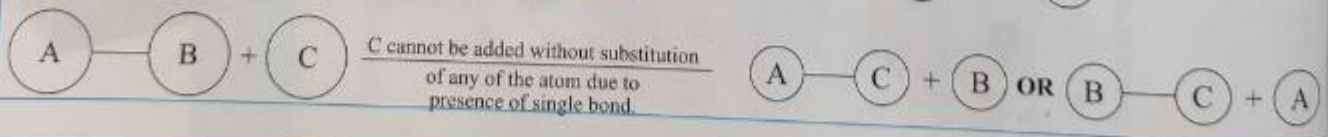
- R.O.R = [C.B]
- Most stable carbocation is formed but no rearrangement occurs.

Simplified Addition Reaction



Presence of Multiple Bond

Simplified Substitution Reaction



Selectivity in the Reaction

Chemo-Selective
When reaction occurs at a specific functional group

Regio-Selective
Regio = Region
There Reaction are Region specific Reactions

Stereo-Selective
One of the stereo isomer is the main product.

Stereo-Specific
Product of this reaction depends on the stereo chemical of substrate

POCO
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Oxidation Reaction

Oxidation Number Increases

Via Abstraction of Hydrogen

- By weak/moderate oxidizing agent
- PCC, PDC, CrO_2Cl_2, Cu/ 573 K Jones reagent - [CrO_3 + dil. H_2SO_4 + acetone]

Via Introduction of Nascent [O]

- Strong oxidizing agent.

Eg.: $KMnO_4$, $K_2Cr_2O_7$, CrO_3, O_3

Reduction Reaction

Oxidation Number Decreases

Via adding of Hydrogen [H^+]

- $(Pd + CaCO_3)/H_2$
- $Ni/Pt/Pd + H_2$

Via introduction of Hydride [H^-]

- $LiAlH_4$ (stronger reducing agent) $NaBH_4$
- Di – BAL – H (diisobutylaluminium hydride)
- $[SnCl_2 + HCl]$ $(H^- + Sn^{+4} + 3Cl^-)$

Acid Base Reaction

*** Most Important Reaction**

***90% students get confused by this reaction**

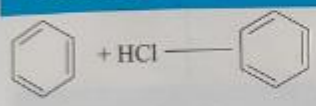
- **70% reactions of organic chemistry are acid base reactions.**
- Fastest Reactions.
- **Salt is produced in this reaction and anionic part of salt can act as Nucleophile.**

Eg.: $\underset{\text{(Acetylene)}}{HC \equiv CH} + \underset{\text{(Base)}}{NaNH_2} \rightarrow HC \equiv C^- Na^+ + NH_3$

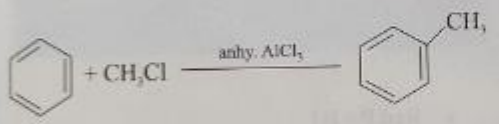
Other Reaction

- **Peri - Cyclic Reaction**
- **Polymerisation Reaction**
- **Rearrangement Reaction**
- **Aromatization Reaction**
- **Condensation Reaction**
- **Isomerisation Reaction**
- **Combustion Reaction**

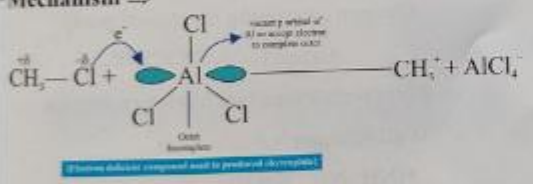
Electrophilic Substitution Reaction

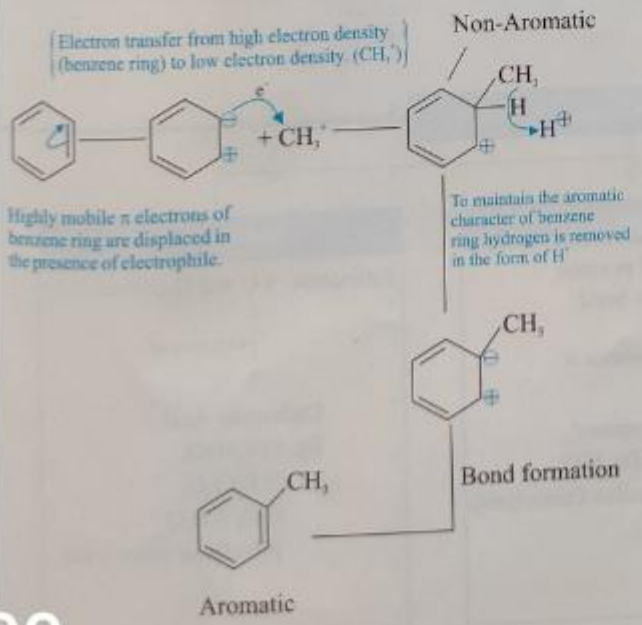


There is no significance of this reaction because H^+ is removed and H^+ is added

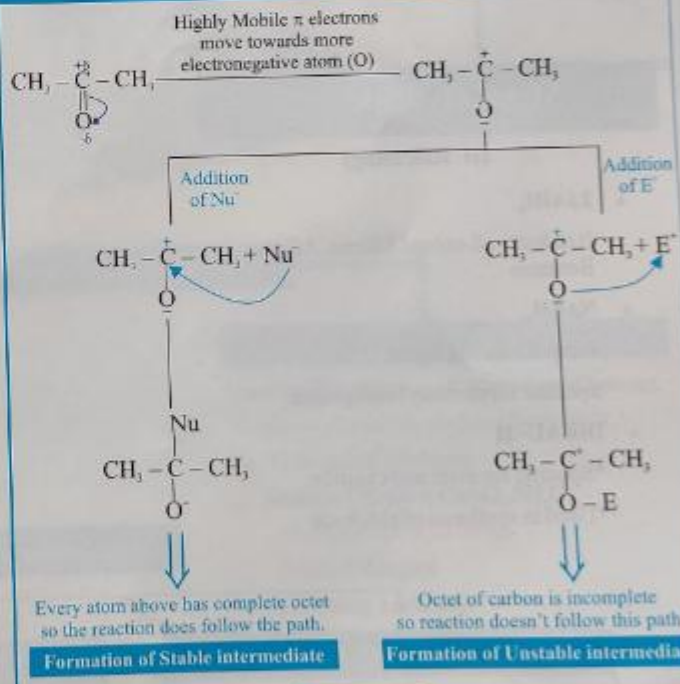


***Mechanism ⇒**





Nucleophilic Addition Reaction



Solvent

- **Non-Polar**
  - CCl_4
  - Benzene
  - Toluene
  - n-hexane
- **Polar**
  - **Polar Protic**
    - Facilitates S_N^1 reaction
    - Facilitates production of ions
    - H_2O
    - CH_3-OH
    - C_2H_5OH
    - CH_3COOH
  - **Polar Aprotic**
    - Facilitate S_N^2 reaction
    - Increases polarization
    - Displacement Increases
    - D.M.S.O. - Di-methyl sulphoxide
    - D.M.A. - Di-methyl acetamide
    - D.M.F. - Di-methyl formamide
    - D.M.P.A. - Di-methyl Propionic acid

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Reduction
In Organic Chemistry

Catalytic Hydrogenation

Syn addition of H^+(F.R.)

Homogeneous

- Catalyst gets dissolved in reaction mixture.
- Eg : (1) Wilkinson's catalyst
  $[Rh(Ph_3P)_3]Cl$
  (2) Metal + H_2 mixed in quinoline.

Heterogeneous

Eg : (1) Raney Ni (Ni + Al)

- More porous
- Size difference in Al and Ni.
- Large surface area.

Eg : (2) Metal + H_2
Ni/Pt/Pd/Ni_2B

- $R-COOH$, $R-\overset{O}{\overset{\|}{C}}-OR$, $R-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-R$, $R-\underset{O}{\underset{\|}{C}}-NH_2$ } Cannot be reduced by catalytic hydrogenation.

The only acid derivative that can be reduce by catalytic hydrogenation is oil halide

Metal with H^+ donor

- **Birch Reduction (Anti addition)**
  Liq. NH_3 + Na
- **Bouveault-Blanc Reduction**
  Na + C_2H_5OH
- **Stephen's Reduction**
  ($SnCl_2$ + HCl)
- **Clemmensen's Reduction**
  [Zn - Hg + HCl]

- **Step 1** – e^- released by metal.
- **Step 2** – Abstraction of H^+ from H^+ donar

Metal Hydride

(H^- Releasing)

- **$LiAlH_4$**
  It reduces all except Alkene, Alkyne, Benzene
- **$NaBH_4$**
  Weak Reducing agent
  Specific for carbonyl compound.
- **DiBAL - H**
  *Specific for ester and cyanide.
  *Used in synthesis of aldehyde

Other

- **Red P + HI**
  Oxygen containing functional group
  Alkanes —Converts into
- **Merrwein Ponndorf Verley reduction**
- **Wolf Kishner's Reduction**
  *[NH_2-NH_2, NaOH]

Oxidation of Alkenes/Alkynes

Weak O.A.

Detection of unsaturated hydrocarbons
| formation of
Vicinal di-ol
Eg. 1) Baeyer's Reagent
(Alkaline solution of **potassium permanganate**)
2) OsO_4 (osmium tetraoxide)
} syn addition of OH
3) Peroxyacids —— Anti addition of OH

Mild O.A.

Detection of position of = and ≡ bond
| formation of
Carbonyl compound
Eg. 1) O_3 + Zn/ H_2O
(Reductive Ozonolysis)

Strong O.A.

Estimation of C and H content
| formation of
Carboxylic Acid
Eg. 1) $KMnO_4$
2) $K_2Cr_2O_7$
3) O_3 + H_2O
[Oxidative ozonolysis]

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Oxidation
In Organic Chemistry

Oxidation of Alcohols

Hydrogen Abstractive O.A. (mild O.A.)/[Limited (O)]

- $R-CH_2-OH \xrightarrow{\text{mild O.A.}} R-CHO$
- $R-\underset{\underset{OH}{|}}{CH}-R \xrightarrow{\text{mild O.A.}} R-\underset{\underset{O}{\|}}{C}-R$
- $R-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-R \xrightarrow{\text{mild O.A.}}$ No Reaction (Due to absence of **C-H bond**)

Mild O.A can reduce only **C-H bond** containing compounds.
C-H bond has tendency to trap [O]

Eg. 1) P.C.C. (Pyridinium chlorochromate) : $[C_5H_5NH]^+[CrO_3Cl]^-$

2) PC - Collin's Reagent

3) PDC (Pyridinium di-chromate)

4) Cu/500°C

5) CrO_3 / H_2SO_4 (Jones' Reagent)

Oxygen Releasing O.A. (Strong O.A.)

Alcohol $(1^\circ / 2^\circ / 3^\circ) \xrightarrow{\text{Strong O.A.}}$ Acid

It Oxidises **C- H bond** as well as **C-C bond.**

Eg. 1) $KMnO_4/H^+$ 2) $K_2Cr_2O_7/H^+$ 3) HIO_4

HIO_4 : (periodic cleavage) It is used for compounds having more than one OH group. Eg.

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Oxidation of Alkane

- Alkanes generally resist oxidation.

Oxidation at 3° H

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H \xrightarrow{KMnO_4} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

- Only alkane which can be oxidized.

Oxidation of Carbonyl Compounds

Strong Oxidizing agent

Eg. $KMnO_4/H^+$, $K_2Cr_2O_7/H^+$

$$R-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Strong O.A.}} R-\underset{\underset{O}{\|}}{C}-OH$$

$$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{\text{Strong O.A.}} R-\underset{\underset{O}{\|}}{C}-OH + R'-\underset{\underset{O}{\|}}{C}-OH$$

Popoff's rule - During the oxidation of ketones, keto group always stays with the smaller alkyl group.

Mild Oxidizing agent

Used in differentiation of aldehyde and ketones.

***Ketones cannot be oxidized by mild O.A.**

Eg. 1) Benedict's Solution

Sodium Citrate + $CuSO_4.5H_2O$

Red ppt. of Cu_2O forms

2) Schiff Reagent

3) Fehling's solution

Fehling A + Fehling B

(Aq. $CuSO_4$) — **Sodium Potassium Tartarate or Roschelle salt**

Red ppt. of Cu_2O forms

4) Tollen's Reagent

It is also known as **Silver Mirror Test**

Ammonical Silver Nitrate – [$AgNO_3$ + NH_4OH]

$$[\overset{(+1)}{Ag}(NH_3)_2]OH \rightarrow \underset{\text{Silver ppt.}}{\overset{(0)}{Ag}}$$

POCO
SHOT ON POCO X2

Chapter – 4 Practical Organic Chemistry

Purification Methods

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 (b.p. = 334 K) and Aniline (b.p. = 457 K)

(ii) Mixture of Ether (b.p. = 308K) & Toluene (b.p. = 384 K)

(iii) Hexane (342K) and Toluene (384K)

(B) Fractional Distillation

When b.p. difference is 10K

Examples

(i) Crude oil in petroleum industry

(ii) Acetone (329K) and Methyl alcohol

(C) Distillation under Reduced Pressure (vacuum distillation)

When liquid boils at higher temperature and it may decompose before b.p. is attained.

Example (i) Concentration of sugar juice

(ii) Recovery of glycerol from spent lye.

(D) Steam Distillation

When the substance is immiscible with water and steam volatile.

$$\underset{\text{atm. pressure}}{P} = \underset{\text{V.P. due to organic liquid}}{P_1} + \underset{\text{V.P. due to water}}{P_2}$$

Example

(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	$Na + C + N \xrightarrow{\Delta} NaCN$	$(NaCN + FeSO_4 + H_2SO_4)$ Boil and cool $+FeCl_3$ + conc. HCl — $Fe_4[Fe(CN)_6]_3$ Prussian blue colour
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$	(i) $Na_2S + Na_2[Fe(CN)_5NO]$ Sodium nitroprusside $\rightarrow Na_4[Fe(CN)_5NOS]$ A deep violet colour (ii) $Na_2S + CH_3COOH + (CH_3COO)_2Pb \rightarrow$ A black ppt. ($PbS\downarrow$)
Halogen	$2Na + X_2 \xrightarrow{\Delta} 2NaX$	$NaX + HNO_3 + AgNO_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl. (ii) Pale Yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 confirms I.
Nitrogen and sulphur together		As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.

Quantitative Analysis of Organic Compounds

Estimation of carbon and hydrogen – Liebig's method

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \xrightarrow{\text{excess}} xCO_2 + y/2H_2O$$

$$\%\text{of C} = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of org. comp.}} \times 100$$

$$\%\text{of H} = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of org. comp.}} \times 100$$

Super Note : Method suitable for estimation if organic compound contains C and H only. If other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which is being absorbed in KOH and will increase the percentage of carbon and therefore following modification should be made.

Estimation of Nitrogen

Duma's method

The nitrogen containing organic compound yields nitrogen gas on heating it with copper (II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.

$$\%\text{of N} = \frac{28}{22400} \times \left(\frac{\text{Vol. of } N_2 \text{ (ml) collected at N.T.P.}}{\text{Wt. of organic compound}}\right) \times 100$$

Super Note : Method can be used to estimate nitrogen in all types of organic compound.

Kjeldahl's Method

In this method nitrogen containing compound on heating with conc. H_2SO_4 in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is.

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

Super Note : Method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (-N = N-) and nitrogen in the ring (pyridine) as Nitrogen of these compounds does not change to ammonium sulphate under these conditions.

POCO
SHOT ON POCO X2

ALKANES

Method of Preparation of Alkanes

$RCOOH \xrightarrow[\text{Soda lime}]{NaOH + CaO\ (3:1)/\Delta}$

- Carbanion intermediate product has one carbon less
- CaO forms $CaCO_3$ with CO_2 prevents backward reaction

$RCOONa \xrightarrow{\text{Kolbe's electrolysis}}$

- Anion of salt form $R^{\bullet}$ due to evolution of CO_2
- Products → Anode → Alkane with even no. of C + CO_2
- Cathode → H_2
- Solution → Base NaOH so pH ↑
- Methane cannot be prepared by this method. F.R. undergo dimerisation

$R\text{–}X \xrightarrow[\text{Wurtz reaction}]{Na / \text{ether}}$

- Methane cannot be prepared by this method
- Only symmetrical alkane can be prepared by this method in good yield.

$R\text{–}X \xrightarrow[\text{Frankland's reaction}]{\text{(i) Zn / Ether (ii) RX}}$

- $R^{\bullet}$ act as a nucleophile

$R\text{–}X \xrightarrow[\text{Corey-House synthesis}]{\text{(i) Li (ii) CuX (iii) R–X}}$

- R_2CuLi known as Gillman's reagent contains $R^{\bullet}$ as the active part
- For synthesis of asymmetrical alkanes

$R\text{–}X \xrightarrow[\text{Reduction}]{Zn/HCl\ (dil.)\ \text{or}\ LiAlH_4\ \text{or Red P/HI}}$ R–H or R–R

$R\text{–}Mg\text{–}X \xrightarrow[\text{or } NH_3 \text{ or } RNH_2]{HOH \text{ or } ROH}$

- $R^{\bullet}$ abstract active hydrogen

$RCOOH$ or ROH or $R\text{–}\underset{\underset{O}{\|}}{C}\text{–}R$ or $RCHO \xrightarrow[\text{Reduction}]{HI / \text{red P} / 140°C}$

- Red phosphors + HI converts all functional group into alkane

$R\text{–}\underset{\underset{O}{\|}}{C}\text{–}R$ or $R\text{–}\underset{\underset{O}{\|}}{C}\text{–}H \xrightarrow[\text{Clemmenson's reduction}]{Zn\text{–}Hg/HCl}$

- Clemmensen's reduction should not be used when the carbonyl compound has a basic group in it. For eg. OH, OR group

$R\text{–}\underset{\underset{R}{|}}{C}{=}O$ or $R\text{–}\underset{\underset{H}{|}}{C}{=}O \xrightarrow[\text{Wolff Kishner reduction}]{H_2N\text{–}NH_2 / KOH}$

- Not used when carbonyl compound has acidic group in it
  Eg. presence of CX bonds

$R\text{–}C{\equiv}CH$ or $R\text{–}CH{=}CH_2 \xrightarrow[\text{Sabatier Senderen's reaction}]{200\text{–}300°C,\ H_2/Ni}$

- Ease of hydroganation is inversely proportional to stearic hinderence near double bond

Some Other Methods of Preparation

1. Preparation of Methane from carbides

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

2. Methane from carbon monoxide

$CO + 3H_2 \xrightarrow[250°C]{Ni+C} CH_4 + H_2O$

POCO
SHOT ON POCO X2

Physical Properties

- **Boiling points and Melting points**

  Melting points and boiling points. $\propto$ Molecular mass $\propto \frac{1}{\text{No. of branches}}$ straight chain alkane have higher b.p. than branched chain alkane
- The even number members have higher m.p. as compared to next alkanes with odd number of carbon atoms. For eg. melting point of ethane > methane > propane.
-

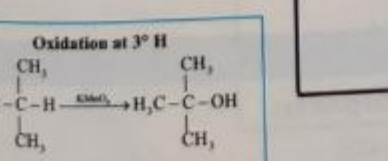
Physical state :	Solubility $\propto \frac{1}{\text{Molecular mass}}$
$C_1 \rightarrow C_4$ Gaseous state $C_5 \rightarrow C_{17}$ Liquid state (except neo pentane) C_{18} & above $\rightarrow$ Solid like wax Alkanes are lighter than water, so it floats over water	Alkanes are soluble in non-polar solvents like benzene, CCl_4, Cs_2 and insoluble in polar solvents like water

Chemical of Alkanes

R–H or R–R

- **Halogenation** — X_2/hv or UV light ($F_2 > Cl_2 > Br_2 > I_2$) → R–X
  - Free radical mechanism reactivity 3° > 2° > 1°
  - F_2 → explosive = occurs in Dark
  - Clorination → non-selective (reactive)
  - Bromination → selective
  - I_2 → slow = needs oxidising agent like HIO_3 to remove HI by forming I_2
- **Nitration** — HNO_3/400°C → R–N(=O)(–O)
  - Lower alkanes do not undergo nitration
  - Mixture of products formed
- **Sulphonation** — $H_2S_2O_7$ → R–SO_3H
  - Lower alkanes do not undergo sulphonation
- **Reed reaction** — $SO_2 + Cl_2$/hv → R–SO_2Cl
- **Isomerisation** — $AlCl_3$/HCl → Branched alkane
  - n-hexane → 2 methyl pentane + 3 methyl pentane
- **Pyrolysis (Cracking)** — 500–700°C → Alkenes + CH_4 or C_2H_6
  - Free radical mechanism
  - Dodecane → heptane + Pentene
  - Kerosene/Petrol → Oil gas/Petrol gas
- **Cr or Mo or V oxide** (Aromatisation/reforming) — $+Al_2O_3$/500°C → Aromatic compound
  - Dehydrogenation reaction
  - Alkane should have 6-Carbon or more
- **CH_2N_2/Δ** — step up reaction → Higher alkane
  - Carbon no. increases
  - Reactive part is methylene
- **O_2** — combustion → $CO_2 + H_2O$
  - $C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$
  - Highly exothermic - alkane used as fuel
  - If incomplete oxidation - carbon black is formed - used in Ink, Filters, Pigments
- **Catalytic Oxidation**
  - O_2 / Cu → R–CH_2OH
  - MoO → R–CHO + H_2O
  - $(AcO)_2$ Mn → R–COOH + $2H_2O$

Oxidation at 3° H



Only 3° Alkane which can be oxidized

POCO
SHOT ON POCO X2

ALKENES

Method of Preparation of Alkenes

$$R{-}CH_2{-}CH_2{-}OH \xrightarrow[-H_2O]{\text{conc. } H_2SO_4/170^\circ C}$$

- Acidic dehydration of alcohol
- H from β-carbon and OH from α-carbon is removed so called β-elimination

$$R{-}CH_2{-}CH_2{-}X \xrightarrow[-HX]{\text{alc. KOH}}$$

- β-dehydrohalogenation
- X = Cl, Br, I
- Rate = RI > RBr > RCl
- Rate = 3° > 2° > 1°

$$R{-}CH_2{-}CH_2{-}X \xrightarrow[-HX]{NaNH_2}$$

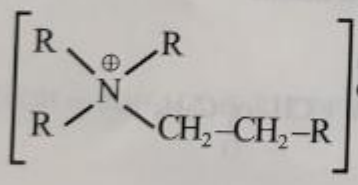
$$R{-}\underset{X}{CH}{-}\underset{X}{CH_2} \xrightarrow[-X_2]{\text{Zn dust}} R{-}CH{=}CH_2 \text{ or } C_nH_{2n}$$

- Vicinal dihalides undergo dehalogenation

$$R{-}C{\equiv}CH \xrightarrow[Pd + BaSO_4/CaCO_3]{H_2}$$

- Partial reduction with calculated amount of H_2
- Palladised charcoal is the catatyst
- Sulphur compounds or quinoline is used as catalytic poison
- Pd-C (lindlar's catalyst) = cis product
- Na-liquid NH_3 = trans product

$$\begin{array}{l} R{-}CH{-}COOK \\ \quad\;\; | \\ R{-}CH{-}COOK \end{array} \xrightarrow{\text{Kolbe's electrolysis}}$$

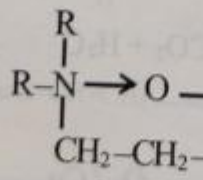


$$\xrightarrow[\text{Pyrolysis}]{\Delta}$$

- β-dehyrogenation
- E^2 elemination reaction
- OH^- abstracts hydrogen from β-position
- 3° amine is formed

$$R{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}R \xrightarrow[\text{Pyrolysis}]{\Delta}$$

- β-dehyrogenation
- E^2 elemination reaction



$$\xrightarrow[\text{Pyrolysis}]{\Delta}$$

- β-dehyrogenation
- E^2 elemination reaction

Physical Properties

- The boiling point of cis–alkenes is usually higher than corresponding trans–alkenes (More polarity).
- *B.P.* and *M.P.* decreases with increasing branches in alkene.
- The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans.

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Chemical Reactions of Alkenes

$R-CH=CH_2$

- $\xrightarrow{HX}$ $R-\underset{\underset{X}{|}}{CH}-CH_3$
  - Electrophilic addition
  - HX = HCl, HBr, HI → Rate = HI > HBr > HCl
  - Markovnikov's rule followed
- $\xrightarrow[\text{Peroxide}]{HBr}$ $R-CH_2-CH_2Br$
  - Anti Markovnikov's rule, kharash effect/peroxide effect
  - Free radical mechanism addition of HBr to unsymmetrical alkene
  - Not observed in HCl because HCl bond is stronger to break
  - Not observed in HI because I combines to form I_2 and does not react with alkene
- $\xrightarrow{X_2}$ $R-\underset{\underset{X}{|}}{CH}-CH_2X$
- $\xrightarrow{HOCl}$ $R-\underset{\underset{OH}{|}}{CH}-CH_2Cl$
  - Cl^+ acts as electrophile
- $\xrightarrow{\text{dil. } H_2SO_4}$ $R-\underset{\underset{OH}{|}}{CH}-CH_3$
  - Cold dilute H_2SO_4 used
  - Markovnikov's rule followed
  - Electrophyllic addition
- $\xrightarrow[(iii)\ NaBH_4]{(i)\ (AcO)_2Hg\ (ii)\ H_2O}$ $R-CH_2-CH_2-OH$ (Anti addition)
  - Addition of water according to Markovnikov's rule without re-arrangement
- $\xrightarrow[\text{Hydroboration}]{BH_3}$ $(RCH_2CH_2)_3B$
  - Addition of water according to anti-Markovnikov's rule
  - $\xrightarrow[\text{Hydrolysis}]{H_2O/H^\oplus}$ $R-CH_2CH_3$
  - $\xrightarrow[\text{Oxidation}]{H_2O_2/OH^-}$ $R-CH_2CH_2-OH$
- $\xrightarrow[\text{Syn addition}]{H_2/Ni\ (\text{Finely divided})}$ $R-CH_2-CH_3$
- $\xrightarrow[\text{Syn addition}]{OsO_4/H_3O^\oplus}$ $R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$
- $\xrightarrow[\text{1\% alkaline } KMnO_4]{\text{Baeyer reagent}}$ $R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$
  - Baeyer reagent - Alkaline cold dilute aqueous $KMnO_4$
  - Decolourisation of $KMnO_4$ = Test for unsaturationn
- $\xrightarrow[\text{Prelischave's reaction}]{\text{per acid}}$ $R-CH\underset{O}{\diagup\diagdown}CH_2 \xrightarrow{H_3O^\oplus} R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$
- $\xrightarrow[\text{ozonolysis}]{O_3 + H_2O + Zn}$ $R-CHO + HCHO$
  - Used to detect position of double bond
  - Addition of O_3 leads to formation of ozonoid ion
  - Ozonoid ion cleaved by Zn - H_2O
- $\xrightarrow[\text{ozonolysis}]{O_3 + H_2O}$ $RCOOH + HCOOH$
- $\xrightarrow[KMnO_4/H^\oplus]{\text{Strong oxidant}}$ $RCOOH + CO_2 + H_2O$
  - Product can be acid or ketone depending on nature of alkene and experimental conditions
- $\xrightarrow[\text{combustion}]{O_2}$ $CO_2 + H_2O$
- $\xrightarrow[500°C]{Cl_2}$ Allylic substitution product ($Cl-H_2C-CH=CH_2$)
- $\xrightarrow{NBS/\Delta}$ Allylic substitution product ($Br-H_2C-CH=CH_2$)
  - NBS releases Br^+ slowly
- $\xrightarrow[200-300°C]{Al_2(SO_4)_3}$ Isomerisation

POCO
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Physical Properties of Alkenes

Alkenes are colourless and odourless.

- These are insoluble in water and soluble in organic solvents.
- **Physical state :** C_2—C_4 ⟶ gaseous
  C_5—C_{15} ⟶ liquid
  C_{16} and above ⟶ solid like wax

Boiling and Melting point $\propto \dfrac{\text{Molecular weight}}{\text{No. of branches}}$

Saytzeff's Rule

- It states that "During dehydration of alcohols and dehydrohalogenation of alkyl halides the product formed is preferentially the one in which maximum number of alkyl groups are attached to the doubly bonded carbon atoms."
- More stable alkene is the major product.
- Good leaving group, less stearic hinderence favour saytzeff's product.
- Elimination from beta carbon having most hydrogen substitutes.
- 2-iodobutane giving 2-butene
- Elemination from β-position with respect to X (halogen).

Hofmann rule

- According to this rule, major product is always least substituted alkene i.e., major product is formed from carbon which has maximum number of hydrogen. Product of the reaction in this case is known as Hofmann product.
- Less stable alkene is the major product.
- Poor leaving group, more stearic hinderence and bulky base favour hofmann's product.
- Elimination from alpha carbon having the least hydrogen substitutes.
- 2-florobutane giving 1-butene in presence of tertiary butoxide ion.
- Elemination from α-position with respect to X-(halogen).

Super Note : Trick for when to apply Hofmann rule
B. S. F.
B → Bulky base
S → Stearic hinderence around β-hydrogen
F → Poor leaving group like florine

Markovnikoff's Rule

"During the addition of unsymmetrical reagents to unsymmetrical alkenes, the negative part of the addendum goes to carbon of double bond with least number of atoms"

$$CH_3-CH=CH_2+HBr \longrightarrow CH_3-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$

- The electrophilic addition to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.

Anti Markovnikoff's Rule

"Here due to presence of peroxide bromine free radicals are formed which attack the carbon (π bond system) which has greater no. of hydrogens.

$$CH_3-CH=CH_2+HBr \xrightarrow{\text{Peroxide}} \underset{\text{(minor)}}{CH_3-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H} + \underset{\text{(major)}}{CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-H}$$

- Only HBr adds on by Anti Markovnikoff's Rule (in presence of organic peroxide) not HCl or HI.

POCO
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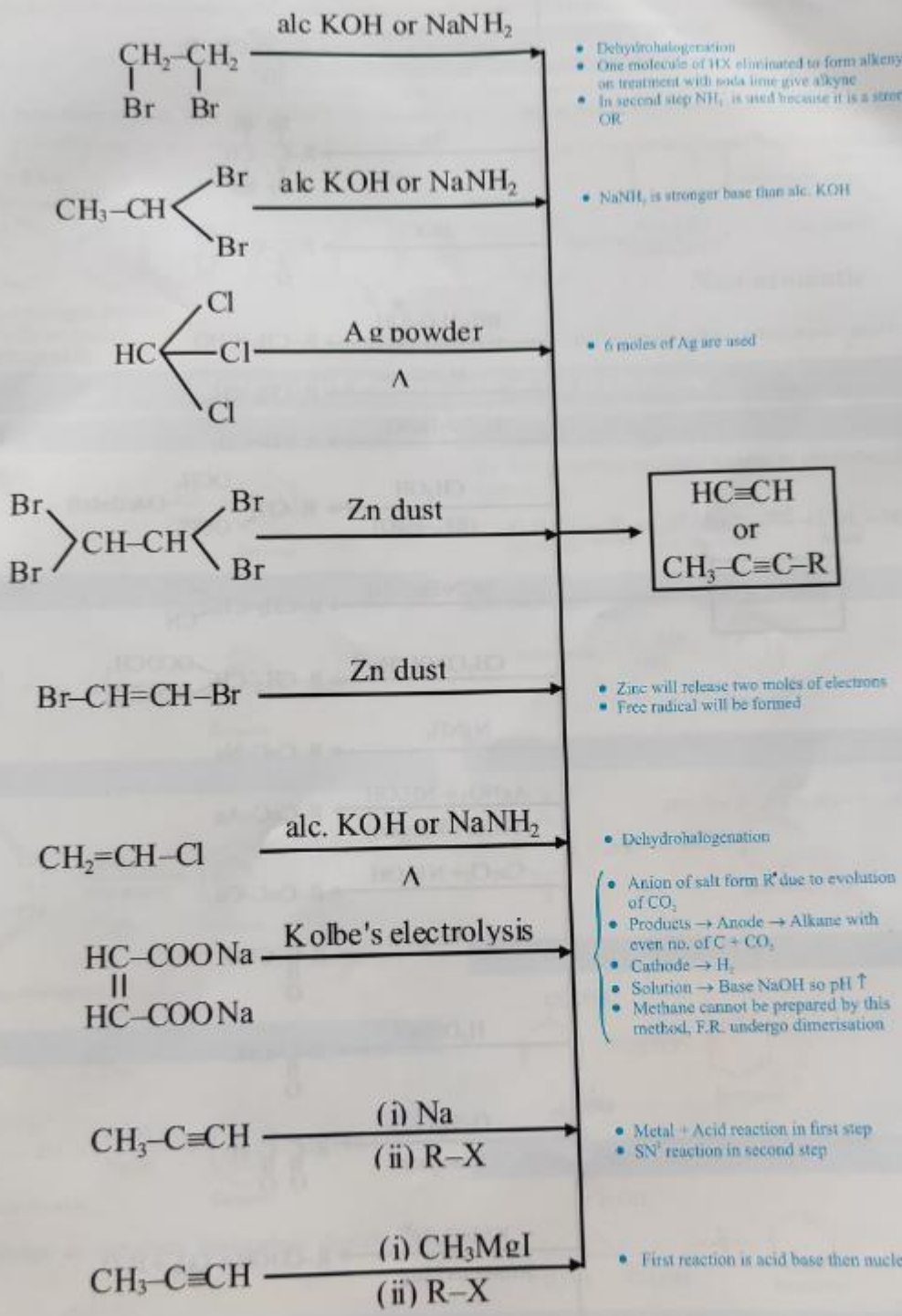
ALKYNES

Method of Preparation of Alkynes



Industrial scale preparation of ethyne from calcium carbide

Step - 1 $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ (Limestone → Quick lime) **Step - 2** $CaO + 3C \longrightarrow CaC_2 + CO$ (Coke → Calcium carbide) **Step - 3** $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + CH \equiv CH$

Important Note : Physical Properties of Alkynes (same as alkene and alkane)

POCO
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Chemical Reactions of Alkynes

- Alkynes give electrophilic addition reaction twice
- Lesser reactive than alkenes because of less stable intermediate
- Gem dihalides are formed

$R-C\equiv CH \xrightarrow{HX} R-\underset{X}{\underset{|}{C}}(X)-CH_3$

$R-C\equiv CH \xrightarrow{HBr/Peroxide} R-\underset{Br}{\underset{|}{CH}}-CH_2-Br$

- Reddish orange colour of solution of bromine in CCl_4 is decolourised
- This is test for unsaturation

$R-C\equiv CH \xrightarrow{Br_2} R-\underset{Br}{\underset{|}{C}}(Br)-\underset{Br}{\underset{|}{CH}}(Br)$

- Cl^+ acts as electrophile

$R-C\equiv CH \xrightarrow{HOCl} R-\underset{O}{\underset{\|}{C}}-CH(Cl)_2$

- Addition of water twice according to anti-Markovnikov's rule

$R-C\equiv CH \xrightarrow{BH_3/H_2O_2/\overset{\ominus}{O}H} R-CH_2-CHO$

$R-C\equiv CH \xrightarrow{H_2/Ni} R-CH_2-CH_3$

$R-C\equiv CH \xrightarrow{H_2/Pd-BaSO_4} R-CH=CH_2$

$R-C\equiv CH \xrightarrow[(BF_3-HgO)]{CH_3OH} R-CH(OCH_3)_2$ (Methylal)

$R-C\equiv CH \xrightarrow{HCN/Ba(CN)_2} R-CH_2-CH(CN)_2$

$R-C\equiv CH \xrightarrow{CH_3COOH/Hg^{+2}} R-CH_2-CH(OCOCH_3)_2$

- Reaction occurs due to acidic nature of hydrogen H attached to sp hybridised carbon
- Acidic nature →
  $HC\equiv CH > CH_3-C\equiv CH >> CH_3-C\equiv C-CH_3$

$R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv C-Na$

$R-C\equiv CH \xrightarrow[\text{(Tollen's Reagent)}]{AgNO_3+NH_4OH} R-C\equiv C-Ag$

$R-C\equiv CH \xrightarrow{Cu_2Cl_2+NH_4OH} R-C\equiv C-Cu$

$R-C\equiv CH \xrightarrow{\text{Baeyer Reagent}} R-\underset{O}{\underset{\|}{C}}-CHO$

$R-C\equiv CH \xrightarrow{H_2O/Hg^{+2}} R-\underset{O}{\underset{\|}{C}}-CH_3$

- Higher alkynes give diketones which are further oxidised to carboxylic acid

$R-C\equiv CH \xrightarrow[\text{ozonolysis}]{O_3/H_2O/Zn} R-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-H$

$R-C\equiv CH \xrightarrow[\text{Strong oxidant}]{KMnO_4/H^{\oplus}} R-COOH + CO_2 + H_2O$

$R-C\equiv CH \xrightarrow{\text{Combustion}} CO_2 + H_2O$

Super Note :

Linear polymerisation of Alkynes $CH\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} (CH=CH-CH=CH)_n$

Under suitable condition polymer conducts electricity

Film of polyacetylene is used as electrode in battery because it is better conductor, lighter and cheaper than metals

POCO
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AROMATIC HYDROCARBON

Aromaticity

Huckel's rule :
For aromaticity the molecule must be planar, cyclic system having delocalised $(4n+2)\pi$ n electrons where n is an integer equal to 0, 1, 2, 3.

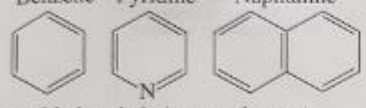
Cyclic Planar Conjugated

Both classes meet these criteria. They only differ in the number of e

When any of the followingtwo criteria are not fulfilled

$4n + 2\ \pi\ e^-$

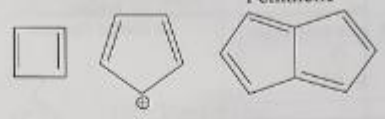
Benzene Pyridine Naphtaline



Double bonded nitrogen doesnot participate in resonance

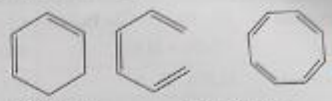
Aromatic

$4n\ \pi\ e^-$



Pentalene

Antiaromatic



Tub shaped

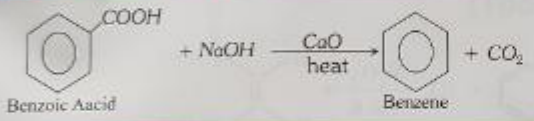
Not fully conjugated

Not planar

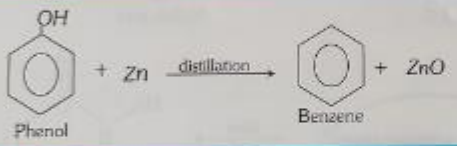
Non-aromatic

Method of Preparation of Benzene

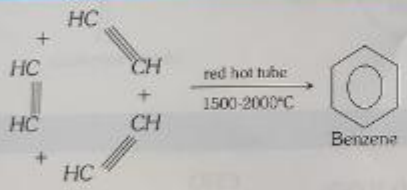
(1) From Benzoic Aacid



(2) From Phenol

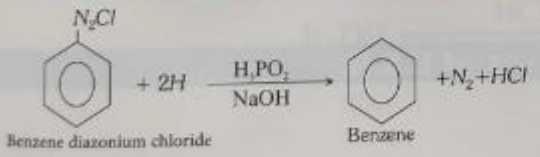


(3) From Alkynes



Three molecules of acetylene

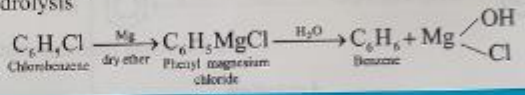
(4) From Benzene Diazonium Salt



Diazonium salt helps to introduce nucleophile directly into benzene ring

(5) From Grignard Reagent

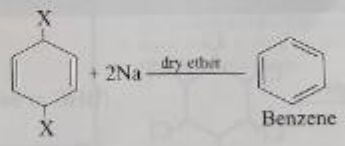
By first preparing grignard reagent of chlorobenzene and then hydrolysis



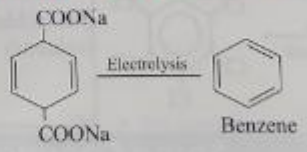
(6) Aromatization

n-hexane $\xrightarrow[500°C]{Cr_2O_3 + Al_2O_3}$ Benzene

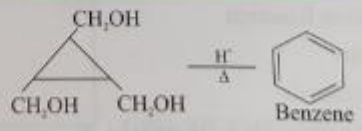
(7) From Wurtz Reaction



(8) From Kolbe's Electrolysis



(9) From Dehydration of Alcohols



Substituents on Benzene Ring

Ortho and para Directing

Electron releasing groups increase electron density at ortho and para position (activating groups)

Strongly activating	Moderatly activity	Weakly activating
$-NH_2$, $-O^-$, $-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OR$	$-NH-\overset{O}{\overset{\|\|}{C}}-CH_3$, $-O-\overset{O}{\overset{\|\|}{C}}-CH_3$	$-CH_3$; $-C_2H_5$, $-C_3H_7$ [Sacrificial hyperconjugation]

Meta Directing

Electron releasing groups decrease electron density at ortho and para position (Deactivating group)

Strongly deactivating	Moderatly deactivating	Weakly deactivating
$-\overset{\oplus}{N}H_3$, $-\overset{\oplus}{N}R_3$, $-CF_3$, $-CCl_3$, $-NO_2$	$-SO_3H$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-CH_3$, $-\overset{O}{\overset{\|}{C}}-OH$	$-Cl$, $-Br$, $-F$ [O & P directing] $-CH_2=CH_2-Cl$

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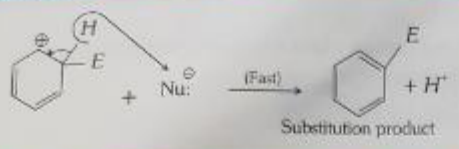
Chemical Reactions of Benzene

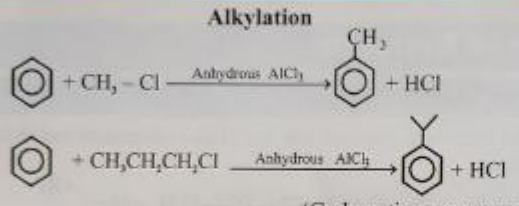
(1) Electrophilic Substitution reactions (Summary)



Reaction	Reagent	Intermediate
(1) Halogenation	Cl_2, Br_2, ($FeCl_3$, $FeBr_3$)	Cl^+ / Br^+
(2) Nitration	$HNO_3 + H_2SO_4$	NO_2^+, Nitronium ion
(3) Sulphonation	H_2SO_4 & Δ	SO_3
(4) Alkylation	CH_3Cl & $AlCl_3$	CH_3^+ / R^+ (can rearrange)
(5) Acylation	$CH_3-\overset{O}{\overset{\|}{C}}-Cl$ & $AlCl_3$	$CH_3-\overset{O}{\overset{\|}{C}}^+$ / $R-\overset{O}{\overset{\|}{C}}^+$

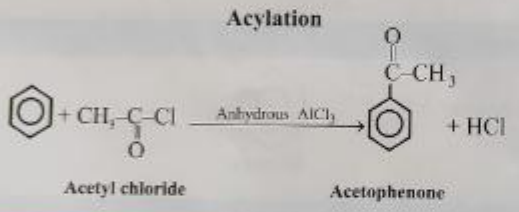
(2) Friedel Crafts Reaction

Alkylation

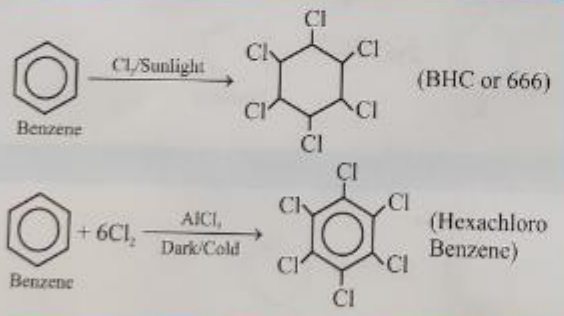


(Carbocation rearrangement)

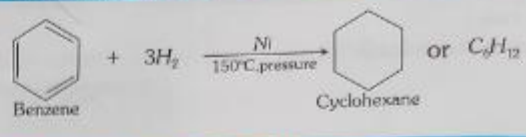
Acylation



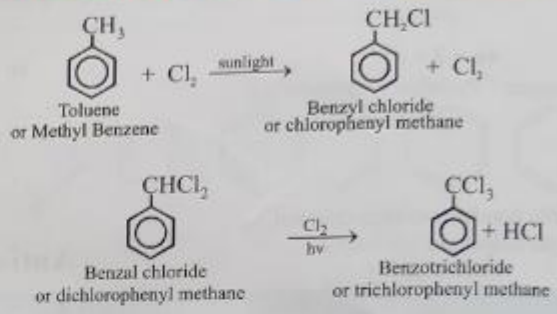
(3) Halogenation of Benzene



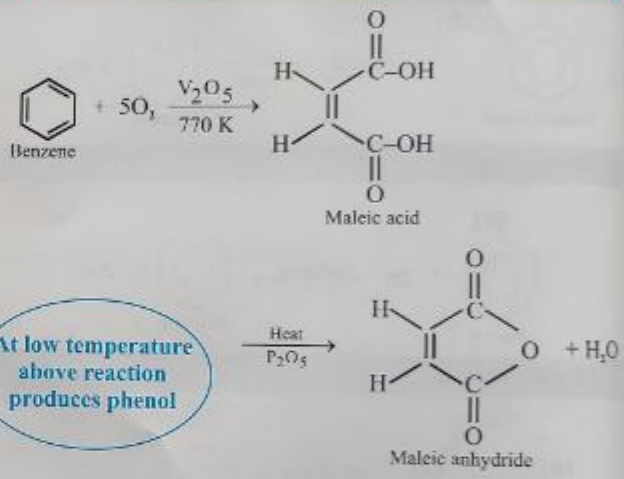
(4) Addition of hydrogen



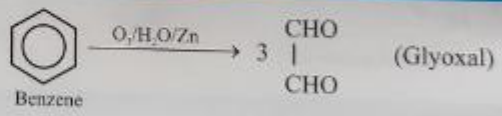
(5) Halogenation of side chain



(6) Oxidation



(7) Ozonolysis of Benzene



Some Common Features of E.S.R.

- Electromeric Effect
- Electrophilic Substitution Reaction
- To Maintain Aromaticity
- H^+ is replaced by Electrophile
- H^+ can not act as Electrophile (HCl, HF, HNO_3)

POCO
SHOT ON POCO X2

ALKYL HALIDE

Method of Preparation of Alkyl Halide

- Order of reactivity of X_2 for a given alkane is, $F_2 > Cl_2 > Br_2 > I_2$
- The reactivity of the alkanes follows the order 3°alkane > 2°alkane > 1°alkane.

$R–H \xrightarrow{X_2/hv}$ R–X
- Free radical mechanism
- Isomeric mono & polyhaloalkanes are formed that are difficult to separate.

$Alkene \xrightarrow{HX}$ R–X
- Electrophilic addition reaction
- Markovnikov's rule is followed

$Alkene \xrightarrow{HBr/Peroxide}$ R–X
- Free radical mechanism
- Anti-Markovnikov's rule is followed

$R–NH_2 \xrightarrow[\text{(Tilden reagent)}]{Cl–N=O}$ R–X

$R–OH \xrightarrow[SOCl_2/Pyridine]{\text{Darzen reaction}}$ R–X
- Preparation by this method is preferred because other product (SO_2, HCl) are gases that escape out

$R–OH \xrightarrow{PCl_3 \text{ or } PCl_5}$ R–X
- Phosphorus tribromide and triiodide are prepared insitu (in reaction mixture) through Red P + Br_2/I_2
- Axial bonds of PCl_5 are reactive because they are longer than equatorial bonds

$R–OH \xrightarrow[NaBr + H_2SO_4]{HI \text{ or } HBr \text{ or}}$ R–X

$R–OH \xrightarrow[\text{(Lucas reagent)}]{HCl + ZnCl_2}$ R–X
- The reactivity order of *HX* (HI > HBr > HCl > HF)
  Reactivity order of alcohols 3° > 2° > 1°

$R–\underset{\underset{O}{\|}}{C}–OAg \xrightarrow[\text{Hunsdiecker reaction}]{Br_2/CCl_4}$ R–X
- Decarboxylation reaction
- AgBr precipitate

Physical Properties of Alkyl Halides

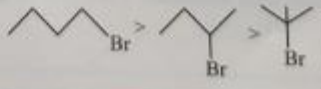
(1) Dipole moment : $CH_3–Cl > CH_3–F > CH_3–Br > CH_3–I$

(2) Bond enthalpies : $CH_3–F > CH_3–Cl > CH_3–Br > CH_3–I$

(3) Density : $n–C_2H_5Cl < n–C_2H_5Br < n–C_2H_5I$

(4) Solubility : slightly soluble in water.

(5) Boiling point : R – I > R – Br > R – Cl > R – F



$$\text{B.p.} \propto \frac{1}{\text{branching}}$$

POCO
SHOT ON POCO X2

Chemical Reactions of Alkyl Halide

- Methane cannot be prepared by this method

(Wurtz reaction) Na/dry ether → R–R

(Frankland reaction) Zn/dry ether → R–R

- R_2CuLi known as Gilman's reagent contains R as the active part
- For synthesis of asymmetrical alkanes

Corey-House reaction → R–R′

(i) Li (ii) CuX (iii) R′–X

- Reduction due to release of H from reagents
- Nascent hydrogen obtained from Zn-Cu couple and alcohol or Zn and HCl or Sn and HCl or Na and alcohol can be used to reduced RX

Reduction → R–H

$LiAlH_4$ or $NaBH_4$ or Ph_3SnH

- Nucleophillic substitution
  All organo metallic reagents release R here

R–MgX or RLi or RNa or R_2Zn or R_2Cd → R–R

or R_2CuLi (Organo metallic reagents)

- For a given alkyl group, the ease of formation of Grignard's reagent is of the order iodide > bromide > chloride

R–CH=CH–MgX → R–CH=CH–R

R–C≡C–Na or R–C≡C–MgX → R–C≡C–R

- Dry acetone is used
- NaX formed is precipitated in dry acetone so forward reaction is favoured (NaX is insoluble in acetone)

(Finkelstein reaction) NaI/acetone → R–I + NaX (X = Cl, Br)

- Other metal flourides that can be used are Hg_2F_2, CoF_2, SbF_3

(Swart reaction) AgF/DMSO → R–F + AgX (X = Cl, Br)

- OR^- is the active part of reagent

(Williamson reaction) RONa → R–O–R

R–X

(Streker reaction) Na_2SO_3 → $R–SO_3Na$

- OR^- is the active part of reagent
- Symmetrical ether formed

$R\ddot{\underset{..}{O}}H$ or dry Ag_2O → $R–\ddot{\underset{..}{O}}–R$

- Nucleophile = OH^-

$H_2\ddot{\underset{..}{O}}$ or aq. NaOH or moist Ag_2O → $R–\ddot{\underset{..}{O}}H$

- Nucleophile = $RCOO^-$

RCOONa or RCOOAg → R–COOR

- Nucleophile = $\ddot{N}H_3$

$\ddot{N}H_3$ → $R–\ddot{N}H_2$

- Nucleophile = $R–\ddot{N}H_2$

$R–\ddot{N}H_2$ → $R–\ddot{N}H–R$

- Nucleophile = $R–\ddot{N}H–R$

$R–\ddot{N}H–R$ → $R_3\ddot{N}$

- Nucleophile = $R_3\ddot{N}$

$R_3\ddot{N}$ → $R_4\overset{\oplus}{N}\overset{\ominus}{X}$

- Nucleophile = CN^- (carbon transfers electrons)

KCN/(Ionic) → R–C≡N

- Nucleophile = Ag – C ≡ $\ddot{N}$ (Nitrogen transfers electrons)

AgCN (covalent) → R–N≡C

- Nucleophile = O = N – O (oxygen transfers electrons)

KO–N=O (Ionic) → R–O–N=O

- Nucleophile = Ag – $\ddot{O}$ – $\ddot{N}$ = $\ddot{O}$:
- N is less electronegative than O so it donates its lonepair

Ag–O–N=O (covalent) → R–N(=O)(→O)

POCO
SHOT ON POCO X2

Nucleophilic substitution reactions

Reactions	S_N2	S_N1
1. No. of Steps	One: $R-L+:\overset{\ominus}{N}u \rightarrow R-Nu+L^-$	Two: (i) $R-L \xrightarrow{Slow} R^+ + :L^-$ (ii) $R^+ + Nu \xrightarrow{Fast} R-Nu$
2. ROR & Order of Reaction	Rate $\propto$ [Substrate] [Nucleophile] Second order	Rate $\propto$ [Substrate] First order
3. Stereochemistry	inversion	Resemization (inversion + Retaintion)
4. Reactivity order of Alkyl Halide	Methyl > 1°>2°>3° halides : $I_2 > Br_2 > Cl_2 > F_2$	3°>2°>1° > methyl halides : $I_2 > Br_2 > Cl_2 > F_2$
5. Intermediate	No I.M. formation	Carbocation
6. Rearrangement	No rearranged product is formed (except for allylic).	Rearranged products can be formed
7. Nature of Nucleophile	Favoured by strong and high concentration of nucleophiles	Favoured by mild and low concentration of nucleophiles
8. Reaction rate determining factor	By steric hindrance.	By electronic factor (stability of $\overset{\oplus}{C}$).
9. Leaving Group	Need good Leaving Group	Need good Leaving Group
10. Solvent	Polar aprotic solvent	Polar protic solvent

Elimination Reaction

Reactions	E_1	E_2
1. No. of Steps	Two step $R-L \rightarrow \overset{\oplus}{R} \rightarrow$ alkene	One Step $R-L+\overset{\ominus}{B} \rightarrow$ alkene + BH + $L^\ominus$
2. Order of Reaction	1st Order Reaction	2nd Order Reaction
3. ROR	ROR $\propto$ [R-L]	ROR $\propto$[R-L][Nu^-]
4. Nucleophile	Weak Nucleophile	Needs Strong [Nu^-]
5. Substrate Reactivity	3° > 2° > 1°	1° > 2° > 3°
6. Intermediate	Carbocation	No I.M. formation
7. Rearrangement	Possible	Not Possible
8. Leaving Group	Needs good L.G.	Needs good L.G.
9. Solvent	Polar Protic Solvent	Polar aprotic Solvent
10. Stereochemistry	Recemisation	Inversion

Order of reactivity of Alkyl Halide towards

$S_N1 \Rightarrow$ Benzylic > Allylic > 3° > 2° > 1°

$S_N1 \propto$ Stability of carbocation

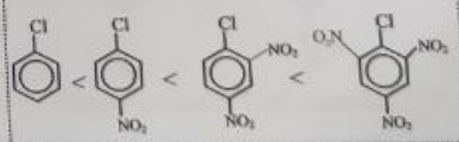
$S_N2 \Rightarrow$ 1° > 2° > 3°

$$S_N2 \propto \frac{1}{\text{Steric hindrance}}$$

Reactivity order of RX towards S_N1 or S_N2 and E_1 or E_2

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

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



Action of heat

$$RCH_2CH_2X \xrightarrow{300°C} \underset{\text{Alkene}}{RCH=CH_2} + HX$$

Iodide > Bromide > Chloride(When same alkyl group is present)

Tertiary > Secondary > Primary (When same halogen is present).

Super Note

Vinylic halides and aryl halides do not give a silver halide precipitate, when treated with alc. $AgNO_3$ because vinylic and phenyl cations are very unstable and therefore, do not form readily.

POCO
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SUMMARY OF S_N1, S_N2, E_1 and E_2 Reaction

	Mechanism	$\overset{\ominus}{Nu}/\overset{\ominus}{B}$	Solvent	Temp.
1°	S_N2	Better Nu: $\overset{\ominus}{O}H, C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E_2	Strong & bulky base $(CH_3)_3C\overset{\ominus}{O}$		High
2°	S_N2	$\overset{\ominus}{H}O; C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E_2	$(CH_3)_3C\overset{\ominus}{O}$		High
	S_N1	Solvent	Polar protic	Low
	E_1	Solvent		High
3°	S_N1	Solvent	Protic	Low
	E_1	Solvent	Protic	High

Preferance of type of reaction for various substituted Alkyl Halide

	Primary (1°)	Secondary (2°)	Tertiary (3°)
Strong nucleophile	$S_N2 >> E_2$	$S_N2 + E_2$ (if weak base, S_N2 favoured)	E_2
Weak nucleophile weak base	Mostly S_N2	Mostly S_N2/S_N1	Mostly S_N1 at low T mostly E_1 at high T
Weak nucleophile strong base	Mostly E_2	Mostly E_2	E_2

Some important chemical reaction of chloroform

(1) Hydrolysis

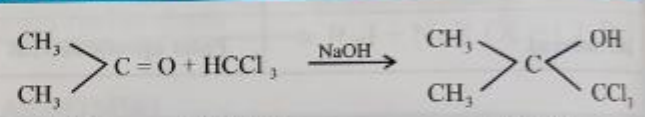
$$\underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{-3KCl} \underset{\text{Unstable}}{CH(OH)_3} \xrightarrow{-H_2O} \underset{\text{Formic acid}}{HCOOH} \xrightarrow[(-H_2O)]{KOH} \underset{\text{Pot. formate}}{HCOOK}$$

(2) Nitration

$$\underset{\text{Chloroform}}{Cl_3CH} + HO.NO_2 \longrightarrow \underset{\text{Chloropicrin}}{Cl_3CNO_2} + H_2O$$

Poisonous gas

(3) Condensation with ketones, *e.g.* acetone



Acetone Chloroform Chloretone

hypnotic agent

Super Note : Tests of chloroform

(i) It gives isocyanide test (Carbylamine test).

(ii) It forms silver mirror with Tollen's reagent.

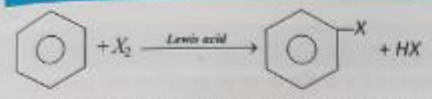
(iii) Pure Chloroform does not give white precipitate with silver nitrate.

POCO
SHOT ON POCO X2

ARYL HALIDE

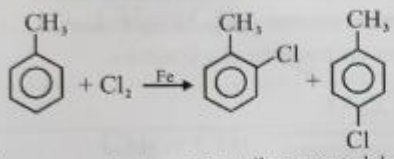
Method of Preparation of Aryl Halide

(1) By direct halogination of benzene ring



Lewis acid = $FeX_3, AlX_3, Tl(OAc)_3$, $X_2 = Cl_2, Br_2$

- Chlorination of toluene in the presence of iron (using equimolar quantities) gives a mixture of o- and p- chlorotoluenes.



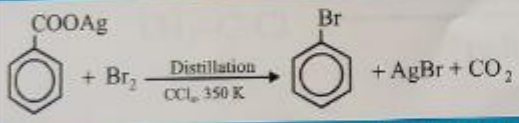
Ortho para products can be easily separated due to large difference in melting point

- Aryl iodides cannot be prepared by direct iodination because the reaction is reversible and hydroiodic acid formed being a strong reducing agent reduces C_6H_5I to C_6H_6.

To overcome this difficulty, iodination is carried out in the presence of oxidizing agent such as nitric acid, mercuric oxide (HgO) or iodic acid, which oxidizes the hydroiodic acid to iodine and thus the reaction proceeds in the forward direction.

- Aryl fluorides cannot be prepared by this method because fluorine is highly reactive and the reaction is very violent and uncontrolable.

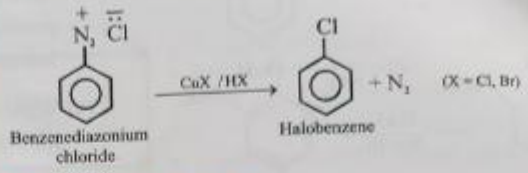
(2) By Hunsdiecker Reaction



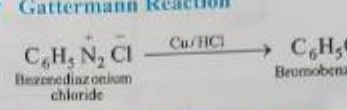
(3) From Diazonium salts

(a) Preparation of chlorobenzene and bromobenzene

- **Sandmeyer's reaction**

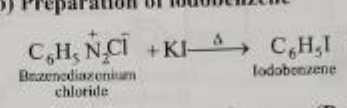


- **Gattermann Reaction**

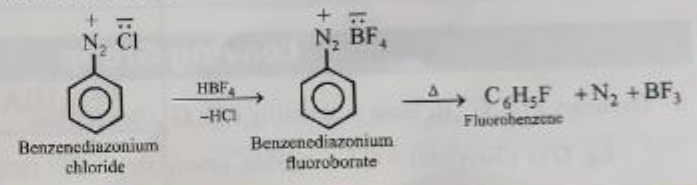


Super Note : Better yield in Sandmeyer reaction Salt is used.

(b) Preparation of iodobenzene



(c) Preparation of fluorobenzene (Balzschiemann reaction).

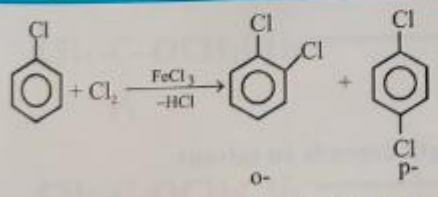


(4) From phenol

Chemical Reactions of Aryl Halide

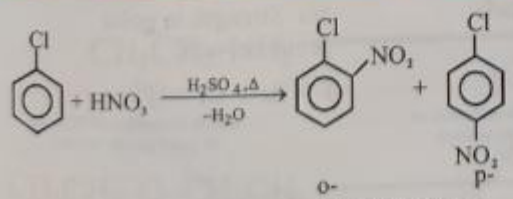
Electrophilic aromatic substitution

Halogenation



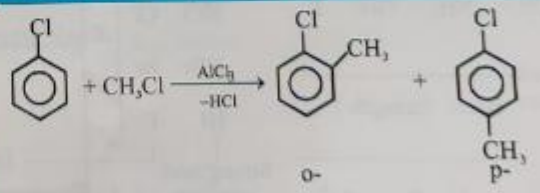
Dichloro benzene

Nitration



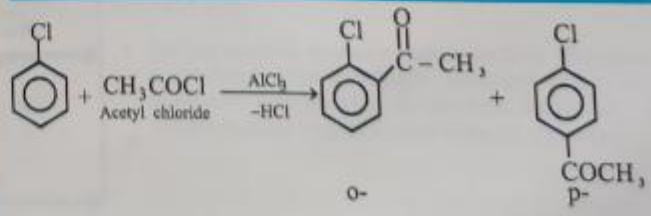
Nitrochlorobenzene

Friedel - craft alkylation reaction



Chloro toluene or Tolyl chloride

Friedel Craft acylation reaction



Chloro acetophenone

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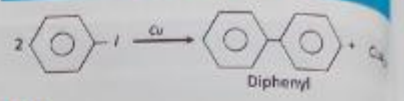
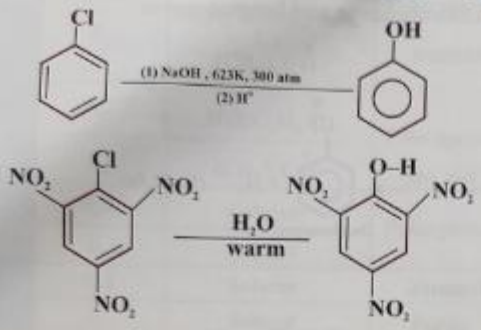
Wurtz – fittig reaction	Formation of grignard reagent	Ullmann reaction
$C_6H_5Br + CH_3Br \xrightarrow[\text{Ether}]{Na} C_6H_5CH_3 + 2NaBr$	$C_6H_5Br \xrightarrow[\text{Ether}]{Mg} C_6H_5MgBr$	

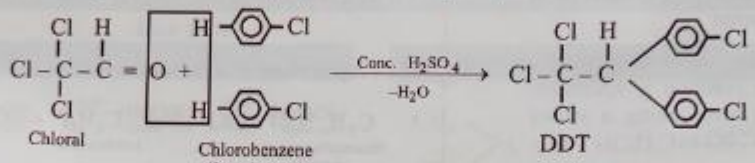
N.S.R. – Nucleophilic Substitution Reaction



(a) Presence of electron-withdrawing groups *e.g.*, $-NO_2$, $-CN$, SO_3H, $-CHO$, $-COOH$, etc. especially at the o- or p- position but not at m-position w.r.t. the halogen increases the ease of replacement of halogen by nucleophile.

(b) While electron donating groups like $-NH_2$, $-OH$, $-OR$ etc. at o- or p-position with respect to halogen atom donates electron due to resonance and thus reduces positive charge on the C-atom of C–Cl bond and thus decreases the reactivity of aryl halides.

Super Note : DDT (p, p' - dichlorodiphenyl trichloroethane)



2, 2–bis–(p–chlorophenyl) 1, 1, 1– trichloroethane

Leaving Group (Beyond NCERT)

- Tendency of L.G. Release ∝ Stability of L.G. after release.

  Eg. OTs^- (Tosylate) > OAc^- > OMe^- (mesylate) > OEt^-

- $H_2O > R\text{-}OH > CH \equiv CH > NH_3 > (CH_2 - CH_2) > CH_4$ **Acidic Strength**
- $OH^- < RO^- < CH \equiv C^- < NH_2^- < CH_2 = CH_2^- < CH_3^-$ **Conjugate base**

$$\text{Basic Strength of C.B.} \propto \frac{1}{\text{Tendency of L.G. to Release}}$$

Strong acid in period

CH_4	NH_3	H_2O	HF	HF	F^-
CH_3^-	NH_2^-	OH^-	F^-	HCl	Cl^-
				HBr	Br^-
				HI	I^-

Basic strength ↓

Periodicity of Bases — Basic Strength ↑

Nu Strength ↑

Strong acid in group

In a group Nu^- strength depends on solvent

Polar Aprotic

Nu^- strength in polar aprotic solvent

$F^- > Cl^- > Br^- > I^-$

due to diffusion of e⁻ in orbitals

Polar Protic

Nu^- Strength in polar protic solvent

$I^- > Br^- > Cl^- > F^-$

due to formation of H-bond in polar protic solvent

POCO
SHOT ON POCO X2

ALCOHOL

Method of Preparation of Alcohol

$CH_2=CH_2 \xrightarrow{H_2O/H^{\oplus}}$
- According to Markovnikoff's rule &
- Rearrangement is possible

$CH_2=CH_2 \xrightarrow{BH_3/H_2O_2/\overset{\ominus}{O}H}$
- According to anti Markovnikoff rule & with no rearrangement

$CH_2=CH_2 \xrightarrow{(AcO)_2\,Hg/H_2O/NaBH_4}$
- According to Markovnikoff's rule & with no rearrangement

$CH_3CH_2{-}Cl \xrightarrow{aq.\ NaOH}$
- The SN2 reaction - A Nucleophilic Substitution in which the Rate Determining Step involves 2 components. -SN2 reactions are bimolecular with simultaneous bond-making and bond-breaking steps.

$H{-}\underset{\underset{O}{\|}}{C}{-}H \xrightarrow{CH_3MgBr/H_3O^{\oplus}}$
- Nucleophilic adition reaction $CH_3^{\ominus}$ acting as nuclephile

$CH_3{-}CH{=}O \xrightarrow[reduction]{H_2/Pd\ or\ LiAlH_4/H^{\oplus}}$
- In case of H_2/Pd. reducing specie is hydrogen free radical. In case of $LiAlH_4/H^-$ reducing specie is part is hydride ion

$CH_3{-}\underset{\underset{O}{\|}}{C}{-}Cl \xrightarrow[reduction]{LiAlH_4/H^{\oplus}}$
- S_{N_1} reaction → **CH_3CH_2OH Ethyl alcohol**

$CH_3{-}\underset{\underset{O}{\|}}{C}{-}OCH_2CH_3 \xrightarrow[reduction]{LiAlH_4/H^{\oplus}}$
- S_{NAC} reaction

$CH_3{-}\underset{\underset{O}{\|}}{C}{-}OCH_2CH_3 \xrightarrow{NaOH}$
- S_{NAE} reaction

$CH_3{-}\underset{\underset{O}{\|}}{C}{-}OCH_2CH_3 \xrightarrow[reversible\ reaction]{H_3O^{\oplus}}$
- S_{NAE} reaction

$CH_3CH_2{-}NH_2 \xrightarrow[or\ HNO_2]{NaNO_2 + HCl}$
- Primary aliphatic diazonium salt to not have conjugated double bonds to get stabilised by resonance so they are much more unstable while the aromatic diazonium salt has benzene ring which stabilises the molecule.

$CH_3CH_2{-}O{-}CH_2CH_3 \xrightarrow[\Delta]{dil.\ H_2SO_4}$

POCO
SHOT ON POCO X2

Physical Properties of Alcohol

(A) Boiling Point

- Due to intermolecular hydrogen bonding boiling points of alcohols are higher than hydrocarbon and ethers.
- 1° alcohol > 2° alcohol > 3° alcohol (B.P. follows the trends)
- If degree of alcohols are same then

$$\text{Boiling point of Alcohol} \propto \frac{1}{\text{No. of branches from parent chain}}$$

(B) Solubility

- The lower alcohols (with small alkyl groups) are miscible in water
- $$\text{Solubility} \propto \frac{1}{\text{Size of alkyl groups}}$$
- Increase in carbon-chain increases organic part hence solubility in water decreases since carbon chain is hydrophobic
- Super Note : Because of the strength of the attraction of the OH group, first three alcohols (methanol, ethanol and propanol) are completely miscible. They dissolve in water in any amount.
  # Patiala peg

Chemical Reactions of Alcohol

(A) Reactions involving cleavage of O – H Bond (Reactions showing acidic behaviour of alcohol)

(1) Reaction with Active metals

$$2RO-H + 2M \rightarrow 2ROM + H_2 \ (M = Na, K, Mg, Al, \text{etc.})$$

(2) Reaction with Grignard Reagent

$$R-MgX + H-OR' \text{ ——— } R-H + R'-OMgX$$

(3) Esterification (S$_N$2 Mechanism)

$$R-\overset{\overset{O}{\|}}{C}-OH + H-O-R' \xrightarrow{H^+} R-\overset{\overset{O}{\|}}{C}-OR' + HOH$$

Super Note : OH is removed from carboxylic acid and H is removed from alcohol.

Super Note : The size of alkyl group increases rate of Esterification decreases both for acid and alcohol

- Alcohols are acidic in nature but they are less acidic than water hence they do not give H^+ in aqueous solution. They do not change the colour of litmus paper.
- Super Note : $HOH > ROH > CH \equiv CH > NH_3 > RH$
  Order of acidic nature
- Acidic nature of alcohol decrease with increase of alkyl groups on – OH bonded carbon due to +I (inductive) effect of alkyl group.

$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH > R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-OH > R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-OH$$

- Alcohols do not react with aqueous alkali, as it does not give H^- in aqueous solution.
- Super Note : Since hydroxide cannot replace alkoxide ion

(B) Reactions Involving Cleavage of C–O Bond

(1) Reaction with HX

$$R-OH + HX(g) \xrightarrow{\text{Anhyd. } ZnCl_2} R-X + H_2O$$

Super Note : The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

Super Note : In this reaction the intermediate is carbocation.

(2) Reaction with Phosphors halides

- $R-OH + PCl_5$ —— $R-Cl + POCl_3 + HCl$

  Super Note : In PCl_5 there are two types of P-Cl bonds;- axial bonds and equitorial bonds. It is found that axial bonds are longer than equitorial bonds . Due to unequal bonds PCl_5 is unstable and highly reactive.
- $3R-OH + PCl_3$ —— $3R-Cl + H_3PO_3$
- $R-OH + SOCl_2$ —— $R-Cl + SO_2 + HCl$ (Darzen's process)

(3) Dehydration of alcohol (reverse of hydration of alkene), Elimination reaction

$$CH_3-CH_2-OH \xrightarrow{H_2SO_4}$$

- $\xrightarrow[170^\circ C]{\text{Conc. } H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$
- $\xrightarrow{140^\circ C} \underset{\text{Diethyl ether}}{C_2H_5O-C_2H_5}$
- $\xrightarrow[H_2SO_4]{110^\circ} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4}$

Super Note : Elimination reaction with carbocation intermediate

Super Note : Protonation of alcohol followed by SN^2 reaction, CH_3-CH_2-OH acting as nucleophile in second step.

Super Note : Elimination reaction followed by electrophillic addition reaction

- Primary alcohols undergo bimolecular elimination (E_2 mechanism, like dehydrohalogenation) while secondary and tertiary alcohols undergo unimolecular elimination (E_1 mechanism).
- The relative reactivity of alcohols in dehydration reactions is ranked as follows: Methanol < primary < secondary < tertiary.
- Primary alcohols dehydrate through the E_2 mechanism. The hydroxyl oxygen donates two electrons to a proton from sulfuric acid (H_2SO_4), forming an alkyloxonium ion. Then the conjugate base, HSO_4^-, reacts with one of the adjacent (beta) hydrogen atoms while the alkyloxonium ion leaves in a concerted process, forming a double bond.
- E_1 Reaction. In the E1 mechanism which is also known as unimolecular elimination, there are usually two steps involved – ionization and deprotonation. During ionization, there is a formation of carbocation as an intermediate. In deprotonation, a proton is lost by the carbocation.

POCO
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Oxidation of Alcohol

- $1^\circ \rightarrow$ $RCH_2OH \rightarrow R-\underset{\underset{\text{Aldehyde}}{H}}{C}=O \rightarrow R-\underset{\underset{\text{Carboxylic acid}}{OH}}{C}=O$
- $2^\circ \rightarrow$ $R-\underset{\underset{\text{Secondary alcohol}}{OH}}{CH}-R' \xrightarrow{CrO_3} R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[\text{Drastic conditions}]{O} RCOOH + CO_2 + H_2O$
- **Super Note :** 3° Alcohol can't be oxidized

- Strong oxidising agent like $KMnO_4$ or $K_2Cr_2O_7$ cause maximum oxidation as above.
- **Super Note :** Jones reagents (chromic acid in aqueous acetone solution) oxidise 1° alcohol to aldehyde and 2° alcohol to ketone without affecting $(C=C)$ double bond

Catalytic oxidation/dehydrogenation

$1^\circ \rightarrow$ $CH_3-CH_2-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-H + H_2$ (Dehydrogenation)

$2^\circ \rightarrow$ $CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[573K]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2$ (Dehydrogenation)

$3^\circ \rightarrow$ $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[573\,K]{Cu} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{C}} + H_2O$

- **Super Note :** In dehydrogenation hydrogen is removed in the form of H^+ ion from oxygen while as H^- ion from α-carbon and double bond is formed in between carbon and oxygen
- Due to lack of hydrogentertiary alcohol undergo dehydration reaction instead of dehydrogenation .

Distinction Between 1°, 2° and 3° Alcohols

Lucas Test

Any alcohol is treated with Lucas reagent (HCl + anhyd. $ZnCl_2$) at room temperature if

- Solution becomes cloudy immediately, alcohol is 3°.
- Solution becomes cloudy after 5-min, alcohol is 2°.
- In solution cloud does not form at room temperature, alcohol is 1°.

Victor Meyer's Method or RBC Test (Beyond NCERT)

- $R-CH_2OH \xrightarrow{P+I_2} R-CH_2I \xrightarrow{AgNO_2} R-CH_2-NO_2 + HNO_2 \xrightarrow{-H_2O} R-\underset{\underset{N\diagdown OH}{\|}}{C}-NO_2 \xrightarrow{NaOH}$ blood red colour
  (1°-alcohol) (Nitrolic acid)
- $R_2CH-OH \xrightarrow{P+I_2} R_2-CH-I \xrightarrow{AgNO_2} RCH-NO_2 + HNO_2 \xrightarrow{-H_2O} R_2\underset{\underset{NO}{|}}{C}-NO_2 \xrightarrow{NaOH}$ blue colour
  (2°-alcohol) Pseudonitrol
- $R_3-C-OH \xrightarrow{P+I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2}$ No reaction $\xrightarrow{NaOH}$ Colourless
  (3°-alcohol)
- **Super Note :** 3° nitro alkanes do not react with HNO_2 because it does not have acidic α-hydrogen

POCO
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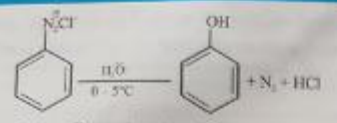
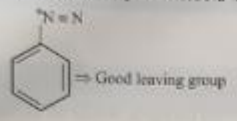
PHENOL

Method of Preparation of Phenol (Carbolic Acid)

(1) From B.D.C.

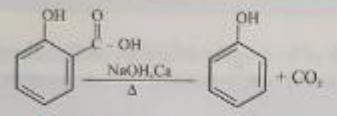


Benzene Di-azonium chloride is used to, directly Introduce Na^+ in Benzene ring.

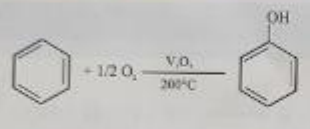


⇒ Good leaving group

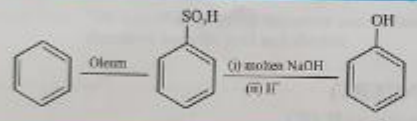
(2) From Salicylic acid



(3) From Benzene

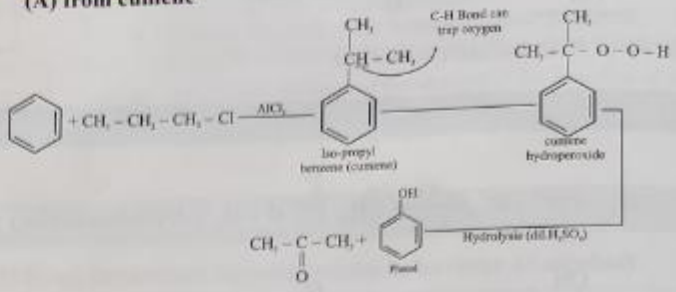


(5) From Benzenesulphonic acid



(4) Industrial method of preparation of phenol

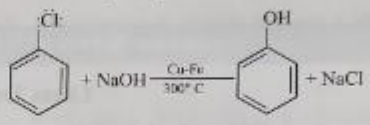
(A) from cumene



Super Note :
Most of the worldwide production of phenol is from cumene
Acetone, a by-product of this reaction, is obtained in large quantities by this method

(B) Dow's Process

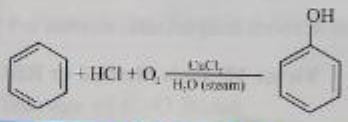
Alkaline Hydrolysis of Chlorobenzene at very high temp.



- Intermediate is sodium phenoside which is acidified to produce phenol

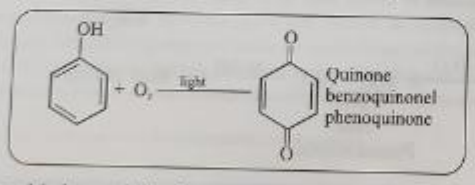
(C) Raschig Process

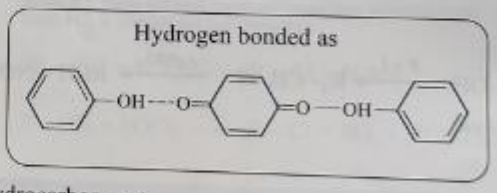
Occurs in presence of O_2 in acidic medium



Physical Properties of Phenol

- Phenol is colour less, Hygroscopic.
- On exposure to air and light it converts into pink colour

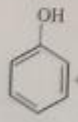




- Phenol is less soluble in water as compare to alcohol due to large Hydrocarbon part.
- It is used as both antiseptic (at low concentration) and disinfactant (at high concentration)

Important points Related to Phenol

- Iodoform test is not given by phenol.



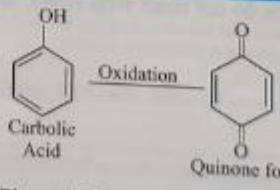
- $+ FeCl_3 \rightarrow$ Violet colour

This test is chracteristic test for phenol.

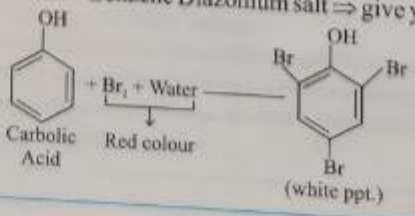
- Phenol is more acidic, since, phenoxide is stable via resonance.

- $+ OH + PCl_3 \rightarrow (C_6H_5)_3P$

Mainly Triphenyl phosphine



- Blue Litmous → red
- Phenol + Benzene Diazonium salt ⇒ give yellow or orange dye



POCO
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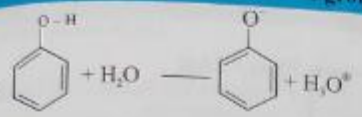
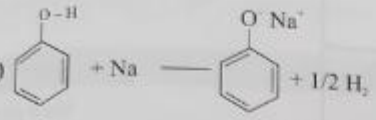
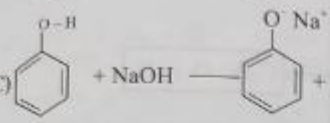
Chemical Reactions of Phenol

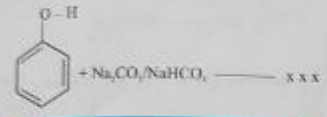
(1) Reaction due to Hydrogen of OH group

(A) 

(B) 

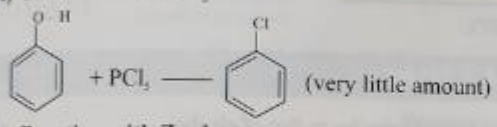
(C) 

(D) Phenol does not decompose $NaHCO_3/Na_2CO_3$, Because Carbolic acid is stronger acid than phenol. so



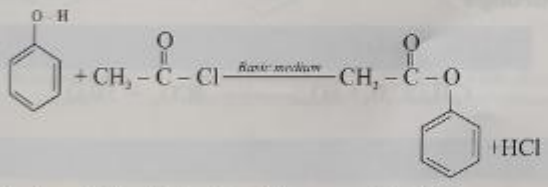
(2) Reactions due to oxygen of OH - group

(A) **Reaction with PCl_5**

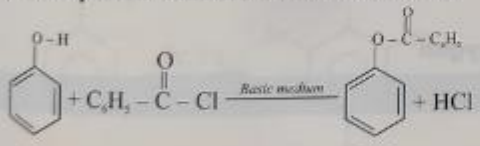


(B) **Reaction with Zn dust**

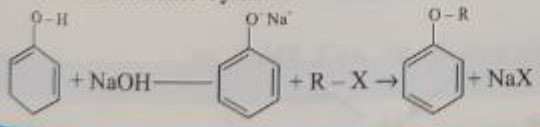
(C) **Acylation**



(D) **Benzoylation/ Schotten-Baumann Reaction**



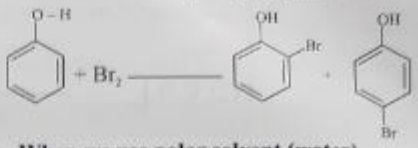
(E) **Williamsom Ether Synthesis**



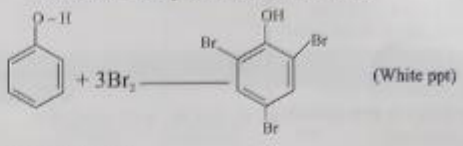
(3) Reaction due to Benzene Ring (E.S.R. reactions)

(A) **Bromination**

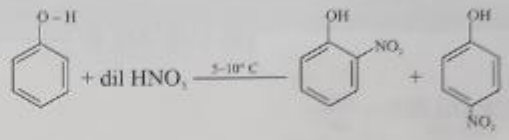
When we use CCl_4 / CS_2/ organic solvent then

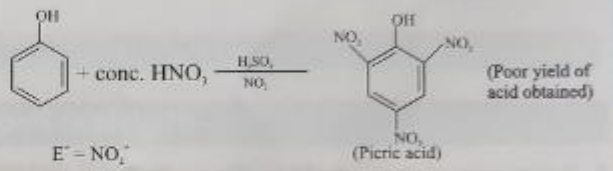


When we use polar solvent (water)

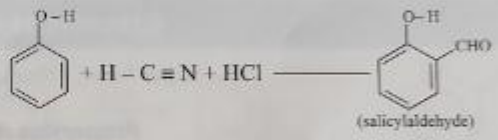


(B) **Nitration**

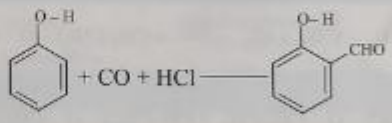




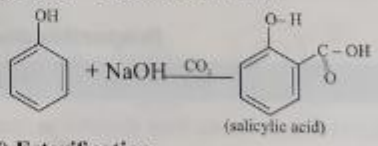
(C) **Gatterman Aldehyde Synthesis**



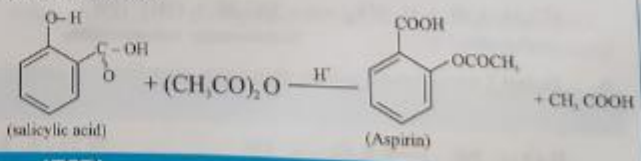
(D) **Gattermann Koch Aldehyde Synthesis**



(E) **Kolbe – Schimdt Reaction**

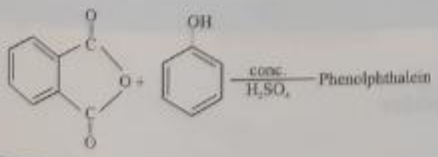


(F) **Esterification**

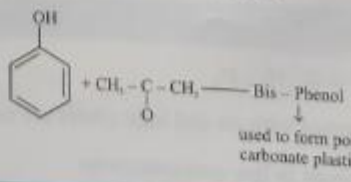


Coupling Reactions (ESR)

(A) **Reaction with Pthalic Anhydride**



(B) **Reaction with Acetone**



POCO
SHOT ON POCO X2

ETHER

Method of Preparation of Alkanes

- It is the laboratory method for the preparation of halide is allowed to react with sodium alkoxide
- Ether containing substituted alkyl groups (2° or 3°) may also be prepared by S_N2 attact of an alkoxide on 1° alkyl halide
- Order of reactivity of primary halide is $CH_3X > CH_3CH_2X > CH_3CH_2CH_2X$
- Tendency of alkyl halide to undergo elimination is 3° > 2° > 1°
- For better yield alkyl halide should be primary and alkoxide should be secondary or tertiary
- Secondary and tertiary alkyl halides readily undergo E_2 elimination in the presence of a strong base to form alkenes.

(1) C_2H_5I —(dry Ag_2O)→ Ether + 2AgI

- Remember that reaction of alkyl halides with moist silver oxide ($Ag_2O + 2H_2O \rightarrow 2AgOH$) gives alcohols $C_2H_5I + Ag_2O$ (moist) $\rightarrow C_2H_5OH + AgI$

(2) C_2H_5I —(C_2H_5ONa)→ Williamson ether synthesis

(3) C_2H_5OH —(Conc. H_2SO_4, 140°C)→ Williamson continuous ether process → $C_2H_5-O-C_2H_5$

- Dehydration reaction (SN_1)
- At 170°C alkene is formed
- When secondary and Tertiary alcohol is taken elimination competes over substitution and alkenes is formed easily

(4) $C_2H_5-Mg-Br$ —($Cl_2-CH_2-O-CH_2-CH_3$)→ Lower ether

- $C_2H_5^-$ acts as a nucleophile

(5) C_2H_5OH —(Al_2O_3, 180-200°C)→

- Dehydration reaction between two molecules of alcohol

Physical Properties of Ether

- Boiling point of ether is similar to alkane
- Miscibility of ether in water is similar to that of alcohol

Chemical Reactions of Ether

Super Note : Ethers are least reactive functional group

Properties due to Alkyl Groups

(1) Halogenation

$$\overset{\beta}{C}H_3-\overset{\alpha}{C}H_2-O-\overset{\alpha'}{C}H_2-\overset{\beta'}{C}H_3 + Cl_2 \xrightarrow{dark} \underset{\alpha\text{-Chloroethyl ether}}{CH_3.CHCl-O-CH_2.CH_3}$$

$$\downarrow Cl_2$$

$$\underset{\alpha,\beta\text{-Dichloroethyl ether}}{CH_2Cl.CHCl-O-CH_2.CH_3} + \underset{\alpha,\alpha'\text{-Dichlorodiethyl ether}}{CH_3CHCl-O-CHCl.CH_3}$$

(2) Combustion

$$C_2H_5OC_2H_5 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

Properties due to Ethereal Oxygen

(1) Basic nature

- Ether behave as Lewis bases Hence they dissolve in strong acids

$$\underset{\text{Diethyl ether}}{(C_2H_5)_2O} + H_2SO_4 \rightarrow \underset{\text{Diethyloxonium hydrogensulphate}}{[(C_2H_5)_2OH]^+HSO_4^-}$$

- Being Lewis bases, ethers also form coordination complexes with Lewis acids like BF_3, $AlCl_3$, RMgX, etc

$$R_2\ddot{O}: + BF_3 \longrightarrow R_2O \rightarrow BF_3$$

$$2R_2O + RMgX \longrightarrow \begin{matrix} R_2O & & R \\ & Mg & \\ R_2O & & X \end{matrix}$$

- It is for this reason that ethers are used as solvent for Grignard reagents.

(2) Formation of peroxide

- $C_2H_5\ddot{O}C_2H_5 + \ddot{O} \rightarrow (C_2H_5)_2O_2$
- On standing in contact with air and light ethers are converted into unstable **peroxides**
- Highly explosive even in low concentrations

POCO
SHOT ON POCO X2

Properties due to carbon-oxygen bond

(Cleavage of C-O bond occurs under drastic condition and with excess of HX)

(1) Hydrolysis

(I) With dilute H_2SO_4

$$C_2H_5-O-C_2H_5 + H_2O \xrightarrow{H_2SO_4} \underset{\text{Ethyl alcohol}}{2C_2H_5OH}$$

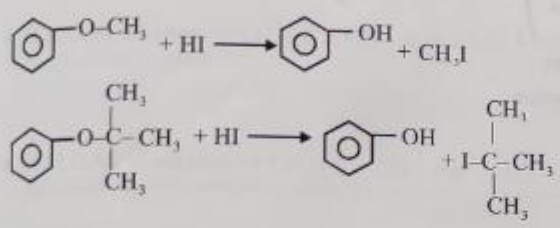
Ethers can never be hydrolysed in alkaline medium

(2) Action of hydroiodic or hydrobromic acid

(I) In Cold

$$\underset{\text{Ethyl ether}}{C_2H_5-O-C_2H_5} + HI \rightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

If one of the group around oxygen is aryl group then I will always attack on the group other than aryl group.



(II) Hot HI

$$R-O-R' + 2HI \xrightarrow{heat} RI + R'I + H_2O$$

(III) With Conc. H_2SO_4

$$C_2H_5-O-C_2H_5 + H_2SO_4\ (conc.) \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + C_2H_5HSO_4$$

$$C_2H_5OH + H_2SO_4(conc.) \rightarrow C_2H_5HSO_4 + H_2O$$

Order of reactivity of HX : HI > HBr > HCl

(3) Reaction of PCl_5

$$R-O-R + PCl_5 \xrightarrow{heat} 2RCl + POCl_3$$

(4) Reaction with acetyl chloride

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} \xrightarrow[\text{heat}]{ZnCl_2} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

(5) Reaction with acid anhydride

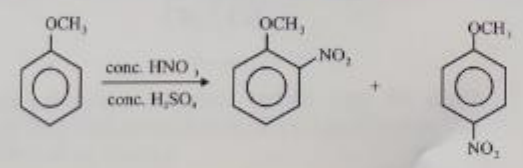
$$\underset{\text{Acetic anhydride}}{CH_3COOOCCH_3} + \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} \xrightarrow[\text{heat}]{ZnCl_2} \underset{\text{Ethyl acetate}}{2CH_3COOC_2H_5}$$

(6) Dehydration

$$C_2H_5OC_2H_5 \xrightarrow[300^\circ C]{Al_2O_3} 2CH_2=CH_2 + H_2O$$

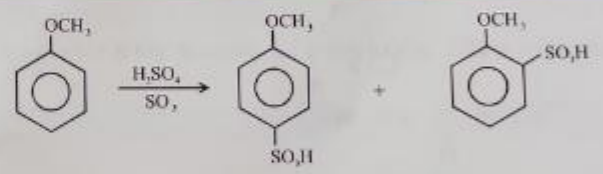
Properties Due to Benzene Nucleus

Nitration



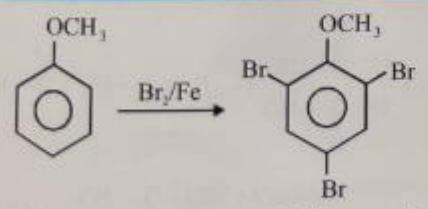
Methylphenyl ether (Anisole) | Methyl 2-nitrophenyl ether or o-Nitroanisole | Methyl 4-nitrophenyl ether or p-Nitroanisole

Sulphonation

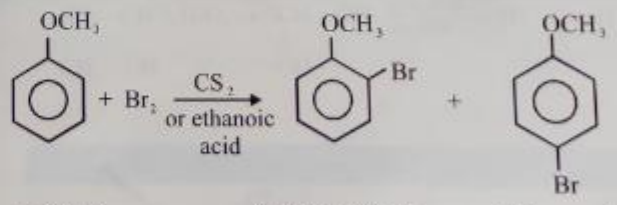


Anisole | p-Methoxybenzene sulphonic acid | o-Methoxybenzene sulphonic acid

Bromination

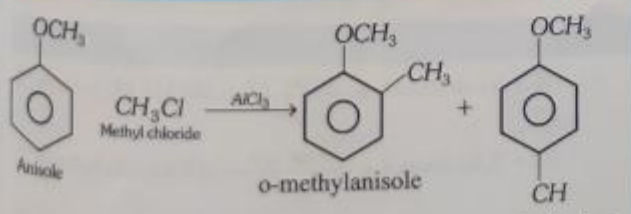


Anisole | 2, 4, 6 Tribromoanisole

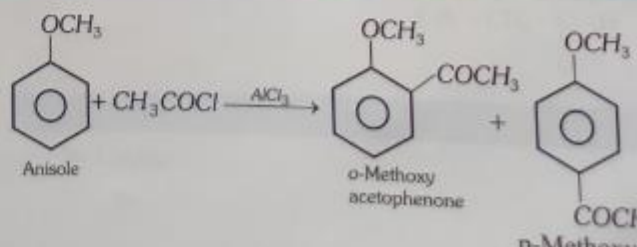


Anisole | 2-Bromoanisole | 4-Bromoanisole (90% para product)

Friedel craft reaction



Anisole | o-methylanisole | p-methylanisole



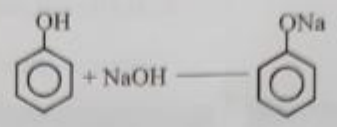
Anisole | o-Methoxy acetophenone | p-Methoxy acetophenone

POCO
SHOT ON POCO X2

Distinction Between Alcohol and Phenols

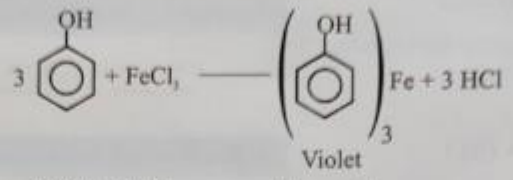
(a) Phenols turns blue litmous into red but alcohols do not

(b) Phenols neutralize base, while alcohols do not.



R-OH + NaOH ——— No reaction

(c) Phenols give violet colour with $FeCl_3$. while alcohols do not



R-OH + $FeCl_3$ ——— No reaction

POCO
SHOT ON POCO X2

ALDEHYDES & KETONES

Methods of Preparation Aldehydes & Ketones

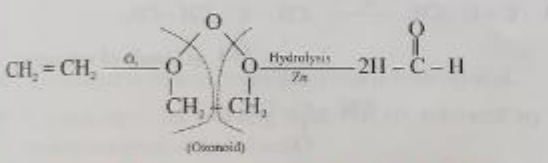
A Reaction used to prepare both aldehydes & ketones

1. Hydration

- **Simple Hydration** → $CH_3-C\equiv CH + H_2O \xrightarrow{H^+} CH_3-\underset{OH}{C}=CH_2 \xrightarrow{\text{Tautomerism}} CH_3-\underset{O}{C}-CH_3$
  - follows markovnikov's rule with rearrangement
- **H.B.O. of alkynes** → $CH_3-C\equiv CH + B_2H_6 / H_2O_2 / NaBH_4 \rightarrow CH_3-CH=\underset{OH}{CH} \xrightarrow{H_2O} CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-OH \rightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$
  Hydroboration oxidation
  - Anti-markovnikov's rule without rearrangement
- **O.M.D.M. of alkynes** → $CH_3-C=CH + Hg^{+2}/H_2O \longrightarrow CH_3-\overset{OH}{\underset{OH}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\underset{O}{C}-CH_3$
  Oxymercuration demercuration
  - follows markovnikov's rule without rearrangement

2. Reductive Ozonolysis of Alkene

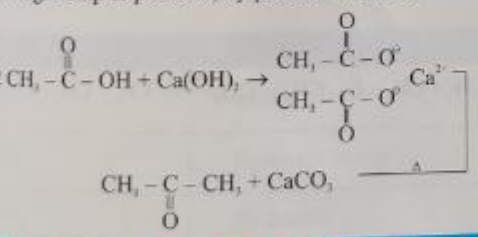
Alkene + O_3 $\xrightarrow[H_2O]{Zn}$ Carbonyl Compound



H_2O_2 formed in reaction, reacts with Zn which prevents further oxidation of carbonyl compounds into carboxylic acid.

3. Dry distillation of Ca salts of organic acids

At high temp & pressure, by product is $CaCO_3$



4. Oxidation of alcohol by P.C.C. [Cr containing O.A.]

1° R–OH → Aldehyde, 2° R–OH → Ketone, 3° R–OH → No reaction

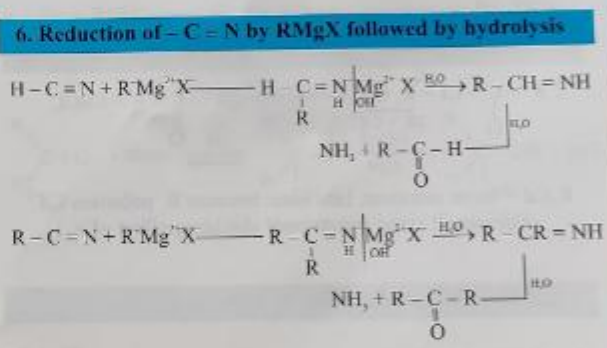
5. Dehydrogenation of Alcohol by Cu.

1° alcohol (RCH_2OH) $\xrightarrow[-H_2]{Cu/300°C}$ Aldehyde (R–CH = O)

2° alcohol (R_2CHOH) $\xrightarrow[-H_2]{Cu/300°C}$ Ketone ($R_2C = O$)

3° alcohol $\xrightarrow[-H_2O]{Cu/300°C}$ Alkene

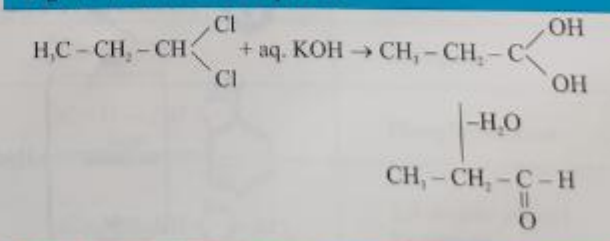
6. Reduction of – C = N by RMgX followed by hydrolysis



7. Oxidation of vicinal di-ol by periodic acid (HIO_4)

$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} + HIO_4 \rightarrow \begin{matrix} CH_2-OH \\ | \\ OH \end{matrix} \xrightarrow[\text{unstable}]{\text{gem di-ol}} 2H-\underset{O}{C}-H$$

8. gem - di halides with aq. KOH



9. Reduction of carboxylic acids

By $LiAlH_4$

POCO
SHOT ON POCO X2

B Reaction used to prepare Aldehydes only

1. Dehydrogenation of 1° alcohol

$$R-CH_2-OH \xrightarrow{Cu/573\,K} R-\underset{\underset{O}{\|}}{C}-H$$

2. Reductive ozonolysis of unbranched alkene

$$CH_3-CH=CH_2+O_3 \xrightarrow{Zn} CH_3-\underset{\underset{O}{\|}}{C}-H+H-\underset{\underset{O}{\|}}{C}-H$$

3. Stephen's Reaction

$$R-C\equiv N+SnCl_2+HCl \rightarrow \underset{\text{Imine}}{R-CH=NH} \xrightarrow{\text{hydrolysis}} R-\underset{\underset{O}{\|}}{C}-H$$

$$Sn^{+2} \rightarrow Sn^{+4}+2e^-$$

$$2e^-+HCl \rightarrow \underset{\text{attacks on carbon of cyanide}}{H^-} + Cl^-$$

4. Rosenmund Reduction

$$R-\overset{:O:}{\overset{\|}{C}}-\dot{\underset{..}{C}}l: + H_2 \xrightarrow[BaSO_4]{Pd} R-\underset{\underset{O}{\|}}{C}-H+HCl$$

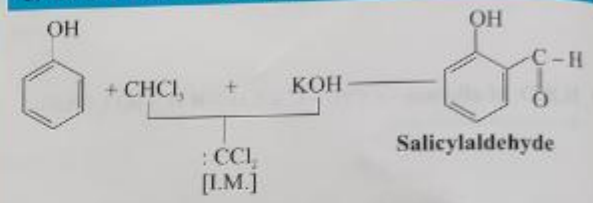
Due to l.p. l.p. repulsion

$$R-\overset{+}{\underset{\underset{O}{\|}}{C}}+Cl^- \xrightarrow{H_2+Pd} H^++H^-$$

(a) Pd Catalyst is poisoned by $BaSO_4$ to check further reduction of aldehyde to alcohol

(b) Formaldehyde cannot be obtained by this method because HCOCl is unstable at room temperature.

5. Riemer-Timann Reaction



Salicylaldehyde

C Reaction used to prepare Ketone only

1. Reactions of -oyl halide with di-alkyl cadmium

$$2R'-\underset{\underset{O}{\|}}{C}-Cl+\underbrace{R_2Cd}_{2R^-+Cd^{+2}} \longrightarrow 2R'-\underset{\underset{O}{\|}}{C}-R+CdCl_2$$

R_2Cd – more covalent, less ionic because R^- polarises Cd^{+2}.
(Cd^{+2} small sized due to poor shielding effect of e^-.)

2. RCN + RMgX (followed by hydrolysis)

$$R-C\equiv N+RMg^{+}X^- \longrightarrow R-\underset{\underset{R}{|}}{C}-N^-Mg^{2+}X \xrightarrow{H_2O} R-\underset{\underset{OH}{|}}{\overset{OH}{C}}R+\underset{H}{\overset{H}{N}}$$

$$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow{-H_2O} R-\underset{\underset{OH}{|}}{\overset{OH}{C}}R$$

3. Hydration of Internal alkynes

$$CH_3-C\equiv C-CH_3 \xrightarrow{H_2O} CH_3-\underset{\underset{OH}{|}}{\overset{OH}{C}}-CH-CH_3$$

(Gemdi-ol unstable)

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$

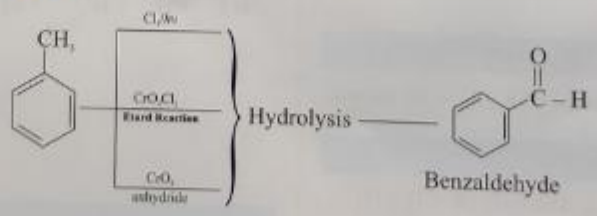
4. Decarboxylation of β-keto acid

Use heat, CO_2 released,
Intermediate is carbanion → which is stabilised by resonance

Eg: $$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-OH$$

$$\xrightarrow{\Delta} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2^{\ominus}+CO_2 \xrightarrow{H^+} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

D Aromatic Aldehyde only



Benzaldehyde

Super Note :

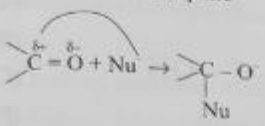
- For industrial scale preparation of aldehydes / ketone, volatile alcohol vapours are passed over heavy metal catalyst (Ag, Cu) that leads to dehydrogenation
- Reduction by DIBAL-H $R-\overset{O}{\overset{\|}{C}}-O-R' \xrightarrow[\text{(ii) } H_2O]{\text{(i) } (iso\text{-}Bu)_2AlH} R-\overset{O}{\overset{\|}{C}}-H$ $\quad C=C-C\equiv N \xrightarrow{DIBAL-H} C=C-CHO$ (Double bond not effected)

POCO
SHOT ON POCO X2

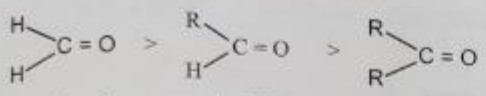
Chemical Reactions of Aldehyde & Ketone

1 Nucleophilic Addition Reactions

- In First Step : Addition of Nucleophile



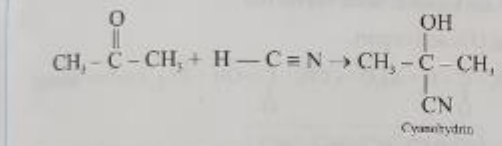
$$Nu^{-}\text{ addition reaction} \propto \frac{\text{Magnitude of + ve charge on C}}{\text{Steric H., e}^{-}\text{ Releasing effect}}$$



- For carbonyl compounds OH^{-} cannot act as a Nucleophille because it forms Gemdiol which again forms carbonyl compound.

(A) Reaction with HCN

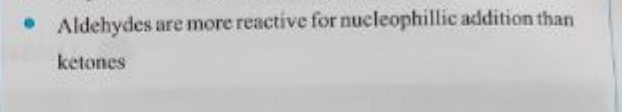
- In basic medium, ionisation of HCN increases leads to formation of CN^{-} (stronger nucleophile than HCN)



- Cyanohydrin on acid hydrolysis gives α-hydroxy acid.
- Cyanohydrin on treating with $NH_3(l)$ followed by acid hydrolysis gives α-amino acid.
- In case of ketone, cyanohydrin formation is reversible due to bulky group of ketone which hinders the formation.

(B) Reaction with $NaHSO_3$

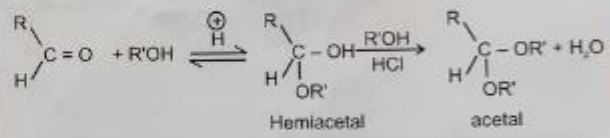
- Reaction used for separation and purification of carbonyl compounds via salt formation (white crystalline)



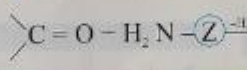
- Sulphur transfers electrons since 'S' is less EN.
- Aldehydes are more reactive for nucleophillic addition than ketones

(C) Reaction with Alcohol

- Reaction is used in the protection of carbonyl group from a Nu.
- Carbonyl compounds can be stored for long time after this reaction
- Since ROH is poor Nu for carbonyl compounds. Dry HCl(g) is used to increase electrophilicity on C of



2 Addition elimination Reactions



Z	Reagent Name	Carbonyl derivative	Product name
-R	Amine	$>C=N-R$	Substituted Imine (Schiff's base)
-OH	Hydroxyl amine	$>C=N-OH$	Oxime
$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
-NH-⬡	Phenylhydrazine	$>C=N-NH$-⬡	Phenylhydrazone
-NH-⬡(NO_2)(NO_2)	2,4 - dinitrophenylhydrazine	$>C=N-NH$-⬡(NO_2)(NO_2)	2,4-dinitro phenyl hydrazone
$-NH-C(=O)-NH_2$	Semi-carbazide	$>C=N-NH-C(=O)-NH_2$	semi - carbazone
-H	Ammonia	$>C=NH$	Imine

POCO
SHOT ON POCO X2

3 Reductions

(1) Reactions in which formation of hydrocarbon occurs

(A) Wolf-Kishner's Reaction

$$>C=O \xrightarrow[KOH,\ H_2O_2]{NH_2-NH_2} >CH_2$$

In the presence of NH_2-NH_2, KOH, H_2O_2 basic medium.

(B) Clemmensen Reaction

$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2$$

In the presence of Zn-Hg & HCl ,acidic medium

(C) Red P+HI

$$>C=O \xrightarrow[P+HI]{Red} >CH_2$$

(2) Reactions in which formation of alcohols occurs

$$>\overset{O}{\overset{\|}{C}} \rightarrow -C-OH$$

(A) H_2 + Ni/Pt/Pd
(B) $LiAlH_4$
(C) $NaBH_4$
(D) RMgX

4 Oxidation Reactions

(C) Oxidation by $K_2Cr_2O_7$ or acidic $KMnO_4$.

- Aldehydes → easy to oxidise → carboxylic Acid. (Due to presence of C-H bond)
- Ketones → difficult to oxidise → require heat
- Popoff's rule (Beyond NCERT) – During the oxidation of unsymmetrical ketones, keto group always stays with the smaller alkyl group. Eg.

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3 \xrightarrow{oxidise} CH_3-\underset{\underset{O}{\|}}{C}-OH + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

(D) Mild oxidising agent.

- To differentiate aldehyde & ketones, ketone not oxidised by mild oxidising agent.

(i) Tollen's Reagent - **Ammonical Silver Nitrate** ⇒ [$AgNO_3$ + NH_4OH],

- It is also known as **Silver Mirror Test**
- Ag_2O is active part.
- $CH_3-\underset{\underset{O}{\|}}{C}-H + \overset{+1}{Ag_2}O \rightarrow CH_3-\underset{\underset{O}{\|}}{C}-OH + 2\overset{0}{Ag}\downarrow$ (silver mirror)

(ii) Fehling's solution → F. solution A → Aq. $CuSO_4$ [Blue]

- F. solution B → Sodium potassium tartarate (Roschelle salt)
- Active part CuO & **ppt. of Cu_2O (Brick red colour) forms**
- It can't oxidise **Aromatic aldehydes**

(iii) Benedict's solution→ **Sodium Citrate+ $CuSO_4.5H_2O$**

- Active part CuO & Red ppt. of Cu_2O forms

5 Oxidation Reactions (Beyond NCERT)

(A) By Selenium dioxide (SeO_2)

α–methylene group converts into $>C=O$

$$H-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow{SeO_2} H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H$$

(glyoxal)

(B) Baeyer villigar oxidation

- In the presence of peroxy carboxylic acid which gives nascent [O].
- Aldehydes convert into carboxylic acid.
- Ketones convert into esters.
- In the oxidation of ketones, [O] trap towards more substituted alkyl group.
- Commonly used peroxy acid.

M.C.P.B.A. (Meta - chloro peroxybenzoic acid)
(It is also used in epoxidation)

Distinction between formaldehyde, acetaldehyde and acetone

S.No.	Reagent / Test	HCHO	CH_3CHO	CH_3COCH_3
1.	Brady reagent / DNP	Coloured crystal	Coloured crystal	Coloured Crystal
2.	Tollen's reagent	Silver mirror	Silver mirror	×
3.	Fehling's solution	Red	Red	×
4.	Benedict's solution	Red	Red	×
6.	Schiff's reagent	Pink	Pink	×
7.	Iodoform test	×	Yellow	Yellow

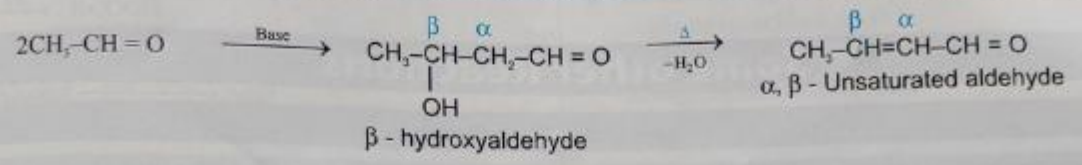
POCO
SHOT ON POCO X2

6 Reaction due to acidic α H

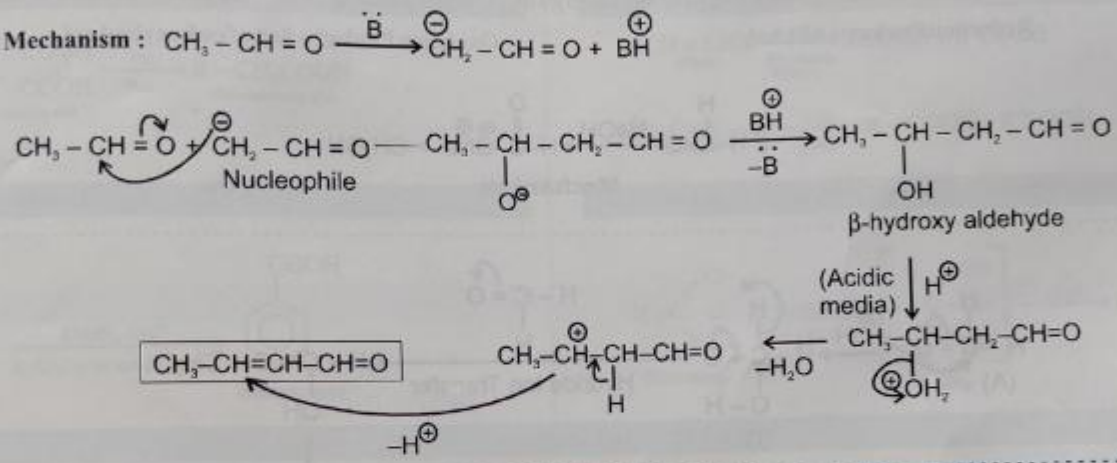
(A) Aldol Condensation

- Acid - Base Reaction followed by N.A.R. , in basic (weak) medium
- Given by Aldehyde/ ketone having α-H and presence of dilute acid is must.
- Formation of

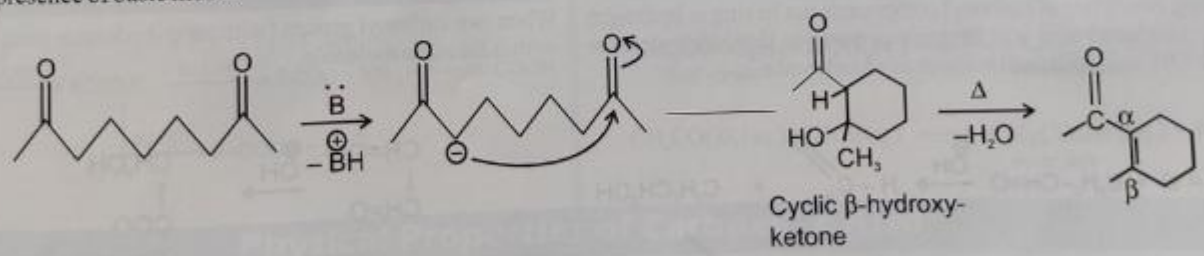
β-hydroxy aldehyde = Aldol
β-hydroxy ketone = Ketol $\xrightarrow[\text{Condensation}]{\Delta}$ [α, β– unsaturated carbonyl compound]



Mechanism :



- **Cross Aldol —** On using two types of carbonyl compounds both having α-hydrogen atoms. We get a mixture of four condensed product because two types of carbonyl compounds will give two types of carbanions which will be nucleophile for itself and other molecule.
- **Intra molecular aldol occurs in 2,5 diketones —** If two carbonyl groups with α-hydrogen atoms are present within the same molecule, then we get cyclic α, β-unsaturated aldehyde / ketones via the formation of cyclic-β-hydroxy aldehyde / ketone in presence of basic media.



Beyond NCERT

(1) 2,7 – diketones form → 3 membered ring

(2) 2, 8 – Diketone form → 6 membered ring

(3) In [2,7], [2,8], or [2,9] Diketones the internal hydrogens are abstracted to generate Nu^-.

(4) In 2,5 Diketones → external hydrogen is abstracted to generate Nu^-.

(B) Haloform Reaction / Test

- This reaction is used to distinguish the presence of $CH_3-\overset{O}{\overset{\|}{C}}-$ and $CH_3-\overset{OH}{\overset{|}{CH}}-$ groups
- Positive haloform test represents presence of 3 acidic Hydrogen (α-H).

POCO
SHOT ON POCO X2

$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Br_2\ /\ NaOH} R-\overset{O}{\overset{\|}{C}}-ONa + CHBr_3 \quad \text{(Bromoform)}$$

Mechanism → involves two step

(a) Halogenation

$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{3Br_2} R-\overset{O}{\overset{\|}{C}}-CBr_3$$

(b) Alkaline hydrolysis

$$R-\overset{O}{\overset{\|}{C}}-CBr_3 \xrightarrow{NaOH} CHBr_3 + R-\overset{O}{\overset{\|}{C}}-ONa$$

Some other Reactions

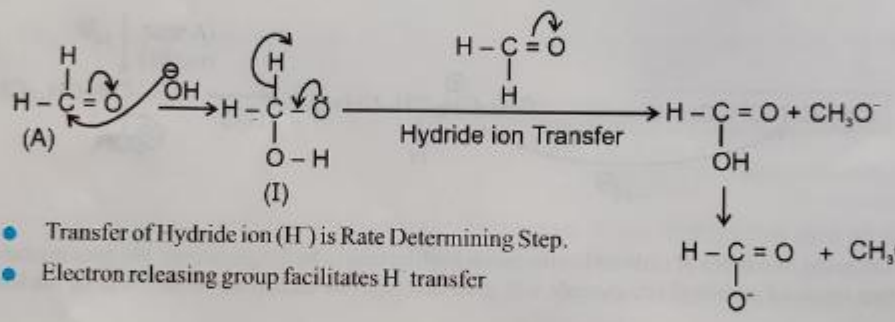
Cannizaro Reaction

- Carbonyl compounds not having α-hydrogen atoms undergo disproportionation or redox reaction in strong basic media.

Reduction Product = Alcohol Oxidation Product = Salt of carboxylic Acid.

$$2\,H-\overset{H}{\overset{|}{C}}=O \xrightarrow{NaOH} H-\overset{O}{\overset{\|}{C}}-\overset{\ominus\oplus}{O}Na + CH_3OH$$

Mechanism



- Transfer of Hydride ion (H^-) is Rate Determining Step.
- Electron releasing group facilitates H transfer

Crossed Cannizaro reaction

On using two types of carbonyl compounds not having α-hydrogen atom, produced acid will be corresponding to that aldehyde over which OH^- will approach without any hinderance.

$$\underset{(A)}{H-\overset{H}{\overset{|}{C}}=O} + \underset{(B)}{C_6H_5-CH=O} \xrightarrow{\overset{\ominus}{O}H} H-C\begin{matrix}O\\ O^-\end{matrix} + C_6H_5CH_2OH$$

Intramolecular Cannizaro reacion

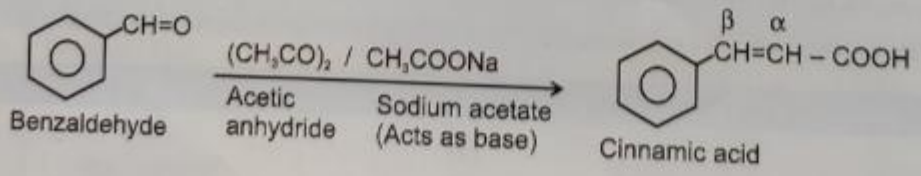
When two carbonyl groups (without α-hydrogen atom) are present within the same molecule.

$$\begin{matrix}CH=O\\ |\\ CH=O\end{matrix} \xrightarrow{\overset{\ominus}{O}H} \begin{matrix}CH_2OH\\ |\\ COO^-\end{matrix}$$

Glycolate ion

Perkin's Reaction

Used to synthesise cinnamic acid.



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Chapter – 9 Carboxylic Acid

Method of Preparation of Carboxylic Acid

(1) By oxidation of alcohols, aldehydes and ketones

$$\underset{\text{alcohol}}{RCH_2OH} \xrightarrow[K_2Cr_2O_7]{[O]} RCHO \xrightarrow[K_2Cr_2O_7]{[O]} \underset{\text{Carboxylic acid}}{RCOOH}$$

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{monocarboxylic acid}}{RCOOH}$$

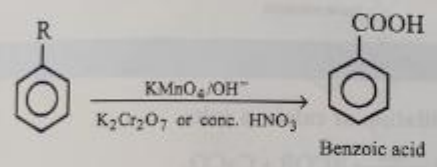
$$\text{Primary Alcohol} \xrightarrow[\text{Jones Reagent}]{CrO_3+H_2SO_4} \text{Acid}$$

- Aldehyde can be oxidized to carboxylic acid with mild oxidising agents such as ammonical silver nitrate solution Ag_2O or $[Ag(NH_3)_2]OH$
- Methanoic acid can not be prepared by oxidation method.
- Ketones can be oxidized under drastic conditions using strong oxidising agent like $K_2Cr_2O_7$.
- Methyl ketones can also be converted to carboxylic acid through the haloform reaction.

(2) By heating on dicarboxylic acid

$$\underset{\text{Substituted malonic acid}}{R-CH\begin{matrix}COOH\\COOH\end{matrix}} \xrightarrow[\text{heat}]{-CO_2} \underset{\text{Monocarboxylic acid}}{R-CH_2COOH}$$

(3) By oxidation of alkyl benzenes

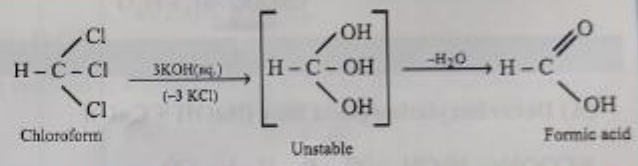


(4) By the Oxidation of alkene and alkyne

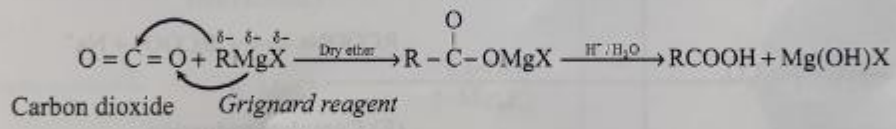
$$\underset{\text{Alkene}}{RCH=CHR'} \xrightarrow[\text{Hot alkaline } KMnO_4]{[O]} RCOOH + R'COOH$$

$$\underset{\text{Alkyne}}{R-C\equiv C-R'} \xrightarrow[(ii)H_2O]{(i)O_3} R-COOH + R'COOH$$

(5) By the hydrolysis of trihalogen derivatives of alkanes



(6) By the reaction of Grignard Reagent



(7) By the hydrolysis of cyanides (nitriles)

$$R\text{-}C\equiv N \xrightarrow{(+H_2O)} RCONH_2 \xrightarrow{H_2O/OH^-} RCOO^- + NH_3 \xrightarrow{H^+} R\text{-}COOH$$

$$RCONH_2 \xrightarrow{H_2O/H^+} R\text{-}COOH + NH_4^+$$

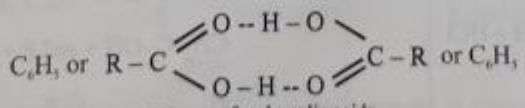
(8) By the hydrolysis of esters

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + KOH(aq.) \xrightarrow{\text{heat}} \underset{\text{Potassium acetate}}{CH_3COOK} + C_2H_5OH$$

$$CH_3COOK(aq.) + HCl(aq.) \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}(aq.) + KCl(aq.)$$

Physical Properties of Carboxylic Acid

Two molecules of carboxylic acids are held together not by one but by two strong hydrogen bonds.



Dimers of carboxylic acids

Super Note : The behaviour of **formic acid is exceptional**. It exists as a dimer in vapour state and a polymer in liquid and solid states. Their H-bonding is so strong that even in vapour state they exist as dimer *i.e.*, H-bond is not broken even in vapour state.

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Chemical Reactions of Carboxylic Acid

(1) Reaction involving hydrogen atom of the –COOH group

Reaction with metals, alkalies, carbonates and bicarbonates.

$$2CH_3COOH + 2Na \rightarrow \underset{\text{Sodium acetate}}{2CH_3COONa} + H_2$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

$$2CH_3COOH + Na_2CO_3 \rightarrow \underset{\text{Sod. acetate}}{2CH_3COONa} + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \rightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + CO_2 + H_2O$$

(2) Reaction involving –OH group of carboxylic acids (*Formation of acid derivatives*).

(A) Formation of acid chloride

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \rightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + SOCl_2 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + HCl$$

(B) Formation of esters (Esterification)

$$RCOOH + H\overset{18}{O}R' \xrightarrow{H^+ \text{ or } OH^-} RCO\overset{18}{O}R' + H_2O$$

- Presence of dehydrating agent makes the reaction in forward direction.
- The greater the bulk of the substituent(s) near the –OH group of alcohol and / or –COOH group of acid, the slower the esterification.
- The reactivity of alcohol towards esterification *tert*-alcohol < *sec*-alcohol < *pri*-alcohol < methyl alcohol
- The acidic strength of carboxylic acid plays only a minor role.

(C) Formation of amides

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \xrightarrow{\text{heat}} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(D) Formation of acid anhydrides

$$\underset{\text{Acetic acid}}{CH_3COOH + CH_3COOH} \xrightarrow[P_2O_5]{\text{Heat}} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

(3) Reaction involving attack of carboxylic group (– *COOH*)

(A) Decarboxylation [soda lime (NaOH + CaO)]

$$\underset{\text{Sodium salt}}{RCOONa} + NaOH \xrightarrow[\text{heat}]{CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

When sodium formate is heated with sodalime, H_2 is evolved. (Exception)

$$HCOONa + NaOH \xrightarrow{CaO} H_2 + Na_2CO_3$$

(B) Heating of ammonium salts

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(C) Dry distillation of calcium salts

$$\underset{\text{Sodium salt}}{(RCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Ketone}}{RCOR} + CaCO_3$$

(D) Electrolysis : (Kolbe's synthesis)

$$RCOONa \longrightarrow RCOO^- + Na^+$$

(E) Complete reduction

$$\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow{P} \underset{\text{Ethane}}{CH_3CH_3} + 2H_2O + 3I_2$$

(4) Reactions involving $-\overset{O}{\overset{\|}{C}}-$ part of the –COOH group

Reduction

$$R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{LiAlH_4} R-CH_2-OH$$

Super Note : Carboxylic acid are reduced to primary alcohol with diborane (better yield of alcohol) but diborane does not easily reduce groups like ester nitro halo etc.

(5) Reaction involving hydrogen of α-carbon

(A) Halogenation In presence of U.V. light

$$-\overset{H}{\underset{|}{C}}-COOH + Cl_2 \xrightarrow{U.V.\Delta} -\overset{Cl}{\underset{|}{C}}-COOH + HCl$$

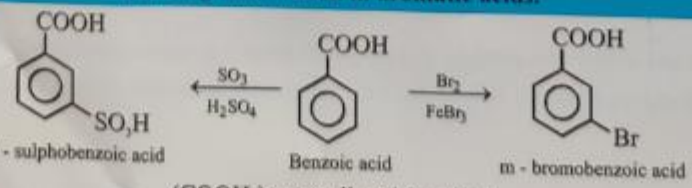
α-chloro acid

(B) Hell-Volhard Zelinsky reaction

$$CH_2\overset{O}{\overset{\|}{C}}-OH + \text{red } P + Cl_2 \longrightarrow CH_2\overset{O}{\overset{\|}{C}}-OH$$

(H and Cl on the α-carbon)

(6) Ring substitution in aromatic acids.



m - sulphobenzoic acid | Benzoic acid | m - bromobenzoic acid

(COOH is meta directing group)

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ALIPHATIC AMINES

Method of Preparation of Aliphatic Amines

- Only for preparation of primary amines
- Migration of an alkyl group takes place from carbonyl carbon of amide to nitrogen
- Carbon number decreases by one in product
- Intermediate → $R-\underset{\underset{O}{\|}}{C}-NBr$, $R-\underset{\underset{O}{\|}}{C}=N$, $R-N=C=O$

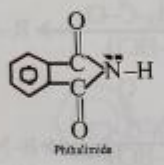
$R-\underset{\underset{O}{\|}}{C}-\ddot{N}H_2 \xrightarrow[\text{Hoffmann bromamide reaction}]{Br_2 + 4KOH}$ Amine + 2KBr + K_2CO_3 + $2H_2O$

$R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\text{Schmidt reaction}]{N_3H/H^{\oplus}}$ Amine + $N_2(g)$ + $CO_2(g)$

- Intermediate → $R-N=C=O$
- Alkaline hydrolysis

$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\text{Curtius reaction}]{(i)\ NaN_3\ (ii)\ H_3O^{\oplus}}$ Amine + $N_2(g)$ + $CO_2(g)$

$R-\underset{\underset{O}{\|}}{C}-\ddot{N}\langle^{H}_{OH} \xrightarrow[\text{Lossen reaction}]{(i)\ \text{dry HCl}\ (ii)\ H_3O^{\oplus}}$



$\xrightarrow[\text{Gabriel phthalimide reaction}]{(i)\ KOH\ (ii)\ R-X\ (iii)\ H_3O^{\oplus}}$

- Used to prepare primary aliphatic amines only
  (i) Acid base reaction
  (ii) Anion of phthalimide react with RX
  (iii) Two times alkaline hydrolysis
- When hydrolysis is difficult N-alkyl phthalimide can be treated with hydrazine to give the required amine

- Nucleophilic attack by ammonia

$>C=O$ (ald./ketone) $\xrightarrow[\text{Reductive amination}]{(i)\ \ddot{N}H_3/H^{\oplus}\ (ii)\ H_2/Pd}$

- NH_3 is the nucleophile

$R-MgCl \xrightarrow[(-MgCl_2)]{Cl-NH_2}$ $R-\ddot{N}H_2$ Alkyl amine

- Nucleophilic substitution reaction
- Order of reactivity RI > RBr > RCl
- The reaction does not give only primary amine as the product rather secondary tertiary amines and quarternary ammonium salt is also obtained

$R-X$ or $R-OH \xrightarrow{NH_3/\Delta}$

- The primary amine may be obtained in a good yield by using a large excess amount of ammonia

$R-N\equiv C \xrightarrow[\text{Complete hydrolysis}]{H_3O^{\oplus}}$

- Hydrolysis occurs thrice

$R-N=C=O \xrightarrow[\text{Wurtz reaction}]{2KOH}$

$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\text{Reduction}]{LiAlH_4/H_2O}$

- Reduction occurs by release of H from the reagent
- H_2O is used as a solvent only

$R-C\equiv N \xrightarrow[\text{Reduction}]{LiAlH_4/H_2O}$

- Reduction occurs by release of H from the reagent
- H_2O is used as a solvent only

$R-N\overset{O}{\underset{O}{\rightleftharpoons}} \xrightarrow[\text{Reduction}]{LiAlH_4/H_2O}$

- Reduction occurs by release of H from the reagent
- H_2O is used as a solvent only

$R-\underset{\underset{COOH}{|}}{CH}-NH_2 \xrightarrow[-BaCO_3,\ -H_2O]{\text{(Baryta water) } Ba(OH)_2}$

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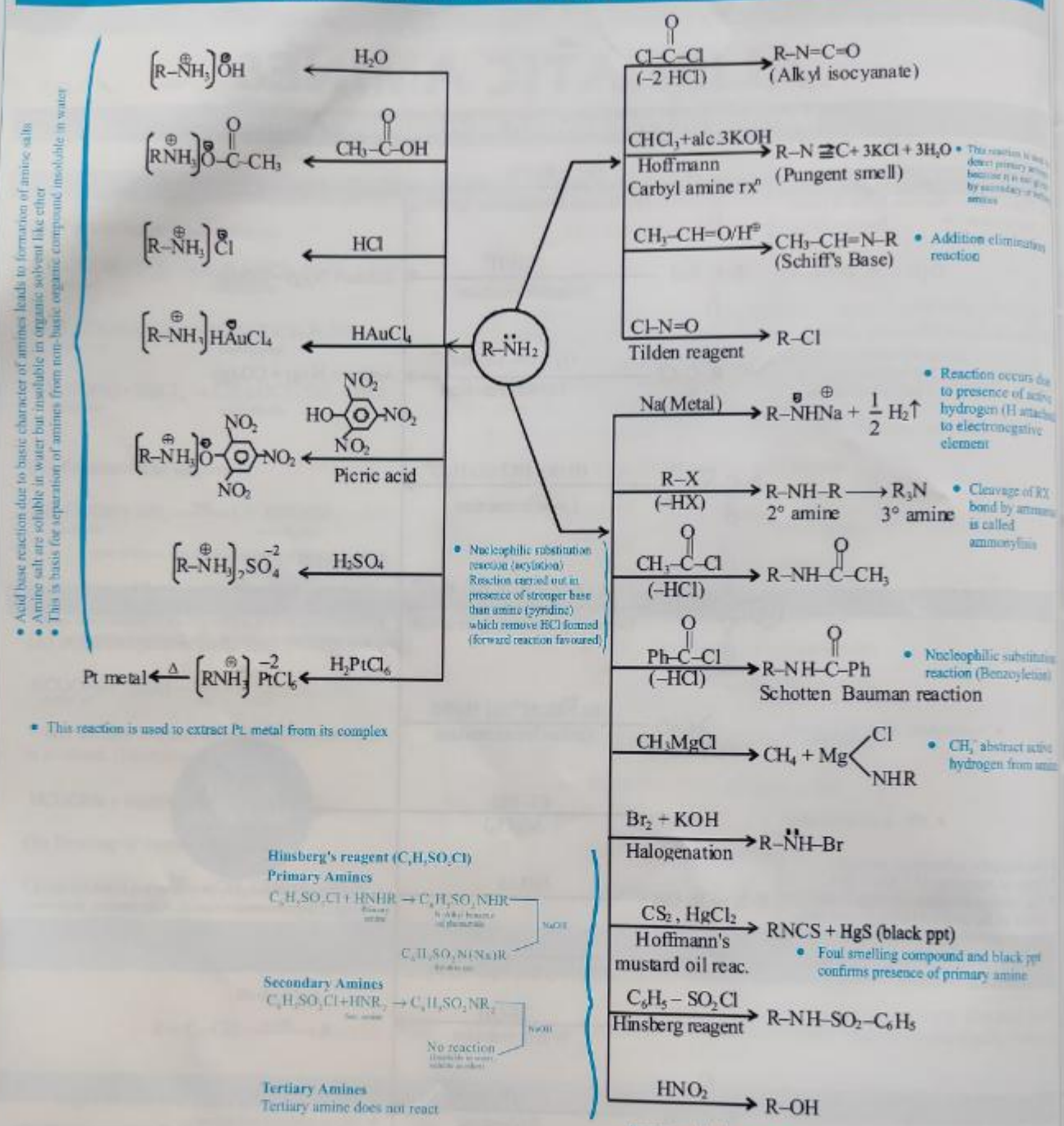
Chemical Reactions of Aliphatic Amines



- Acid base reaction due to basic character of amines leads to formation of amine salts
- Amine salt are soluble in water but insoluble in organic solvent like ether
- This is basis for separation of amines from non-basic organic compound insoluble in water

- Nucleophilic substitution reaction (acylation) Reaction carried out in presence of stronger base than amine (pyridine) which remove HCl formed (forward reaction favoured)

- This reaction is used to extract Pt metal from its complex

- This reaction is used to detect primary amines because it is not given by secondary or tertiary amines

- Addition elimination reaction

- Reaction occurs due to presence of active hydrogen (H attached to electronegative element

- Cleavage of RX bond by ammonia is called ammonolysis

- Nucleophilic substitution reaction (Benzoylation)

- CH_3^- abstract active hydrogen from amine

- Foul smelling compound and black ppt confirms presence of primary amine

Hinsberg's reagent ($C_6H_5SO_2Cl$)

Primary Amines

$C_6H_5SO_2Cl + HNHR \rightarrow C_6H_5SO_2NHR$ (N-Alkyl benzene sulphonamide)

$C_6H_5SO_2NHR \xrightarrow{NaOH} C_6H_5SO_2N(Na)R$

Secondary Amines

$C_6H_5SO_2Cl + HNR_2 \rightarrow C_6H_5SO_2NR_2$

$C_6H_5SO_2NR_2 \xrightarrow{NaOH}$ No reaction (Insoluble in water, soluble in alkali)

Tertiary Amines

Tertiary amine does not react

Reaction with nitrous acid

$(NaNO_2 + HCl) \rightarrow HNO_2 + NaCl$

Primary amines

$RNH_2 + HONO \rightarrow ROH + N_2 + H_2O$

Exception

$CH_3NH_2 + 2HONO \rightarrow CH_3-O-CH_3 + CH_3-O-N=O + N_2 + 2H_2O$

Secondary amines

$R_2NH + HONO \longrightarrow R_2NNO + H_2O$

Nitrosoamines are water-insoluble yellow oils and when warmed with a crystal of phenol and a few drops of conc. H_2SO_4 produce a green solution which turns blue on adding alkali. This reaciton is known as **Liermann's nitroso reaction and may be used as a test for secondary amines.**

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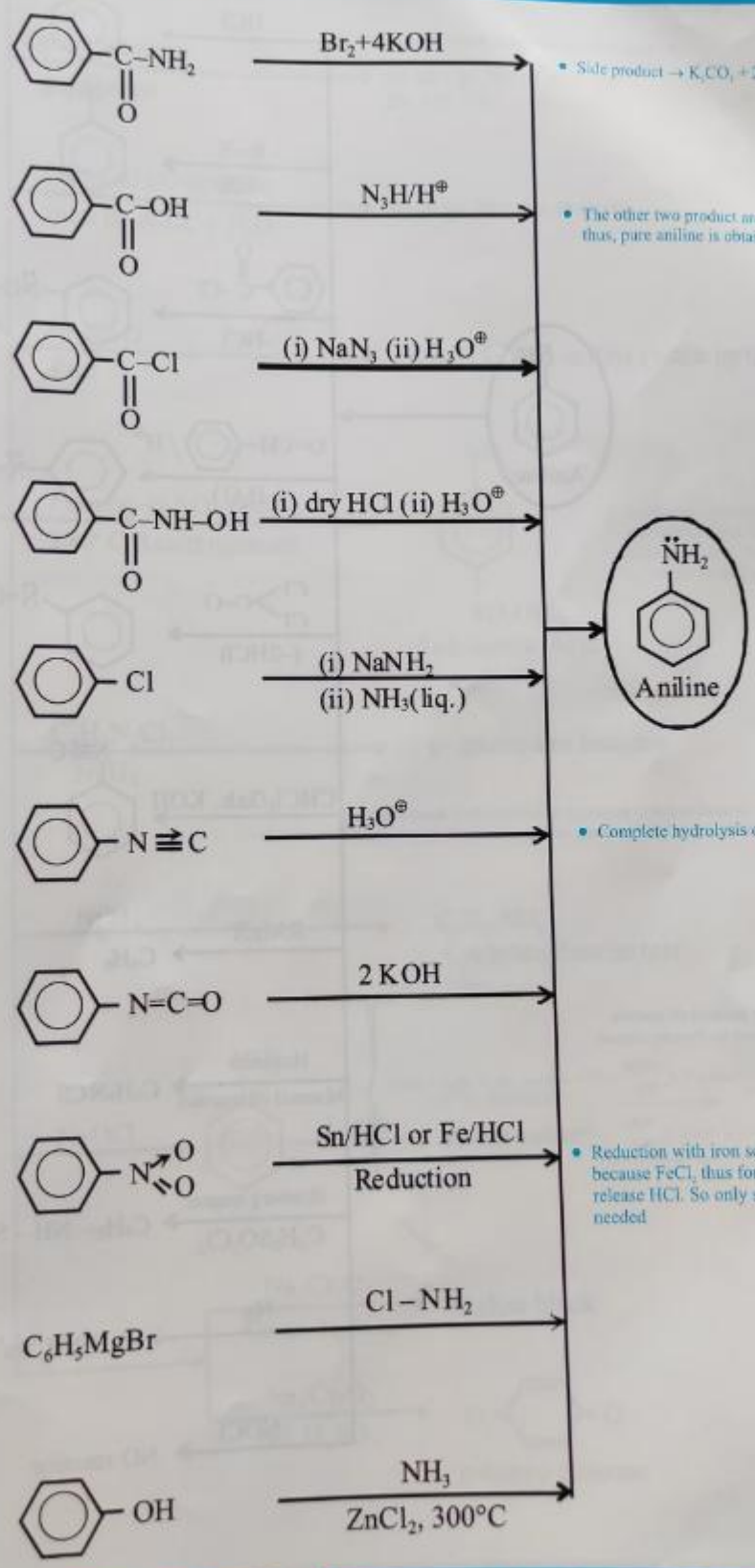
ANILINE

Method of Preparation of Aniline



General Method of Preparation

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \xrightarrow{Sn,HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

On a commercial Scale

$$2C_6H_5NH_2 + SnCl_4 + 2HCl \rightarrow \underset{\text{Double salt}}{(C_6H_5NH_3)_2SnCl_6}$$

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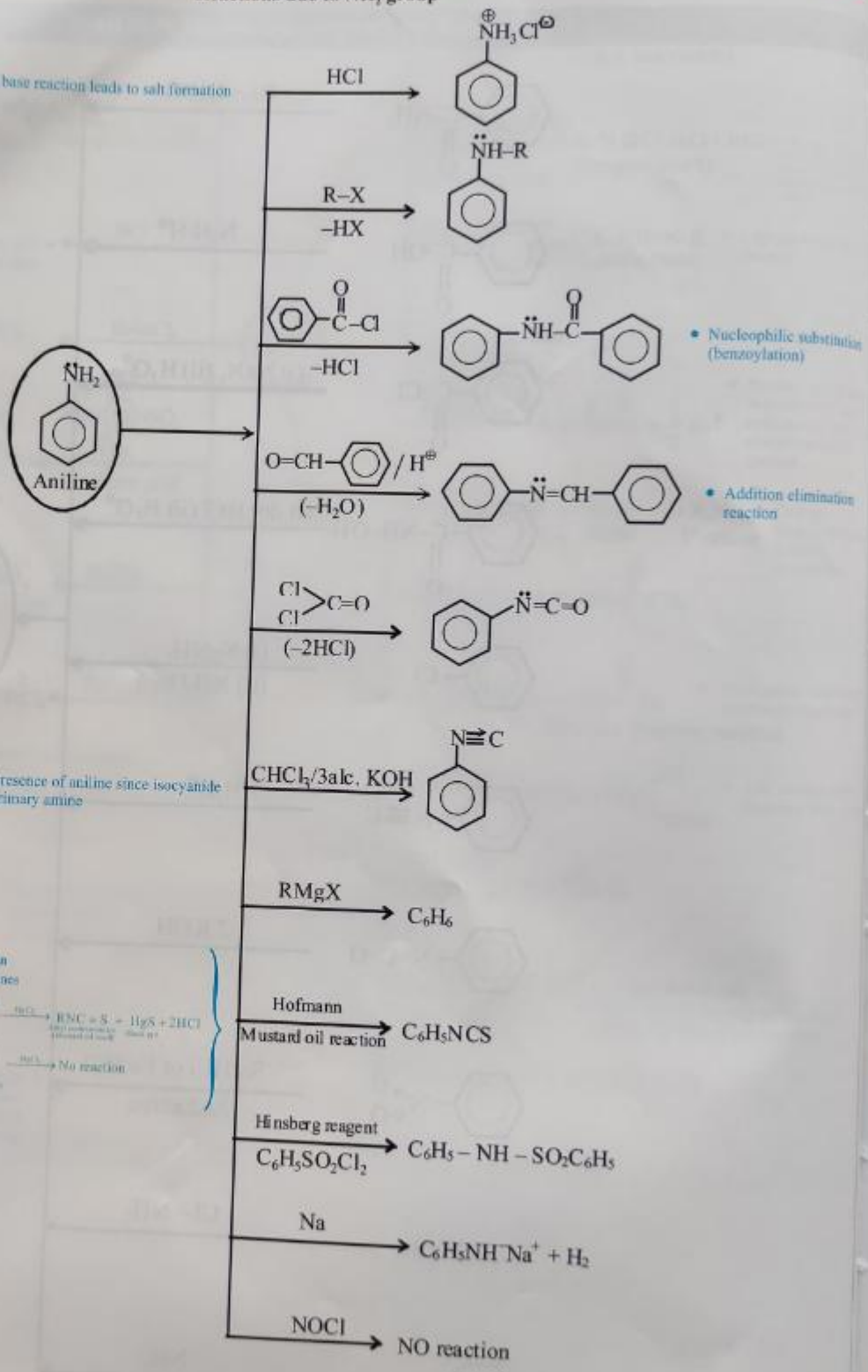
Chemical Reactions of Aniline

Reactions due to NH_2 group



- Acid base reaction leads to salt formation
- Nucleophilic substitution (benzoylation)
- Addition elimination reaction
- Reaction is used to detect presence of aniline since isocyanide formation occurs only by primary amine

Hofmann's mustard oil reaction

This is the test for Primary Amines

$$RNH_2 \xrightarrow{S=C=S} S=C\begin{matrix}NHR\\SH\end{matrix} \xrightarrow{HgO} RNC=S + HgS + 2HCl$$

$$R_2NH \xrightarrow{S=C=S} S=C\begin{matrix}NR_2\\SH\end{matrix} \xrightarrow{HgO} \text{No reaction}$$

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Reaction due to ring

- Acetic anhydride in pyridine leads to formation of acetanilide so aniline does not form anilinium ion and so meta product is very less

$(CH_3CO)_2O$ pyridine, then nitration mix → o- & p- Nitro aniline + H_2O

- Aniline being basic in nature reacts with acid (in nitrating mixture) to form anilinium ion which is meta directing

Direct nitration, Exception → o- m - p- Nitro aniline
2% 47% 51%

- Para product is major product

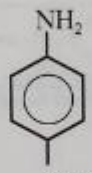
$(CH_3CO)_2O$ pyridine, then $Br_2/CCl_4 + H_2O$ → o- & p- Bromo aniline

- The reaction occurs at room temperature
- Electrophilic substitution

Br_2/H_2O, Test → 2,4,6-Tribromo aniline (white ppt) + 3 HBr

Aniline

Fuming-H_2SO_4 (oleum), 180° C Rearrangement →



Sulphanilic Acid

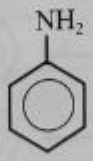
- Anilinium hydrogensulphate is the intermediate that on heating gives sulphanilic acid (sulphanilic acid occurs in zwitter ionic form)

- Electrophilic substitution reaction
- Electron donating group on BDC decrease rate of reaction
- Electron withdrawing group on BDC increase rate of reaction

$C_6H_5N_2Cl$, Ni/H_2 → p- amino azo benzene

Ni/H_2 → $C_6H_{11}NH_2$
Cyclohexylamine test

NaOCl →



Light → Voilet colour

$Na_2Cr_2O_7$, Conc. H_2SO_4 → Aniline black

$Na_2Cr_2O_7$, dil. H_2SO_4 →

p-benzo quinone

Super Note : Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

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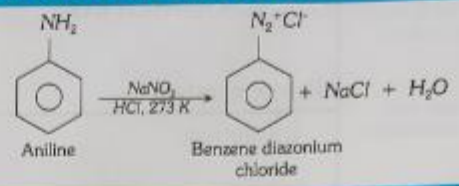
DIAZONIUM SALT

Method of Preparation of Diazonium Salt

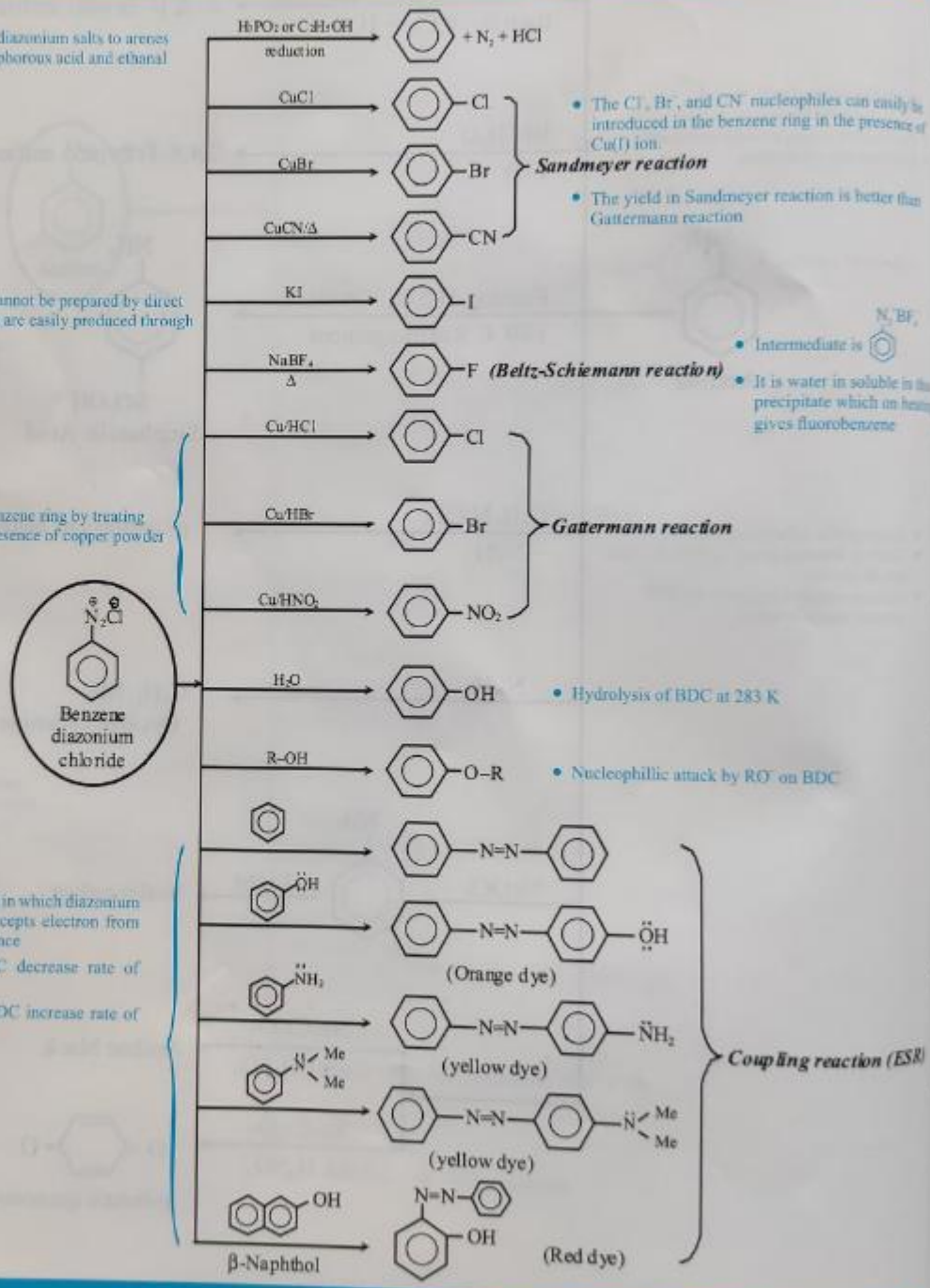
Diazonium Salt is used to enter nucleophile directly into benzene ring

$[NaNO_2 + HCl \rightarrow NaCl + HONO]$



Chemical Reactions of Diazonium Salt

- Phosphinic acid and ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal respectively



- The Cl^-, Br^-, and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion.
- The yield in Sandmeyer reaction is better than Gattermann reaction
- Aryl fluorides and iodides cannot be prepared by direct halogenation of benzene but are easily produced through BDC
- Intermediate is
- It is water in soluble in the precipitate which on heating gives fluorobenzene
- Cl, Br, NO_2 can be introduced in benzene ring by treating BDC with corresponding acid in presence of copper powder
- Hydrolysis of BDC at 283 K
- Nucleophillic attack by RO^- on BDC
- Coupling reaction is a ESR reaction in which diazonium salt acts electron acceptor and accepts electron from para position to avoid steric hinderance
- Electron donating group on BDC decrease rate of reaction
- Electron withdrawing group on BDC increase rate of reaction

Super Note : BDC is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state. Benzenediazonium fluoroborate (N_2BF_4) is water insoluble and stable at room temperature.

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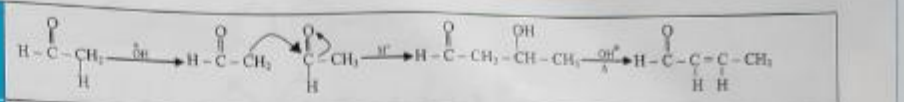
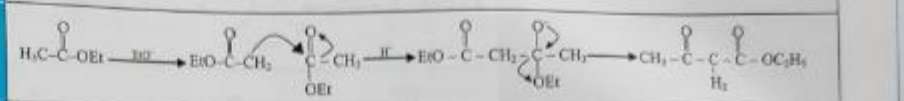
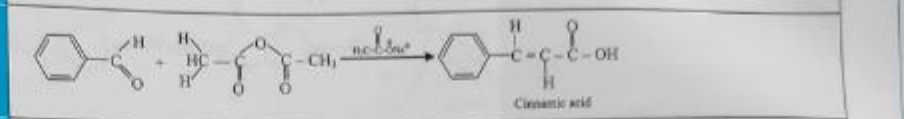
- *Aldol Condensation*



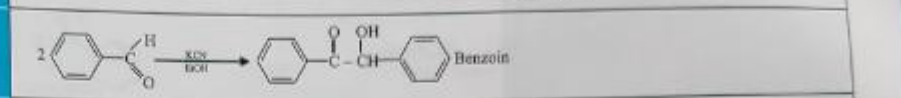
- *Claisen Condensation*



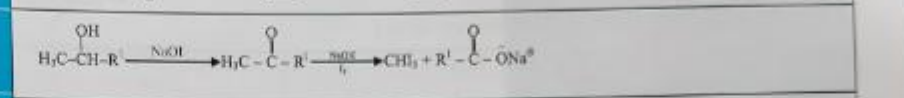
- *Perkin Condensation*



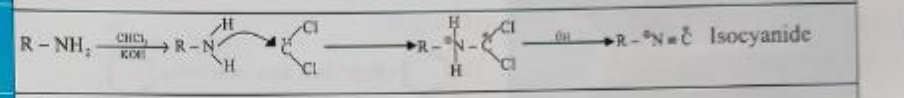
- *Benzoin Condensation*



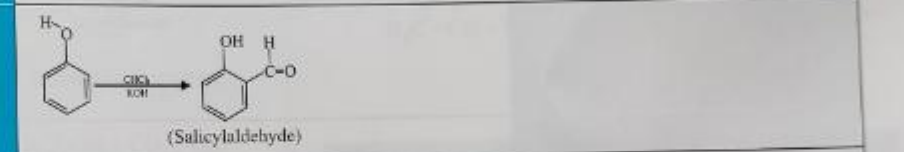
- *Haloform Reaction*



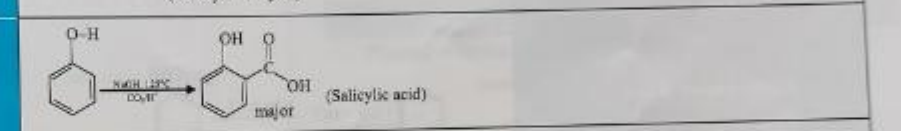
- *Carbylamine Test*



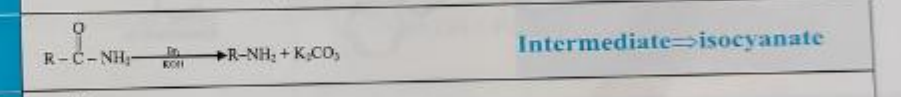
- *Reimer Tiemman Reaction*



- *Kolbe's Schimdt Reaction*



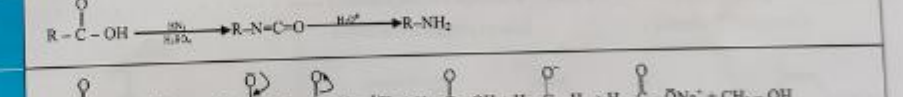
- *Hoffmann Bromamide Degradation*



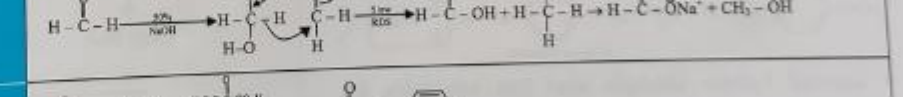
Intermediate⇒isocyanate

- *Curtius Reaction*

- *Schimdt Reaction*

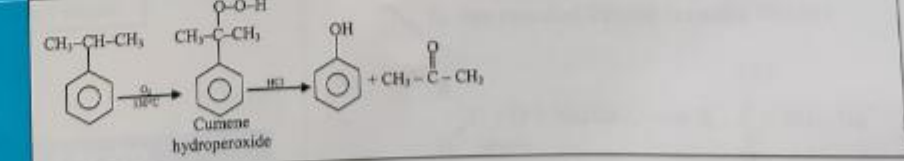


- *Cannizzaro Reaction*

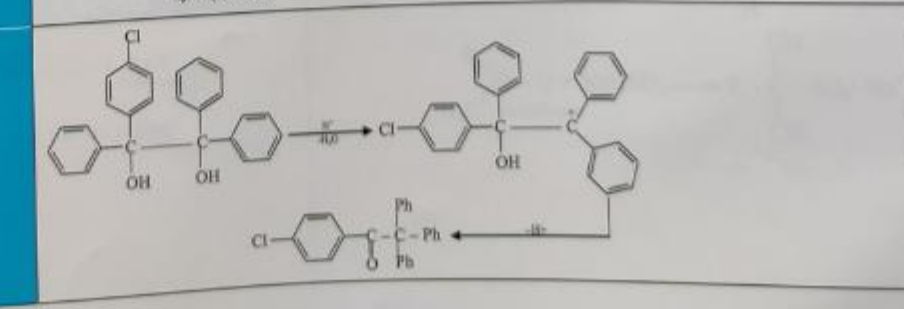


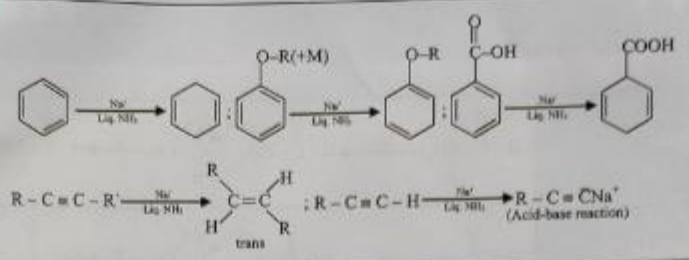
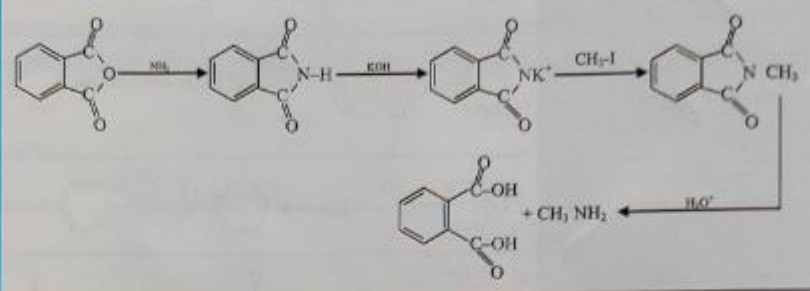
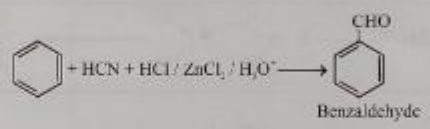
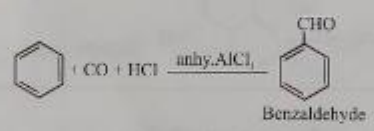
- *Baeyer villiger oxidation*

- *Cumene*



- *Pinacol-Pinacolone rearrangement*



• ***Birch Reduction***	
• ***Gabriel Phthalimide Synthesis***	
Gattermann Aldehyde Synthesis	
Gattermann Koch Reaction	

POCO
SHOT ON POCO X2

Chapter – 12 Distinction between pairs of Compound

UNSATURATION TEST

(a) Double / Triple bonded compounds (C=C) / (C≡C) + Br_2 in CCl_4 (Brown colour) —— Colourless compound

$$\underset{\text{(Alkene)}}{R-CH=CH-R} + \underset{\text{(Brown)}}{Br_2} \xrightarrow{CCl_4} \underset{\text{(Colourless)}}{R-\underset{Br}{\underset{|}{CH}}-CH-R}$$ [Anti addition]

$$\underset{\text{(Alkyne)}}{R-C\equiv C-R} + \underset{\text{(Brown)}}{Br_2} \xrightarrow{CCl_4} \underset{\text{(Colourless)}}{R-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-R}$$

(b) Double/triple bonded Compound + Baeyer's reagent (Pink colour) → Brown precipitate [Syn addition]

$$\underset{\text{(Alkene)}}{R-CH=CH-R} + \underset{\text{(Cold, dilute)}}{KMnO_4} \rightarrow \underset{\text{(Colourless)}}{R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R} + \underset{\text{Brown ppt.}}{MnO_2}$$

$$R-C\equiv C-R' + \underset{\text{(Hot, dilute)}}{KMnO_4} \rightarrow \underset{\text{Brown ppt}}{MnO_2} + RCOOH + R'COOH$$

$$\underset{\text{(Alkyne)}}{R-C\equiv C-H} + \underset{\text{(Hot, dilute)}}{KMnO_4} \rightarrow \underset{\text{Brown ppt.}}{MnO_2} + \underset{\text{(Colurless)}}{RCOOH} + CO_2 + H_2O$$

- Baeyer's reagent is cold, dilute $KMnO_4$ solution having pink colour.
- The above test are not given by Benzene, Although it has unsaturation

TEST FOR TERMINAL ALKYNE

Terminal Alkyne

Ammonical silver nitrate → White ppt.

Ammonical cuprous chloride → Red ppt.

$$NH_4NO_3 + H_2O + \underset{\text{White ppt.}}{R-C\equiv C-Ag} \xleftarrow{AgNO_3 + NH_4OH} \underset{\text{Terminal alkyne}}{R-C\equiv CH}$$

$$NH_4Cl + H_2O + \underset{\text{Red ppt.}}{R-C\equiv C-Cu} \xleftarrow{Cu_2Cl_2 + NH_4OH} \underset{\text{Terminal alkyne}}{R-C\equiv CH}$$

NATURE OF X-GROUP IN C-X BOND

$$R\text{–}X + \text{aqueous KOH} \rightarrow R\text{–}OH + KX \xrightarrow[AgNO_3]{HNO_3} \underset{\text{Precipitate}}{AgX}$$

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

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOLS

$$\underset{\text{Tertiary alcohol}}{R_3C-OH} \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} \underset{\text{Cloudiness appears immediately}}{R_3C-Cl}$$

$$\underset{\text{Secondary alcohol}}{R_2CH-OH} \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} \underset{\text{Cloudiness appears within five minutes}}{R_2CH-Cl}$$

$$\underset{\text{Primary alcohol}}{R-CH_2-OH} \xrightarrow[\text{Heat}]{\text{Lucas reagent}} \underset{\text{Cloudiness appears after 30 minutes}}{R-CH_2-Cl}$$

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

$H_3C-\overset{OH}{\overset{|}{C}H}-R$ type of alcohol gives iodoform test.

$$H_3C-\overset{OH}{\overset{|}{C}H}-R + I_2 \xrightarrow[\text{Iodoform test}]{NaOH} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + RCOO^-Na^+$$

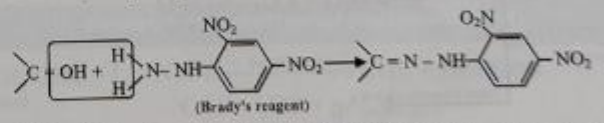
PHENOL

Phenol + ferric chloride —— Violet colouration
(neutral)

$$6\,C_6H_5-OH + FeCl_3 \rightarrow 3H^+ + \underset{\text{Violet colouration}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

CARBONYL GROUP

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



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

In this reaction Proton transfer Occurs

$$\underset{\text{Aldehyde}}{R(H)C=O} + NaHSO_3 \longrightarrow R-\overset{OH}{\overset{|}{C}}H-SO_3^-Na^+$$

$$\underset{\text{Methyl ketone}}{R(H_3C)C=O} + NaHSO_3 \longrightarrow R-\overset{OH}{\overset{|}{C}}(CH_3)-SO_3^-Na^+$$

POCO
SHOT ON POCO X2

Aliphatic Aldehyde Group

Aldehyde + Tollen's reagent → Silver mirror

$$R-\underset{\underset{O}{\|}}{C}-H + 3OH^{\ominus} + 2[Ag(NH_3)_2] \longrightarrow RCOO^{\ominus} + 2H_2O + 4NH_3 + 2Ag\downarrow$$
(silver mirror)

Aldehyde + Fehling's solution → Reddish brown precipitate

$$R-\overset{\overset{O}{\|}}{C}-H + 2Cu^{2+} + 5OH^{-} \rightarrow RCOO^{\ominus} + 3H_2O + Cu_2O$$
(Reddish brown ppt)

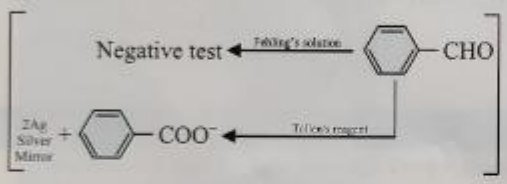
$H_3C-\overset{\overset{O}{\|}}{C}-$ group also gives Iodoform test.

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

AROMATIC ALDEHYDE GROUP

Aromatic aldehyde + Tollen's reagent → Silver mirror

Aromatic aldehyde + Fehling's solution → Negative Test

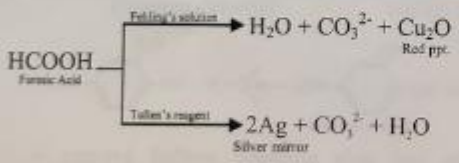


CARBOXYLIC GROUP

Carboxylic acid + Sodium bicarbonate → effervescence

$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2\uparrow$

FORMIC ACID



AMINES (1°)

Primary amine + KOH + $CHCl_3$ $\xrightarrow{\text{Carbylamine reaction}}$ Isonitrile (Offensive smell)

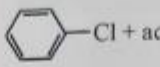
Amines (1°, 2° & 3°) (Hinsberg's test)

- Primary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{KOH}$ Soluble
- Secondary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{KOH}$ insoluble
- Tertiary amine+Benzenesulphonyl chloride → no reaction

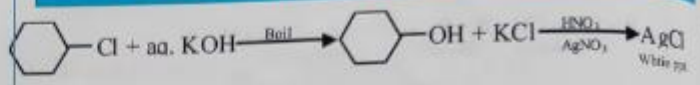
NOTE : Benzenesulphonyl chloride is called Hinsberg's reagent.

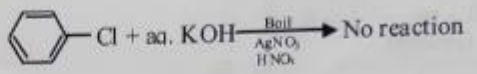
Chloroethane and Chlorobenzene

$$C_2H_5-Cl + aq.KOH \xrightarrow{Boil} C_2H_5OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$$
White ppt.



Chlorocyclohexane and chlorobenzene



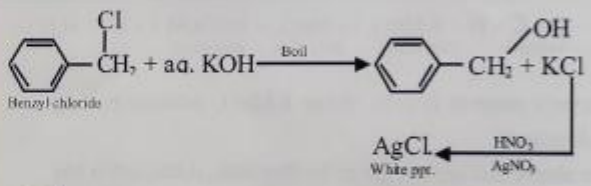


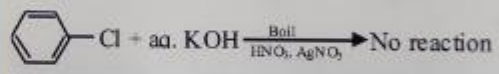
Chloroethane and bromoethane

$$\underset{\text{(Chloroethane)}}{C_2H_5-Cl} + aq.KOH \xrightarrow{Boil} C_2H_5-OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$$
White ppt.

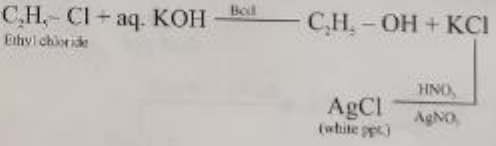
$$\underset{\text{(Bromoethane)}}{C_2H_5-Br} + aq.KOH \xrightarrow{Boil} C_2H_5-OH + KBr \xrightarrow[AgNO_3]{HNO_3} AgBr$$
Yellow ppt.

Benzyl chloride and chlorobenzene





Ethyl chloride and vinyl chloride



$$\underset{\text{Vinyl Chloride}}{H_2C=CH-Cl} + aq.KOH \xrightarrow[HNO_3, AgNO_3]{Boil} \text{No reaction.}$$

n-propyl alcohol and iso-propyl alcohol

$$CH_3CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2Cl$$

No cloudiness at room temp.

$$H_3C-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[HCl]{ZnCl_2} H_3C-\overset{\overset{Cl}{|}}{CH}-CH_3$$

Cloudiness within 5 minutes

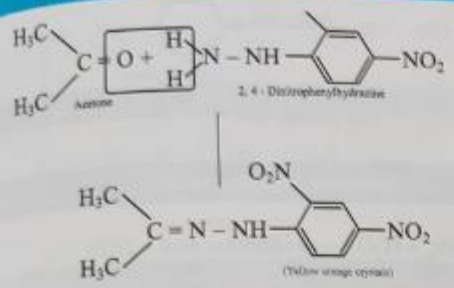
POCO
SHOT ON POCO X2

Ethyl alcohol and methyl alcohol (Iodoform test)

$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa$ (Yellow ppt.)

$CH_3OH + 4I_2 + 6NaOH \rightarrow$ No yellow ppt.

Ethyl alcohol and acetone (2, 4 – DNP)



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

Phenol and Benzoic Acid ($NaHCO_3$)

Benzoic acid + sodium bicarbonate → effervescence

$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$

Phenol + Sodium bicarbonate → No effervescence

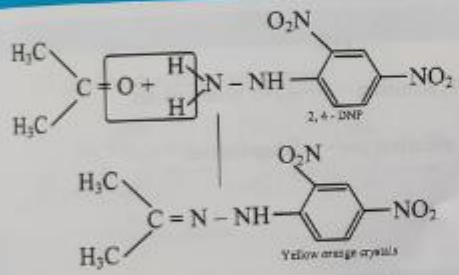
(Phenol is less acidic than benzoic acid)

Phenol and ethyl alcohol (Neutral $FeCl_3$)

Phenol + $FeCl_3$ → Violet coloration

Ethyl alcohol + $FeCl_3$ → No colour

Propanone and propanol (2, 4 – DNP)



Propanol + 2, 4 – Dinitrophenylhydrazine ——No crystals

Ethanal and propanal (Iodoform test)

$H_3C-\underset{\text{Ethanal}}{\overset{O}{\overset{\|}{C}}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + HCOONa$

$H_3C-CH_2-\underset{\text{Propanal}}{\overset{O}{\overset{\|}{C}}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No Yellow ppt.

Propanal and Propanone (Tollen's and Fehling's reagent)

Propanal + Tollen's reagent ——Silver Mirror

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 3OH^- + 2[Ag(NH_3)_2]^+$

$CH_3CH_2COO^- + 2H_2O + 4NH_3 + \underset{\text{(silver mirror)}}{2Ag\downarrow}$

Propanal + Fehling's solution → Reddish brown precipitate

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 2Cu^{2+} + 5OH^-$

$CH_3CH_2COO^- + 3H_2O + \underset{\text{(Reddish brown ppt.)}}{Cu_2O}$

Propanone — Fehling's solution — Negative Test

Propanone — Tollen's reagent — Negative Test

Pentan 2 one and pentan 3 one (Iodoform test)

$H_3C-CH_2-CH_2-\underset{\text{(Pentan -2- one)}}{\overset{O}{\overset{\|}{C}}}-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$

$\underset{\text{Iodoform (yellow ppt.)}}{CHI_3} + CH_3CH_2CH_2COONa$

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_3-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Propanal and benzaldehyde (Fehling's solution)

Propanal + Fehling's solution → Reddish brown precipitate (Cu_2O)

$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H + \underset{\text{Fehling's solution}}{2Cu^{2+} + 5OH^-} \rightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$

Benzaldehyde + Fehling's solution → No precipitate

$-CHO + 2Cu^{2+} + 5OH^- \longrightarrow$ No Reaction

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

HCOOH — Fehling's solution — $H_2O + CO_3^{2-} + Cu_2O$ (Reddish Brown ppt.)

HCOOH — Tollen's reagent — $2Ag\downarrow + CO_3^{2-} + H_2O$ (Silver Mirror)

Ethanoic acid — Fehling's solution — No brown ppt

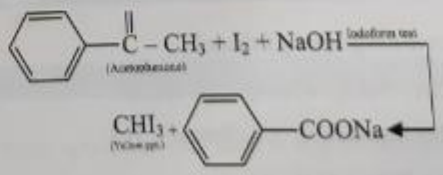
Ethanoic acid — Tollen's reagent — No silver mirror

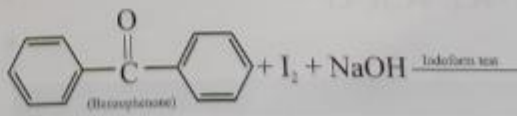
Ethanal and methanal (Iodoform test)

$\underset{\text{Ethanal}}{CH_3CHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (yellow ppt.)}}{CHI_3} + HCOONa$

$\underset{\text{Methanal}}{HCHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Acetophenone and benzophenone (Iodoform test)





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

POCO
SHOT ON POCO X2

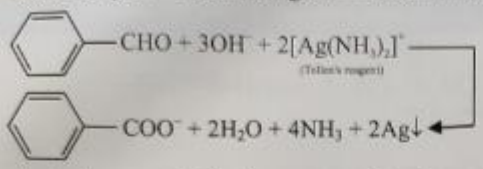
Benzoic acid and ethylbenzoate

$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$
Effervescence

Ethyl benzoate + Sodium bicarbonate → No effervescence

Benzaldehyde and acetophenone (Tollen's test)

Benzaldehyde + Tollen's reagent → Silver mirror



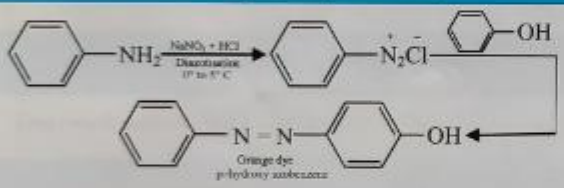
Acetophenone + Tollen's reagent → No silver mirror

Methyl amine and dimethyl amine (Isocyanide test)

$\underset{\text{(Methyl amine)}}{CH_3NH_2} + CHCl_3 + 3KOH \underset{\text{(alc.)}}{\rightarrow} \underset{\substack{\text{Methylisocyanide}\\ \text{(Offensive smell)}}}{CH_3NC} + 3KCl + 3H_2O$

$\underset{\text{Di-methyl amine}}{H_3C-\overset{\overset{CH_3}{|}}{N}H} + CHCl_3 + 3KOH\,(alc.) \rightarrow$ No offensive smell

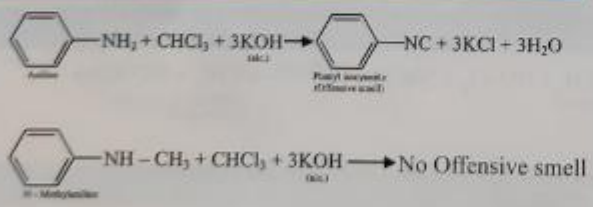
Aniline and ethyl amine (Diazotisation)



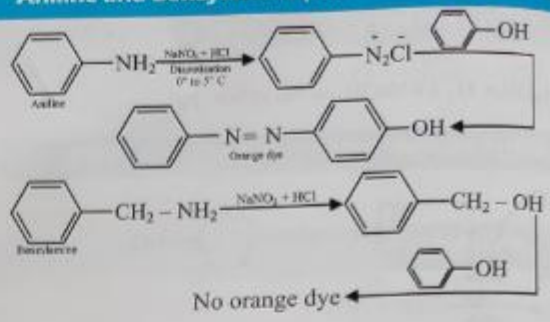
$CH_3CH_2NH_2 \xrightarrow{NaNO_2 + HCl} CH_3CH_2OH$ —OH

No Orange dye

Aniline and N-methylaniline (Isocyanide test)



Aniline and Benzylamine (Diazotisation + Phenol



Glucose and fructose

$\underset{\text{(Brown colour)}}{Glucose + Br_2 + H_2O} \longrightarrow \underset{\text{(Colourless)}}{Gluconic\ acid} + 2HBr$

$\underset{\text{(Brown colour)}}{Fructose + Br_2 + H_2O} \longrightarrow \underset{\text{(No change in colour)}}{Brown\ colour}$

Glucose and Sucrose

Glucose + Tollen's reagent —— Silver mirror

Sucrose + Tollen's reagent —— No silver mirror

Glucose and starch

Glucose + Fehling's solution —— Red ppt.

Starch + Fehling's solution —— No red ppt.

OR

Glucose + I_2 solution —— No blue colour

Starch + I_2 solution —— Blue colour

Some Important points related to Ethanol

- Iodoform test is given by Ethanol
- $C_2H_5-OH + FeCl_3 \rightarrow$ No specific colour
- $C_2H_5O^-$ (No Resonance, +I effect of C_2H_5)
- $C_2H_5-OH + PCl_5 \rightarrow C_2H_5-Cl$
- $C_2H_5-OH \xrightarrow{oxidation}$ Aldehyde / acid
- C_2H_5OH not change colour of litmous paper because C_2H_5OH is less acidic than H_2O.
- Ethanol + Benzene diazonium chloride → No dye formation
- Ethanol + Br_2 + Water → No white ppt.

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Chapter – 13 Organic Reagents

1. Alcoholic KOH

R–X → Alkene ; Elimination reaction

2. Aluminium Ethoxide

$$\underset{\text{(Aldehyde)}}{RCH=O} \rightarrow \underset{\text{(Ester)}}{R-\underset{\underset{O}{\|}}{C}-O-CH_2R}$$ (Tishchenko Reaction)

3. Aqueous KOH/NaOH

R–X→ROH

Nucleophilic substitution reaction also used for Cannizzaro reaction with aldehyde.

4. Baeyer's Reagent (Alkaline cold dilute $KMnO_4$)

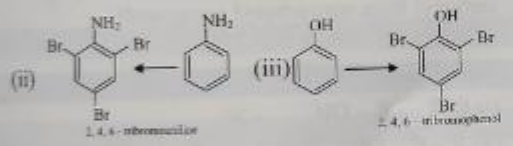
$$RCH=CHR' \rightarrow \underset{OH}{RCH}-\underset{OH}{CHR'}$$ (Syn)

Alkene → 1, 2 diol

(used to detect unsaturation)

5. Bromine water

(i) used to detect unsaturation:



6. Benedict's solution

Used to detect aldehyde group

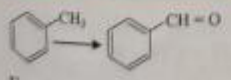
RCHO → RCO_2^-
[ketone gives –ve test]

7. $Cu_2Cl_2 + NH_4OH$

Used to Detect terminal Alkyne

Red Precipitate observed

8. CrO_2Cl_2

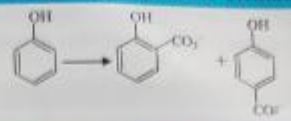


Etard reaction

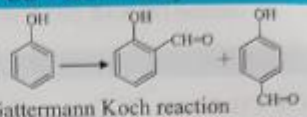
9. CrO_3

(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C=O$
(iii) R_3COH → no reaction

10. $CCl_4 + OH^-$ (Reimer Tiemann reaction)

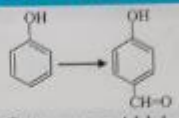


11. $CO + HCl + AlCl_3$



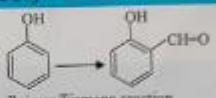
Gattermann Koch reaction

12. $HCN + HCl + AlCl_3$



Gattermann Aldehyde Synthesis

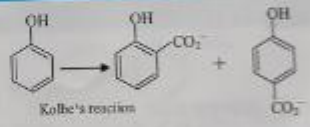
13. $CHCl_3 + KOH$

(i) 

Reimer Tiemann reaction

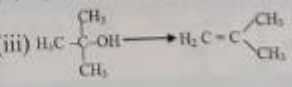
(ii) $RNH_2 \rightarrow RNC$ (Carbylamine reaction) (Isocyanide test)
(Used to detect 1° Amine)

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



Kolbe's reaction

15. Cu/Δ

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

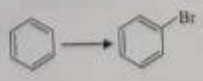
16. 2,4 – di-nitro phenyl hydrazine (2, 4 - D.N.P.)

Used to detect carbonyl group (orange ppt observed)

17. di-methyl sulphoxide (D.M.S.O.)

Polar aprotic solvent used in S_N2 mechanism

18. $Fe + Br_2/FeBr_3$



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19. Fehling solution

(Fehling solution A = aq.$CuSO_4$)

(Fehling solution B = Alkaline sodium potassium tartarate (Rochelle salt)

Used to identify –CH=O group

PhCHO gives –ve test

Observation: red ppt of Cu_2O formed

20. Grignard Reagent

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

21. H_2(Pd/$CaCO_3$) Quinoline (Lindlar catalyst)

R–C≡C–R→R–CH=CH–R (cis)

22. H_3PO_2

23. $N_3H + H_2SO_4$

$$R-\underset{\underset{O}{\|}}{C}-OH \rightarrow RNH_2$$

(Schmidt Reaction)

24. H_3PO_4/Δ

$H_3PO_4 \Rightarrow$ same as H_2SO_4/Δ

25. H_2SO_4/Δ

$$\underset{\underset{OH}{|}}{RCH}-CH_3 \rightarrow RCH=CH_2$$

Saytzeff Product; C^- intermediate

Rearranged alkene can be formed

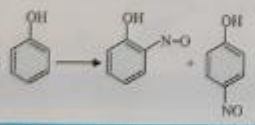
26. HNO_2 ($NaNO_2$ + HCl)

(i) $RNH_2 \rightarrow R-OH$;

(ii) $PhNH_2 \xrightarrow{0°-5°C} PhN_2^+Cl^-$

(iii) $PhNH_2 \rightarrow PhOH$ (high temperature)

(iv)



27. HIO_4 (Periodic acid)

$$\underset{\underset{OH}{|}}{RCH}-\underset{\underset{OH}{|}}{CH}-R' \rightarrow RCH=O + R'CH=O$$

oxidative cleavage of diols

28. H_2(Ni) can reduce

(i) $R-\underset{\underset{O}{\|}}{C}-R \rightarrow R_2CHOH$

(ii) $R-\underset{\underset{O}{\|}}{C}-H \rightarrow RCH_2OH$

(iii) $RCN \rightarrow RCH_2NH_2$; $-C\equiv C- \rightarrow -CH_2-CH_2-$, $-HC=CH- \rightarrow -CH_2-CH_2-$

29. H_2(Pd/$BaSO_4$)

Quinoline

$$R-\underset{\underset{O}{\|}}{C}-Cl \rightarrow RCH=O$$

(Rosenmund reduction)

30. Jones Reagent (CrO_3 + dil. H_2SO_4 + acetone)

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

31. $KHSO_4$ Dehydrating Reagent

$$\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH}-CH_2OH \rightarrow CH_2=CH-CH=O$$

32. $K_2Cr_2O_7/H^+$

(i) $RCH_2OH \rightarrow RCO_2H$; (ii) $R_2CHOH \rightarrow R_2C=O$

33. MnO_2

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

(ii) $PhCH_2OH \rightarrow PhCH=O$

To oxidize allylic/ benzylic hydroxyl group into corresponding carbonyl.

34. $NaHCO_3$

$$RCO_2H \xrightarrow{NaH^{14}CO_3} RCO_2^-Na^+ + {}^{14}CO_2 \uparrow$$

35. $NaHSO_3$

$$R-\underset{\underset{O}{\|}}{C}-R \rightarrow R_2C\begin{cases}OH\\SO_3^-Na^+\end{cases}$$

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

36. NaOH (aq.)

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

(ii) $R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[(H_2O)]{NaOH} R-\underset{\underset{O}{\|}}{C}-O^- + R'OH$

Basic hydrolysis of ester

(iii) $HCHO \xrightarrow{OH^-} HCO_2^- + CH_3OH$ (cannizzaro)

(iv) $H_3C-CH=O \xrightarrow[\Delta]{OH^-} H_3C-CH=CH-CH=O$

(Alcohol condensation)

37. Ninhydrin

Detection of amino acid

Observation : Purple coloured solution in presence of amino acid

38. NaOR

Strong base:

(i) $\underset{\underset{X}{|}}{RCH}-CH_2R \rightarrow R-CH=CH-R$

(Saytzeff Product : E_2 elimination)

(ii) $H_3C-\underset{\underset{O}{\|}}{C}-OEt \rightarrow H_3C-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt$

(claisen condensation) (β keto ester)

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39. NaOH + X_2 or NaOX

(i) $R-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow RCO_2 + CHX_3$ (Haloform reaction)

(ii) $R-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow RNH_2$ (Hoffman Degradation)

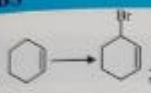
40. NaOH + CaO

$RCO_2H \rightarrow RH$

41. MnO / 300°C

$R-\underset{\underset{O}{\|}}{C}-O-\boxed{H+HO}-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-\underset{\underset{O}{\|}}{C}-R + CO_2 + H_2O$

42. NBS

(i) 

; (ii) $PhCH_3 \rightarrow PhCH_2-Br$

43. $NaNO_2$ + HCl

$RNH_2 \rightarrow R-OH$

44. $NaNH_2$ in paraffin

Non-terminal Alkyne → Terminal Alkyne
(2-Butyne → 1-Butyne)

45. Na/EtOH

Reduces all except C/C double & triple bond

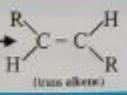
46. Zn(Hg) + HCl [Clemmensen's reduction]

$R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-CH_2-R$

47. NH_2-NH_2/OH^- [Wolf Kishner reduction]

$R-CO-R \rightarrow R-CH_2-R$

48. Na in Liq. NH_3 [Birch reduction]

$R-C\equiv CR \longrightarrow$ 

(trans alkene)

49. $OsO_4 + H_2O$

$RCH=CHR \longrightarrow R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R$
(syn addition)

50. O_3

$R-CH=CH-R \xrightarrow[H_2O/Zn]{O_3} R-CHO + R-CHO$
(Ozonolysis product)

51. Oxirane followed by H^+ (2C increase in chain)

$RMgX \rightarrow RCH_2-CH_2-OH$

52. PCC (Mild oxidizing reagent)

(i) $RCH_2OH \rightarrow RCHO$,

(ii) $R_2CHOH \rightarrow R_2C=O$

(iii) R_3COH → no reaction

53. P(red) + Br_2

(i) $CH_3CO_2H \longrightarrow H_2\underset{\underset{Br}{|}}{C}-CO_2H$ (HVZ reaction)

(ii) $ROH \rightarrow R-Br$

54. P (red) + HI

$CH_3CO_2H \rightarrow CH_3-CH_3$

$CH_3CH=O \rightarrow CH_3-CH_3$

$CH_3CH_2OH \rightarrow CH_3-CH_3$

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

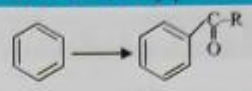
55. Perbenzoic acid [Baeyer Villiger Oxidation]

$R-\underset{\underset{O}{\|}}{C}-R' \longrightarrow R-\underset{\underset{O}{\|}}{C}-OR'$

R' having more migrating tendency then R.

56. RCl + $AlCl_3$ [Friedel craft's alkylation]

57. RCOCl + $AlCl_3$ [Friedel craft's acylation]

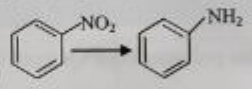


58. ROH + RCOOH (Esterification reaction)

$ROH + R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{conc.\ H_2SO_4} R-\underset{\underset{O}{\|}}{C}-OR$ Ester formed

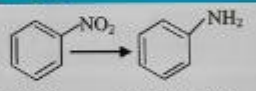
59. $SnCl_2$ + HCl (Produce H + 3Cl + Sn^{++})

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

(ii) 

(iii) $RCN \rightarrow RCH=O$ [Stephen's reduction]

60. Sn + HCl

(i) 

(ii) $RCN \longrightarrow R-CH_2NH_2$

61. Silver salt RCOOAg (Hunsdiecker reaction)

$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

62. AgOH/ moist Ag_2O

$R_4\overset{-}{N}\overset{-}{X} \rightarrow R_4\overset{+}{N}\overset{-}{O}H$

63. $SOCl_2$ (thionyl chloride)

$R-\underset{\underset{O}{\|}}{C}-OH/R-OH \longrightarrow R-\underset{\underset{O}{\|}}{C}-Cl/R-Cl$

64. Tollen's reagent Test

(i) Terminal alkyne gives
(ii) Aldehyde Group gives
(iii) Ketone gives –ve test
(iv) α-hydroxy ketone gives
(v) HCOOH gives
(vi) Hemiacetal gives
(vii) PhNH-OH gives **(Phenyl hydroxyl amine)**

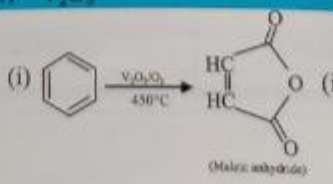
65. Benzene sulphonyl chloride (Hinsberg reagent)

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

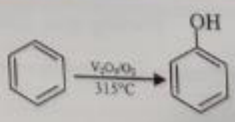
66. Tetra ethyl lead (TEL)

Used as antiknock compound

67. V_2O_5

(i) 

(Maleic anhydride)

(ii) 

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Chapter – 14 Polymers

Classification Based on Source

Natural polymers	Semi-synthetic polymers	Synthetic polymers
Proteins, cellulose, starch, some resins and rubber	Cellulose acetate (rayon) and cellulose nitrate	Nylon 6,6 and Buna - S

Classification Based on Structure of Polymers

Linear polymers	Branched chain polymers	Cross linked or Network polymers
High density polythene and PVC	Low density polythene	Bakelite and melamine

Polymers and Intermolecular Forces

Thermosetting	Fibres	Thermoplastic polymers	Elastomers
Bakelite and urea-formaldelyde resins	Polyamide (nylon 6, 6) and polyesters (terylene)	Polythene, polystyrene and polyvinyls	Buna-S, Buna-N and neoprene

Super Note : Strength of intermolecular forces in polymers:-Thermosetting polymers > Fibres > Thermoplastic polymers > Elastomers

Natural Rubbers

- Natural rubber is hydrocarbon polymer built up from the monomer isoprene.

$$\underset{\text{Isoprene}}{n\,H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2} \xrightarrow[\text{(1, 4–Addition)}]{\text{Polymerisation}} \underset{\text{Cis 1, 4 polyisoprene (Natural rubber)}}{\left[CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2\right]_n}$$

Vulcanisation

- Natural rubber becomes soft at high temperature (>335 K) and brittle at low temperatures (< 283 K) and shows high water absorption capacity. It is soluble in non-polar solvents and is non-resistant to attack by oxidising agents to improve it is vulcanised.
- In viulcanisation process, raw rubber is mixed with 1-3% S is used in rubber bands and 5% of sulphur for tyre rubber and heated.
- This sulphur reacts with polymer molecules and form a cross-linked network (which provide strength and elasticity).

Biodegradable polymers

1. ***Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV)***
- It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3 - hydroxypentanoic acid.
- PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs.
- PHBV undergoes bacterial degradation in the environment.

2. ***Nylon 2–nylon 6***
- It is an alternating polyamide copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid [$H_2N\ (CH_2)_5$ COOH].
- It undergoes bacterial degradation in the environment.

Super Note : Triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) is used for synthesis of high density polythene.

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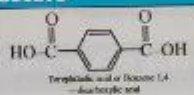
Addition Polymers

S. No	Name of Polymer	Starting Materials	Nature of Polymer
		I. Polyolefins	
1.	Polyethylene or Polyethene	$CH_2=CH_2$	Low density homopolymer (branched chain growth)
2.	Polypropylene or Polypropene	$CH_3CH=CH_2$	Homopolymer, linear, chain growth
3.	Polystyrene	$C_6H_5CH=CH_2$	Homopolymer, linear, chain growth
		II. Polydienes	
1.	Neoprene (Synthetic rubber)	$CH_2=CH-\overset{Cl}{\overset{\vert}{C}}=CH_2$ Chloroprene or 2-Chloro–1,3–butadiene	Homopolymer, chain growth
2.	Buna S (Styrene-Butadiene, Rubber) SBR or GRS	$CH_2=CH-CH=CH_2$ and $C_6H_5CH=CH_2$ 1,3 – butadiene Styrene	Copolymer, chain growth
3.	Buna N (Nitrile Butadiene Rubber) NBR	$CH_2=CH-CH=CH_2$ and $CH_2=CH-CN$ 1,3 - Butadiene Acrylonitrile	Copolymer
		III. Polyacrylates	
1.	Polymethylmethacrylate (Flexiglass Lucite, Acrylite or Perspex) PMMA	$H_2C=\overset{CH_3}{\overset{\vert}{C}}-COOCH_3$	Homopolymer
2.	Polyethylacrylate	$H_2C=CH-COOC_2H_5$	Homopolymer
3.	Polyacrylonitrile or Orion (PAN)	$CH_2=CH-CN$	Homopolymer
		IV. Polyhalofins	
1.	Polyvinyl chloride (PVC)	$CH_2=CH-Cl$	Homopolymer, chain growth
2.	Polytetrafluoroethylene or Teflon (PTFE)	$F_2C=CF_2$	Homopolymer
3.	Polymonochlorotrifluoro-ethylene (PCFE)	$ClFC=CF_2$	Homopolymer

Condensation Polymers

S. No	Name of Polymer	Starting Materials	Nature of Polymer
		I. Polyesters	
1.	Terylene or Dacron	$HO-CH_2-CH_2-OH$ (Ethylene glycol or Ethane 1,2 diol) And  (Terephthalic acid or Benzene 1,4 – dicarboxylic acid)	Copolymer, step growth, linear
2.	Glyptal or Alkyl resin	$HO-CH_2-CH_2-OH$ (Ethylene glycol) And (Phthalic acid or Benzene 1,2 dicarboxylic acid)	Copolymer, linear step growth
		II. Polyamides	
1.	Nylon-6,6	$HO-\overset{O}{\overset{\Vert}{C}}(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-OH$ (Adipic acid) and $H_2N-(CH_2)_6-NH_2$ (Hexamethylenediamine)	Copolymer, linear, step growth
2.	Nylon-6,10	$H_2N(CH_2)_6NH_2$ (Hexamethylene diamine) and $HOOC(CH_2)_8COOH$ (Sebacic acid)	Copoymer, linear, step growth
3.	Nylon -6	Caprolactum	Homopolymer, linear
		III. Formaldehyde resins	
1.	Phenolformaldehyde resin or Bakelite	Phenol and formaldehyde	Copolymer, step growth
2.	Melamine formaldehyde resin	Melamine and formaldehyde	Copolymer, step growth

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CARBOHYDRATES

- Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or the compound which produce such units on hydrolysis.
- **Monosaccharide ($C_nH_{2n}O_n$):** A carbohydrate that cannot be hydrolyzed to simpler compounds is called monosaccharide. Monosaccharide which have six carbon are either aldohexoses or ketohexoses.

MONOSACCHARIDES

On the Basis of No. of Carbon	On the Basis of Functional group	
	Aldose group (–CHO)	Ketose group (>C = O)
Triose (3C)	Glyceraldehyde	Dihydroxy acetone
Tetrose (4C)	Erythrose, Threose	Erythrulose
Pentose (5C)	Ribose, Deoxy-ribose	Ribulose
Hexose (6C)	Glucose, Galactose	Fructose
Haptose (7C)	———	Sedohaptulose

- **Anomers** : Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new asymmetric carbon is referred to as Anomeric carbon.

- **Epimers** : Diastereomers which differ in conformation at any one chiral carbon.
  Eg. D-Glucose & D-mannose & D-Glucose & D-Galactose
- **Oligosaccharides/di-saccharides** : gives two to ten monosaccharides on hydrolysis
- Disaccharides (by glycosidic linkage)

Sucrose $\xrightarrow{H_3O^+}$ α – D – Glucose + β – D – Fructose;
(1,2 Glycosidic linkage)

Maltose $\xrightarrow{H_3O^+}$ 2α – D – Glucose unit
(1,4 Glycosidic linkage)

Lactose $\xrightarrow{H_3O^+}$ β – D – Glucose + β - D - Galactose
(1,4 Glycosidic linkage)

Reducing Sugars

Carbohydrates reducing fehling reagent or Tollen's reagent are termed as reducing carbohydrates.

E.g. all monosaccharides and disaccharides (except sucrose).

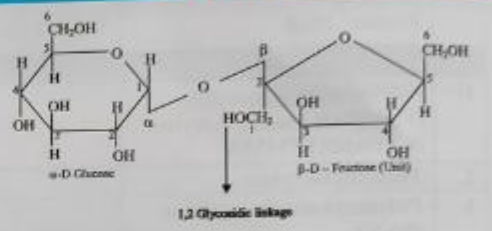
Non-reducing Sugars

Carbohydrates which do not reduce such reagents are known as non-reducing carbohydrates

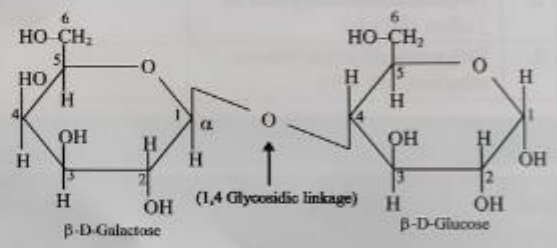
Eg. : sucrose and polysaccharides.

Disaccharides (by glycosidic linkage)			
Reducing Sugar		Non- reducing Sugar	
L Lactose	M Maltose	T Trehalose	S Sucrose
β1 galactose	α1 glucose	α1 glucose	α1 glucose
β4 glucose	α4 glucose	α1 glucose	β2 fructose

Sucrose



Lactose



- **Polysaccharide:** Contain more than ten monosaccharide units.
  $(C_6H_{10}O_5)_n$: Starch & Cellulose

	Monosaccharide	Di-saccharide/ Oligosaccharide	Polysaccharide
Unit	Single saccharide unit	2-10 unit of Monosaccharide	10-100s unit of Monosaccharide
Suffix	'ose'	'ose'	'an'
Soluble in water	Yes	Yes	No
Hydrolysis	Not Possible	Possible	Possible
Direct Oxidation	Yes	No	No
Taste	Sweet in taste	Sweet in taste	Tastless
Example	Glucose, Galactose fructose, Ribose	Lactose, Maltose, Trehalose, Sucrose	Cellulose, Starch, Glycogen Chitin

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olecules

dic linkage)

on- reducing Sugar	
alose	S Sucrose
ose	α1 glucose
ose	β2 fructose

D - Fructose (Unit)

β-D-Glucose

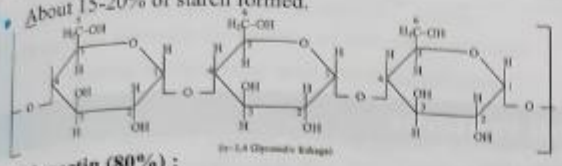
monosaccharide

le/ ide	Polysaccharide
de	10-100s unit of Monosaccharide
	'an'
	No
	Possible
	No
	Tastless
	Cellulose, Starch, Glycogen Chitin

Starch : (Amylose & Amylopectin)

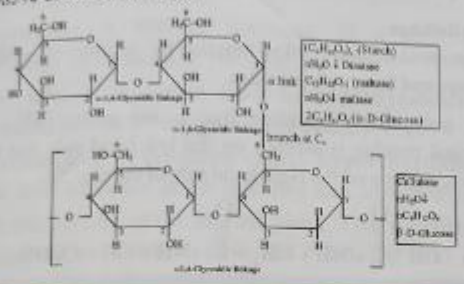
Amylose (20%) :

- An unbranched water soluble polymer.
- Soluble in H_2O & gives blue colour with I_2
- About 15-20% of starch formed.

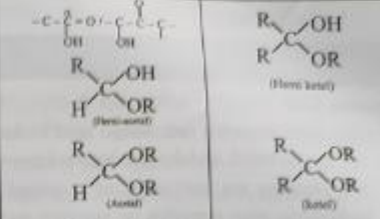


Amylopectin (80%) :

- A branched water insoluble polymer.
- Insoluble in H_2O
- 80-85% of starch formed

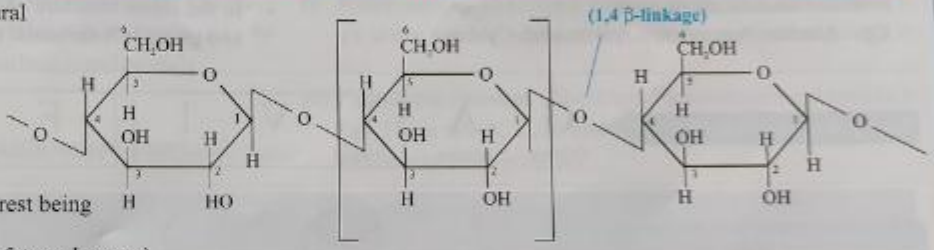


Types of Sugar

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		
Example	• **All Monosaccharide** Glucose, Fructose, Mannose, Galactose • **Disaccharides** Maltose, Lactose	• **Disaccharide** Sucrose, Trehalose • **Polysaccharides** Starch, Cellulose

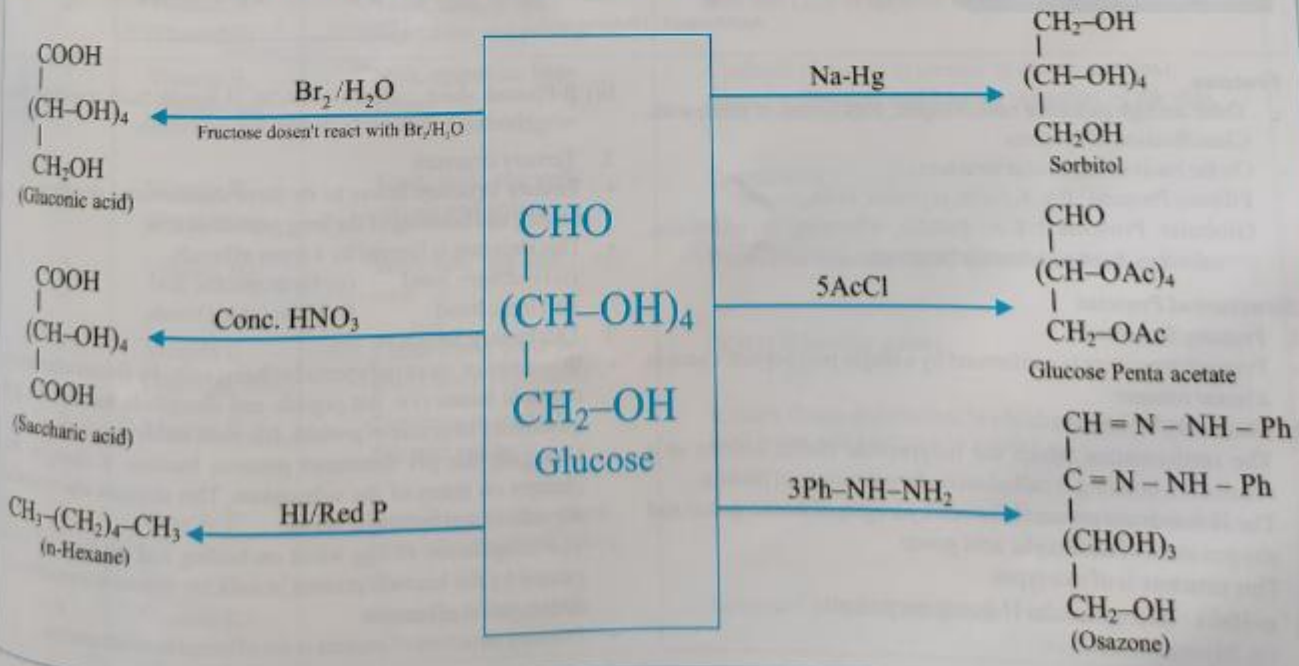
Cellulose $(C_6H_{10}O_5)_n$

- It is the most abundant and structural polysaccharide of plants. It is important food source of some animals. It is polymer D(+)β-glucose.
- The Chief of source of cellulose are wood (contains 50% cellulose rest being lignin, resins etc) and cotton (contains 90% cellulose rest being fats and waxes)



Structure of Cellulose

Reactions of Glucose (Open Chain structure)



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Super Note :

- Glucose is also known as dextrose, because the glucose found in nature is dextrorotatory. [d or (+)]
- Fructose is also known as Levulose because the fructose found in nature is levorotatory. [l or (–)]
- All the carbohydrates which is present in nature are generally. D-configured. (Molecule configuration has no connection with optical rotation)
- All the α-amino acids which is present in nature are generally L-configured.

D/L	d/l
It denotes configuration of molecule w.r.t. glyceraldehyde	It denotes direction of rotation of plane polarized light
It is theortical quantity.	It is a experimental quantity.

Amino Acids and Proteins

Amino Acid

- The bond between two amino acid molecules is **peptide bond** 'or' amide bond, and the resultant is known as dipeptide.
- All proteins are polymers of α-amino acids and on partial hydrolysis give peptides of varying molecular masses which upon complete hydrolysis give α-amino acids.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha - \text{amino acids}$$

Classification of Amino Acid

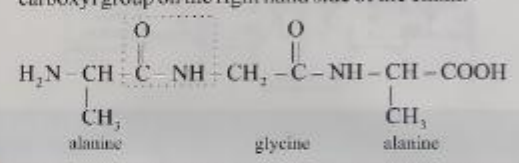
- **Essential amino acid**
- Amino acids which are necessarily be present in our diet are called essential amino acids.
  Eg. : Leucine, Isoleucine, Lysine, Histidine, Methionine, Phenylalanine, Threonine, Tryptophan and Valine
- **Non essential amino acid**
- 10 amino acids that are synthesis in our body and these are said to be non essential amino acids
  Eg. : Alanine, Aspargine, Aspartic acid, Cystine

Properties

- **Except glycine** all other naturally occuring α-amino acids are **optically active,** since α-carbon is asymmetric. L-amino acids are represented by writting the $-NH_2$ group on the left hand side.

Peptide linkage

- Amino acid units are linked together by peptide $-\underset{\underset{O}{\|}}{C}-NH-$ linkage and form polypeptides.
- In a polypeptide structure free amino group (NH_2) i.e. N-terminal residue is written on the left hand side and the free carboxyl group on the right hand side of the chain.



- In the above structure **–COOH group is C-terminal residue and group is N-terminal residue.**

Non-polar amino acid	G Glycine	A Alanine	L Leucine	V Valine	I Isoleucine	F Phenylalanine	M Methionine	W Tryptophan	P Proline	
Polar uncharged amino acid	C Cysteine	S Serine	T Threonine	Y Tyrosine	N Asparagine	Q Glutamine				
Polar charged amino acid	D Aspartic acid	E Glutamic acid	H Histidine	R Arginine	K Lysine					

Proteins

- These are high molecular mass complex, biopolymers of amino acids.
  Classification of Proteins
- On the basis of molecular structure :
  Fibrous Proteins : E.x. Keratin, myosine, collagen, etc.
  Globular Proteins : E.x. Insulin, albumin, thyoblobulin, antiadiodies, haemoglobin fibrinogen etc.

Structure of Proteins

1. Primary Structure :
- Primary struciture is conformed by a single polypeptide chain in a linear manner.

2. Secondary Structure :
- The conformation which the polypeptide chains assume as a result of H-bonding is called secondary structure of protein.
- The H-bonds are present between hydrogen of amino group and oxygen atom of carboxylic acid group.
- This structure is of two types

(i) α-Helix : Intermolecular H-bonds are present.
Eg. Myosin, Keratin etc.

(ii) β-Pleated sheet : Intermolecular H-bonds hold together the neighboring polypeptide chains. Eg. Silk fibres.

3. Tertiary structure
- Tertiary structure refers to its three dimensional structure, i.e. folding and bonding of the long peptide chains.
- This structure is formed by 4 types of bonds.
  (i) Hydrogen bond (ii) Hydrophobic acid
  (iii) Ionic bond (iv) Disulphide bonds

4. Quaternary Structure
- When two or more polypeptide chains unite by forces other than covalent bonds (i.e. not peptide and disulphide bonds), we get quaternary structure of protein. It is most stable structure.
- Changing the pH denatures proteins because it changes the charges on many of the side chains. This disrupts electrostatic attractions and hydrogen bonds.
- The coagulation of egg white on boiling and curdling of milk caused by the bacteria present in milk are common examples of denaturation of protein.
- Primary structure of protein is not affected in denaturation.

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Hormones

- These are molecules that act as ***intercellular messengers.***
- These are produced by **endocrine glands.**
- Chemically, they are **steroids** (e.g. estrogens & androgens), **polypeptides** (e.g. insulin & endorphins) or **amino acid derivatives** (e.g. epinephrine & norepinephrine).
- Hormones maintain the balance of biological activities.

Some hormones and their functions

- **Glucagon & Insulin:** They regulate blood glucose level. Glucagon increases glucose whereas Insulin decreases it.
- **Epinephrine & norepinephrine**: They mediate responses to external stimuli.
- **Growth hormones & sex hormones:** They play role in growth and development.
- **Thyroxine:** A thyroid hormone. It is an iodinated derivative of amino acid tyrosine.

Low level of thyroxine leads to **hypothyroidism.** It is characterized by lethargyness and obesity.

Increased level of thyroxine causes **hyperthyroidism.**

Low level of iodine in the diet may lead to hypothyroidism and enlargement of the thyroid gland. This is controlled by adding sodium iodide to table salt ("Iodised" salt).

- **Steroid hormones from adrenal cortex:**

Glucocorticoids: Control the carbohydrate metabolism, modulate inflammatory reactions, and are involved in reactions to stress.

Mineralocorticoids: Control the level of excretion of water and salt by the kidney.

Improper functioning of adrenal cortex results in **Addison's disease** characterized by hypoglycemia, weakness and increased susceptibility to stress. It should be treated by glucocorticoids & mineralocorticoids.

- **Steroid hormones from gonads:** Responsible for development of secondary sex characters.

Testosterone: Male sex hormone. It is responsible for development of secondary male characteristics (deep voice, facial hair, general physical constitution).

Estradiol: Female sex hormone. It is responsible for development of secondary female characteristics and regulates menstrual cycle.

Progesterone: Responsible for preparing the uterus for implantation of fertilised egg.

Vitamins

- Vitamins may be defined as a group of biomolecules which are required in small amounts for normal metabolic process and for the life, growth and health of human beings and animals.

Classification of Vitamins

- The vitamins are broadly classified into two categories.

(i) Water soluble vitamins : Vitamin B-complex and vitamin C are water soluble vitamins and must be supplied regularly in diet.

(ii) Fat soluble vitamins : These are oily substances and soluble in fats **These are A, D, E and K.** They are stored in liver and adipose (fat storing) tissues.

Sr. No.	Name of Vitamins	Sources	Deficiency diseases
1.	Vitamin A	Fish liver oil, carrots butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2.	Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
3.	Vitamin B_2 (Riboflavin)	Milk, eggwhite, liver kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk cereals and grams	Convulsions
5.	Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6.	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
7.	Vitamin D	Exposure to sunlight fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
8.	Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
9.	Vitamin K	Green leafy vegetables	Increased blood clotting time

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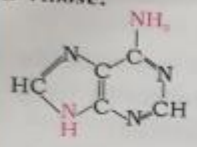
NUCLEIC ACIDS

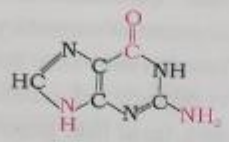
- These are the biomolecules present in chromosomes (hereditary particles made up of proteins & nucleic acids).
- They are 2 types: **Deoxyribonucleic acid (DNA)** and **Ribonucleic acid (RNA).**
- Nucleic acids are long chain polymers of **nucleotides,** so they are also called **polynucleotides.**

Chemical Composition of Nucleic Acids

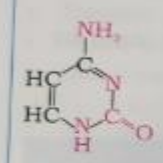
- Complete hydrolysis of DNA or RNA yields a pentose sugar, phosphoric acid & nitrogen bases.
- In DNA, the sugar is **β-D-2-deoxyribose.** In RNA, it is **β-D-ribose.**



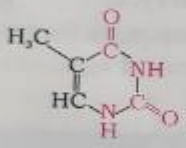
Adenine (A)



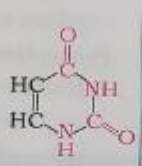
Guanine (G)



Cytosine (C)



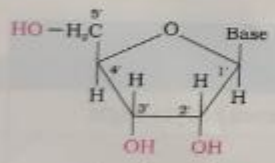
Thymine (T)



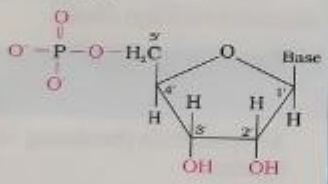
Uracil (U)

Structure of Nucleic Acids

- When a base is linked to 1′ position of sugar, it forms **nucleoside.**
- When a nucleoside is linked to phosphoric acid at 5′-position of sugar, it gives a **nucleotide.**

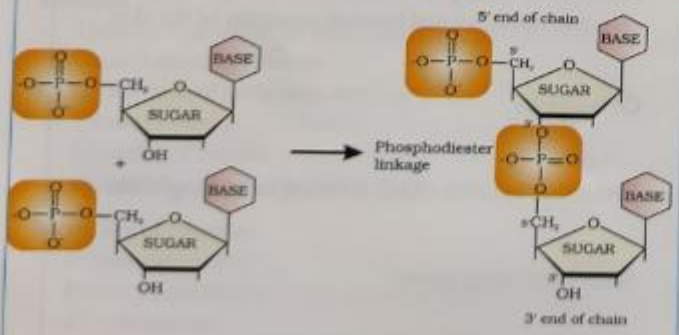


A nucleoside

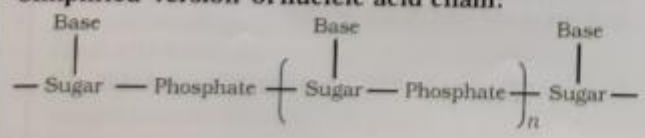


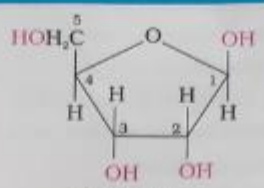
A nucleotide

- Nucleotides are joined together by **phosphodiester linkage** between 5′ and 3′ carbon atoms of the pentose sugar.

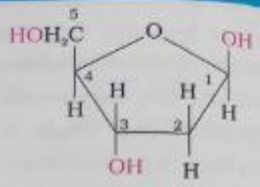


- **Simplified version of nucleic acid chain:**





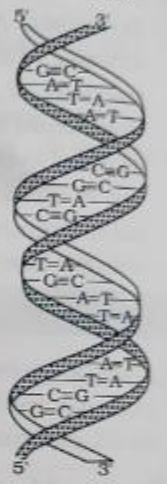
β-D-ribose



β-D-2-deoxyribose

- Nitrogen bases are N- containing heterocyclic compounds.
- 4 bases in DNA: Adenine (A), Guanine (G), Cytosine (C) & Thymine (T).
- 4 bases in RNA: Adenine (A), Guanine (G), Cytosine (C) & Uracil (U).

- Information regarding sequence of nucleotides in a nucleic acid chain is called its **primary structure.**
- **James Watson & Francis Crick** gave a double strand **helix structure (secondary structure)** for DNA.
- Two nucleic acid chains are coiled each other and held together by **hydrogen bonds** between pairs of bases.
- The two strands are complementary to each other. Adenine pairs with thymine and cytosine pairs with guanine.
- In secondary structure of RNA, single stranded helices are present. Sometimes they fold back on themselves to form a double helix structure.



- RNA are 3 types: **messenger RNA (m-RNA), ribosomal RNA (r-RNA) & transfer RNA (t-RNA).**

DNA Fingerprinting

- A sequence of bases on DNA is unique for a person and information regarding this is called **DNA fingerprinting.**
- It is same for every cell and cannot be altered.

Uses of DNA fingerprinting:

- In forensic laboratories for identification of criminals.
- To determine paternity of an individual.
- To identify the dead bodies in any accident by comparing the DNA's of parents or children.
- To identify racial groups to rewrite biological evolution.

Biological Functions of Nucleic Acids:

- DNA is the chemical basis of heredity and the reserve of genetic information.
- DNA maintains the identity of different species.
- DNA undergoes self-duplication during cell division and identical DNA strands are transferred to daughter cells.
- Protein synthesis in the cell.

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Chapter – 16 Chemistry in Everyday Life

Drugs and their Classification

- Drugs are chemicals of low molecular mass. Interact with macromolecular targets to produce biological response.
- If a drug produces therapeutic biological response then drug is called medicine.
- This process is called chemotherapy.
- Drugs are classified on the basis of :
  - **Pharmacological Effect :** Useful to doctors
    - Analgesics have pain killing effect
    - Antiseptics kill or arrest microbe growth
  - **Drug action :** Biochemical response
    - Antihistamine block histamine
  - **Chemical Structure :** Drugs that share common structure and have same pharmacological effect
  - **Molecular Target :** Most useful in medicine

Drug Target Interaction

Catalytic action of enzymes

- Active sites on enzyme hold substrate via ionic bonds, H-bonds, vander wall force and dipole-dipole interactions
- Enzymes provide functional groups that will attact on the substract

Drug enzyme interaction

- Drug inhibit any one of function of enzyme
- Such drugs are called enzyme inhibitors
  - Competitive inhibitors : Fight for binding to active site
  - Non competitive : Bind to allostearic site & change shape of active site
- Enzyme inhibitor bond : Strong covalent then bond does not break rather enzyme inhibitor complex is degraded

Receptors as drug targets

- Active site containing part is projected outward where as other part embedded
- To accomodate a messenger shape of receptor site changes
- Receptors show specificity due to
  - Different shapes
  - Different structure
  - Different amino acid composition
- Antagonist : Block message
- Agonist : Increases message transfer

Therapeutic Action of Drugs

Neurologically Active Drugs

- Affect message transfer mechanism

(a) **Tranquilizers :** Stress & mental diseases

- Decreases anxiety, stress, irritability & excitement
- Essential part of sleeping pills

(i) **Antidepressant :** If neurotransmittor ↓, depression ↑
It degrade enzyme that harms neurotransmittor
Iproniazid, phenelzine

(ii) **Mild Tranquilizer :** Relieves tension
Chlordiazepoxide, Meprobamate

(iii) **Depression hypertension :** Equanil

(iv) **Hypnotic Barbiturates :** Vernol, Amytal, Seconal, Nembutal, Luminal

(v) **Other :** Valium., Serotonin

(b) **Analgesics :** Reduce or abolish pain without causing loss of consiousness

(i) **Non-narcotic :** Paracetamol
Aspirin : Inhibits prostaglandins (inflammatory)
Used in heart attack patients

- Relieve skeletal pain as in arthritis
- Antipyretic action
- Does not cause platelet coagulation

(ii) **Narcotic :** Morphine & derivatives

- Medicine relieve pain, increase sleep, reduce pain in child birth
- High dosage cause stupor, coma, convulsions, death
- Called opiates (opium poppy)

Antihistamines

- **Histamin :** Vasodialation
  Contract muscles of bronchi & gut
  Relaxes muscles of blood vessels
  Nasal congestion in cold
  Activates in pollen allergy
- Brompheniramine (Dimetapp)
- Terpenadine (Seldane)
- These two are competitive inhibitors
- Above two not used as antacid because Aantiallergic & Antacid have different receptors

Antacids

- Cimetidine (Tegamet)
- Zantac (ranitidine)
- More acid produced in stomach causes ulcers
- Metal hydroxides used cause an increase in pH avove 7
- This treatment is not permanent
- Permanent treatment is stopping histamine as it increases HCl and pepsine
- Cimetidine was largest selling drug until zantac arrived

Antifertility

- Contain progesteron : Decreases ovulation
- Synthetic progesterone better than natural
- Nor ethindrone : Progesteron only
- Ethynylestradiol (novestrol) : oestrogen + progesteron

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Antibiotics

- The chemical substances produced from some micro organism (fungi, bacteria or mold) and are used to inhibit the growth of other micro organism.
- These are effective in the treatment of infections diseases, e.g. Penicillin - It is highly effective drug for pneumonia,
- Bronchitis, abcesses, sore throat etc.
- Synthetic antibiotics are Streptomycin (Tuberculosis),
- Chloromycetin - (Typhoid, Meningitis, Pneumonia, diarrhoea, dysentary etc.)
- Tetracyclins - (Acute fever, trachoma, dysentery & urinarytract infection)

Antimicrobials

- **Antiseptics :** Living tissues
  Furacine
  Soframycine
- Dettol : Chloroxylend terpencol
- Soaps : Bithional (ol)
- Tincture of Iodine : 2-3% I_2 in $-OH/H_2O$
- Boric acid : Dilute aq. solution for eyes
- Phenol : 0.2%
- **Disinfectant :** Non living
- Chlorine : 0.2 - 0.4 ppm
- SO_2 : Low conc.
- Phenol : 1%

Chemicals in Food

- Enhancing appeal, Nutritive valve, Preservation
- Main categories of additives
- Food colour, Fat emulsifies, Antioxidant, Nutrition, Sweetness, Flavour, Preservatives

Sweetness

- **Aspartame :** Most successful - cold food
- 100 times more sweet than natural sugar.
- methyl ester of dipeptide of asparctic acid & phenylalanin
- Unstable at temperature of cooking

- **Saccharin :** Ortho sulphobenzimide - first discovered for diabetic patients.
- 550 times more sweet than natural sugar.
- **Alitame :** Control difficult as it is 2000 times more sweet than natural sugar
- **Sucralose :** Trichloroderivative of sucrose
  600 times more sweet than natural sugar.
  Appearance & taste like sugar
  No calories

Food presenatives

- Sodium benzoate, salts of sorbic acid, propanoic acid, NaCl, Oils etc.

Soaps and Detergent

$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \end{array} + 3NaOH \rightarrow 3C_{17}H_{35}COONa + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Glyceryl ester of stearic acid (Fat) | Sodium hydroxide | Sodium stearate | Glycerol (or Glycerine)

- Soaps containing sodium salts are formed by heating fat (i.e., glyceryl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as **saponification**

Anionic Detergents

$$\underset{\text{Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} \xrightarrow{H_2SO_4} \underset{\text{Lauryl hydrogensulphate}}{CH_3(CH_2)_{10}CH_2OSO_3H}$$

$$\xrightarrow{NaOH(aq)} CH_3(CH_2)_{10}CH_2OSO_3^-\overset{+}{N}a$$

Cationic Detergents

- Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions.
- Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom

$$\left[CH_3(CH_2)_{15}-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N}}}}-CH_3\right]^+ Br^-$$

Cetyltrimethyl ammonium bronide

Non-ionic Detergents

$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethyleneglycol}}{HO(CH_2CH_2OH} \xrightarrow{-H_2O}$$

$$CH_3(CH_2)_{16}COO(CH_2CH_2O)_n CH_2CH_2OH$$

- The branching of the hydrocarbon chain is controlled and kept to the minimum because unbranched chains can be biodegraded more easily and hence pollution is prevented.

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st discovered for

times more sweet

ral sugar.

anoic acid, NaCl,

um salts of amines

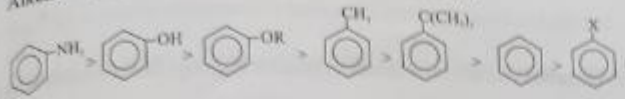
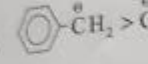
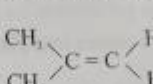
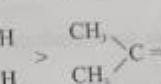
ain and a positive

$\xrightarrow{H_2O}$

$H_2O)_n CH_2CH_2OH$

ntrolled and kept to

an be biodegraded

1. $RCOCl > RCOOCOR > RCOOR > RCONH_2$ Nucleophilic substitution reaction.
2. $HI > HBr > HCl > RCOOH > C_2H_5OH > H_2O > ROH > CH \equiv CH > NH_3$ (Acidic nature).
3. $CCl_3CHO > HCHO > CH_3CHO > CH_3COCH_3$ Nucleophilic addition reaction.
4. Alkene > Alkynes (Electrophilic addition reaction).
5.  (Electrophilic Substitution Reaction)
6. $CH_2Cl > Cl-CH_2-CH=CH_2 > C_6H_5Cl > CH_2=CH-Cl$ (Nucleophilic Substitution Reaction)
7. $(\triangleright)_3\overset{\oplus}{C} > (C_6H_5)_3\overset{\oplus}{C} > C_6H_5\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_2-CH=CH_2$ (Carbocation stability)
8. $(\triangleright)_3C-Cl > (C_6H_5)_3C-Cl$ $-CH_2Cl > C_6H_5Cl$ (Nucleophilic Substitution Reaction)
9.  $\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_2-C=CH_2 > \overset{\ominus}{C}H_3 > 1^\circ > 2^\circ > 3^\circ$ (Carbanion stability)
10. $(CH_3)_2C=C(CH_3)_2 > CH_3-CH=C-(CH_3)_2 > CH_3-CH=CH-CH_3 > CH_3-CH=CH_2$ (Stability)
11. $CH_2=CH_2 > CH_3-CH=CH_2 > CH_3-CH=CH-CH_3 >$  $>$  (Heat of Hydrogenation)
12. $\overset{\ominus}{N}H_2 > \overset{\ominus}{O}H > NH_3 > H_2O$ (Basic strength)
13. $NI_3 > NBr_3 > NCl_3 > NF_3$ (Basic strength)
14. $Br_2 > Cl_2 > I_2$ (Selectivity for halogenation)
15. Halogenation of alkenes by cyclic halonium state, so anti attack takes place (Anti Addition).
16. Hydroboration followed by oxidation is always anti markownikoff's addition due to steric effect. (No rearrangement)
17. Oximercuration - demercuration is markownikoff's addition of water because some carbocation character in cyclic mercurium state. (No rearrangement)
18. $CHCl_3$ in the presence of strong bases forms biradical : CCl_2 which undergo addition with double or triple bonds.
19. $:CCl_2$ is intermediate in Reimer tiemann reaction & carbyl amine test
20. Ozonolysis of cyclo alkene forms one mole dialdehyde while ozonolysis of cyclo alkadiene forms two moles of dialdehyde.
21. Ozonolysis in the present of Zn is known as reductive ozonolysis (Zn prevents further oxidation of aldehydes).
22. Hydration of alkyne occurs in $HgSO_4$ and dil H_2SO_4.
23. 1-alkynes (terminal alkynes) forms ppt with $Ag(NH_3)_2^+$ and $Cu(NH_3)_2^+$
24. Cis-2-butene reacts with Br_2 to forms dl(±) pair of enantiomers of 2,3-dibromobutane while in case of trans-2-butene forms meso-2,3-dibromo butane due to anti addition always.
25. Haloform test given by species with CH_3CO-group but not in case of Acetoacetic ester and tert. Butyl alcohol.
26. Chloral reacts with chloro benzene in con. H_2SO_4 to form insectiside DDT.
27. NBS is used for free radical allylation (Bromination at allylic position).
28. Rate for S_N1 reaction is $3^\circ > 2^\circ > 1^\circ$ in protic polar solvent (Polar solvents have active hydrogen).
29. Rate for S_N2 reaction is $1^\circ > 2^\circ > 3^\circ$ in polar aprotic solvent like DMSO, DMF, Acetone.

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30. If cyclo 1,3-penta diene reacts with $CHCl_3$ and potassium tert. butoxide to form chlorobenzene.

31. Alkyl halides reacts with AgCN to form isocyanides due to ambident nature of nucleophile with KCN it forms cyanides.

32. In dehydration of alcohols active species is carbocation so rearrangement occurs like hydride shift, methyl shift, phenyl shift, ring expansion and ring contraction.

33. Dehydration of cyclobutyl methyl alcohol ring expansion takes place, formation of cyclo pentene occurs.

34. In esterification where acid reacts with alcohol to form ester, - OH given by acid while - H by alcohol

$$CH_3\overset{18}{C}OOH + C_2H_5\overset{16}{O}H \xrightarrow{\overset{+}{H}} CH_3COOC_2H_5 + H_2\overset{18}{O}$$

35. For faster esterification reaction R groups should be small both in carboxylic acid and alcohol (smaller R group, faster esterification).

36. Ether's reacts with HI to form alcohol and halide where fission of lower ether by S_N2 mechanism while higher ethers like ter. butyl methyl ether or benzyl methyl ether by S_N1 mechanism.

37. If unsymmetrical cyclic ether undergo fission it depends upon medium weather it is acid or basic like in acidic medium some character of carbocation so nucleophile goes to carbon where more alkyl groups are there while reverse in basic medium due to steric factor.

38. Aldehydes are reducing agent while ketones are not.

39. Aldehydes and ketones are separated by tollen's reagent.

40. Carbonyl and noncarbonyl are separated by sodium bi sulphite and Brady's reagent.

41. ROH / Ethlene glycol in acidic medium is used to protect carbnyl bond from nucleophile attack.

42. As the size of alkyl group increases steric hindrance comes into play, reactivity towards nucleophilic addition decreases.

43. Aldehydes with hydrogen atom in the presence of dil base undergo enolization and form carbonian to give aldol product.

44. If there is two-CHO group with hydrogen atom to form cyclic intra aldol product.

45. Aldehydes without -hydrogen atom in the presence of con. alkali to form each molecule of acid and alcohol by hydride active species.

46. Glyoxal reacts with con. KOH to form glycolate ion by Intra Cannizaro's.

47. Cyclo hexanoneoxime on beckmann's reaction gives caprolectum which on reaction with to give polymer nylon-6

48. 2-methyl propanal even contains -hydrogen atom but does not give aldol reaction.

49. Aldol reaction occurs due to acidic hydrogen of carbonyl compound.

50. In Cannizaro's reaction hydride transfer is slowest step as well as R.D.S.

51. If formaldehyde and benzaldehyde undergo Cannizaro's reaction, formaldehyde get oxidised.

52. Benzaldehyde do not respond to benedict's and fehling's solution due to less reducing power of aromatic aldehyde.

53. HCOOH respond to oxidising agent due to presence of - CHO group.

54. $RCOOH > H_2CO_3 > C_6H_5OH > H_2O > CH \equiv CH > NH_3 > CH_3-C \equiv CH > CH_2 = CH_2 > CH_4$ this is decreasing acidic nature.

55. Acids with -hydrogen atom when reacts with halogen in the presence of Red P to form -haloacid (HVZ).

56. For reactivity of acid derivatives use funda weaker the base better the leaving group.

57. Reactivity of acid derivatives : O > N > E > M. (O = Oil Halide, N = Anhydride, E = Ester, M = Amide) [Trick : ONEM]

58. Anhydride on reaction with carbonyl compound in the presence of base (carbanian) forms ,-unsaturated carboxyllic acid (perkin reaction)

59. Amide on reaction with Br_2 and alkali to form primary amine of lower homologue. Intermediate species is nitrene which undergo intra rearrangement to form RNH_2.

60. For a compound to be aromatic it must be cyclic, planar and obey (4n + 2) electron rule.

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61. Stability order : Aromatic > Non-aromatic > Anti-aromatic

62. Antiaromatic compounds are not stable even at room temperature.

63. Cyclo-octatetraene is non aromatic compound while pyrrole, pyredene, furan, cyclopentadieneyl anion all are aromatic (on the basis of number of Pi-electrons, it should be Anti-aromatic but it is Non-aromatic (tub shaped, non planar)).

64. In aromatic electrophilic substitution reaction there is no hydrogen isotopic effect except sulphonation and iodination.

65. m- directing groups like nitrobenzene and benzaldehyde cannot undergo fridel craft reaction.

66. $NaHCO_3$ is used to differentiate between carboxylic acid and phenol.

67. Phenol is less acidic than general carboxylic acid, cannot react with $NaHCO_3$.

68. $FeCl_3$ used for the detection of phenol and phenolic compounds.

69. Aniline is more reactive than phenol towards electrophillic substitution reaction because less energy difference between nitrogen and carbon. (NH_2 has more + R, than – OH)

70. Benzene diazonium chloride reacts with phenol or aniline to form azo compounds.

71. Benzene diazonium salt is used to introduce nucleophile directly into benzene ring.

72. $C_6H_5NH_2 > C_6H_5OH > C_6H_5OR > C_6H_5Br > C_6H_5NO_2$ (Reactivity towards electrophillic substitution reaction.

73. Carbanion is reactive part in grignard reagent.

74. $LiAlH_4$, $NaBH_4$, Di-BAL-H all releases H– (hydride ion) and act as reducing agent.

75. $LiAlH_4$ is stronger reducing agent than $NaBH_4$.

76. R Mg X (grignard reagent), R_2CuLi (Gillman's Reagent), R_2Cd all are source of R^- i.e. carbanion.

77. Free radical is intermediate of Wurtz, Wurtz - fitting, fitting, Kolbe's electrolysis reaction.

78. Carbanion is intermediate of soda lime de-carboxylation.

79. Dehydrohalogenation is an example of E^2 reaction, while dehydration of alcohols is E^1 reaction.

80. For dehydro halogenation hydogen & halogen must be anti-parralel.

81. Condensation of aldols is an example of ElCB reaction. (Aldol condensation)

82. P.C.C. & PDC are hydrogen abstracting oxidising agents while $KMnO_4$ & $K_2Cr_2O_7$ are oxygen releasing oxidising agents. (PDC = Pyridinium di-chromate)

83. Alcoholic & Aqueous KOH have OR^- & OH^- reactive species respectively.

84. $NaNH_2$ is stronger base than alcoholic KOH.

85. In S_N1 reaction both inversion and retention of configuration occurs but in S_N2 only inversion occurs.

86. In Sn1 reaction inversion is more than retention, so 90-95% racemization occurs.

87. Pinacol pinacolone type reactions involve protonation, deprotonation and alkyl shift.

88. Aldol, Perkin, reformatsky and knovengel's reactions are classified as carbanian active reaction.

89. In Beckmann's rearrangement migration of group which is anti to-OH group takes place.

90. Beckmann's rearrangent is a reaction of oximes in the presence of H_2SO_4 or PCl_5 to produce N-alkyl amide derivatives.

91. Migratory attitude of alkyl group in Pinacol-pinacolone, beckmann's and bayer villegar oxidation is $-C_6H_5 > (CH_3)_3C- > (CH_3)_2CH- > C_2H_5- > CH_3-$

92. By wittig reaction carbonyl compounds are converted into E-Z form of alkene.

93. When conjugated diene reacts with alkene or alkyne it is known as diel's elder synthesis.

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PHYSICAL CHEMISTRY

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Chapter – 1 Mole Concept

Classification of Matter

Physical Classification

Solid – Definite Volume & Definite Shape

Liquid – Definite Volume & Indefinite Shape

Gas – Indefinite Volume & Indefinite Shape

Chemical Classification

- **Mixture** (Mixed two or more substance)
  - **Homogeneous** (Uniform mixture)
  - **Heterogeneous** (Non-uniform mixture)
- **Pure Substance** (Fixed ratio of masses of constituents)
  - **Elements** (Same type of atom)
    - Metal
    - Metalloids
    - Non-Metal
  - **Compound** (Two or more type atom)
    - Organic
    - Inorganic

Mass

Atomic Mass – Mass of one atom

Gram Atomic Mass – Mass of one mole of atom in gram.

Molecular Mass – Mass of one molecule

$$\text{Relative Atomic Mass} = \frac{\text{mass of one atom of the substance}}{\frac{1}{12} \times \text{mass of one} - \text{C-12 atom}}$$

Gram Molecular Mass – Mass of one mole of molecule in gram.

$$\text{Relative Molecular Mass} = \frac{\text{mass of one molecule of the substance}}{\frac{1}{12} \times \text{mass of one} - \text{C-12 atom}}$$

- Weight of one atom of any element = Atomic Mass (a.m.u.).
- 1 a.m.u. (Atomic Mass Unit) = $1/N_A$ gram = 1.67×10^{-27} Kg.

$$\text{Average Atomic Mass} = \frac{\Sigma(\%\text{ of } I_i \times A_i)}{\Sigma(\%\text{ of } I_i)}$$

A_i = Atomic Mass of Isotope, I_i = Isotopes

Lowest atomic mass < AAM < Highest atomic mass
Average Atomic Mass closer to isotope having high %.

$$\text{Average molecular mass} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{\Sigma n_i \times M_i}{\Sigma n_i}$$

n_i = No. of moles, M_i = Molar Mass

Density

Absolute density – It is same for solid, liquid and gas.

Absolute density = mass/ volume , unit = kg/m^3 or gm/cm^3

Relative density

(a) For solid and liquid relative density is taken relative to water. It is also known as **specific gravity**. It is unit less.

$$\text{specific gravity} = \frac{\text{density of solid or liquid}}{\text{density of water at } 4°C = 1\text{ gm/ml}}$$

(b) For gases relative density is known as vapour density (V.D.)

$$\text{V.D.} = \frac{\text{Molar mass of gas}}{2} \quad \text{(for single gas)}$$

$$\text{V.D.} = \frac{\text{Average molecular mass}}{2} \quad \text{(for mixture of gases)}$$

Chemical Laws of Combination

- **Law of Mass Conservation** – In a chemical change total mass remains conserved. i.e. mass before reaction is always equal to mass after reaction
- **Law of Constant or Definite proportion** – All chemical compounds are found to have constant composition irrespective of their method of preparation or sources.
- **Law of Multiple Proportion** – When one element combines with the other element to form two or more different compounds, the mass of one element, which combines with a constant mass of the other, bear a simple ratio to one another.
- **Gay – Lussac's Law of Combining Volume** – According to him elements combine in a simple ratio of atoms, gases combine in a simple ratio of their volumes provided all measurements should be done at the same temperature and pressure
- **Law of Reciprocal Proportion** – The ratio of weight of two elements A and B which combined with fixed weight of third element C is either the same or a simple multiple or the ratio of weights of A and B with directly combined with each other.

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Avogadro's Hypothesis

Equal volume of all gases have equal number of molecules (not atoms) at same temperature and pressure condition.

S.T.P. (Standard Temperature and Pressure)

At S.T.P. condition : temperature = 0°C or 273 K

pressure = 1 atm = 760 mm of Hg

Volume of one mole of gas at STP is found to be experimentally equal to 22.4 litres which is known as molar volume.

Molecular formula & Emperical Formula

Molecular Formula – Actual No. of atoms of elements present in a molecule.

Emperical Formula – Simplest ratio (whole no.) of atoms of element in a molecule.

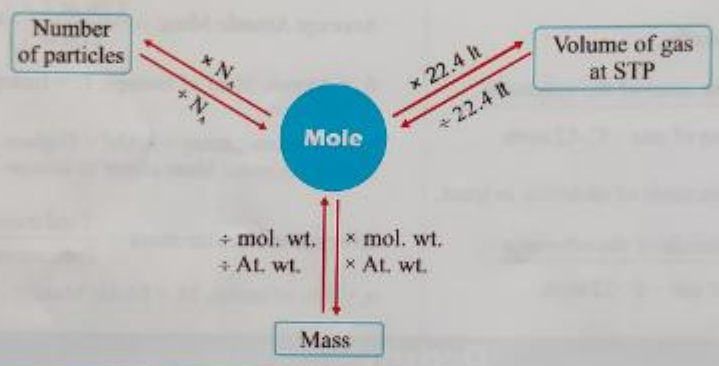
Molecular Formula = $(\text{Emperical formula})_n$

$$n = \frac{\text{molar mass of substance in molecular formula}}{\text{molar mass of substance in emperical formula}}$$, where n is an Integer Number.

Mole Concept (n)

One mole of any substance contains 6.023×10^{23} particles and this no is known as avogadro No. (N_A)

Avogadro No. = 6.023×10^{23}



Stoichiometry

- For stoichiometry calculations reaction should be balanced.
- **Stoichiometry Coefficient** – In a balanced reaction balancing coefficient are konwn as stoichiometry coefficient.

  For Ex. in given reaction $aA + bB \rightarrow cC + dD$

  a, b, c, d are stoichiometry coefficient.

NOTE : Stoichiometry coefficient can be used as mole, molecules, volume, but can not use as mass.

Mole - Mole Analysis

- This is the simplest method to determine product or reactant (volume, atoms, moles, mass, etc.) To comparing mole of one substance to comparing mole of another substance.

$$\frac{\text{Moles of reactant}}{\text{Stoichiometric coefficient}} = \frac{\text{Moles of product}}{\text{Stoichiometric coefficient}}$$

CASE 1 - Only single reactant containing reaction. In this type of reaction we can calculate amount of product from moles of reactant by direct comparing moles.

Ques. Calculate moles of KCl produce when 367.5 gram of $KClO_3$ are heated.

Sol. $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

Mole of $KClO_3$ = 367.5 / 122.5 = 3

from stoichiometry moles of KCl produce = (3/2) × 2 = 3

CASE 2 - More then one reactant containing reaction. (Information about1 reactant is given) In these type of reaction we will take reference of that reactant about which information is given.

Ques. Calculate mole of HCl, HCl required to neutralise 80 gm of NaOH.

Sol. $NaOH + HCl \longrightarrow NaCl + H_2O$

Moles of NaOH = 80/40 = 2.

from stoichiometry moles of HCl required to neutralise NaOH = 2

$$\frac{\text{Moles of NaOH}}{\text{S.C. of NaOH}} = \frac{\text{Moles of HCl}}{\text{S.C. of HCl}} = \frac{\text{Moles of NaCl}}{\text{S.C. of NaCl}}$$

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CASE 3 - More then one reactant containing reaction. (Information about atleast 2 reactant is given) In these type of reaction we have to decide which reactant is completely consume in reaction and which is remaining.

- Completely consumed reagent is known as **Limiting Reagent (LR)**. Reagent which is present in excess that is known as **Excess Reagent (ER)**.

$$\frac{\text{Moles of LR}}{\text{S.C. of LR}} = \frac{\text{Moles of product}}{\text{S.C. of product}}$$

- **Amount of excess reagent left and amount of product formed is always decided by LR.**

Determination of Limiting Reagent

- First of all reaction should be balanced.
- Calculate moles of reagents on the basis of given information.
- Then divide the given moles of reactant with there respective stoichiometry coefficient.
- Reactant for which this ratio is minimum will be limiting reagent.

POAC Method

- This method is used for multistep reaction.
- POAC is conservation of mass. Atoms are conserved, moles of atoms shall also be conserved in a chemical reaction (but not in nuclear reactions.)
- This method is helpful for solving those problem in which either reaction is difficult to balance or impossible to balance.
- The strategy here will be around a particular atom. We focus on a atom and conserve it in that reaction.
- This principle can be understand by the following example.

For Example : $H_2S + HNO_3 \rightarrow NO + S + H_2O$ (Unbalanced eq.)

POAC atoms H, S, N, O.

POAC on 'H' atom : $2 \times n_{H_2S} + 1 \times n_{HNO_3} = 2 \times n_{H_2O}$

POAC on 'S' atom : $1 \times n_{H_2S} = 1 \times n_S$

POAC on 'N' atom : $1 \times n_{HNO_3} = 1 \times n_{NO}$

POAC on 'O' atom : $3 \times n_{HNO_3} = 1 \times n_{NO} + 1 \times n_{H_2O}$

Question :

Q. 5 moles of SO_2 and 5 mole of O_2 are reacting with each other to form SO_3. Determine weight of LR and ER left and amount of SO_3 formed.

Sol. $2SO_2 + O_2 \longrightarrow 2SO_3$

$5/2 = 2.5$ (LR) $5/1 = 5$ (ER)

Left mole $\rightarrow 0$ $5 - (5/2) = 2.5$ $(2/2) \times 5 = 5$

Weight of O_2 left $= 2.5 \times 32 = 80$ gm

weight of SO_3 formed $= 5 \times 30 = 400$ gm

$$\% \text{ yield of reaction} = \frac{\text{moles actual produced}}{\text{moles theoretical produced}} \times 100$$

$$\% \text{ Purity of Sample} = \frac{W_{\text{reactant}}}{W_{\text{given}}} \times 100$$

- **Any sample is not 100 % pure**
- **Impurities are taken inert which will not take participate in reaction only pure form of substance will react.**

Volume strength of H_2O_2

Volume strength of H_2O_2 is expressed by X 'V'.

It is define as volume of oxygen in litre at STP produced by the decomposition by all the H_2O_2 present in 1 litre of solution according to the given equation.

$$2H_2O_2(aq) \longrightarrow 2H_2O(g) + O_2(g)$$

$M = X / 11.2$; $S = (X / 5.2) \times 17$

$N = X / 5.6$; $\% (w/V) = (X/5.6) \times 17/10$

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Percentage Labelling of Oleum (for JEE)

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

% labelling of oleum sample $= (100 + X)\%$ X = mass of H_2O required for the complete conversion of SO_3 in H_2SO_4

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

Super Note : Maximum % labelling of oleum = 122.7 %

Determination of Available chlorine from given sample of Bleaching powder (for JEE)

Weight % of available Cl_2 when sample of bleaching powder is treated with dilute acid or CO_2 is known as available chlorine.

$$CaOCl_2 + H_2SO_4 \text{ ——— } CaSO_4 + H_2O + Cl_2$$

$$CaOCl_2 + 2HCl \text{ ——— } CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + CO_2 \text{ ——— } CaCO_3 + Cl_2$$

$$\% \text{ Available of } Cl_2 = \frac{3.55 \times M \times V(\text{ml.})}{W_{CaOCl_2}}$$

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Chapter – 2

Atomic Structure

Discovery of Fundamental Particles

Electron (e)/ cathode rays

It was discovered by J.J. Thomson

Mass = 9.1×10^{-31} kg = 9.1×10^{-28} g,

Mass = 0.000549 amu

Charge = -1.6×10^{-19} C

e/m of electron is found to be independent of nature of gas & electrode used

Proton (p) /anode rays

It was discovered by Eugen Goldstein

Mass = 1.67×10^{-27} kg = 1.67×10^{-24} g,

Mass = 1.00750 amu

Charge = $+1.6 \times 10^{-19}$ C

e/m value is dependent on the nature of gas taken in discharge tube

Neutron (n)

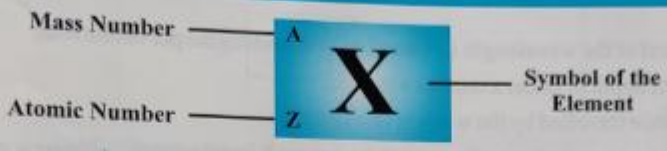
It was discovered by James Chadwick

Mass = 1.67×10^{-27} kg = 1.67×10^{-24} g,

Mass = 1.00850 amu

Charge = Neutral

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 in nucleus.

  A = Number of proton (Z) + Number of neutrons (n)
- **Isotopes:** same atomic number but different mass number.

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

  Ex. ${}_1H^3, {}_3H^3$
- **Isodiaphers:** Same difference of number of neutrons & protons

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

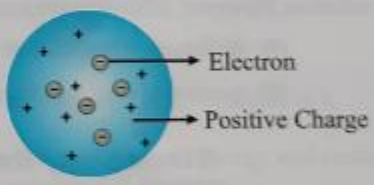
  Ex. CO_2, N_2O
- **Isoelectronic:** Species having same no. of electrons

  Ex. Cl , Ar

Atomic Models

(1) Thomson's Model of the Atom

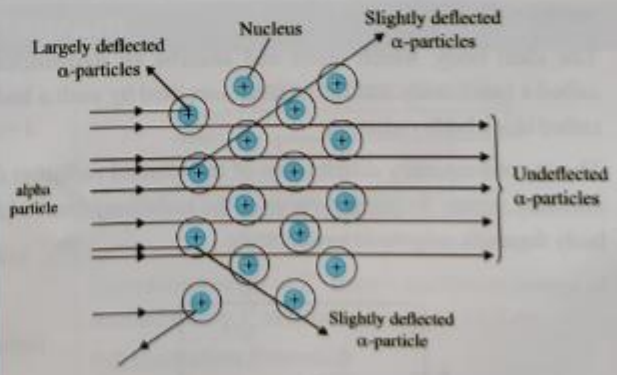
- He proposed that the positive charge is spread over a sphere of the size of the atom (i.e. 10^{-8} cm radius) in which electrons are embedded to make the atom as whole neutral.
- This model could not explain the experimental results of Rutherfords α-particle scattering, therefore it was rejected.



(2) Rutherford's Experiment

Observation

- Most of the α-particles passed straight through the gold foil without suffering any deflection from their original path.
- A few of them were deflected through small angles, while a very few were deflected to a large extent.
- A very small percentage (1 in 20000) was deflected through angles ranging from 90° to 180°.



Rutherford's nuclear concept of the atom

- The atom of an element consists of a small positively charged 'nucleus' which is situated at the centre of the atom and which carries almost the entire mass of the atom.
- The electrons are distributed in the empty space of the atom around the nucleus in different concentric circular paths, called orbits.
- The number of electrons in orbits is equal to the number of positive charge (protons) in the nucleus. Hence, the atom is electrically neutral.
- The volume of the nucleus is negligibly small as compared to the volume of the atom.
- Most of the space in the atom is empty.

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

[A mass number, R_N = Radius of nucleus]

$V_{atom} = 10^{15} \times V_{nucleus}$

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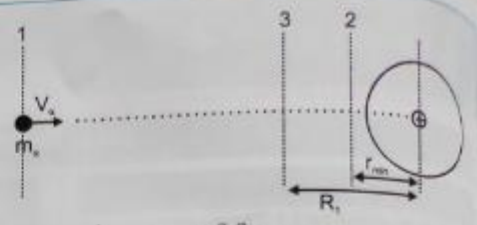
Drawbacks of Rutherford's Model :

- This was not according to the classical theory of electromagnetism proposed by Maxwell. According to this theory, every accelerated charged particle must emit radiations in the form of electromagnetic waves and loses it total energy.
- Since energy of electrons keep on decreasing, so radius of the circular orbitals should also decrease and ultimately the electron should fall in nucleus.
- It could not explain the line spectrum of H–atom.



$$\frac{1}{2} m_\alpha v_\alpha^2 = K \frac{q_1 q_2}{r_{min}}$$

Electromagnetic Wave Radiation

Wavelength (λ) : The shortest separation between two consecutive crests and troughs.

Frequency (ν) : It is the number of waves or cycles passing through a particular point per unit time.

$\nu = 2$ Two waves are passing through "P" per unit time.

or $\nu = \frac{c}{\lambda}$

Wave number : It is the reciprocal of the wavelength i.e., number of wavelengths per centimeter.

Amplitude : It is the height of depth of either a crest or a trough.

Velocity (v) : The linear distance travelled by the wave in one second.

Relationship between velocity, wavelength and frequency of a wave

As frequency is the number of waves passing through a point per second and λ is the length of each wave, hence their product will give the velocity of the wave. Thus $v = \nu \times \lambda$

Order of wavelength in Electromagnetic spectrum

Cosmic rays < γ – rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

Super Trick : Radio waves **RaMesh** Infrared **I** **Saw** Ultraviolet rays **Ur** **X** γ-rays **Gf** **Comolica**
Micro waves, Visible, X-rays, Cosmic rays

Order of ($\lambda\downarrow, \nu\uparrow, E\uparrow$)

Particle Nature of Electromagnetic Radiation : Planck's Quantum Theory

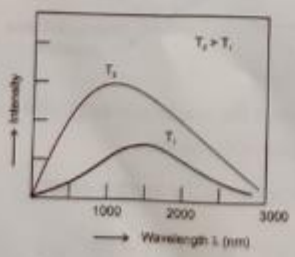
Some of the experimental phenomenon such as diffraction and interference can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained

(i) the nature of emission of radiation from hot bodies (black - body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

Black Body Radiation

- When solids are heated they emit radiation over a wide range of wavelengths.
- The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation.
- The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature.



Photoelectric Effect

When certain metals (for example Potassium, Rubidium, Caesium etc.) were exposed to a beam of light electrons were ejected. This phenomenon is called **Photoelectric effect**.

For each metal, there is a characteristic minimum frequency, ν_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

$$h\nu = h\nu_0 + 1/2\, m_e v^2$$

where m_e is the mass of the electron and v is the velocity associated with the ejected electron.

Some Important Point :

- For photoelectric effect, for each incident photon, only one electron is emitted.
- There is no time lap between striking of photon and emission of photoelectron.
- Not all ejected photoelectrons have $KE = KE_{max}$. Some photo electrons may have $KE < KE_{max}$.

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Quantum Theory of Light

The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation is called as quantum of light.

According to Planck, the light energy coming out from any source is always an integral multiple of a smallest energy value called quantum of light.

$E_0 = h\nu$ (ν - Frequency of light)

$h = 6.626 \times 10^{-34}$ J-Sec (h - Planck const.)

$E_0 = hc/\lambda$ (c - speed of light) (λ - wavelength)

Bohr's Atomic Model

Assumptions of Bohr's model

- There are certain orbits around the nucleus such that if electron will be revolving in these orbit, then it not emit any electromagnetic radiation. These are called stationary orbit.

$$\frac{mv^2}{r} = \frac{Ke^2Z}{r^2}$$

- Angular momentum of the electron in these stationary orbit is always an integral multiple of $h/2\pi$

$$mvr = \frac{nh}{2\pi}$$

- Electron can make jump from one stationary orbit to another stationary orbit by absorbing or emitting a photon of energy equal to difference in the energies of the stationary orbit.

$$\frac{hc}{\lambda} = \Delta E$$

ΔE – difference in the energy of orbit

Mathematical Forms of Bohr's Postulates

Radius of the Bohr's Orbit

$$r_n = 0.529 \times \frac{n^2}{Z} \text{ Å}$$

Velocity of an electron in Bohr's Orbit

$$v_n = 2.18 \times 10^6 \times \frac{Z}{n} \text{ m/sec}$$

Time Period, $T = \frac{2\pi r}{v}$ $\quad T \propto n^3$

Frequency, $f = \frac{v}{2\pi r}$

Energy of an electron in Bohr's Orbit

$$E_n = -13.6\frac{Z^2}{n^2} \text{ eV/atom} = -21.8 \times 10^{-19}\frac{Z^2}{n^2} \text{ J/atom}$$

$$= -1313.6\frac{Z^2}{n^2} \text{ kJ/mole} = -313.6\frac{Z^2}{n^2} \text{ kCal/mole}$$

$$\Delta E = 13.6 \times Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ eV/atom}, \; n_2 > n_1$$

KE : PE : TE = 1 : – 2 : – 1

E_{max} / v_{max} / λ_{min} ⇒ n_1 = lowest & n_2 = Highest

E_{min} / v_{min} / λ_{max} ⇒ n_1 = Highest & n_2 = Closest to n_1

On increasing the value of n (shell) energy and radius will increase but velocity will decrease.

Failures / Limitations of Bohr's Theory

- He could not explain the line spectra of atoms containing more than one electron.
- He also could not explain the presence of multiple spectral lines.
- He was unable to explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect)
- No conclusion was given for the principle of quantisation of angular momentum.
- He was unable to explain the de-broglie's concept of dual nature of matter.
- He could not explain heisenberg's uncertainty principle.

Energy Level Diagram

(i) Ground state

Lowest energy state of any atom or ion is called ground state of the atom It is n = 1.

(ii) Excited State

States of atom other than the ground state are called excited states :

n = 2 (first excited state), n = 3 (second excited state), n = n + 1 (n^{th} excited state)

(iii) Ionisation energy (IE)

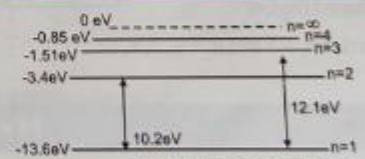
Minimum energy required to move an electron from ground state to n = ∞ is called ionisation energy of the atom or ion.

(iv) Ionisation Potential (I.P.)

Potential difference through which a free electron must be accelerated from rest, such that its kinetic energy becomes equal to ionisation energy of the atom is called ionisation potential of the atom.

(v) Excitation Energy

Energy required to move an electron from ground state of the atom to any other state of the atom is called excitation energy of that state.



Energy level diagram of H-atom

Excitation energy of 2nd state = excitation energy of 1st excited state = 1st excitation energy = 10.2 ev.

(vi) Excitation Potential

Potential difference through which an electron must be accelerated from rest to so that its kinetic energy become equal to excitation energy of any state is called excitation potential of that state.

(vii) Binding Energy 'or' Seperation Energy

Energy required to move an electron from any state to n = ∞ is called binding energy of that state.

Binding energy of ground state = I.E. of atom or Ion.

Spectrum

A collection of radiations of different wavelength

Absorption spectrum

It is obtain when light is passed through a solution of a substance which can absorb certain wavelengths

Dark lines are obtain on a coloured background

Emission spectrum

It is obtain when light from a source is passed through a prism

Coloured light are obtain on a dark background.

Continuous spectrum

When two colours can not be differentiated

Discontinuous spectrum

When two colours can be easily differentiated

Band spectrum

Discrete band of different colours are obtained.

Formed by molecules.

Line spectrum

Discrete line of different colours are obtained.

Formed by atom.

Spectrum Line Series

Lyman Series

$\lambda_{max} = \frac{4}{3R_H}$ and $\lambda_{min} = \frac{1}{R_H}$

It has ultra violet region

for this series $n_1 = 1$ and $n_2 = 2, 3, 4, ...$

Balmer Series

$\lambda_{max} = \frac{36}{5R_H}$ and $\lambda_{min} = \frac{4}{R_H}$

It has visible region

for this series $n_1 = 2$ and $n_2 = 3, 4, 5, ...$

Paschen Series

$\lambda_{max} = \frac{144}{7R_H}$ and $\lambda_{min} = \frac{9}{R_H}$

It has infrared region

for this series $n_1 = 3$ and $n_2 = 4, 5, 6, ...$

Bracket Series

$\lambda_{max} = \frac{400}{9R_H}$ and $\lambda_{min} = \frac{16}{R_H}$

It has infrared region

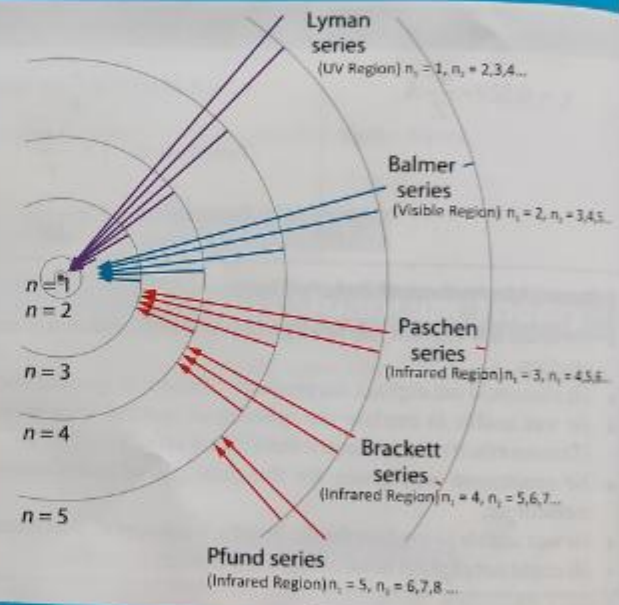
for this series $n_1 = 4$ and $n_2 = 5, 6, 7, ...$

Pfund Series

$\lambda_{max} = \frac{900}{11R_H}$ and $\lambda_{min} = \frac{25}{R_H}$

It has infrared region

for this series $n_1 = 5$ and $n_2 = 6, 7, 8, ...$



Humphery Series

$\lambda_{max} = \frac{1764}{13R_H}$ and $\lambda_{min} = \frac{36}{R_H}$

It has far infrared region

for this series $n_1 = 6$ and $n_2 = 7, 8, 9 .....$

Hydrogen Emission Spectrum

- Rydberg's Equation $\frac{1}{\lambda} = \bar{v} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$
- $1/R_H = 912Å$ (approx)
- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_α line means $n_2 = n + 1$, similarly H_β line means $n_2 = n + 2$.
- If an electron is in any higher state $n = n_2$ and makes a transition to another excited state $n = n_1$, then total no. of different photons emitted is equal to $\Delta n(\Delta n + 1)/2$, where $\Delta n = n_2 - n_1$.
- $R_H \cong 109700 cm^{-1}$ = Rydberg constant

Super Note :

- If an electron is in any higher state n = n and makes a transition to ground state, then total no. of different photons emitted = n × (n − 1)/2
- In case of single isolated atom if electron make transition from n state to the ground state then max. number of spectral lines observed = (n−1)

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De-broglie Hypothesis

- Wave mechanical theory of matter.
- According to this theory, the electrons protons and even atom when in motion possess wave properties. (dual nature of light)
- According to de-broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation,

$$\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2mKE}} = \frac{h}{\sqrt{2mqV}}$$

where h is planck's constant

(i) For electron $\lambda = \frac{12.27}{\sqrt{V}}\text{Å} = \sqrt{\frac{150}{V(\text{volts})}}\text{Å}$

(ii) for proton $\lambda = \frac{0.286}{\sqrt{V}}\text{Å}$

(iii) For α particles $\lambda = \frac{0.101}{\sqrt{V}}\text{Å}$

(iv) For neutrons $\lambda = \frac{h}{\sqrt{2Em}} = \frac{0.286}{\sqrt{E(eV)}}\text{Å}$

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.

Heisenberg Uncertainity Principle

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

- $\Delta x.\Delta p \geq \frac{h}{4\pi}$ or $(\Delta x)(\Delta v) \geq \frac{h}{4\pi m}$ $\quad \Delta x \to 0 ; \Delta v \to \infty \quad \Delta v \to 0 ; \Delta x \to \infty$
- $\frac{h}{4\pi} = 5.27 \times 10^{-35}$ Js (In SI Unit)
- Heisenberg replaced the concept of orbit by that of orbital.

Quantum Numbers

(A) Principal Quantum number (n)

- Given by Bohr
- Indicates = Size and energy of the orbit, distance of e^- from nucleus
- Values n = 1, 2, 3, 4, 5
- Angular momentum = n × h/2π.
- Total number of e^- s in an orbit = $2n^2$
- Total number of orbitals in an orbit = n^2
- Total number of subshell in an orbit = n

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

- Given by = Sommerfeld
- Indicates = Sub shell/ sub orbit / sub level
- Values = 0, 1 ..... (n – 1)
- Total no. of e^- s in a suborbit = 2 (2*l* + 1)
- Total no. of orbitals in a suborbit = (2*l* + 1)
- Orbital angular momentum $\sqrt{l(l+1)}\frac{h}{2\pi} = \sqrt{l(l+1)}\hbar$

  h = Plank's constant

Value of *l*	Subshell
0	*s*
1	*p*
2	*d*
3	*f*

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

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

(C) Magnetic Quantum number (m)

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

m for p sub shell =

p_x	p_y	p_z
-1	+1	0

m for d sub shell =

dxy	dyz	dz^2	dxz	dx^2-y^2
– 2	–1	0	+1	+2

(D) Spin Quantum number (m_s or s)

- Given by Uhlenback & Goudsmit
- Values of s = ½
- Total values of spin in an atom = 1/2 × number of unpaired electrons.
- Spin Angular momentum = $\sqrt{s(s+1)}\frac{h}{2\pi}$

Pauli's exclusion principle

No two electrons in an atom can have the same set of all the four quantum numbers, i.e., an orbital cannot have more than 2 electrons because three quantum numbers (principal, azimuthal and magnetic) at the most may be same but the fourth must be different, i.e., spins must be in opposite directions.

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Aufbau principle

Aufbau is a German word meaning building up. The electrons are filled in various orbitals in order of their increasing energies. An orbital of lowest energy is filled first. The sequence of orbitals in order of their increasing energy is :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, ...

The energy of the orbitals is governed by $(n + l)$ rule.

Hund's Rule

No electron pairing takes place in the orbitals in a sub - shell until each orbital is occupied by one electron with parallel spin. Exactly half filled and fully filled orbitals make the atoms more stable, i.e., p^3, p^6, d^5, d^{10}, f^7 and f^{14} configuration are most stable.

'n + l' Rule

The relative order of energies of various sub-shell in a multi electron atom can be predicated with the help of '$n + l$' rule
The sub-shell with lower value of $(n + l)$ has lower energy and it should be filled first.

eg.

3d	4s
$(n+l) = 3+2$	$(n+l) = 4+0$
$= 5$	$= 4$

Since, $(n + l)$ value of 3d is more than 4s therefore, 4s will be filled before 3d.

If two sub-shell has same value of $(n + l)$ then the sub-shell with lower value of n has lower energy and it should be filled first.

eg.

3d	4p
$(n+l) = 3+2$	$(n+l) = 4+1$
$= 5$	$= 5$

3d is filled before 4p.

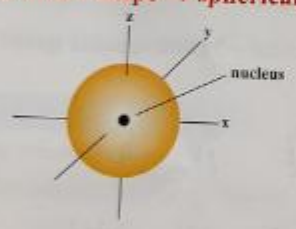
(i)	Total nodes = n – 1	(ii)	Angular nodes = l	(iii)	Radial nodes = $n - l - 1$

Orbital

An orbital may be defined as the region of space around the nucleus where the probability of finding an electron is maximum (90% to 95%)

Orbitals do not define a definite path for the electron, rather they define only the probability of the electron being in various regions of space around the nucles.

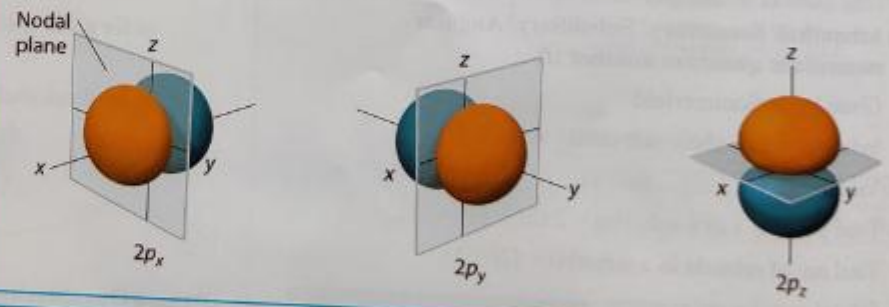
s- orbital : shape → spherical



s- orbital is non directional and it is closest to the nucleus, having lowest energy.
s-orbital can accomodate maximum no. of two electrons.

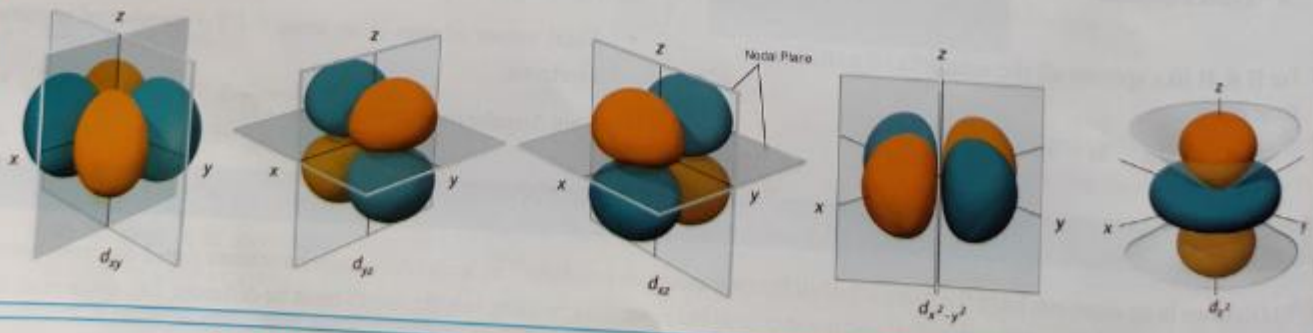
p-orbital : shape → dumb bell

Dumb bell shape consists of two lobes which are separated by a region of zero probability called node.
p - orbital can accomodate maximum no. of six electrons.



d - orbital : shape → double dumb bell

d - orbital can accomodate maximum no. of 10 electrons.



f - orbital : shape → leaf like – f - orbital can accomodate maximum no. of 14 electrons

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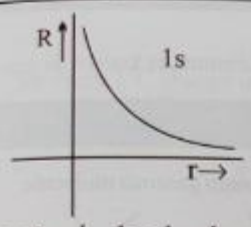
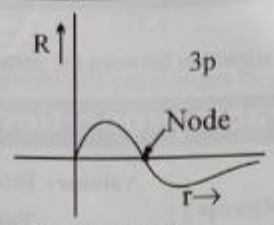
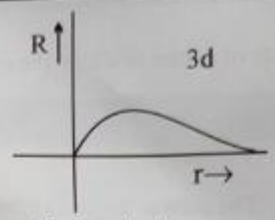
Wave Mechanical Model (for JEE)



Nodes = $n - l - 1 = 1 - 0 - 1 = 0$

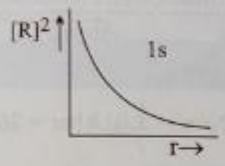


Nodes = $3 - 1 - 1 = 1$

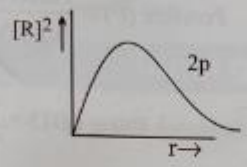


Nodes = $3 - 2 - 1 = 0$

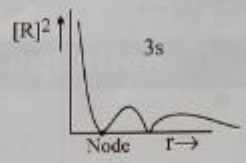
Radial probability density $[R^2]$



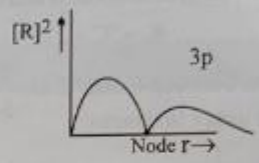
Node = $1 - 0 - 1 = 0$



Node = $2 - 1 - 1 = 0$

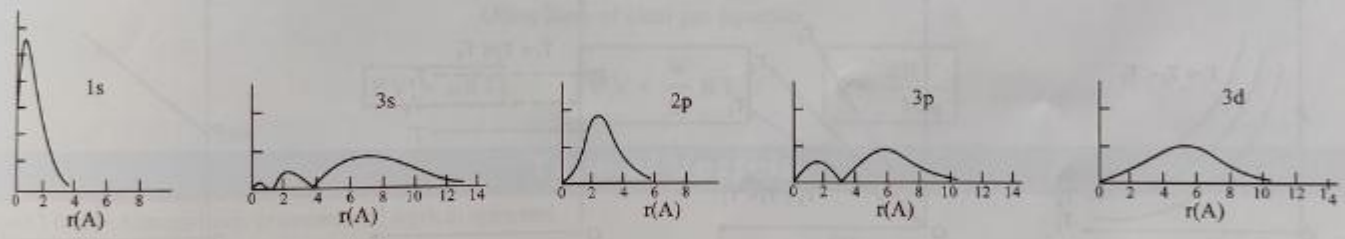


Node = $3 - 0 - 1 = 2$



Node = $3 - 1 - 1 = 1$

Radial probability functions $D = 4\pi r^2 R^2$



Radial probability density for some orbitals of the hydrogen atom. Ordinate is proportional to $4\pi r^2 R^2$, and all distributions are to the same scale.

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Chapter – 3 Gaseous State

The state of matter in which the molecular forces of attraction between the particles of matter are minimum, is known as *gaseous state*.

Measurable properties of gases

Mass - The mass of the gas is related to the number of moles of the gas

$$\text{moles of gas } (n) = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{m}{M}$$

Temperature - Degree of hotness and coldness

$$K = {}^{\circ}C + 273$$

Relation between F and °C is $\frac{{}^{\circ}C}{5} = \frac{F^{\circ} - 32}{9}$

Volume - Free space available between gaseous molecule

For Ideal gas, $V_{container} = V_{gas}$

$1L = 1000\,mL$, $1\,mL = 1cc$ or $1\,cm^3$, $1L = 1\,dm^3 = 10^{-3}\,m^3$.

Pressure - Pressure of the gas is the force exerted by the gas per unit area of the walls of the container in all directions

$$\text{Pressure } (P) = \frac{\text{Force}(F)}{\text{Area}(A)} = \frac{\text{Mass}(m) \times \text{Acceleration}(a)}{\text{Area}(a)}$$

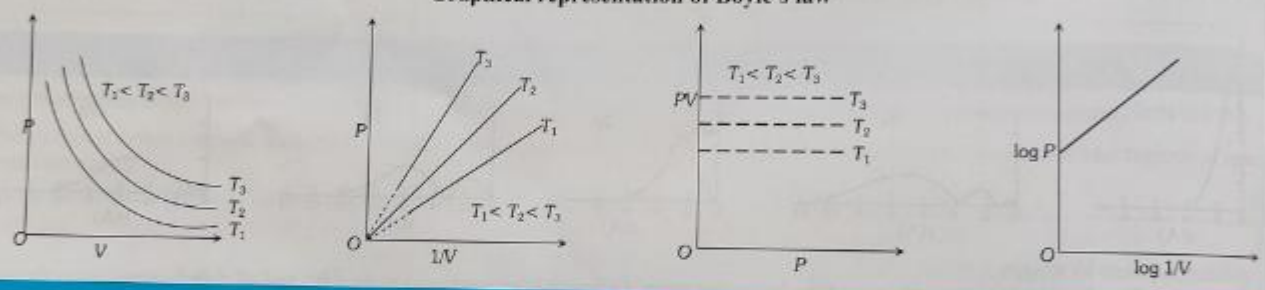
$$1 \text{ atm} = 1.013 \text{ bar}$$

$$1 \text{ atm} = 1.013 \times 10^5\ N/m^2 = 1.013 \text{ bar} = 760 \text{ torr}$$

Boiye's Law

$P \propto \frac{1}{V}$ at constant n and T. $\Rightarrow P_1V_1 = P_2V_2$

Graphical representation of Boyle's law



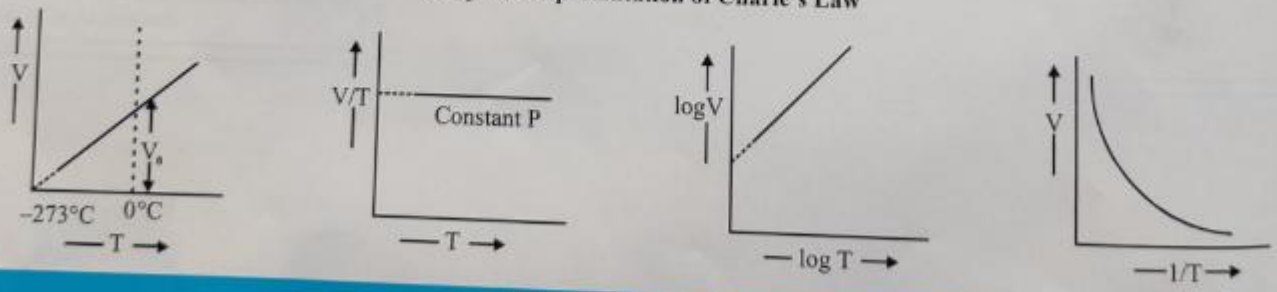
Charle's Law

$V \propto T(K)$ at constant n and P $\Rightarrow V_1/V_2 = T_1/T_2$

$$V_t = V_0\left(1 + \frac{t}{273}\right)$$

For every 1°C change in temperature, the volume of a gas changes by $\frac{1}{273.15}\left(\approx \frac{1}{273}\right)$ of the volume at 0°C

Graphical representation of Charle's Law



Avogadro's Law

$V \propto n$ at constant P and T

1 mole of every gas at STP occupies volume = 22.4 lit.

$\frac{V_1}{n_1} = \frac{V_2}{n_2}$ Applicable under the condition of high temperature & low pressure that is for ideal gas

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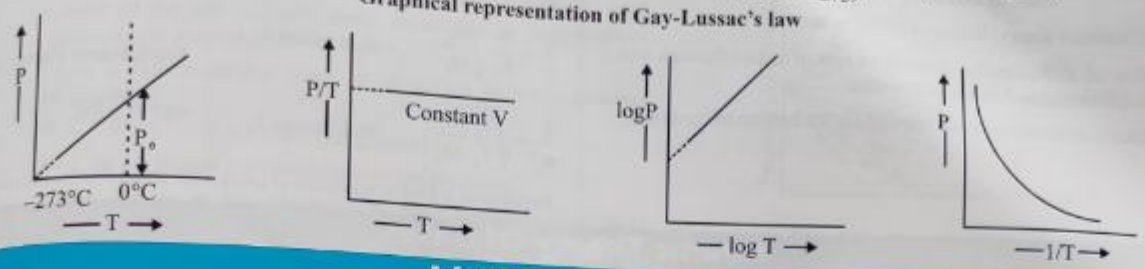
Gay-Lussac's law (Amonton's law) - $P \propto T$ (K) at constant n and V $\Rightarrow P_1/P_2 = T_1/T_2$

$$P_t = P_0\left(1 + \frac{t}{273}\right)$$

for every 1°C change in temperature, the pressure of a gas changes by $\frac{1}{273.15}\left(\approx \frac{1}{273}\right)$ of the pressure at 0°C.

Graphical representation of Gay-Lussac's law



Ideal gas equation

Boyle's law	$P \propto \frac{1}{V}$ or $V \propto \frac{1}{P}$	(n and T constant)	
Charle's law	$V \propto T$	(n and P constant)	$\Rightarrow PV = nRT$ (R = Ideal gas constant) **Ideal Gas Equation**
Avogadro's law	$V \propto n$	(T and P constant)	

Numerical value of R

$= 0.0821$ litre atm K^{-1} mol^{-1}

$= 8.314$ J K^{-1} mol^{-1}

$= 1.987 = 2$ cal K^{-1} mol^{-1}

Other form of ideal gas equation.

$$\boxed{PV = nRT} \quad \boxed{PV = \frac{W}{M}RT} \quad \boxed{P = \frac{dRT}{M}}$$

Type of Vessels

Open Vessel - Atmospheric pressure will work at open end.

Close Vessel - It has two types

a) **Rigid vessel** - wall's of vessel is fixed mole of gases constant & volume is also constant

b) **Non Rigid vessel** - Wall's of vessel is movable, moles of gases is constant but volume is not constant.

Connecting vessel - Vessels can be rigid or non rigid, connected by a tube having negligible volume. Moles will be constant.

Moles before connecting = moles after connecting.

$\frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2} = \frac{PV_1}{RT_1} + \frac{PV_2}{RT_2}$, After connecting tube pressure will be come in both container.

Dalton's Law Of Partial Pressure

The total pressure exerted by a mixture of two or more **non-reacting gases** in a definite volume is equal to the sum of individual pressures which each gas would exert if it occupies the same volume at a constant temperature

$P_{total} = P_1 + P_2 + P_3 + ...$

Where $P_1, P_2, P_3, ...$are partial pressures of gas number 1, 2, 3 .....

Partial pressure

$$P_x = \text{Mole fraction of gas} \times \text{Total pressure} = \frac{\text{no. of moles of gas}}{\text{Total no. of moles of all gases}} \times \text{Total pressure}$$

P (moist) = P (dry gas) + P (H_2O vapours)

P (dry gas) = P (moist) – aq. tension.

Limitations of Dalton's Law

This law is applicable only when the component gases in the mixture do not react with each other. For example, N_2 and O_2, CO and CO_2, N_2 and Cl_2, CO and N_2 etc. But this law is not applicable to gases which combine chemically. For example, H_2 and Cl_2, CO and Cl_2, NH_3, HBr and HCl, NO and O_2 etc.

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Graham's Law of Diffusion and Effusion

Diffusion - escaping gas through a small hole or orifice

Effusion - spontaneous intermixing of two or more gases.

Rate of diffusion = Rate of effusion

- Effusion is always followed by diffusion.
- Rate of diffusion also depends on area of orifice through which it diffuses as well as on temperature
- Due to diffusion gases do not settle at the bottom of container.

$r \propto \frac{1}{\sqrt{M}}$ at constant P & T

$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$ at constant P & T

$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$ at constant T

$\frac{r_1}{r_2} = \sqrt{\frac{T_1}{T_2}\frac{M_2}{M_1}}$ at different T

Enrichment of Gases

at constant T

$\left(\frac{n_1}{n_2}\right)_f = \frac{n_1}{n_2}\left(\sqrt{\frac{M_2}{M_1}}\right)^n$

Enrichment Factor (f)

$\log f = \frac{n}{2}\log\left(\frac{M_2}{M_1}\right)$

Enrichment is used in separation of isotopes by different diffusion rate

Kinetic Theory Of Gases

The postualates

(1) The gaseous molecules are considered to be the point masses.

(2) The volume of a molecule is negligible as compared to total volume of the gas.

(3) The molecules do not posses appreciable attraction.

(4) The collisions are perfectly elastic i.e. there is no loss of energy during the molecular collisions.

(5) The average kinetic energy of molecules is directly proportional to the absolute temperature of the gas.

(6) The effect of gravity on molecular motion is negligible.

Kinetic gas equation

$$PV = \frac{1}{3}mnu^2_{rms}$$

where, P = pressure exerted by the gas
V = volume of the gas
m = average mass of each molecule
n = number of molecules
u = root mean square (*RMS*) velocity of the gas

Calculation of kinetic energy

$KE = \frac{3}{2}nRT$ for n mole molecule

$KE = \frac{3}{2}KT$ for 1 molecule

Where $K = R/N_A$ = Boltzman constant

$K = 1.38 \times 10^{-23}\ J\ K^{-1}\ Molecule^{-1}$

Kinetic energy only depends on temperature.

$KE \propto T$

Molecular speeds or velocities

Root mean square velocity (U_{rms})

$$u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + ...u_n^2}{n}}$$

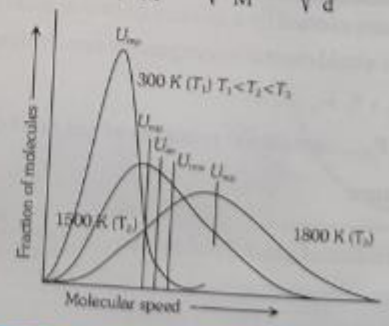
$$u_{rms} = \sqrt{\frac{3PV}{(mN_0) = M}} = \sqrt{\frac{3RT}{(mN_0) = M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3KT}{m}} = \sqrt{\frac{3P}{d}}$$

Average velocity (U_{av})

$$u_{av} = \frac{u_1 + u_2 + u_3 + ...u_n}{n}; \quad u_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

Most probable velocity (u_{mp})

$$u_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{d}}$$



Relation between molecular speeds or velocities

u_{mp}	:	u_{av}	:	u_{rms}
$\sqrt{2}$	:	$\sqrt{\frac{8}{\pi}}$	:	$\sqrt{3}$
1.414	:	1.595	:	1.732
1	:	1.128	:	1.224

Collision Theory (for JEE)

KTG considered only biomolecular collision only

Collision diameter (σ) = 2r

Collision frequency (z_1) = $\pi\sigma^2 U_{av}\left(\frac{N}{V}\right)$ for 1 molecule

when all molecules moving (z_{11}) = $\frac{1}{\sqrt{2}}\pi\sigma^2 U_{av}\left(\frac{N}{V}\right)^2$

Mean free path (λ) = $\frac{KT}{\sqrt{2}\pi\sigma^2 P}$, $\lambda \propto \frac{T}{P}$

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Real and Ideal gases

Gases which obey gas laws or ideal gas equation (PV=nRT) at all temperatures and pressures are called ideal gases.
"real gas is that which obeys the gas laws under low pressure or high temperature".

Causes of deviations of real gases from ideal behaviour

(1) The volume of a molecule is not negligible as compared to total volume of the gas. Actually gases molecules do posses some volume which account for the deviation.

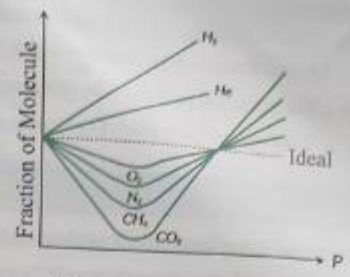
(2) There is intermolecular force of attraction between gaseous molecules.

$$Z = PV/RT \text{ [for 1 mole]}$$

(a) $Z = 1$, the gas is ideal at all temperatures and pressures.

(b) $Z > 1$, the gas is less compressible than expected from ideal behaviour and shows positive deviation, usually at high P *i.e.* $PV > RT$

(c) $Z < 1$, the gas is more compressible than expected from ideal behaviour and shows negative deviation, usually at low P *i.e.* $PV < RT$.



Some gases like CO_2 show both negative and positive deviation.

Due to low molecular masses of H_2 and He and attraction forces will be insignificant at normal temperature so these gases shows positive deviation.

Vander Waal's Equation

Volume correction [v-nb] — *Volume correction for finite size of molecules*

Constant b - The effective size of gas molecules. Greater is the value of b, larger is the size and smaller is the compressible volume
Unit of 'b' is : $Lmol^{-1}$

Pressure correction $\left(P + \frac{n^2 a}{V^2}\right)$ — *Pressure correction for molecular attraction*

Constant a - a indirect measure of magnitude of attractive forces between the molecules. Greater is the value of a, more easily the gas can be liquefied
Unit of 'a' is : $atm.L^2mol^{-2}$

Vander waal's Equation : $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

When pressure is low

In condition of law pressure volume will be high so we can neglect b in comparison to V

$V - b \approx V$

So,

$$\frac{PV}{RT} = 1 - \frac{a}{VRT} \quad \text{or} \quad Z = 1 - \frac{a}{VRT}$$

$Z < 1$, negative deviation (molecular attraction available).

When pressure is high

In the condition of high pressure a/V^2 term can be negligible w.r.t. P

$$\left(P + \frac{a}{V^2}\right) \approx P$$

$$PV = RT + Pb; \quad \frac{PV}{RT} = 1 + \frac{Pb}{RT} \quad \text{or} \quad Z = 1 + \frac{Pb}{RT}$$

$Z > 1$, positive deviation (effective only molecular size).

Exceptional behavior of H_2 and He	$a_{H_2} \approx 0$ & $a_{He} \approx 0$ (due to small size) $P(V - b) = RT$ $Z = 1 + \frac{Pb}{RT}$ (+ve deviation at all pressure)

Critical Points (for JEE)

(1) Critical temperature (T_c) :

It is the temperature above which a real gas can not be liquefied whatever applied pressure may be, $T_c = \frac{8a}{27Rb}$

(2) Critical pressure (P_c) :

It is the minimum pressure required to liquefy the gas at critical temperature. $P_c = \frac{a}{27b^2}$

(3) Critical volume (V_c) :

The volume occupied by 1 mole of the gas at critical temperature and critical pressure is known as critical volume.

$$V_c = 3b$$

$V_c = 3 \times 4V_m = 12V_m$ (Since $b = 4V_m$)

(4) Critical coefficient of a gas :

It is ratio of $\frac{RT_c}{P_c V_c}$ which is equal to 2.66 and remain constant for all the gases.

(5) Boyle's temperature (T_B) :

The temperature at which a real gas obey ideal gas equation at very low pressure is known as Boyle's temperature.

$$T_B = \frac{a}{Rb}$$

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Chapter – 4 Thermodynamics

Basic Terms of Thermodynamics

Systems : A specified part of the universe which is under observation is called the *system*

Surroundings : The remaining portion of the universe which is not a part of the system is called the *surroundings*.

Boundary : The limits of the system. The system and the surroundings can interact across the boundary. It can be real or Imaginary.

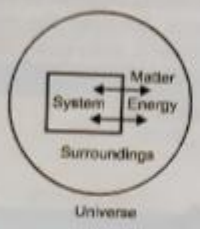
Types of System

(i) **Isolated system** : A system which neither exchanges energy nor matter with its surroundings is called an isolated system. For example a liquid in contact with its vapour in an insulated closed vessel is an isolated system.

(ii) **Closed system** : A system which may exchange energy but not matter with its surroundings is called a closed system. If in the above example the vessel containing liquid in contact with its vapour is closed one but is not insulated. It is a closed system.

(iii) **Open system** : A system which may exchange both energy and matter with its surrounding is called an open system. The evaporation of water in an open vessel is an example of open system. Water absorbs heat from the surroundings and escapes into surroundings as water vapour.

Whole Universe is a perfect isolated system.



Open System

Close System

Isolated system

Extensive and Intensive Variables

(a) Extensive property of a system are those whose magnitude depends on the amount of matter present in the system. It is an additive property. For example volume, internal energy, enthalpy, entropy, mass etc.

(b) The property whose magnitude does not depend upon quantity of matter present in a system is known as intensive property of the system. It is not an additive property and don't alter with time. Example are; temperature, pressure, density etc.

State Function and Path Function

State Function

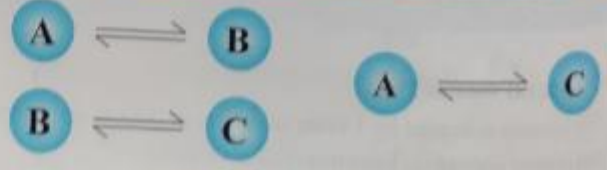
- Property of a system which is dependent only on the state of the system i.e. it is a point function
- It is independent of the path adopted to attain a particular state.
- Temperature, Pressure, Volume, Total internal energy (E or U), Enthapy (H), Gibbs free energy (G), Entropy (S) are all state functions.

Path Function

- Quantities which are dependent on the path/way. The system has achieved a particular state.
- Heat, work, Heat capacities (Molar heat capacities, specific heat capacities etc) are path functions.
- These quantities are define when there is a process going on.
- These can not have any definite (particular) value in any particular state of the system.

Zeroth law of Thermodynamics

If a system A is in thermal equilibrium with a system C and if B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other whatever the composition of the system.



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Thermodynamics Processes

The change of thermodynamics state from one condition to another condition is called thermodynamics process.

(i) **Isothermal process** : In this process operation is done at constant temperature. $dT = 0$ thus $\Delta E = 0$.

(ii) **Adiabatic process** : In this process there is no exchange of heat takes place between the system and surroundings. The system is thermally isolated, i.e., $dQ = 0$ and its boundaries are insulated.

(iii) **Isobaric process** : In this process the pressure remains constant throughout the change i.e., $dP = 0$.

(iv) **Isochoric process** : In this process volume remains constant throughout the change, i.e., $dV = 0$.

(v) **Cyclic process** : When a system undergoes a number of different processes and finally return to its initial state, it is termed cyclic process. For a cyclic process $dE = 0$ and $dH = 0$.

(vi) **Reversible process** : A process which occurs infinitesimally slowly, i.e. opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be reversible process.

(vii) **Irreversible process** : When the process occurs from initial to final state in single step in finite time and cannot be reversed, it is termed an irreversible process. Amount of entropy increases in irreversible process.

Irreversible processes are spontaneous in nature. All natural processes are irreversible in nature

Heat Capacity

Heat required to increase temperature of given amount of substance by 1°C or 1 K.

$C = q / \Delta T \Rightarrow q = C.\Delta T$

at constant pressure : $\Delta H = C_p \Delta T$ at constant volume : $\Delta E = C_v \Delta T$

Specific heat capacity (S)

Heat required to raise temperature of unit mass (generally 1 g) of a substance by 1°C

$$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT} \; Jg^{-1} K^{-1}$$

$$q = \int dq = \int mSdT = mS\Delta T$$

- **S is intensive path function**
- S_p is specific heat capacity at constant pressure
- S_v is specific heat capacity at constant volume
- S_p & S_v are intensive but not a path function

Molar heat capacity (C)

Heat required to raise temperature of 1 mole of a subtance by 1°C

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT} \; J\ mole^{-1} K^{-1}$$

$$q = \int nCdT = nC\Delta T$$

- **C is intensive path function**
- C_p is molar heat capacity at constant pressure
- C_v is molar heat capacity at constant volume
- C_p and C_v are intensive but not a path function

Relation between C_p and C_v

$C_p - C_v = R = 2\ Cal = 8.314\ J$

$C_p / C_v = \gamma$

For monoatomic gas

$\gamma = 5/3$ $C_v = 3/2\ R$ $C_p = 5/2\ R$

For diatomic or triatomic linear gas

$\gamma = 7/5$ $C_v = 5/2\ R$ $C_p = 7/2\ R$

For triatomic Non - Linear gas

$\gamma = 4/3$ $C_v = 3\ R$ $C_p = 4\ R$

Units of Heat and Work

- The S.I. unit of heat is Joule (J) or KiloJoule. The Joule (J) = Newton – metre (1 J = 1 Nm).
- Work is measured in terms of ergs or Joules. The S.I. unit of work is Joule.

1 Joule = 10^7 ergs = 0.2390 cal.

1 cal > 1 Joule > 1 erg

Internal Energy, Heat And Work

Internal Energy (E or U)

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

$$E = E_{translational} + E_{rotational} + E_{vibrational} + E_{bonding} + E_{electronic} + \ldots$$

Change in internal energy (ΔE) : It is neither possible nor necessary to calculate the absolute value of internal energy of a system then, $\Delta E = E_f - E_i$.

Heat (q)

Heat is a form of energy. It flows from one system to another because of the difference in temperature between them. Heat flows from higher temperature to lower temperature.

Heat given to system = +ve **Heat given by system = –ve**

Work (w)

Work is said to be performed if the point of application of force is displaced in the direction of the force. It is equal to the force multiplied by the displacement (distance through which the force acts).

Work done by the system = –ve **Work done on the system = +ve**

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First Law of Thermodynamics

(a) Energy can be transformed from one form to another but energy can neither be created nor destroyed.

(b) The total mass and energy of an isolated system remains constant

(c) There is an exact equivalence between work and heat

(d) Whenever a quantity of one kind of energy is produced, an exactly equivalent amount of another kind of energy must disappear

$$\boxed{\Delta E = q + w}$$

Isochoric Process
$q = \Delta E, w = 0$

Adiabatic Process
$\Delta E = w, q = 0$

Cyclic Process
$q = -w, \Delta E = 0$

Enthalpy and Enthalpy Change

Heat content of a system at constant pressure is called enthalpy denoted by 'H'.

Heat change at constant pressure can be given as $\Delta q = \Delta E + P\Delta V$

At constant pressure heat can be replaced at enthalpy $\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + \Delta n_g RT$ Δn_g = number of moles of gaseous product – number of moles of gaseous reactant.

$\therefore \Delta H$ = Heat change or heat of reaction (in chemical process) at constant pressure

ΔE = Heat change or heat of reaction at constant volume.

Work Done in Different Process

Isothermal Process

$\Delta T = 0, \ \Delta E = 0 \Rightarrow w = -q$

Reversible Isothermal Expansion

$w_{rev} = -2.303\ nRT \log [V_2/V_1] = -2.303\ nRT \log [P_1/P_2]$

Irreversible Isothermal Expansion

$w_{irr} = -P_{ext}(V_2 - V_1)$

Super Note : for expansion $w_{rev} > w_{irr}$, for compression $w_{rev} < w_{irr}$

Adiabatic Process

$q = 0, w = \Delta E$

Reversible Adiabatic

$$w_{rev} = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

Irreversible Adiabatic

$\Delta E = w_{irr}$

$nC_v (T_2 - T_1) = -P_{ext}(V_2 - V_1)$

Adiabatic Expansion Process

$(w_{gas})_{rev} > (w_{gas})_{irrev} \Rightarrow \Delta E_{rev} > \Delta E_{irrev}$

$\therefore (T_2)_{rev} < (T_2)_{irrev}$

Adiabatic Compression Process

$(w_{gas})_{rev} < (w_{gas})_{irrev} \Rightarrow \Delta E_{rev} < \Delta E_{irrev}$

$\therefore (T_2)_{rev} < (T_2)_{irrev}$

Isochoric Process

$\Delta V = 0, w = 0$

Free expansion

Always going to be irreversible and since $P_{ext} = 0$

So, $dw = -P_{ext} \cdot dV = 0$

If no heat is supplied $q = 0$

then $\Delta E = 0$ So, $\Delta T = 0$.

Chemical Reaction

$w = -P_{ext}\Delta V = -\Delta n_g RT$

Comparison between Isothermal and Adiabatic Process

Always remember that adiabatic curves are more steeper than isothermal curves

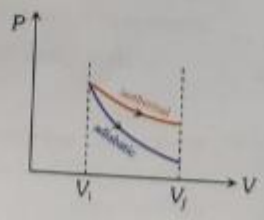
(i) Expansion :

$w_{isothermal} > w_{adiabatic}$

$P_{isothermal} > P_{adiabatic}$

$T_{isothermal} > T_{adiabatic}$

$(Slope)_{isothermal} < (Slope)_{Adiabatic}$



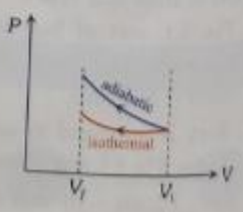
(ii) Compression :

$w_{adiabatic} > w_{isothermal}$

$P_{adiabatic} > P_{isothermal}$

$T_{adiabatic} > T_{isothermal}$

$(Slope)_{isothermal} < (Slope)_{Adiabatic}$



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Second Law of Thermodynamics

It can be defined in number of ways as follows

1. All spontaneous processes (or naturally occurring processes) are thermodynamically irreversible.
2. Without the help of the an external agency, a spontaneous process cannot be reversed e.g., heat cannot by itself flow from a colder to hotter body.
3. The complete conversion of heat into work is impossible without leaving some effect elsewhere.
4. All spontaneous processes are accompanied by a net increase of entropy.
5. The entropy of the universe is increasing.
6. The entropy is a time arrow.

Entropy and Entropy Change

Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature.

$$\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T} \quad JK^{-1} \quad \text{or} \quad \text{cal deg}^{-1}$$

(i) Entropy is an extensive property. Its value depends upon the amount of the substance present in the system.

(ii) Entropy of a system is a state function. It depends upon the state variables (T, P, V, n)

(iii) The change in entropy in going from one state to another is independent of the path

(iv) The total entropy change of an isolated system is equal to the entropy change of system and entropy change of the surroundings. The sum is called *entropy change of universe*.

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr}$$

Process		ΔS_{system}	ΔS_{surr}	ΔS_{Total}
Isothermal	Reversible	$\Delta S_{(system)} = nR\ln(V_2/V_1)$	$\Delta S_{surr} = -nR\ln(V_2/V_1)$	$\Delta S_T = 0$
	Irreversible	$\Delta S_{(system)} = nR\ln(V_2/V_1)$	$\Delta S_{surr} = -q_{rev}/T$	$\Delta S_T > 0$
Adiabetic	Reversible	$\Delta S_{(system)} = 0$	$\Delta S_{surr} = 0$	$\Delta S_T = 0$
	Irreversible	$\Delta S_{(system)} = nR\ln(V_2/V_1)$ $\Delta S_{(system)} = nR\ln(T_2/T_1)$	$\Delta S_{surr} = 0$	$\Delta S_T > 0$
Free expansion (irrversible)	Isothermal	$\Delta S_{(system)} = nR\ln(V_2/V_1)$	$\Delta S_{surr} = 0$	$\Delta S_T > 0$
	Adiabatic	$\Delta S_{(system)} = nR\ln(V_2/V_1) + nC_v\ln(T_2/T_1)$	$\Delta S_{surr} = 0$	$\Delta S_T > 0$

Gibb's Free energy and Free energy change

Gibb's free energy is defined as, the energy available in the system for conversion into useful work.

It is that thermodynamic quantity of a system, the decrease in whose value during a process is equal to the useful work done by the system.

$\Delta G = \Delta H - T\Delta S$ (Gibb's Helmotz equation) $\Delta H = H_2 - H_1$ is the enthalpy change of the system

Spontaneous Process ($\Delta G < 0$)

- A process which can take place by itself under the given set of conditions once it has been initiated if necessary, is said to be a spontaneous process.
- A spontaneous process is a process that can occur without work being done on it. The spontaneous processes are also called feasible or probable processes.

Examples

The diffusion of the solute from a concentrated solution to a dilute solution occurs when these are brought into contact. , Mixing of different gases. Heat flows from a hot reservoir to a cold reservoir . , Electricity flows from high potential to low potential. , Expansion of an ideal gas into vacuum through a pinhole.

Non Spontaneous ($\Delta G > 0$)

- The processes which are forbidden and are made to take place only by supplying energy continuously from outside the system are called non-spontaneous processes.
- Non spontaneous processes can be brought about by doing work.

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ΔH	ΔS	ΔG	Reaction characteristics
−	+	Always negative	Reaction is spontaneous at all temperatures
+	−	Always positive	Reaction is non spontaneous at all temperatures
−	−	Negative at low temperature but positive at high temperature	Reaction is spontaneous at low temperature but becomes non spontaneous at high temperature
+	+	Positive at low temperature but negative at high temperature	Reaction is non spontaneous at low temperature but becomes spontaneous at high temperature

(Relation between ΔG° and Equilibrium constant (K) : $\Delta G^\circ = -2.303RT \log K$ **)**

Third Law of Thermodynamics

It states that, "Entropy of all perfectly crystalline solids may be taken as zero as the absolute zero of temperature." Third law of thermodynamics may also be defined as

(i) The entropy of a solid is zero at the absolute zero of temperature.

(ii) It is impossible to reduce the temperature of any system to absolute zero by any process.

(iii) At any pressure, the entropy of every crystalline solid in thermodynamic equilibrium at absolute zero is zero.

(iv) At the absolute zero, increment in entropy for isothermal process in crystalline approaches zero as the limit.

(v) At absolute zero, every crystal becomes ideal crystal.

Thermochemistry

Exothermic Reactions

The chemical reactions which proceed with the ***evolution of heat*** energy are called exothermic reactions.

$$\Delta H = H_p - H_r; \quad H_p < H_r; \quad \Delta H = -ve$$

Endothermic Reactions

The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions.

$$\Delta H = H_p - H_r; \quad H_p > H_r; \quad \Delta H = +ve$$

Heat of Reaction or Enthalpy of Reaction

Heat of Formation

It is the quantity of heat evolved or absorbed (i.e. the change in enthalpy) when one mole of the substance is formed from its constituent elements under given conditions of temperature and pressure. It is represented by ΔH_f.

$$\Delta H^\circ = [\Sigma \Delta H^\circ_{(products)} - \Sigma \Delta H^\circ_{(Reactants)}]$$

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g); \quad \Delta H_{(g)} = -11\,kcal$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl; \quad \Delta H_f = -22\,kcal$$

Heat of Combustion

It is the amount of heat evolved or absorbed (*i.e.* change in enthalpy) when one mole of the substance is completely burnt in air or oxygen.

$$\Delta H^0 = [\Sigma \Delta H^0_{f(Products)} - \Sigma H^0_{f(Reactants)}]$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \Delta H = -192\ kcal$$

$$C_2H_6(g) + 3.5\,O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l); \ \Delta H = -372.8\ kcal$$

Heat of Neutralisation

It is the amount of heat evolved (i.e., change in enthalpy) when one equivalent of an acid is neutralised by one equivalent of a base in fairly dilute solution

$$HCl(aq.) + NaOH\ (aq.) \rightarrow NaCl(aq.) + H_2O$$

$$\Delta H = -13.7\ kcal$$

Heat of Fusion

When a solid is allowed to melt, it changes into liquid state with the absorption of heat (increase in enthalpy) and when a liquid is allowed to freeze, it changes into solid with the evolution of heat (decrease in enthalpy). The change in enthalpy of such type of transformations is called enthalpy of fusion.

$$H_2O(ice) \rightarrow H_2O(liquid); \quad \Delta H = +1.44\ kcals\ (+6.02\ kJ)$$

$$H_2O\ (liquid) \rightarrow H_2O\ (ice); \quad \Delta H = -1.44\ kcals\ (-6.02\ kJ)$$

Heat of Solution

It is the amount of heat evolved or absorbed (i.e., change in enthalpy) when one mole of the solute is dissolved completely in excess of the solvent (usually water).

$$NH_4Cl(s) + H_2O(l) \rightarrow NH_4Cl(aq.); \quad \Delta H = +3.90\ kcal$$

$$BaCl_2(s) + H_2O(l) \rightarrow BaCl_2(aq.); \quad \Delta H = -2.70\ kcal$$

Heat of Hydration

It is the amount of heat evolved or absorbed (i.e change in enthalpy) when 1mole of an anhydrous or a partially hydrated salt combines with the required number of moles of water to form a specific hydrate.

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s); \ \Delta H = -18.69\ kJ/mol$$

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Laws of Thermochemistry

Levoisier and Laplace Law

According to this law enthalpy of decomposition of a compound is numerically equal to the enthalpy of formation of that compound with opposite sign.

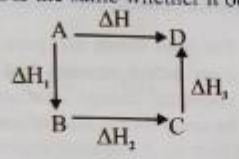
Example: $C(s) + O_2 \rightarrow CO_2(g); \Delta H = -94.3\,kcal$

$CO_2(g) \rightarrow C(s) + O_2(g); \Delta H = +94.3\,kcal$

Hess's Law

If a reaction is the sum of two or more constituent reactions, then ΔH for the overall process must be sum of the ΔH of the constituent reactions.

The enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps.



For $A \rightarrow D$, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Applications of Hess's Law

(a) For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

(b) For the determination of enthalpies of extremely slow reactions.

(c) For the determination of enthalpies of transformation of one allotropic form into another.

(d) For the determination of resonance energy.

(e) For the determination of lattice energy

(f) For the determination of bond energies.

$\Delta H_{reaction} = \Sigma$ Bond energies of reactants $- \Sigma$ Bond energies of products.

Note : Bond energy is only place where we do reactant – product, everywhere else we do product – reactant.

Super Note

(1) Relation between ΔG and ΔG°

$\Delta G = \Delta G^\circ + 2.303RT \log Q$ (Q = concentration coefficient)

(2) **ΔG° and equilibrium constant :**

at equilibrium $\Delta G = 0$ and $Q = K$

$\therefore \quad \Delta G^\circ = -RT \ln K$

$= -2.303RT \log K$

(3) **ΔG and work :** $\Delta G = -w$ (non expansion) useful.

(4) **ΔG and electrical work done :** $\Delta G = -nFE_{cell}$

$\Delta G^\circ = -nFE^\circ_{cell}$

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Chapter – 5 Chemical Equilibrium

Basic Theory of Equilibrium

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

Equilibrium State

Consider a Reversible Reaction $aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$

According to mass action law → rate ∝ concentration of reactants

- Only gaseous element considered
- Solid/ liquids active mass taken unity

Forward reaction rate $r_f = k_f[A]^a [B]^b$,

Backward reaction rate $r_b = k_b [C]^c[D]^d$,

At Equilibrium State

Rate of forward reaction (r_f) = Rate of backward reaction (r_b)

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

Types of Equilibrium Constant

(1) K_c is a constant and is called the **equilibrium constant in terms of concentration.** where all the concentrations are at equilibrium and are expressed in moles/litre

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

(2) K_p → **Equilibrium constant in terms of partial pressure.** It is defined for the equilibrium reaction which contains at least one gaseous component.

e.g. $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

$$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} \quad \text{(In terms of Partial Pressure)}$$

(3) K_x → **Equilibrium constant in terms of mole fraction .** It is unit less

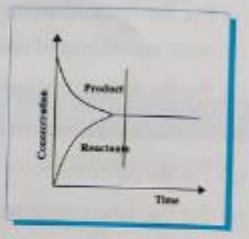
$$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b} \quad \text{(In terms of Mole fraction)}$$

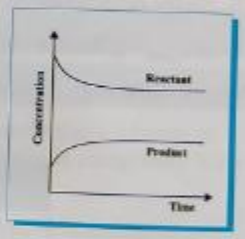
- Partial pressure of solid is taken as unity & in calculation of partial pressure of solids, their number of moles are not considered.
- In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.

- For pure solids and pure liquids, although they have their own active masses but they remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.

e.g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_c = [CO_2]$, $K_p = P_{CO_2}$





Units of Equilibrium Constants

- Unit of $K_C = (\text{mol/litre})^{\Delta n_g}$
- Unit of $K_P = (\text{atm})^{\Delta n_g}$

Equilibrium constant only depends on temperature

Relation between K_p & K_c

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

- If $\Delta n_g = 0$ then $K_P = K_C$
- If $\Delta n_g > 0$ then $K_P > K_C$
- If $\Delta n_g < 0$ then $K_P < K_C$

Δn_g = (No. of moles of gaseous product) - (No. of moles of gaseous reactant

Characteristics of Equilibrium Constant & Factors Affecting it

Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached

The equilibrium constant does not give any idea about time taken to attain equilibrium.

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K depends on the stoichiometry of the reaction

If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 . K_2$

		Equilibrium constant
	$A(g) \rightleftharpoons B(g)$	K_1
	$B(g) \rightleftharpoons C(g)$	K_2
On adding	$A(g) \rightleftharpoons C(g)$	$K = K_1 . K_2$

If the reaction having eq. constant K is reversed then resulting equation has eq. constant $1/K_1$

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

On reversing, $C(g) + D(g) \rightleftharpoons A(g) + B(g)$ $\quad K = \frac{1}{K_1}$

If a chemical reaction having equilibrium constant K_1 is multiplied by a factor n then the resulting equation has equilibrium constant $K = (K_1)^n$, n can be fraction

eg. $D_2(g) \rightleftharpoons 2A(g)$ $\quad K_1$

Multiplying by $\left(\frac{1}{2}\right)$ $\quad \frac{1}{2}D_2(g) \rightleftharpoons A(g)$ $\quad K = (K_1)^{1/2} = \sqrt{K^1}$

$A \rightleftharpoons B$	$K_C = K_1$	$2C \rightleftharpoons 2B$	$K_C = K_2$
$D \rightleftharpoons C$	$K_C = K_3$ then	$A \rightleftharpoons D$	$K_C = \frac{K_1}{\sqrt{K_2} \times K_3}$

Equilibrium constant is dependent only on the temperature.

It means K_c and K_p will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

However if temperature is changed,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]; \Delta H = \text{Enthalpy of reaction}$$

If $T_2 > T_1$ then

$K_2 > K_1$ provided $\Delta H = +ve$ (endothermic reaction)

$K_2 < K_1$ if $\Delta H = -ve$ (exothermic reaction)

In the above equation, the unit of R and $\Delta H/T$ should be same.

Relation between equilibrium constant & standard free energy change.

$$\Delta G^\circ = -2.303\ RT \log K$$

Where ΔG° = standard free energy change

T = Absolute temperature,

R = universal gas constant.

Application of Equilibrium constant

(1) Predicting the direction of the reaction

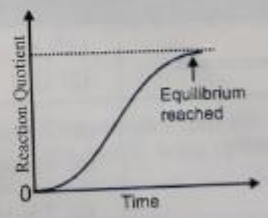
Reaction Quotient (Q) is expressed in the same way as for equilibrium constant, except that the concentrations may not necessarily be at equilibrium. In general for the reversible reaction

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

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{(In terms of concentration)}$$

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

- The reaction quotient is a variable quantity with time.
- It helps in predicting the direction of a reaction.
- if $Q > K_c$ reaction will proceed in backward direction until equilibrium in reached.
- if $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
- if $Q = K_c$ Reaction is at equilibrium.



- **Degree of dissociation (α)**

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

- **Degree of Dissociation from Vapour pressure**

$n_1 A \rightleftharpoons n_2 B + n_3 C$

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

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

D_0 = Observed vapour density.

(2) More is the value of K_p and K_c more is the extent of reaction.

(3) Stability of reactant increases when value of K decreases.

(4) Stability of Product increases when value of K increase.

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Relation between K_{eq}, Q, Gibb's energy change ΔG and ΔH

- ΔG = -ve (spontaneous process)
- ΔG = +ve (non spontaneous process)
- $\Delta G = \Delta G^\circ + RT\,lnQ$

  at equilibrium $\Delta G = 0, Q = K_{eq}$

  $\Delta G^\circ = -RT\,lnK_{eq}$
- More negative value of ΔG° then more positive value of K_{eq}.
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

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

- If $\Delta G^\circ = 0$, then $K_{eq} = 1$.
- If $\Delta G^\circ > 0$, then $K_{eq} < 1$. So reverse reaction is possible. (less concentration of product at equilibrium)
- If $\Delta G^\circ < 0$, then $K_{eq} > 1$. So forward reaction is possible. (large concentration of product is observed till the point of equilibrium is attained).

Super Note : Negative value of ΔG° never indicates the complete transformation of the reactants into products. Similarly a positive value of ΔG° does not indicate the absence of product formation.

Physical Equilibrium

Those reaction in which change in only & only physical state of substances takes place without any chemical change.

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

$$H_2O\,(s) \rightleftharpoons H_2O\,(l) \qquad \Delta H = +ve$$

Density Low	Density High
Volume High	Volume Low

Melting of ice is favourable at high temperature and high pressure.

(ii) Boiling of water

$$H_2O\,(l) \rightleftharpoons H_2O\,(g) \qquad \Delta H = +ve$$

Density High	Density Low
Volume Low	Volume High

On increasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward. Hence, on increasing pressure, the boiling point increases.

(iii) Solubility of gases in liquid

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

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

Le-Chatelier's Principle

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

S.No.	Effect due to change in		$\Delta n_g = 0$ A⇌B	$\Delta n_g > 0$ A⇌2B	$\Delta n_g < 0$ 2A⇌B
(1)	Concentration	(i)↑[A] (ii) ↓[A]	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
(2)	Pressure	(i) ↑ in pressure (ii) ↓ in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
(3)	Volume	(i) ↑ in Volume (ii) ↓ in Volume	Unchanged Unchanged	Forward direction Backward direction	Backward direction Forward direction
(4)	Temperature	(i) ↑ in Endothermic (ii) ↑ in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
(5)	Dissociation	(i) ↑ in pressure (ii) ↓ in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Decreases	Dissociation Decreases Dissociation Decreases
(6)	Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Decreases Unchanged	Dissociation Decreases Unchanged

- Favourable condition or suitable condition means forward direction or more product.
- Conversion of a solid into liquid, liquid into gas is favoured by high temperature in most of the cases.
- Melting of solids is accompained by increase of volume so low pressure favours their melting while high pressure favours solidification.
- The **melting of ice** is endothermic process favourable condition is **high temperature** and **high pressure.**
- Addition or removal of pure solid or pure liquid can not disturb the equilibrium because concentration of pure solid / liquid is constant.

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Chapter – 6 Ionic Equilibrium

All The substances can be classified into

Non electrolytic Substance

- Does not dissociate into ions on dissoving in solvent like water.
- Solution will not conduct electricity eg. C_6H_6, diethyl ether

Electrolytic Substance

- Will Dissociate on dissolving in water into ions.
- Solution will conduct electricity. Eg. All acids, bases, all salts, Hg_2Cl_2 dissolve but dissociate negligible

Strong electrolyte

- α = Unity (100% ionisation)
- Eg. Strong acids (generally $HClO_4$, HI, HBr, HCl, H_2SO_4, HNO_3), Strong bases (generally NaOH, KOH, RbOH, CsOH and $Ba(OH)_2$) All type of soluble salts (SASB, SAWB, WASB or WAWB.)

Weak electrolyte

- α <<< 10% or $\alpha < 0.1$ (generally valid if $K_{eq} < 10^{-5}$) electrolytes not 100% dissociated.
- Eg. Weak acids (CH_3COOH, HCN), weak bases (Nh_3, $Zn(OH)_2$). All sparingly soluble salts AgCl, $BaSO_4$ etc.

Acid Base Theory

Arrhenius concept

Arrhenius Acid

Substance which gives H^+ ion on dissolving in water (H^+ donor)

eg. HNO_3, $HClO_4$, HCl, HI, HBr, H_2SO_4, H_3PO_4 etc.

- H_3BO_3 is not Arrhenius acid.
- H^+ ion in water is extremely hydrated (in form of H_3O^+, $H_5O_2^+$, $H_9O_4^+$) and high charge density.
- The structure of solid $HClO_4$ is studied by X-ray, It is found to be consisting of H_3O^+ and ClO_4^-.

$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$ (better representation)

Arrhenius Base

Any substance which releases OH^- (hydroxyl) ion in water (OH^- ion donor)

E.g. NaOH, $Mg(OH)_2$, $Ba(OH)_2$

- OH^- ion also in hydrated form of $H_2O_2^-$, $H_3O_4^-$, $H_4O_3^-$
- First group elements (except Li.) form strong bases.

Major Limitation : Defined only in water solvent

Fails to explain acidic and basic nature of substance

Ex. NH_3, $AlCl_3$, BF_3 etc.

Bronsted - Lowry Concept : (Conjugate acid - base concept) (Protonic concept)

Acid

Substances which donate H^+ are Bronsted Lowry acids (H^+ donor)

Base

Substances which accept H^+ are Bronsted Lowry bases (H^+ acceptor)

Conjugate acid - base pairs

In a typical acid base reaction

$$HX + B \rightleftharpoons X^- + HB^+$$

HX (acid) + B (base) ⇌ HB^+ (Conjugate acid) – X (Conjugate base)

Conjugate pair

☞ **Forward Reaction** – Here HX, being a proton donor, is an acid. B, being a proton acceptor, is a base.

☞ **Backward Reaction** – Here HB^+, being a proton donor, is an acid. X, being a proton acceptor, is a base.

- Conjugate acid - base pair differ by only one proton
- Strong acid will have weak conjugate base and vice versa
- Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

Fails to explain acid & basic nature of substance without proton transfer.

Ex. SO_2, BF_3, $AlCl_3$, $COCl_2$ etc.

Lewis Concept (electronic concept)

Acid

An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Acid → e pair acceptor

e.g. Electron deficient molecules : BF_3, $AlCl_3$

Cations : H^+, Fe^{2+}, Na^+

Molecules with vacant orbitals : SF_4, PF_5

Base

A base is any molecule/ion which has a lone pair of electrons which can be donated.

Base → (electron pair donor)

e.g. Molecules with lone pairs (ligands) : NH_3, PH_3, H_2O, CH_3OH

Fails to explain acid and base practically According to this concept neutralization process is slow but actually acid base neutralization is fast process.

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Super Note :

- All the Lewis bases are bronsted bases but all lewis acids are not bronsted acids
- All Arrhenius acids are bronsted acid. but it is not so for bases.
- Relative strength of weak acid or weak base = $\sqrt{\frac{K_1 C_1}{K_2 C_2}}$

Ostwald's Dilution Law (for Weak Electrolytes)

For a weak electrolyte A^+B^- dissolved is water, if α is the degree of dissociation then

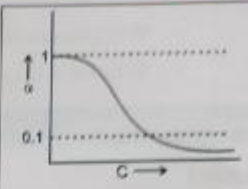
	$AB(aq) \rightleftharpoons$	$A^+(aq)$ +	$B^-(aq)$
initial conc.	C	0	0
conc-at eq.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Then according to law of mass action,

$$K_a = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha . C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$ = dissociation constant of the weak electrolyte

For very weak electrolytes, $\alpha < 5\%$ or 0.05 then $(1-\alpha) = 1$

$$K_{eq} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{eq}}{C}} = \sqrt{K_{eq} . V}$$



$\alpha \propto \frac{1}{\text{concentration}}$

- On dilution V increases, C decreases & α increases
- At infinite dilution $V \to \infty$, $\alpha \to 1$ means weak electrolyte will behave like strong electrolyte.

Properties of Water

(i) Amphoteric in nature

In pure water $[H^+] = [OH^-]$ so it is Neutral.

(ii) Molar concentration / Molarity of water –

$$M = \text{No. of moles/litre} = \frac{1000 \text{ gm/litre}}{18 \text{ gm/mole}} = 55.55 \text{ M}$$ (density = 1 gm/cc)

(iii) Ionic product of water $[K_w]$

According to Arrhenius concept

$H_2O \rightleftharpoons H^+ + OH^-$ so, ionic product of water,

$K_w = [H^+][OH^-] = 10^{-14}$ at 25° (exp.), $pK_w = pH + pOH$

dissociation of water, is endothermic, so on increasing temperature K_{eq} increases, K_w increases with increase in temperature

Now **$pH = -\log[H^+] = 7$** and
$pOH = -\log[OH^-] = 7$
$(pH)_{pure\ water} = pK_w / 2$
for water at 25° (experimental)

pH = 7 = pOH	⇒	neutral	at 25°C
pH < 7 or pOH > 7	⇒	acidic	at 25°C
pH > 7 or pOH < 7	⇒	Basic	at 25°C

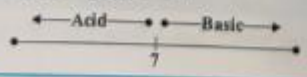
- **Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.**
- **pH of an acidic solution is always less than pH of pure water.**
- **pH of a basic solution is always greater than pH of pure water**

Super Note : Pure water is neutral at any temperature and boiling water has pH = 6.5625 (Neutral)

Different values at Different Temperature

At 25°C

1. $K_W = 10^{-14}$
2. $(pH)_{pure\ water} = (pOH)_{pure\ water} = 7$
3. $pH + pOH = 14$



on increasing temperature K_W ↑ →

on increasing temperature $(pH)_{pure\ water}$ decreases →

At 90°C

1. $K_W = 10^{-12}$
2. $(pH)_{pure\ water} = (pOH)_{pure\ water} = 6$
3. $pH + pOH = 12$

Common ion Effect

- Minimum two electrolytes are required having one common ion.
- Common ion effect operates only on weak electrolyte.
- [Common ion] increases → more common ion effect and α decreases.

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pH Calculations Of Different Types Of Solutions

Type I: Single Substances

Strong Acid

(i) If concentration is greater than 10^{-6} M, In this case H^+ ions coming from water can be neglected, so **$[H^+]$ = normality of strong acid solution.**

(ii) If concentration is less than 10^{-6} M, In this case H^+ ions coming from water cannot be neglected, So

$[H^+]$ = normality of strong acid + H^+ ions coming from water in presence of this strong acid

Strong Base

$[OH^-] = N_{Base} + 10^{-7}$ (from water)

We can neglect smaller values. If it is atleast 100 times smaller than other

$pOH = -\log[OH^-]$

$pH = pK_W - pOH$

Weak Acid

For monobasic acid

$[H^+] = \sqrt{K_a C}$

K_a = dissociation constant of acid

C : Initial concentration of acid

So $pH = \frac{1}{2}(pK_a - \log C)$

on increasing dilution ⇒ $C \downarrow \Rightarrow \alpha \uparrow$ and $[H^+] \downarrow \Rightarrow pH \uparrow$

Weak Base

(for monoacidic base)

$[OH^-] = \sqrt{K_b C}$

K_b = dissociation constant of base

C : Initial concentration of base

So $pOH = \frac{1}{2}(pK_b - \log C)$

$pH = pKw - pOH$

Type II: More than one substance (Non reacting)

$(SA)_I + (SA)_{II}$

- Initially same Beaker (If individual volume is not given): $[H^+] = N_1 + N_2$
- Initially in different beaker (individual volume is given): $[H^+] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

$(SB)_I + (SB)_{II}$

- Same Beaker (initially): $[OH^-] = N_1 + N_2$
- Different Beaker (Initially): $[OH^-] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

SA + WA or SB + WB

We can ignore $[H^+]/[OH^-]$ coming from weak part as compared to strong part due to common ion effect.

Type III: More than one substance (Reacting)

$$\underset{N_1V_1}{SA} + \underset{N_2V_2}{SB} \rightarrow \text{Salt of SASB} + H_2O$$

a) If $N_1V_1 = N_2V_2$

Then salt of SASB is left in beaker after reaction.

Salt of SASB:

Does not hydrolyse

Solution remain neutral

(pH = 7 at 25°C)

b) If $N_1V_1 > N_2V_2$

Then SA + Salt of SASB is left in solution among which only SA is the contributing substance toward pH.

$$[H^+] = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

c) If $N_1V_1 < N_2V_2$

Then SB + salt of SASB is left in solution among which only SB is contributing substance toward pH.

$$[OH^-] = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

Salt Hydrolysis (Reverse Of Neutralisation)

Salt + Water ⇌ acid + base

(i) Salt of strong acid and strong base

Neither of the ions will undergo hydrolysis so the Solution contain only the equilibrium of ionization of water.

$$2H_2O(l) \rightleftharpoons H_3O^+ + OH^-$$

$$pH = pK_w/2$$

(ii) Salt of strong acid and weak base

$N_1V_1 = N_2V_2$

Cationic hydrolysis

The *Examples* can be NH_4Cl, $(NH_4)_2SO_4$, $AlCl_3$ Only the cation will undergo hydrolysis and the solution will be acidic in nature. $K_h \times K_b = K_w$

$$h = \sqrt{\frac{K_h}{C}} \qquad [H^+] = \sqrt{\frac{K_w}{K_b} \times C}$$

$$pH = -\log[H^+] = =1/2[pK_w - pK_b - \log C]$$

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(iii) Salt of weak acid and strong base

$N_1V_1 = N_2V_2$

Anionic hydrolysis

$K_a \times K_s = K_w$

The ***Examples*** can be CH_3COONa, KCN, $Na_2C_2O_4$, K_3PO_4

$$h = \sqrt{\frac{K_h}{C}} \qquad [OH^-] = \sqrt{\frac{K_w}{K_a} \times C}$$

$$pH = -\log[H^+] = \frac{1}{2}[pK_w + pK_a + \log C]$$

(iv) Salt of weak acid and weak base

Examples can include CH_3COONH_4, NH_4CN, $Ca(CH_3COO)_2$, MgC_2O_4

$$K_a \times K_w \times K_b = K_w$$

$$\left(\frac{h}{1-h}\right) = \sqrt{K_h}$$

$$[H^+] = K_a \times \sqrt{K_h} = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$\mathbf{pH = -\log[H^+] = 1/2\,[pK_w + pK_a - pK_b]}$$

Hydrolysis of Amphiprotic Anion (Cation is not Hydrolysed)

Amphiprotic ions are those ions which acts as acid as well as base.

$NaHCO_3$, NaHS, etc., can undergo ionisation to from H^+ ion and can undergo hydrolysis to form OH^-

(Na^+ ion is not hydrolysed)

(i) $HCO_3^- + H_2O \xrightleftharpoons{\text{Ionisation}} CO_3^{2-} + \underset{\text{acid}}{H_3O^+}$

(ii) $HCO_3^- + H_2O \xrightleftharpoons{\text{Hydrolysis}} H_2CO_3 + \underset{\text{base}}{OH^-}$

$$pH(HCO_3^-) = \left(\frac{pKa_1 + pKa_2}{2}\right)$$

Similarly for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions.

$$pH(H_2PO_4^-) = \left(\frac{pKa_1 + pKa_2}{2}\right) \text{ and } pH(HPO_4^{2-}) = \left(\frac{pKa_2 + pKa_3}{2}\right)$$

Buffer Solution

(if the acids and bases are mixed in different amounts (equivalents))

Buffer ***Solution***s are those, which resist a change in pH upon addition of small amount of acid or base. this does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred.

Acidic Buffer

Buffer of weak acid and its salt with a strong base

If $N_1V_1 > N_2V_2$

[Left : WA + salt of WASB] Acidic buffer

$$pH = pK_a = +\log\frac{[Salt]}{[Acid]} \text{ ([C] in normality)}$$

Basic Buffer

Buffer of a weak base and its salt with a strong acid.

If $N_1V_1 < N_2V_2$

[left : WB + salt of SAWB] Basic Buffer

$$pOH = pK_b + \log\left(\frac{[Salt]}{[Acid]}\right)$$

Key point

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] (α = 50%) Best Buffer ⇒ pH = pKa	pH of Amphiprotic species : ($NaHPO_4$, $NaHCO_3$) which can donate as well as accept H^+ $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
Basic Range ($pK_a - 1$) to ($pK_a + 1$)	**Buffer in blood** $H_2CO_3 + NaHCO_3$	

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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.

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

Solubility product (K_{sp})

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

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

Solubility product (K_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

Expression of K_{sp} $A_xB_y \rightleftharpoons xA^{+y} + yb^{x-}$

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

In terms of 'S' $\Rightarrow K_{sp} = (xS)^x (yS)^y = x^x . y^y (S)^{x+y}$

Ionic Product (Q_{sp})

$$A_X B_Y \rightleftharpoons xA^{+y} + yB^{-x} ; Q_{sp}[A^{y+}][B^{x-}]^y$$

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

Applications:

I. If $Q_{sp} < K_{sp}$ [Unsaturated]

II. If $Q_{sp} = K_{sp}$ [Saturated]

III. 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 (ion which have opposite nature to the ion which is present in solution) increases the solubility but has no effect on K_{sp}.

Qualitative Analysis (for JEE)

Group	Radicals	Condition for precipitation (Group reagent)	Forms of precipitation
Zero	Na^+, K^+, NH_4^+	1-2 drop of CH_3COOH	-
First	Pb^{+2}, (Hg_2^{2+}), Ag^+	By mixing of dilute HCl	Chloride AgCl, Hg_2Cl_2, $PbCl_2$
Second	Pb^{+2}, Cu^{+2}, Hg^{+2}, Cd^{+2}, Bi^{+3}, As^{+3}, Sb^{+3}, Sn^{+2}, Sn^{+4}	H_2S gas passed in the presence of acidic medium	Sulphide PbS, HgS, CuS, CdS, SnS, SnS_2, As_2S_3, Sb_2S_3, Bi_2S_3
Third	Al^{+3}, Cr^{+3}, Fe^{+3}	NH_4OH mixed in the presence of NH_4Cl	Hydroxide $Al(OH)_3$, $Fe(OH)_3$ $Cr(OH)_3$
Fourth	Zn^{+2}, Ni^{+2}, Mn^{+2}, Co^{2+}	H_2S gas passed in presence of basic medium	Sulphide MnS, CoS, NiS, ZnS
Fifth	Ba^{+2}, Sr^{+2}, Cr^{+2}	$(NH_4)_2CO_3$ mixed in the presence of NH_4Cl	Carbonate $BaCO_3$, $SrCO_3$, $CaCO_3$
Sixth	Mg^{+2}	By mixing of Na_2HPO_4	Hydrogen phosphate ($MgHPO_4$)

Acid Base Titration and Indications (for JEE)

Name of Indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
Methyl Orange (MeOH)	Orange red	Yellow	3.1 to 4.5
Methyl red	Red	Yellow	4.2 to 6.2
Phenol red	Yellow	Red	6.2 to 8.2
Phenolphthalein (Hph)	Colour Less	Pink	8.2 to 10.2

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

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Chapter – 7 Redox Reaction

Concept of Oxidation & Reduction

Oxidation

- **Addition of Oxygen**
  Ex. $2Mg + O_2 \rightarrow 2MgO$
- **Removal of Hydrogen**
  Ex. $H_2S + Cl_2 \rightarrow 2HCl + S$
- **Increase in positive charge**
  Ex. $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- **Increase in oxidation number**
  Ex. $\overset{(+2)}{SnCl_2} \rightarrow \overset{(+4)}{SnCl_4}$
- **Removal of electron**
  Ex. $Sn^{2+} \rightarrow Sn^{4+} + 2e$

Reduction

- **Removal of Oxygen**
  Ex. $CuO + C \rightarrow Cu + CO$
- **Addition of Hydrogen**
  Ex. $S + H_2 \rightarrow H_2S$
- **Decrease in positive charge**
  Ex. $Fe^{3+} + e^- \rightarrow Fe^{2+}$
- **Decrease in oxidation number**
  Ex. $\overset{(+7)}{MnO_4^-} \rightarrow \overset{(+2)}{Mn^{2+}}$
- **Addition of electron**
  Ex. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Oxidation Number

(1) Oxidation no. is given positive sign if electrons are lost. oxidation no. is given negative sign if electrons are gained.

(2) Oxidation no. represents real charge in case of ionic compounds. However, in covalent compounds it represents imaginary charge.

The rules to derive oxidation number or oxidation state

(a) The O.S. of an element in its free state is zero.
Example O.S.'s of Na, Cu, I_2, Cl_2, O_2 etc. are zero

(b) Sum of O.S.'s of all the atoms in neutral molecule is zero.

(c) Sum of O.S.'s of all the atoms in a complex ion is equal number of charge present on it.

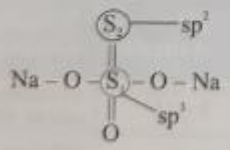
(d) In complex compounds, O.S. of some neutral molecules (ligands) is zero. Example CO, NO, NH_3, H_2O.

(e) Generally O.S. of oxygen is –2 but in H_2O_2 it is –1 and in OF_2 it is +2.

(f) Generally O.S. of Hydrogen is +1 but in metallic hydrides it is –1.

(g) Generally O.S. of halogen atoms is –1 but in interhalogen compounds it changes.

NOTE : Some times same atom in a compound has different O.S. For example, structure of $Na_2S_2O_3$ is



Here S_1 and S_2 both are sulphur atoms but they have different O.S.

O.S. of $S_1 = 6$, O.S. of $S_2 = -2$ (it is accepting two electrons from S_1 because EN of sp^2 > EN of sp^3)

Average O.S. of S $= (6-2)/2 = 2$

(h) Generally, O.S. of alkali metals is +1 and that of alkaline earth metals is +2.

(i) O.S. of transition elements vary from compound to compound. Mn has O.S. from +1 to +7.
$Mn_2O \rightarrow +1$, $MnO \rightarrow +2$, $Mn_3O_4 \rightarrow 8/3$, $MnO_2 \rightarrow +4$, $Mn_2O_3 \rightarrow +5$, $MnO_4^{2-} \rightarrow +6$, $MnO_4^- \rightarrow +7$

(j) O.S. of an atom may be fractional, negative, zero as well as Positive.

Super Note :

- Oxidation state of F is always –1
- Oxidation number can be zero, +ve, –ve (integer or fraction)
- Maximum oxidation no. of an element is = Group no. (Except O and F)
- Minimum oxidation no. of an element is = Group no. – 8 (Except metals)

Concept of Oxidising and Reducing Agent

Oxidising Agent and Oxidant

- Oxidises other and reduces itselves.
- Show electronation so decrease in oxidation number during a redox change.

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

Reducing Agent or Reductant

- Reduces others and oxidises itselves.
- Show de-electronation so increase in oxidation no. during a redox change.

E.g. : KI, $Na_2S_2O_3$ etc. are powerful reducing agent.

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Identification of Oxidizing and Reducing Agent

1. If an element is in its highest possible oxidation state in a compound, it can function as an oxidizing agent, e.g. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, H_2SO_4, $HClO_4$ etc.
2. If an element is in its lowest possible oxidation state in a compound, it can function as a reducing agent, e.g. H_2S, $FeSO_4$, $Na_2S_2O_3$, $SnCl_2$ etc.
3. If an element is in its intermediate oxidation state in a compound, it can function both as an oxidizing agent as well as reducing agent, e.g. H_2O_2, H_2SO_3, HNO_2, SO_2 etc.
4. If highly electronegative element is in its higher oxidation state in a compound, that compound can function as a powerful oxidizing agent, e.g. $KClO_4$, $KClO_3$, KIO_3 etc.
5. If an electronegative element is in its lowest possible oxidation state in a compound or in free state, it can function as a powerful reducing agent, e.g. I^-, Br^-, N^{3-} etc.

Redox Reaction

A reaction in which oxidation and reduction simultaneously take place is called a redox reaction

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

$$Zn(s) + Cu^{+2}(aq) \longrightarrow Zn^{+2}(aq) + Cu$$

Reduction

Oxidation

In the above redox reaction Zn is acting as reducing agent and Cu^{+2} as oxidising agent.

Types of Redox Reaction

Intermolecular redox Reaction

It occurs between the compound or reactants.

$$\overset{+2}{Cu}SO_4 + \overset{0}{Zn} \longrightarrow \overset{+2}{Zn}SO_4 + \overset{0}{Cu}$$

Reduction

Oxidation

Intramolecular redox Reaction

It occurs within the compound in which one component act as reactant and other act as oxidant.

$$(\overset{-3}{N}H_4)_2\overset{+6}{Cr_2}O_7 \xrightarrow{\Delta} \overset{0}{N_2} + \overset{+3}{Cr_2}O_3 + H_2O + \text{Heat}$$

Reducation

Oxidation

Combination Reaction

Molecular species are formed by combination of elements present in their standard state.

$$\overset{0}{C} + \overset{0}{O_2} \longrightarrow \overset{+4}{C}\overset{-2}{O_2}$$

Redox Thermal Decomposition

In which molecular species dissociate into smaller species and oxidation state of element changes during thermal decomposition.

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$$

Displacement Reaction

(a) Metal Displacement Reaction – Metal Cation is displaced by more electro positive metal form its Salt Solution.

$$\overset{+2}{Cu}SO_4 + \overset{0}{Zn} \longrightarrow \overset{+2}{Zn}SO_4 + \overset{0}{Cu}$$

(b) Non Metal Displacement Reaction – Non metal ion is displaced by metal or more electronegative non metal from its solution.

$$\overset{0}{Cl_2} + K\overset{-1}{I} \longrightarrow K\overset{-1}{Cl} + \overset{0}{I_2}$$

Disproportionation Reaction

In which an element from same oxidation state is converted to different oxidation states.

$$(X = Cl, Br, I) \quad \overset{0}{X_2} + NaOH \longrightarrow Na\overset{-1}{X} + Na\overset{+1}{O}X + H_2O$$

NOTE : F does not undergo disproportionation as it is strong O.A.

Comproportionation Reaction

In which an element from different oxidation state is converted to same oxidation state.

$$Nax + NaOX \xrightarrow{H^+} X_2$$

Balancing of Redox Reactions

Balancing of Half Reactions. **(Short method)**

(1) **Balance Atom other then O and H.**

(2) **Balancing of O atom using desired medium.**

Acidic - Add required no. of H_2O molecule on the site deficient with oxygen and twice the number of H^+ ion on opposite side.

Basic - Add required no. of H_2O molecule on the site rich with O and twice the number of OH^- ion on the opposite side.

(3) **Balancing of H atom using H^+ ion :** Add required number of H^+ ion on the side deficient with hydrogen.

(4) **Balancing of Charge :** charge is balanced by electron. Add required number of electron on the site deficient with charge.

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Oxidation number method

To balance the redox reactions by oxidation number method we are to follow the procedure as per the given sequences.

1. Write the equation representing a chemical change and complete it if it is incomplete.
2. By knowing O.Ns of elements, identify which atom (s) is (are) undergoing oxidation and reduction. Write separate equations for oxidation and reduction.
3. Balance the atoms undergoing oxidation and reduction.
4. Add appropriate number of electrons on the right of oxidation reaction and on the left of reduction reaction. Make sure that the net charge on both the sides of the equations is same.
5. Multiply the oxidation and reduction equations by suitable numbers to make the number of electron released in oxidation equal to the number of electrons accepted in reduction reactions.
6. Transfer the coefficient of the oxidizing and reducing agents and their product to the main equation.
7. Balance all atoms other than hydrogen and oxygen. Also balance the charge.
8. Balance H and O by addition of suitable number of H_2O to appropriate side.

Ion electron method

Balancing of redox reaction can be carried out in three medium viz, acidic, alkaline and neutral. To balance a redox reaction by ion electron method, following sequence will be followed.

1. Write the equation representing chemical change and complete it, if it is incomplete.
2. Divide the complete equation into two half equations, one representing oxidation and the other reduction.
3. Balance each half equation separately as below:
   (i) Balance atoms undergoing oxidation or reduction.
   (ii) Add suitable number of electrons to suitable side on the basis of difference in O.S.
   (iii) Balance all other atoms except H and O.
   (iv) Balance the total charge by adding H^+ in acidic medium and OH^- in alkaline medium.
   (v) Add suitable number of H_2O to the side deficient in H and O.
4. Multiply the two half reactions by suitable integers so that total number of electrons in both equations become equal.
5. Add the two balanced half reactions and remove the common terms from the both sides.

Normality

It is define as no. of equivalent of a solute present in one litre of solution

$$N = \frac{\text{Equivalent of solute}}{\text{Volume of solution in litre}} = \frac{\text{Weight of solute}}{\text{Equivalent weight of solute} \times \text{V in litre}}$$

Normality = n-factor × molarity of solution

Law of Equivalence

The law states that one equivalent of an element combine with one equivalent of the other. In a chemical reaction, equivalents and milli equivalents of reactants react in equal amount to give same number of equivalents or milliequivalents of products separately.

Accordingly

(i) $aA + bB \rightarrow mM + nN$; meq of A = meq of B = meq of M = meq of N

(ii) In a compound M_xN_y; meq of M_xN_y = meq of M = meq of N

(iii) In general we can write for the two reacting substances X and Y as, $\frac{\text{wt. of X}}{\text{wt. of Y}} = \frac{\text{Equiv wt. of X}}{\text{Equiv wt. of Y}}$

(iv) No. of equivalents = w/E $= \frac{w}{M/n-\text{factor}} = \frac{w}{M} \times$ n-factor

Some Common Oxidising and Reducing Agents

Oxidants and Reductants

(a) List of common oxidants :

1. O_2 2. O_3 3. H_2O_2 4. H_2SO_4 5. HNO_3 6. $HClO_4$ 7. $KClO_3$
8. $(K_2Cr_2O_7/H_2SO_4)$ 9. $(KMnO_4/H_2SO_4)$ 10. $(KMnO_4/KOH)$ 11. F_2, Cl_2, Br_2

(b) List of Common Reductants :

1. H_2 2. HI 3. H_2S 4. $LiAlH_4$ 5. $NaBH_4$ 6. SO_2 7. C
8. O_3 9. H_2O_2 10. (Sn/HCl) 11. (Na/C_2H_5OH) 12. Metallic Salts (Ous) like $SnCl_2$, $FeSO_4$
13. Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$

(c) Substance acting as oxidant as well as Reductant

HNO_2, O_3, H_2O_2, SO_2 etc.

Super Note : Equivalent weight of $KMnO_4$ (Mol.wt. 158) in acidic, alkaline & neutral media is respectively : 31.6, 158, 52.6

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be carried out in three
eutral. To balance a redox
llowing sequence will be

chemical change and

two half equations, one
reduction.
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7. $KClO_3$

7. C

6, 158, 52.6

Important Oxidation & Reduction Part

(a) Oxidation Part (Half reaction)

1. Fe^{2+} - Fe^{3+}
2. H_2O_2 - O_2 (basic med.)
3. Zn - Zn^{2+}
4. SO_3^{2-} - SO_4^{2-}
5. Cl^- - Cl_2 (Or $X^- \rightarrow X_2$)
6. S^{2-} - S
7. $C_2O_4^{2-}$ - CO_2
8. $S_2O_3^{2-}$ - $S_4O_6^{2-}$
9. I_2 - IO_3^-
10. AsO_3^{3-} - AsO_4^{3-}
11. Sn^{2+} - Sn^{4+}
12. Cu^+ - Cu^{+2}
13. SO_2 - SO_4^{2-}

(b) Reduction Part (Half Reaction)

1. Fe^{3+} - Fe^{2+}
2. H_2O_2 - H_2O
3. CrO_4^{2-} - Cr^{3+}
4. SO_4^{2-} - SO_2
5. OCl - Cl
6. $[Fe(CN)_6]^{3-}$ - $[Fe(CN)_6]^{4-}$
7. I_2 - I (Or $X_2 \rightarrow X^-$)
8. ClO_3 - Cl
9. VO^{2+} - V_2O_3
10. NO_3^- - NO_2 (In Conc.HNO_3)
11. NO_3^- - NO (In dil. HNO_3)

$KMnO_4$
- Basic — K_2MnO_4; n = 1
- Acidic — MnO ; n = 5
- Neutral — MnO_2 ; n = 3

BANI 53

$K_2Cr_2O_7 \xrightarrow{\text{Acidic}} Cr^{3+}$

In basic medium $K_2Cr_2O_7$ will not act as OA because it is unstable in basic medium and converts into cromate ion

Equivalent Weight

Number of parts by mass of an element which reacts or displaces from a compound. 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of that element

$$\text{Equivalent weight (E)} = \frac{\text{Atomic or molecualr weight}}{\text{n - factor}}$$

$$\text{No. of equivalents of solute} = \frac{\text{Wt}}{\text{Eq. wt.}} = \frac{\text{W}}{\text{E}} = \frac{\text{W}}{\text{M / n}}$$

No. of equivalents of solute = No. of moles of solute × n-factor

- Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.
- The equivalent mass of substance may have different values under different conditions.
- There in no hard and fast rule that equivalent weight will be always less than the molecular mass.

Calculation of 'n' Factor (for JEE)

(A) For Acid-Base Reactions/Neutralization reactions

The number of H^+ ion(s) furnished per molecule of the acid is its n-factor also called basicity. Similarly the number of OH^- ion(s) furnished by the base per molecule is its n-factor, also called acidity.

$\underset{(n=1)}{HCl} \longrightarrow H^+ + Cl^-$ $\quad$ $\underset{(n=1)}{H_2SO_4} \longrightarrow H^+ + HSO_4^-$ $\quad$ $\underset{(n=2)}{H_2SO_4} \longrightarrow 2H^+ + SO_4^{2-}$

$\underset{(n=1)}{NaOH} \longrightarrow Na^+ + OH^-$ $\quad$ $\underset{(n=3)}{Al(OH)_3} \longrightarrow Al^{3+} + 3OH^-$ $\quad$ $\underset{(n=1)}{Ba(OH)_2} \longrightarrow [Ba(OH)]^+ + OH^-$

(B) For Redox Reactions

(i) When only one atom undergoing either reduction or oxidation then we consider the change in oxidation state of atom undergoing oxidation or reduction change per molecule as the n-factor of the species.

$$\underset{n=5}{\overset{+7}{MnO_4^-}} \xrightarrow{H^+} \overset{+2}{Mn^{2+}} \quad \text{n-factor} = |(+2) \times 1 - (+7) \times 1| = 5$$

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(ii) Salts which react in such a way that only one atom undergoes change in oxidation state but goes in two products with different oxidation state as a result of either only oxidation or only reduction.

$$3\overset{+7}{Mn}O_4^- \longrightarrow 2\overset{+2}{Mn}^{2+} + \overset{+6}{Mn}^{+6}$$

total decrease in oxidation state of Mn.

$= |[2 \times (+2) - 2 \times (+7)]| + |[1 \times (+6) - 1 \times (+7)]|$

$= |4 - 14| + |6 - 7| = 11$

So, n-factor = 11/3

(iii) Salts which react in such a way that only one atom undergoes change in oxidation state in two product, in one product with changed oxidation state and in other product with same oxidation state as that of reactant.

In such case also one cannot calculate the n-factor without knowing the balanced chemical equation because one must know how much of atom has changed its oxidation state.

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

"n" factor = net exchange of electron / Stoichiometry coefficient of compound

(iv) Salts which react in such a way that two or more atoms in the salt undergoes change in oxidation states as a result of either oxidation or reduction.

calculate the n-factor of the salt as the total increase or decrease in oxidation state per mole of the salt

$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2$

Total change in oxidation state

$= |1 \times (+2) - 1 \times (+3)| + |2 \times (+3) - 2 \times (+4)| = 1 + 2 = 3$

So, n-factor of FeC_2O_4 is 3

(v) Salts which react in such a way that two atoms undergoing change in oxidation state but one undergoing oxidation and other reduction reaction. In such a case one has to calculate the change in oxidation state of either the atom being oxidized or the atom being reduced.

For example.

$$\overset{-3\times2}{(NH_4)_2}\overset{+6\times2}{Cr_2O_7} \longrightarrow \overset{0\times2}{N_2} + \overset{+3\times2}{Cr_2O_3} + 4H_2O$$

n-factor of $(NH_4)_2Cr_2O_7$ considering oxidation $= |(-3) \times 2 - (0) \times 2| = 6$

n-factor of $(NH_4)_2Cr_2O_7$ considering reduction $= |(+6) \times 2 - (+3) \times 2| = 6$

(C) **Species which undergoes disproportionation reaction:** Those reaction in which oxidant and reductant are the same species or the same element from the species is getting oxidized as well as reduced.

n-factor = $(n_1 \times n_2)/(n_1 + n_2)$

n_1 = No. of electrons in oxidation, n_2 = No. of electron in oxidation

(D) **Precipitation/Double Decomposition Reactions:**

In such reaction, there is no change in oxidation state of any atom. The n-factor of the salt can be calculated by multiplying the oxidation state of the cation/anion by total no. of atoms per molecule of the salt. For example

$$\underset{n=2}{BaCl_2} + \underset{n=2}{Na_2SO_4} \longrightarrow BaSO_4 \downarrow + 2NaCl$$

for $BaCl_2$

n-factor = Oxidation state of Ba atom in $BaCl_2$ × number of Ba atoms in 1 molecule of $BaCl_2$

$= (+2) \times 1 = 2$

for Na_2SO_4

n-factor = Oxidation state of Na × number of Na-atoms in 1 molecule of Na_2SO_4

$= (+1) \times 2 = 2$

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Chapter – 8 Solid State

The solids are the substances which have definite volume and definite shape. In terms of kinetic molecular model, solids have regular order of their constituent particles (atoms, molecules or ions).

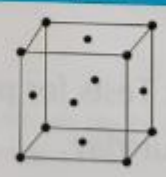
Distinction between Crystalline and Amorphous Solids

Crystalline	Amorphous
These solids have definite characteristic shape	These solids have irregular shape.
Definite melting point & heat of fusion	Indefinite melting point & heat of fusion.
Cleavage surfaces are smooth	Cleavage surfaces are irregular.
Anisotropic in nature	Isotropic in nature.
Long range order.	Short range order.
Ex. : NaCl, Quartz, Metal, Diamond etc.	Ex. Glass, Quartz Glass, Rubber, Plastics etc.

Classification of Crystalline Solids

Types of Solid	Constituents	Bonding	Examples	Physical Nature	M.P.	B.P.	Electrical Conductivity
Ionic	Positive and negative ions network systematically arranged	Coulombic (Electrostatic force)	NaCl, KCl, CaO, MgO, LiF, ZnS, $BaSO_4$ and K_2SO_4, CaF_2 etc.	Hard but brittle	High	High	Insulator in solid state but conductor (in molten state and in aqueous solution)
Covalent	Atoms connected in covalent bonds	Electron sharing	SiO_2 (Quartz), SiC, C (diamond), C(graphite) etc.	Hard Hard Soft	Very high	Very high	Insulator except graphite
Molecular	Polar or non-polar molecules	(i) Molecular interactions (intermolecular forces) (ii) Hydrogen bonding	I_2, S_8, P_4, CO_2, CH_4, CCl_4 etc.	Soft	Low	Low	Insulator
			Starch, sucrose, dry ice or drycold (solid CO_2)	Soft	Low	Low	Insulator
			H_2O (ice) etc.	Hard			
Metallic	Cations in a sea of delocalised electrons	Metallic	Sodium, Au, Cu, Fe, Ag, magnesium, metals and alloys	Ductile malleable	High	High	Conductor All states
Atomic	Atoms	London dispersion force	Noble gases	Soft	Very low	Very low	Poor thermal and electrical conductors

Space Lattice/Crystalline Lattice/3–D Lattice

	Contents	SCC	BCC	FCC/CCP	HCP
1.	Geometry				
2.	No. of atoms/ UC	1	2	4	6
3.	Coordination No.	6	8	12	12
4.	Example	Mn	IA; Group V & Cr; Ba, Fe	Ca, Sr, Al, Group VIII Co, Ni, Cu All inert gases except He	Remaining d – block elements.Be & Mg

Contribution of different Lattice point in one Cubical unit cell

(i) Contribution from one corner lattice point = 1/8

(ii) Contribution from one face centered lattice point = 1/2

(iii) Contribution from edge centered lattice point = 1/4

(iv) Contribution from body centered lattice point = 1

Elements of Symmetry

The total no. of planes, axes and centre of symmetries possessed by a crystal is termed as its elements of symmetry. A cubical crystal possesses a total of 23 elements of symmetry.

- Planes of symmetry = 3 + 6 = 9
- Axis of symmetry = 3 + 4 + 6 = 13
- Centre of symmetry = 1
- Total number of symmetry elements = 23

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Bravais Lattice

On basis of geometrical consideration, main seven crystal system are present also known as seven primitive unit cells, which differ three-dimensionally in axial edge length (a, b and c) and axial angles (α, β, γ).

Crystal System	Features	Unit cell found	Examples
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	SCC, BCC, FCC	NaCl, ZnS, Fe, Al, Cu, C (diamond), CsCl, CaF_2, Na_2O, KCl, Pb, Alum.
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	SCC, BCC	Sn (white tin), SnO_2, TiO_2, ZnO_2, $NiSO_4$, Urea.
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	SCC, BCC, FCC, ECC	Rhombic sulphur, $BaSO_4$, KNO_3, $PbCO_3$, $CaCO_3$ (aragonite)
Rhombohedral or Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	SCC	$CaCO_3$ (Calcite), HgS (Cinnabar), $NaNO_3$, ICL
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	SCC	Graphite, ZnO, CdS, Mg, Pb_2I, SiC
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90°$; $\beta \neq 120°, \neq 90°, \neq 60°$	SCC, ECC	Monoclinic sulphur, $PbCr_2O$, $Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	SCC	$K_2Cr_2O_7$, $CuSO_4 \bullet 5H_2O$, H_3BO_3

In 3-D 14 different types of unit cell are found and these are also known as 14 Bravais lattice.

Co-ordination Number

The number of nearest neighbouring particles around a specific particle in a given crystalline substance is called as co-ordination number of that crystalline substance.

Packing Efficiency

"Packing efficiency is defined as the ratio of volume occupied by the atoms to the total volume of the crystalline substance"

$$P.E = \frac{Z \times \text{Volume of sphere}}{\text{Volume of the unit cell}}$$

Z = number of atoms per unit cell

Volume of cube = a^3

Volume of sphere = $4/3\ \pi r^3$

Density of the Crystal (d or r)

$$\rho = \frac{Z \times M}{a^3 \times N_0}$$

Z = Number of particles per unit cell

M = Atomic mass or molecular mass

N_0 = Avogadro number

a = Edge length of the unit cell

Unit Cell

- **Primitive Unit Cell**
  Same type of particles are present at corners only
- **Centered Unit Cell**
  Same type of particles are present besides corners
  - Face centered (FC)
  - Body centered (BC)
  - End centered (EC)

- In End centered same type of particles are present at corners and any two opposite face centres.
- End centered type of Bravais lattice is present only in orthorhombic and monoclinic type of unit cell.

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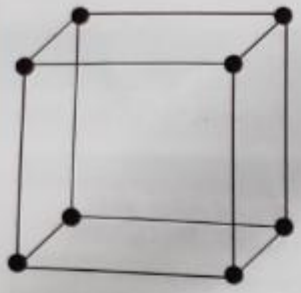
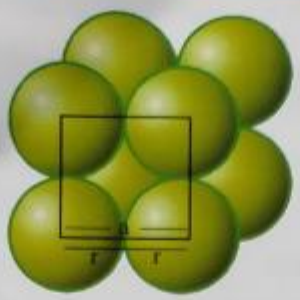
Simple/Primitive/Basic Cubic Unit Cell (SCC)





(i) Relation between 'a' and 'R'

corner atoms are touching each other so, $a = 2R$.

(ii) Effective no. of atom (Z) (per unit cell).

$Z = 8\,[\text{corner}] \times 1/8 = 1$ atom.

(iii) Packing Efficiency :

$$\text{P.E.} = \frac{1 \times \frac{4}{3}\pi R^3}{(2R)^3} = \frac{\pi}{6} = 52.33\%.$$

(iv) Co-ordination number : CN = 6

Body Centered Cubic Unit Cell (BCC)

(I) Relation between 'a' and 'R' :

Sphere are not touching along edge. They touching along the body diagonal. So, $\sqrt{3}\,a = 4\,R$.

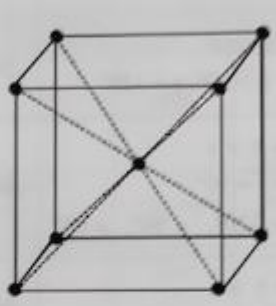
(ii) Effective No. of atom (Z) (per unit cell).

$8 \times [\text{corner}] \times 1/8 + 1 = 2$

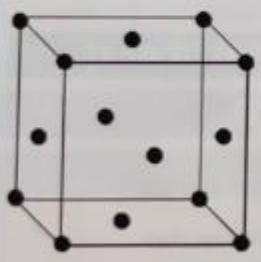
(iii) Packing Efficiency

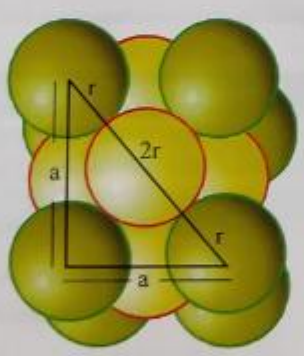
$$\text{P.E.} = \frac{2 \times \frac{4}{3}\pi R^3}{\left(\frac{4R}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\pi}{8} = 68\%.$$

(iv) Co-ordination No. (CN) = 8.



Face Centred Cubic Unit Cell (FCC)





(i) Relation between 'a' and 'R' : $a \neq 2R$

$\sqrt{2}a = 4R$ (sphere are touching along the face diagonal)

(ii) Effective No. of atom (Z) (per unit cell).

$$Z = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$$

(iii) Packing Efficiency :

$$\text{P.E.} = \frac{4 \times \frac{4}{3}\pi R^3}{4 \times 4 \times 4\,R^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74(\ 74\%\ )$$

(iv) Co-ordination Number : CN = 12

Close Packing in Crystalline Solids

Close packing in Two Dimensions

Square Close Packing

In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form square. In this arrangement each sphere is in contact with four spheres.

Hexagonal Close Packing

In which the spheres in every second row are seated in the depression between the spheres of first row. The spheres in the third row are vertically aligned with spheres in first row. The similar pattern is noticed throughout the crystal structure. In this arrangement each sphere is in contact with six other spheres.

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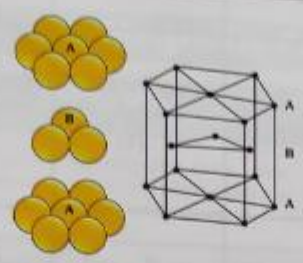
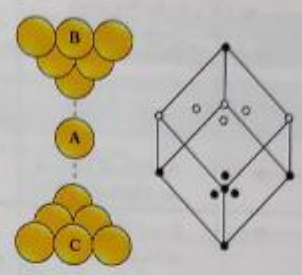
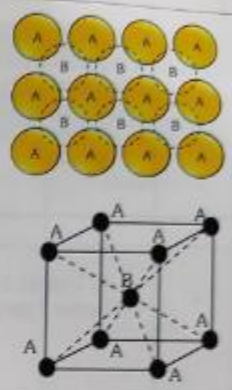
Close Packing in 3D

Property	hcp	ccp	bcc
Arrangement of packing	Close packed	Close packed	Not close packed
Type of packing	AB AB A...	ABC ABC A...	AB AB A...
Available space occupied	74%	74%	68%
Coordination number	12	12	8
Malleability and ductility	Less malleable, hard, brittle	Malleable and ductile	
3D Structure			
Example	Be, Mg, Zn, Cd, Sc, Y, Ti, Zr, Tc, Ru.	Cu, Ag, Au, Ni, Pt, Pd, Co, Rh, Ca, Sr.	Li, Na, K, Rb, Ba, Cs, V, Nb, Cr, Mo, Fe.

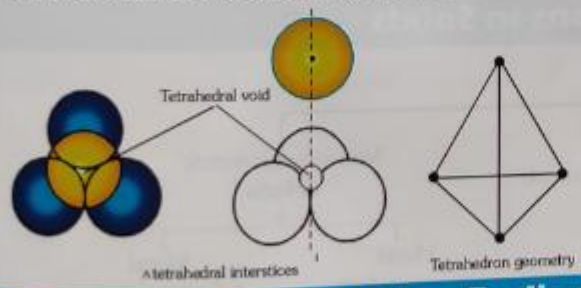
Interstitial Sites in Close Packing

Tetrahedral void

The number of tetrahedral voids is double the number of spheres in the crystal structure.

$$\frac{r}{R} = 0.225$$

r is the radius of the tetrahedral void
R is the radius of spheres forming tetrahedral void

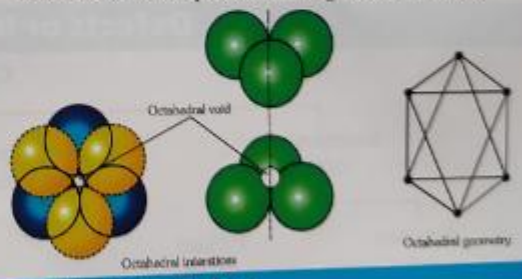


Octahedral void

The number of octahedral voids is equal to the number of spheres.

$$\frac{r}{R} = 0.414$$

r is the radius of the octahedral void
R is the radius of spheres forming octahedral void



Limiting Radius Ratio of void to Particles

The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular ___0.225___ Tetrahedral ___0.414___ Octahedral ___0.732___ Cubic

Limiting Radius Ratio	Coordination No. of cation	Geometry of Voids	Void found in	Location of Void	No. of Void	Example
$0.155 \le r/R < 0.225$	3	Plane Trigonal	-	-	-	Boron oxide (B_2O_3)
$0.225 \le r/R < 0.414$	4	Tetrahedral	FCC, HCP	On body diagonal at $\sqrt{3}\,a/4$ distance from corner of the unit cell	2	ZnS, SiO_2, Na_2O, CaF_2
$0.414 \le r/R < 0.732$	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

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Ionic Crystals

S.No.	Type of Ionic Crystal	Geometry	Coordination Number	No. of formula per U.C.	Examples
1.	NaCl (1:1) (Rock salt Type)	CCP → Cl^- : Every element of 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_4X.
2.	CsCl Type (1 : 1)	BCC Type → Cl^- : At Every Corner; BCC Type → Cs^+ : At Body Centre	8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	• Halides of 'Cs' • TlCl, TlBr, CaS
3.	ZnS Type (1:1) (Zinc Blende Type) (Sphalerite)	CCP → S^{-2} : Every element of CCP; CCP → Zn^{+2} : At 50% of THV or At Alternate THV	4 : 4	$4Zn^{+2} + 8F^{-1}$ $4CaF_2$ (4)	Bes, BeO, CaO, AgI, CuCl, CuBr, CuI
4.	CaF_2 Type (1:2) (Fluorite Type)	CCP → Ca^{+2} : Every element of CCP; CCP → F^- : At every THV	$4Ca^{+2}$ → 8; $8F^-$ → 4	$4Ca^{+2} + 8F^{-1}$ $4CaF_2$ (4)	$BaCl_2$, BaF_2, $SrCl_2$, SrF_2, $CaCl_2$, CaF_2
5.	Na_2O Type (2:1) (Antifluorite Type)	CCP → Na^+ : At every THV; CCP → O^{-2} : Every element of CCP	$8Na^+$ → 4; $4O^{-2}$ → 8	$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S, Na_2O, Na_2S, K_2O, K_2S
6.	ZnS Type (1:1) (Wurtzite) another geometry of ZnS	HCP → 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

Defects or Imperfections In Solids

Crystal Defects

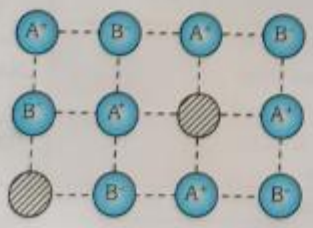
- Stoichiometric defects
  - Schottky defect
  - Frenkel defect
- Impurity defects (some external impurity is mixed)
- Non stoichiometric defects
  - Metal excess defect
  - Metal deficiency defect

Stoichiometric Defect

In these defects stoichiometric ratio of constituent ions is not disturbed.

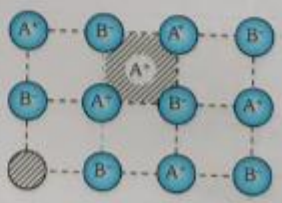
(a) **Schottky Defect :** When equal number of cation and anion are missing from its normal site Schottky defect is created. This defect causes decrease in density of crystal.

NaCl, KCl, CsCl and KBr etc.,



In AgBr both Schottky and Frenkel defects occur simultaneously.

(b) **Frenkel Defect :** Found mostly in ionic solids. The ion leaves its position in the lattice and occupies an interstitial void. This defect does not affect density of crystal. This is majorly shown by crystals having lessC.N. (e.g., ZnS). ZnS, AgCl and AgI



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Non Stoichiometric Defect

In these defects stoicheometric ratio of constituent ions is changed.

(a) **Metal excess defect :** Extra cations occupying voids. Neutrality is maintained by additional electrons occupying nearby sites. It is possible by some anion vacancies; also charge is balanced by electrons occupying these vacancies (F–centres). These electrons are responsible for imparting colour (Farbe = colour).

Crystals with either type of metal excess defect possess free electrons and if they migrate they conduct electric current. But the amount of current conducted is very small and so these material resulting from interstitial cation are called n–type semiconductors.

Further free electrons may be excited to higher energy levels causing colour. ZnO is yellow when hot and white when cold.

(b) **Metal deficiency :** defect occurs when the metal shows variable valency. It is due to missing of a cation and the presence of the cation having higher charge (e.g +2 instead of +1) in adjacent site. FeO, FeS etc.

Magnetic Properties of Solids

Properties	Description	Alignment of Magnetic Dipoles	Examples	Applications
Diamagnetic	Feebly repelled by the magnetic fields. Non-metallic elements (excepts O_2, S) inert gases and species with paired electrons are diamagnetic	All paired electrons ↑↓ ↑↓ ↑↓	TiO_2, V_2O_5, NaCl, C_6H_6 (benzene)	Insulator
Paramagnetic	Attracted by the magnetic field due to the presence of permanent magnetic dipoles (unpaired electrons). In magnetic field, these tend to orient themselves parallel to the direction of the field and thus, produce magnetism in the substances.	↑↓ ↑ ↑ At least one unpaired electron	O_2, Cu^{2+}, Fe^{3+}, TiO, Ti_2O_3, VO, VO_2 CuO	Electronic appliances
Ferromagnetic	Permanent magnetism even in the absence of magnetic field. Above a temperature called **Curie** temperature, there is no ferromagnetism	Dipoles are aligned in the same direction ↑ ↑ ↑ ↑ ↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio and video tapes
Antiferromagnetic	This arises when the dipole alignment is zero due to equal and opposite alignment.	↑ ↓ ↑ ↓ ↑ ↓	MnO, MnO_2, Mn_2O, FeO, Fe_2O_3; NiO, Cr_2O_3, CoO, Co_2O_3	–
Ferrimagnetic	This arises when there is net dipole moment	↑ ↓ ↓ ↓ ↑ ↓	Fe_3O_4, ferrites	–

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Concentration Terms

Temperature Independent

Mass Related concentration terms

- % by Mass (w/M) $= \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 100$
- mole fraction $(X) = \frac{n_A}{n_A + n_B}$ or $\frac{n_B}{n_A + n_B}$
- Molality $(m) = \frac{\text{No. of moles of solute}}{\text{Amount of solvent (g)}} \times 1000$
- PPM(by mass) $= \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 10^6$

Temperature dependent

Volume Related concentration terms

- % by volume $(v/V) = \frac{\text{Volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$
- %mass by volume (w/V) $= \frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 100$
- Molarity(M) $= \frac{\text{No. of Moles of solute}}{\text{Volume of solution (L)}}$
- Normality (N) $= \frac{\text{No. of Gram Equivalents of solute}}{\text{Volume of solution (L)}}$

Relation Between Concentration Terms

$\% w/V = (\%w/W) \times d$

$M = \frac{10 \times \%w/V}{M.wt_{solute}} = \frac{(\%w/W) \times d \times 10}{M.wt_{solute}}$

$m = \frac{1000 \times M}{1000 \times d - M \times M.wt_{solute}}$

$m = \frac{X_{solute}}{X_{solvent}} \times \frac{1000}{M.wt_{solvent}}$

- **Molarity on Dilution**

  n_{solute} = constant

  V increase, M decrease

  $M_1V_1 = M_2V_2$

- Normality = Molarity × n-factor

- **Molarity on mixing**

  $M = \sum_{i=1}^{x} \frac{M_iV_i}{V_i}$

- This is valid when substance is same or one ion is common.

Vapour Pressure

The pressure exerted by the vapour (molecules in the vapour phase) over the surface of the liquid at the equilibrium in a closed container at given temperature is called the vapour pressure of the liquid. In case of water it is also known as aqueous tension.

Pure Liquid Vapour Pressure = P°

- If $P^\circ \neq 0 \rightarrow$ Volatile Substance
- If $P^\circ = 0 \rightarrow$ Non–volatile Substance

Factors affecting Vapour Pressure

Temperature

[Vapour pressure $\propto$ Temperature]

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called its **boiling point (T_b).**

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Nature of liquid

Vapour pressure of liquid $\propto \frac{1}{\text{The strength of intermolecular forces acting between molecules}}$

Vapour pressure $\propto \frac{\text{Intramolecular H-bonding}}{\text{Intermolecular H-bonding}}$

Heat of vaporization $\propto \frac{\text{Intramolecular H-bonding}}{\text{Intermolecular H-bonding}}$

At vapour pressure

Rate of vaporization = Rate of condensation

Raoult's Law

Vapour Pressure of a Solution Containing Non Volatile Solute

Acccording to Raoult's law, the partial pressure of any volatile constituent in a soluion at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

$$P_A \propto X_A \qquad P_A = P_A^\circ X_A, \qquad P_A < P_A^\circ$$

$$P_{total} = P_A^\circ X_A = \frac{n_A}{n_A + n_B} \times P_A^\circ (\because P_B^\circ = 0)$$

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Relative lowering in vapour pressure $(RLVP) = \frac{P_A^o - P_S}{P_A^o} = X_B$

Derived from RLVP $\frac{P_A^o - P_S}{P_S} = \frac{n_B}{n_A}$

Lowering of vapour pressure $= \Delta P = P_A^o - P_S$

Super Note :
On adding non volatile solute vapour pressure decreases and boiling point increases.

Vapour Pressure of a Solution Containing Two Volatile Liquids

Mole fraction of A in liquid, $X_A = \frac{n_A}{n_A + n_B}$, $P_A = P_A^o X_A$

Raoult's Law: (Valid only in liquid state)

Assuming $P_A^o > P_B^o$

$$P_S = P_A^o X_A + P_B^o X_B$$

$$P_S = P_A^o + (P_B^o - P_A^o) X_B$$

$$P_S = P_B^o + (P_A^o - P_B^o) X_A$$

$$\boxed{P_A^o > P_S > P_B^o}$$

Mole fraction of B in liquid, $X_B = \frac{n_B}{n_A + n_B}$, $P_B = P_B^o X_B$

Mole fraction of A in Vapour phase $Y_A = \frac{P_A^o X_A}{P_S}$

Mole fraction of B in Vapour phase $Y_B = \frac{P_B^o X_B}{P_S}$

Super Note :

$$\frac{Y_A}{Y_B} = \frac{P_A^o X_A}{P_B^o X_B} = \frac{P_A^o n_A}{P_B^o n_B}$$

Valid for vapour phase solution

Types of Solution

Ideal Solution

Conditions for Forming Ideal Solution

Two liquids on mixing form an ideal solution only when

- Both have similar structures and polarity so that they have similar molecular environment.
- Both have similar molecular sizes.
- Both have identical intermolecular forces.

Characteristics of Ideal Solution :
Mixing of two substances results in an ideal solution only when:

- They obey Raoult's Law
- $\Delta H_{mixing} = 0 \Rightarrow$ that is no heat is absorbed or released during dissolution
- $\Delta V_{mixing} = 0 \Rightarrow$ that is the total volume of the solution is equal to the sum of the volume of the pure liquids mixed to form the solution.

Examples

benzene + toluene

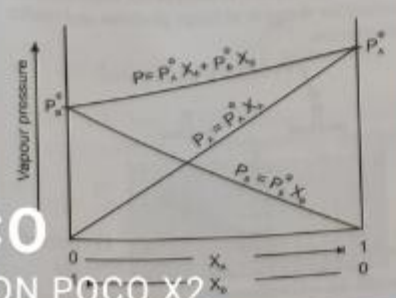
chlorobenzene + bromobenzene

ethyl bromde + ethyl iodide

n-butyl chloride + n-butyl bromide

ethyl alcohol + methyl alcohol

Graphical Representation



Non-Ideal Solution

Non ideal solutions showing +ve deviation

Condition for forming non-ideal solution showing +ve deviation from Raoult's law.
Two liquids A and B on mixing form this type of solution when

- A – B attractive force should be weaker than A – A and B – B attractive forces.
- 'A' and 'B' have different shape, size and character.
- 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

Characteristic of non-ideal solution showing +ve deviation

- Do not obey Raoult's law
- $\Delta H_{mix} > 0$. (endothermic dissolution heat is absorbed.)
- $\Delta V_{mix} > 0$. (Volume is increased after dissolution)
- $P_A > P_A^o X_A; P_B > P_B^o X_B$,
  $P = P_A + P_B > P_A^o X_A + P_B^o X_B$

Examples

acetone + ethanol

water + methanol

CCl_4 + toluene

acetone + benzene

cyclohexane + ethanol

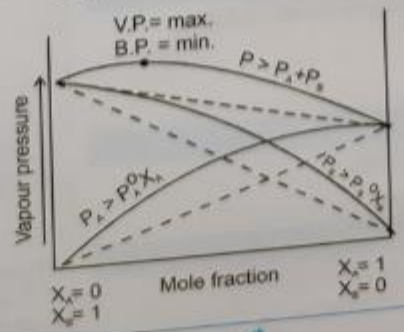
acetone + CS_2

water + ethanol

$CCl_4 + CHCl_3$

$CCl_4 + CH_3OH$

Graphical Representation



Non ideal solutions showing –ve deviation.

Condition for forming non-ideal solution showing –ve deviation from Raoult's law.
Two liquids A and B on mixing form this type of solution when

- A—B attractive force should be greater than A—A and B—B attractive forces.
- 'A' and 'B' have different shape, size and character
- Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

Characteristic of non-ideal solution showing +ve deviation

- Do not obey Raoult's law.
- $\Delta H_{mix} < 0$. (Exothermic dissolution; heat is evolved.)
- $\Delta V_{mix} < 0$. (Volume is decreased during dissoluton)
- $P_A < P_A^o X_A; P_B < P_B^o X_B$,
  $P = P_A + P_B < P_A^o X_A + P_B^o X_B$

Examples

acetone + aniline; $CH_3OH + CH_3COOH$

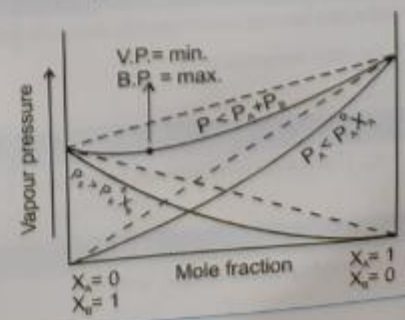
chloroform + diethyl ether

acetic acid + pyridine

chloroform + benzene, $H_2O + HNO_3$

water + HCl

Graphical Representation



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Azeotropes

The non-ideal solution showing large deviations from Raoult's law can not be purified by distillation. A solution at certain composition which continues to boil at constant temperature without change in the composition of the solution and its vapour is called an AZEOTROPE or constant boiling mixture.

Maximum Boiling Azeotropes

Shows large negative deviation from Raoult's Law

Also known as Minimum vapour pressure Azeotropes

Minimum Boiling Azeotropes

Shows large positive deviation from Raoult's Law

Also known as Maximum vapour pressure Azeotropes

Components of mixture are separated by azeotropic distillation.

Colligative Properties

The property of a solution which depends upon the fraction of solute particles and solvent particles and not upon the chemical nature of solute is called a colligative property. Greater the no. of particles of solute in solution, greater is the extent to which colligative property is affected.

Factors that affect the Colligative Property

The no. of solute particles in solution. To be more accurate, the colligative property depends upon the fraction of solute and solvent particles in solution.

(1) Nature of the solvent

(2) Independent of the nature of the solute

(3) Extent of association and dissociation of solute particles in solution.

1 Relative Lowering in Vapour Pressure (RLVP)

For dilute solution, $(n_B << n_A)$

$$\frac{P_A^\circ - P_s}{P_A^\circ} \approx \frac{n_B}{n_A}, \quad \Delta P \propto \frac{n_B}{n_A}$$

RLVP depends upon relative number of solute particles

Ostwald–Walker Method

Loss in weight of solution containers $\propto P_s$.

Loss in weight of solvent containers $\propto (P - P_s)$

gain in weight of dehydrating agent $\propto P$.

$$\frac{P - P_s}{P_s} = \frac{\text{loss in weight of solvent}}{\text{loss in weight of solution}}$$

$$\frac{P - P_s}{P} = \frac{\text{loss in weight of solvent}}{\text{gain in weight of dehydrating agent}}$$

Weight loss → vapour pressure more → concentration decrease

Weight gain → vapour pressure less → concentration increase

2 Osmotic Pressure

Osmosis

The spontaneous flow of solvent particles from solvent side to solution side or from solution of low concentration side to solution of high concentration side through a semipermeable membrane (SPM) is known as osmosis.

Osmotic Pressure

It is defined as the pressure which must be applied to the concentrated solution in order to stop osmosis

$$\pi = CRT = \frac{n}{V}RT$$

Reverse Osmosis

If the pressure applied on the solution side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is known as reverse osmosis.

$$\pi = \text{atm.} \begin{cases} C \text{ - mol/lit} \\ R \text{ - } 0.082 \text{ lit. atm. mol}^{-1} K^{-1} \\ T \text{ - kelvin} \end{cases}$$

Super Note : Osmosis, diffusion, Boiling point, Freezing point and vapoour pressure are not colligative properties.

Addition of HgI_2 to KI (aq.) shows an increase in vapour pressure due to complex formation no. of solute particles in solution decrease.

$$2KI + HgI_2 \rightarrow K_2[HgI_4]$$

On the Basis of Osmotic pressure type of solution

Isotonic Solution

Two solutions having same osmotic pressure are consider as isotonic solution.

$\pi_1 = \pi_2$ (at same temperature)

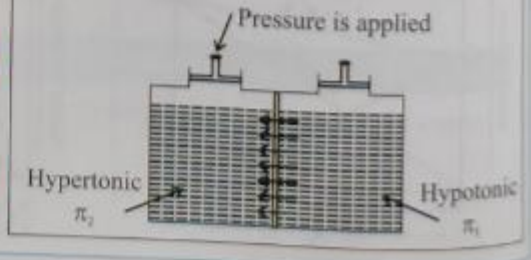
Hypertonic Solution

If $\pi_1 > \pi_2$, 1st solution is hypertonic solution w.r.t. 2nd solution

Hypotonic Solution

2nd solution is hypotonic w.r.t. 1st solution.

Osmotic pressures can be determined quite accurately, hence it is used in the determination molecular weights of large proteins and similar substances.



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3 Elevation in Boiling point (ΔT_b)

Boiling point

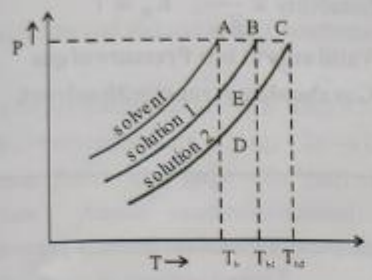
The temperature at which vapour pressure of a liquid becomes equal to the external pressure present at the surface of the liquid is called boiling point of liquid at that pressure.

$$\Delta T_b = (T_b)_{solution} - T_b^0 = m \times K_b$$

K_b = molal elevation constant or ebullioscopic constant for a solvent

$$K_b = \frac{RT_b^2 \times (M.wt)}{1000 \times \Delta H_{vapour}}, \quad K_b = \frac{RT_b^2}{1000 \times L_{vapour}}$$

Units of K_b : $\frac{\Delta T_b}{\text{molality}} = \frac{K}{\text{mol/kg}} = K\ kg\ mol^{-1}$



K_b & K_f are characteristic property of solvent

4 Depression in freezing point (ΔT_f)

Freezing point

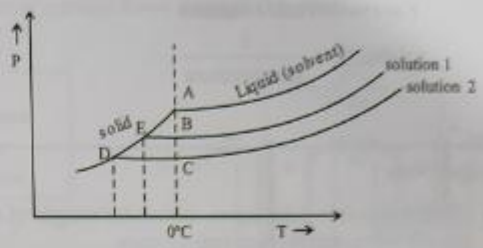
Temperature at which vapour pressure of solid becomes equal to vapour pressure of liquid is called freezing point of liquid or melting point of solid.

$$\Delta T_f = (T_f^0) - (T_f)_{solution} = m \times K_f$$

K_f = molal depression constant or cryoscopic constant for a solvent

$$K_f = \frac{RT_f^2 \times (M.wt)}{1000 \times \Delta H_{fusion}}, \quad K_f = \frac{RT_f^2}{1000 \times L_{fusion}}$$

Units of K_f : $\frac{\Delta T_f}{\text{molality}} = \frac{K}{\text{mol/kg}} = K\ kg\ mol^{-1}$



Abnormal Colligative Properties

If solute gets associated or dissociated in solution then experimentable / observed / actual value of colligative property will be different from theoretically predicted value so it is also known as **abnormal colligative property.**

For electrolytic solutes the No. of particles would be different then the No. of particles actually added, due to dissociation or association of solute.

Vant – Hoff Factor (i)

The actual extent of dissociation/association can be expressed as a correction factor known as vant Hoff factor (i).

$$i = \frac{\text{number of solute particle actually present in solution}}{\text{number of solute particle dissolve}} = \frac{\text{Observed colligative property}}{\text{normal colligative property}}$$

$$= \frac{\text{observed molality}}{\text{normal molality}} = \frac{\text{normal molecular weight of solute}}{\text{observed molecular weight of solute}}$$

Calculation of Degree of Dissociation of solute particles

	A_n	$\rightleftharpoons$	nA
No. of moles dissolved	1 mol		0
No. of moles after dissociation	$1-\alpha$		$n\alpha$

Total number of moles present in solution $= (1-\alpha) + n\alpha$

Van't Hoff factor, $i = \frac{\text{moles of solute actually present in solution}}{\text{Moles of solute dissolved}}$

$$= \frac{(1-\alpha)+n\alpha}{1} = 1 + (n-1)\alpha$$

$$i = 1 + (n-1)\alpha \text{ or } \alpha = \frac{i-1}{n-1}$$

The Van't Hoff factor for a solute can be calculated by the following modified equations:

(i) $\frac{P_A^0 - P_A}{P_A^0} = i X_B$ (ii) $\Delta T_f = iK_f m$

(iii) $\Delta T_b = iK_b m$ (iv) $\pi = iCRT$

where C = molarity of the solution.

Calculation of Degree of Association of solute particles

Let n moles of the solute, A, associate to form $(A)_n$. If α is the degree of association.

	nA	$\rightleftharpoons$	A_n
No. of moles dissolved	1 mol		0
No. of moles after dissociation	$1-\alpha$		α/n

Total number of moles present in solution $= (1-\alpha) + \alpha/n$

$$i = 1 + \left(\frac{1}{n} - 1\right) \times \alpha \quad \text{or} \quad \alpha = \frac{i-1}{\frac{1}{n}-1}$$

Super Note :
Unless otherwise mentioned, always assume $\alpha = 1$
For non-electrolytes: $i = 1$
For electrolytes; $i > 1$ (If solute particles undergo Dissociation in the solution)
$i < 1$ (If solute particles undergo Association in the solution)

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Solubility

Solubility of solid in liquid

1) **Effect of Hydration energy and Lattice energy.**
   HE > LE soluble
   HE < LE Insoluble
2) **Nature of solute and solvent.**
   (Like dissolve Like)
   Polar solute dissolve in polar solvent
   Non polar solute dissolve in Non polar solvent.
3) **Effect of Temperature (T) :**
   For endothermic reaction
   solubility $\propto$ Temperature.
   For exothermic reaction
   solubility $\propto \frac{1}{\text{Temperature}}$

Raoult's law is special case of Henry's law

Solubility of gas in liquid

1) **Like dissolve Like**
   Polar gases dissolve in polar solvent
   Non polar gases dissolve in Non polar solvent.
2) **Effect of Temperature (T) :**
   solubility of gases $\propto$ 1/Temperature.
3) **Effect of Pressure (Henry's Law)**
   $X \propto P \Rightarrow X = KP \Rightarrow X \times \frac{1}{K} = P$

   $P = K_H \times X$

   Solubility $\propto \frac{1}{K_H}$, $K_H \propto T$

   ***Valid only at low Pressure of gas**
   ***Gas should not react with solvent.**

Super Note :

- Best method to determines molecular weight of macromolecules like protein is osmotic pressure because osmotic pressure can be easily measured at room temperature.
- 0.91 % W/V NaCl solution is isotonic with blood
- When density < 1 = m > M
- When density > 1 = m < M

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Chapter – 10 Electrochemistry

ELECTROCHEMICAL CELL

Galvanic cell or Voltaic cell		Electrolytic cell
Chemical energy → Electrical energy	Conversion of electrical to chemical & chemical to electrical energy	Electrical energy → Chemical energy
Spontaneous redox reaction		Nonspontaneous redox reaction

Galvanic Cell

- It has two half–cells,each having a beaker containing a metal strip that dips in its aqueous salt solution.
- The metal strips are called electrodes and are connected by a conducting wire.
- Two solutions are connected by a salt bridge.
- The oxidation and reduction half reactions occur at separate electrodes and electric current flows through the wire.

At anode: (-ve) oxidation $Zn(s) \rightarrow Zn^{+2}(aq) + 2e^-$

At cathode : (+ve) reduction $Cu^{+2}(aq) + 2e^- \rightarrow Cu(s)$

Cell Reaction : $Zn(s) + Cu^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cu(s)$

Current Flow : Anode → cathode (internal circuit)

Cathode → Anode (External circuit)

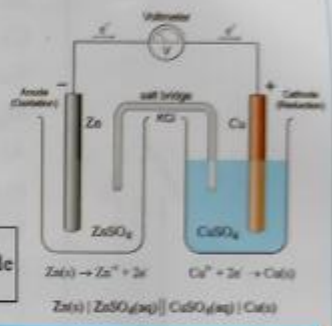
$[Zn^{+2}]$ ions in anode solution ↑

$[Cu^{+2}]$ ions in cathode solution ↓

Mass of Zn rod ↓ while mass of Cu rod ↑

Trick

- L → Left
- O → Oxidation
- A → Anode
- N → Negative



Cell Representation

Anode	Anode Half cell electrolyte (concentration)	Cathode half cell electrolyte (concentration)	cathode

Salt Bridge & Its Function

- Salt bridge is U – shaped glass tube filled with a gelly like substance, agar – agar (plant gel) mixed with an electrolyte like KCl, KNO_3, NH_4NO_3 etc.
- The electrolyte in salt bridge should be such that speed of it's cation is nearly equal to speed of it's anion.

Functions

- It connects the solution of two half cell to complete the circuit
- It maintains the electrical neutrality of the solution.
- If the salt bridge is removed then voltage drops to zero.
- It prevents the liquid -liquid junction potential.

Electrode Potential

- The potential difference between the electrode and electrolytic solution is called **electrode potential.**
- Electrode potential measured at 1 bar and temperature 298 K when concentration of all the ions is 1 M is called **standard electrode potential.**

Oxidation Potential (O.P.)

The electrode potential for oxidation half reaction

$M(s) \rightarrow M^{+n}(aq) + ne^-$; $E_{M/M^{+n}} = O.P$

Greater the O.P. greater will be the tendency to get oxidised

Reduction Potential (R.P.)

The electrode potential for reduction half reaction

$M^{+n}(aq) + ne^- \rightarrow M(s)$; $E_{M^{+n}/M} = R.P.$

Greater the R.P. greater will be the tendency to get reduced.

Electrode potential depends upon :

- Concentration of the solution
- Nature of the metal
- Pressure temperature conditions.

Reference Electrode

Standard Hydrogen Electrode **(SHE)** is taken as standard reference electrode. Its electrode potential is arbitrarily assumed to be 0.00 volt.

When acts as anode

$H_2(g) \rightleftharpoons 2H^+ + 2e^-$

$E^0_{H^+/H_2(g)} = SOP$

Representation : Pt, $H_2(g)$ | H^+ (1M)

For SHE electrode potential is arbitrarily assumed to be zero at all temperature

SOP = –SRP = 0 for SHE.

When acts as cathode

$2H^+ + 2e^- \rightleftharpoons H_2(g)$

$E^0_{H^+/H_2(g)} = SRP$

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Cell Potential

The difference in electrode potentials of the two half cell reactions (oxidation half cell and reduction half cell) is known as emf of the cell or cell potential.

E°_{cell} = SRP of cathode – SRP of anode {when all values are in SRP}

E°_{cell} = SRP of cathode + SOP of anode {when oxidation potential of anode (SOP) and reduction potential of anode (SRP)}

E°_{cell} = SOP of anode – SOP of cathode {when all values are in SOP}

E°_{cell} is intensive property so on multiplying/Dividing cell reaction by any number, the E°_{cell} value would not change.

Electrochemical Series

Increasing strength of reducing agent ↑

Electrode	Reaction	SRP (at 298 K)
Li	$Li^{+} + e^{-} \rightarrow Li(s)$	–3.05 V
K	$K^{+} + e^{-} \rightarrow K(s)$	–2.93 V
Ba	$Ba^{+2} - 2e^{-} \rightarrow Ba$	–2.91 V
Ca	$Ca^{+2} + 2e^{-} \rightarrow Ca(s)$	–2.87 V
Na	$Na^{+} + e^{-} \rightarrow Na(s)$	–2.71 V
Mg	$Mg^{+2} + 2e^{-} \rightarrow Mg(s)$	–2.36 V
Al	$Al^{+3} + 3e^{-} \rightarrow Al$	–1.66 V
Mn	$Mn^{+2} + 2e^{-} \rightarrow Mn$	–1.18 V
H_2O	$H_2O(l) + e^{-} \rightarrow H_2 + OH^{-}$	–0.828 V
Zn	$Zn^{+2} + 2e^{-} \rightarrow Zn(s)$	–0.76 V
Cr	$Cr^{+3} + 3e^{-} \rightarrow Cr(s)$	–0.74 V
Fe	$Fe^{2+} + 2e^{-} \rightarrow Fe$	–0.44 V
Cd	$Cd^{+2} + 2e^{-} \rightarrow Cd(s)$	–0.40 V
Co	$Co^{+2} + 2e^{-} \rightarrow Co$	–0.28 V
Ni	$Ni^{+2} + 2e^{-} \rightarrow Ni(s)$	–0.25 V
Sn	$Sn^{+2} + 2e^{-} \rightarrow Sn(s)$	–0.14 V
Pb	$Pb^{+2} + 2e^{-} \rightarrow Pb(s)$	–0.13 V
H_2	$2H^{+} + 2e^{-} \rightarrow H_2(g)$	0.00 V
Cu	$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$	0.34 V
I_2	$I_2 + 2e^{-} \rightarrow 2I^{-}$	0.54 V
Fe	$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	0.77 V
Hg	$Hg_2^{2+} + 2e^{-} \rightarrow Hg(l)$	0.79 V
Ag	$Ag^{+} + e^{-} \rightarrow Ag$	0.80 V
Hg	$Hg^{2+} + 2e^{-} \rightarrow Hg(l)$	0.85 V
Br_2	$Br_2 + 2e^{-} \rightarrow 2Br^{-}$	1.09 V
Pt	$Pt^{+2} + 2e^{-} \rightarrow Pt$	1.20 V
O_2	$O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O(l)$	1.23 V
Cl_2	$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$	1.36 V
Au	$Au^{+3} + 3e^{-} \rightarrow Au(s)$	1.40 V
F_2	$F_2 + 2e^{-} \rightarrow 2F^{-}$	2.87 V

Increasing strength of oxidising agent ↓

Applications of Electrochemical Series

Oxidising and reducing power

Oxidising power $\propto$ SRP $\propto \frac{1}{SOP}$

Reducing power $\propto$ SOP $\propto \frac{1}{SRP}$

Reactivity of metals

In ECS reactivity of metal decreases from top to bottom. Li is most reactive metal.

Reactivity of non-metals

In ECS reactivity of non-metal increases from top to bottom F_2 is most reactive non-metal

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Displacement reactions in solution

More reactive metal / non-metal displaces less reactive metal / non-metal in their solution.

- $Cu + 2\,AgNO_3 \rightarrow Cu(NO_3)_2 + 2\,Ag$

  $Ag + Cu(NO_3)_2 \rightarrow$ No reaction

- $I_2 + 2\,KCl + Cl_2 \rightarrow 2\,KCl + I_2$

  $I_2 + 2\,KCl \rightarrow$ No reaction

Metal above hydrogen displaces H_2 from dilute acid solution

$Zn + H_2SO_4(aq) \rightarrow ZnSO_4 + H_2(g)$

$Cu + H_2SO_4(dilute) \rightarrow$ No reaction

Nernst Equation

It is a relation between electrode potential, emf of cell, temperature and concentration of ions in solution represented by the equation

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\ln\frac{[P]}{[R]}$$

At 25°C, $E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log_{10}\frac{[P]}{[R]}$

E_{cell} = EMF of cell at new concentration

R = Gas constant = 8.314 $JK^{-1}\,mol^{-1}$.

n = Number of electrons

[P] = Concentration of product in mol L^{-1}

E^{o}_{cell} = Standard emf of cell (1M, 25°C and 1 atm)

T = Absolute temperature

F = Faraday constant = 96500 C

[R] = Concentration of reactants in mol L^{-1}

For the reaction

$M^{n+} + ne^- \rightarrow M$, $E = E^{o} - \frac{RT}{nF}\ln\frac{M}{[M^{n+}]}$ or $E = E^{o} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$ at 298K

Super Note :

If $[M^{n+}]\uparrow \Rightarrow E_{red}\uparrow \Rightarrow E_{ox}\downarrow$

$[M^{n+}]\downarrow \Rightarrow E_{red}\downarrow \Rightarrow E_{ox}\uparrow$

For Concentration Cell $E^{o}_{Cell} = 0$ $\quad E_{cell} = -\frac{0.0591}{n}\log_{10}\frac{[Product(C_1)]}{[Reactant\ (C_2)]}$, $E_{cell} = +ve$ if $C_2 > C_1$

Thermodynamic Property of Cell

From thermodynamics : $W_{electrical} = \Delta G = -nFE_{cell}$

- For cell to be spontaneous (working) $\Rightarrow$ $\Delta G < 0$, So $E_{cell} > 0$
- For cell to be Non-spontaneous (Non-working) $\Rightarrow$ $\Delta G > 0$, So $E_{cell} < 0$
- At equilibrium condition $\Delta G > 0$, So $E_{cell} = 0$

$E^{o}_{Cell} = \frac{0.0591}{n}\log_{10} K_{eq}$ [K_{eq} : Equlibrium constant] $\quad \Delta G^{o} = -2.303\,RT\log_{10} K$

Electrolytic Cell and Electrolysis

- Device in which non-spontaneous redox reaction($\Delta G > 0$) is used to convert electrical energy into chemical energy is called **Electrolytic Cell.**
- The decomposition of an electrolyte on passing current through its molten state or aqueous solution is called **Electrolysis**
- Electrolysis is a process of oxidation and reduction due to current in the electrolyte.
- Cation (+ve) $\rightarrow$ Cathode (-ve) Reduction and Anion (-ve) $\rightarrow$ Anode (+ve) Oxidation
- **Sign of cathode & anode are opposite in Galvanic cell & Electrolytic cell.**

Efficiency of cell $(\eta) = \frac{\Delta G}{\Delta H} = \frac{\eta FE}{\Delta H}$

Active vs Inactive electrodes

- Active electrodes are metal electrodes in cell which participate in cell reaction.
- Inactive electrodes are those electrodes which does not participate in cell reaction. E.g. : most commonly rods of graphite or platinum

Preferential Discharge Theory

- When an electrolytic solution consists of more than two ions and the electrolysis is done.
- All the ions are not discharged from the electrodes simultaneously but certain ions are liberated from the electrodes in preference to others.
- This is explained by preferential discharge theory.
- It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least energy.
- The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge potential or deposition potential.
- The values of discharge potential are different for different ions.

For electrolysis ΔG = +ve, So it is non-spontaneous process.

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S.No.	Electrolyte	Electrode	Product at anode	Product at cathode	pH change
1.	Fused/ Molten NaCl	Pt or Graphite	Cl_2	Na	No change
2.	Aqueous NaCl	Pt or Graphite	Cl_2	H_2	pH↑
3.	Dilute NaCl	Pt or Graphite	O_2	H_2	No change
4.	Aqueous NaCl	Hg	Cl_2	Reduction of Na; H_2 ↑	No change
5.	Fused NaOH	Pt or Graphite	O_2	Na	No change
6.	Aqueous $CuSO_4$	Pt or Graphite	O_2	Cu	pH↓
7.	Aqueous $CuSO_4$	Cu	Cu oxidize to Cu^{2+}	Cu	No change
8.	Aqueous $CuCl_2$	Cu	Cu oxidizes to Cu^{+2}	Cu	No change
9.	Aqueous $AgNO_3$	Pt or Graphite	O_2	Ag	pH↓
10.	Aqueous $AgNO_3$	Ag	Ag^+	Ag	No change
11.	Aqueous $NiSO_4/Ni(NO_3)_2$	Ni	Ni^{2+}	Ni	No change
12.	Aqueous $NiSO_4$	Pt or Graphite	O_2	Ni	pH↓
13.	Aqueous Na_4SO_4	Pt or Graphite	O_2	H_2	No change
14.	Dilute H_2SO_4	Pt or Graphite	O_2	H_2	No change

Quantitative Aspects of Electrolysis

First Law of Electrolysis

According to this law the mass of a substance oxidised or reduced at an electrode is directly proportional to the amount of charged supplied.

$W \propto Q$, W = amount of substance deposited, Q = charge in coulomb

$\Rightarrow W = Z \times Q \Rightarrow W = Z \times I \times t \quad \because Q = I \times t$ and Z (electrochemical equivalent) $= \frac{E}{96500}$

$\Rightarrow W = \frac{E \times I \times t}{96500}$

Second Law of Electrolysis

When equal charge is passed through 2 electrolytic cells and this cells are connected in series then mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses.

$$\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2} \text{ (Q = same)}$$

Conductors

Substances which allow electric current to flow through them are called conductors

Examples - Metals, Aqueous solution of acids, bases and salts, fused salts and impure water etc

Metallic conductors or electronic conductors

1. Passage of current by movement of electrons in the metallic lattice, E.g., Cu, Ag, etc.
2. Passage of current brings in only physical changes.
3. It generally shows no transfer of matter.
4. It generally shows an increase in resistance during the passage of current due to increase in temperature. Thermal motion of metal ions hindering the flow of electrons increases with increase in temperature.

Electrolytic conductors or ionic conductors

1. Passage of current by ions in molten state or in aqueous solution of electrolytes, E.g., NaCl (aq) or NaCl (fused).
2. Passage of current brings in physical as well as chemical changes.
3. It involves transfer of matter in the form of ions.
4. It generally shows a decrease in resistance due to decrease in viscosity of the medium and degree of hydration of ions with increase in temperature.

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Electrolytic Conductance

Resistance (R)

Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference (V) to the current (I) flowing.

$R = V/I$ R is expressed in ohms

Specific resistance/Resistivity (ρ)

The resistance (R) of a conductor is directly proportional to its length (ℓ) and inversely proportional to its area of cross section (A).

$$R \propto \frac{\ell}{A} \quad ; \quad R = \rho\frac{\ell}{A}$$

Therefore resistance offered by 1 cm^3 electrolytic solution is known as resistivity.

Unit of $\rho \rightarrow$ ohm cm

Conductance (G)

It is the property by virtue of which it favours flow of current. The conductance of a conductor is equal to reciprocal of resistance

$G = 1/R$

Unit of G is **mho** or **ohm^{-1}** or **Siemens (S)**

Specific conductance/ Conductivity (κ)

It is defined as the reciprocal of specific resistance, $\kappa = 1/\rho$

$$\frac{1}{\rho} = \frac{1}{R}\cdot\frac{\ell}{A} \qquad R = \rho\frac{\ell}{A} \qquad \kappa = G \times G^*$$

Specific conductance = Conductance × Cell constant Hence specific conductivity of a solution is defined as the conductance offered by 1 cm^3 of electrolytic solution

Unit of κ is $ohm^{-1}\ cm^{-1}$

Molar conductivity or Molar conductance

It is defined as the conductance of all the ions produced by one mole of electrolyte present in the given volume of solution.

$$\lambda_m = \kappa \times V = \frac{\kappa \times 1000}{M}$$

Unit of $\lambda_m = ohm^{-1}\ cm^2\ mol^{-1}$

Relation between Λ_{eq} and Λ_m

$$\Lambda_{eq} = \frac{\Lambda_m}{V.F.}$$

Equivalent conductivity or Equivalent conductance

It is defined as the conductance of all the ions produced by one gram equivalent of the electrolyte in the given volume of solution

$$\lambda_{eq} = \kappa \times V = \frac{K \times 1000}{N}$$

Unit of $\lambda_{eq} \rightarrow ohm^{-1}\ cm^2\ eq^{-1}$

Factors Affecting Electrolytic Conductance

(a) Inter ionic attraction - If inter ionic attraction between ions of solute is more, then the conductance will be less.

(b) Polarity of solvent - If solvent has high-dielectric constant then the ionization and conductance will be higher.

(c) Viscosity of medium - On increasing the viscosity of medium, the conductance decreases.

(d) Temperature - As the temperature of electrolytic solution is increased, the conductance increases because K.E. of the ions increases and all types of attraction forces decrease and the viscosity of medium decreases.

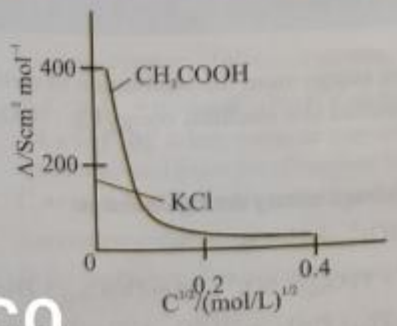
(e) Hydrated size - Due to hydration of ions conductance decreases.

(f) Dilution - (i) On increasing the dilution conductance (G) increases. For strong electrolyte on dilution interionic force of attraction decreases therefore conductance increases. For weak electrolyte with dilution degree of dissociation (α) increases therefore conductance increases.

(ii) On dilution specific conductance decreases because on dilution number of ions in 1 ml solution decreases.

(iii) On dilution equivalent and molar conductance increases because with dilution normality or molarity decreases

Debye Huckel Onsager Equation



$$\Lambda_m = \Lambda_m^0 - b\sqrt{C}$$ Only for strong electrolyte

where Λ_m = molar conductance at concentration C,

Λ_m^0 = molar conductance at ∞ dilution,

b = constant and its value is same for a particular type of electrolyte.

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change with dilution is due to increases in the number of ions in total volume of solution that contains 1 mol of electrolyte

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Kohlrausch's Law

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions."

$$\Lambda_{eq}^{\infty} = \lambda_c^{\infty} + \lambda_a^{\infty}$$

λ_c^{∞} = equivalent conductance of cation at infinite dilution.

λ_a^{∞} = equivalent conductance of anion at infinite dilution.

$$A_xB_y \rightarrow xA^{y+} + yB^{x-}$$

In terms of molar conductances of cation and anion

$$\Lambda_{eq}^{\infty} = \frac{1}{x}\lambda_{m(c)}^{\infty} + \frac{1}{y}\lambda_{m(a)}^{\infty}$$

$\lambda_{m(c)}^{\infty}$ = Limiting molar conductance of cation

$\lambda_{m(a)}^{\infty}$ = Limiting molar conductance of anion

y = Charge of cation

x = Charge of anion

$$\Lambda_m^{\infty} = x\lambda_{m(c)}^{\infty} + y\lambda_{m(a)}^{\infty}$$

x = Stoichiometric coefficient of cation

y = Stoichiometric coefficient of anion

Applications of Kohlrausch's Law

(A) To calculate degree of dissociation :

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_{eq}}{\Lambda_{eq}^{\infty}} = \frac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at infinite dilution}}$$

$$\text{or } \alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}} = \frac{\text{molar conductance at a given concentration}}{\text{molar conductance at infinite dilution}}$$

(B) To calculate dissociation constant of weak electrolyte

$$K_a = \frac{C\alpha^2}{(1-\alpha)} \qquad \text{If } \alpha \le 5\% \text{ then } K = C\alpha^2$$

(C) To calculate Solubility (S) and K_{sp} of any sparingly soluble salt

Sparingly soluble salt means salt with very less solubility

Saturated solution of sparingly soluble salt can be considered as infinitely dilute solution.

In a saturated solution of sparingly soluble salt

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

M = Solubility (S)

$$\Lambda_m(\text{saturated}) = \Lambda_m^{\infty} = \frac{\kappa \times 1000}{\text{Solubility}}; S = \frac{k \times 1000}{\Lambda_m^{\infty}}$$

Corrosion

- Corrosion is the process of change of metal surface into salts like oxides, sulphides, carbonates etc. due to attack of atmospheric gases.
- Rust is hydrated ferric oxide $Fe_2O_3.xH_2O$.
- Factors which enhance corrosion are:
  - (a) Presence of impurities in metal.
  - (b) Presence of moisture (Eg. Rainy season)
  - (c) Presence of electrolyte. (Eg. Saline water)
- Corrosion can be prevented by Barrier protection (oil/grease), sacrificial protection (Galvanisation). Electrical protein.
- H_2O_2 fuel cell was the source of drinking water & electrical energy in Appollo Moon flight.
- Mercury cell gives constant voltage throughout its life.
- Dry cell have short life because acidic NH_4Cl corrodes Zn Container.

Cell

Name of the cell/battery	Anode	Cathode	Electrolyte
Dry Cell	Zinc	Graphite; $MnO_2 + C$ (touching cathode)	$NH_4Cl + ZnCl_2$ (touching anode)
Mercury Cell (Used in watches, hearing aids)	Zinc/mercury Amalgum	Paste of HgO & carbon	Paste of KOH & ZnO
Lead storage battery	Lead	Lead Dioxide	H_2SO_4 (38%)
Ni-Cd cell	Cadmium	Nickel dioxide	KOH solution
H_2-O_2 fuel cell	Porous carbon containing catalysts (H passed)	Porous carbon containing catalysts (O_2 passed)	aq. NaOH solution

- Primary Cell cannot be recharged. Eg. Dry cell & Mercury Cell
- Secondary cells can be recharged. Eg. Ni-Cd cell & Lead storage battery.
- Fuel cell produces energy from the combustion of fuels which can be converted into electrical energy Eg. : H_2-O_2 fuel cell.
- Reactions in lead storage battery during discharge:
- At anode : $Pb_{(s)} + SO_4^{2-} \rightarrow PbSO_{4(s)} + 2e^-$
- At cathode : $4H^+ + PbO_{2(g)} + SO_4^{2-} + 2e^- \rightarrow PbSO_{4(g)} + 2H_2O$
- Complete reaction: $Pb_{(s)} + PbO_{2(g)} + 2H_2SO_4 \rightarrow 2PbSO_{4(g)} + 2H_2O$

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Chapter – 11

Chemical Kinetics

Kinetics of Chemical Reactions

Type of Reaction

Very Fast Reaction : Complete within fraction of seconds

- Ionic reactions

Very Slow Reaction : Requires years for completion.

- Rusting of Iron

Moderate Reaction : Require finite time for completion.

- Molecular Reactions

Types of Rate of Reactions

Average Rate $\frac{\Delta[C]}{\Delta t}$	Instantaneous Rate $\frac{d[C]}{dt}$
• Measured over a finite interval of time.	• Measured at a particular instant.
• Must know concentration of substance at two different time.	• Obtained by tracing tangent at that time in given graph.

- Always take mole ratio not mass ratio for calculation of rate.

Rate of Reaction (ROR)

- Change in concentration of reactant and product per unit time, (change in concentration/time taken)
- Unit of Rate

In aq. : $\frac{\text{mole / litre}}{\text{time}}$ In gaseous phase : $\frac{\text{atm or bar}}{\text{time}}$

- Rate in (atm/ sec) = Rate in (molarity/sec) RT
- Relation between related and product (ROR)

$nA \rightarrow mB$

Rate of disappearance of A = –d[A]/dt

Rate of formation of B = +d[B]/dt

$$ROR = \frac{dx}{dt} = \frac{1}{n}\frac{-d[A]}{dt} = \frac{1}{m}\frac{+d[B]}{dt}$$

- – and + shows decrease and increase concentration time respectively.
- Overall rate is positive.

Super Note : Rate of reaction value is dependent on the stoichiometric coefficients used in the reaction while rate of any species will be fixed value under given conditions.

Rate Law (Dependence of Rate on Concentration of Reactants)

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law.

It can only be established by experiments.

Rate $\propto$ (conc.)^{order} $\Rightarrow$ Rate = K (conc.)^{order}

This is the differential rate equation or rate expression.

Where K = Rate constant / specific reaction rate unit of K = (conc)$^{1-order}$ time^{-1}

Super Note :
Value of K is a constant for a given reaction, depends only on temperature.

Molecularity

- Total molecules involved in reactant of an elementry reaction.
- It is a theoretical concept.
- Mostly molecularity of reaction lies between 1 to 3.
- Molecularity can not be greater than 3, If it is greater than 3 then reaction will be multi step or complex.
- Molecularity of a reaction can not be zero, negative, fractional and infinite.

Order of Reaction

- It is sum of powers of all concentration terms appearing in Rate Law Expression.
- $m_1A + m_2B \rightarrow$ products Now, if on the basis of experiment, we find that $R \propto [A]^p [B]^q$ Where p may or may not be equal to m_1 and similarly q may or may not be equal to m_2, p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is **overall order of the reaction.**
- **C_0 or (a) is initial concentration and C_t or (a-x) is concentration at time 't'.**
- It is experimentally determined
- Order can be zero & fractional but can not be infinite. Order with respect to a particular reactant may be negative but overall order can not be negative.
- [illegible] overall order is defined which is calculated from R.D.S. or slow step.

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Elementary Reactions

- These type of reactions complete in single step
- If $n_1A + n_2B$ Product, Rate Law = $K[A]^{n_1}[B]^{n_2}$, Order = $n_1 + n_2$
- For elementary reaction fractional order is not possible. In elementary reaction molecularity is equal to its order. Zero order reactions can never be elementary reaction

Complex Reactions

- These type of reactions complete in multi step:
- Eg.: $2N_2O_5 \rightarrow 4NO_2 + O_2$

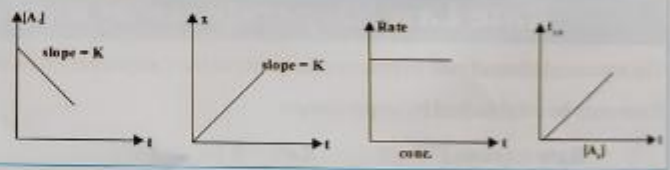
  (i) $2N_2O_5 \rightleftharpoons 2NO_2 + 2NO_3$ (Fast) (ii) $NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ (Slow) (iii) $NO + NO_3 \rightarrow 2NO_2$
- Here rate law is written in terms of slowest step (R.D.S.) which must be free from intermediates.
- Rate law = $K[N_2O_5]$, Order = 1
- Molecularity of each reaction step is defined separately
- Total molecularity of complex reaction is not defined.
- If not defined is not in the option then molecularity is equal to order of reaction. (Then in this case molecularity will be 1)

Zero Order Reaction

- Rate doesn't depend on the concentration of reactant
- $r = K$ [concentration of reanctant]$^0 \Rightarrow r = K$
- Unit of K = (mol/litre)sec^{-1}.
- $P_t = P_0 - Kt$ for gaseous phase reaction
- $a_t = a_0 - Kt$ for aqueous phase reaction
- Life time = a_0 / K
- Half life time ($t_{1/2}$) = $a_0/2K$
- $\alpha = x/a_0 = Kt/a_0$
- Ex. Photochemical reaction, Enzyme catalyste reaction, Dissociation of gases on solid surface at very high pressure etc.

$$t_{1/2} \propto a_0$$

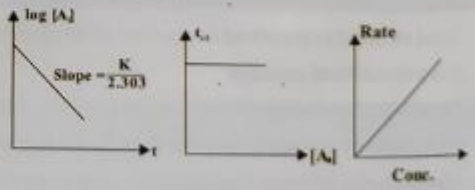
Differential Rate of Equation	Integrated Rate Equation
$R = -d[A]/dt = K[A]^0$	$[A]_t = [A]_0 - Kt$; $x = Kt$
Half Life Reaction	**Time of completion**
$t_{1/2} = t_{50\%}$ $[A]_0 / 2K$	$t_{100\%} = [A]_0 / K = 2t_{1/2}$



1st Order Reaction

- $r = K[a_0]^1$
- $a_t = a_0 e^{-Kt} \Rightarrow K = \frac{2.303}{t}\log\left(\frac{a_0}{a_0 - x}\right)$
- $\alpha = 1 - e^{-Kt}$
- $r = Ka_0e^{-Kt}$
- $t_{1/2} = 0.693/K$
- life time = ∞
- Ex. Radioactivity reaction, growth or decay of bacteria, Inversion of cane sugar, Acidic Hydrolysis of ester etc.

$$t_{1/4} = t_{75\%} = 2t_{1/2}$$



Super Note : $t_{1/2}$ is independent of initial concentration

Progress Monitoring (Related to first order reaction) (for JEE)

Pressure Related	When P_0 & P_t is given $K = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$	When P_∞ & P_t is given $K = \frac{2.303}{t}\log\frac{P_\infty}{2(P_\infty - P_t)}$
Volume Related (Atleast one product should be gaseous)	$K = \frac{1}{t}\ln\left(\frac{V_\infty}{V_\infty - V_t}\right)$ V_t = Volume of gaseous product at t = t, V_∞ = Volume of gaseous product at t = ∞	**Redox Titration** $K = \frac{1}{t}\ln\left(\frac{V_0}{V_t}\right)$ V_0 = Volume of Std. solution used at t = 0, V_t = Volume of Std. solution used at t = t
Acid-Base Titration	$K = \frac{1}{t}\ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$ V_0 = Volume of Std. solution A/B required for titration at t = 0, V_t = Volume of Std. solution A/B required for titration at t = t, V_∞ = Volume of Std. solution A/B required for titration at t = ∞	**Optical Rotation** $K = \frac{1}{t}\ln\left(\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}\right)$ θ_0 = angle of rotation of PPL at t = 0, θ_t = angle of rotation of PPL at t = t, θ_∞ = angle of rotation of PPL at t = ∞

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Parallel first order reaction (for JEE)

$A \xrightarrow{K_1} mB$, $A \xrightarrow{K_2} nC$ $\quad K_{avg} = (K_1 + K_2)$, $\quad -d[A]/dt = K_{avg}[a_t]$

$K_{avg} = \frac{2.303}{t}\log\left(\frac{a_0}{a_t}\right)$, $\quad x = a_0\left[1 - e^{-K_{avg}t}\right]$ $\quad [B_t] = \frac{mK_1.x}{K_{avg}}$

$[C_t] = \frac{nK_2.x}{K_{avg}}$

Sequential first order reaction (for JEE)

$A \xrightarrow{K_1} B \xrightarrow{K_2} C$

$a_0 = a_t + b_t + c_t$ $\quad [b_t] = \frac{K_1}{K_2 - K_1}a_0[e^{-K_1t} - e^{-K_2t}]$

$[a_t] = a_0e^{-K_1t}$ $\quad t_{max} = \frac{1}{K_2 - K_1}\ln\left(\frac{K_2}{K_1}\right)$

Time taken for B to attain max value of B

Pseudo First Order Reaction

- Reaction in which kinetics of reaction is studied by decreased order. It is due to (1) Any Particular reactant in excess (2) Rate law involves catalyst.
- Ex. Inversion of cane sugar, Acidic hydrolysis of ester, etc.

n^{th} Order Reaction

$$r = K[a_0]^n \qquad Kt = \frac{1}{(n-1)}\left[\frac{1}{a_t^{n-1}} - \frac{1}{a_0^{n-1}}\right] \qquad t_{1/2} = \frac{1}{K}\frac{(2^{n-1}-1)}{(n-1)a_0^{n-1}}$$

Valid for all order reaction except 1st order

Methods to Determine Order of Reaction

(1) Initial rate method

$r = K[A]^a[B]^b[C]^c$ $\quad$ if $[B]$ = constant $\quad [C]$ = constant

then for two different initial concentrations of A we have

$$\left.\begin{aligned} r_{0_1} &= K[A_0]_1^a \\ r_{0_2} &= K[A_0]_2^a \end{aligned}\right\} \frac{r_{0_1}}{r_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^a$$

In log form $\quad a = \frac{\log(r_{0_1}/r_{0_2})}{\log([A_0]_1/[A_0]_2)}$

(2) Integrated rate law method

It is method of trial and error.

(3) Method of half lives

$$t_{1/2} \propto \frac{1}{[R_0]^{n-1}} \qquad \frac{t_{1/2}}{t'_{1/2}} = \frac{(R_0')^{n-1}}{(R_0)^{n-1}}$$

(4) Ostwald's isolation method

This method is useful for reaction which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess except that of one, so if B is in large amount

$$\text{rate} = K[A]^a[B]^b = K_0[A]^a$$

Then value of 'a' can be calculated by previous methods and similarly 'b' can also be calculated

Factors Affecting Rate of Reaction

(a) Nature of Reactant & Product

- ROR : Gas > Liquid > Solid
- ROR : Homogeneous > Hetergeneous.
- **Homogeneous Gaseous Reaction ⇒ ROR is maximum**
- ROR ∝ Surface area
- ROR $\propto \frac{\text{Stability of Product}}{\text{Stability of Reactant}}$

(b) Concentration of Reactant

- $r = K[\text{concentration}]^{order}$; rate law expression.

  Where K is rate constant or velocity constant or specific reaction rate. **(only depends on temperature)**

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right], \quad T_2 > T_1$$

- Unit of $K = \left(\frac{\text{mole}}{\text{litre}}\right)^{1-n}\text{time}^{-1}$, n = order

(c) Catalyst

- Positive catalyst increases rate of reaction and negative catalyst decreases rate of reaction.
- Due to catalyst average energy level, thermodynamic behavior of reaction do not change.
- Catalyst is not consumed in reaction nor initiate reaction.
- Variation in K on adding catalyst $\log\left(\frac{K'}{K}\right) = \frac{E_a - E_a'}{2.303RT}$

(d) Temperature

- The effect of temperature on reaction rate was expressed in terms of **temperature coefficient** which was defined as the ratio of rate of reaction at two different temperature differing by 10°C (usually these temperatures were taken as 25°C and 35°C

$$\frac{r_{t+\Delta t}}{r_t} = \alpha^{\frac{\Delta t}{10}}, \quad 2 < \alpha < 3$$

- On increasing temperature by 10° C ROR increase by 2 to 3 times.
- Generally we take $\alpha = 2$.

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Collision Theory

The basic requirement for a reaction to occur is that the reacting species must collide with one another. This is the basis of **collision theory** for reactions.

(a) Collision Frequency

The number of collisions that takes place per second per unit volume of the reaction

(b) Effective Collisions

The collisions that actually produce.

For a collision to be effective, the following two barriers are to be cleared

(i) Energy Barrier or Threshold Energy (E_T)

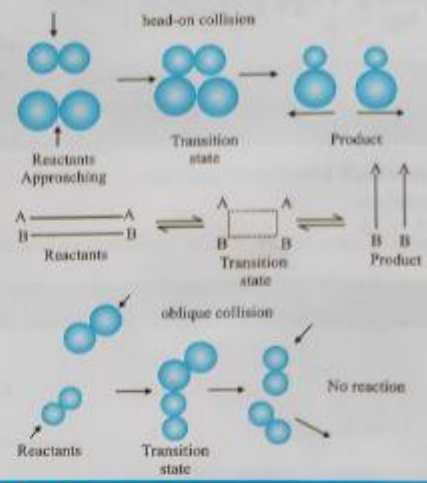
The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur.

If $E_R < E_T \Rightarrow$ Non effective collision (No Products are formed)

If $E_R \geq E_T \Rightarrow$ Chance of effective collision

(ii) Orientation Barrier

The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed.



The main points of Collision Theory

- For a reaction to occur, there must be collisions between the reacting species.
- Only a certain fraction of the total number of collisions is effective in forming the products.
- For effective collisions, the molecules should possess sufficient energy as well as orientation.

Concept of Activation Energy

Extra energy given to reactant molecules above their average energy level to make participate in reaction.

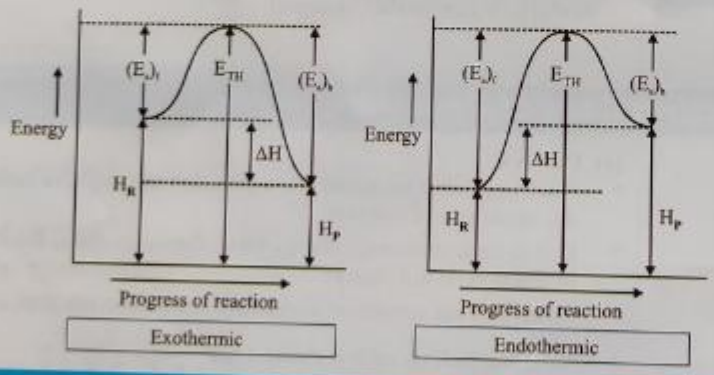
$E_T = E_a + E_R$ for reaction : $\Delta H = (E_a)_f - (E_a)_b$ If ΔH = -ve, exothermic If ΔH = +ve, endothermic

Activation energy = Threshold energy – average kinetic energy of reacting molecules

(a) Zero activation energy = Fraction of effective collision (f) will be very large = Very fast reaction (Instantaneous reaction).

(b) Low activation energies = Fraction of effective collision (f) will be large = Fast reactions.

(c) High activation energies = Fraction of effective collision (f) will be small = Slow reaction.



E_{TH} = Threshold Energy, H_R = Enthalpy or Energy or Potential of reactants.

H_P = Enthalpy or Energy or Potential of product, $(E_a)_f$ = Activation energy for forward reaction.

$(E_a)_b$ = Activation energy for backward reaction.

Arrhenius Equation

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

A = frequency factor

E_a = activation energy

T = absolute temperature

R = gas constant

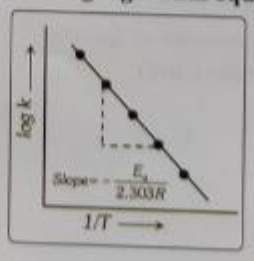
Taking logarithm equation

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

log K plotted against 1/T

intercept = log A

slope $\frac{-E_a}{2.303\,R}$



Rate constants for the reaction at two different temperatures T_1 and T_2,

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

- Fraction of molecules crossing barrier = $e^{-E_a/RT}$
- $K = Ae^{-E_a/RT}$, where A is collision factor having unit same as K
- **Arrhenius equation not applicable for radioactivity problems and for zero order reaction.**

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Chapter – 12 Surface Chemistry

Adsorption

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting in to higher concentration of the molecules on the surface is called **adsorption**.

Reason : $F_{ad} \neq 0$ on the surface particle of adsorbent.

Example : Ammonia gas placed in contact with charcoal gets adsorbed on the charcoal whereas ammonia gas placed in contact with water gets absorbed into water.

Basic Terminology used in Adsorption

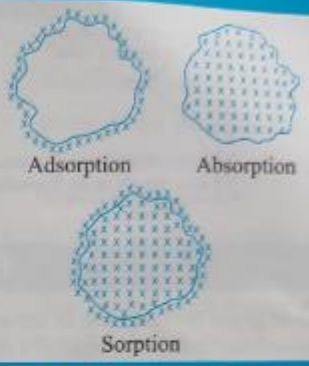
Adsorbate - The substance which gets adsorbed on any surface.

Adsorbent - The substance on the surface of which adsorption takes place.

Absorption - When the molecules of a substance are uniformly distributed throughout the body of a solid or liquid.

Desorption - The removal of the adsorbed substance from a surface.

Sorption - The phenomenon in which adsorption and absorption occur simultaneously.



There are two types of adsorption :

(i) Physical adsorption (ii) Chemical adsorption

Physical adsorption or Physisorption	Chemical adsorption or Chemisorption
1. Enthalpy of adsorption usually is of the order of 20-40 kJ mol^{-1} *i.e.* exothermic	1. Enthalpy of adsorption is of the order of 80-240 kJ mol^{-1}.
2. Molecule of adsorbate and adsorbent are held by Van der Waal interaction	2. Molecules of adsorbate and adsorbent are held by chemical bonds
3. It usually takes place at low temperature and decreases with increasing temperature	3. It takes place relatively at high temperature
4. It is not very specific *i.e.* all gases are adsorbed on all solids to some extent	4. It is highly specific and take place when there is some possibility of compound formation between adsorbate and adsorbent molecule.
5. Multimolecular layers may be formed on adsorbent	5. Usually monomolecular layer is formed on the adsorbent

Thermodynamics of Adsorption

- Adsorption is accompanied by decrease in the ΔG of the system when $\Delta G = 0$, **adsorption equilibrium is said to be established.**
- Adsorption is an exothermic process. **ΔH of adsorption is always negative.**
- When a gas is adsorbed, the freedom of movement of its molecules becomes restricted decrease in the entropy of the gas after adsorption, i.e. **ΔS is negative.**
- For a process to be spontaneous, $\Delta G < 0$, $\Delta G = \Delta H - T\Delta S$ can be negative if ΔH has sufficiently high negative value and $T\Delta S$ **has positive value.**

Difference between Adsorption and Absorption

Adsorption	Absorption
• It is a surface phenomenon	• It concerns with the whole mass of the absorbent.
• In it, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid.	• It implies that a substance is uniformly distributed, through the body of the solid or liquid.
• In it the concentration of the adsorbed molecules is always greater at the free phase.	• In it the concentration is low.
• It is rapid in the beginning and slows down near the equilibrium.	• It occurs at the uniform rate.
• Examples : (i) Water vapours adsorbed by silica gel. (ii) NH_3 is adsorbed by charcoal.	• Examples : (i) Water vapours absorbed by anhydrous $CaCl_2$ (ii) NH_3 is absorbed in water forming NH_4OH

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Factors affecting the Extent of Adsorption

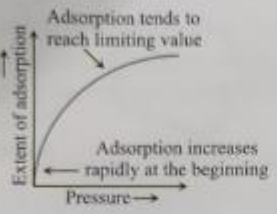
Nature of the adsorbate (gas) and adsorbent (solid)

In general, easily liquefiable gases e.g., CO_2, NH_3, Cl_2 and SO_2 etc. are adsorbed to a greater extent than the elemental gases e.g. H_2, O_2, N_2, He etc.

Effect of pressure on the adsorbate gas

An increase in the pressure of the adsorbate gas increases the extent of adsorption

At low temperature, the extent of adsorption increases rapidly with pressure

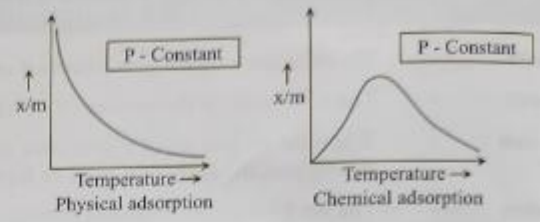


Surface area of the solid adsorbent

The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. larger the surface area of the adsorbent, greater is the extent of adsorption.

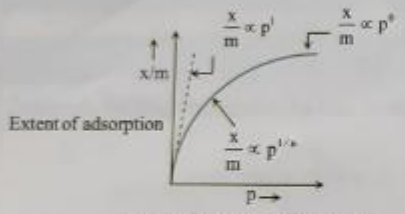
Effect of temperature

Magnitude of adsorption should decrease with rise in temperature



Freundlich Adsorption Isotherm

A relation or graph between x/m (x are number of moles of adsorbate and m is the mass of adsorbent) and the pressure (P) of the gas at a constant temperature is called adsorption isotherm.

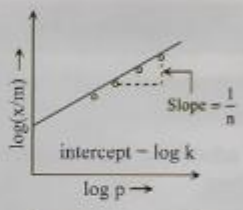


Freundlich adsorption isotherm: plot of x/m against p

$$\frac{x}{m} = kp^{\frac{1}{n}} \text{ (Freundlich adsorption isotherm)}$$

- At low pressure, the extent of adsorption varies linearly with pressure. $\frac{x}{m} \propto p^1$
- At high pressure, it becomes independent of pressure $\frac{x}{m} \propto p^0$
- At moderate pressure x/m depends upon pressure raised to powers $\frac{x}{m} \propto p^{\frac{1}{n}}$

- **Calculation of 1/n**



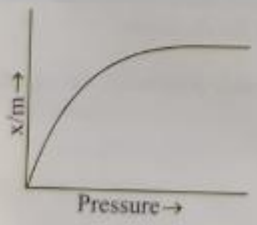
$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

- **Limitation :**
  High Pressure behaviour can'not be explain by freundlich isotherm and it is not valid at high pressure 1/n can be calculated by measuring the slope of

$$\frac{x}{m} \propto (P)^{1/n}$$

The Langmuir - Adsorption Isotherms

Langmuir considered that adsorption to consist of the two opposing processes *i.e.* adsorption and desorption both take place and dynamic equilibrium established between the above two processes. He also assumed that the layer of the adsorbed gas was only one molecule thick *i.e.* unimolecular and for chemisorption.



$$\frac{x}{m} = \frac{aP}{1+bP}$$ where a and b are two Langmuir parameters

- $\frac{x}{m} = \frac{a}{b}$ (At very high pressure $1 + bP \simeq bP$)

  and $\frac{x}{m} = aP$ (At very low pressure $1 + bP \cong 1$)
- So at high pressure of the gas x/m remains constant and nature of graph is linear at very high pressure
- In order to determine the parameters a and b, we may write
- $\frac{m}{x} = \frac{1+bP}{aP} = \frac{b}{a} + \frac{1}{aP}$

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Catalyst

- A catalyst remains unchanged in mass and chemical composition but can change their physical state.
- Only a very small amount of catalyst is sufficient to catalyse a reaction.
- A catalyst does not initiate a reaction but participate in mechanism of reaction.
- Solid catalyst is more efficient when used in finely divided form.
- Generally catalyst does not change the nature of products.
- 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.
- The catalyst are generally specific in nature.
- Does not change free energy of reaction.

Type of Catalysation

Homogeneous Catalysation
Physical State of reactant and catalyst is same.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$$

Heterogeneous Catalysation
Physical State of reactant and catalyst is different.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{Pt_{(s)}} 2SO_{3(g)}$$

Enzyme Catalyst

- It is a macro molecule of nitrogen containing compound which has specific type of cavity for specific reactant on its surface. That's why it is also known as shape selective catalyst.
- It works on key-lock system.

Type of Catalyst

1. **Positive Catalyst** - Which increases rate of reaction.
2. **Negative Catalyst** - Which decreases rate of reaction.
3. **Auto Catalyst** - If one of the product behaves like a catalyst in the reaction and it is known as auto catalyst.
4. **Induced Catalyst** - If one of the chemical reaction behaves like a catalyst from another reaction then such reaction is known as induced catalyst.

Shape Selective Catalysis By Zeolites

- Zeolites are the most important metal oxide or aluminosilicates catalysts. These catalysts are widely used in the petrochemical industries for (i) cracking of hydrocarbons and (ii) for aromatisation. Zeolites are microporous silicates having the general formula
- Shape-selectivity is the most remarkable feature of zeolite catalysts. The reactions depend on the size of the cavities (Cages) and pores (apertures) present on the surface of zeolite. The pore size varies between 260pm and 760pm.
- Hence depending upon the size of the reactant and product molecules, as compared to the size and the shape of the cavities and the pores of the zeolite, the reactions can move in a specified manner.
- A special catalyst, called ZSM-5, is used to convert alcohols such as methanol, ethanol directly to gasoline or petrol.

$$\underset{\text{Methanol}}{xCH_3OH} \xrightarrow[\text{Catalyst}]{\text{ZSM-5}} \underset{\text{Gasoline}}{(CH_2)_x} + xH_2O$$

- Zeolites are also used in water softening.

Colloids

Colloidal state of matter is a state in which the size of particles is such (10Å – 1000Å) that they can pass through filter paper but not through animal or vegetable membrane.

Classification of Colloids

(i) **Based on physical state of dispersed phase and dispersion medium**–The physical state of dispersed phase and dispersion medium may be solids, liquids or gases, eight types of colloidal system are possible.

Dispersed Phase	Dispersion Medium	Name	Examples
Solid	Solid	Solid Sol	Some coloured glasses, gem stones
Solid	Liquid	Sol	Some paints, cell fuids, muddy water
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud
Gas	Solid	Solid foam	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Gas mixed with another gas form a homogeneous mixture and not a colloidal system (hetrogeneous mixture).

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(ii) 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 substances.	Formation by aggregation of big size molecules. These are polymers with high molecular mass	These are the substances which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal solution. These associated particles are also called micelles.
Ex → Gold sol (Au) Sulphur sol (S_8)	Ex → Starch, Cellulose, Protein etc.	Ex. → Soap & Detergent

(iii) Based on nature of interaction between dispersed phase and dispersion medium–

S.No.	Properties	Lyophilic Sols	Lyophobic Sols
1.	Nature	Reversible	Irreversible
2.	Preparation	Prepared by direct mixing with liquid dispersion medium i.e. solvent loving	Cannot be prepared directly but by special method i.e. solvent hating
3.	Stability	Quite stable and not easily precipitated or coagulated	Precipitated by adding small amount of suitable electrolyte
4.	Hydration	Highly hydrated	Not much hydrated
5.	Nature & substances	These sols are usually formed by the organic substances like starch, gum, proteins etc.	These are usually formed by the inorganic materials like metals, their sulphides etc.
6.	Viscosity	Much higher than that of medium	Almost same as that of medium
7.	Surface tension	Lower than that of dispersion medium	Nearly same as that of dispersion medium

Emulsions and Its Type

Insoluble liquids form Emulsion.

Emulsions are colloids in which both dispersed phase and dispersion medium are liquids and broadly classified into two types

(i) **Oil in water emulsion** – In this type of emulsion oil act as dispersed phase and water act as dispersion medium.
Ex.– Milk, vanishing cream etc.

(ii) **Water in oil emulsion** – In this type of emulsion water act as dispersed phase and oil act as dispersion medium.
Ex.– Cold cream, butter, cod liver oil etc.

Preparation of Colloids

Prepared by two types of methods : (i) Dispersion method (ii) Condensation method

Dispersion Methods

In this method large particles of the substance are broken into particles of colloidal dimensions in the presence of dispersion medium and stabilised by adding some suitable stabilizer. Some methods given below:

(i) **Mechanical dispersion** – In this method, the course suspension of the substance is brought into a colloidal state in dispersion medium by grinding it in a colloidal mill, ball mill or ultrasonic disintegrator.

(ii) **Electrical disintegration or Bredig's arc method** - This process involves dispersion as well as condensation colloidal sols of metals such as gold, silver, platinum etc. can be prepared by this method. Electric arc is struck between electrodes of metals immersed in the dispersion medium. The intense heat produced vaporises the metal, which then condenses to form particles of colloidal size.

(iii) **Peptization** – It is a process of converting the precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte (Peptising agent)

During peptization the precipitate adsorb one of the ion (cation or anion) which is common ion.

Ex – When freshly precipitated $Fe(OH)_3$ is shaken with aqueous solution of $FeCl_3$ (Peptizing agent) it adsorbs Fe^{+3} ion (common ion) and there by breaks up into small sized particles.

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Condensation Methods

Physical Method	
Exchange of solvent	**Excessive cooling**
When a true solution is mixed with an excess of other solvent in which the solute is insoluble but solvent is miscible. Ex– when a solution of sulphur in alcohol is poured in excess of water sol of S is obtained	A sol of ice in $CHCl_3$ or ether by freezing the water in the solvent

Chemical method

$As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposition}} As_2S_3(sol) + 3H_2O$

$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$

$2AuCl_3 + 3HCHO + 3H_2O_2 \xrightarrow{\text{Reduction}} 2Au\ (sol) + 3HCOOH + 6HCl$

$FeCl + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3 + 3HCl\ (sol)$

General Properties of Colloids

(i) **Colligative properties** – Due to high average molecular masses of colloidal particles, mole fraction of dispersed phase is very low and the value of colligative properties observed experimentally are very small.

(ii) **Optical properties–Tyndall effect** – If a strong beam of light is passed through a colloidal sol placed in the dark place the path of the beam gets illuminated. This phenomenon is called Tyndall effect, which is due to scattering of light by the colloidal particles. Tyndall effect not found in true solution.

(iii) **Mechanical properties–Brownian movement** – Colloidal particles are found to be in continuous zig–zag motion called Brownian movement, it arises because of the impact of the molecules of the dispersion medium with the colloidal particles.

(iv) **Electrical Properties-Electrophoresis.** The particles of colloids are electrically charged and are positively or negatively charge. The dispersion medium has an equal and opposite charge making the system neutral as a whole. The existance of charge is shown by the phenomenon of electrophoresis. It involves the movement of colloidal particles either towards the cathode or anode under the influence of electric field.

Positively charged collidal particles	Negatively charged colloidal particles
Metal hydroxides [$Fe(OH)_3$, $Al(OH)_3$, $Ca(OH)_2$, $Cr(OH)_3$], Oxides (TiO_2) haemoglobin, basic dye (Methyl blue, Prussian blue) etc.	Metal, starch, clay, metal sulphides (As_2S_3,CdS), Acidic dye (congo red) etc.

(v) **Coagulation (Flocculation) of Colloids** – The phenomenon of precipitation of a colloidal solution by the addition of excess of an electrolyte is called coagulation or flocculation.

- **Coagulation value :** Amount of electrolyte in milimoles which can coagulate a 1 litre colloidal solution.

Coagulation value ∝ 1/coagulating power

Hardy–Schulze Rule

- The ions carrying charge opposite to that of sol particles are effective in causing the coagulation of the sol
- The minimum concentration of an electrolyte which is required to cause coagulation of a sol is known as coagulation value and expressed in millimoles / litre.

Coagulating power ∝ Magnitude of opposite charge.

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).

$$\text{Protection capacity} \propto \frac{1}{\text{Protection number (gold number)}}$$

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

Purification of Colloids

Following methods are used

(i) **Dialysis** – A bag made-up of parchment paper or cellophone membrane is filled with colloidal solution and is the suspended in fresh water, the electrolyte particles passout leaving behind the colloidal sol Movement of ions across the membrane can be expedited by applying electric potential through two electrodes. This method is faster than simple dialysis and is known as electrodialysis

(ii) **Ultrafiltration** – In this method the colloidal solution is filtered through ultra-filters which allow to pass electrolytes only.

(iii) **Ultra–centrifugation** – In this method colloidal sol is taken in a tube which is placed in an ultra-centrifuge. On rotation of the tube w high speeds the colloidal particles settle down at the bottom of the tube and the impurities remain in solution called the centrifugate. T settle colloidal particles are mixed with an appropriate dispersing medium to regenerate the sol.

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