Chemistry 3 Hours

CHEMISTRY

Mole Concept

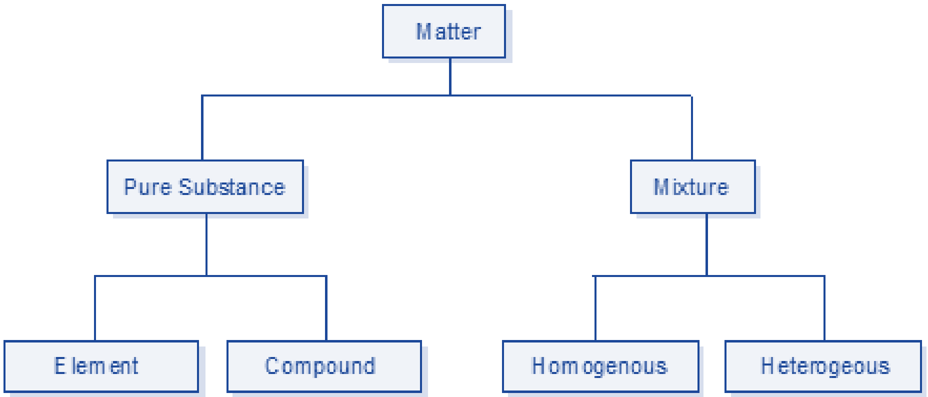
Matter:

Anything that exhibits inertia is called matter.

The quantity of matter is its mass.

Classification of Matter:-

Based on chemical composition of various substances..



Measurement of Temperature

Three scales of temperature

- Kelvin scale (K)
- Degree Celsius scale ($^{\circ}$C)
- Degree Fahrenheit scale ($^{\circ}$F)

Relations between the scales:

- $^{\circ}F = 9/5(^{\circ}C) + 32$
- $K = {}^{\circ}C + 273$

0 K temperatures is called absolute zero.

Dalton's Atomic Theory:

- Every matter consists of indivisible atoms.
- Atoms can neither be created nor destroyed.
- Atoms of a given element are identical in properties
- Atoms of different elements differ in properties.
- Atoms of different elements combine in a fixed ratio to form molecule of a compound.

Laws of Chemical Combination:

Law of conservation of mass:

"For any chemical change total mass of active reactants are always equal to the mass of the product formed"

Law of constant proportions:

"A chemical compound always contains same elements in definite proportion by mass and it does not depend on the source of compound".

Law of multiple proportions:

"When two elements combine to form two or more than two different compounds then the different masses of one element B which combine with fixed mass of the other element bear a simple ratio to one another"

Law of reciprocal proportion:

" If two elements B and C react with the same mass of a third element (A), the ratio in which they do so will be the same or simple multiple if B and C reacts with each other".

Gay Lussac's law of combining volumes:

"At given temperature and pressure the volumes of all gaseous reactants and products bear a simple whole number ratio to each other".

Atomic and Molecular Masses:

Atomic Mass:

- Mass of an atom.
- Reported in atomic mass unit "amu" or unified mass "u"
- One atomic mass unit i.e. amu, is the mass exactly equal to one-twelfth the mass of one carbon-12 atom.

Molecular Mass:

- Mass of a molecule of covalent compound.
- It is equal to the sum of atomic masses of all the elements present in the molecule.

Formula Unit Mass

- Mass of a molecule of an ionic compound
- It is also equal to the sum of atomic masses of all the elements present in the molecule

Mole Concept:

Mole:

- Unit of amount of substance.
- One mole amount of substance that contains as many particles or entities as there are atoms in exactly 12 g of the ^{12}C isotope.

Molar mass:

- Mass of one mole of a substance in gram
- Molar mass in gram in numerically equal to atomic/molecular/formula mass in amu or u.

?Percentage composition:

Mass percentage of an element in a compound = (Mass of that element in the compound / Molecular mass of the compound)×100

Percentage yield:

- It is the ratio of actual yield of the reaction to the theoretical yield multiplied by 100.
- % yield = (Actual yield /Theoretical yield) ×100

Empirical formula and molecular formula:

Molecular Formula:-

Represents the actual number of each individual atom in any molecule is known as molecular formula.

Empirical Formula:-

Expresses the smallest whole number ratio of the constituent atom within the molecule.

Molecular formula = (Empirical formula)$_n$

Molecular weight = n × Empirical weight

also,

Molecular weight = 2 × Vapour density

Limiting Reagent:

The reactant which is totally consumed during the course of reaction and when it is consumed reaction stops.

For a balanced reaction reaction:

$A + B \rightarrow C + D$

B would be a limiting reagent if $n_A / n_B > n_B / n_A$

Similarly, A is a limiting reagent if $n_A / n_B < n_B / n_A$

Concentration of the solutions:

Mass by Mass Percentage:-

Amount of solute in gram present per 100 gm of the solution.

Mass percentage of solute = [(Mass of solute)/(Mass of solution)] x100

Mass by Volume Percentage:-

Amount solute in gram present per 100 mL of the solution.

Volume by Volume Percentage:-

Volume of solute per 100 mL of the solution

Volume by volume percentage of solute = [(Volume of solute)/(volume of solution)] x100

Parts per million (ppm) :-

The amount of solute in gram per million (106) gram of the solution.

ppm = [(mass of solute/mass of solution)]x 106

Mole fraction:-

Ratio of the moles of one component of the solution to the total number of moles of solution

Total mole fraction of all the components of a solution is equal to 1.

For binary solutions having two components A and B

Mole fraction of A

$X_A = (n_A)/(n_A+n_B)]$

Mole fraction of B

$X_B = (n_B)/(n_A+n_B)]$

or $X_B = 1- X_A$

Molarity(M):-

Number of moles of solute per 1000 mL of the solution.

M = (Number of moles of solute)/(Volume of solution in L)

Molality(m):-

number of moles of solute per 1000 gram of the solvent.

m = (Number of moles of solute)/(Weight of solvent in kg)

Gaseous & Liquid State

Revision Notes on States of Matter

Thus matter is classified mainly into three categories depending upon its physical state namely solid, liquid and gaseous states.

Distinction between three states of matter:

Sr. No	Property	Solid	Liquid	Gas
1	Shape	Definite shape	Indefinite shape	Indefinite shape
2	Volume	Definite Volume	Definite Volume	Indefinite Volume
3	Inter particular Forces	Strong Inter particular Forces	Comparatively weaker Inter particular Forces	Interparticular forces are negligible
4	Inter particular Space	Negligible inter particular space	Comparatively large inter particular space	Very large Inter particular space
5	Particular Motion	Particle motion is restricted to vibratory motion.	Particle motion is very slow	Particle motion is very rapid and also random.
6	Packing of Particles	Particles are very Closely packed	Particles are loosely packed	Particles are very loosely packed
7	Compressibility	Incompressible	Compressible	Highly Compressible
8	Density	Very High Density	Low Density	Very low density

Parameters of Gases

The characteristics of gases are described in terms of following four parameters

- Mass
- Pressure
- Volume
- Temperature

1. **Mass (m):**

The mass of the gas is related to the number of moles as

$n = w/M$

Where n = number of moles

w = mass of gas in grams

M = molecular mass of the gas

2. Volume (V):

Since gases occupy the entire space available to them, therefore the gas volume means the volume of the container in which the gas is enclosed.

Units of Volume: Volume is generally expressed in **litre (L), cm^3** & **dm^3**
$1m^3 = 10^3$ litre $= 10^3\ dm^3 = 10^6\ cm^3$.

3. Pressure:

Pressure of the gas is due to its collisions with walls of its container *i.e.* the force exerted by the gas per unit area on the walls of the container is equal to its pressure.

$$P(pressure) = \frac{F(Force)}{A(Area)} = \frac{Mass \times Accelaration}{Area}$$

Pressure is exerted by a gas due to kinetic energy of its molecules.

As temperature increases, the kinetic energy of molecules increases, which results in increase in pressure of the gas. So, pressure of any gas is directly proportional to its temperature.

Units of Pressure:

The pressure of a gas is expressed in **atm, Pa, Nm^{-2}, bar** and **lb/In^2 (psi).**
760 mm = 1 atm = 10132.5 KPa = 101325 Pa = 101325 Nm^{-2}
760 mm of Hg = 1.01325 bar = 1013.25 milli bar = 14.7 $lb/2n^2$ (psi)

3. Temperature (T):

Temperature is defined as the degree of hotness. The SI unit of temperature is Kelvin. °C and °F are the two other units used for measuring temperature. On the Celsius scale water freezes at 0°C and boils at 100°C where as in the Kelvin scale water freezes at 273 K and boils at 373 K.

K = °C + 273.5

F = (9/5) °C + 32

Gas Laws:

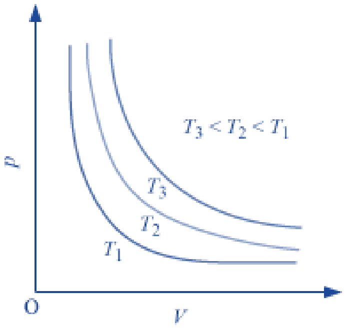
1. Boyle's Law:-

"At constant temperature, the pressure of a fixed amount (i.e., number of moles n) of gas varies inversely with its volume".

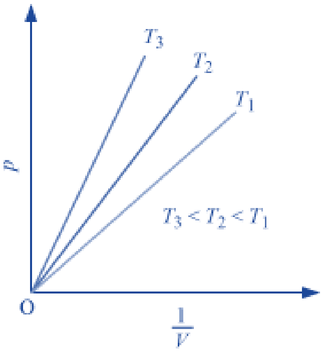
$$P_1V_1 = P_2V_2 = Constant \Rightarrow \frac{P_1}{P_2} = \frac{V_1}{V_2}$$

Graphical Representation of Boyle's Law :

- A plot of *P* versus 1/*V* at constant temperature for a fixed mass of gas would be a straight line passing through the origin.
- A plot of *P* versus *V* at constant temperature for a fixed mass of a gas would be a rectangular hyperbola.

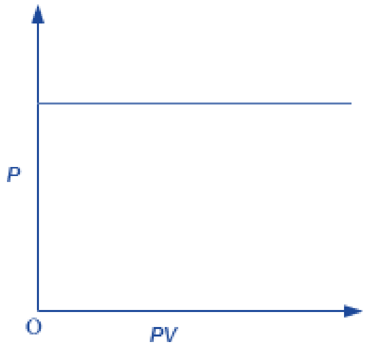


p vs V graph



p vs $\frac{1}{V}$ graph

- A plot of *P* (or *V*) versus *PV* at constant temperature for a fixed mass of a gas is a straight line parallel to the *PV axis.*



P vs PV graph

2. **Charles' Law:-**

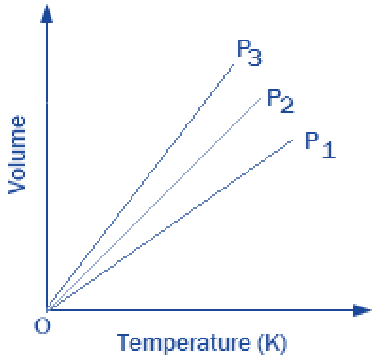
"At constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature"

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = constant$$

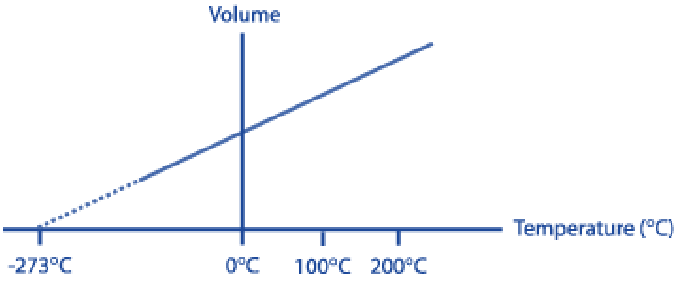
Or log V – log T = Constant

Graphical Representation of Charles's Law :

1. For a definite mass of the gas a plot of V vs T (^{o}K) at constant pressure is a straight line passing through the origin.



2. A plot of V vs t (^{o}C) at constant pressure is a straight line cutting the temperature axis at -273 ^{o}C



3. **Combined Gas Law:-**

This law states that "*at constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature".*

The combination of Boyle's Law and Charles' Law:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

4. **Gay Lussac's Law:**

$$P \alpha T \text{ (at constant volume)}$$

$$\Rightarrow P = kT \Rightarrow \frac{P}{T} = k = constant$$

Where,

***P* = Pressure of Gas**

***T* = Absolute Temperature**

If the pressure and temperature of a gas changes from P_1 & T_1 to P_2 & T_2, volume remaining constant, we have

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = constant$$

$$\text{or } \log P - \log T = \text{constant}$$

$$P_t = P_0(1 + \frac{t}{273.15})$$

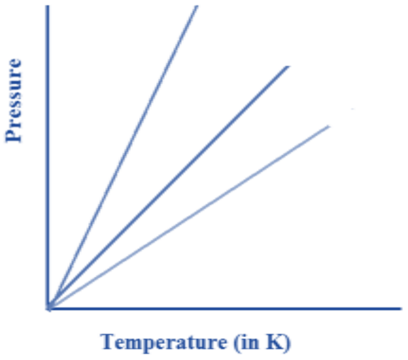
where,

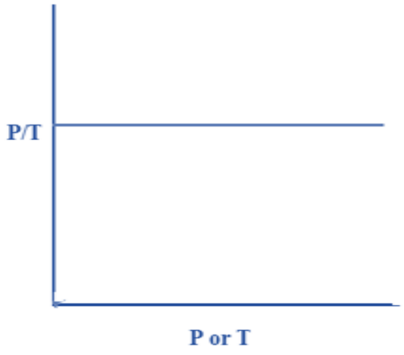
P_t = Pressure of gas at t °C

Po = Pressure of gas at 0 °C

t = Temperature in °C.

Graphical Representation of Gay-Lussac's Law





5. **Avogadro Law:**

   "Samples of different gases which contain the same number of molecules (any complexity, size, shape) occupy the same volume at the same temperature and pressure".

   It follows from Avogadro's hypothesis that $V \alpha n$ (when T and P are constant).

   Mathematically

$$V \alpha n \Rightarrow V = kn$$

$$\Rightarrow \frac{V}{n} = k = Constant$$

6. **Ideal Gas Equation:**

   Ideal gas obey all the three laws i.e. Boyle's, Charles's, and Avogadro's law strictly.

   pv = nRT

   Where,

   where R is the constant of proportionality or universal gas constant

   The value of R was found out to be

   R = 8.314 J mol^{-1} K^{-1}

$R = 0.0821$ litre atm K^{-1} mol^{-1}

$R = 2$ cal K^{-1} mol^{-1}

Ideal gas equation is also known as equation of state.

7. **Dalton's law of partial pressures:**

The total pressure of mixture of non-reactive gases at constant temperature and pressure is equal to the sum of the individual partial pressures of the gases.

$p_{total} = p_1 + p_2 + p_3 + p_4 \ldots$

$p_1 = x_1 \, p_{total}$

$p_2 = x_2 \, p_{total}$

$p_3 = x_3 \, p_{total}$

Aqueous tension:-

Pressure exerted by saturated water vapour.

$p_{dry\ gas} = p_{Total}$ –Aqueous Tension

Gas Eudiometry:

Gas	Absorbing Reagent used:
O_3	Turpentine oil
O_2	Alkaline pyrogallol
NO	$FeSO_4$ solution
CO_2,SO_2	Alkali solution (NaOH, KOH, $Ca(OH)_2$, $HOCH_2CH_2NH_2$, etc.)
NH_3	Acid solution or $CuSO_4$ solution

Equation for combustion of hydrocarbons:

$C_xH_y + (x + y/4)\ O_2 \longrightarrow xCO_2 + y/2\ H_2O$

Kinetic molecular theory of gases:

- Gases are made of large number of identical particles (atoms or molecules), which are very small and perfectly hard spheres.
- The actual volume of the molecules is negligible as compare to the space between them and hence they are considered as the point masses.
- Interaction between the particles is negligible.
- Particles of a gas are always in constant and random motion and the collision between them is perfectly elastic.
- The average kinetic energy of the particles of a gas is directly proportional to the absolute temperature.
- Pressure of the gas is due to the collision between gas molecules and walls of the container.

The Kinetic Equation

$$pV = \frac{1}{3}mnu^2$$

$$\Rightarrow u^2 = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}}$$

Velocities of gas molecules

- **Average Velocity**

Average velocity =

$$\frac{u_1 + u_2 + u_3 + u_4 + u_n}{n} = \frac{n_1u_1 + n_2u_2 + n_3u_3 + . + n_nu_n}{n_1 + n_2 + n_3 + . + n_4}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8pV}{\pi M}}$$

- **Root Mean Square Velocity:-**

Maxwell proposed the term U_{rms} as the square root of means of square of all such velocities.

$$U_{rms}^2 \frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + u_n^2}{n} = \frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + . + n_nu_n^2}{n_1 + n_2 + n_3 + . + n_4}$$

also

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV}{M}}$$

- **Most probable velocity:-**

It is the velocity which is possessed by maximum no. of molecules.

$$U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2pV}{M}}$$

Furthermore

$$u_{mp} : u_{av} : u_{rms} ::: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : 1.224$$

$$\Rightarrow u_{mp} : u_{av} : u_{rms} ::: 1 : 1.128 : 1.224$$

Kinetic Energy of Gas

As per kinetic equation

$$pV = \frac{1}{3}mnu^2$$

For 1 mole m × n = Molecular Mass (M)

$$pV = \frac{1}{3}Mu^2 = \frac{2}{3} \times \frac{1}{2}Mu^2 = \frac{2}{3} \times \frac{2}{3} \times K.E./mole = \frac{3}{2}RT$$

Also

$$\frac{K.E.}{Molecule} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT$$

Where k is the Boltzmann constant (k = R / N)

Graham's Law of Diffusion/Effusion:

1. **Diffusion:** ability of a gas to spread and occupy the whole available volume irrespective of other gases present in the container
2. **Effusion:** process by which a gas escapes from one chamber of a vessel through a small opening or an orifice

$$R = \frac{Volume\ Diffused}{Time\ Taken} = \frac{V}{T}$$

r ∝ 1 / √d

where r is the rate of diffusion and d is the density of the gas.

Now, if there are two gases A and B having r_1 and r_2 as their rates of diffusion and d_1 and d_2 their densities respectively. Then

$r_1 \propto \frac{1}{\sqrt{d_1}}_1$

and

$r_2 \propto \frac{1}{\sqrt{d_2}}$

or

$$,\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}\ (at\ same\ T\ and\ P)$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

The rate of diffusion (r) of a gas at constant temperature is directly preoperational to its pressure

$$\frac{r_1}{r_2} = \frac{P_2}{P_1} = \sqrt{\frac{M_2}{M_1}}$$

Deviation from ideal gas behavior:

For ideal gas,

Compressibility factor i.e. Z = PV/nRT =1

For non-Ideal gas, Z ≠1

Thus for non-ideal gas,Z can be < 1 or > 1

When Z < 1, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour.

When Z > 1, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behaviour.

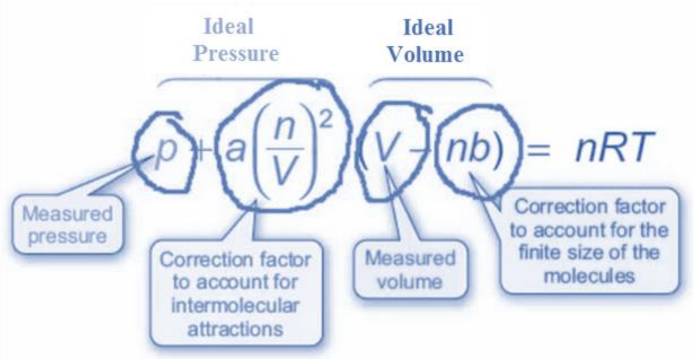
1. **Causes of deviation from ideal behaviour:**

   The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.
   The forces of attraction between gas molecules are negligible.

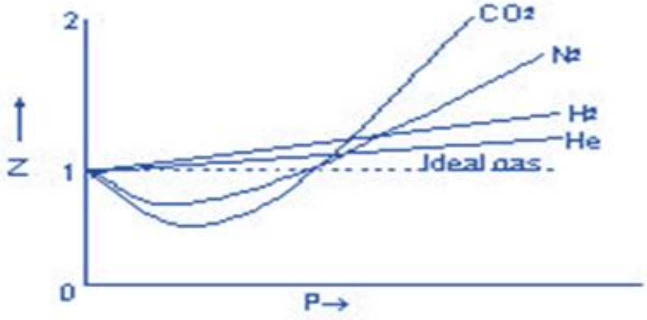
2. **Van der waals Equation:**

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

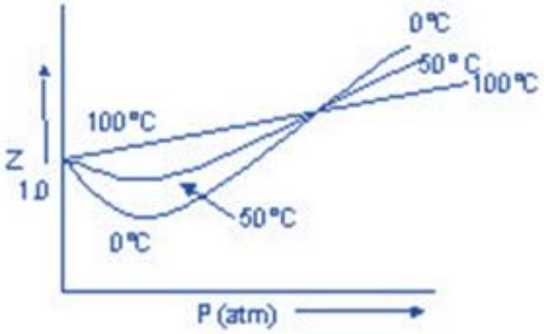
Where,
a and b are van der waals constants.
At low pressures:
PV = RT – a/V
or
PV < RT
This accounts for the dip in PV vs P isotherm at low pressure



At fairly high pressures



a/V^2 may be neglected in comparison with P. The Vander Waals equation becomes
PV = RT + Pb
or
PV > RT
This accounts for the rising parts of the PV vs P isotherm at high pressures



Boyle's Temperature (T_b) :- Temperature at which real gas obeys the gas laws over a wide range of pressure.

$T_b = a / Rb = 1/2\ T_1$

Liquefaction of gases:

- **Critical temperature (Tc):-** temperature at which a gas liquefies. $T_c = 8a / 27Rb$
- **Critical Volume: (V_c) :-** volume of one mole of a gas at critical temperature.$V_c = 3b$
- **Critical pressure (pc):-** pressure of A gas at its critical temperature. $P_c = a/27b^2$
- **Molar heat capacity of ideal gases:-**the amount of heat required to raise the temperature of 1 mole of a gas trough 1^0C.

  $C_P - C_V = R$ &

  Poisson's ratio (γ) = C_P/C_V

  For monatomic gas C_p = 5 cal and C_v =3 cal

  γ = 5/3 = 1.67

  For diatomic gas C_p = 7 cal and C_v = 5 cal

  γ =7/5 = 1.4

  For polyatomic gas C_p = 8 cal and C_v= cal

  γ = 8/6 = 1.33

  Also $C_p = C_p m$,

  Where, C_p and C_v are specific heat and m, is molecular weight.

Liquid State:

1) Surface Tension (γ):- It is the force acting at right angles to the surface along one centimeter length of the surface.

Surface tension (γ) = Work done / Change in area

Units: **CGS:** dcm^{-1}

SI: Nm^{-1}

The surface of the liquid tends to contract to the smallest possible area for a given volume of the liquid i.e. spherical shape.

Surface Tension of liquid decreases with increase of temperature and becomes zero at its critical temperature.

Surface Tension in everyday life:

- Cleansing action of soap and detergents.
- Efficacy of tooth pastes, mouth washes and nasal jellies.

Viscosity:

It is the force of friction which one part of the liquid offers to another part of the liquid.

Coefficient of viscosity: is the force per unit area required to maintain unit difference of velocity between two parallel layers in the liquid one unit apart.

Units: CGS: $dscm^{-1}$

S.I: Nsm^{-1}

Viscosity of liquid decreases with increase in temperature.

Solid State

Revision Notes on Solid State

Classification of solids:

Crystalline and Amorphous solids:

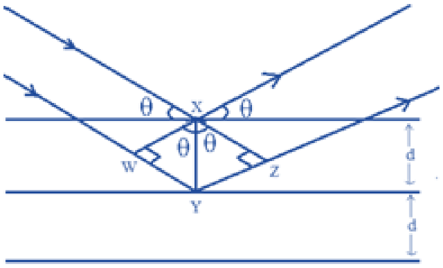
Based on binding forces:

Bragg Equation:

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

Where

- d= distance between the planes
- n = order of refraction
- θ= angel of refraction
- λ = wavelength



Crystal Systems:

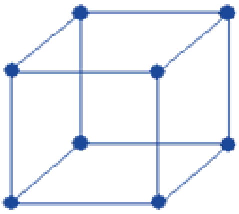
- Total number of crystal systems: 7
- Total number of Bravais Lattices: 14

Crystal Systems	Bravais Lattices	Intercepts	Crystal angle	Example
Cubic	Primitive, Face Centered, Body Centered	a = b = c	$a = b = g = 90^o$	Pb,Hg,Ag,Au Diamond, NaCl, ZnS
Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	a ≠ b ≠ c	$a = b = g = 90^o$	KNO_2, K_2SO_4
Tetragonal	Primitive, Body Centered	a = b ≠ c	$a = b = g = 90^o$	TiO_2,SnO_2
Monoclinic	Primitive, End Centered	a ≠ b ≠ c	$a = g = 90^o, b \neq 90^o$	$CaSO_4,2H_2O$
Triclinic	Primitive	a ≠ b ≠ c	$a \neq b \neq g \neq 90^0$	$K_2Cr_2O_7$, $CaSO_45H_2O$
Hexagonal	Primitive	a = b ≠ c	$a = b = 90^0, g = 120^o$	Mg, SiO_2, Zn, Cd
Rhombohedra	Primitive	a = b = c	$a = g = 90^o, b \neq 90^o$	As, Sb, Bi, $CaCO_3$

Number of atoms in unit cells.

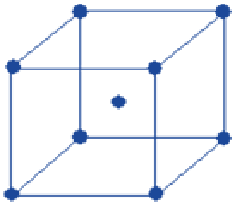
Primitive cubic unit cell:

- Number of atoms at corners = 8×1/8 =1
- Number of atoms in faces = 0
- Number of atoms at body-centre: = 0
- Total number of atoms = 1



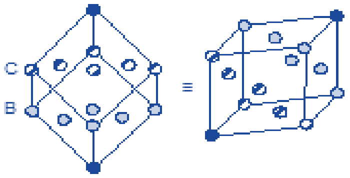
Body-centred cubic unit cell:

- Number of atoms at corners = 8×1/8 =1
- Number of atoms in faces = 0
- Number of atoms at body-centre: =1
- Total number of atoms = 2



Face-centred cubic or cubic-close packed unit cell:

- Number of atoms at corners = 8×1/8 =1
- Number of atoms in faces = 6×1/2 = 3
- Number of atoms at body-centre: = 0
- Total number of atoms = 4



Packing Efficiency

Packing Efficiency = (Volume occupied by all the atoms present in unit cell / Total volume of unit cell)×100

Close structure	Number of atoms per unit cell ‘*z*’.	Relation between edge length ‘*a*’ and radius of atom ‘*r*’	Packing Efficiency
hcp* and *ccp* or *fcc	4	r = a/(2√2)	74%
bcc	2	r = (√3/4)a	68%
Simple cubic lattice	1	r = a/2	52.4%

Density of crystal lattice:

r = (Number of atoms per unit cell × Mass number)/(Volume of unit cell × N_A)

$$r = \frac{Number\ of\ unit\ cells \times Mass\ number}{Volume\ of\ Unit\ Cells \times N_A}$$

or

$$r = \frac{z \times M}{V \times N_A}$$

Octahedral and Tetrahedral Voids:

Number of octahedral voids = Number of effective atoms present in unit cell

Number of tetrahedral voids = 2×Number of effective atoms present in unit cell

So, Number of tetrahedral voids = 2× Number of octahedral voids.

Coordination numbers and radius ratio:

Coordination numbers	Geometry	Radius ratio (x)	Example
2	Linear	$x < 0.155$	BeF_2
3	Planar Triangle	$0.155 \leq x < 0.225$	$AlCl_3$
4	Tetrahedron	$0.225 \leq x < 0.414$	ZnS
4	Square planar	$0.414 \leq x < 0.732$	$PtCl_4^{2-}$
6	Octahedron	$0.414 \leq x < 0.732$	NaCl
8	Body centered cubic	$0.732 \leq x < 0.999$	CsCl

Classification of Ionic Structures:

Structures	Descriptions	Examples
Rock Salt Structure	Anion(Cl^-) forms fcc units and cation(Na^+) occupy octahedral voids. Z=4 Coordination number =6	NaCl, KCl, LiCl, RbCl
Zinc Blende Structure	Anion (S^{2-}) forms fcc units and cation (Zn^{2+}) occupy alternate tetrahedral voids Z=4 Coordination number =4	ZnS, BeO
Fluorite Structures	Cation (Ca^{2+}) forms fcc units and anions (F^-) occupy tetrahedral voids Z= 4 Coordination number of anion = 4 Coordination number of cation = 8	CaF_2, UO_2, and ThO_2
Anti- Fluorite Structures	Oxide ions are face centered and metal ions occupy all the tetrahedral voids.	Na_2O, K_2O and Rb_2O.
Cesium Halide Structure	Halide ions are primitive cubic while the metal ion occupies the center of the unit cell. Z=2 Coordination number of = 8	All Halides of Cesium.
Pervoskite Structure	One of the cation is bivalent and the other is tetravalent. The bivalent ions are present in primitive cubic lattice with oxide ions on the centers of all the six square faces. The tetravalent cation is in the center of the unit cell occupying octahedral void.	$CaTiO_3$, $BaTiO_3$
Spinel and Inverse Spinel Structure	Spinel :$M^{2+}M_2^{3+}O_4$, where M^{2+} is present in one-eighth of tetrahedral voids in a FCC lattice of oxide ions and M^{3+}ions are present in half of the octahedral voids. M^{2+} is usually Mg, Fe, Co, Ni, Zn and Mn; M^{3+} is generally Al, Fe, Mn, Cr and Rh.	$MgAl_2O_4$, $ZnAl_2O_4$, Fe_3O_4,$FeCr_2O_4$ etc.

Defects in crystal:

Stoichiometric Defects

1. **Schottky Defects**
   - Some of the lattice points in a crystal are unoccupied.
   - Appears in ionic compounds in which anions and cations are of nearly same size.
   - Decreases the density of lattice
   - Examples: NaCl and KCl

2. **Frenkel Defects**
   - Ion dislocate from its position and occupies an interstitial position between the lattice points
   - Appears in crystals in which the negative ions are much larger than the positive ion.
   - Does not affect density of the crystal.
   - Examples: AgBr, ZnS

Non-Stoichiometric Defects

1. **Metal Excess defect:**
   - Metal excess defect occurs due to
   - anionic vacancies or
   - presence of extra cation.
   - F-Centres: hole produced due to absence of anion which is occupied by an electron.

2. **Metal deficiency defect:**
   - Metal deficiency defect occurs
   - Due to variable valency of metals
   - When one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring two charges instead of one

Structure of Atom

Structure of Atom

Subatomic Particles:

Name	Electron	Proton	Neutron
Symbol	e-	p	n
Approximate relative mass	1/1836	1	1
Mass in kg	9.109×10^{-31}	1.673×10^{-27}	1.675×10^{-27}
Mass in amu	5.485×10^{-4}	1.007	1.008
Charge (coulomb)	1.602×10^{-19}	1.602×10^{-19}	0
Actual Charge (e.s.u)	4.8×10^{-10}	4.8×10^{-10}	0

Atomic Models:

Thomson's Atomic Model (Plum – pudding model):-

Postulate: -Atom is a sphere of positive charge in which number of electrons are embedded.

Limitations: - Could not satisfactorily explain the results of scattering experiment carried out by Rutherford.

Rutherford's Model:

Postulates:-

- Almost all the positive charge and mass of atom is present in its nucleus.
- Electrons revolve around the nucleus in circular orbits.
- There is strong electrostatic attraction between nucleus and electrons

Limitations: - Could not explain stability and electronic structure of atom.

Atomic Terms

Terms	Definition / Explanation
Atomic Number (Z)	Number of protons or electrons of neutral atom.
Mass Number (A)	Total number of protons and neutrons in an atom
Nucleons	Protons and neutrons are present in a nucleus. So, these fundamental particles are collectively known as nucleons
Isotopes	Atoms of the element with same atomic number but different mass number e.g. $_1H^1$, $_1H^2$, $_1H^3$.

Isobars	Atoms having the same mass number but different atomic numbers, e.g. ${}_{15}P^{32}$ and ${}_{16}S^{32}$
Isotones	Atoms having the same number of neutrons but different number of protons or mass number, e.g. ${}_{6}C^{14}$, ${}_{8}O^{16}$, ${}_{7}N^{15}$
Isoelectronic	Atoms, molecules or ions having same number of electrons e.g. N_2,CO, CN^-
Nuclear isomers	atoms with the same atomic number and same mass number but with different radioactive properties. Example of nuclear isomers is Uranium –X (half life 1.4 min) and Uranium –Z (half life 6.7 hours
Isosters	Molecules having same number of atoms and also same number of electrons are called isosters. E.g., N_2 and CO

Electromagnetic Waves

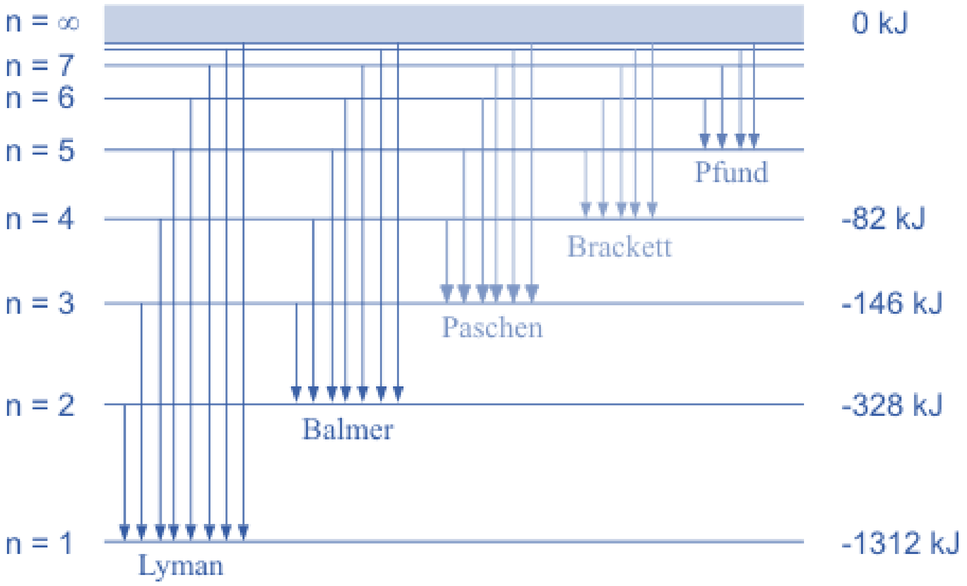
Atomic spectrum of hydrogen atom:

$$\frac{1}{\lambda} = \bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

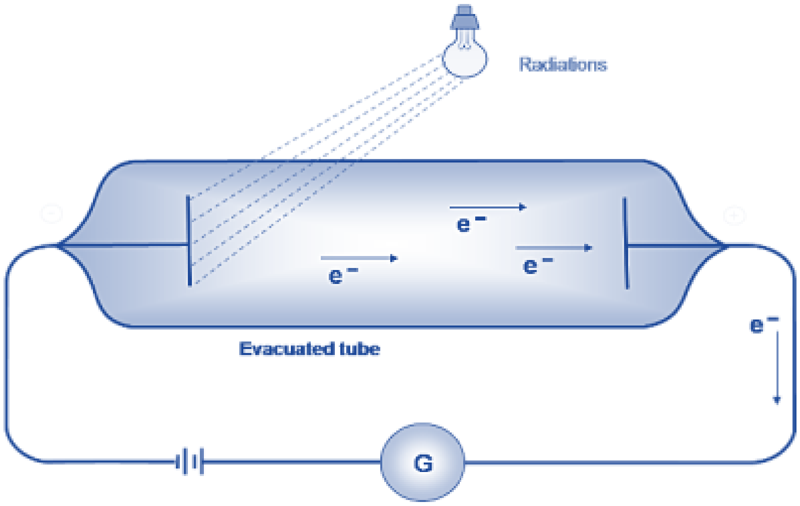
Where, R_H = Rydberg constant (108978 cm^{-1})

n_1 and n_2 have integral values as follows

n_1	n_2	Spectral Series	Spectral region
1	2,3,4…	Lyman	UV
2	3,4,5…	Balmer	Visible
3	4,5,6…	Pascher	IR
4	5,6,7…	Brackett	IR
5	6,7,8…	Pfund	IR



Photoelectric effect:



- Ejection of electrons takes place from the surface of metal when light of suitable frequency fall on it.
- Minimum frequency required for ejection of electron is called threshold frequency (v_o).
- Energy of the ejected electrons is directly proportional to the frequency of radiation.
- Number of electrons ejected per second depends on the intensity of radiation.
- $hv - hv_o = 1/2 m_e v^2$

Planck's quantum theory:

Substances radiate or absorb energy discontinuously in the form of energy packets

The smallest packet of energy is called quantum. In case of light the quantum is known as photon.

The energy of a quantum is directly proportional to the frequency of the radiation.

E = hv were v is the frequency of radiation and h is Planck's constant having the value 6.626×10^{-27} erg sec or 6.626×10^{-34} J sec.

A body can radiate or absorb energy in whole number multiples of quantum hn, 2hv,3hv………..nhv, where n is the positive integer.

Bohr's atomic model:

Electrons revolve around the nucleus in circular orbits of fixed energy.

Electron revolve only in those orbits whose angular momentum (mvr) is an integral multiple of h/2Π.

Electron absorbs energy in the form of EMR, when it jumps from lower energy level (ground state) to higher energy level (excited state) and vice-versa.

Energy absorbed or released in an electron jump, (dE) is given by $dE = E_2 – E_1 = hv$
Energy of stationary state oh hydrogen atom $(E_n) = -R_H (1/n^2)$
For an hydrogen like species i.e. He^+, Li^{2+} with atomic number Z
Radius of nth orbit $(r_n) = 52.9 \times n^2/z$ pm
Energy of nth orbit $(E_n) = -2.18\times10^{-18}(Z^2/n^2) = –13.6 \times(Z^2/n^2)$ eV $= 313.6 \times(Z^2/n^2)$ kcal /mole
Velocity of electron $(v) = (2.18 \times10^8)\ z/n$ cms^{-1}

Where n = 1,2,3,4…

Limitations of Bohr's theory:

- Failed to explain the spectra of atoms having more than one electron.
- Failed to account for the splitting of spectral line source of a spectrum is placed in a strong magnetic or electric field.
- Dual nature of particle and the uncertainty principle was ignored in the Bohr's atomic model.

de- Broglie equation:

λ = h/mv = h/p

Heisenberg's uncertainty principle:

$$\Lambda x \times \Delta v \geqslant \frac{h}{4\pi m}$$

It is impossible to determine simultaneously, the exact position and exact momentum of an electron.

Quantum Numbers:

Principal quantum number (n):

- It tells the main shell in which the electron resides and the approximate distance of the electron from the nucleus.
- Maximum number of electrons a shell can accommodate is $2n^2$.

Azimuthal or angular momentum quantum number (l):

- It represents the number of subshells present in the main shell.
- These subsidiary orbits within a shell will be denoted as s,p,d,f…
- This tells the shape of the subshells.
- For a given value of n, there are n possible values of l starting from 0 to (n-1)

Value of l	0	1	2	3	4
Notation of sub shell	s	p	d	f	g

The magnetic quantum number (m):

- It determines the number of preferred orientations of the electron present in a subshell.
- For a given value of l, there are (2l+1) possible values of m starting from –l to +l.

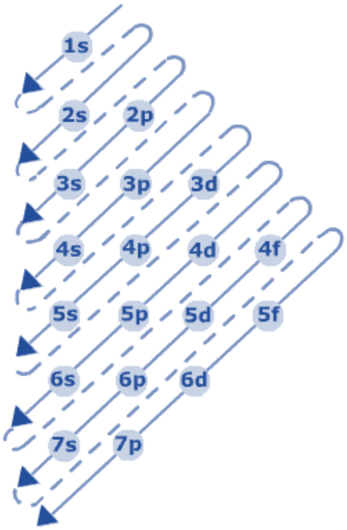
Value of l	0	1	2	3
Notation of sub shell	s	p	d	f
Values of m	0	-1,0,1	-2,-2,0,1,2	-3,-2,-1,0,1,2,3

The spin quantum number (s)

- It determines the direction of spin of electron in an orbit.
- There are only two possible values for spin quantum number i.e. -1/2 ,+1/2.

Rules for filling of electrons in various orbitals :

Aufbau Principle:



- Electrons are added one by one to the various orbitals in order of their increasing energy starting with the orbital of lowest energy.
- In neutral isolated atom, the lower the value of (n+ l) for an orbital, lower is its energy
- The increasing order of energy of various orbital is : 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d ..

Pauli's Exclusion principle :-

An orbital can contain a maximum number of two electrons and these two electrons must be of opposite spin.

Hund's rule of maximum multiplicity :-

Electron pairing in p, d and f orbital cannot occur until each orbital of a given subshell contains one electron each or is singly occupied".

Exceptional Configurations

Stability of half filled and completely filled orbitals

Cu has 29 electrons. Its expected electronic configuration is

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^9$

But a shift of one electron from lower energy 4s orbital to higher energy 3d orbital will make the distribution of electron symmetrical and hence will impart more stability.

Thus the electronic configuration of Cu is

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

Fully filled and half filled orbitals are more stable

Chemical Bonding

Revision Notes on Chemical Bonding

Chemical bond:-

Chemical bond is the attractive force which holds various constituents together in a molecule.

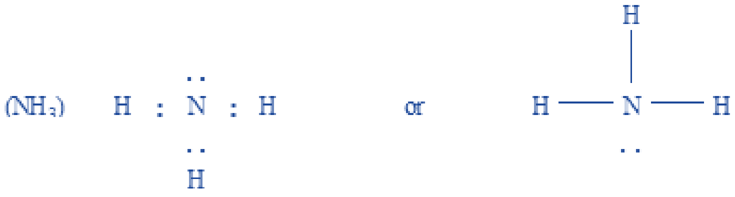
There are three types of chemical bonds: Ionic Bond, Covalent Bond, Co-ordinate Bond.

Octet Rule:

Atoms form chemical bonds in order to complete their octet i.e. eight electrons in their valence shell.

Lewis Structures:

- Pair of bonded electrons is by means of a 'dash' (-) usually called a 'bond'.
- Lone pairs or 'non-bonded' electrons are represented by 'dots'.
- Electrons present in the last shell of atoms are called valence electrons.



Exceptions to the Octet Rule:

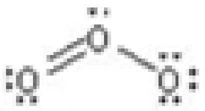
- Species with odd number of electrons**:** NO, NO_2,
- Incomplete octet for the central atom: LiCl, BeH_2 and BCl_3
- Expanded octet for the central atom: PF_5, SF_6 and H_2SO_4

Formal Charge:

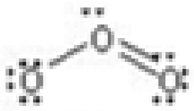
- Formal charge is the difference between the number of valence electrons in an isolated atom and number of electrons assigned to that atoms in Lewis structure.
- Formal charge = [Total number of valence electrons in the free atom) - (Total number of lone pairs of electrons) -1/2(Total number of shared electrons i.e. bonding electrons)]

Resonance:

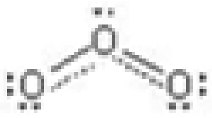
- For molecules and ions showing resonance it is not possible to draw a single Lewis structure.
- All the properties of such species can only be explained by two or more Lewis structures. Example: Resonance of O_3



(A)



(B)

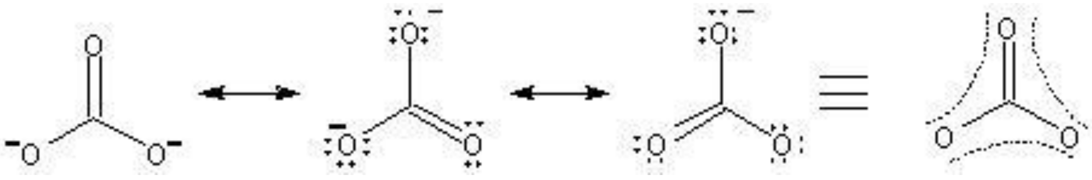


(C)

A and B are resonating or canonical structures and C is the resonance hybrid

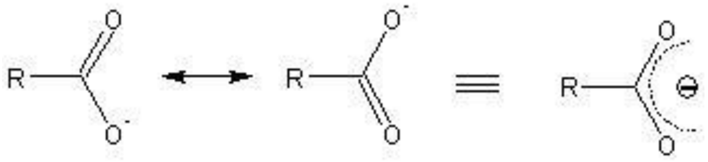
Some other examples

(i) CO_3^{2-} ion



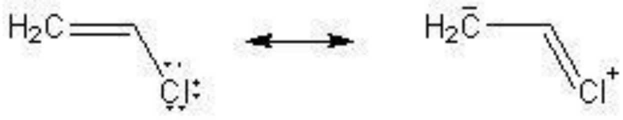
Example

(ii) Carbon-oxygen bond lengths in carboxylate ion are equal due to resonance.



(iii) Benzene

(iv) Vinyl Chloride



Ionic Bonding:

Formation of Ionic Bond:

- Formation of ionic bond takes place between a metal and a non-metal by transfer of electron.
- Steps involved in formation of an ionic bond:

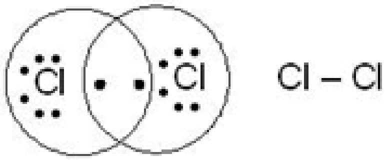
Steps	Equation	Energy involved
Formation of gaseous cations	$A(g) + I.E. \rightarrow A^{+}(g) + e$	Ionization Energy
Formation of gaseous anions	$X(g) + e \rightarrow X^{-}(g) + E.A$	Electron Affinity
Packing of ions of opposite charges to form ionic solids	$A^{+}(g) + X^{-}(g) \rightarrow AX(s) + \text{Energy}$	Lattice energy

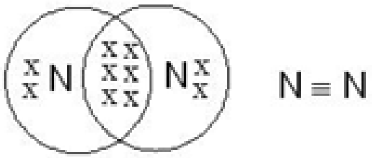
Conditions required of formation of ionic bonds:

- Low I.E of cation.
- High E.A of anion.
- High lattice energy.

Covalent Bonding:

- Covalent bond is formed between two non-metals by sharing of electrons.
- Electron pairs which participate in bonding are called bond pairs.
- Electron pairs which do not participate in bonding are called lone pairs.
- There could be single, double or triple covalent bonds between two elements depending on the number of electrons being shared.





VSEPR (Valence Shell Electron Pair Repulsion) Theory:

X	Shape	Examples
2	Linear	$HgCl_2/BeCl_2$
3	Triangular planar	BF_3
3	Angular	$SnCl_2$, NO_2
4	Tetrahedral	CH_4, BF_4^-
4	Trigonal Pyramidal	NH_3, PCl_3
4	Angular	H_2O
5	Trigonal bipyramidal	PCl_5, PF_5
5	Irregular tetrahedral	SF_4, IF_4^+
5	T-shaped	ClF_3, BrF_3
5	Linear	XeF_2, I_3^-
6	Octahedral	SF_6, PF_6^-
6	Square Pyramidal	IF_5
6	Square planar	XeF_4, ICl_4

- The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell.
- Order of the repulsion: Lone pair↔ Lone pair > Lone pair↔ Bond pair > Bond pair↔ Bond pair.
- Repulsion among the bond pairs is directly proportional to the bond order and electro negativity difference between the central atom and the other atoms.

Determination of shape of molecules using VSEPR theory:

- Calculate X using following method.

X = (No. of valence electrons of central atom) + (No. of other atoms) + (Negative charge on the molecule) – (Positive charge on the molecule)

Use the following chart to find the shape.

Rule:

It accounts for the covalent character in ionic compounds.

Covalency is favoured by

- Smaller cation .
- Larger anion and
- Large charge on either ion.

Dipole Moment:

- Dipole moment of any bond is the product of the net positive or negative charge and distance between the two charged ends, i.e., the bond length. i.e.

  Dipole moment (m) = electronic charge (e) × Distance (d) Dipole moment is measured in debye unit (D);
- Dipole moment of a molecule is vector addition of all the individual bond moments.

Percentage Ionic Character:

The percent ionic character =

$$\frac{Observed\ dipole\ moment}{Expected\ dipole\ moment} \times 100$$

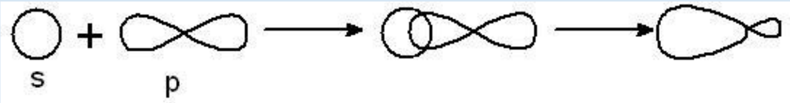
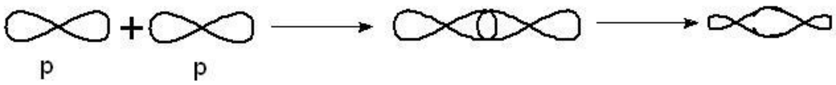
Hydrogen Bonding:

- Hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule or a part of a molecule and an electronegative atom (such as F,O, N) of another molecule (Inter-molecular hydrogen bonding) or another part of the same molecule (intramolecular hydrogen bonding).
- Intermolecular hydrogen bonding increases boiling point of the compound and also its water solubility
- Intramolecular hydrogen bonding decreases the boiling point of the compound and also its water solubility

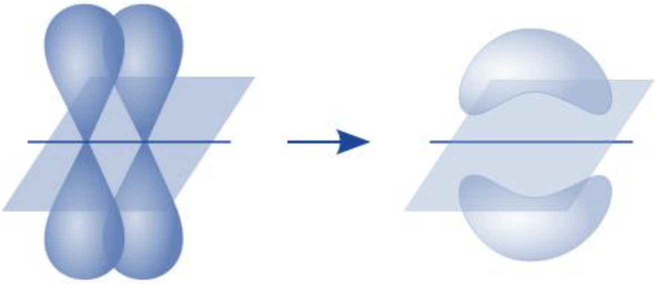
Valence bond theory (VBT):

- A covalent bond is formed by overlapping of valence shell atomic orbital of the two atoms having unpaired electron.
- There is maximum electron density between the bonding atoms.
- Greater the overlapping of atomic orbital higher is the strength of chemical bond.

- The bond formed by lateral overlap of two atomic orbitals having maximum overlapping on both sides of the line connecting the centres of the atoms is called a **π-bond**. A π-bond possess a plane of symmetry, often referred to as the nodal plane.
- **σ-Bond :** When covalent bond is formed by overlapping of atomic orbitals along the same axis it is called s - bond. Such type of bond is symmetrical about the line joining the two nuclei e.g.

(a) s-s overlapping	
(b) s-p overlapping	
(c) p-p overlapping	

- **π - Bond:** This type of bond is formed by the sidewise or lateral overlapping of two half filled atomic orbitals.



- |The strength of a bond depends upon the extent of overlapping of half-filled atomic orbitals. The extent of overlapping is between two atoms is always greater when there is end to end overlapping of orbitals than, when there is sidewise overlapping of orbitals. Hence s-bond is always stronger than p-bond.
- The average distance between the nuclei of the two bonded atoms in a molecule is called bond length and the energy required to break one mole of bonds of particular type in gaseous state is called Bond energy or Bond strength. The same amount of energy is released in formation of one mole of particular bond.

Hybridization:

- The mixing of dissimilar orbital of similar energies to form new set of hybrid orbital.
- Number of hybrid orbital formed is equal to the no. of orbital taking part in hybridization.
- Depending upon the different combination of s and p orbitals, these types of hybridization are known.

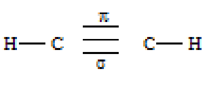
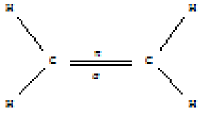
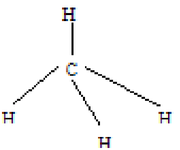
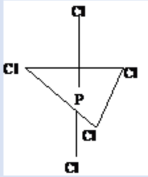
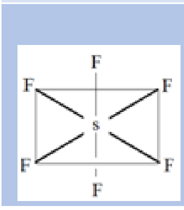
sp^3 hybridization: In this case, one s and three p orbitals hybridize to form four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals are oriented in a tetrahedral arrangement.

sp^2 hybridization: In this case one s and two p orbitals mix together to form three sp^2 hybrid orbitals and are oriented in a trigonal planar geometry.

The remaining p orbital if required form side ways overlapping with the other unhybridized p orbital of other C atom and leads to formation of $p_2C = CH_2$ bond as in H

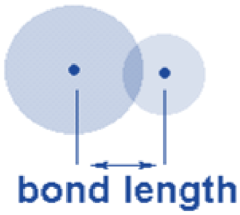
sp hybridization: In this case, one s and one p orbital mix together to form two sp hybrid orbitals and are oriented in a linear shape.

The remaining two unhybridised p orbitals overlap with another unhybridised p orbital leading to the formation of triple bond as in $HC\equiv CH$.

Hybridization	Total Number of orbitals taking part	Shape	Examples
sp	2 (one s and one p)	Linear	
sp^2	3 (one s and two p)	Trigonal planar	
sp^3	4 (one s and three p)	Tetrahedral	
sp^3d	5 (one s ,three p and one d)	Trigonal bipyramidal	
sp^3d^2	6 (one s ,three p and two d)	Octahedral	

Bond Characteristics:

Bond Length:



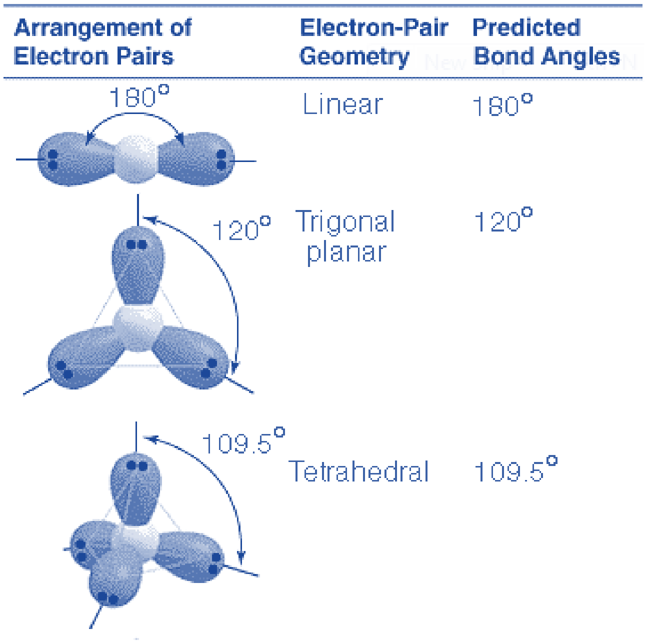
- The distance between the nuclei of two atoms bonded together is called bond length.
- It is expressed in angstrom (Å) units or picometer (pm).
- Bond length in ionic compound = $r_c^+ + r_a^-$
- Bond length in covalent compound (AB) = $r_A + r_B$

Important features of bond length

1. The bond length of the homonuclear diatomic molecules are twice the covalent radii.
2. The lengths of double bonds are less than the lengths of single bonds between the same two atoms, and triple bonds are even shorter than double bonds.Single bond > Double bond > Triple bond (decreasing bond length)
3. Bond length decreases with increase in s-character since s-orbital is smaller than a p – orbital.
   sp^3 C – H = 1.112Å: sp^2 C – H = 1.103Å; sp C – H = 1.08Å;
   (25% s-character as in alkanes) (33.3% s-character as in alkenes) (50% s-character as in alkynes)
4. Bond length of polar bond is smaller than the theoretical non-polar bond length.

Bond Angle:

Bond angel is the angle between two adjacent bonds at an atom in a molecule made up of three or more atoms.



Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
	Linear	180°
	Trigonal planar	120°
	Tetrahedral	109.5°

Bond angles mainly depend on the following three factors:

- **Hybridization:** Bond angle depends on the state of hybridization of the central atom

Hybridization	Bond angle	Example
sp^3	$109^o28'$	CH_4
sp^2	120^o	BCl_3
sp	180^o	$BeCl_2$

Generally s- character increase in the hybrid bond, the bond angle increases.

- **Lone pair repulsion:** Bond angle is affected by the presence of lone pair of electrons at the central atom. A lone pair of electrons at the central atom always tries to repel the shared pair (bonded pair) of electrons. Due to this, the bonds are displaced slightly inside resulting in a decrease of bond angle.
- **Electronegativity:** If the electronegativity of the central atom decreases, bond angle decreases.

Bond Energy or Bond Strength:

- The amount of energy required to break a bond in molecule is called bond energy.
- Bond energy of sigma bond is more than that of a π-bond.
- Bond energy increases with decrease in bond length

  $C \equiv C > C = C > C - C$ (decreasing bond length)

  $s < p < sp < sp^2 < sp^3$
- The bond energy decreases with increase in number of lone pairs on the bonded atom.

Molecular Orbital Theory:

- Molecular orbital are formed by linear combination of atomic orbital (LCAO)
- Atomic orbital of all the atoms are assumed to interfere with each other in the form of waves.
- Bonding molecular orbital are formed by constructive interference of atomic orbital.
- Anti-bonding orbital are formed by destructive interference of atomic orbital.
- Anti-bonding MO is of higher energy than Bonding MO.
- In simple homonuclear diatomic molecules the order of MO's based on increasing energy is

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s \begin{vmatrix} \pi\ 2p_y \\ \pi\ 2p_z \end{vmatrix}, \sigma 2p_x, \begin{vmatrix} \pi^*\ 2p_y \\ \pi^*\ 2p_z \end{vmatrix}, \sigma^* 2p_x, - - - - -$$

- For molecules including O_2 and above, the order is
-

$$\sigma 1s,\ \ \sigma^* 1s,\ \sigma 2s, \sigma^* 2s,\ \sigma 2p_x \begin{vmatrix} \pi\ 2p_y \\ \pi\ 2p_z \end{vmatrix},\begin{vmatrix} \pi^*\ 2p_y \\ \pi^*\ 2p_z \end{vmatrix},\ \sigma^* 2p_x,\ - - - - -$$

- **Bond Order:** Bond-order = 1/2 (no. of bonding electrons - No. of anti-bonding electrons).

Application of MOT to Homonuclear Diatomic Molecules

Species	Total number of electrons	Electronic configuration	Bond order	Magnetic Behaviour
H_2^+	1	s $1s^1$	(1-0)/2 =1/2	Paramagnetic
H_2	2	s $1s^2$	(2-0)/2 = 1	Diamagnetic
He_2^+	3	$s1s^2$, s^* $1s^1$	(2-1)/2 = 1/2	Paramagnetic
He_2	4	$s1s^2$, s^* $1s^2$	(2-2)/2 = 0	Molecule does not exist
O_2	16	$s1s^2$, s^* $1s^2$, $s2s^2$, s^*2s^2, $s2p^2_{x\,,}$ $p2p_y^2$, $p2p_z^2$, $p^*2p_y^1$, $p2p_z^1$	(10-6)/2 =2	Paramagnetic

Application of MOT to Heteronuclear Diatomic Molecules

Molecules/Ions	Total No. of electrons	Magnetic behaviour
CO	14	Diamagnetic
NO	15	Paramagnetic
NO^+	14	Diamagnetic
NO^-	16	Diamagnetic
CN	13	Paramagnetic
CN^-	14	Diamagnetic

Chemical Thermodynamics

Revision Notes on Chemical Thermodynamics:

Basic Terminology:

Terms	Explanation
System	Part of the universe under investigation.
Open System	A system which can exchange both energy and matter with its surroundings.
Closed System	A system which permits passage of energy but not mass, across its boundary.
Isolated system	A system which can neither exchange energy nor matter with its surrounding.
Surroundings	Part of the universe other than system, which can interact with it.
Boundary	Anything which separates system from surrounding.
State variables	The variables which are required to be defined in order to define state of any system *i.e.* pressure, volume, mass, temperature, surface area, etc.
State Functions	Property of system which depend only on the state of the system and not on the path. Example: Pressure, volume, temperature, internal energy, enthalpy, entropy etc.
Intensive properties	Properties of a system which do not depend on mass of the system *i.e.* temperature, pressure, density, concentration,
Extensive properties	Properties of a system which depend on mass of the system*i.e.* volume, energy, enthalpy, entropy etc.
Process	Path along which state of a system changes.
Isothermal process	Process which takes place at constant temperature
Isobaric process	Process which takes place at constant pressure
Isochoric process	Process which takes place at constant volume.
Adiabatic process	Process during which transfer of heat cannot take place between system and surrounding.
Cyclic process	Process in which system comes back to its initial state after undergoing series of changes.
Reversible process	Process during which the system always departs infinitesimally from the state of equilibrium *i.e.* its direction can be reversed at any moment.
Irriversible Process	This type of process is fast and gets completed in a single step. This process cannot be reversed. All the natural processes are of this type

Heat, energy and work:

Heat (Q):

- Energy is exchanged between system and surround in the form of heat when they are at different temperatures.
- Heat added to a system is given by a positive sign, whereas heat extracted from a system is given negative sign.
- It is an extensive property.
- It is not a state function.

Energy:

- It is the capacity for doing work.
- Energy is an extensive property.
- Unit : Joule.

Work (W):

- Work = Force × Displacement *i.e.* dW = Fdx
- Work done on the system is given by positive sigh while work done by the system is given negative sign.
- Mechanical Work or Pressure-Volume Work: work associated with change in volume of a system against an external pressure.
- Work done in reversible process: W=

$$\int_{V_1}^{V_2} PdV$$

W = – 2.303 nRT log v_2/v_1 = –2.303 nRT log p_1/p_2

- Wok done in isothermal reversible contraction of an ideal gas: ?W = – 2.303 nRT log v_2/v_1 = –2.303 nRT log p_1/p_2
- Unit : Joule.

Internal Energy (E or U):

- Sum of all the possible types of energy present in the system.
- ΔE = heat change for a reaction taking place at constant temperature and volume.
- ΔE is a state function.
- It is an extensive property.
- Value of ΔE is -ve for exothermic reactions while it is +ve for endothermic reactions.

First Law of Thermodynamics:

Energy can neither be created nor destroyed although it can be converted from one form to another.

or

Energy of an isolated system is constant**.**

Mathematical Expression

Heat observed by the system = its internal energy + work done by the system. *i.e.* $q = dE + w$

For an infinitesimal process

$dq = dE + dw$

Where, q is the heat supplied to the system and w is the work done on the system.

For an ideal gas undergoing isothermal change $\Delta E = 0$.

so $q = -w$.

- **For an isolated system, d*q=0***

so, $dE = - dw$

- **For system involving mechanical work only**

$\Delta E = q - pdV$

- **At constant volume i.e. isochoric process**

$\Delta E = q_v$

- **For Isothermal Process**

$\Delta E = 0$
or
$q = - pdV = -W$

- **For adiabatic process**

?q = 0

or

$\Delta E = W$

Enthalpy (H):

$H = E+PV$

At constant pressure:

$dH = dE + pdV$

For system involving mechanical work only

$dH = Q_P$ (At constant pressure)

For exothermic reactions:

dH = -ve

For endothermic reactions:

dH = +ve

Relation between dH and dE:

$dH = dE + dn_g RT$

Where,

dn_g = (Number of moles of gaseous products - Number of moles of gaseous reactants)

Heat capacity:

- Amount of heat required to rise temperature of the system by one degree.

$C = q / dT$

- **Specific heat capacity:** Heat required to raise the temperature of 1 g of a substance by one dgree.

C_s = Heat capacity / Mass in grams

- **Molar heat capacity**: Heat required to raise the temperature of 1 g of a substance by one dgree.

C_m = Heat capacity / Molar mass.

- **Heat capacity of system at constant volume:**

$C_v = (dE/dT)_v$

- **Heat capacity of system at constant pressure:**

$C_p = (dE/dT)_p$

$C_p - C_v = R$

- **Variation Of Heat Of Reaction With Temperature:**

$dC_P = (dH_2 - dH_1)/(T_2-T_1)$ & $dC_V = (dE_2 - dE_1)/(T_2-T_1)$

- **Bomb Calorimeter:**

?

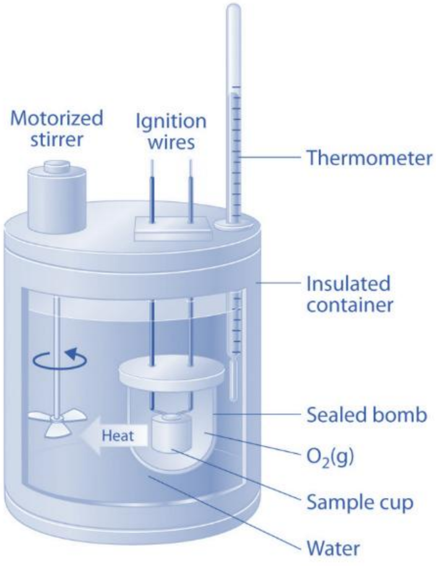
Heat exchange = Z × ΔT

Z–Heat capacity of calorimeter system

ΔT– Rise in temp.

Heat changes at constant volumes are expressed in ΔE and Heat changes at constant

pressure are expressed in dH.

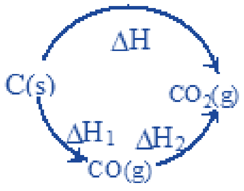


Enthalpies of Reactions:

Hess's Law of constant heat summation:

?The total enthalpy change of a reaction is the same, regardless of whether the reaction is completed in one step or in several steps.

According to Hess's law: $\Delta H = \Delta H_1 + \Delta H_2$

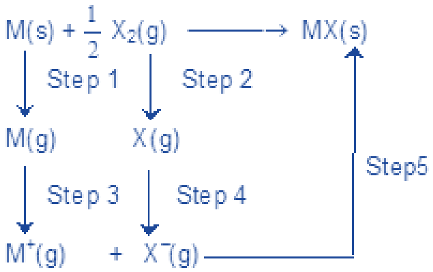


Born–Haber Cycle:

Applying Hess's law we get

$\Delta H_1 + 1/2\ \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = \Delta H_f$ (MX) (Lattice energy)

Lattice energy: The change in enthalpy that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions.



Born – Haber cycle

Second law of thermodynamics

Statement:

It is impossible to take heat from a hot reservoir and convert it completely into work by a cyclic process without transferring a part of it to a cold reservoirs.

Mathematically:

- $\Delta S = q_{rev}/T$

Where,

ΔS is entropy change.

- Entropy is the degree of randomness thus it increases with increase in randomness of particles of the system*i.e.* ΔS is positive for melting of ice.
- At equilibrium, $\Delta S = 0$
- For a spontaneous process, $\Delta S > 0$
- Entropy change in an isothermal reversible expansion of a gas $\Delta S = 2.303\ nR\ log\frac{V_2}{V_1} = 2.303\ nR\ log\frac{P_1}{P_2}$
- **Spontaneous Processes:** These type of physical and chemical changes occur of its own under specific circumstances or on proper initiations. For example: Flow of liquids from higher to lower level.
- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} gt; 0 = \Delta S_{universe} gt; 0$

Gibbs free energy(ΔG):

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = nRT \ln K_{eq}$
- $\Delta G = nFE_{cell}$
- At equilibrium, $\Delta G = 0$
- For spontaneous process, $\Delta G < 0$

Bond Energies:

Average amount of energy required to break one mole bonds of that type in gaseous molecules.

$H–OH(g) \rightarrow 2H(g) + ½O(g)$ $\Delta H = 498$ kJ

$O–H(g) \rightarrow H_2(g) + ½O_2 (g)$ $\Delta H = 430$ Kj

$\Delta H_{O–H} = (498 + 430)/2 = 464$ kJ mol^{-1}

- **Efficiency of a heat engine (carnot cycle):**

$W = R (T_2 – T_1) \ln v_2/v_1$

$q_2 = RT_2 \ln v_2/v_1$

$W = q_2$

$$\frac{T_2 - T_1}{T_2}$$

Efficiency (h). h =

$$\frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

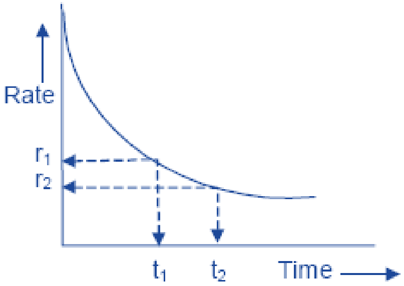
Chemical Kinetics

Revision Notes on Chemical Kinetics:

Rate of Reaction:

- Rate of change of extent of reaction is the rate of reaction.
- Rate of reaction is positive for product and negative for reactant.
- For reaction aA →bB

  Rate $=1/b(\Delta[B]/\Delta t) = -1/a(\Delta[A]/\Delta t)$
- It goes on decreasing as the reaction progress due to decrease in the concentration(s) of the reactant(s).



- Unit of rate of reaction : mol L^{-1} s^{-1}
- The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.
- In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentration of the reactants decreases, i.e., products are produced.
- The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.

Order of Reaction

For reaction aA + bB + ….. → cC+ ….

$R \propto [A]^m[B]^n$ or $R = k[A]^m[B]^n$….

Where m and n may or may not be equal to a & b.

m is order of reaction with respect to A and n is the order of reaction with respect to B.

m + n +… is the overall order of the reaction.

Elementary Reaction:

- It is the reaction which completes in a single step.
- A reaction may involve more than one elementary reactions or steps also.
- Overall rate of reaction depends on the slowest elementary step and thus it is known as rate determining step.

Molecularity of Reaction:

- Number of molecules taking part in an elementary step is known as its molecularity.
- Order of an elementary reaction is always equal to its molecularity.
- Elementary reactions with molecularity greater than three are not known because collisions in which more than three particles come together simultaneously are rare.

Differential and Integrated Rate Laws:

Zero Order Reactions:

For Reaction: A → Product

$[A]_0 - [A]_t = k_0 t$

Where,

$[A]_0$ = Initial concentration of A

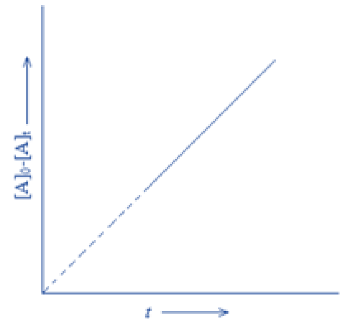
$[A]_t$ = Concentration of A at time t.

k_0 = Rate constant for zero order reaction.

Half Life:

$t_{1/2} = [A]_0/2k$

Unit of rate constant = mol $dm^{-3}s^{-1}$



Examples:

- Enzyme catalyzed reactions are zero order with respect to substrate concentration.
- Decomposition of gases on the surface of metallic catalysts like decomposition of HI on gold surface.

First Order Reactions:

A → Product

$(\Delta [A] / A) = -k_1 \Delta t$

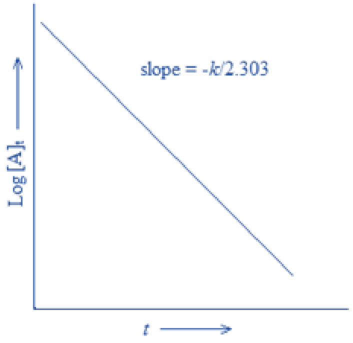
or $k_1 = (2.303/t) \log ([A]_0 / [A]_t)$

Half Life:

$t_{1/2} = 0.693/k_1$

Half life is independent of the initial concentration of the reactant for a first order reaction.

Units of k_1 = s^{-1}



Examples:

$N_2O_5 \rightarrow 2NO_2 + 1/2O_2$

$Br_2 \rightarrow 2Br$

$2HNO_3 \rightarrow 2NO + H_2O$

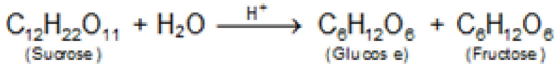
$H_2O_2 \rightarrow H_2O + 1/2O_2$

Pseudo First Order Reactions:

These are the reactions in which more than one species is involved in the rate determining step but still the order of reaction is one.

Examples:

- **Acid hydrolysis of ester:** $CH_3COOEt + H_3O^+ \rightarrow CH_3COOH + EtOH$
- **Inversion of cane sugar:**



$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(Glucos e)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

- Decomposition of benzenediazonium halides $C_6H_5N{=}NCl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$

Half – Life of a nth Order Reaction:

$kt_{1/2} = (2^{n-1}-1)/(n-1)[A_0]^{n-1}$

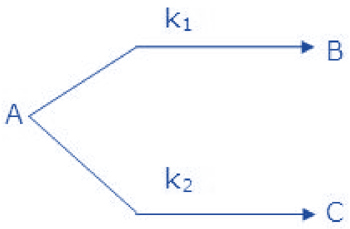
Where, n = order of reaction ≠1

Parallel Reactions:

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.

If we assume that both of them are first order, we get.

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$



k_1 = fractional yield of B × k_{av}

k_2 = fractional yield of C × k_{av}

If $k_1 > k_2$ then

A → B main and

A → C is side reaction

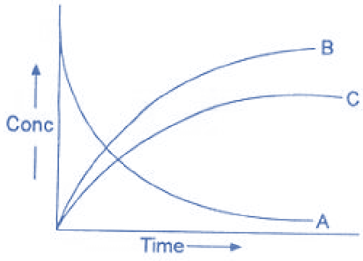
Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

$$\frac{x}{y} = \frac{k_1}{k_2}$$

i.e

$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2.



Sequential Reactions:

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

A → B → C and so on

$$A \overset{k_1}{\to} B \overset{K_2}{\to} C$$

$$-\frac{d[A]}{dt} = k_1[A] \text{.......(i)}$$

$$\frac{d[B]}{dt} = k_1[A] - K_2[B] \text{.........(ii)}$$

$$\frac{d[C]}{dt} = k_2[B] \text{..........(iii)}$$

Integrating equation (i), we get

$$[A] - [A]_o e^{-k_1 t}$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

$$[\mathrm{C}] = \frac{[\mathrm{A}]_0}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right]$$

$$t_{\max} = \frac{1}{k_1 - k_2} \ln\frac{k_1}{k_2}$$

$$\mathrm{B}_{\max} = [\mathrm{A}]_o \left[\frac{k_2}{k_1}\right]^{k_2/k_1 - k_2}$$

Arrhenius Equation:

$k = A \exp(-E_a/RT)$

Where, k = Rate constant

A = pre-exponential factor

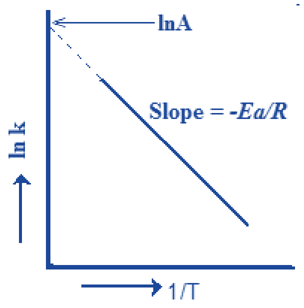
E_a = Activation energy

Temperature Coefficient:

The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperature differing by 10°C.

μ = Temperature coefficient= $k_{(r+10)}/k_t$

Let temperature coefficient of a reaction be ' μ ' when temperature is raised from $T_1$to T_2; then the ratio of rate constants or rate may be calculated as



$$\frac{k_{T2}}{k_{T1}} = \mu^{\frac{T_2-T_1}{10}} = \mu^{\frac{\Delta T}{10}}$$

$$log\frac{k_{T2}}{k_{T1}} = \mu^{\frac{T_2-T_1}{10}} = \Delta T log\mu$$

$$\frac{k_{T2}}{k_{T1}} = antilog[\frac{\Delta T}{10}]log\mu$$

Its value lies generally between 2 and 3.

Collision Theory of Reaction Rate

- A chemical reaction takes place due to collision among reactant molecules.
- The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
- The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.
- Every collision does not bring a chemical change.
- The collisions that actually produce the products are effective collisions.
- The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and
- disperse in different directions with different velocities.
- For a collision to be effective, the following two barriers are to be cleared.

1. Energy Barrier
2. Orientation Barrier

Radioactivity:

All radioactive decay follow 1^{st} order kinetics

For radioactive decay A ->B

$-(dN_A/dt) = l N_A$

Where, l = decay constant of reaction

N_A = number of nuclei of the radioactive substance at the time when rate is calculated.

Arrhenius equation is not valid for radioactive decay.

Integrated Rate Law: $N_t = N_o e^{-lt}$

Half Life: $t_{1/2}$= 0.693/λ

Average life time: Life time of a single isolated nucleus, t_{av}= 1/λ

Activity: Rate of decay

A = dN_A/dt, Also, $A_t = A_o e^{-lt}$

Specific Activity**:** activity per unit mass of the sample.

$$\text{Specific activity} = \frac{\left(\lambda \times \frac{w}{M} \times Av\right)}{w} = \frac{\lambda \times Av}{M}$$

Units: dps or Becquerrel

Chemical Equilibrium

Revision Notes on Chemical and Ionic Equilibrium

Equilibrium

- Equilibrium is the state of a process in which the properties like temperature, pressure, and concentration etc of the system do not show any change with passage of time.
- In all processes which attain equilibrium, two opposing processes are involved.
- Equilibrium is attained when the rates of the two opposing processes become equal.
- If the opposing processes involve only physical changes, the equilibrium is called **Physical Equilibrium.**
- If the opposing processes are chemical reactions, the equilibrium is called **Chemical Equilibrium**.

Physical Equilibrium

- **Solid – liquid Equilibrium:** $H_2O(s) \rightleftharpoons H_2O(l)$
- **Liquid – Gas Equilibrium:** $H_2O(l) \rightleftharpoons H_2O(g)$
- **Solid – Solution Equilibrium:** Salt(Solid) $\rightleftharpoons$ Salt(in solution)
- **Gas –Solution equilibrium:** $CO_2(g) \rightleftharpoons CO_2$(in solution)

Equilibrium in Chemical Process

- **Reversible reaction:** A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions Examples: $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
- **Irreversible reaction:** A reaction cannot take place in the reverse direction, i.e. the products formed do not react to give back the reactants under the same condition. Example: $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(g)$
- Generally, a chemical equilibrium is represented as $a\,A + b\,B \rightleftharpoons c\,C + b\,D$

  Where A, B are reactants and C, D are products.

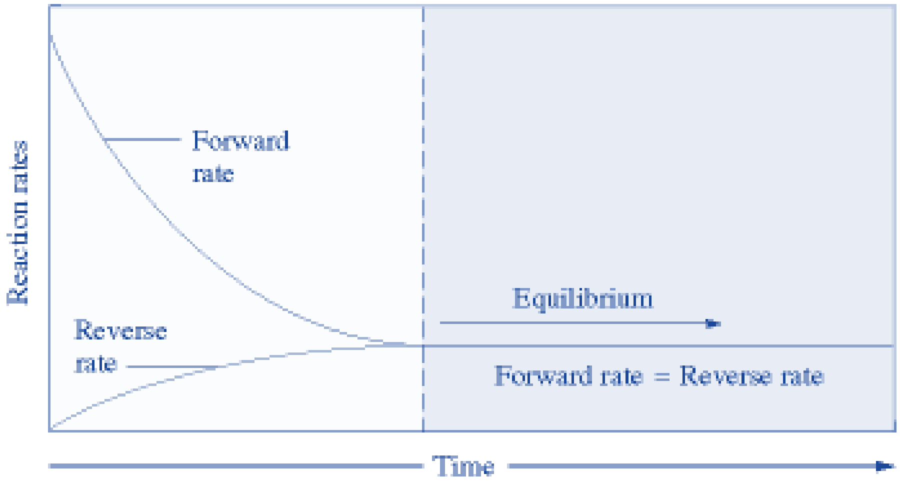
Note:

The double arrow between the left hand part and right hand part shows that changes are taking place in both the directions.

On the basis of extent of reaction, before equilibrium is attained chemical reactions may be classified into three categories.

- **Those reactions which proceed to almost completion.**
- **Those reactions which proceed to almost only upto little extent.**
- **Those reactions which proceed to such an extent, that the concentrations of reactants and products at equilibrium are comparable.**

- The equilibrium state is dynamic and not static in nature. A reaction is said to have attained equilibrium when the rate of forward reaction equals that of backward reaction



?

- **Homogeneous Equilibrium: A**ll the reactants and products of any reaction under equilibrium are in same physical state. Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- **Heterogeneous Equilibrium** :Physical state of one or more of the reacting species may differ i.e. all the reactants and products are not in same physical state.
  Example
  $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(l)$?

Characteristics of Equilibrium State

- It can be attained only if the reversible reaction is carried out in closed vessel.
- It can be attained from either side of the reaction.
- A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium.
- It is dynamic in nature i.e. reaction does not stop but both forward and backward reactions take place at equal rate.
- Change of pressure, concentration or temperature favours one of the reactions (forward or backward) resulting in shift of equilibrium point in one direction.

Law of Mass Action & Equilibrium Constant

"The rate at which a substance reacts is directly proportional to its active mass and rate of a chemical reaction is directly proportional to product of active masses of reactants each raised to a power equal to corresponding stoichiometric coefficient appearing in the balanced chemical equation".

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

Rate of reaction $\propto [A]^a.[B]^b$

or rate of reaction = $K[A]^a[B]^b$

where K is rate constant or velocity constant of the reaction at that temperature.

Unit of rate constant (K)

$$K = \frac{Rate\ of\ reaction}{[A]^a[B]^b} = \frac{molL^{-1}s^{-1}}{(molL^{1)a+b}} = (molL^{-1})^{1\ to\ n}\ s^{-1}$$

(where n is order of reaction.)

For unit concentration of reactants rate of the reaction is equal to rate constant or specific reaction rate.

Applying Law of mass action for general reversible reaction

aA + bB $\rightleftharpoons$ cC + dD

Rate of forward reaction α $[A]^a[B]^b$

or $R_f = K_f\,[A]^b\,[B]^b$

Similarly for backward reaction

$R_b = K_b[C]^c\,[D]^d$

At equilibrium $K_f[A]^a[B]^b = K_b[C]^c[D]^d$

$$\Rightarrow \frac{K_f}{K_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_c$$

The above equation is known as equilibrium equation and Kc is known as equilibrium constant.

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

$$\Rightarrow K_f = \frac{1}{K_b}$$

Expression of K_C

Let"a" moles of PCl_5 be taken in a closed vessel of volume 'V' litre. Suppose "*x*" mole is dissociated at equilibrium.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Initial Conc:	**a**	**0**	**0**
At. eqbm	***a-x***	**x**	**x**
Active mass	**(a-x)/V**	**x/V**	**x/V**

According to law of mass action

$$K_c = \frac{[Product]}{[Reactant]} = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{a-x}{v}} = \frac{x^2}{(a-x)V}$$

Equilibrium Quotient or Mass Action Ratio:

Consider the equilibrium

aA +bB $\rightleftharpoons$ cC +dD

At equilibrium

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

When the reaction is not at equilibrium this ratio is called ‘Q_C’ i.e., Q_C is the general term used for the above given ratio at any instant of time. And at equilibrium Q_C becomes K_C.

- If the reaction is at equilibrium, $Q = K_c$
- A net reaction proceeds from left to right (forward direction) if $Q < K_C$.
- A net reaction proceeds from right to left (the reverse direction) if $Q > K_c$

The Le–Chatelier’s Principle:

Statement:

“When a chemical reaction at equilibrium is subjected to any stress, then the equilibrium shifts in that direction in which the effect of the stress is reduced.”

Effect of Addition of Inert Gases:

- Addition of inert gas at constant volume: No effect on equilibrium.
- Addition of inert gas at constant pressure: Equilibrium shifts in a direction where there is increase in number of moles of gases.

Effect of Change in Temperature:

- In a system at equilibrium, both exothermic and endothermic reactions take place simultaneously.
- Increase in temperature would shift the equilibrium in the direction of endothermic reaction.
- Decrease in temperature would shift the equilibrium in the direction of exothermic reaction.

Effect of Change in Concentration:

- When the concentration of reactants increased, equilibrium shifts in forward direction.
- When the concentration of the products is increases, equilibrium shifts in backward direction.\

Effect of Change in Pressure:

- Increase in pressure shifts the equilibrium in the direction of lesser number of gaseous molecules.
- Decrease in pressure shifts the equilibrium in the direction of larger number of gaseous molecules.

Effect of Catalyst:

Catalyst does not change the equilibrium.

Thermodynamics of chemical equilibrium:

$\Delta G = \Delta G^0 + 2.303\ RT \log Q$

At equilibrium:

$\Delta G = \Delta G^0 + 2.303\ RT \log K = 0$

or

$\Delta G^0 = - 2.303\ RT \log K$

Also

$$\log K = \frac{-\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303RT}$$

Assuming ΔH^0 to be constant in temperature range T_1 and T_2

$$\frac{d \log K}{dT} = \frac{\Delta H^0}{2.303RT^2}$$

Acids and Bases:

1. **Arrhenius Definition:**
   a. Acids give H^+ ions aqueous solutions.
   b. Bases give OH^- ions in aqueous solution.

2. **Bronsted – Lowry Definition:**
   a. Acid is a proton donor .
   b. Base is a proton acceptor.

3. **Strong and Weak Acids:**
   a. Strong acid dissociate completely in aqueous solution.

      Example: HCl

   b. Weak acid dissociates partially in aqueous solution.

      Examples: CH_3COOH

      Degree of dissociation (a) =$(Ka/C)^{1/2}$

      Where,

      $K_a = [CH_3COO^-][H^+]/[CH_3COOH]$

      And

      C = Initial concentration of acid.

      Also

      $[H^+] = Ca = (Ka \times C)^{1/2}$

      c. Ionic Product of Water:

      H_2O $H^+ + OH^-$

      $K[H_2O] = [H^+]\,[OH^-] = 10^{-14}$

Common Ion effect:

The addition of an ion to equilibrium, having the same ion makes the equilibrium `reaction move in a direction to consume that ion.

$$HCl \rightleftharpoons H+ + Cl^-$$

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

This implies that water would dissociate less in the presence of HCl.

Hydrolysis of salts:

1. Salt of a Weak Acid and Strong Base:

   $[H^+] = (K_w K_a / C)^{1/2}$

2. Salt of a Weak Base and Strong Acid

   $[H^+] = (K_w / K_b C)^{1/2}$

3. Salt of a Weak Acid and Weak Base

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

- **Buffer Solutions:** Resists change in its pH when such a change is caused by the addition of a small amount of acid or base.

1. **Weak acid–Salt buffer:**

   Formed by combination of a weak acid and a salt of the acid with a strong base. Example, CH_3COOH & CH_3COONa

   $pH = pK_a + \log [\text{Conjugated base}]/ [\text{Acid}]$

   For weak dibasic acid

   $pH = (pK_{a1} + pK_{a2})/2$

   Where pK_{a1} and pK_{a2} are 1st and 2nd dissociation constant of the acid.

2. **Weak base–salt buffer:** Formed by combination of a weak base and a salt of the base with a strong acid. Example, NH_4OH and NH_4Cl

   $pH = pK_b + \log [\text{Conjugated acid}]/ [\text{Base}]$

Solubility and Solubility Product :

1. Amount (moles) of the salt that has made the solution saturated per liter of solution is called the solubility of the salt.
2. For salt AB.

   $AB \leftrightarrow A^+ + B^-$

   $K_{sp} = [A^+][B^-]$
3. Solution cannot have the product of the concentration of the ions more than K_{SP} of the salt in solution.

Ionic Product:

a) Product of ionic concentration due to ions already present in water or from a salt.

b) I.P. may be and may not be equal to K_{sp}.

c) If ionic Product (IP) > K_{sp} ; precipitation takes place till I.P. equals K_{sp}

d) If Ionic Product < K_{sp} ; a precipitate will not be formed and the solution will be unsaturated.

e) If Ionic Product = K_{sp} ; a precipitate will not form an the solution is saturated in that salt.

Solution & Colligative Properties

Type of Solutions

Vapour Pressure:

S.No.	Solute	Solvent	Example
1	Gas	Gas	Air
2	Gas	Liquid	Aerated water ($CO_2 + H_2O$)
3	Gas	Solid	Hydrogen in palladium
4	Liquid	Liquid	Alcohol in water, benzene in toluene
5	Liquid	Solid	Mercury in zinc amalgam
6	Liquid	Gas	CO_2 dissolved in water
7	Solid	Liquid	Sugar in water, common salt in water
8	Solid	Gas	Smoke
9	Solid	Solid	Various alloys

Raoult's Law:

"The partial vapour pressure of any component in the solution is directly proportional to its mole fraction".

For a binary solution of two components A and B,

$P_A = X_A$

$P_B = X_B$

Where

P^0_A = vapour pressure of component A in pure state.

P_A = vapour pressure of component A in the solution.

P^0_B = vapour pressure of component B in pure state.

P_B = vapour pressure of component B in the solution

Limitations of Raoult's Law

- Raoult's law is applicable only to very dilute solutions.
- It is applicable to solutions containing non-volatile solute only.
- It is not applicable to solutes which dissociate or associate in a particular solution

Raoult's Law in Combination with Dalton's Law of Partial Pressure:

$P_T = X_A P^0{}_A + X_B P^0{}_B = P^0{}_B + (P^0{}_A - P^0{}_B) X_A$

Where

P_T = Total Vapour Pressure of the Solution.

Ideal and Non-Ideal Solutions:

- **Ideal Solution:**

  For Ideal Solution:

  1. $dH_{mixing} = 0$, i.e. no heat should be absorbed or evolved during mixing
  2. $dV_{mixing} = 0$, i.e. no expansion or contraction on mixing

Examples , Ethyl chloride and ethyl bromide, n–hexane and n–heptane , CCl_4 and $SiCl_4$

- **Non-Ideal Solution:**

  ?These solutions deviate from ideal behaviour and do not obey Raoult's law over entire range of composition.

  For non ideal solutions,

  1. $dH_{mixing} \neq 0$
  2. $dH_{mixing} \neq 0$

  Here we may have two cases

  A) **Positive Deviation*:***
     1. $P_A > X_A$ **&** $P_B > X_B$
     2. $dH_{mix} > 0$
     3. $dV_{mix} > 0$

     Example: Cyclohexane and Ethanol

  B) **Negative Deviation:**
     1. $P_A > X_A$ **&** $P_B > X_B$
     2. $dH_{mix} < 0$
     3. $dV_{mix} < 0$

Colligative Properties

Lowering of Vapour Pressure by a Non-Volatile Solute

Elevation of Boiling Point by a Non-Volatile Solute :

Depression of Freezing Point by a Non-Volatile Solute:

Osmosis and Osmotic Pressure:

- **Osmosis:** The phenomenon of the passage of pure solvent from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane.
- **Osmotic Pressure:** Excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane.

$V = nRT$

where

= Osmotic pressure

V = volume of solution

n = no. of moles of solute that is dissolved

R = Gas constant

T = Absolute temperature

Isotonic Solutions: A pair of solutions having same osomotic pressure is called isotonic solutions.

Abnormal Molecular Weight and Van't Hoff Factor:

Van't Hoff Factor:

Van't Hoff, in order to account for all abnormal cases introduced a factor **i** known as the Van't Hoff factor, such that

Degree of Association:

Let a be the degree of association, then,

The number of unassociated moles = $1-\alpha$

The number of associated moles = α/n

Total number of effective moles = $1-\alpha+\alpha/n$

Obviously, $i < 1$

Degree of Dissociation

The fraction of the total number of molecules which dissociates in the solution, that is, breaks into simpler molecules or ions.

$KCl \leftrightarrow K^+ + Cl^-$

$1-\alpha \quad \alpha \quad \alpha$

Thus, the total number of moles after dissociation $= 1-\alpha+\alpha+\alpha = 1+\alpha$

Hence, $i = (1+\alpha)/1$

$i = 1+ \alpha = 1+ (2–1)\alpha$

In general, **$i = 1+ (n–1) \alpha$,**

Where, n = number of particles (ions) formed after dissociation

From the above formula, it is clear that **$i > 1$**

Redox Reactions and Electrochemistry

Conductors and Non Conductors

- **Non-Conductors:** Those substances which do not allow electric current to pass through them are called non-conductors or insulators. Example: - wood, plastic glass, rubber etc.
- **Conductors:** Those substances which allow electric current to flow through tem are called conductors. Examples: Copper, Iron, Gold, Silver, Graphite, salt solution etc.

Conductors can further be divided into two groups

- **Metallic Conductors:** These conductors conduct electricity or electric current by movement of electrons without undergoing any chemical change during the process. These conduct electricity in both solid as well as molten state. Example: All the metals and Graphite
- **Electrolytes:** Those substances which conduct electricity only when they are present in aqueous solution and not in solid form are called electrolytes. These conduct electricity by movement of ions in solutions.

S.No	Metallic Conduction	Electrolytic Conduction
1	Electric current flows by movement of electrons.	Electric current flows by movement of ions.
2	No chemical change occurs.	Ions are oxidized or reduced at the electrodes.
3	It does not involve the transfer of any matter.	It involves transfer of matter in the form of ions.
4	Ohm's law is followed.	Ohm's low is followed.
5	Resistance increases with increase of temperature.	Resistance decreases with increase of temperature.
6	Faraday law is not followed.	6Faraday law is followed.

Comparison of Electrolytic and Metallic Conduction

Electrolytic Conductance:

Specific Resistance or resistivity (ρ):

$R = \rho \times l / A$

Where,

R = Resistance

A=Area of cross sections of electrodes

l = Distance between the electrodes.

Specific Conductance or Conductivity (κ):

$\kappa = 1/\rho$

Units: $W^{-1}\ cm^{-1}$ or Sm^{-1}

Equivalent Conductance (Λ):

Conducting power of all the ions produced by one g-equivalent i.e. one equivalent of an electrolyte in a given solution

$\Lambda = 1000\ \kappa / C$

Where, C be the normality of solution i.e. concentration of electrolytic solution in equivalent/L.

Units: $W^{-1}cm^{2}$

Molar Conductance (Λ_m):

Conductance of solution due to all the ions produced by one mole of the dissolved electrolyte in a given solution.

$\Lambda_m = \kappa / c$

Where, c = concentration of solution in mol m^{-3}.

$\Lambda_m = \kappa \times 1000 / M$

Where, M is molarity of solution.

Units: $S\ cm^2\ mol^{-1}$

Relation between Λ and Λ_m

$\Lambda_m = n\ \Lambda$

Where n = n-factor of the electrolyte = total charge carried by either ion = M/E

Variation of Conductance with Dilution:

Specific conductance: Decrease with dilution due to decrease in number of ions per c.c. of the solution.

Molar and Equivalent Conductance: Increases with increase in dilution.

- Weak electrolyte: Increase is due to increase in extent of ionization.
- Strong electrolyte: Increase is due to increase in mobility of ions because of decreased inter-ionic attraction.

Debye-Hückel-Onsager Equation

$\Lambda_m = \Lambda^0_m - (A + B\ \Lambda^0_m)\ \sqrt{C}$

Where,

A & B = Debye-Hückel constants.

C = Molar concentration

$\mathbf{\Lambda}^0_m$ = Limiting molar conductivity i.e. molar conductivity at infinite dilution.

At 298 K,

$\mathbf{\Lambda}_m = \mathbf{\Lambda}^0_m - (60.2 - 0.299\ \mathbf{\Lambda}^0_m)\sqrt{C}$

Kohlransch's Law of Independent Migration of Ions:

"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", i.e., anions and cations. Thus,

$$\lambda_{eq}^{\infty} = \lambda_c^{\infty} + \lambda_a^{\infty}$$

where,

$$\lambda_{eq}^{\infty} = Equivalence\ Conductivity\ at\ Infinite\ Dilution$$

$$\lambda_c^{\infty} = Conductivity\ of\ Cation$$

$$\lambda_a^{\infty} = Equivalence\ Conductivity\ of Anion$$

According to Kohlrausch'slaw. "conductivity of ions is constant at infinite dilution and it does not depend on nature of co-ions."

For A_xB_y type electrolyte,

$$A_xB_y \overset{H_2O}{\rightarrow} xA^{+y} + YB^{-x}$$

$$\lambda_{eq}^{\infty} = \frac{1}{z}\lambda_B^{\infty} + \frac{1}{z^-}\lambda_A^{\infty}$$

Here $Z^+$and Z^- are the charges present on cation and anion.

$$\lambda_m^{\infty} = m\lambda_c^{\infty} + n\lambda_a^{\infty}$$

Here m and n are the number of moles of cations and anions.

$$\lambda_{BaCl_2}^{\infty} = \frac{1}{2}\lambda_{Ba^{2+}}^{\infty} + \frac{1}{1}\lambda_{Cl^-}^{\infty}$$

$$\lambda_{AlCl_3}^{\infty} = \frac{1}{3}\lambda_{Al^{3+}}^{\infty} + \frac{1}{1}\lambda_{Cl^-}^{\infty}$$

$$\lambda_{Al_2(SO_4)_3}^{\infty} = \frac{1}{3}\lambda_{Al^{3+}}^{\infty} + \frac{1}{2}\lambda_{SO_4^{2-}}^{\infty}$$

Faraday's Laws of Electrolysis:

<u>First Law:</u> "The mass of a substance deposited or liberated at any electrode is directly proportional to the amount of charge passed."

w = zQ

Where z = electrochemical equivalent i.e. the mass of the substance in grams deposited or liberated by passing one coulomb of charge,

Second Law: "Mass of a substance deposited or liberated at any electrode on passing a certain amount of charge is directly proportional to its chemical equivalent weight".

Charge on one mole electrons = 1 F = 96487 C

That is w a E where w is the mass of the substance in grams while E is its chemical equivalent weight in gms per equivalent=

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}.$$

The charge possessed by 1 mole of electrons = $1.6 \times 10^{-19} \times 6.023 \times 10^{23} \approx 96500$ C

This charge is called as **1 Faraday.**

If we pass one Faraday of charge, it means that we are passing one mole of electron and by passing 1 Faraday of charge 1gm equivalent weight of the substance will be deposited or liberated.

$$W = \frac{q}{96500} \times E$$

By combining the first and second law, we get

$$Z = \frac{E}{96500}$$

Electrochemical Cells:

Difference in Electrolytic Cell and Galvanic Cell:

Electrolytic Cell	Galvanic cell
Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
Anode positive electrode. Cathode negative electrode	Anode negative electrode. Cathode positive electrode.
Ions are discharged on both the electrodes.	Ions are discharged only on the cathode
If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire
Both the electrodes can be fitted in the same compartment	The electrodes are fitted in different compartment

Standard electrode potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K)

IUPAC Cell Representation: Anode (Molarity of electrolyte at anode) || Cathode (Molarity of electrolyte at cathode)

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

Example:

$$\underbrace{\underset{(C_1)}{Zn / ZnSO_4}}_{\text{Anode}} \| \underbrace{\underset{(C_2)}{CuSO_4 / Cu}}_{\text{Cathode}}$$

The Nernst Equation:

For a general reaction such as

$M_1A + m_2B$ ..... $n_1X + n_2Y$ + ...(i)

Occurring in the cell, the Gibbs free energy change is given by the equation

$$G = \triangle G^0 + 2.303RTlog_{10}\frac{(a_x^{n1} \times a_y^{n2})}{(a_A^{m1}a_B^{m2})}.(ii)$$

where

'a' represents the activities of reactants and products under a given set of conditions and

?G^o refers to free energy change for the reaction when the various reactants and products are present at standard conditions.

The free energy change of a cell reaction is related to the electrical work that can be obtained from the cell, i.e.,

?G^o = -nFE$_{cell}$ and ?G^o = -nFE^o.

On substituting these values in Eq. (ii) we get

$$nFE_{cell} = -nFE^o + 2.303RTlog_{10}\frac{(a_x^{n1} \times a_y^{n2})}{(a_A^{m1}a_B^{m2})}.(iii)$$

$$\Rightarrow E_{cell} = E^o - 2.303RTlog_{10}\frac{(a_x^{n1} \times a_y^{n2})}{(a_A^{m1}a_B^{m2})}.(iv)$$

This equation is known as **Nearnst equation**.

Some other important relations:

- $K_{eq} = e^{nE/FRT}$
- $\Delta H = nF\,[T(dE/dT)-E]$
- $\Delta S = nF(dE/dT)_P$

Some Important Half Cells:

Hydrogen Electrode:

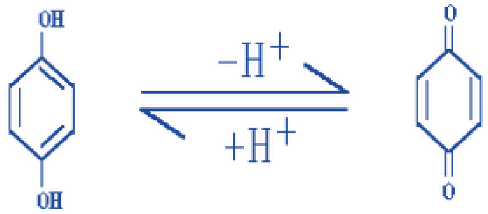
- **<u>The electrode reaction</u> :** H_2 -> $2H^+ + 2e^-$
- **<u>Electrode representation</u>:** Pt | H_2 (1 atm) | H^+ (1M).

Ferrous – Ferric Electrode:

- **<u>Electrode reaction</u>:** $Fe^{3+} + e^-$ -> Fe^{2+}
- **<u>Electrode representation</u>:** Pt | Fe^{2+} (C_1), Fe^{3+} (C_2).

Quin – Hydrone Electrode:

- **Electrode reaction:**



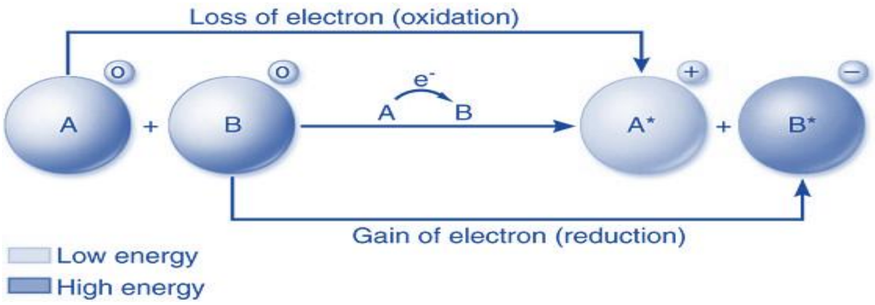
- **Electrode representation**: Pt.|QH_2,Q,H^+ (C)

Calomel electrode :

- **Electrode reaction :** ½ Hg_2Cl_2 +e^- ↔ Hg +Cl^-
- **Electrode is representation:** Cl^- (1M) | Hg_2Cl_2, Hg?

?Oxidation and Reduction

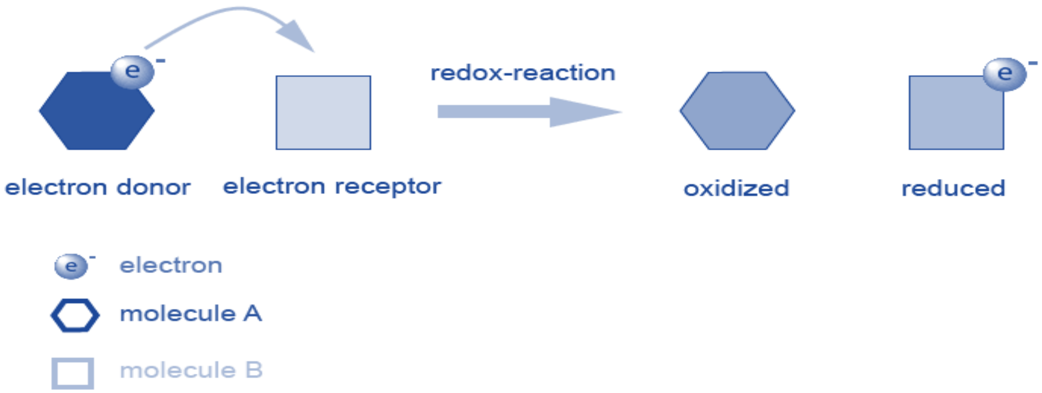
- Oxidation is defined as the loss of electrons by a chemical species (atom, ion or molecule).
- Reduction is the gain of electrons by a chemical species (atom, ion or molecule).
- An oxidising agent that chemical species which takes electrons thus it is an electron acceptor.
- A reducing agent is the chemical species that gives electrons and thus acts as an electron donor.



- When Fe^{2+}(aq) ions are being oxidised they are acting as reducing agents, and when Fe^{3+}(aq) ions are being reduced they are acting as oxidising agents. In general ;

$$\text{O.A.} + \text{electrons} \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \text{R.A.}$$

- $\underset{\text{(R.A.)}}{Fe^{2+}_{(aq)}} \xrightarrow{\text{Oxidation}} \underset{\text{(O.A.)}}{Fe^{3+}_{(aq)}} + e^-$ $\qquad Fe^{3+}_{(aq)} + e^- \xrightarrow{\text{reduction}} Fe^{2+}_{(aq)}$



- Neither reduction nor oxidation occurs alone. Both of them occur simultaneously. Since both these reactions must occur at the same time they are often termed as "redox reactions". The oxidation or reduction portion of a redox reaction, including the electrons gained or lost can be determined by means of a Half-Reaction ?Oxidation Number
- The oxidation number for an element in a covalent compound is by taking the oxidation number to be equal to the charge that the element would carry, if all the bonds in the compound were regarded as ionic instead of covalent.
- The sum of the oxidation numbers of all the atoms in an uncharged compound is zero. In case of an ion, the algebraic sum of the oxidation numbers of all the atoms is equal to the charge on the ion.
- Oxidation number of any element in its elementary state is zero.
- Fluorine is the most electronegative element. Its oxidation number is always -1 .
- Oxygen after fluorine is the second most electronegative element. It shows an oxidation state of -2 in almost all the compounds excepts peroxides and superoxides,
- In all compounds, except ionic metallic hydrides, the oxidation number of hydrogen is +1.
- In any compounds has more than two elements, the oxidation number of any one of them may have to be obtained by first assigning reasonable oxidation numbers to the other elements.

Oxidation Number / State Method For Balancing Redox Reactions:

This method is based on the principle that the number of electrons lost in oxidation must be equal to the number of electrons gained in reduction. The steps to be followed are :

- Write the equation (if it is not complete, then complete it) representing the chemical changes.
- By knowing oxidation numbers of elements, identify which atom(s) is(are) undergoing oxidation and reduction. Write down separate equations for oxidation and reduction.
- Add respective electrons on the right of oxidation reaction and on the left of reduction reaction. Care must be taken to ensure that the net charge on both the sides of the equation is same.
- Multiply the oxidation and reduction reactions by suitable numbers to make the number of electrons lost in oxidation reactions equal to the number of electrons gained in reduction reactions.
- Transfer the coefficient of the oxidizing and reducing agents and their products to the main equation.

- By inspection, arrive at the co-efficients of the species not undergoing oxidation or reduction.
- Some elements like manganese, chromium, nitrogen and chlorine show variable oxidation states.
- When an element is oxidised its oxidation number gets increased while reduction on any element decreases its oxidation number. Change in oxidation number can be used to decide whether an oxidation or a reduction has taken place. In the change from chloromethane to dichloromethane, for example,

  $C\ H_3\ Cl \quad C\ H_2\ Cl_2$

  -2 +1 -1   0 +1 -1

  The oxidation number of carbon is increased from -2 to 0. The carbon is therefore being oxidised.

Half-Reaction or Ion-Electron Method For Balancing Redox Reactions

This method involves the following steps :

- Divide the complete equation into two half reactions, one representing oxidation and the other reduction.
- Balance the atoms in each half reaction separately according to the following steps:
  - First of all balance the atoms other than H and O.
  - In a reaction taking place in acidic or neutral medium, oxygen atoms are balanced by adding molecules of water to the side deficient in oxygen atoms while hydrogen atoms are balanced by adding H^+ ions to the other side deficient in hydrogen atoms. On the other hand, in alkaline medium (OH^-), every excess of oxygen atom on one side is balanced by adding one H_2O to the same side and $2OH^-$ to the other side. In case hydrogen is still unbalanced, then balance by adding one OH^-, for every excess of H atom on the same side as the excess and one H_2O on the other side.
  - Equalize the charge on both sides by adding a suitable number of electrons to the side deficient in negative charge.
  - Multiply the two half reactions by suitable integers so that the total number of electrons gained in one half reaction is equal to the number of electrons lost in the other half reaction.

Common Oxidising and Reducing Agents

Oxidising agent	Effective Change	Decrease in Oxidation Number
$KMnO_4$ in acid solution	$MnO_4^- \rightarrow Mn^{2+}$	5
$KMnO_4$ in alkaline solution	$MnO_4^- \rightarrow MnO_2$	3
$K_2Cr_2O_7$ in acid solution	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	3
dilute HNO_3	$NO_3^- \rightarrow NO$	3
concentrated HNO_3	$NO_3^- \rightarrow NO_2$	1
concentrated H_2SO_4	$SO_4^{2-} \rightarrow SO_2$	2
manganese (IV) oxide	$MnO_2 \rightarrow Mn^{2+}$	2
chlorine	$Cl \rightarrow Cl^-$	1
chloric (I) acid	$ClO^- \rightarrow Cl^-$	2
KIO_3 in dilute acid	$IO_3^- \rightarrow I$	5
KIO_3 in concentrated acid	$IO_3^- \rightarrow I^-$	4
Reducing agent	**Effective Change**	**Increase in Oxidation Number**
iron (II) salts (acid)	$Fe^{2+} \rightarrow Fe^{3+}$	1
tin (II) salts (acid)`	$Sn^{2+} \rightarrow Sn^{4+}$	2
ethanedioates (acid)	$C_2O_4^{2-} \rightarrow CO_2$	1
sulphites (acid)	$SO_3^{2-} \rightarrow SO_4^{2-}$	2
hydrogen sulphide	$S^{2-} \rightarrow S$	2
iodides (dilute acid)	$I^- \rightarrow I$	1
iodides (concentrated acid)	$I^- \rightarrow I^+$	2
metals, e.g. Zn	$Zn \rightarrow Zn^{2+}$	2
hydrogen		

Surface Chemistry

Revision Notes on Surface Chemistry:

Adsorption

Reversible and irreversible adsorption

The adsorption is **reversible,** if the adsorbent can be easily removed from the surface of the adsorbent by physical methods. It is called **irreversible adsorption**, if the adsorbate cannot be removed from the surface of the adsorbent.

A gas adsorbed on a solid surface can be completely removed in vacuum. It is, therefore, reversible adsorption. Examples of irreversible adsorption are adsorption of oxygen on tungsten adsorbate and adsorption of CO on tungsten surface

Adsorbent, Adsorbate and Interface

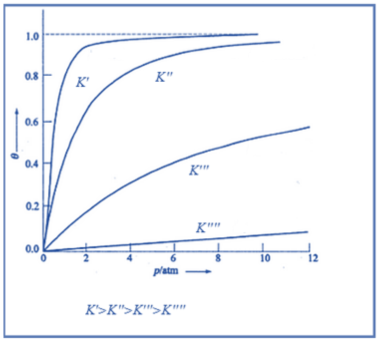
- The substances upon whose surface the change of concentration occurs, is called ***absorbent***.
- The substance taken up on the surface is call ***adsorbate***.
- The common surface between the two phases where the adsorbed molecules concentrate is called the ***interface.***

Physisorption and Chemosorption:

Physisorption	Chemisorption
Only van der Waals force are present between adsorbate and surface of adsorbent	Chemical bonds are formed between adsorbate and surface of adsorbent
Low enthalpy of adsorption ie, in the order of 20 kjmol-1.	High enthalpy of adsorption i.e, order of 200 kjmol-1.
Reversible	Irreversible
It is usually takes place at low temperature and does not require any activation energy.	It takes place at **high temperature** and require activation energy..
Multi molecular layer of adsorbate are formed on the surface	Only **monomolecular layers** are formed.
Not specific.	Highly specific.

Langmular Isotherm:

If A, B & AB represents the adsorbed, absorbent and the absorbed – adsorbent complex then,



$A + B \leftrightarrow AB$

k_a = Equilibrium constant for adsorption = [AB]/[A][B]

k_d = Equilibrium constant for desorption = [A][B]/[AB]

K = Distribution coefficient = k_a/k_b

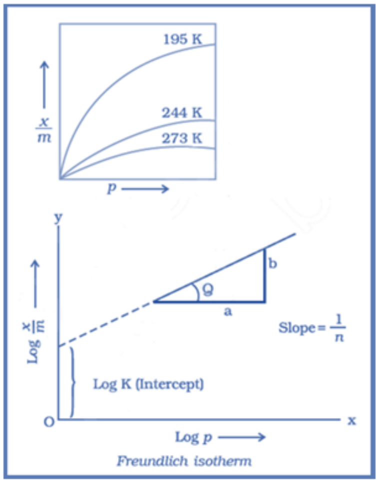
Θ = Fraction of the surface of adsorbent available for adsorption.

P = pressure

So,

$\Theta = KP/(1+KP)$ (Langmular Equation)

Freundlich Isotherm:



Freundlich isotherm

x= Mass of the gas adsorbed

m = Mass of absorbent

p = Pressure

K and n = constants

$x/m = k.p^{(1/n)}$ [n >1]

or

$\log x/m = \log k + 1/n \log P$

Factors Affecting Adsorption:

- **Temperature:** An increase of temperature leads to a decrease in amount adsorbed and vice – versa.
- **Pressure or concentration:** It has been found that in most cases, the adsorption is reversible and an increased pressure of a gases vapour or an increase in concentration of a solute causes increased adsorption.
- **Nature of Adsorbate and Adsorbent:** The amount of the gas adsorbed depends upon the nature of adsorbent and the gas (adsorbate), which is to be adsorbed. It has been found that easily liquifiable gases such as NH_3, HCl, Cl_2, SO_2 CO_2 etc. are more readily adsorbed than so the called permanent gases such as O_2,N_2, H_2 etc. This is because that molecules of the former type of gases have greater Vander waal's or molecular force of attraction.

Colloids

Dispersed Phase:

The phase which is dispersed or scattered through the dispersion medium is called Dispersed phase or discontinuous phase.

Dispersion Medium:

The phase in which the scattering is done is called the dispersion medium or continuous medium.

Dispersed Phase	Dispersion Medium	Name	Typical example
Solid	Liquid	Sol	Gold sol, Mud, $Fe(OH)_3$ sol,
Solid	Solid	Solid sol	Gems, Ruby glass, Minerals
Solid	Gas	Aero sols	Smoke (Carbon in air) Volcanic dust
Liquid	Solid	Gel	Curd, Cheese, Jellies
Liquid	Liquid	Emulsion	Milk, water in benzene, cream
Liquid	Gas	Liquid aero sol	Clouds, fog (water in air) mist
Gas	Solid	Solid foam	Lava, Pumica
Gas	Liquid	Foam	Froth on beer , whipped cream

Lyophobic and Lyophilic Colloids:

Those substance whose colloidal solution cannot be prepared by bringing them in contact with a solvent are called *Lyophobic* (disliking, fearing or hating a liquid). On the other hand those substances whose colloidal solutions can be prepared by bringing them in contact with a liquid solvent are called *lyophilic colloids* (loving a solvent).

Emulsions:

- **Emulsion of oil in water:** Those emulsions in which the dispersed phase is oil and water is the dispersion medium. These emulsion are generally represented as O in W emulsions. Examples are milk, vanishing cream etc.
- **Emulsions of water in oil:** Those emulsion in which the dispersed phase is water while oil is the dispersion medium. These emulsion are generally represented as W in O emulsions. Examples are butter, ice cream etc.

Difference between True Solutions, Suspension & Colloids

True solution	Suspension	Colloid
Homogenous	Heterogeneous	Heterogeneous
Particle size less than 1nm	Particle size more than 1000nm	Particle size between 1-1000nm
Don't settle down	Settle down under the influence of gravity	Don't settle down
Complements cannot be separated out by filtration	Can be filtered	Can be filtered using special filter papers
Don't show tyndrall effect	Show tyndrall effect	Show tyndrall effect

Methods of preparation of colloids

Chemical Methods:

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decompostion}} As_2S_3(sol) + 3H_2O$$

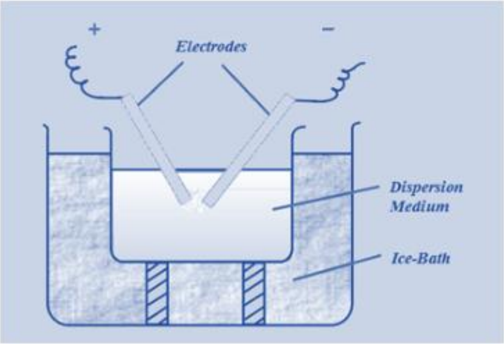
$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2\ AuCl_3 + 3\ HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (sol) + 3HCl$$

Bredig's method:

An electric arc is struck between two metallic electrodes immersed in dispersion medium. The arc produced vapourises the metal which on further condensation produces particles of colloidal size.



- **Peptization:**

Process of converting a precipitate into colloidal sol by shaking it with electrolyte in dispersion medium.

Hardy Schulze Rule:

- Ion carrying charge opposite to the colloidal particle has capacity to coagulate the colloid.
- Greater the valency of ion, greater will be the coagulating power.
- Gold Number: The minimum amount of lyophilic colloid in milligrams which can prevent the coagulation of 10 ml gold sol against 1 ml of 10% NaCl solution.

Surfactants

substances which gets preferentially adsorbed at the air – water and solid – water interfaces forming an oriented monolayer where the hydrophilic groups point towards the aqueous phase and the hydrocarbon chain point towards the air or towards the oil phase.

- Anionic surfactants : NSodium salts of higher fatty acids such as sodium palmitate ($C_{15}H_{31}COONa$), sodium stereate ($C_{17}H_{35}COONa$) and sodium Oleate ($C_{17}H_{33}COONa$).
- Catiuonic Surfactants: Those which dissociates in water to yield positively charged ions ***examples:*** $C_{18}H_{37}$, $C_{16}H_{33}(CH_3)_3$ etc.
- Non ionogenic: Those whose molecules cannot undergo dissociation when an alcohol having a higher molecular weight reacts with several molecules of ethylene oxide, a non – ionogenic surfactant is produced.

Periodic Table

Modern Periodic Law:

- Properties of elements are the periodic function to their atomic numbers.
- The periodicity in properties is due to repetition of similar outer shell electronic configuration at a certain regular intervals.
- In modern periodic table is based on modern periodic law in which elements are arranged in increasing order of their atomic numbers.
- In the modern periodic table, the elements are arranged in rows and columns. These rows and columns are known as periods and groups respectively.
- The table consists of 7 periods and 18 groups
- Period indicates the value of 'n' (principal quantum number) for the outermost or valence shell.
- Same number of electrons is present in the outer orbitals (that is, similar valence shell electronic configuration

IUPAC Nomenclature for Elements with Atomic Number ? 100

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Classification of Elements:

Elements:	**Valence Shell Electronic Configuration**	**Nature**	**Position in Modern Periodic Table**
s-block elements	ns^{1-2} (n = 1 to 7).	Metals	1 and 2 group elements
p – block elements	ns^2np^{1-6} (n = 2 to 7).	Metalloids & non metals but some of them are metals also.	groups 13 to 18
d-Block Elements	$(n-1)d^{1-10}\ ns^{1-2}$ (n = 4 to 7).	Metals	3 to 12 groups 3d series – Sc(21) to Zn (30) 4d series – Y (39) to Cd (48) 5d series – La (57), Hf (72) to Hg (80
f-Block Elements	$(n-2)f^{1-14}\ (n-1)s^2\ (n-1)p^6\ (n-1)d^{0-1}ns^2$ (n = 6 and 7).	Radioactive	group 3 4f series – Lanthanides – 14 Elements Ce (58) to Lu (71) 5f series – Actinides – 14 Elements Th (90) to Lw (103)

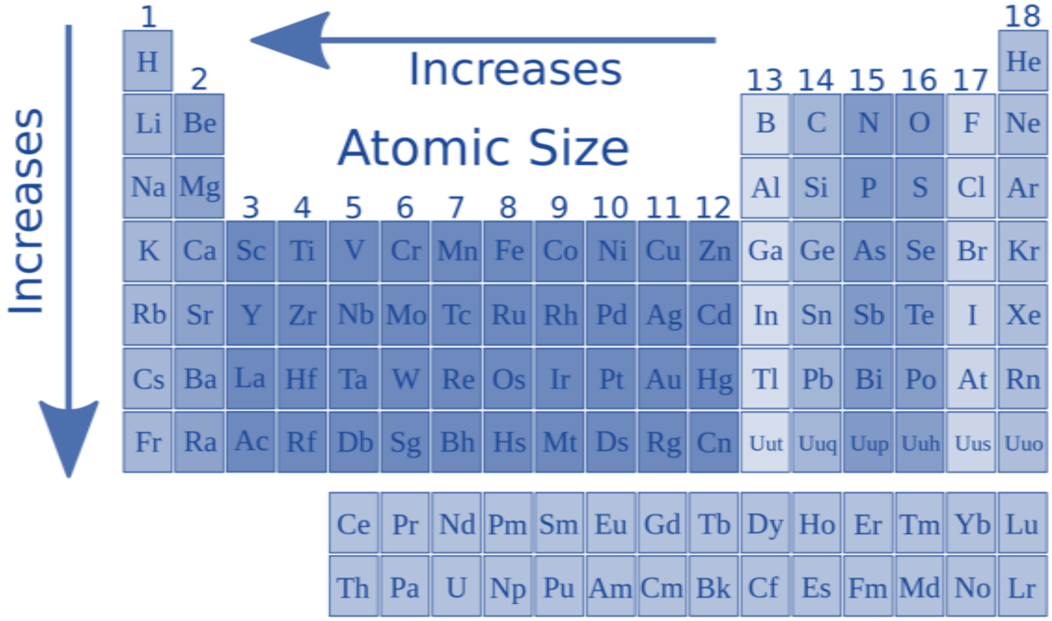
Periodicity in Atomic Properties:

1. Atomic Radius:

- Within a given period atomic radius **decreases from left to right**. This is due to the effect of increase in nuclear charge while the electrons are being added to the same shell.
- Within a given group atomic radius increases down the group. This is due to the increase in number of shells.

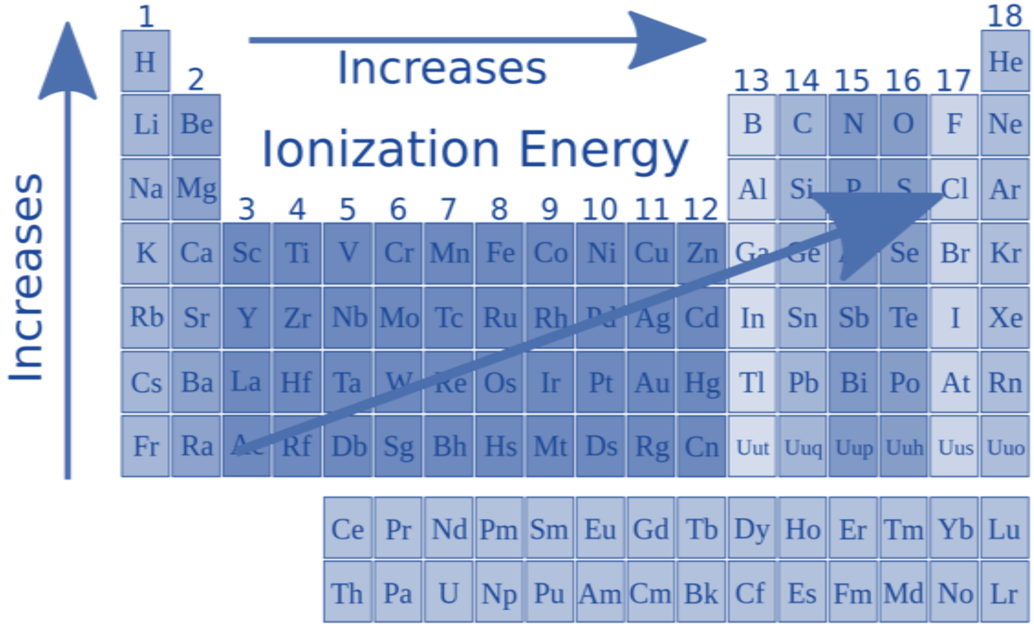
Period	**Group**							
	IA	**IIA**	**IIIA**	**IVA**	**VA**	**VIA**	**VIIA**	**Zero**
1.	H 0.37							He 0.93
2.	Li 1.34	Be 0.90	B 0.82	C 0.77	N 0.73	O 0.74	F 0.72	Ne 1.31
3.	Na 1.54	Mg 1.30	Al 1.18	Si 1.11	P 1.06	S 1.02	Cl 0.99	Ar 1.74

- In the first transition series the atomic size slightly decreases from Sc to Mn because effect of effective nuclear charge is stronger than the shielding effect. The atomic size from Fe to Ni remains almost the same because both the effects balance each other.
- The atomic size from Cu to Zn slightly increases because shielding effect is more than effective nuclear charge due to d^{10} structure of Cu and Zn.
- Inner transition elements – As we move along the lanthanide series, there is a decrease in atomic as well as ionic radius. The decrease in size is regular in ions but not so regular in atoms. This is called lanthanide contraction.



2) Ionisation potential or Ionisation Energy:

Ionization energy increases along the period while decreases down the group.



Factors which influence I.E.

- Atomic size: the larger the size of the atom, the smaller the I.E. i.e., I.E. µ
- Effective nuclear charge: The greater the effective charge on the nucleus of an atom, the more difficult it would be to remove an electron from the atom because electrostatic force of attraction between the nucleus and the outermost electron increases. So greater energy will be required to remove the electron.
- Penetration effect of orbitals: The order of energy required to remove electron from s,p,d-and¦-orbitals of a shell is s>p>d>¦.
- Shielding or screening effect: Screening effect results in decrease of force of attraction between the nucleus and the outermost electron and lesser energy is required to separate the electron. Thus the value of I.P. decreases.
- Stability of half-filled and fully-filled orbitals: According to Hund's rule the stability of half filled or completely filled degenerate orbitals is comparatively high. So comparatively more energy is required to separate the electron from such atoms.

Successive Ionisation Energies

Element	IE_1	IE_2	IE_3	IE_4
Li	520.1	7297	11813	—
C	1086.2	2352	4620	6221
N	1402.1	2856	4577	7474

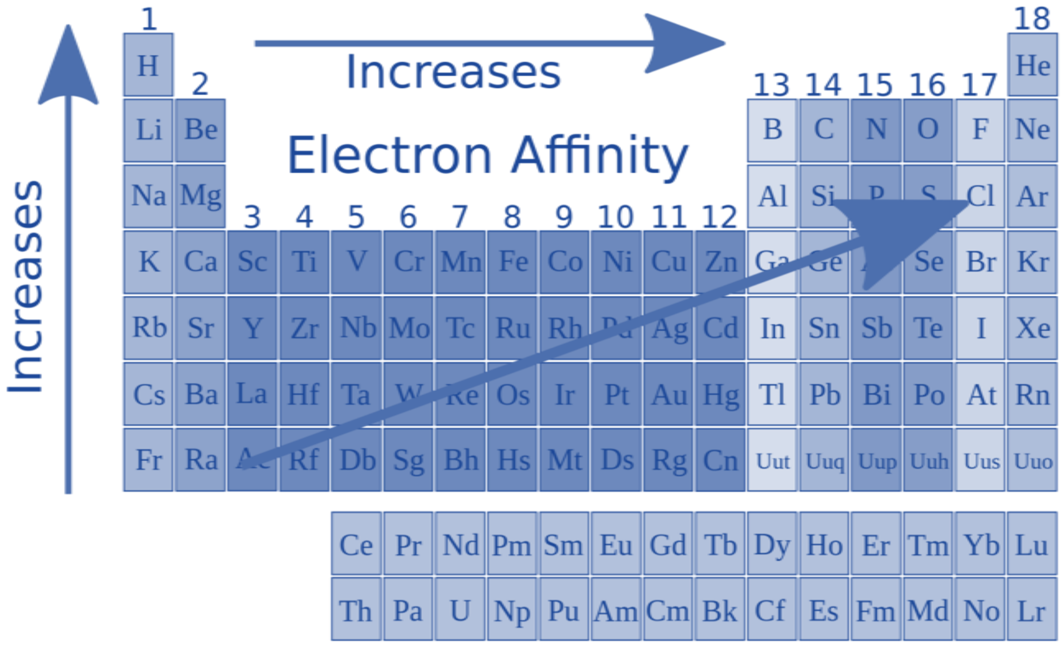
3) Electron Affinity:

Electron affinity increases along the period while decreases down the group.

Factors affecting the magnitude of electron affinity

- Atomic size – In general electron affinity value decreases with the increasing atomic radius because electrostatic force of attraction decreases between the electron being added and the atomic nucleus due to increase of distance between them.
- Effective nuclear charge – Electron affinity value of the element increase as the effective nuclear charge on the atomic nucleus increases because electrostatic force of attraction between the electron being added and the nucleus increases. As the electrostatic force of attraction increases, amount of energy released is more.
- Screening or Shielding effect – Electron affinity value of the elements decreases with the increasing shielding or screening effect. The shielding effect between the outer electrons and the nucleus increases as the number of electrons increases in the inner shells.

Stability of half filled and completely filled orbitals – The stability of half filled and completely filled degenerate orbitals of a sub shell is comparatively more, so it is difficult to add electron in such orbitals and lesser energy is released on addition of electron hence the electron affinity value will decrease.



? Electron Affinities (kJ mol^{-1}), $M_{(g)} + e^{-}$ ® $M_{(g)}^{-}$ + energy

Group 1	2	13	14	15	16	17	18
H							He
72							< 0
Li	Be	B	C	N	0	F	
57	< 0	27	122	< 0	142	333	
Na	Mg	Al	Si	P	S	Cl	Ne
53	< 0	44	134	72	200	349	< 0
K	Ca	Ga	Ge	As	Se	Br	Ar
48	< 0	29	116	77	195	324	< 0
Cs				Bi	Te	1	Xe
43							

Isolation of Metals

General Principles & Processes of Isolation of Metals

Types of Ores:

Ores may be divided into four groups

- **Native Ores:** These ores contain the metal in free state eg. Silver gold etc. These are usually formed in the company of rock or alluvial impurities like clay, sand etc.
- **Oxidised Ores**: These ores consist of oxides or oxysalts (eg. carbonates, phosphate) and silicate of metal. Important oxide ore includes, Fe_2O_3, $Al_2O_3.2H_2O$ etc. and important cabonate ores are limestone ($CaCO_3$), Calamine ($ZnCO_3$) etc.
- **Sulphurised Ores**: These ores consist of sulfides of metals like iron, lead, mercury etc. Examples are iron pyrites (FeS2). galena (PbS), Cinnabar (HgS)
- **Halide ores**: Metallic halides are very few in nature. Chlorides are most common examples include horn silver (AgCl) carnallite KCl. $MgCl_2.6H_2O$ and fluorspar (CaF_2) etc.

Metallurgy:

It is the process of extracting a metal from its ores. The following operations are carried out for obtaining the metal in the pure form.

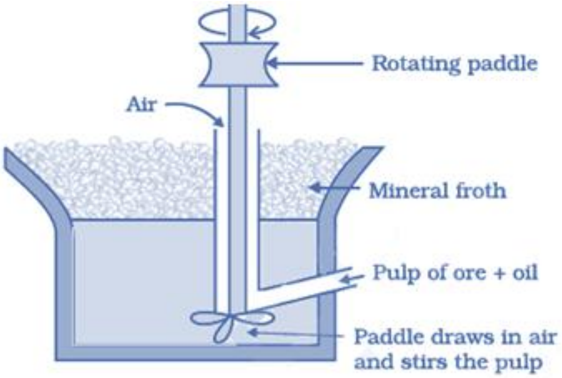
- Crushing of the ore
- Dressing or concentration of the ore.
- Reduction of metal.
- Purification or refining of the metal

Concentration

Physical Method

Gravity separation: The powdered ores is agitated with water or washed with a running stream of water. The heavy ore particles of sand, clay etc. are washed away.

Froth Floatation Process*:* The finely divided ore is introduced into water containing small quantity of oil (e.g. Pine Oil). The mixture is agitated violently with air a froth is formed which carries away along with it the metallic particles on account of the surface tension forces. The froth is transferred to another bath where gangue-free ore settles down**.**



Electro Magnetic Separator*:*. A magnetic separator consists of a belt moving over two rollers, one of which is magnetic. The powdered ore is dropped on the belt at the other end. Magnetic portion of the ore is attracted by the magnetic roller and falls near to the roller while the non-magnetic impurity falls farther off

Chemical Methods

Calcination: Carbonate or hydrated oxide ores are subjected to the action of heat in order of expel water from hydrated oxide and carbon dioxide from a carbonate.

Examples:

$ZnCO_3$ --> $ZnO + CO_2$
$CaCO_3$ --> $CaO + CO_2$
$Al_2O_3 \times 2H_2O$ --> $Al_2O_3 + 2H_2O$
$2Fe_2O_3 \times 3H_2O$ --> $2Fe_2O_3 + 3H_2O$

Roasting: Sulphide ores either are subjected to the action of heat and air at temperatures below their melting points in order to bring about chemical changes in them.

Examples:

$2PbS + 3O_2$ --> $2PbO + 2SO_2$
$PbS + 2O_2$ --> $PbSO_4$
$2ZnS + 3O_2$ --> $2ZnO + 2SO_2$
$ZnS + 2O_2$ --> $ZnSO_4$
$CuS + 2O_2$ --> $CuSO_4$
$2Cu_2S + 3O_2$ --> $2Cu_2O + 2SO_2$

Leaching: It involves the treatment of the ore with a suitable reagent as to make it soluble while impurities remain insoluble. The ore is recovered from the solution by suitable chemical method.
$Al_2O_3 + 2NaOH$ -->$2 NaAlO_2 + H_2O$

Reduction of Free Metal:

Smelting:

Reduction of a metal from its ore by a process involving melting
Several reducing agents such as sodium, magnesium and aluminium are used for reduction.
The calcinated or roasted ore is mixed with carbon (coal or coke) and heated in a reverberatory or a blast furnace.
Carbon and carbon monoxide produced by incomplete combustion of carbon reduce the oxide to the metal.

$$\left.\begin{array}{l} PbO + C \rightarrow Pb + CO \\ PbO + CO \rightarrow Pb + CO_2 \\ SnO_2 + 2C \rightarrow Sn + 2CO \end{array}\right\}\text{Carbon reductionprocess}$$

$$\left.\begin{array}{l} Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 \\ 3Mn_3O_4 + 8Al \rightarrow 9Mn + 4Al_2O_3 \end{array}\right\}\text{Alumin iumreduction process(Gold - Schimidt alumino thermic process)}$$

Flux:

The ores even after concentration contain some earthy matter called gangue which is heated combine with this earthy matter to form an easily fusible material. Such a substance is known as flux and the fusible material formed during reduction process is called slag.

- **Acidic fluxes** like silica, borax etc are used when the gangue is basic such as lime or other metallic oxides like MnO, FeO, etc
- **Basic fluxes** like CaO, lime stone ($CaCO_3$), magnesite ($MgCO_3$), hematite (Fe_2O_3) etc are used when the gangue is acidic like silica, P_4O_{10} etc.

Refining

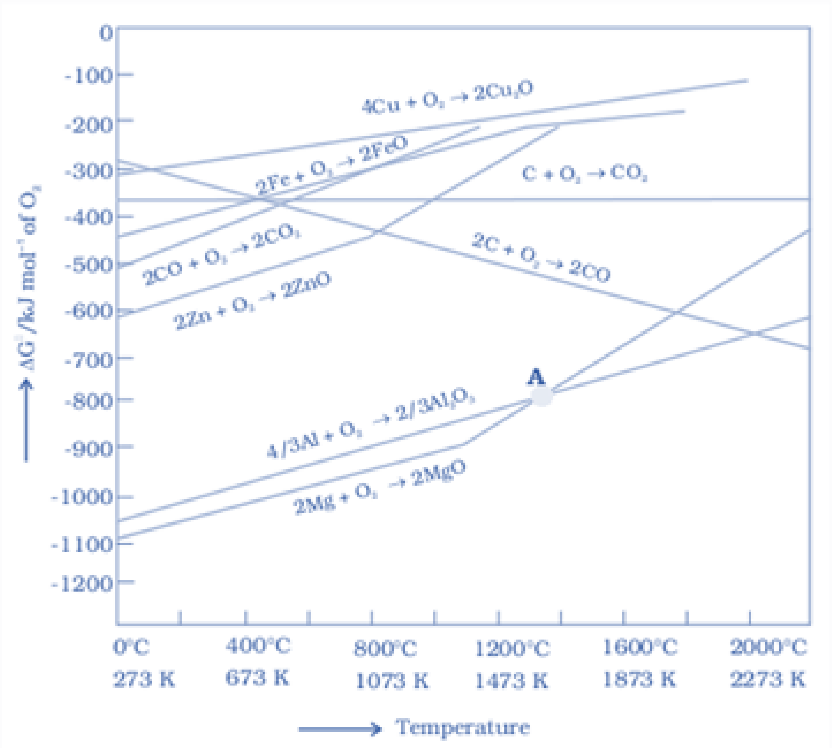
The metals obtained by the application of above reduction methods from the concentration ores are usually impure. The impure metal is thus subjected to some purifying process known as refining in order to remove undesired impurities. Various process for this are

a) Liquation process	b) Distillation process
c) Cupellation	d) Poling
e) Electrolytic refining	f) Bessemerisation

Thermodynamic Principles of Metallurgy:

$\Delta G = \Delta H - TS$

or $\Delta G^0 = -RT \ln K$



An element A can reduce element B if ΔG value for oxidation of A to AO is lower than the ΔG value for oxidation of B to BO.

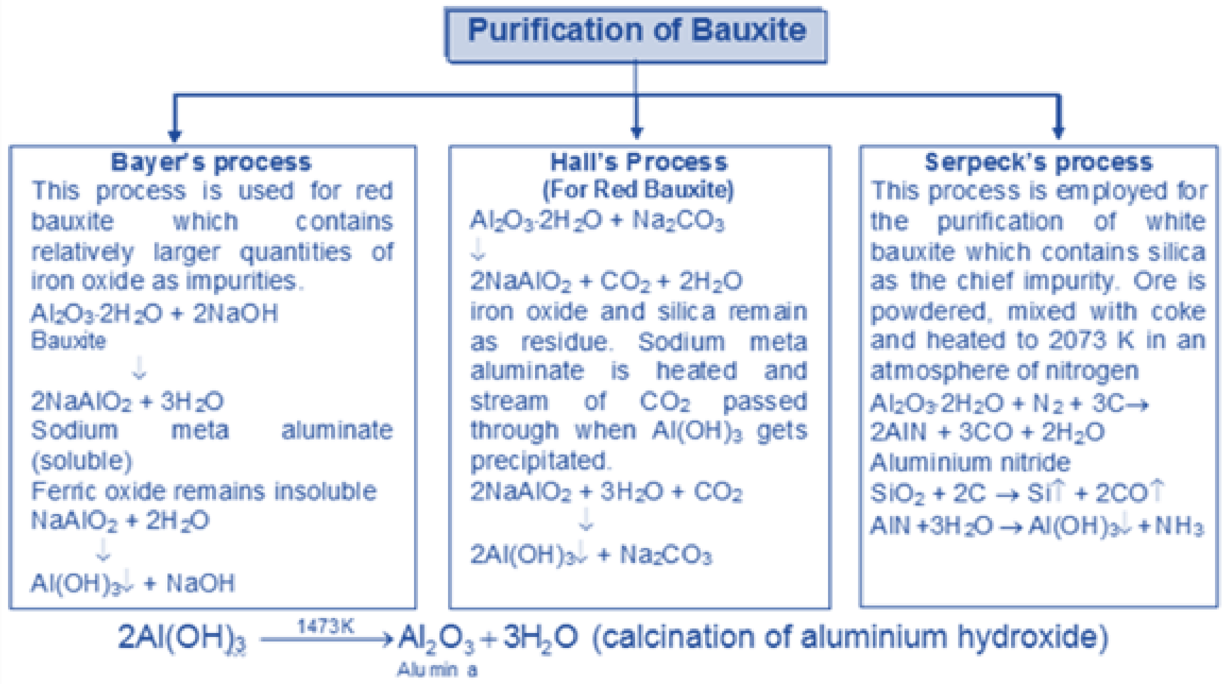
i.e. $\Delta G_{(A \rightarrow AO)} < \Delta G_{(B \rightarrow BO)}$

Extraction of Aluminium:

Important Ores of Aluminium:

- Bauxite : $Al_2O_3\times2H_2O$Cryolite: Na_3AlF_6
- Feldspar: $K_2OAl_2O_3\times6SiO_2$ or $KAlSi_3O_8$
- Mica: $K2O\times3Al_2O_3\times6SiO_2\times2H_2O$
- Corundum: Al_2O_3
- Alumstone or Alunite: $K_2SO_4\times Al_2(SO_4)_3\times4Al(OH)_3$

Purification of Bauxite



Purification of Bauxite

Bayer's process

This process is used for red bauxite which contains relatively larger quantities of iron oxide as impurities.

$Al_2O_3 \cdot 2H_2O + 2NaOH$
Bauxite
$\downarrow$
$2NaAlO_2 + 3H_2O$
Sodium meta aluminate (soluble)

Ferric oxide remains insoluble

$NaAlO_2 + 2H_2O$
$\downarrow$
$Al(OH)_3\downarrow + NaOH$

Hall's Process (For Red Bauxite)

$Al_2O_3 \cdot 2H_2O + Na_2CO_3$
$\downarrow$
$2NaAlO_2 + CO_2 + 2H_2O$

iron oxide and silica remain as residue. Sodium meta aluminate is heated and stream of CO_2 passed through when $Al(OH)_3$ gets precipitated.

$2NaAlO_2 + 3H_2O + CO_2$
$\downarrow$
$2Al(OH)_3\downarrow + Na_2CO_3$

Serpeck's process

This process is employed for the purification of white bauxite which contains silica as the chief impurity. Ore is powdered, mixed with coke and heated to 2073 K in an atmosphere of nitrogen

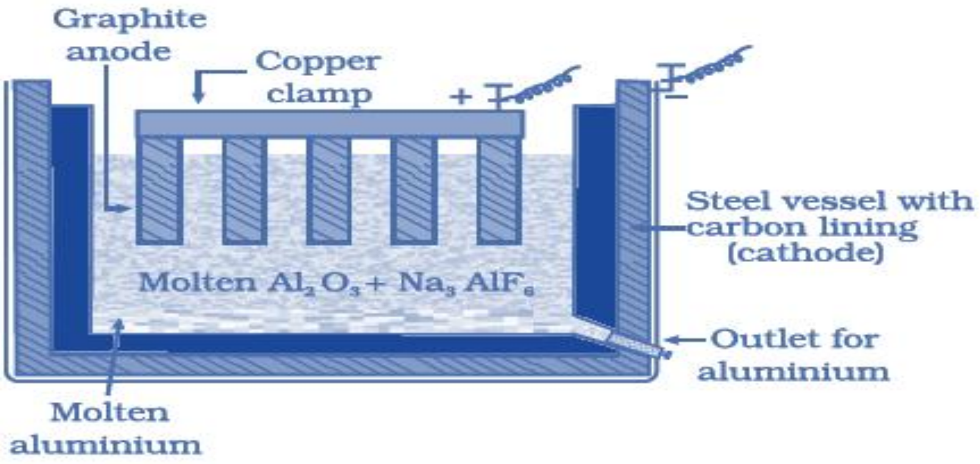
$Al_2O_3 \cdot 2H_2O + N_2 + 3C \rightarrow$
$2AlN + 3CO + 2H_2O$
Aluminium nitride

$SiO_2 + 2C \rightarrow Si\uparrow + 2CO\uparrow$

$AlN + 3H_2O \rightarrow Al(OH)_3\downarrow + NH_3$

$$2Al(OH)_3 \xrightarrow{1473K} \underset{\text{Alumina}}{Al_2O_3} + 3H_2O$$ (calcination of aluminium hydroxide)

Electrolysis of fused pure alumina (Hall & Herwlt Method)



The addition of cryolite (Na_3AlF_6) and fluorspar (CaF_2) makes alumina a good conductor of electricity and lowers its Fusion temperature from 2323 to 1140 K. the reaction taking place during electrolysis.

$$Na_3AlF_6 \rightleftharpoons 3NaF + AlF_3$$

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

At cathode

$$Al^{3+} + 3e^- \longrightarrow Al$$

At anode

$$F^- \longrightarrow F + e^-$$

$$2Al_2O_3 + 12\,F \longrightarrow 4AlF_3 + 3O_2$$

$$2C + O_2 \longrightarrow 2CO$$

$$2CO + O_2 \longrightarrow 2CO_2$$

Refining of Aluminium:

The graphite rods dipped in pure aluminium and Cu–Al alloy rod at the bottom in the impure aluminium work as conductors. On electrolysis, aluminium is deposited at cathode from the middle layer and equivalent amount of aluminium is taken up by the middle layer from the bottom layer (impure aluminium). Therefore, aluminium is transferred from bottom to the top layer through middle layer while the impurities are left behind. Aluminium thus obtained is 99.98% pure.

Hydrometallurgy (solvent extraction)

Solvent extraction is the latest separation technique and has become popular because of its elegance, simplicity and speed. The method is based on preferential solubility principles.

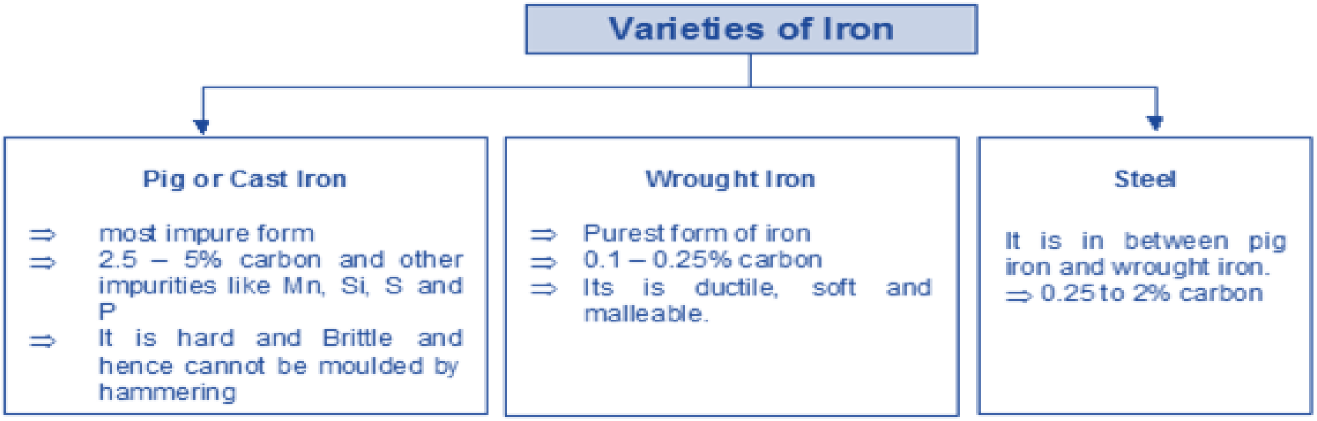
Solvent or liquid-liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other an organic solvent such as benzene, carbon tetrachloride or chloroform. In certain cases, the solute can be more or less completely transferred into the organic phase.

Extraction of Iron:

a) Important Ores of Iron:

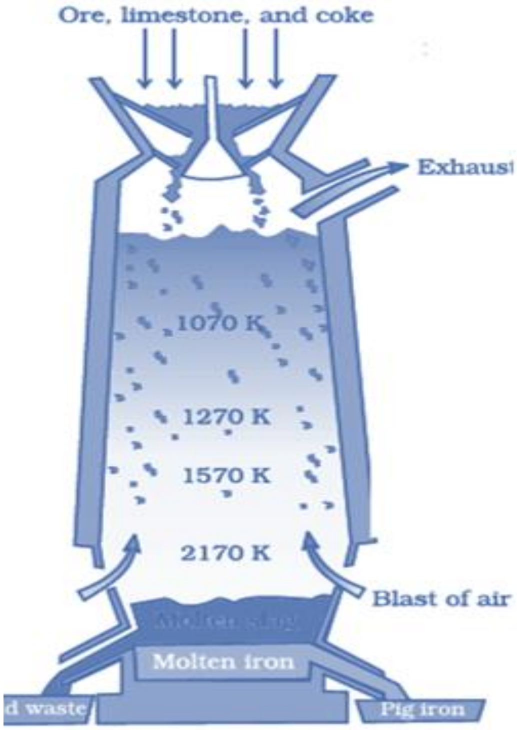
Hematite Fe_2O_3 (red oxide of iron)

Limonite $Fe_2O_3 \times 3H_2O$ (hydrated oxide of iron)



Magnetite Fe_3O_4 (magnetic oxide of iron)

Extraction of Cast Iron:



Reactions taking place in the blast furnace

Zone of combustion

$$\underset{\text{(Coke)}}{C} + O_2 \longrightarrow CO_2$$

Zone of reduction

$$Fe_2O_3 + 3CO \longrightarrow Fe + CO_2$$

Zone of reduction

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

Zone of slag formation

$$\underset{\text{(lim e stone)}}{CaCO_3} \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow \underset{\text{Fusible slag}}{CaSiO_3}\ ;$$

Zone of fusion

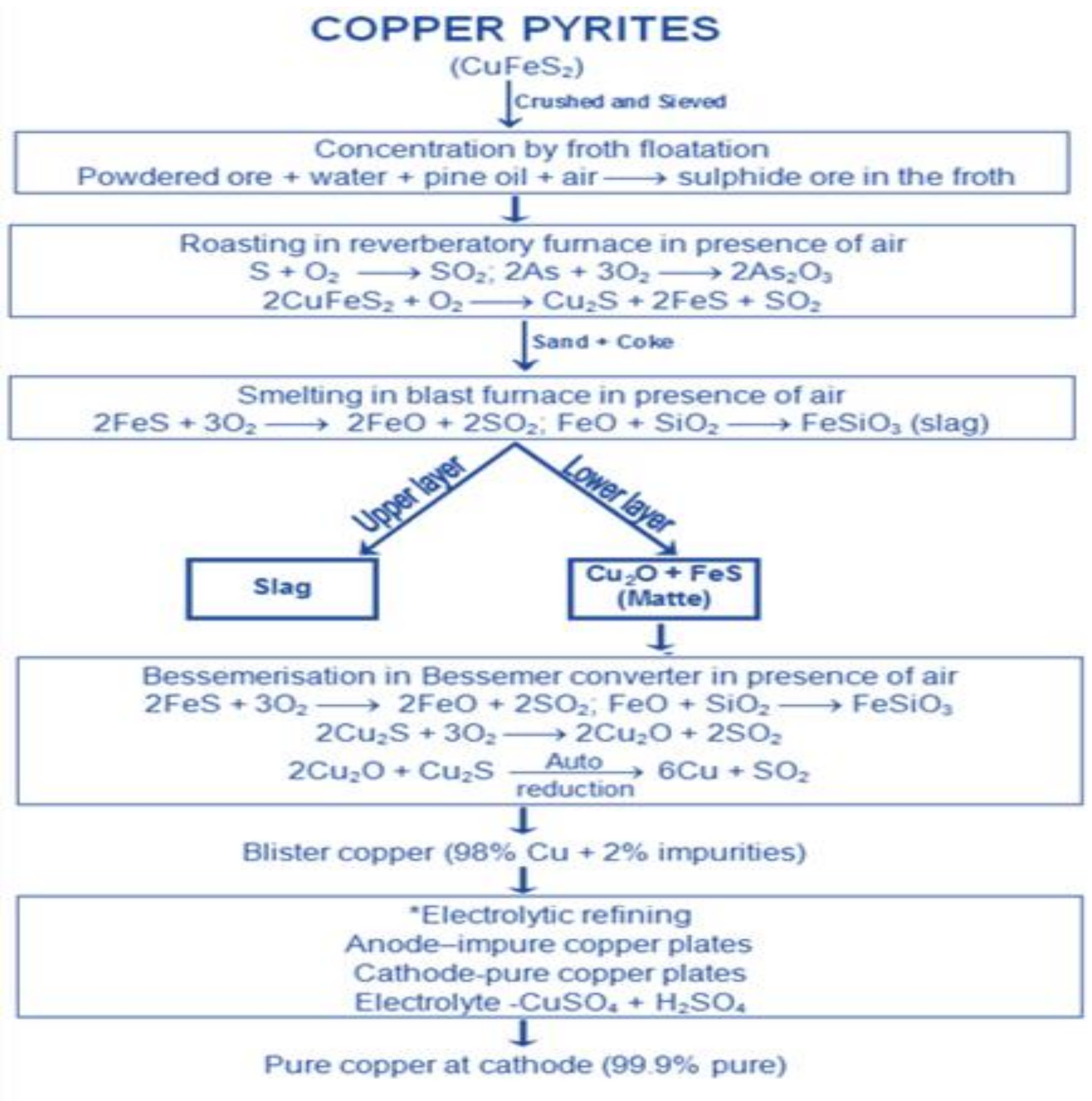
lower part of furnace

Molten iron is heavier than from molten slag. The two liquids are periodically tapped off. The molten iron tapped off from the furnace is solidifed into blocks called 'pigs'.

Extraction of Copper:

Ores of Copper:

- Copper glance (chalcocite) : Cu_2S
- Copper pyrites (Chalopyrites): $CuFeS_2$
- Malachite : $Cu(OH)_2 \times CuCO_3$
- Cuprite or Ruby copper: Cu_2O
- Azurite : $Cu(OH)_2 \times 2CuCO_3$



Refining of Metals:

Zone refining (Fractional crystallization): This method is employed for preparing extremely pure metals. This method is based upon the principle that when a molten solution of the impure metal is allowed to cool, the pure metal crystalises out while the impurities remain in the melt.

Electro-refining: In this method, the impure metal is converted into a block which forms the anode while cathode is a rod or plate of pure metal. These electrodes are suspended in an electrolyte which is the solution of a soluble salt of the metal usually a double salt of the metal. When electric current is passed, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ion. The soluble impurities present in the crude metal anode go into the solution while the insoluble impurities settle down below the anode as anode mud.

Van-Arkel Method: In this method, the metal is converted into it volatile unstable compound such as iodide leaving behind the impurities. The unstable compound thus formed is decomposed to get the pure metal.

$$\mathrm{Ti(s)} + 2\mathrm{I_2(s)} + \xrightarrow[540\mathrm{K}]{} \mathrm{TiI_4(g)} \xrightarrow[\mathrm{Ti(s)}]{1700\mathrm{K}} \mathrm{Ti} + 2\mathrm{I_2(g)}$$

Cupellation and Poling are used for refining of metals, cupellation is contain impurities of other metals with traces of lead are removed from silver by heating impure silver with a blast of air in a cupel (an oval shaped pan made up of bone ash) in which lead is oxidised to lead oxide (PbO) which being volatile escapes leaving behind pure silver.Poling is used for refining of such metals which contain impurities of its own oxide.

Study of Representative Elements (spdf blocks)

Revision Notes on s-Block Elements:

Alkali Metals (Group I elements of modern periodic table):

Poperty		**Elements**					
		Li	**Na**	**K**	**Rb**	**Cs**	**Fr (Radioactive)**
Atomic Number		3	11	19	37	55	87
Electronic Configuration		2s’	3s’	4s’	5s’	6s’	7s’
Atomic Mass		6.94	22.99	39.10	85.47	13.91	223
Metallic radius (pm)		152	186	227	248	265	375
Ionic radius (M$^+$/pm)		76	102	138	152	167	180
Ionization enthalpy (kJ mol^{-1})	I	520	496	419	403	376	–
	II	7298	3562	3051	2633	2230	–
Electro negativity (Pauling Scale)		0.98	0.93	0.82	0.82	0.79	
Density/g cm^{-3} (at 298K)		0.53	0.97	0.86	1.53	1.90	
Melting point/K		454	371	336	312	302	
Boiling point/K		1615	1156	1032	961	944	
E°(V) at 298K for M$^+$(aq) + e$^-$ → M(s)		−3.04	−2.714	−2.925	−2.930	−2.927	
Occurrence in Atmosphere		18*	227**	1.84**	78.12*	2.6*	

*ppm (parts per million)

** percentage by weight

Physical Properties of Alkali Metals:

- These are soft in nature and can be cut with the help of knife except the lithium.
- The atoms of alkali metals have the largest size in their respective periods.
- The first ionization energy of the alkali metals are the lowest as compared to the elements in the other group.
- The alkali metals show +1 oxidation state.
- The alkali metals have low values of reduction potential (as shown in table-I) and therefore have a strong tendency to lose electrons and act as good reducing agents.
- The melting and boiling points of alkali metals are very low because the intermetallic bonds in them are quite weak.
- ll the alkali metals form ionic (electrovalent) compounds.
- The alkali metals are good conductors of heat and electricity.
- Alkali metals (except Li) exhibit photoelectric effect
- The alkali metals and their salts impart a characteristic colour to flame

	Li	Na	K	Rb	Cs
Color	Crimson Red	Golden Yellow	Pale Violet	Violet	Sky Blue
l/nm	670.8	589.2	766.5	780.0	455.5

Hydroxides of Alkali Metals:

a) All the alkali metals, their oxides, peroxides and superoxides readily dissolve in water to produce corresponding hydroxides which are strong alkalies.

- $2Na + 2H_2O \rightarrow 2NaOH + H_2$
- $Na_2O + 2H_2O\ 2NaOH$
- $Na2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$
- $2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$

b) The basic strength of these hydroxides increases as we move down the group Li to Cs.

c) All these hydroxides are highly soluble in water and thermally stable except lithium hydroxide.

d) Alkali metals hydroxides being strongly basic react with all acids forming salts.

- $NaOH + HCl \rightarrow NaCl + H_2O$
- $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Halides of Alkali metals:

$M_2O + 2HX \rightarrow 2MX + H_2O$

$MOH + HX \rightarrow MX + H_2O$

$M_2CO_3 + 2HX \rightarrow 2MX + CO_2 + H_2O$ (M = Li, Na, K, Rb or Cs)

(X = F, Cl, Br or I)

a) Standard enthalpies of formation in (kJ/mol^{-1})

Element	MF	MCl	MBr	MI
Li	-612	-398	-350	-271
Na	-569	-400	-360	-288
K	-563	-428	-392	-328
Rb	-549	-423	-389	-329
Cs	-531	-424	-395	-

b) Covalent Character:

- Small cation and large anion favors covalency.
- Order: LiCl > NaCl > KCl > RbCl > CsCl & . LiI > LiBr > LiCl > LiF
- Greater the charge on the cation greater is its polarizing power and hence larger is the covalent character: $Na^+Cl^- < Mg^{+2}Cl_2 < Al^{+3}\,Cl_3$
- Greater the charge on the anion, more easily it gets polarized thereby imparting more covalent character to the compound formed eg covalent character increase in the order. $NaCl < Na_2SO_4 < Na_3PO_4$

c) Lattice Energies: Amount of energy required to separate one mole of solid ionic compound into its gaseous ions.

Greater the lattice energy, higher is the melting point of the alkali metals halide and lower is its solubility in water

d) Hydration Energy: Amount of energy released when one mole of gaseous ions combine with water to form hydrated ions.

- M^+ (g) + aq $\rightarrow$ M^+ (aq) + hydration energy
- X^- (g) + aq $\rightarrow$ X^- (aq) + hydration energy

Higher the hydration energy of the ions greater is the solubility of the compound in water.

The solubility of the most of alkali metal halides except those of fluorides decreases on descending the group since the decrease in hydration energy is more than the corresponding decrease in the lattice energy.

Due to high hydration energy of Li^+ ion, Lithium halides are soluble in water except LiF which is sparingly soluble due to its high lattice energy.

For the same alkali metal the melting point decreases in the order

fluoride > chloride > bromide > iodide

For the same halide ion, the melting point of lithium halides are lower than those of the corresponding sodium halides and thereafter they decrease as we move down the group from Na to Cs.

The low melting point of LiCl (887 K) as compared to NaCl is probably because LiCl is covalent in nature and NaCl is ionic.

Anomalous Behavior of Lithium and diagonal relationship with Magnesium:

Li has anomalous properties due to

- Very small size
- High polarizing Power

Lithium show diagonal relationship with magnesium because both elements have almost same polarizing power.

- The melting point and boiling point of lithium are comparatively high.
- Lithium is much harder than the other alkali metals. Magnesium is also hard metal.
- Lithium reacts with oxygen least readily to form normal oxide whereas other alkali metals form peroxides and superoxides.
- LiOH like $Mg(OH)_2$ is weak base. Hydroxides of other alkali metals are strong bases.
- Due to their appreciable covalent nature, the halides and alkyls of lithum and magnesium are soluble in organic solvents.
- Unlike elements of group 1 but like magnesium. Lithium forms nitride with nitrogen.$6Li + N_2 \rightarrow 2Li_3N$
- LiCl is deliquescent and crystallizes as a hydrate, $LiCl2H_2O$. Other alkali metals do not form hydrates. also forms hydrate, $MgCl_2.8H_2O$.
- Unlike other alkali metals lithium reacts directly with carbon to form an ionic carbide. Magnesium also forms a similar carbide.

- The carbonates, hydroxides and nitrates of lithium as well as magnesium decompose on heating.
    - $Li_2CO_3 \rightarrow Li_2O + CO_2$
    - $MgCO_3 \rightarrow MgO + CO_2$
    - $2LiOH \rightarrow Li_2O + H_2O$
    - $Mg(OH)_2 \rightarrow MgO + H_2O$
    - $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$
    - $2Mg(NO_3)_2 \rightarrow 2Mg + 4NO_2 + O_2$
- The corresponding salts of other alkali metals are stable towards heat.

Lithium nitrate, on heating, decomposes to give lithium oxide, Li_2O whereas other alkali metals nitrate decomposes to give the corresponding nitrite.

- $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$
- $2NaNO_3 \rightarrow 2NaNO_2 + O_2$
- $2KNO_3 \rightarrow 2KNO_2 + O_2$
- Li_2CO_3, LiOH, LiF and Li_3PO_4 are the only alkali metal salts which are insoluble in water. The corresponding magnesium compounds are also insoluble in water.
- Hydrogen carbonates of both lithium and magnesium can not be isolated in solid state. Hydrogen carbonates of other alkali metals can be isolated in solid state.

Sodium Hydroxide (NaOH):

a. Properties

- NaOH is stable towards heat but is reduced to metal when heated with carbon

  $2NaOH + 2C \rightarrow 2Na + 2CO + H_2$
- $FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$
- $NH_4Cl + NaOH \rightarrow NaCl + NH_3$ (pungent smell) $+ H_2O$
- $HgCl_2 + 2NaOH \rightarrow HgO$ (yellow powder) $+ 2NaCl + H_2O$
- $Zn(OH)_2 \uparrow + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2Oh$
- $Al_2O_3 \uparrow + 2NaOH \rightarrow 2NaAlO_2 + H_2O$
- $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
- $3P + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
- $2Al + 2NaOH + 2H_2O \rightarrow 3H_2 + 2NaAlO_2$

b. Uses

- It is used in the manufacture of paper, soap and artificial silk.
- It is used in petroleum refining.
- It is used for mercerizing cotton.
- It is used for the preparation of sodium metal and many salts of sodium.

Sodium Carbonate (Washing soda) (Na_2CO_3):

a. Preparation:

Solvay process:

Carbon dioxide gas is bubbled through a brine solution saturated with ammonia and it results in the formation of sodium hydrogen carbonate.

- $NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$
- $NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$

Sodium hydrogen carbonate so formed precipitates out because of the common ion effect caused due to the presence of excess of NaCl. The precipitated $NaHCO_3$ is filtered off and then ignited to get Na_2CO_3.

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

b. Properties

1. The aqueous solution absorbs CO_2 yielding sparingly soluble sodium bicarbonate.
    - $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$
2. Dissolves in acids with an effervescence of carbon dioxide and is causticised by lime to give caustic soda.
    - $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
    - $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$
3. Fusion with silica, sodium carbonate yields sodium silicate.
    - $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$
4. Hydrolysis – being a salt of a strong base (NaOH) and weak acid (H_2CO_3), when dissolved in water sodium carbonate. Undergoes hydrolysis to form an alkaline solution
    - $Na_2CO_3 + 2H_2O \rightarrow H_2CO_3 + 2NaOH$

c. Uses

- It is used for softening hard water.
- A mixture of sodium carbonate & potassium carbonate is used as fusion mixture.
- As an important laboratory reagent both in qualitative and quantitative analysis.
- It is used in paper, paints and textile industries.
- It is used for washing purposes in laundry.
- It is used in the manufacture of glass, borax, soap and caustic soda.

Alkali Earth Metals (Group II elements of modern periodic table):

Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra).

- **Physical Properties of Alkali Earth Metals:**

1. **Alkali earth metals are almost similar in properties to the corresponding alkali metals.**
    - Higher melting points than alkali metals
    - Higher boiling points alkali metals
    - Higher densities alkali metals
    - Harder than the corresponding alkali metals

2. **Atomic and ionic radii**

   The atomic radii as well as ionic radii of the members of the family are smaller than the corresponding members of alkali metals.

3. **Ionization energy:** The alkaline earth metals owing to their large size of atoms have fairly low values of ionization energies as compared to the p – block elements. However with in the group, the ionization energy decreases as the atomic number increases. It is because of increase in atomic size due to addition of new shells and increase in the magnitude of screening effect of the electrons in inner shells. Because their $(IE)_1$ is larger than that of their alkali metal neighbours, the group IIA metals trend to the some what less reactive than alkali metals. The general reactivity trend is Ba > Sr > Ca > Mg > Be.

4. **Oxidation state:** The alkaline earth metal have two electrons in their valence shell and by losing these electrons, these atoms acquire the stable noble gas configuration. Thus, unlike alkali metals, the alkaline earth metals exhibit +2 oxidation state in their compounds.

   $M \rightarrow M^{+2} + 2e^-$

   [noble gas]

5. **Characteristic flame colouration:**

Ion	Colour
Ca^{2+}	Brick-red
Sr^{2+}	Crimson
Ba^{2+}	Apple green
Ra^{2+}	Carmine – red

Difference between alkali metals and alkali earth metals:

	Properties	Alkaline earth metals	Alkali metals
1.	Electronic configuration	Two electrons are present in the valency shall. The configuration is ns^2 (bivalent)	One electron is present in the valency shell. The configuration is ns^1 (monovalent) more electropositive
2.	Valency	Bivalent	Monovalent
3.	Electropositive nature	Less electropositive	More electropositive
4.	Hydroxides	Weak bases, less soluble and decompose on heating.	Strong bases, highly soluble and stable towards heat.
5.	Bicarbonates	These are not known in free state. Exist only in solution.	These are known in solid state.
6.	Carbonates	Insoluble in water. Decompose on heating.	Soluble in water. Do not decompose on heating ($LiCO_3$ is an exception)
7.	Action of nitrogen	Directly combine with nitrogen and form nitrides	Do not directly combine with nitrogen except lithium
8.	Action of carbon	Directly combine with carbon and form carbides	Do not directly combine with carbon
9.	Nitrates	Decompose on heating evolving a mixture of NO_2 and oxygen	Decompose on heating evolving only oxygen
10.	Solubility of salts	Sulphates, phosphates fluorides, chromates, oxalates etc are insoluble in water	Sulphates, phosphates, fluorides, chromates, oxides etc are soluble in water.
11.	Physical properties	Comparatively harder. High melting points. Diamagnetic.	Soft, low melting points paramagnetic.
12.	Hydration of compounds	The compounds are extensively hydrated. $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $BaCl_2.2H_2O$ are hydrated chlorides.	The compounds are less hydrated. NaCl, KCl, RbCl form non – hydrated chlorides
13.	Reducing power	Weaker as ionization potential values are high and oxidation potential values are low.	Stronger as ionization potential values are low and oxidation potential values are high.

Chemical Properties of Alkali Earth Metals:

1. Reaction with water :

- $Mg + H_2O \rightarrow MgO + H_2$
- or, $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$
- $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

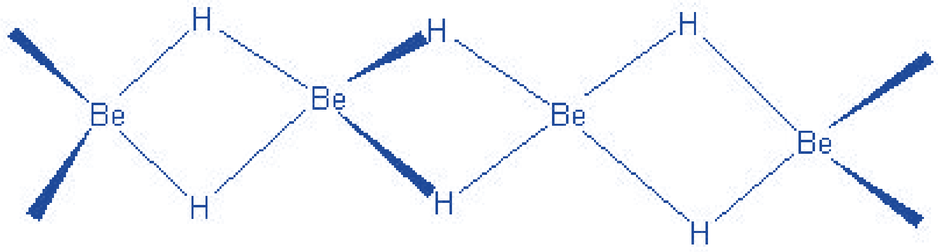
2. **Formation of oxides and nitrides**
   - Be + O_2 (air) +Δ→ 2BeO
   - 3Be + N2 (air) +Δ → Be_3N_2
   - Mg + air + Δ → MgO + Ng_3N_2

3. **Formation of Nitrides**
   - 3M + N_2 + Δ → M_3N_2
   - Be_3N_2 + Δ → 3Be + N_2
   - Ba_3N_2 + $6H_2O$ + Δ → 3Ba $(OH)_2$ + $2NH_3$
   - Ca_3N_2 + $6H_2O$ + Δ → 3Ca $(OH)_2$ + $2NH_3$

4. **Reaction with hydrogen:**

   M + H_2 + Δ → MH_2

   Both BeH_2 and MgH_2 are covalent compounds having polymeric structures in which H – atoms between beryllium atoms are held together by three centre – two electron (3C - 2e) bonds as shown below:



5. **Reaction with carbon – (Formation of carbides)**

   When BeO is heated with carbon at 2175 – 2275 K a brick red coloured carbide of the formula Be_2C is formed

$$2BeO + 2C \xrightarrow{2175-2275K} Be_2C + 2CO$$

   It is a covalent compound and react water forming methane.

   $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$

6. **Reaction with Ammonia:**

   Like alkali metal, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solution from which ammoniates $[M(NH_3)_6]^{2+}$ can be recovered.

Anamolous Behaviour of Beryllium:

- Be is harder than other members of its group.
- Be is lighter than Mg.
- Its melting and boiling points are higher than those of Mg & other members.
- Be does not react with water while Mg reacts with boiling water.
- BeO is amphoteric while MgO is weakly basic.
- Be forms covalent compounds whereas other members form ionic compounds.
- Beryllium carbide reacts with water to give methane whereas carbides of other alkaline earth metals gives acetylene gas.
    - $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$
    - $Mg_2C_2 + 2H_2O \rightarrow Mg(OH)_2 + C_2H_2$
    - $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$
- Beryllium does not exhibit coordination number more than four as it has four orbitals in the valence shell. The other members of this group has coordination number

Diagonal relationship of Be with Al:

- Unlike groups – 2 elements but like aluminium, beryllium forms covalent compounds.
- The hydroxides of Be, [$Be(OH)_2$] and aluminium [$Al(OH)_3$] are amphoteric in nature, whereas those of other elements of group – 2 are basic in nature.
- The oxides of both Be and Al i.e. BeO and Al_2O_3 are high melting insoluble solids.
- $BeCl_2$ and $AlCl_3$ have bridged chloride polymeric structure.
- The salts of beryllium as well as aluminium are extensively hydrolysed.
- Carbides of both the metal reacts with water liberating methane gas.
    - $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$
    - $Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$
- The oxides and hydroxides of both Be and Al are amphoteric and dissolve in sodium hydroxide as well as in hydrochloric acid.
    - $BeO + 2HCl \rightarrow BeCl_2 + H_2O$
    - $BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$
    - $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + H_2O$
    - $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$
- Like Al, Be is not readily attacked by acids because of the presence of an oxide film.

Calcium Carbonate ($CaCO_3$):

It occurs in nature as marble, limestone, chalk, coral, calcite, etc. It is prepared as a white powder, known as precipitated chalk, by dissolving marble or limestone in hydrochloric acid and removing iron and aluminium present by precipitating with NH_3, and then adding ammonium carbonate to the solution; the precipitate is filtered, washed and dried.

$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4Cl$

It dissolves in water containing CO_2, forming $Ca(HCO_3)_2$ but is precipitated from solution by boiling.

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

Plaster of Paris, $CaSO_4.1/2\ H_2O$ or $(CaSO_4)_2.H_2O$:

It occurs in nature as gypsum and the anhydrous salt as anhydride. It is prepared by precipitating a solution of calcium chloride or nitrate with dilute sulphuric acid.

The effect of heat on gypsum or the dihydrate presents a review of interesting changes. On heating the monoclinic gypsum is first converted into orthorhombic form without loss of water. When the temperature reaches 120°C, the hemihydrate or plaster of paris is the product. The latter losses water, becomes anhydrous above 200°C and finally above 400°C, it decomposes into calcium oxide.

$2CaSO_4 \rightarrow 2CaO + 2SO_2\uparrow + O_2\uparrow$

The addition of common salt accelerates the rate of setting, while a little borax or alum reduces it. The setting of plaster of paris is believed to be due to rehydration and its reconversion into gypsum.

$2CaSO_4.\ 1/2\ H_2O + 3H_2O \rightarrow 2CaSO_4.\ 2H_2O$

Plaster of Paris Gypsum

Uses

- Plaster of pairs is used for producing moulds for pottery and ceramics & casts of statues & busts.
- It is used in surgical bandages used for plastering broken or fractured bones.
- It is also used in dentistry

Industrial uses of lime and Limestone

Uses of lime

- Calcium oxide is called lime or quick lime. It main industrial uses are
- It is used in steel industry to remove phosphates and silicates as slag.
- It is used to make cement by mixing it with silica, alumina or clay.(iii) It is used in making glass.
- It is used in lime soda process for the conversion of Na_2CO_3 to NaOH & vice versa.
- It is used for softening water, for making slaked lime $Ca(OH)_2$ by treatment with water and calcium carbide CaC_2.

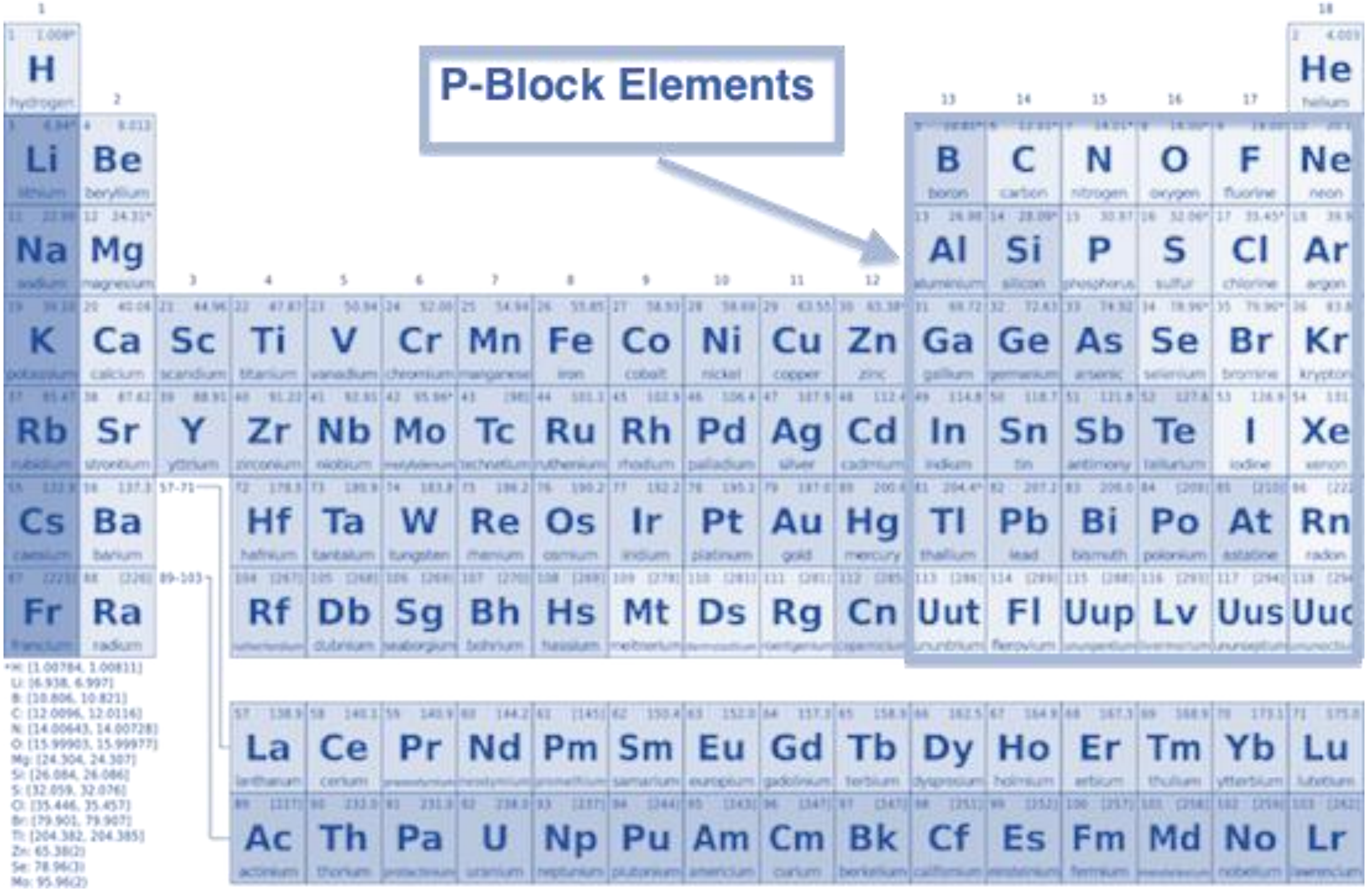
Uses of Slaked lime [$Ca(OH)_2$]

- Slaked lime is used as a building material in form of mortar. It is prepared by mixing 3 – 4 times its weight of sand and by gradual addition of water. Its sets into a hard mass by loss of H_2O and gradual absorption of CO_2 from air.
- In manufacture of bleaching powder by passing Cl_2 gas.
- In making glass and in the purification of sugar and coal gas.
- It is used in softening of hard water.

Uses of lime stone ($CaCO_3$)

- It is used as building material in form of marble.
- In manufacture of quick lime.
- It is used as a raw material for the manufacture of Na_2Co_3 in solvay – ammonia process.
- Commercial limestone contains iron oxide, alumina, magnesia, silica & sulphur with a CaO content of 22 – 56% MgO content upto 21%. It is used as such as a fertilizer.

Revision Notes on p-Block Elements:



Boron Family (Group 13 Elements)

- **Members:** B, Al, Ga, In & Tl
- **Melting Point**: Decreases from B to Ga and then increases up to Tl.
- **Ionization Energies:** 1st <<< 2nd < 3rd
- **Metallic Character:** Increases from B to Tl. B is non-metal

Boron

Preparation of Boron:

- From Boric Acid: $B_2O_3(s) + 3Mg(s) \rightarrow 2B(s) + 3 MgO(s)$
- From Boron Trichloride
  - (at 1270 k): $2BCl_3 + 3H_2 (g) \rightarrow 2B(s) + 6HCl (g)$
  - (at 900 ^{0}C): $2BCl_3(g) + 3Zn (s) \rightarrow 2B(s) + 3 ZnCl_2 (s)$
- By electrolysis of fused mixture of boric anhydride (B_2O_3) and magnesium oxide (MgO) & Magnesium fluoride at 1100 ^{0}C
  - $2 MgO- \rightarrow 2Mg + O_2(g)$
  - $B_2O_3 + 3Mg \rightarrow 2B + 3MgO$

- By thermal decomposition of Boron hydrides & halides:
  B_2H_6 (g) + Δ → 2B(s) + $3H_2$ (g)

Compounds of Boron:

Orthoboric acid (H_3BO_3)

Preparation of Orthoboric acid

- **From borax** : $Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$
- **From colemanite** : $Ca_2B_6O_{11} + 2SO_2 + 11H_2O \rightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

Properties of Orthoboric acid

- **Action of Heat**:

$$4H_3BO_3 \xrightarrow[-4H_2O]{373\,k} 4HBO_2 \xrightarrow[-H_2O]{413\,k} H_2B_4O_7 \xrightarrow[-H_2O]{\text{Read heat}} 2B_2O_3$$

Metaboric acid Tetraboric acid Boron trioxide

- **Weak monobasic acidic behavior:**
  $B(OH)_3 \leftrightarrow H_3BO_3 \leftrightarrow H^+ + H_2O +$
  Thus on titration with NaOH, it gives sodium metaborate salt
  $H_3BO_3 + NaOH \leftrightarrow NaBO_2 + 2H_2O$

- **Reaction with Metaloxide:**

$$B(OH)_3 + MO \xrightarrow{\text{Fusion}} M - \text{borates}$$

Where M stands for a bivalent metal

- **Reaction with Ammonium boro fluoride:**

$$B(OH)_3 \xrightarrow[\text{Fusion}]{NH_4HF_2} NH_4BF_4 \xrightarrow[\text{heat}]{B_2O_3} BF_3$$

Ammonium boro fluoride

Borax (sodium tetraborate) $Na_2B_4O_7.\ 10H_2O$

Preparation from Boric Acid

$4H_3BO_3 + Na_2CO_3 \dashrightarrow Na_2B_4O_7 + 6H_2O + CO_2$

Properties of Borax

- **Basic Nature**:-
  Aqueous solution of borax is alkaline in nature due to its hydrolysis
  $Na_2B_4O_7 + 3H_2O \rightarrow NaBO_2 + 3H_3BO_3$
  $NaBO_2 + 2H_2O \rightarrow NaOH + H_3BO_3$

- **Action of heat:**

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{heat} Na_2B_4O_7 \xrightarrow{740^\circ C} 2NaBO_2 + B_2O_3$$

Diborabe(B_2H_6)

<u>Preparation of Diborane:</u>

Reduction of Boron Trifluoride:

$BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3\ LiAl\ F_4$

From $NaBH_4$:

$2NaBH_4 + H_2SO_4 \rightarrow B_2H_6 + 2H_2 + Na_2SO_4$

$2NaBH_4 + H_3PO_4 \rightarrow B_2H_6 + 2H_2 + NaH_2PO_4$

Properties of Diborane:

- **Reaction with water**: $B_2H_6 + H_2O$ -->$2H_3BO_3 + 6H_2$
- **Combustion:** $B_2H_6 + 2O_2$ --? $B_2O_3 + 3H_2O$ $\Delta H = -2615$ kJ/mol

Compounds of Aluminium:

Aluminium Oxide or Alumina (Al_2O_3)

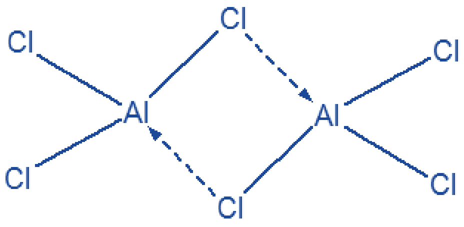
$2Al(OH)_3 + Heat \rightarrow Al_2O_3 + 2H_2O$

$2Al(SO_4)_3 + Heat \rightarrow Al_2O_3 + 2SO_3$

$(NH_4)_2Al_2(SO_4)_3 \cdot 24H_2O$ --> $2NH_3 + Al_2O_3 + 4SO_3 + 25\ H_2O$

Aluminum Chloride $AlCl_3$:

Structure of Aluminium Chloride:



<u>Properties of Aluminium Chloride</u>

- White, hygroscopic solid
- Sublimes at 183 ^{0}C
- Forms addition compounds with NH_3, PH_3, $COCl_2$ etc.
- Hydrolysis: $AlCl_3 + 3H_2O$ --> $Al(OH)_3 + 3HCl + 3H_2O$
- Action of Heat: **2**$AlCl_3$.$6H_2O$ --> $2Al(OH)_3$ à Al_2O_3+ $6HCl + 3H_2O$

Carbon Family (Group 14 Elements):

- **Members:** C, Si, Ge, Sn, & Pb
- **Ionization Energies:** Decreases from C to Sn and then increases up to Pb.
- **Metallic Character:** C and Si are non metals, Ge is metalloid and Sn and Pb are metals
- **Catenation:** C and Si show a tendency to combine with its own atoms to form long chain polymers

Compounds of Carbon:

Carbon Monoxide

<u>Preparation of Carbon Monoxide</u>

- By heating carbon in limited supply of oxygen: $C + 1/2O_2 \longrightarrow CO$.
- By heating oxides of heavy metals e.g. iron, zinc etc with carbon.
  - $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$
  - $ZnO + C \rightarrow Zn + CO$
- By passing steam over hot coke: $C + H_2O \rightarrow CO + H_2$ (water gas)
- By passing air over hot coke: $2C + O_2 + 4N_2 \rightarrow 2CO + 4N_2$ (Producer gas)

?<u>Properties of Carbon Monoxide</u>:

- A powerful reducing agent : $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
  $CuO + CO \rightarrow Cu + CO_2$
- Burns in air to give heat and carbon dioxide: $CO + 1/2O_2 \rightarrow CO_2$ + heat.

Tests For Carbon Monoxide:

- Burns with blue flame
- Turns the filter paper soaked in platinum or palladium chloride to *pink or green*.

Carbon di-oxide

<u>Preparation of Carbon di-oxide</u>

- By action of acids on carbonates: $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
- By combustion of carbon: $C + O_2 \rightarrow CO_2$

<u>Properties of Carbon di-oxide</u>

- It turns lime water milky $Ca(OH)_2 + CO_2 \rightarrow CaCO_3{}^{-} + H_2O$,
- Milkiness disappears when CO_2 is passed in excess
  $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$
- Solid carbon dioxide or *dry ice* is obtained by cooling CO2 under pressure. It passes from the soild state straight to gaseous state without liquefying (hence dry ice).

Carbides:

- **Salt like Carbides :** These are the ionic salts containing either C_2^{2-} (acetylide ion) or C^{4-} (methanide ion)e.g. CaC_2, Al_4C_3, Be_2C.
- **Covalent Carbides :** These are the carbides of non-metals such as silicon and boron. In such carbides, the atoms of two elements are bonded to each other through covalent bonds. SiC also known as *Carborundum*.
- **Interstitial Carbides :** They are formed by transition elements and consist of metallic lattices with carbon atoms in the interstices. e.g. tungsten carbide WC, vanadium carbide VC.

Compounds of Silicon:

Sodium Silicate (Na_2SiO_3):

?Prepared by fusing soda ash with pure sand at high temperature:

$Na_2CO_3 + SiO_3 \rightarrow Na_2SiO_3 + CO_2$

Silicones:

Silicon polymers containing Si – O – Si linkages formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation.

Silicates:

Salts of silicic acid, H_4SiO_4 comprised of SiO_4^{4-} units having tetrahedral structure formed as result of sp^3hybridization.

Nitrogen Family (Group 15 Elements)

- **Members:** N, P, As, Sb & Bi
- **Atomic Radii:** Increases down the group. Only a small increases from As to Bi.
- **Oxidation state:** +3, +4 & +5.Stability of +3 oxidation state increases down the group.
- **Ionization energy:** Increases from N to Bi.

Nitrogen

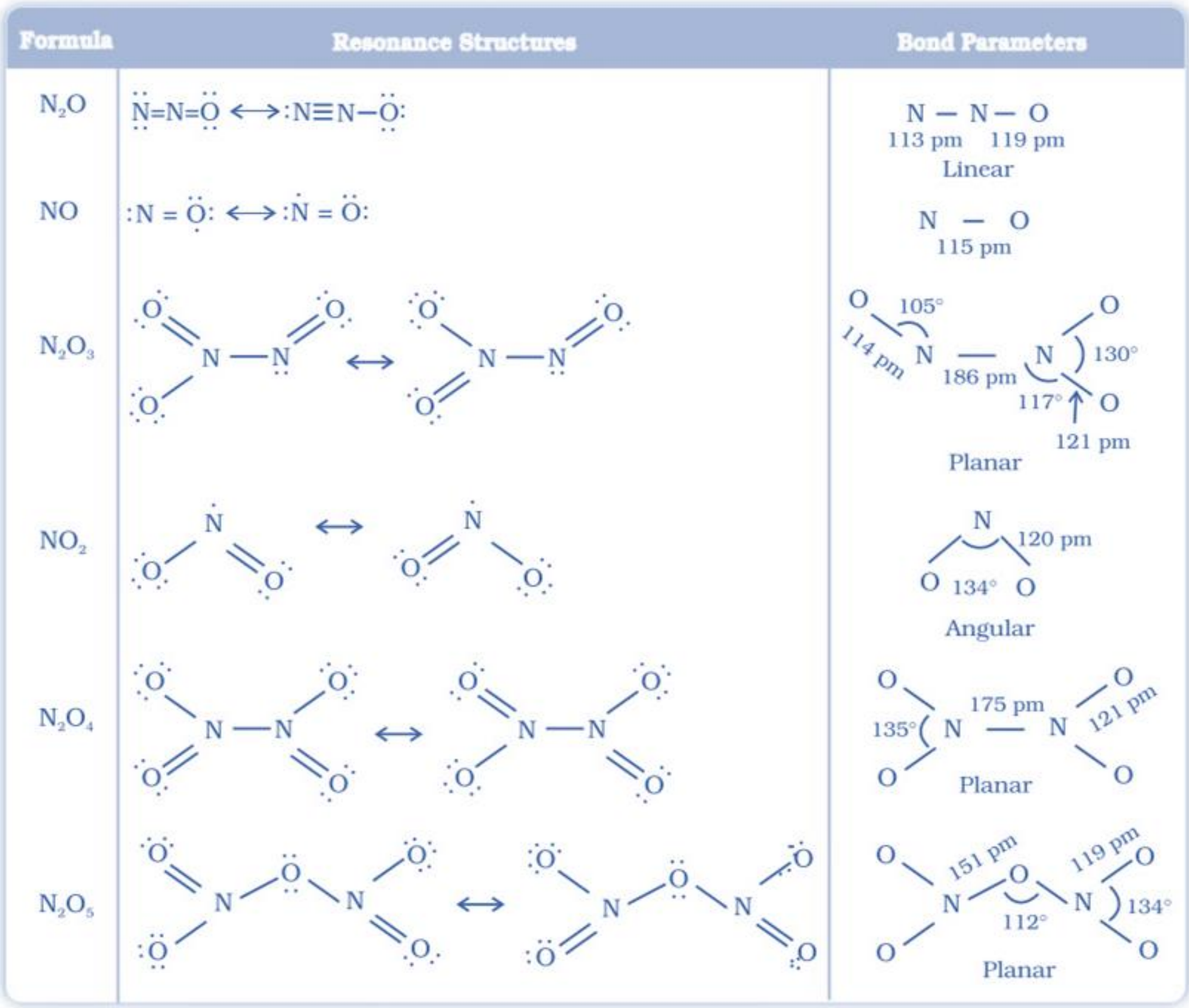
Preparation of Nitrogen:

- $3CuO + 2NH_3 + \text{Heat} \dashrightarrow N_2 + Cu + 3H_2O$
- $CaOCl_2 + 2NH_3 + \text{Heat} \dashrightarrow CaCl_2 + 3H_2O + N_2$
- $NH_4NO_2 + \text{Heat} \dashrightarrow 3H_2O + N_2 + Cr_2O_3$

Properties of Dinitrogen:

- Formation of Nitrides (with Li, Mg, Ca & Al): $Ca + N_2 + \text{Heat} \rightarrow Ca_3N_2$
- Oxidation: $N_2 + O_2 \rightarrow 2NO$
- Reaction with carbide (at 1273 K): $CaC_2 + N_2 \rightarrow CaCN_2 + C$

Oxides of Nitrogen



Oxy -Acids of Nitrogen :

Oxy Acids	Name of oxy – acid
1. $H_2N_2O_2$	Hyponitrous acid
2. $H_2\ NO_2$	Hydronitrous acid
3. HNO_2	Nitrous acid
4. HNO_3	Nitric acid
5. HNO_4	Per nitric acid

Ammonia (NH_3):

Preparation of Ammonia:

- By heating an ammonium salt with a strong alkali ;$NH_4Cl + NaOH \dashrightarrow NH_3 + NaCl + H_2O$
- By the hydrolysis of magnesium nitride: $Mg_3N_2 + 6H_2O \dashrightarrow 3Mg(OH)_2 + 2NH_3$.
- Haber's process : $N_2(g) + 3H_2(g) \dashrightarrow 2NH_3(g)$.

Properties of Ammonia:

- **Basic nature :** Its aq. solution is basic in nature and turns red litmus blue. $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$

- **Reaction with halogens :**
    - $8NH_3 + 3Cl_2 \dashrightarrow 6NH_4Cl + N_2$
    - $NH3 + 3Cl_2$ (in excess) $\rightarrow NCl_3 + 3HCl$
    - $8NH3 + 3Br_2 \rightarrow 6NH4Br + N_2$
    - $NH_3 + 3Br_2$ (in excess) $\rightarrow NBr_3 + 3HBr$
    - $2NH_3 + 3I_2 \rightarrow NH_3.NI_3 + 3HI$
    - $8NH_3.NI_3 \rightarrow 6NH_4I + 9I_2 + 6N_2$

- **Complex formation :**
    - $Ag^+ + NH_3 \rightarrow [Ag(NH_3)_2]^+$
    - $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$
    - $Cd^{2+} + 4NH_3 \rightarrow [Cd(NH_3)_4]^{2+}$

Precipitation of heavy metal ions from the aq. solution of their salts :

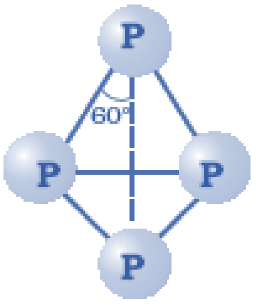
- $FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$
  Brown ppt.
- $AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$
  White ppt.
- $CrCl_3 + 3NH_4OH \rightarrow Cr(OH)_3 + 3NH_4Cl$
  Green ppt.

Phosphorus:

Allotropy of Phosphorus:

a) White phosphorus:

- Translucent white waxy solid
- Extremely reactive
- Poisonous and insoluble in water



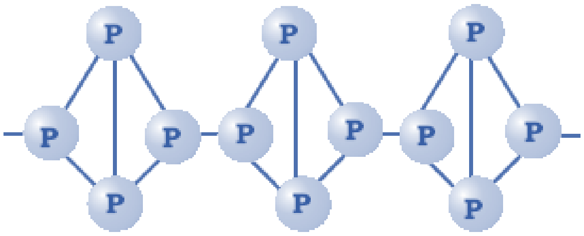
b) Red Phosphorus:

- Formed by heating white phosphorus in absence of air.
- Does not burn spontaneously at room temperature.

c) Black Phosphorus: Formed by further heating of red phosphorus.

Compounds of Phosphorus:

a) Phosphine, PH_3:



<u>Preparation of Phosphine</u>

- $Ca_3P_2 + 6H_2O \rightarrow 2 PH_3 + 3 Ca(OH)_2$
- $4H_3PO_3 + Heat \rightarrow PH_3 + 3 H_3PO_4$
- $PH_4I + KOH \rightarrow PH_3 + KI + H_2O$
- $P_4 + 3KOH + 3H_2O \rightarrow PH_3 + 3KH_3PO_2$

Properties of Phosphine:

- Formation of Phosphonic Iodide: $PH_3 + HI$ à PH_4I
- Combustion: $PH_3 + 2O_2$ à H_3PO_4

b) Phosphorous Halides:

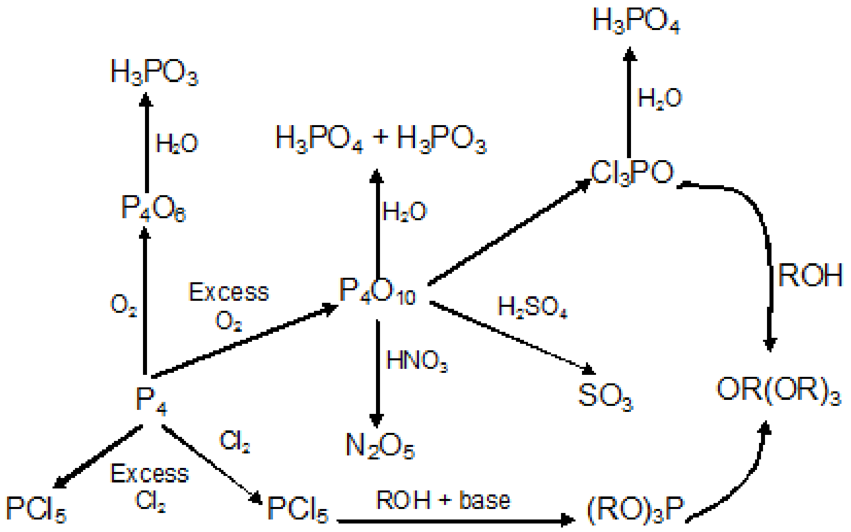
Preparation:

- $P_4 + 6Cl_2 \rightarrow 4PCl_3$
- $P_4 + 10Cl_2 \rightarrow 4PCl_5$
- $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
- $P_4 + 10SOCl_2 \rightarrow 4PCl_5 + 10SO_2$

Properties:

- $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
- $PCl_5 + 4H_2O \rightarrow POCl_3$ à $H_3PO_4 + 5HCl$
- $PCl_3 + 3CH_3COOH \rightarrow 3 CH_3COCl + H_3PO_3$
- $PCl_5 + CH_3COOH \rightarrow CH_3COCl + POCl_3 + HCl$
- $2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$
- $2Sn + PCl_5 \rightarrow SnCl_4 + 2PCl_3$
- $PCl_5 + Heat \rightarrow PCl_3 + Cl_2$

?C) Oxides of Phosphorus:



d) Oxy – Acids of Phosphorus:

Oxo acid	Name
H_3PO_2	Hypophosphorus acid
H_3PO_3	Phosphorus acid
$H_4P_2O_6$	Hypophosphoric acid
H_3PO_4	Orthophosphoric acid
$H_4P_2O_7$	Pyrophosphoric acid
HPO_3	Metaphosphoric acid

Oxygen Family (Group 16 Elements) :

Sr. No.	Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
1.	Configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]4s^2 4p^4$	$[Kr]5s^2 5p^4$	$[Xe]6s^2 6p^4$
2.	Common oxidation state	-2	-2, +4, +6	+4, +6	+4, +6	
3.	Atomic radius (pm)	66	104	116	143	167
4.	First ionization energy (KJ/mol)	1314	1000	941	869	812
5.	Electronegativity	3.5	2.5	2.4	2.1	2.0

Chemical Properties of Group 16:

Formation of volatile Hydrides:

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

$$Na_2Se + 2HCl \longrightarrow 2NaCl + H_2Se$$

Formation of Halides:

$$\frac{1}{8}S_8(s) + 3F_2(g) \longrightarrow SF_6(g)$$

$$\frac{1}{4}S_8(\ell) + Cl_2(g) \longrightarrow S_2Cl_2(\ell)$$

$$Te(s) + 2Cl_2(g) \longrightarrow TeCl_4(s)$$

$$Te(s) + 2I_2(g) \longrightarrow TeI_4(s)$$

Formation of Oxide:

a) All elements (except Se) forms monoxide.

b) All elements form dioxide with formula MO_2, SO_2 is a gas, SeO_2 is volatile solid. While TeO_2 and PoO_2 are non – volatile crystalline solids.

c) **Ozone:** It is unstable and easily decomposes into oxygen. It acts as a strong oxidising agent due to the case with which it can liberate nascent oxygen.

Oxyacids:

Sulphur	Selenium	Tellurium
Sulphurous acid H_2SO_3. **Sulphuric acid H_2SO_4** **Peroxomonosulphuric acid H_2SO_5(Caro's acid)** **Peroxodisulphuric acid** **$H_2S_2O_8$ (Marshell's acid)** **Thio sulphuric acid $H_2S_2O_3$** **Dithiconic acid $H_2S_2O_6$** **Pyrosulphuric acid $H_2S_2O_7$**	Selenious acid H_2SeO_3 Selnenic acid H_2SeO_4	Tellurous acid H_2TeO_3. Telluric acid H_2TeO_4.

Allotropes of Sulphur :

Rhombic sulphur:

- It has bright yellow colour.
- It is insoluble in water and carbon disulphide. Its density is 2.07 gm cm^{-3} and exists as S_8 molecules. The 8 sulphur atoms in S_8 molecule forms a puckered ring.

Monoclinic Sulphur :

- Stable only above 369 K. It is dull yellow coloured solid, also called *b - sulphur*. It is soluble in CS_2 but insoluble in H_2O.
- It slowly changes into rhombic sulphur. It also exist as S_8 molecules which have puckered ring structure. It however, differs from the rhombic sulphur in the symmetry of the crystals

Plastic Sulphur:

- It is obtained by pouring molten sulphur to cold water.
- It is amorphous form of sulphur.
- It is insoluble in water as well as CS_2.

Sulphuric Acid:

- Due to strong affinity for water, H_2SO_4 acts as a powerful dehydrating agent.
- Concentrated H_2SO_4 reacts with sugar, wood, paper etc to form black mass of carbon. This phenomenon is called charring.
- It is moderately strong oxidizing agent.

$$C + 2H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + CO_2$$

$$\frac{1}{8}S_8 + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$$

$$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$$

$$H_2S + H_2SO_4 \longrightarrow 2H_2O + S + SO_2$$

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$$

- Decomposes carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites at room temperatures.

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2 \uparrow$$

$$H_2SO_4 + 2NaHCO_3 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2 \uparrow$$

$$H_2SO_4 + Na_2S \longrightarrow Na_2SO_4 + H_2S \uparrow$$

- Salts like chlorides, fluorides, nitrates, acetates, oxalates are decomposed by hot conc. H_2SO_4 liberating their corresponding acids.

$$H_2SO_4 + CaCl_2 \longrightarrow CaSO_4 + 2HCl \uparrow$$

$$H_2SO_4 + CaF_2 \longrightarrow CaSO_4 + 2HF$$

? $$H_2SO_4 + 2KNO_3 \longrightarrow K_2SO_4 + 2HNO_3$$

Halogen Family (Group 17 Elements)

Inter halogen compounds:

Type XX'_1 (n = 1) (with linear shape)	Type XX'_3 (n = 3) (with T-shape)	XX'_5 (n = 5) (with square pyramidal shape)	XX'_7 (n = 7) with pentagonal bipyramidal shape)
ClF	ClF_3	ClF_5	
BrF BrCl	BrF_3	BrF_5	
ICl, IBr, IF	ICl_3, IF_3	IF_5	IF_7

Hydrogen Halides:

Properties of Hydrogen Halides:

- All the three acids are reducing agents HCl is not attacked by H_2SO_4.
  - $2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2$
  - $2HI + H_2SO_4 \rightarrow 2H_2O + SO_2 + I_2$
- All the three react with $KMnO_4$ and $K_2Cr_2O_7$
  - $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl2 + 8H_2O + 5Cl_2$
  - $K_2Cr_2O_7 + 14HBr \rightarrow 2KBr + 2CrBr_3 + 7H_2O + 3Br_2$
- Other reactions are similar.
  - Dipole moment : HI < HBr < HCl < HF
  - Bond length: HF < HCl < HBr < HI
  - Bond strength: HI < HBr < HCl < HF
  - Thermal stability: HI < HBr < HCl < HF
  - Acid strength: HF < HCl < HBr < BI
  - Reducing power: HF < HCl < HBr < HI

Pseudohalide ions and pseudohalogens:

Ions which consist of two or more atoms of which at least one is nitrogen and have properties similar to those of halide ions are called pseudohalide ions. Some of these pseudohalide ions can be oxidised to form covalent dimers comparable to halogens (X_2). Such covalent dimers of pseudohalide ions are called pseudohalogens.

The best known psuedohalide ion is $CN^{-\backslash}$

Pseudohalide ions	**Name**
CN^-	Cyanide ion
OCN^-	Cyanate ion
SCN^-	Thiocyante ion
$SeCN^-$	Selenocyanate ion
NCN^{2-}	Cyanamide ion
N_3^-	Azide ion
OMC^-	Fulminate ion

Pseudohalogen

- $(CN)_2$ cyanogen
- $(SCM)_2$ thiocyanogen

Some important stable compound of Xenon

- XeO_3 Pyramidal
- XeO_4 Tetrahedral
- $XeOF_4$ Square pyramidal
- XeO_2F_2 Distorted octahedral

First rare gas compound discovered was $Xe^+ (PtF_6]^-$ by Bartlett.

Oxyacids of Chlorine

Formula	Name	Corresponding Salt
HOCl	Hypochlorous acid	Hypochlorites
$HClO_2$	Chlorous acid	Chlorites
$HClO_3$	Chloric acid	Chlorates
$HClO_4$	Perchloric acid	Perchlorates

Acidic Character: Acidic character of the same halogen increases with the increase in oxidation number of the halogen: $HClO_4 > HClO_3 > HClO_2 > HOCl$

Preparation

HOCl :

- $Ca(OCl)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2HOCl$

$HClO_2$:

- $BaO_2 + 2ClO_2 \rightarrow Ba(ClO_2)_2$ (liquid) $+ O_2$
- $Ba(ClO_2)_2 + H_2SO_4$(dil.) $\rightarrow BaSO_4$ ¯ $+ 2HClO_2$

$HClO_3$:

- $6Ba(OH)_2 + 6Cl_2 \rightarrow 5BaCl_2 + Ba(ClO_3)_2 + 6H_2O$
- $Ba(ClO_3)_2 + H_2SO_4$(dil.) $\rightarrow BaSO_4$ ¯ $+ 2HClO_3$

$HClO_4$:

- $KClO_4 + H_2SO_4 \rightarrow KHSO_4 + HClO_4$
- $3HClO_3 \rightarrow HClO_4 + 2ClO_2 + H_2O$

The Noble Gases (Group 18 Elements):

The noble gases are inert in nature. They do not participate in the reactions easily because they have

- stable electronic configuration i.e. complete octet.
- high ionization energies.
- low electron affinity.

Compounds of Xenon

$$\underset{(1:2)}{Xe + F_2} \xrightarrow[673\,K]{\text{Nickel tube}} XeF_2$$

$$\underset{(1:5)}{Xe + 2F_2} \xrightarrow[5-6\text{ atm}]{\text{Nickel tube, }673\,K} XeF_4$$

$$\underset{(1:20)}{Xe + 3F_2} \xrightarrow[50-60\text{ atm}]{\text{Nickel tube, }575\,K} XeF_6$$

Molecule	Total electron pairs (BP + LP)	Hybridisation	Shape
XeF_2	5s	Sp^{3}d	Linear
XeF_4	6	Sp^{3}d^2	Square planar
XeF_6	7	sp^{3}d^3	Distorted octahedral

Uses of Nobles gas

The noble gases are used in following ways:

(A) Helium

- It is used to fill airships and observation balloons.
- In the oxygen mixture of deep sea divers.
- In treatment of asthma.
- Used in inflating aeroplane tyres.
- Used to provide inert atmosphere in melting and welding of easily oxidizable metals.

(B) Neon

- It is used for filling discharge tubes, which have different characteristic colours and are used in advertising purposes.
- Also used in beacon lights for safety of air navigators as the light possesses fog and stram perpetrating power.

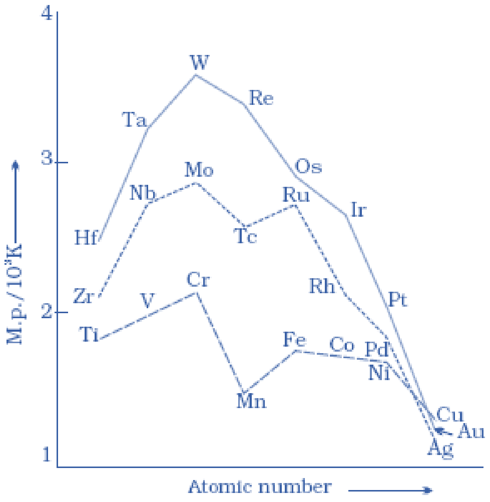
(C) Argon

Along with nitrogen it is used in gas – filled electric lamps because argon is more inert than nitrogen.

Revision Notes on Transition Elements:

Physicochemical Properties

a. Melting and Boiling Points:

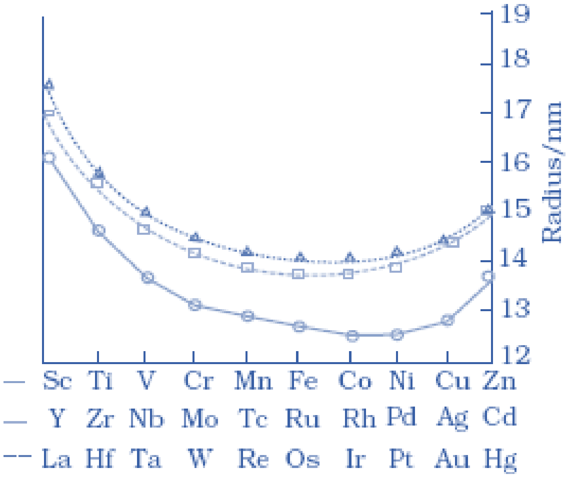


Melting and boiling points show no definite trends in the three transition series.

The metals having the highest melting and boiling points are towards the middle of each transition series.

b. Atomic (Covalent) and Ionic Radii:

Atomic and ionic radii values decrease generally, on moving from left to right in the period.



The atomic radii for the elements from Cr to Cu are very close to one another.

Radii of 5d series elements are virtually the same as those of corresponding members of 4d series due to lanthanoid contraction.

c. Ionisation Potentials:

- **First Ionization Potentials:** I_1 values for the first four 3d block elements (Sc, Ti, V and Cr) differ only slightly from one another. The value of I_I 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 I_{II} 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.

d. Oxidation States:

- The higher oxidation state of 4d and 5d series elements are generally more stable than those of the elements of 3d series,
- In short it may be said that in going down a sub-group the stability of the higher oxidation states increases while that of lower oxidation states decreases.
- Transition elements cannot form ionic compounds in higher oxidation states because the loss of more than three electrons is prevented by the higher attractive force exerted (on the electrons) by the nucleus

e. Colour: Transition elements with partially filled d orbitals form coloured compounds.

f. **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.

g. **Catalytic properties:**

Transition metals and their compounds are known to act as good catalyst due to

1. variable oxidation state, they form unstable intermediate compounds and provide a new path with lower activation energy for the reaction (Intermediate compound formation theory)
2. In some cases the finely divided metals or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to the closer contact(Adsorption theory)

h. **Magnetic Properties:**

Magnetic moment is which is related to the number of unpaired electrons as follows

$$\mu = \sqrt{n(n+2)}\ \text{B.M.}$$

n = number of unpaired electrons

B.M. = Bohr Magneton, unit of magnetic moment

More the magnetic moment more is the paramagnetic behavior

i. **Formation of Alloys:**

As the transition elements have similar atomic sizes hence in the crystal lattice, one metal can be readily replaced by another metal giving solid solution and smooth alloys. The alloys so formed are hard and have often high melting point.

j. **Interstitial Compounds:**

Transition metals form no. of interstitial compounds, in which they take up atoms of small size e.g. H, C and N in the vacant spaces in the their lattices. The presence of these atoms results in decrease in malleability and ductility of the metals but increases their tensile strength.

Potassium Dichromate ($K_2Cr_2O_7$)

a. Preparation

It is prepared from the ore called chromate or ferrochrome or chrome iron, $FeO.Cr_2O_3$.

Steps: 1, Preparation of sodium chromate

$4FeO.Cr_2O_3 + O_2 \rightarrow Fe_2O_3 + 4Cr_2O_3$

$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 \rightarrow 4Na_2CrO_4 + 4CO_2$

Step: 2, Conversion of sodium chromate into sodium dichromate.

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

Step: 3, Conversion of sodium dichromate into potassium dichromate.

$Na_2Cr2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

b. Properties

1. Action of heat: When heated, it decomposed to its chromate

$4K_2Cr_2O_7 + \Delta \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

2. Action of alkalis

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

$2K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$

3. Action of conc. H_2SO_4 solution

(a) In cold conditions

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

(b) In hot conditions

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

4. Oxidising propertiesIt is a powerful oxidising agent.

In the presence of dil. H_2SO_4 it furnishes 3 atoms of available oxygen.

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

Some of the oxidizing properties of $K_2Cr_2O_7$ are

It liberates I_2 from KI

$K_2Cr_2O_7 + 7H_2SO_4 + 6Kl \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

It oxidises ferrous salts to ferric salts

$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 2H_2O$

It oxidises S^{-2} to S

$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

It oxidises nitrites to nitrates

$K_2Cr_2O_7 + 4H_2SO_4 + 3NaNO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3NaNO_3 + 4H_2O$

It oxidises SO_2 to SO_4^{2-}

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3H_2O$

It oxidises ethyl alcohol to acetaldehyde and acetic acid.

5. Chromyl chloride test

When heated with conc. HCl or with a chloride in the presence of sulphuric acid, reddish brown vapours of chromyl chloride are obtained.

$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$

Thus reaction is used in the detection of chloride ions in qualitative analysis.

c. Uses

In volumetric analysis for the estimation of Fe^{2+} and I^-.

In chrome tanning in leather industry.

In photography and in hardening gelatin film.

Potassium Permanganate

a. Preparation:

It is prepared from the mineral pyrolusite, MnO_2.

Step:1, Conversion of MnO_2 into potassium manganate.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

Step:2, Oxidation of potassium manganate into permanganate

Chemical oxidation

K_2MnO_4 is oxidised to $KMnO_4$ by bubbling CO_2 or Cl_2 or ozone into the former.

$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$

Electrolytic oxidation

$2K_2MnO_2 + H_2O + O \rightarrow 2K_2MnO_4 + 2KOH$

b. Properties

$KMnO_4$ exists as deep purple prisms. It is moderately soluble in water at room temperature and its solubility in water increases with temperature.

(i) Action of heat

When heated it decomposes to K_2MnO_4.

$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(ii) Action of conc. H_2SO_4

With cold conc. H_2SO_4 it gives Mn_2O_7 which on warming decomposes to MnO_2.

$2MnO_2 + 2H_2SO_4 \rightarrow Mn_2O_7 + 2KHSO_4 + 2H_2O$

$2Mn_2O_7 + \Delta \rightarrow 4MnO_2 + 3O_2$

With hot Conc. H_2SO_4 O_2 is evolved

$4KMnO_4 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_{21}$

(iii) Oxidising properties

$KMnO_4$ is a powerful oxidizing agent. The actual oxidizing action depends upon themedium i.e. acidic, basic or neutral.

(a) In neutral solution, it acts as moderate oxidizing agent.

$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O$

Some oxidizing properties of $KMnO_4$ in neutral medium are

$2KMnO_4 + 3Na_2S_2O_3 + H_2O \rightarrow 3K_2SO_4 + 8MnO_2 + 3Na_2SO_4 + 2KOH$
$2KMnO_4 + 4H_2S \rightarrow 2MnS + S + K_2SO_4 + 4H_2O$

(b) In strong alkaline solution, it is converted into

$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$

Some reaction in alkaline medium are

$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$

(c) In acidic medium, Mn^{+7} is converted into Mn^{+2}

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

Some other reactions are

(i) $2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5S$

(ii) $2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(iii) $2KMnO_4 + 3H_2SO_4 + 5KNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5KNO_3$

(iv) $2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

(v) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

(vi) $2KMnO_4 + 3H_2SO_4 + 10KI \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$

c. Uses

(i) Used in volumetric analysis for estimation of ferrous salts, oxalates, iodides & H_2O_2.

(ii) Used as oxidizing agent in the laboratory as well as in industry.

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] $4f^{n+1}$ $5d^{\circ}$ $6s^2$ 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 down the group 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.

Co-ordination Compounds

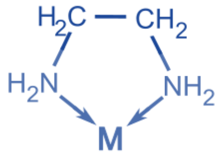
Revision Notes on Coordination Compounds

Ligands: an ion or molecule capable of donating a pair of electrons to the central atom via a donor atom.

- Unidentate ligands: Ligands with only one donor atom, e.g. NH_3, Cl^-, F^- etc.
- Bidentate ligands: Ligands with two donor atoms, e.g. ethylenediamine, $C_2O_4^{2-}$(oxalate ion) etc.
- Tridentate ligands: Ligands which have three donor atoms per ligand, e.g. (dien) diethyl triamine.
- Hexadentate ligands: Ligands which have six donor atoms per ligand, e.g. EDTA.

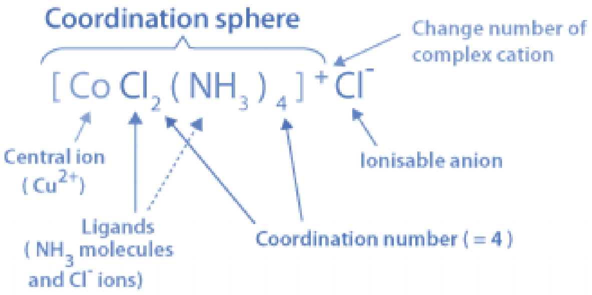
Chelating Ligands:

- Multidentate ligand simultaneously coordinating to a metal ion through more than one site is called chelating ligand. Example: Ethylenediamine ($NH_2CH_2CH_2NH_2$)
- These ligands produce a ring like structure called chelate.
- Chelation increases the stability of complex.



Werner's Theory:

- Metals possess two types of valencies i.e. primary (ionizable) valency and secondary (nonionizable) valency.
- Secondary valency of a metal is equal to the number of ligands attached to it i.e. coordination number.
- Primary valencies are satisfied by negative ions, while secondary valencies may be satisfied by neutral, negative or positive ions.



- Secondary valencies have a fixed orientation around the metal in space.

  $[Co(NH_3)_6]Cl_3$
  Primary Valencies = 3 Cl^-
  Secondary Valencies = 6 NH_3
  Coordination Sphere = $[Co(NH_3)_6]^{3-}$

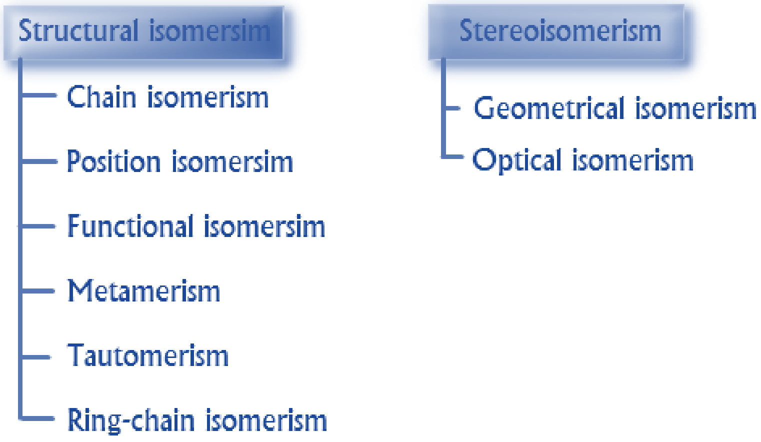
Nomenclature of Complexes:

- Positive ion is named first followed by negative ion.
- Negative ligands are named by adding suffix - o.
- Positive ligands are named by adding prefix – ium.
- Neutral ligands are named as such without adding any suffix or prefix.
- Ligands are named in alphabetical order.
- Name of the ligands is written first followed by name of metal with its oxidation number mentioned in roman numbers in simple parenthesis.
- Number of the polysyllabic ligands i.e. ligands which have numbers in their name, is indicated by prefixes bis, tris etc,
- Number and name of solvent of crystallization if any, present in the complex is written in the end of the name of complex.
- When both cation and anion are complex ions, the metal in negative complex is named by adding suffix-ate.
- In case of bridging ligands:
  [Name of the groups to the left of bridging ligand (Oxidation state)] –µ – [Name of the groups to the right of bridging ligand (Oxidation state)] – [Name of negative ion]

Ligands	Name
Negative	
CH_3COO^-	Acetato
CN^-	Cyano
Br^-	Bromo
Cl^-	Chloro
F^-	Fluoro
OH^-	Hydrido
N^{3-}	Nitrido
$C_2O_4^{2-}$	Oxalato
SO_3^{2-}	Sulfito
O_2^-	Superoxo
O_2^{2-}	Peroxo
O^{2-}	Oxo
NH^{2-}	Imido
SO_4^{2-}	Sulphato
$S_2O_3^{2-}$	Thiosulfato
HS^-	Mercapto

Positive	
NO^+	Nitrosonium
$NH_2NH_3^+$	Hydrazinium
Neutral	
H_2O	Aqua
NH_3	Ammine
CO	Carbonyl
CH_3NH_2	Methylamine
NO	Nitrosyl
C_5H_5N	Pyridine

Isomerism in coordination compounds



Structural Isomerism

- Ionization Isomerism: Exchange of ligands between coordinate sphere and ionization sphere $[Pt(NH_3)_4Cl_2]Br_2$ & $[Pt(NH_3)_4Br_2]Cl_2$
- Hydrate Isomerism: Exchange of water molecules between coordinate sphere and ionization sphere
  $[Cr(NH_3)_3(H_2O)_3]Br_3$ & $[Cr(NH_{32})_3(H_2O)_2 Br]Br_2 H_2O$
- Linkage Isomerism: Ambient legend binds from the different binding sites to the metal atom. $K_2[Cu(CNS)_4]$ & $K_2[Cu(SCN)_4]$
- Coordination Isomerism: Exchange of the metal atom between coordinate sphere and ionization sphere when both are complex ions.
  $[Cr(NH_3)_6][CoF_6]$ & $[Co(NH_3)_6][CrF_6]$.

- Ligand Isomerism: Different isomers of the same ligands attached to the metal.

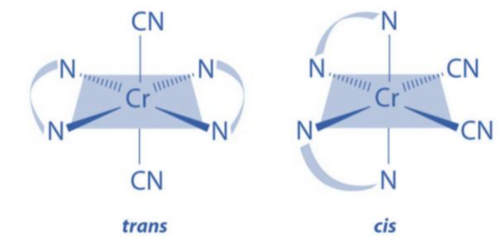
  $[Co(pn)_2Br]Cl_2$ & $[Co(tn)_2Br]Cl_2$ Where,

  pn = 1,2- Diaminopropane

  tn = 1,3-Diaminopropane.

Stereoisomerism:

a. Geometrical Isomerism: When two similar ligands are on adjacent position the isomer is called cis isomer while hen they are on opposite positions, the isomer is called trans isomer.



b. Optical Isomerism: In order to show optical isomerism, the complex should form a non superimposible mirror image which rotates the place of polarized light in opposite direction.

Valence Bond Theory:

Hybridization:

Find out the hybridization of central metal ion using following steps:

- Write down the electronic configuration of metal atom.
- Find out oxidation state of metal atom.
- Write down the electronic configuration of metal ion.
- Write down the configuration of complex to find out hybridization.
- Strong field ligands cause the pairing of electrons.

  Strong Field Ligands: CO, CN^-, NO_2^-, en, py, NH_3.

  Weak Filed Ligands: H_2O, OH^-, F^-, Cl^-, Br^-, I^-

When the d orbital taking part in hybridization is inside the s and p orbital taking part in hybridization with respect to the nucleus, it is called an inner orbital complex.

Example: d^2sp^3 hybridization of $[Co(NH_3)_6]^{3+}$ involves 3d, 4s and 4p orbital, hence it is an inner orbital complex.

When the d orbital taking part in hybridization outside the s and p orbital taking part in hybridization with respect to the nucleus, it is called an outer orbital complex.

Example: sp^3d^2 hybridization of $[CoF_6]^{3-}$ involves 4*d*, 4*s* and 4*p* orbital, hence it is an inner orbital complex.

Coordination Number	Hybridization	Geometry
4	sp^3	Tetrahedral
	dsp^2	Square Planar
6	d^2sp^3 & sp^3d^2	Oct

Geometry:

Magnetic Properties:

- Diamagnetic: All the electrons paired.
- Paramagnetic: Contains unpaired electrons.

Spin:

- Spin paired: All electrons paired.
- Spin free: Contains unpaired electrons.

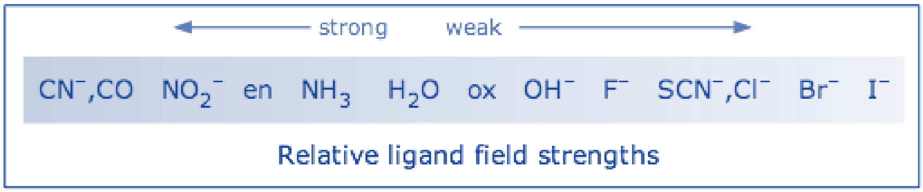
Colour:

Compound must contain free electrons in order to show colour.

Crystal Field Theory:

Strong field ligand causes greater repulsion and thus results in the formation of low spin complexes by pairing of electrons.

- Weak field ligands result in the formation of high spin complexes
- Order of strength of ligands: CO > CN^- > NO_2^- > en > py = NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- >I^-



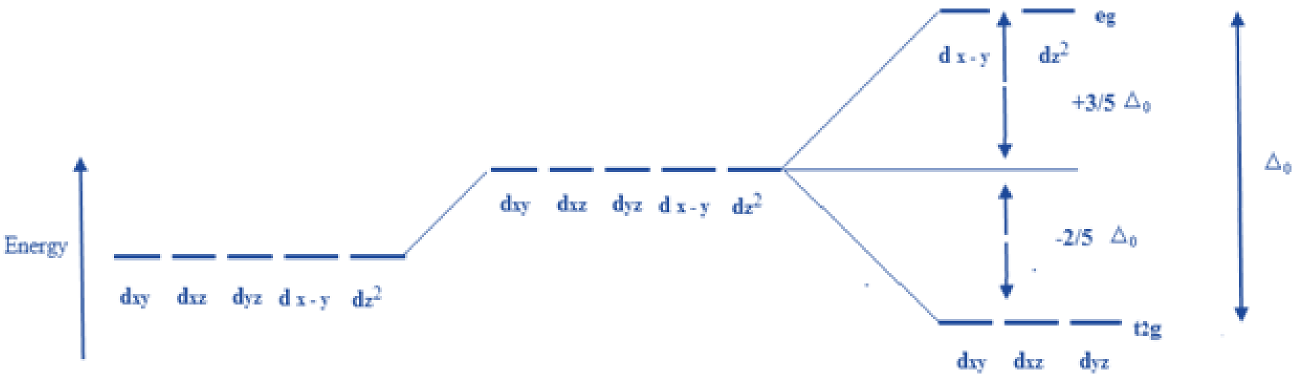
strong weak

CN^-,CO NO_2^- en NH_3 H_2O ox OH^- F^- SCN^-,Cl^- Br^- I^-

Relative ligand field strengths

?

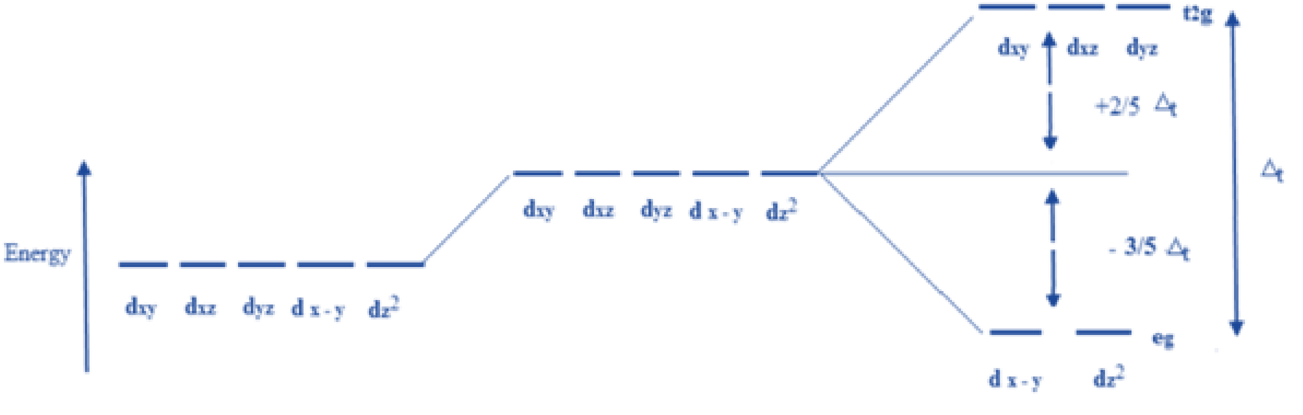
- Octahedral Complexes: e_g orbital are of higher energy than t_{2g} orbital.



Metal Ion in Octhedral Crvstal Field

- Tetrahedral Complexes: e_g orbitals are of lower energy than t_{2g} orbitals.

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



Metal Ion in Tetrahedral Crystal Field

Crystal Field Stabilization Energy:

System	High Spin		Low Spin	
	Electronic Configuration	**CFSE**	**Electronic Configuration**	**CFSE**
Octahedral Complex				
d^4	$t_{2g}^3\ e_g^1$	$-(3/5)\Delta_0$	$t_{2g}^4\ e_g^0$	$-(8/5)\Delta_0+P$
d^5	$t_{2g}^3\ e_g^2$	0	$t_{2g}^5\ e_g^0$	$-(10/5)\Delta_0+2P$
d^6	$t_{2g}^4\ e_g^2$	$-(2/5)\Delta_0+P$	$t_{2g}^6\ e_g^0$	$-(12/5)\Delta_0+3P$
d^7	$t_{2g}^5\ e_g^2$	$-(4/5)\Delta_0+2P$	$t_{2g}^6\ e_g^1$	$-(9/5)\Delta_0+3P$
Tetrahedral Complexes				
d^4	$e_g^2\ t_{2g}^2$	$-(2/5)\Delta_t$	$e_g^4\ t_{2g}^0$	$-(12/5)\Delta_t+2P$
d^5	$e_g^2\ t_{2g}^3$	0	$e_g^4\ t_{2g}^1$	$-2\ \Delta_t+2P$
d^6	$e_g^3\ t_{2g}^3$	$-(3/5)\Delta_t+P$	$e_g^4\ t_{2g}^2$	$-(8/5)\Delta_t+2P$

Magnetic Properties: Complexes with unpaired electrons are paramagnetic while with no unpaired electron are diamagnetic.

Basic Concepts of Organic Chemistry

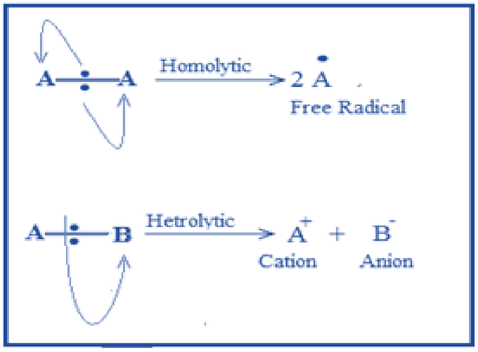
General Organic Chemistry:

Bound Fission:

a) **Homolytic fission:** Each atom separates with one electron, leading to the formation of highly reactive entities called radicals, owing their reactivity to their unpaired electron.

b) **Heterolytic fission:** One atom holds on to electrons, leaving none for the other, the result in the above case being a negative and positive ion, respectively, the result being the formation of an *ion pair*.

Reactions involving radicals tend to occur in the gas phase and in solution in non-polar solvents, and to be catalyzed by light and by the addition of other radicals. Reactions involving ionic intermediates take place more readily in solution in polar solvents, because of the greater ease of separation of charges therein and very often because of the stabilization of the resultant ion pairs through solvation.



Electronic Displacement in Covalent Bonds

The following four types of electronic effects operates in covalent bonds

a) Inductive effect

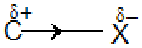
b) Mesomeric and Resonance effect

c) Electromeric effects

d) Hyperconjugation

Inductive Effect:

a) **Negative inductive Effect: (–I Effect):**This is due to electron - attracting groups (X); it develops positive charge on the chain and is said to exert a negative inductive denoted by (– I)



$\overset{\delta+}{C}\rightarrow\overset{\delta-}{X}$

1) It decreases as one goes away from group X (electron attracting): X-C_1-C_2-C_3

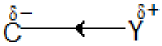
C_1(d+) > C_2(dd+) > C_3(ddd+) and after third carbon charge is negligible

D and L configuration:

a) The configuration of an enantiomer is related to a standard, glyceraldehydes.

Order: $^+NH_3NO_2$ > F > COOH > Cl > Br > I > OH > C_6H_5

a) **Positive Inductive Effect (+I):** This is due to electron-releasing group (Y). It develops an negative charge on the chain and is said to exert a positive inductive effect denoted by (+I)



$\overset{\delta-}{C}\leftarrow\overset{\delta+}{Y}$

1) It also decreases as we go away group Y (electron - releasing):Y-C_1-C_2-C_3

C_1(d–) > C_2(dd–) > C_3(ddd–)

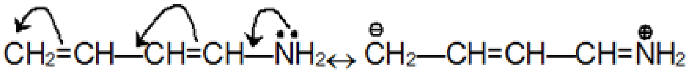
2) Order: $(CH_3)_3C$ -R > $(CH_3)_2CH$-R > CH_3CH_2-R > CH_3-R

	(–I) effect	**(+I) Effect**
Acidic nature –	Increases	Decreases
Basic nature–	Decreases	Increases

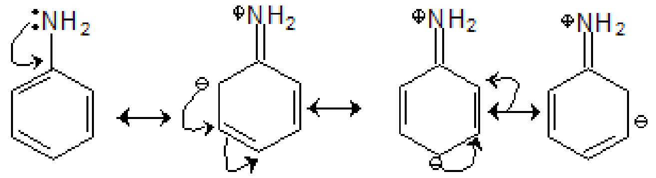
Mesomeric Effect or Resonance Effect:

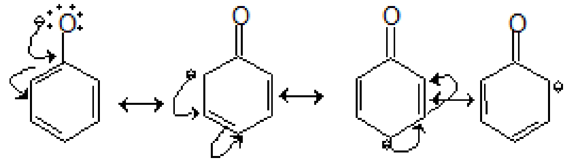
In conjugated systems, p-electrons shifting takes place consecutively giving permanent polarity on the chain.

a) **Positive Mesomeric Effect (+M):** A group or atom is said to have +M effect when the direction of electron -displacement is away from it.

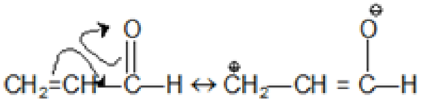


This effect extends the degree of delocalization and imparts stability to the molecule

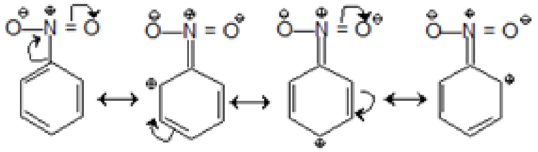


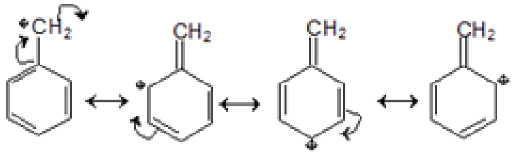


a) Negative Mesomeric Effect (–M): A group or atom is said to have +M effect when the direction of electron -displacement is toward it.

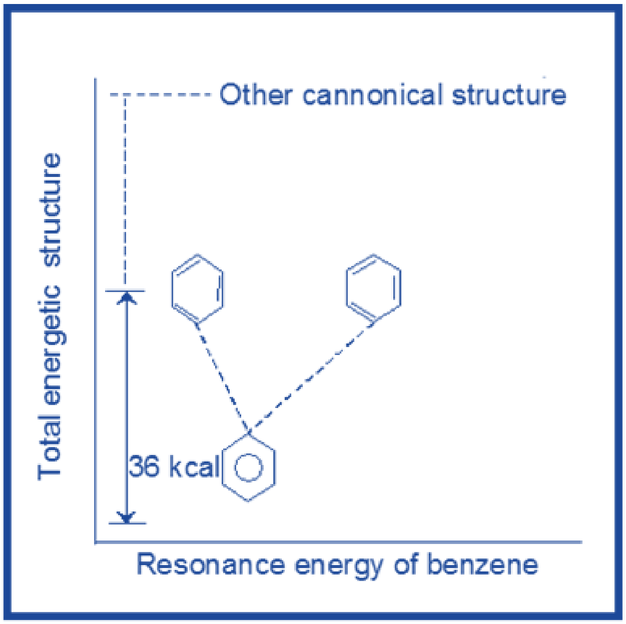


$$CH_2=CH-\overset{O}{\overset{\|}{C}}-H \leftrightarrow \overset{+}{C}H_2-CH=\overset{O^{-}}{\overset{|}{C}}-H$$





a) Resonance Energy: The difference in energy between the hybrid and the most stable canonical structure is called as Resonance energy

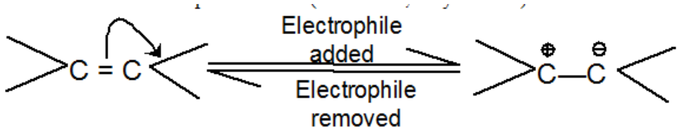


Electromeric Effect:

Complete transfer of p-electrons from one atom to other to produce temporary polarity on atoms joined by multiple bonds, in the presence of an electrophile is known as electromeric effect. Effect is reversible and temporary.

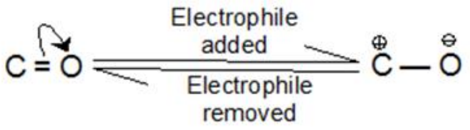
a) Positive Electromeric Effect:

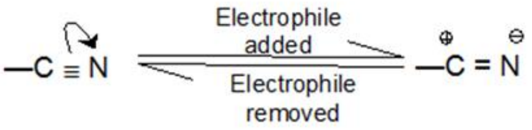
p-electrons transfer takes place C to C (as alkenes, alkynes etc.)



a) Negative Electromeric Effect:

p-electrons transfer takes place to more electronegative atom (O,N,S) joined by multiple bonds.





Hyperconjugation:

Delocalization of sigma electrons also known as sigma-pi – conjugation or no bond resonance. It is a permanent effect.

a) Occurrence

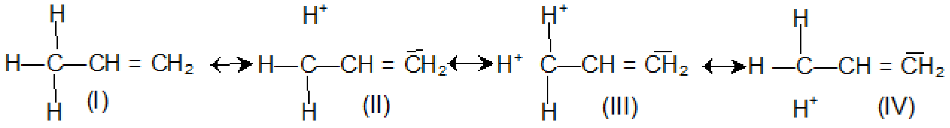
Alkene, alkynes

Free radicals (saturated type) carbonium ions (saturated type)

b) Condition

Presence of a–H with respect to double bond, triple bond carbon containing positive charge (in carbonium ion) or unpaired electron (in free radicals)

Example



Note: Number of hyperconjugative structures = number of a-Hydrogen. Hence, in above examples structures I,ii,iii,iv are hyperconjugate structures (H-structures).

a) Effects of Hyperconjugation:

Bond Length: Hyperconjugation also affects bond lengths because during the process the single bond in compound acquires some double bond character and vice-versa

Dipole moment: Since hyperconjugation causes this development of charges, it also affects the dipole moment of the molecule.

Stability of carbonium Ions: Tertiary > Secondary > Primary

Stability of Free radicals:

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

Reactive Intermediates:

Species	Geometry	Stability
Carbocation	sp^2 hybridized with a planar structure and bond angles are of about 120°. There is a vacant unhybridized p orbital which (e.g. in the case of CH_3^+) lies perpendicular to the plane of C—H bonds	Any structural feature which tends to reduce the electron deficiency at the tricoordinate carbon stabilizes the carbocation Order: 3°> 2° > 1° > CH_3^+
Carbanions	sp^3 hybridized with the unshared pair occupying one apex of the tetrahedron. Pyramidal structures similar to those of amines.	Any structural feature which tends to reduce the electron deficiency at the tricoordinate carbon stabilizes the carbocation Order: 3°< 2° < 1° < CH_3^-
Free Radicals	sp^2 hybridized with planar (trigonal) structure.. and sp^3 hybridized with pyramidal structure.	Hyperconjugation increases the stability of free radical. Order: : 3°> 2° > 1°

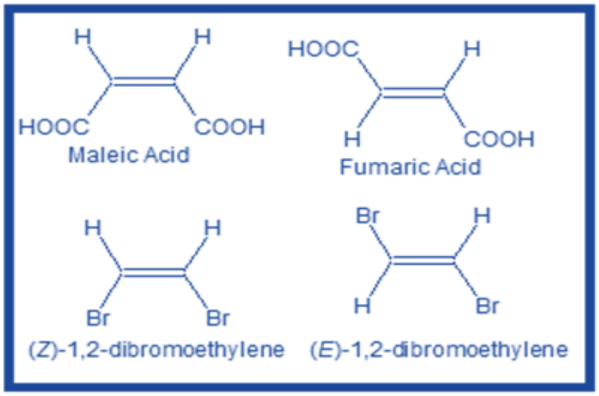
Isomerism :

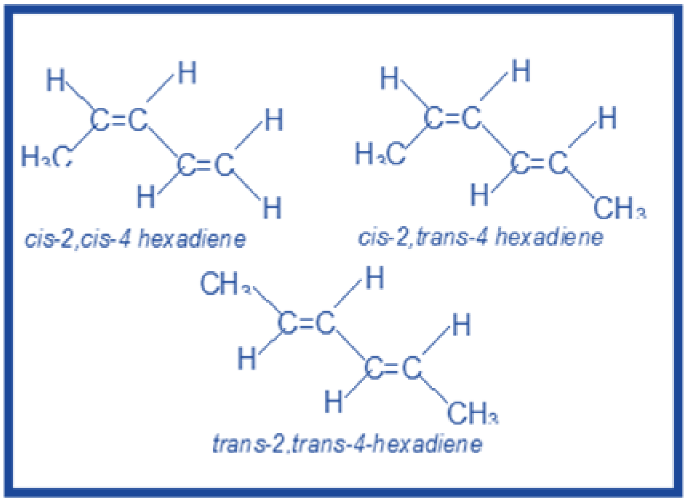
Geometrical Isomerism:

The isomers possess the same structural formula containing a double bond and differ only in respect of the arrangement of atoms or groups about the double bond.

This isomerism is shown by alkenes or their derivatives in which two different atoms or groups are attached to each carbon containing the double bond.

Thus the compounds having the formula abC = Cxy or the simple structure *abC = Cab* occur in two forms and exhibit geometrical isomerism.





a) The *trans* isomers of alkenes are usually more stable than their corresponding *cis* isomers.

b) The *trans* isomers have normally less dipole moments than their corresponding *cis* isomers.

c) The *trans* isomer has greater symmetry than the corresponding *cis* isomer. Thus it packs more easily in the crystal lattice and hence has higher melting points.

Optical Isomerism:

a) Optical Activity: The property of a substance of rotating the plane of polarized light.

b) Specific Rotation: The number of degrees of rotation observed when light is passed through 1 decimeter (10 centimeters) of its solution having concentration 1 gram per milliliter.

$$[\alpha]_D^{t^\circ} = \frac{a_{obs}}{l \times c}$$

a) **Laevorotatory or (-) - form:** rotates the plane of polarized light to the left.

b) **Dextrorotatory or (+)- form :** rotates the plane of polarized light to the right.

c) Racimic Mixture or (±)– mixture : An inactive from which does not rotate the plane of polarized light at all. This is a mixture of equal amounts of (+)– and (–)– forms and hence its optical inactivity

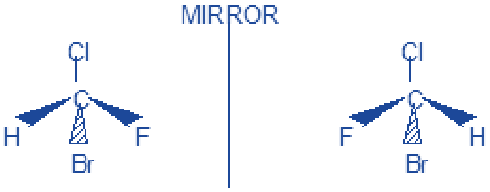
Asymmetric Carbon atom: A carbon atom which is attached to four different atoms

Chirality:

a) All organic compounds which contain an asymmetric carbon (C* *abde*) atom are *chiral* and exist in two tetrahedral forms.

b) A molecule must have chirality in order to show optical activity.

Enantiomers: Two optical isomers which are non superimposable mirror images of each other.



a) Meso compounds: Compound containing two or more chiral carbon which do not show optical activity due to presence of centre of symmetry (indicated by thick dot).

b) Compounds which have unsymmetrical molecule with one or more chiral centres: In such compounds if 'n' is the number of chiral carbons, then

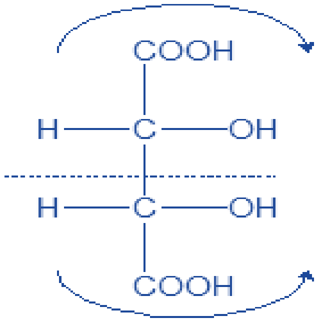
No. of optically active isomers (a) = 2^n

No. of racemic forms (r) = a/2

No. of meso forms (m) = 0

c) compounds having a symmetrical molecule (compounds having chiral carbons but molecule as a whole is achiral): (a) compounds with even number of carbons atoms: In such compounds if number of chiral carbons in n, we have a = 2^{n-1}, r = a/2, and m=$2^{(n/2-1)}$

d) Compounds with odd number of carbon atoms: In such compounds if n is the number of asymmetric carbons then total optical isomers are given by 2^{n-1} whereas m = $2^{(n-2)/2}$. Thus, a = $2^{n-1} - 2^{(n-1)/2}$.



Inactivity of Meso Tartaric acid by Internal Compesnation

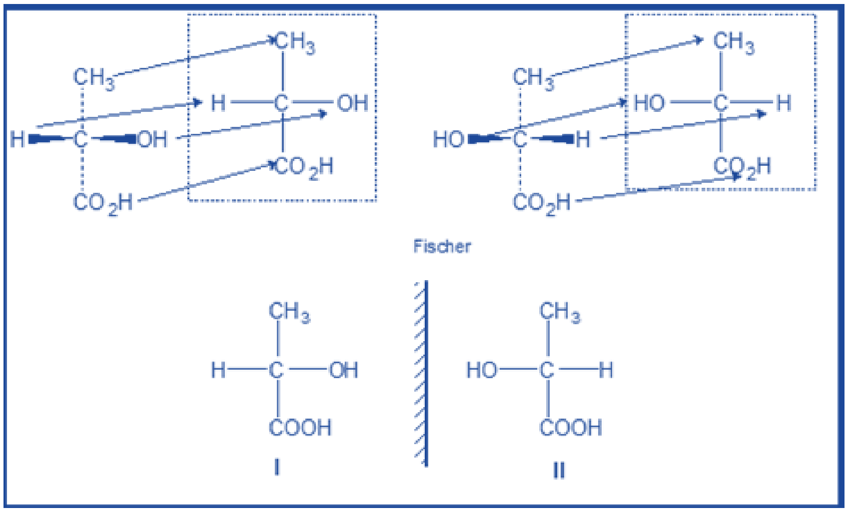
The force of rotation due to one half of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to **internal compensation.** It occurs whenever a compound containing two or more

Fischer Projections:

a) Representing three dimensional structures on a two dimensional surface.

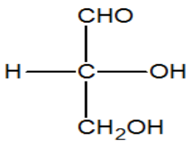
b) Asymmetric carbon atom drawn in a prescribed orientation and then projected into a planar surface.

c) Planar formulas of the asymmetric carbon are obtained by placing it so that the two substituents are horizontal and project out towards the viewer (shown by thick wedge-like bonds), while the two other substituents are vertical and project away from the viewer (shown by dotted bonds).



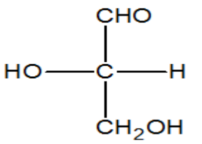
D and L configuration:

a) The configuration of an enantiomer is related to a standard, glyceraldehydes.



(+)-glyceraldehyde

D configuration



(-)-glyceraldehyde

L configuration

b) If the configuration at the asymmetric carbon atom of a compound can be related to D (+)-glyceraldehyde, it belongs to D-series.

c) By convention for sugars, the configuration of the highest numbered asymmetric carbon is referred to glyceraldehyde to determine the overall configuration of the molecule.

R and S System:

The **sequence rules** to determine the order of priorities of groups are :

The atoms or groups directly bonded to the asymmetric carbon are arranged in order of decreasing atomic number and assigned priority 1, 2, 3, 4, accordingly

a) Thus in chlorobromofluoromethane (CHClBrF), the substituents Br (at no = 35), Cl (at no = 17), F (at no = 9) and H (at no = 1) give the order of priorities.

Br > Cl > F > H

(1) (2) (3) (4)

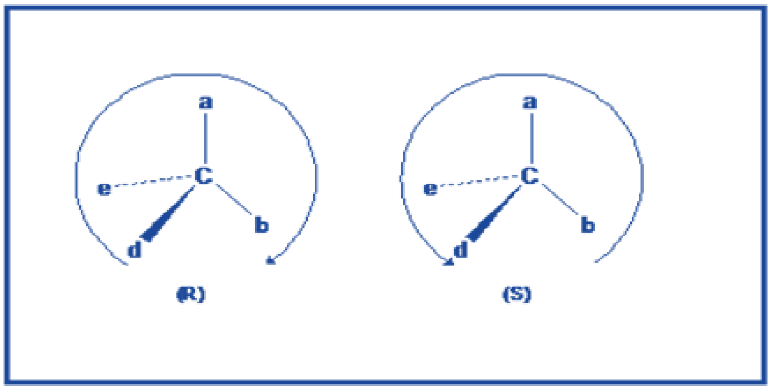
b) When two or more groups have identical first atoms attached to asymmetric carbon, the priority order is determined by considering the atomic numbers of the second atoms; and if the second atoms are also identical the third atoms along the chain are examined.

c) If the first atoms of the two groups have same substituents of higher atomic number, the one with more substituents takes priority.

Thus —$CHCl_2$ has a higher priority than —CH_2Cl.

d) A doubly or triply bonded atom 'A' present in a group appended to asymmetric carbon, is considered equivalent to two or three singly bonded 'A's, respectively. Thus, R= A equals A-R-A.

If in a molecule, order of priority for groups a,b,c,d, & e is $a > b > d > e$



Diastereomers :

- Stereoisomers which are optically active isomers but not mirror images, are called diasteriomers.
- Diastereoisomers have different physical properties. Thus they have different melting points, boiling points, solubilities in a given solvent, densities, and refractive indices.
- They also differ in specific rotations; they may have the same or opposite signs of rotations.
- Like geometrical isomers, the diastereoisomers may be separated from each other :–
  - by fractional distillation due to their difference in boiling points;
  - by fractional crystallisation due to their difference in solubility;
  - by chromatography due to their different molecular shapes and polarity.

Alkanes, Alkenes, Alkynes & Aromatic Compounds

Hydrocarbons

Compounds of carbon and hydrogen.

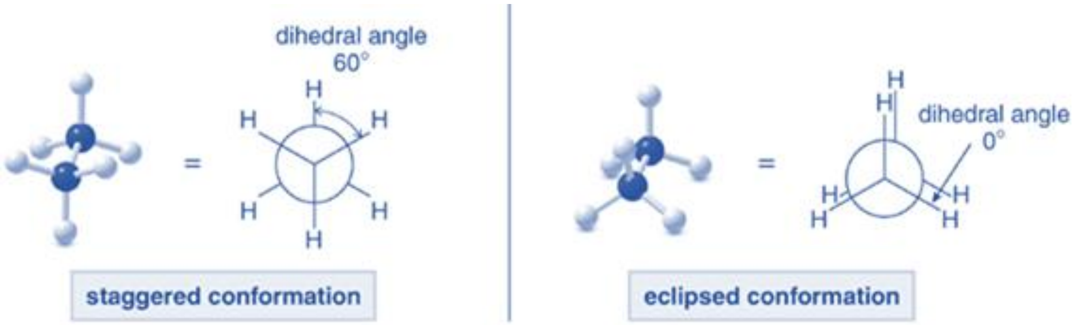
Classification of Hydrocarbons:

Alkane

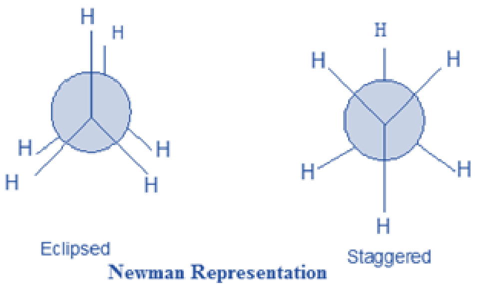
- Open chain saturated hydrocarbon with general formula (C_nH_{2n+2}).
- All the C atoms are single bonded i.e. sp^3 hybridised.

Conformations of Alkane

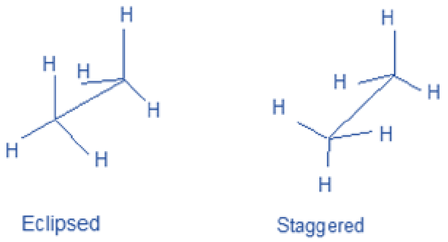
- Conformations are the different arrangement of atoms that can be converted into one another by rotation about single bonds.
- Eclipsed Conformation: H atoms on two adjacent carbon atoms are closest to each other i.e. dihedral angle is 0.



- Staggered Conformation: H atoms on two adjacent carbon atoms are farthest to each other i.e. dihedral angle is 60.



Newman Representation



Sawhorse Representation

Preparation of Alkanes:

- Reduction of Alkyl Halides:

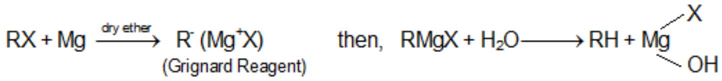
  $RX + Zn: + H^+ \rightarrow RH + Zn^{2+} + X^-$

  $4RX + LiAlH_4 \rightarrow 4RH + LiX + AlX_3$ ($X \neq F$)

  $RX + (n - C_4H_9)_3SnH \rightarrow R\text{-}H + (n - C_4H_9)_3SnX$

- Grignard Reagent:

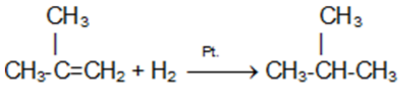
  $RX + 2Li \xrightarrow{\text{dry ether}} R^- Li^+ + LiX$ then $R^- Li^+ + H_2O \longrightarrow RH + LiOH$



  $RX + Mg \xrightarrow{\text{dry ether}} \underset{\text{(Grignard Reagent)}}{R^-(Mg^+X)}$ then, $RMgX + H_2O \longrightarrow RH + Mg\begin{matrix} X \\ OH \end{matrix}$

  ?

- Hydrogenation of Alkenes:



  $$CH_3\text{-}\overset{CH_3}{\overset{|}{C}}=CH_2 + H_2 \xrightarrow{Pt.} CH_3\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}CH_3$$

- Wurtz Reaction:

  $2RX + 2Na \rightarrow R\text{-}R + 2NaX$

  $2Na + 2CH_3CH_2CH_2Cl \rightarrow CH_3CH_2CH_2CH_2\text{-}CH_2CH_3 + 2NaCl$

- Corey House Reaction:

  $R\,MgX \text{ or } RLi \xrightarrow[RX]{CuX} R\text{-}R'$ ($R = 1°, 2°$ or $3°$; $R' = 1°$)

- Decarboxylation of a mixture of the sodium salt of a carboxylic acid:

  $RCOONa + NaOH(CaO) \rightarrow RH + Na_2CO_3$

- Kolbe's electrolytic method:

  $2\,RCOOK + 2H_2O \rightarrow R\text{-}R + 2CO_2 + H_2 + 2KOH$

Chemical Properties of Alkane

- Direct Halogenation

  $RH + X_2 \rightarrow RX + HX$

  Order of Reactivity of X_2: $F_2 > Cl_2 > Br_2$; I_2 does not react

  ?a. Initiation Step

  $Cl\text{-}Cl \xrightarrow{uv} 2Cl^\cdot$

b. Propagation Step

$H_3C\text{-}H + Cl^{\cdot} \rightarrow H_3C^{\cdot} + H\text{-}Cl$
$H_3C^{\cdot} + Cl\text{-}Cl \rightarrow H_3C\text{-}Cl + Cl^{\cdot}$

c. Termination Step

$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl\text{-}Cl$
$H_3C^{\cdot} + H_3C^{\cdot} \rightarrow H_3C\text{-}CH_3$
$Cl^{\cdot} + H_3C^{\cdot} \rightarrow Cl\text{-}CH_3$

- Nitration

  Nitration of alkane is made by heating vapours of alkanes and HNO_3 at about 400oC to give nitroalkanes.

  ¨This is also known as vapour phase nitration.

  $$CH_{4(g)} + HNO_{3(g)} \xrightarrow{400^{\circ}C} CH_3NO_2 + H_2O$$

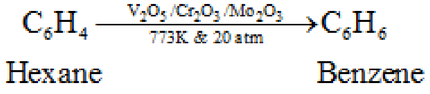
- Combustion:

  ?Alkanes burn readily with non luminous flame in presence of air or oxygen to give CO_2 & water along with evolution of heat.

  $C_2H_6 + 7O_2 \rightarrow CO_2 + 6H_2O$ + heat

- Aromatization

  ?¨Alkanes having six to 10 carbon atoms are converted into benzene and its homologues at high pressure and temperature in presence of catalyst.

  $$\underset{\text{Hexane}}{C_6H_4} \xrightarrow[773K\ \&\ 20\,atm]{V_2O_5/Cr_2O_3/Mo_2O_3} \underset{\text{Benzene}}{C_6H_6}$$

- Oxidization of 3^0 alkane:?

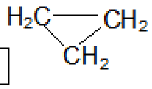
  Tertiary alkanes are oxidized to tertiary alcoholsby KMnO4

  $R_3CH + KMnO_4 \rightarrow R_3COH$

Alkene (olefins)

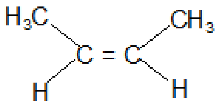
- Open chain, Unsaturated hydrocarbons with general formula (CnH_2n).
- At least one >c=c< (double bond) group i.e. sp2 hybridisation, is present throughout the chain.
- Allene: alkene molecule in which at least one C has double bonds with each of the adjacent carbon i.e. -c=c=c- group.
- Isomeric with saturated cycloalkanes.

$CH_3CH = CH_2$

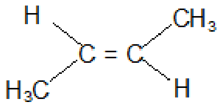


$\boxed{C_3H_6}$

Geometric Isomers:

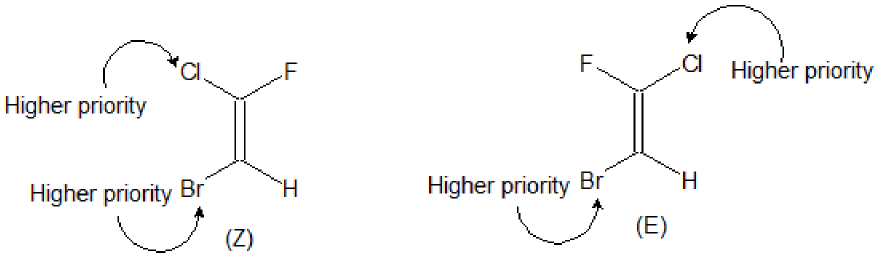


CH_3's on same side
called *cis-*

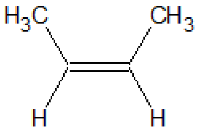


CH_3's on opposite sides :
called trans-

Z is used if the higher - priority substituents on each C are on the same side of the double bond.letter E is used if they are on opposite sides

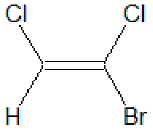


CH > H

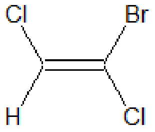


(2*Z*)-but-2-ene

CH > H
Br > Cl



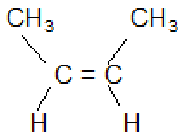
(*E*)-1-bromo-1,2-dichloroethylene



(*Z*)-1-bromo-1,2-dichloroethylene

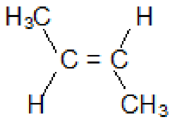
Heats of Hydrogenation: Heat of hydrogenation increases with increase in stability of alkene.

$$\underset{\text{1 - Butene}}{CH_3CH_2CH = CH_2} + H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3 \quad \Delta H° = -30.3\ Kcal\ mol^{-1}$$



cis –2 - Butene

$$+ H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3 \quad \Delta H° = -28.6\ Kcal\ mol^{-1}$$



trans –2 - Butene

$$+ H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3 \quad \Delta H° = -27.6\ Kcal\ mol^{-1}$$

Order of heat of hydrogenation: 1-Butene> cis-2-Butene > trans-2-Butene

Order of stability: 1-Butene> cis-2-Butene > trans-2-Butene

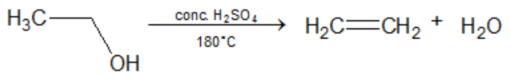
Preparation of Alkenes:

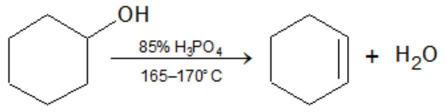
1. Cracking of petroleum: $R-CH_2-CH_3 \xrightarrow{\text{Pt or Pd}} R-CH=CH_2+H_2$

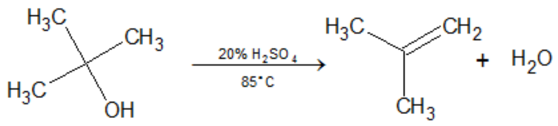
2. Dehydrohalogenation of alkyl halides: RCH_2CH_2X + alc.KOH → $RCH = CH_2$

3. Dehydration of Alcohols :

Saytzeff Rule: In dehydration and dehydrohalogenation the preferential order for removal ofan H is 3° > 2° > 1°

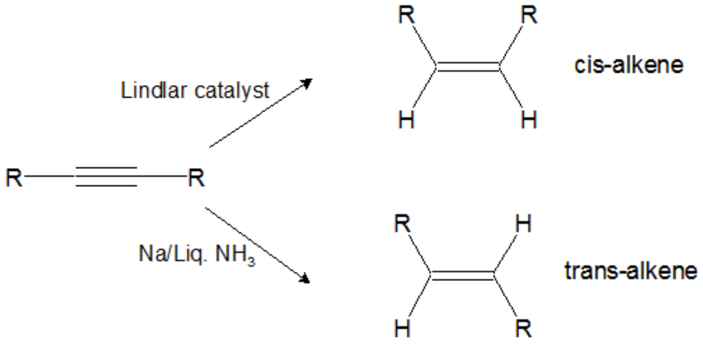






Order of reactivity of alcohols: 1°>2°> 3°

4. Reduction of alkynes:



Chemical Properties:

1. Electrophilic Polar Addition Reactions

Reagent		Product	
Name	**Structure**	**Name**	**Structure**
Halogens (Cl_2, Br_2 only)	X:X	Ethylene dihalide	CH_2XCH_2X
Hydrohalic acids	H:X	Ethyl halide	CH_3CH_2X
Hypohalous acids	X:OH	Ethylene halohydrin	CH_2XCH_2OH
Sulfuric acid (cold)	$H:OSO_2OH$	Ethyl bisulfate	$CH_3CH_2OSO_3H$
Water (dil. H_3O^+)	H:OH	Ethyl alcohol	CH_3CH_2OH
Borane	$H_2B:H$	Ethyl borane	$(CH_3CH_2BH_2) \rightarrow (CH_3CH_2)_3B$
Peroxyformic acid	H:O-OCH=O (HCO_3H)	Ethylene glycol	CH_2OHCH_2OH

2. Addition of Hydrogen Halides to Alkenes: Markovnikov's Addition:

$R - CH = CH_2 + HBr \rightarrow R - CHBr - CH_3$

Mechanism:

$R - CH = CH_2 + HBr \rightarrow R - CH^+ - CH_3 + Br^-$
$R - CH^+ - CH_3 + Br^- \rightarrow R - CHBr - CH_3$

Anit- Markovnikov's Addition (Peroxide Effect):

$R - CH = CH_2 + HBr + (C_6H_5CO)_2O_2 \rightarrow R - CHBr - CH_3$

Mechanism

Initiation:

$R - O - O - R \rightarrow 2RO^{\cdot}$

$RO^{\cdot} + HBr \rightarrow Br^{\cdot} + ROH$

Propagation

$CH_3CH = CH_2 + Br^{\cdot} \rightarrow CH_3{\cdot}CH - CH_2Br$

$CH_3{\cdot}CHCH_2Br + HBr \rightarrow CH_3CH_2CH_2Br + Br^{\cdot}$

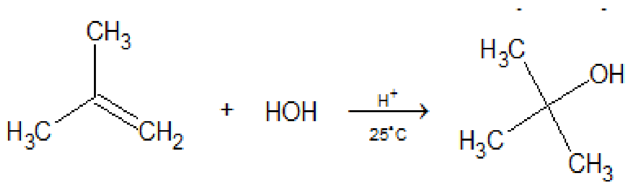
Termination:

$2RO^{\cdot} \rightarrow R - O - O - R$

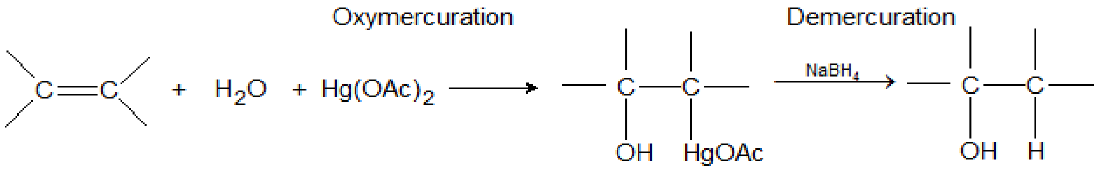
$Br^{\cdot} + Br^{\cdot} \rightarrow Br_2$

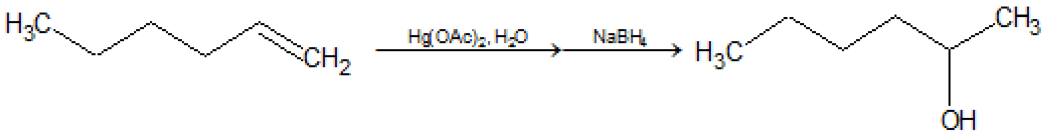
3. Addition of Water to Alkenes: Acid Catalyzed Hydration:

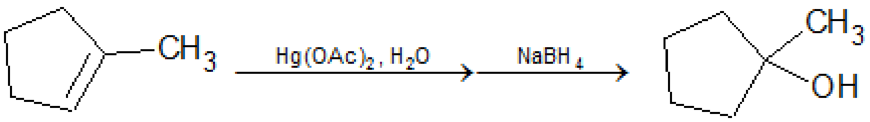
Reagent		**Product**	
Name	**Structure**	**Name**	**Structure**
Halogens (Cl_2, Br_2 only)	X:X	Ethylene dihalide	CH_2XCH_2X
Hydrohalic acids	H:X	Ethyl halide	CH_3CH_2X
Hypohalous acids	X:OH	Ethylene halohydrin	CH_2XCH_2OH
Sulfuric acid (cold)	$H:OSO_2OH$	Ethyl bisulfate	$CH_3CH_2OSO_3H$
Water (dil. H_3O^+)	H:OH	Ethyl alcohol	CH_3CH_2OH
Borane	$H_2B:H$	Ethyl borane	$(CH_3CH_2BH_2)$®$(CH_3CH_2)_3B$
Peroxyformic acid	H:O - OCH = O (HCO_3H)	Ethylene glycol	CH_2OHCH_2OH

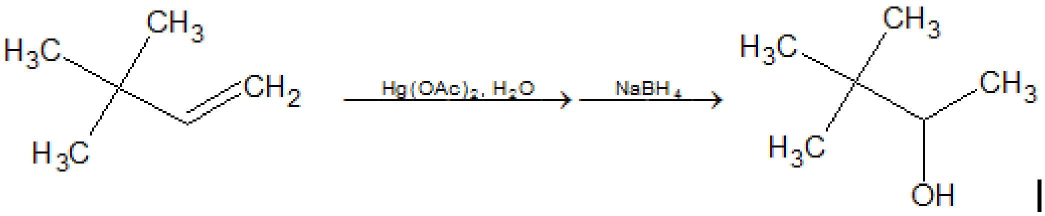


1. Oxymercuration-Demercuration:









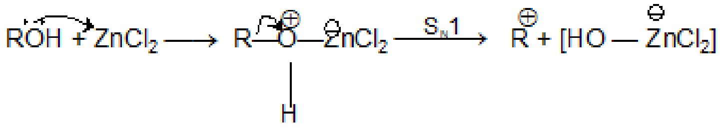
Halogen Derivatives of Organic Compounds

Organic Compounds Containing Halogens can be divided into two groups:

- **Alkyl Halides:** Aliphatic carbon chain with halogen atom(s) as substitution. Example: Chlorobutane.
- **Aryl Halides:** Aromatic carbon ring with halogen atom(s) as substitution on ring. Example: Chlorobenzene.

Methods of Preparation of Alkyl Halides:

Grove's process: Replacement of "OH" group in primary and secondary alcohols with an "X' atom in presence of Zinc chloride.



The reaction follows S_N2 mechanism when the concentration of zinc chloride is low.

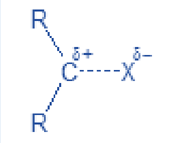
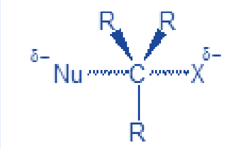
Darzen Process: Reaction of thionyl chloride with straight-chain primary alcohols without presence or absence of pyridine.
In presence of pyridine:
$ROH + SOCl_2 \rightarrow HCl + ROSOCl$
$HCl+C_5H_5N \rightarrow C5H5NH^{+}+Cl^{-}$
$ROSOCl + Cl^{-} \rightarrow RCl + SO_2$ (S_N2)

- **Action of a phosphorus halide on the alcohol:** $ROH + PCl_5 \rightarrow RCl + HCl + POCl_3$.
- **By addition of Halogen to an alefins:** $R\text{-}CH{=}CH_2 + Br_2 + CCl_4 \rightarrow R\text{-}CH(Br)CH_2Br$
- **Photohalogenation:** $CH_4 + Cl_2 + hv \rightarrow CH_3Cl + HCl$
- **Displacement of one halogen atom by another:** $RCl + NaI \rightarrow RI + NaCl$
- **Bonodine – Hünsdiecker Reaction:** $RCO_2Ag + Br_2 \rightarrow RBr + CO_2 + AgBr$
- **Hydrohalogenation of unsaturated hydrocarbons:**
  - In absence of peroxide: $RCH{=}CH_2 + HBr \rightarrow RCH(Br)CH_3$
  - In presence of peroxide: $RCH{=}CH_2 + HBr + \text{Peroxide} \rightarrow RCH_2CH_{2Br}$

Methods of Preparation of aryl halides

- **Halogenation:** Ar-H + X_2 +Lewis Base → Ar-x + HX
- **From diazonium salts:**
  - $C_6H_5N_2Cl + HBF_4 \rightarrow C_6H_5F$ (Schiemann Reaction)
  - $C_6H_5N_2Cl + CuCl \rightarrow C_6H_5Cl$ (Sandmeyer Reaction)
  - $C_6H_5N_2Cl$ + Cu powder $\rightarrow C_6H_5Cl$ (Gatterman Reaction)
  -

S_N1 and S_N2 mechanism:

	S_N1	**S_N2**
Steps	Two : (1) R:Xl → $R^+ + X^-$ (2) $R^+ + Nu^-$ l →RNu	One : R:X + Nu^- l → RNu + X^-
Rate	=K [RX] (1st order)	=K[RX] [:Nu^-] (2nd order)
TS of slow step		
Stereochemistry	Inversion and racemization	Inversion (backside attack)
Molecularity	Unimolecular	Bimolecular
Reactivity structure of R **Determining Factor** **Nature of X** **Solvent effect on rate**	$3^o > 2^o > 1^o > CH_3$ Stability of R^+ RI> RBr> RCl> RF Rate increases in polar solvent	$CH_3 > 1^o > 2^o > 3^o$ Steric hindrance in R group RI> RBr> RCl> RF with Nu^- there is a large rate increase in polar aprotic solvents.
Effect of nucleophile	No effect as it does not appear in the rate expression.	Rate depends on nucleophilicity $I^- > Br^- > Cl^-$; $RS^- > RO^-$
Catalysis	Lewis acid, eg. Ag^+, $AlCl_3$, $ZnCl_2$	None
Competitive reaction	Elimination, rearrangement	Elimination

Reactions of Alkyl Halides:

- **Hydrolysis: :** $RX + OH^{-} \rightarrow ROH + X^{-}$
- **Williamson Synthasis:** R-ONa +R'X → R-R' + NaX
- **Reaction with dry silver oxide:** $2R\text{-}X + Ag_2O \rightarrow R\text{-}O\text{-}R$
- **Reaction with sodio-Alkynides:** R-C≡C-Na +X-R→ R-C=C-R +NaX
- **Reaction with potassium-cyanide:** KCN+X-R→ RCN +KX
- **Reaction with silver-cyanide:** AgCN+X-R→ RNC +AgX
- **Reaction with silver-nitrite:** $AgNO_2 + X\text{-}R \rightarrow RNO_2 + AgX$
- **Reaction with potassium-nitrite:** $KNO_2 + X\text{-}R \rightarrow R\text{-}O\text{-}N{=}O + KX$
- **Fridal Craft Reaction:** $R\text{-}X + C_6H_6 + AlCl_3 \rightarrow C_6H_5\text{-}R$
- **Malonic Ester Synthasis:** $R\text{-}X + {}^{-}CH(CO_2C_2H_5)_2 \rightarrow R\text{-}CH(CO_2C_2H_5)_2 + HX$
- **Acetoacetic Ester Synthasis:** $R\text{-}X + {}^{-}CH(CO_2CH_3)_2 \rightarrow R\text{-}CH(CO_2CH_3)_2 + HX$
- **Reaction with Ammonia:** $R\text{-}X + NH_3 \rightarrow R\text{-}NH_2 + HX$
- **Wurtz Reaction:** 2R-I+ 2Na →R—R + 2NaI
- **Dehydrohalogenation:** $CH_3.CH_2.CH_2Br + \text{alco.}KOH \rightarrow CH_3{-}CH = CH_2 + KBr + H_2O$
- **Reaction with alcoholic $AgNO_3$:** $R\text{-}X + AgNO_3 \rightarrow R^{+} + AgX\downarrow + HNO_3$

Substitution Versus Elimination:

CH_3X	RCH_2X	R_2CHX	R_3CX
Methyl	1°	2°	3°
Bimolecular reactions only			S_N1/E1 or E_2
Gives S_N2 reactions	Gives mainly S_N2 except with a hindered strong base [e.g., $(CH_3)_3CO^{-}$] and then gives mainly E2.	Gives mainly S_N2 with weak bases (e.g., I^{-}, CN^{-}, RCO_2^{-}) and mainly E2 with strong bases (e.g., RO^{-})	No S_N2 reaction. In solvolysis gives S_N1/E1, and at lower temperature S_N1 is favoured. When a strong base (e.g., RO^{-}) is used. E2 predominates.

Haloform(Tri halide):

- **Preparation:** It can be prepared from any alcohol having $-CH(OH)CH_3$ group or from the aldehydes and ketones formed from above type of alcohols i.e, from a carbonyl compound having three a - hydrogen atoms by the action of $X_2$and an alkali or Na_2CO_3.
- **Laboratory Preparation of $CHCl_3$:**

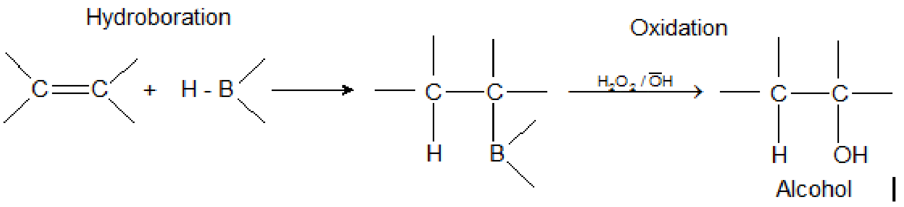
$$CH_3CH_2OH \xrightarrow{\text{oxidation by } Cl_2} CH_3CHO \xrightarrow{\text{chlorination}} CCl_3CHO \xrightarrow[\text{hydrolysis}]{Ca(OH)_2} CHCl_3$$

- **Physical properties of $CHCl_3$:** colourless liquid with sweet smell and test. It is heavier than water and insoluble in it but soluble in alcohol and ether.

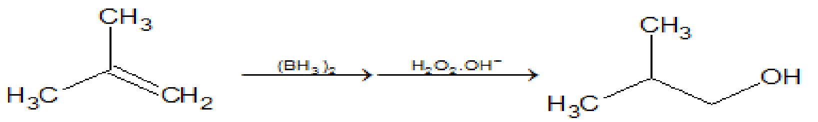
Chemical Reactions of $CHCl_3$:

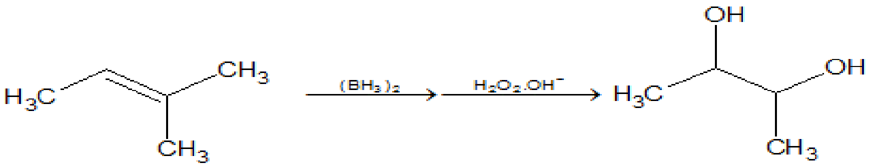
- **Oxidation:** $CHCl_3 + 1/2\ O_2 \rightarrow HCl + COCl_2$ (phosgene)
- **Hydrolysis:** $CHCl_3 + 4NaOH \rightarrow HCOONa + 3NaCl + 2H_2O$
- **Carbyl amine reactions:** $CHCl_3 + CH_3NH_2 + 3NaOH \rightarrow CH_3N{\equiv}C + 3NaCl + 3H$

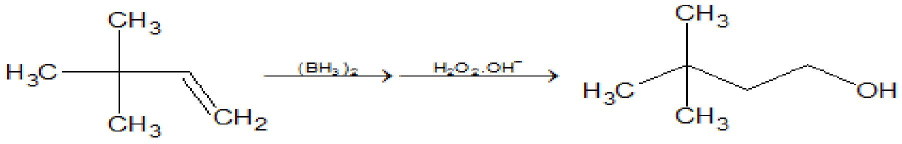
5. Hydroboration-Oxidation:



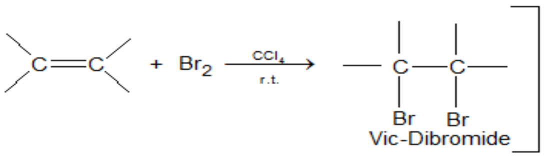
Examples:





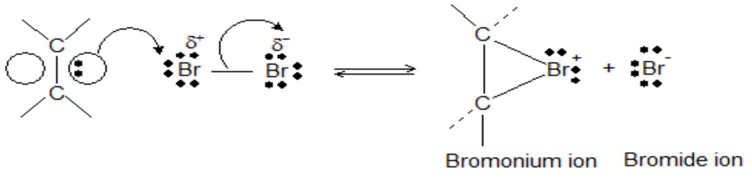


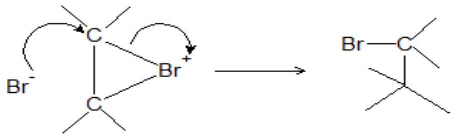
6. Halogen Addition in Non-polar Solvent:



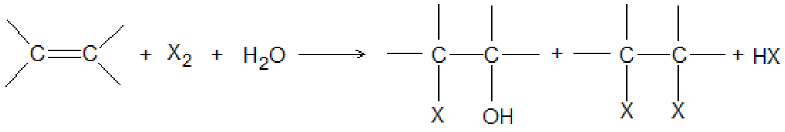
rapid decolourization of Br_2/CC is a test for alkenes and alkynes

Mechanism:



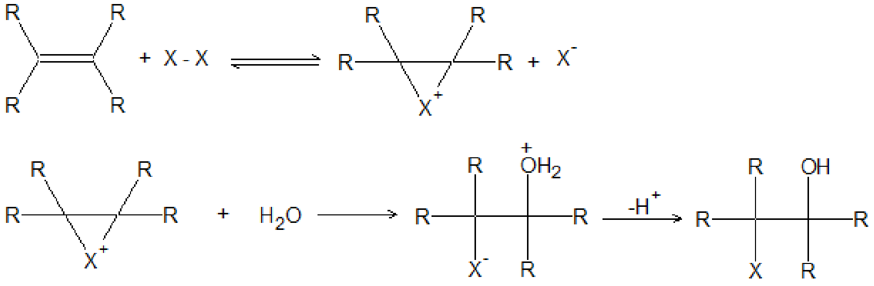


7. Halogen Addition in Aqueous Medium:

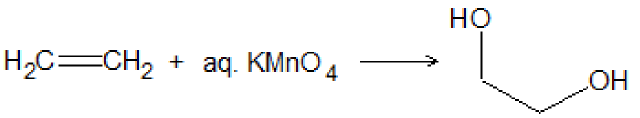


X = Cl_2 or Br_2

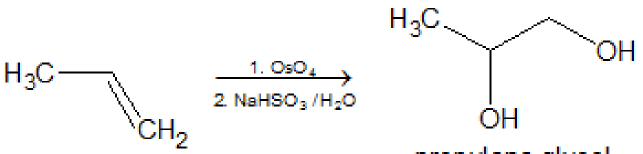
Mechanism:



8. Syn – Hydroxylation: Formation of di-oles.

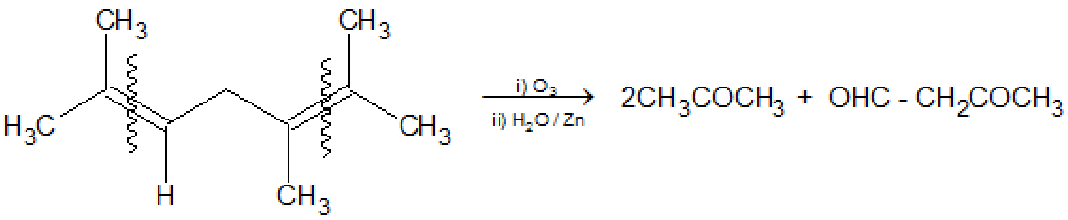


ethylene glycol



propylene glycol

9. Ozonolysis of Alkenes:

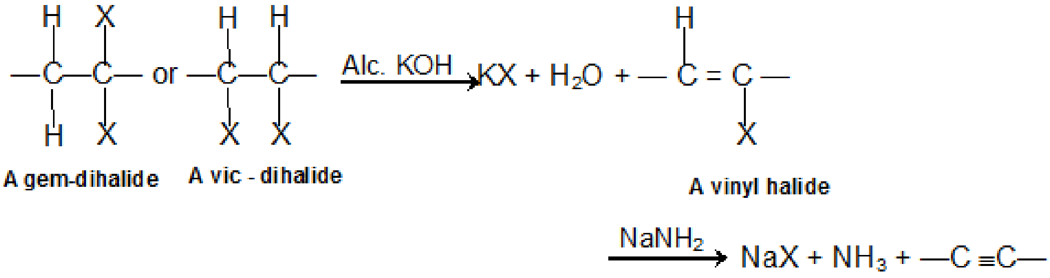


Alkyne

- Saturated open chain hydrocarbon with general formula (C_nH_{2n-2}).
- At least one -c≡c- (triple bond) group i.e. sp hybridisation, is present throughout the chain.
- Physical properties of alkynes are similar to those of the corresponding alkenes

Preparation

1. Dehydrohalogenation of vic-Dihalides or gem-Dihalides



2. Dehalogenation of vic-Tetrahalogen Compounds

$$\underset{\text{2,2,3,3-Tetrabromobutane}}{CH_3—CBr_2—CBr_2—CH_3} + 2Zn \xrightarrow[\text{heat}]{\text{EtOH}} \underset{\text{2-butyne}}{CH_3—C\equiv C—CH_3} + 2ZnBr_2$$

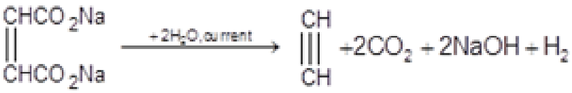
3. Alkyl Substitution in Acetylene; Acidity of º C-H

$$HC\equiv CH + NaNH_2 \xrightarrow[-33^\circ C]{\text{liq. }NH_3} HC\equiv CNa^+ \xrightarrow{n\text{-}C_4H_9Br} \underset{\text{1-hexyne}}{CH_3(CH_2)_3C\equiv CH}$$

4. From Calcium Carbide:

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

5. Kolbe's Electrolysis:



$$\begin{matrix} CHCO_2Na \\ \| \\ CHCO_2Na \end{matrix} \xrightarrow{+2H_2O,\text{current}} \begin{matrix} CH \\ ||| \\ CH \end{matrix} + 2CO_2 + 2NaOH + H_2$$

Chemical Properties

1. **Hydrogenation: $RC \equiv CCH_2CH_3 + 2H_2 \rightarrow CH_3CH_2CH_2CH_2CH_3$**
2. **Hydro-halogenation:**

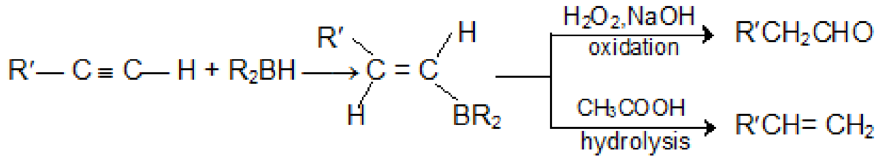
Markovnikov addition: $RC\equiv CH + HBr \rightarrow RCBr{=}CH_2 + HBr \rightarrow RCBr_2\text{-}CH_3$

Anti-markovnikov addition: $RC\equiv CH + HBr + \text{peroxide} \rightarrow RCH{=}CHBr$

3. Hydration:

$$CH \equiv CH + H_2O \xrightarrow[Hg^{2+}]{H_2SO_4} [CH_2 = CHOH] \longrightarrow CH_3CHO$$

4. Addition of boron hydride:

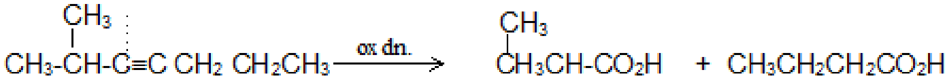


5. Dimerization:

$$2\,H\text{—}C \equiv C\text{—}H \xrightarrow[H_2O]{Cu(NH_3)_2^+Cl^-} \underset{\text{Vinylacetylene}}{H_2C{=}CH\text{—}C{\equiv}CH}$$

6. Oxidation:

$$CH_3CH_2C{\equiv}C\text{-}CH_3 + 2KMnO_4 \rightarrow CH_3CH_2COOK + CH_3COOK + 2MnO_2 + 2H_2O$$



$$CH_3\text{-}\overset{\overset{CH_3}{|}}{CH}\text{-}C{\equiv}C\,CH_2\,CH_2CH_3 \xrightarrow{\text{ox dn.}} \overset{CH_3}{\overset{|}{CH_3CH}}\text{-}CO_2H + CH_3CH_2CH_2CO_2H$$

(Two isomeric acids each having M.F. $C_4H_8O_2$)

7. Ozonolysis-Hydrolysis:

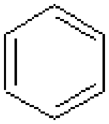
$$\underset{\text{2-Pentyne}}{CH_3C{\equiv}CCH_2CH_3} \xrightarrow[\text{2. hydrolysis}]{\text{1. } O_3} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Propanoic acid}}{HOOCCH_2CH_3}$$

8. Cyclic polymerization:

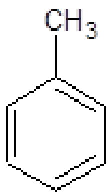
Aromatic Hydrocarbons:

For being aromatic a hydrocarbon should

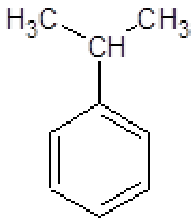
- be a cyclic compounds.
- have planarity in geometry.
- have complete delocalization of electrons over ring.
- follow Huckel Rule i.e. number of ?? electrons in ring = (4n+2). :



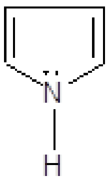
Benzene



Toluene



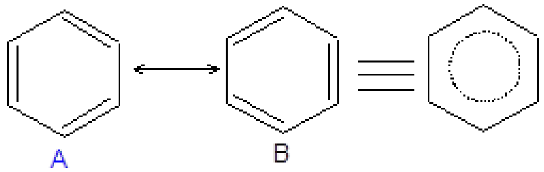
Isopropyl benzene
(Cumene)



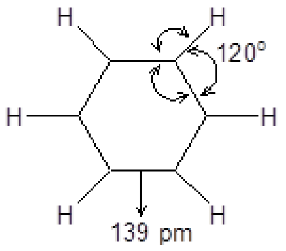
Pyrrole

Benzene (C_6H_6)

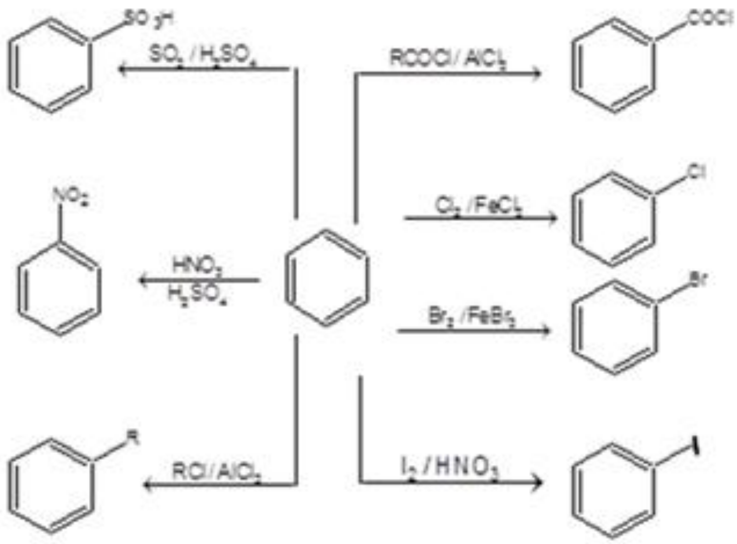
1. Structure:

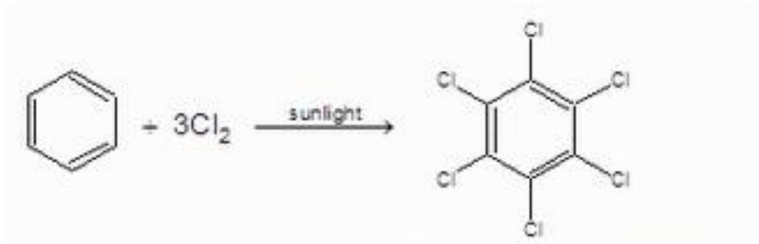


Kekule Structures



2. Chemical Reactions of Benzene:





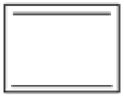
Benzene hexachloride

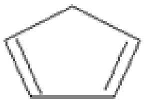
Anti-aromatic Hydrocarbons:

Highly unstable compounds.

Number of π electrons in ring = 4n.

Example:





Alcohols, Phenols & Ethers

Revision Notes on Alcohols, Phenols and Ether:

Alcohols

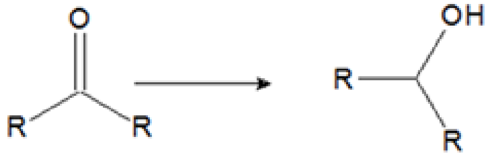
Preparation of Alcohols:

- **By hydrolysis of haloalkanes** : R-X + aq. KOH →ROH +KX
- **By reduction of Carbonyl compounds**

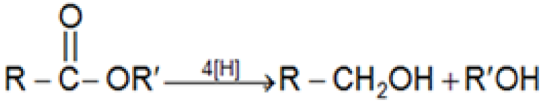
$$4RCOOH + 3LiAlH_4 \rightarrow 4RCH_2OH \ (1^o alcohol)$$

$$CH_3(CH_2)_{14}COOC_2H_5 \xrightarrow{LiAlH_4} CH_3(CH_2)_{14}CH_2OH$$

$$R-CHO \longrightarrow RCH_2OH(1^O \text{ alcohol})$$



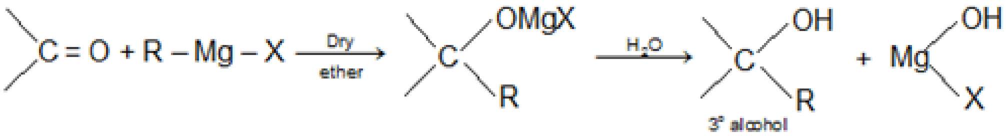
$(2^0$ alcohol)



$$R-\overset{\overset{O}{||}}{C}-OR' \xrightarrow{4[H]} R-CH_2OH + R'OH$$

$$CH_3CH_2COOCH_3 \xrightarrow{Cr_2O_4} CH_3CH_2CH_2OH + CH_3OH$$

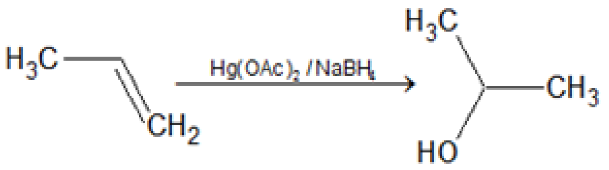
- **By the action of Grignard's Reagent on aldehydes, ketones and esters**



- **By Aliphatic Primary Amines: $RCH_2NH_2 + HNO_2 \rightarrow RCH_2OH + N_2 + H_2O$**
- **Hydration of alkenes:**

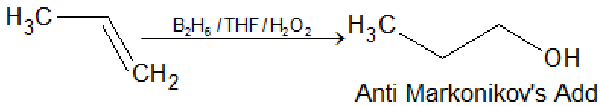
$$CH_2 = CHR + \underset{\text{Concentrated}}{H_2SO_4} \xrightarrow[H_2O]{\text{Boil}} CH_3 - CH(R)OH$$

- **Oxymercuration-demercuration:**



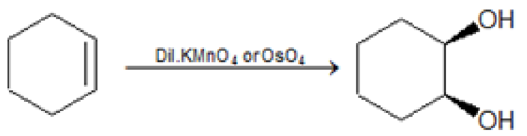
Markonikov's Addition

- **Hydroboration-oxidation:**

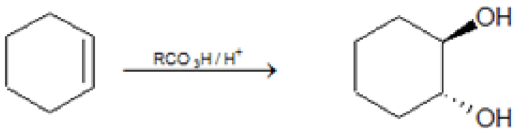


Anti Markonikov's Addition

- **Hydroxylation of alkenes:**



syn-Hydroxylation



anti-Hydroxylation

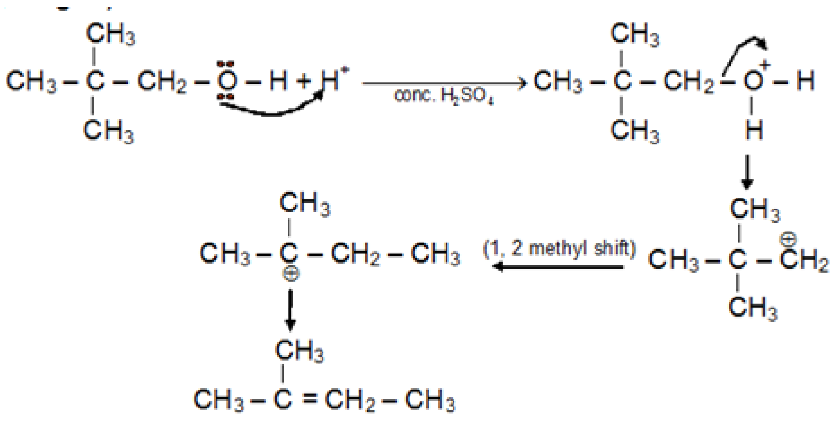
Physical Properties of Alcohol:

- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.

Chemical Properties of Alcohol:

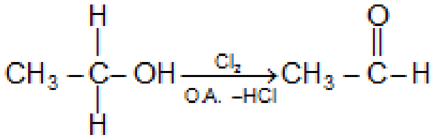
- **Alcohol's reaction with metal:** $ROH + Na \rightarrow 2RO^{+}Na^{-} + H_2$
- **Formation of Halides:**
  - $3ROH + P + I_2 \rightarrow 3RI + H_3PO_3$
  - $ROH + SOCl_2/PCl_3/PCl_5 \rightarrow RCl$
  - $ROH + HX \rightarrow RX$
  - $ROH + NaBr, H_2SO_4 \rightarrow R\text{-}Br$
  - $ROH + Zn + HCl \rightarrow R\text{-}Cl$
  - $R_2C\text{-}OH$ alcohol + $HCl \rightarrow R_2CCl$
- **Reaction with HNO_3:** $R\text{-}OH + HO\text{-}NO_2 \rightarrow R\text{-}O\text{-}NO_2$
- **Reaction with carboxylic acid (Esterification) :** $R\text{-}OH + R'\text{-}COOH + H^{+} \leftrightarrow R'\text{-}COOR$
- **Reaction with Grignard reagent:** $R'OH + RMgX \rightarrow RH + R'OMgX$
- **Reduction of alcohol :** $ROH + 2HI + \text{Red } P \rightarrow RH + I_2 + H_2O$
- **Dehydration of Alcohol:** Dehydration of alcohols takes place in acidic medium. Intra-molecular dehydration leads to the formation of alkene while inter molecular dehydration which forms ether. Ease of dehydration: 3° > 2° > 1

- **Satyzeff's Rule :** Elimination through b carbon containing minimum b hydrogen



- **Oxidation of Alcohol**:
  RCH_2-OH + [O] → RCHO → RCOOH
  RCH_2-OH + [O] +PCC → RCHO

- **Haloform Reaction:** Compound containing CH_3CO- group (or compound on oxidation gives CH_3CO – group) which is attached with a C or H, in presence of halogen and mild alkali gives haloform.CH_3-CH_2-$COCH_2$-CH_3, CH_3-CO-Cl, CH_3COOH will not respond to haloform reaction wile CH_3CH_2OH will respond to haloform Reaction.



$$CH_3-\underset{H}{\overset{H}{C}}-OH \xrightarrow[O.A.\ -HCl]{Cl_2} CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3CH_2OH \xrightarrow{Cl_2+NaOH} CHCl_3$$

?

Test for Alcohols:

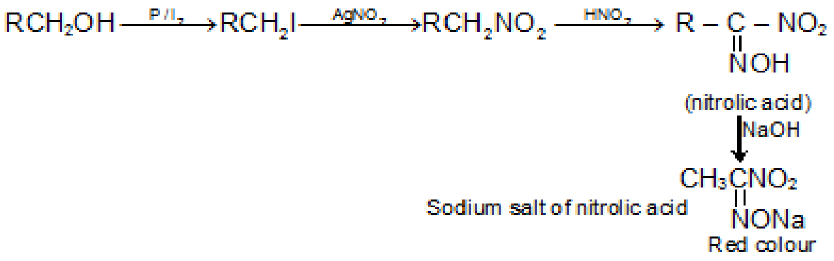
1. **Lucas Test:**

   Alcohols + $ZnCl_2$ + HCl

- 1^o Alcohol: RCH_2OH + $ZnCl_2$ +HCl → No reaction at room temperature
- 2^0 Alcohol: R_2CHOH + $ZnCl_2$ +HCl → R_2CHCl White turbidity after 5-10 min.
- 3^0 Alcohol: R_3CHOH + $ZnCl_2$ +HCl → R_3CHCl white turbidity instantaneously.

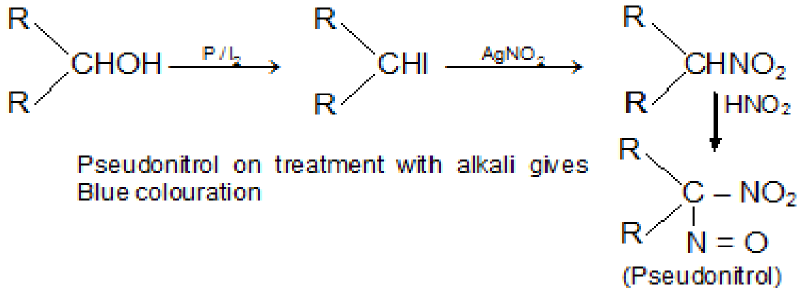
2. Victor Meyer Test

1° alcohol:



Nitrolic acid on treatment with alkali gives colouration

2° alcohol:



Pseudonitrol on treatment with alkali gives Blue colouration

3° alcohol:

$$R_3C-OH \xrightarrow{P/I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2$$

$$\downarrow HNO_2$$

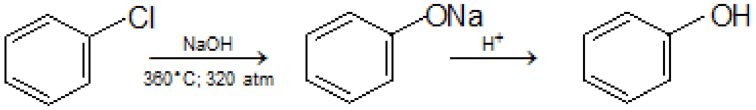
No reaction

(colour less)

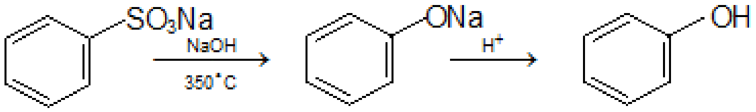
Phenols:

Preparation:

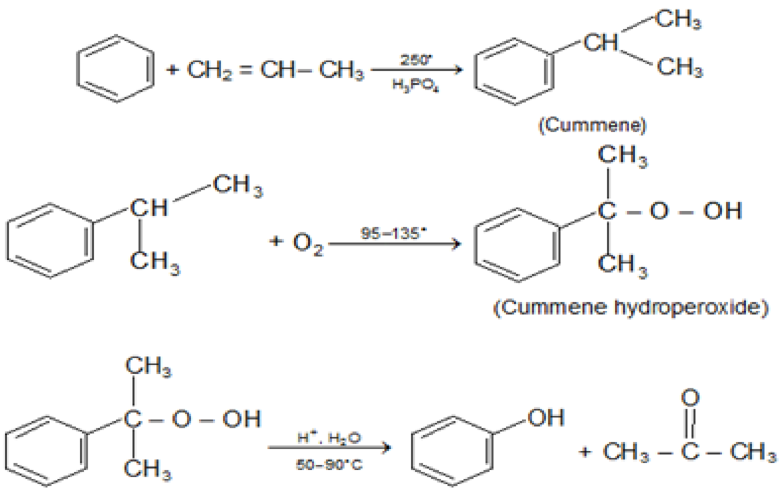
a. Hydrolysis of chlorobenzene: (Dow's process)



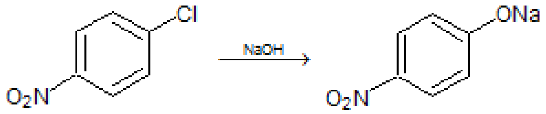
b. Alkali fusion of Sodium benzene sulfonate



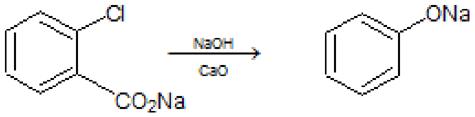
c. From Cummene Hydroperoxide



d. Aromatic Nucleophilic Substitution of Nitro Aryl Halides



e. Distillation of phenolic acids with soda-lime produces phenols, e.g. sodium salicylate gives phenol.



Physical Properties of Phenols

- Phenol is a colorless, toxic, corrosive, needle shaped solid.
- Phenol soon liquifies due to high hygroscopic nature.
- Phenol is less soluble in water, but readily soluble in organic solvents.
- Simplest phenols, because of hydrogen bonding have quite high boiling points.
- o-nitrophenol is, steam volatile and also is less soluble in water because of intramolecular hydrogen bonding

Chemical Properties of Phenols

a) Formation of Esters

Phenyl esters (RCOOAr) are not formed directly from RCOOH. Instead, acid chlorides or anhydrides are reacted with ArOH in the presence of strong base

$(CH_3CO)_2O + C_6H_5OH + NaOH \rightarrow CH_3COOC_6H_5 + CH_3COONa + H_2O$

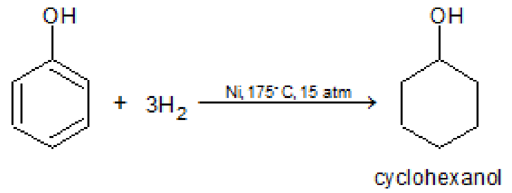
Phenyl acetate

$C_6H_5COCl + C_6H_5OH + NaOH \rightarrow C_6H_5COOC_6H_5 + Na^+Cl^- + H_2O$

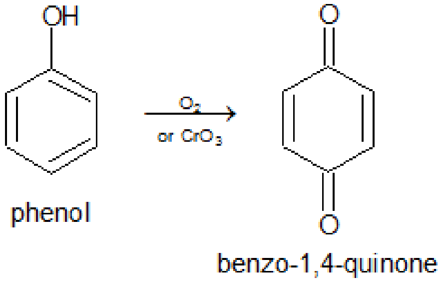
Phenyl benzoate

b) Displacement of OH group: $ArOH + Zn \xrightarrow{\Delta} ArH + ZnO$ (poor yields)

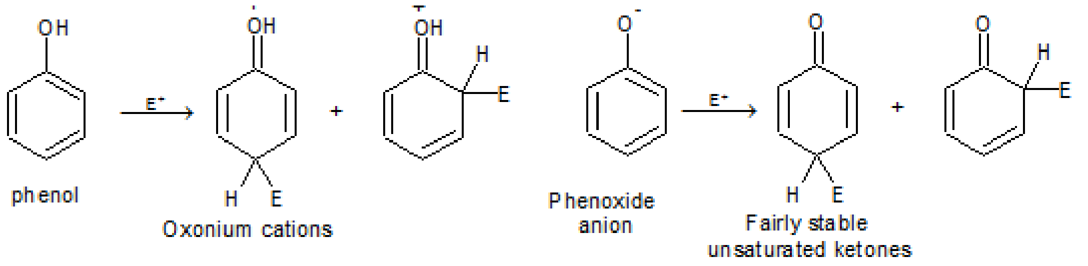
c) Hydrogenation



d) Oxidation to Quionones

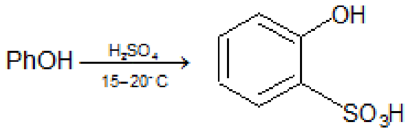


e) Electrophilic Substitution The —OH and even more so the —O(phenoxide) are strongly activating ortho ,para - directing

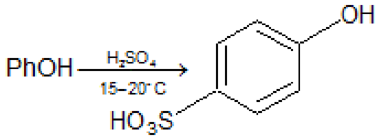


Special mild conditions are needed to achieve electrophilic monosubstituion in phenols because their high reactivity favors both polysubstitution and oxidation.

j) Sulfonation



(rate-controlled)



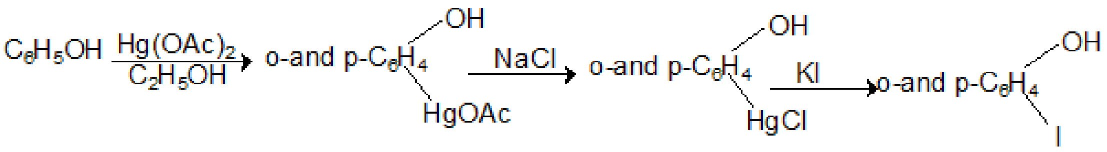
(eqbm-controlled)

k) Diazonium salt coupling to form azophenols

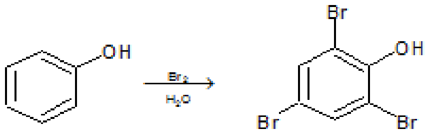
Coupling (G in ArG is an electron – releasing group)

$ArN_2^+ + C_6H_5G \longrightarrow p\text{-}G-C_6H_4-N=N-Ar$ (G = OH, NR_2,NHR, NH_2)

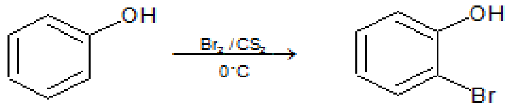
l) Mercuration



f) Halogenation

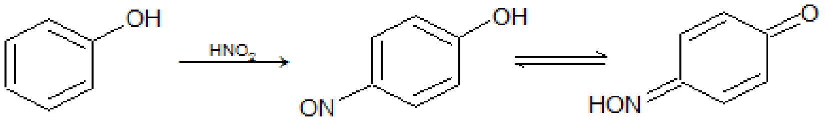


(goes via ArO; no monobromophenols)



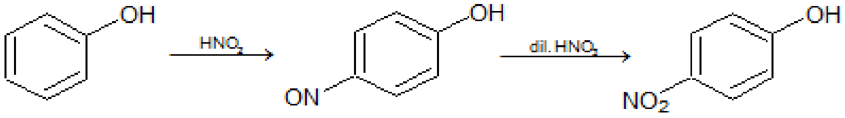
2-bromophenol

h) Nitrosation

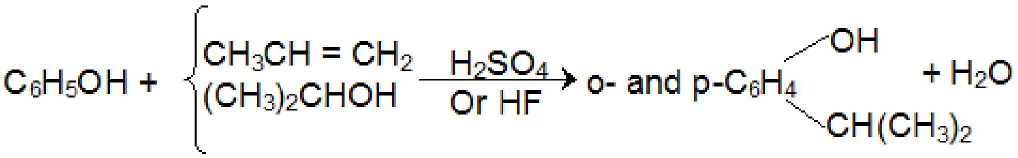


p-nitrosophenol Quinone monoxime

i) Nitration



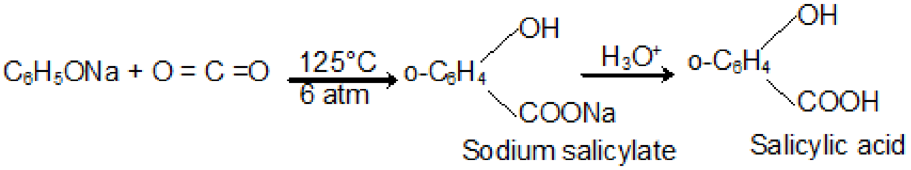
m) Ring alkylation



$$C_6H_5OH + \left\{\begin{matrix} CH_3CH=CH_2 \\ (CH_3)_2CHOH \end{matrix}\right. \xrightarrow[\text{Or HF}]{H_2SO_4} \text{o- and p-}C_6H_4\begin{matrix} OH \\ CH(CH_3)_2 \end{matrix} + H_2O$$

RX and $AlCl_3$ give poor yields because $AlCl_3$ coordinates with O.

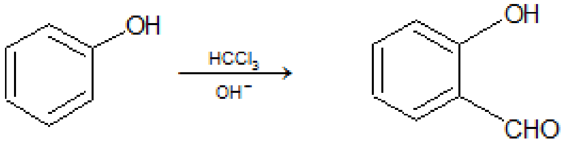
n) Kolbe synthesis of phenolic carboxylic acids



$$C_6H_5ONa + O=C=O \xrightarrow[6\text{ atm}]{125°C} \text{o-}C_6H_4\begin{matrix} OH \\ COONa \end{matrix} \xrightarrow{H_3O^+} \text{o-}C_6H_4\begin{matrix} OH \\ COOH \end{matrix}$$

Phenoxide carbanion adds at the electrophilic carbon of CO_2, para product is also possible.

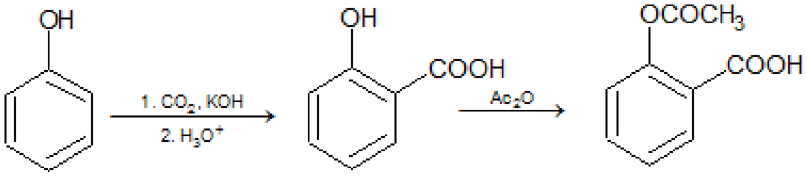
o) Reimer – Tiemann synthesis of phenolic aldehydes



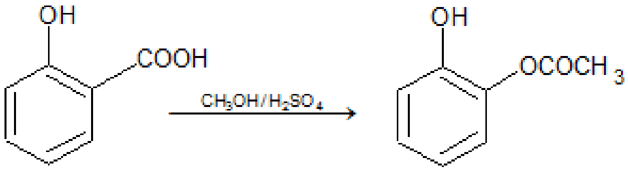
The electrophile is the dichlorocarbene, :CCl_2, formation of carbene is an example of α-elimination. $\overline{O}H + HCCl_3 \xrightarrow{-HCl} \ddot{C}Cl_2$

p) Synthesis of (a) aspirin (acetylsalicylic acid) (b) oil of wintergreen (methyl salicylate)

a)



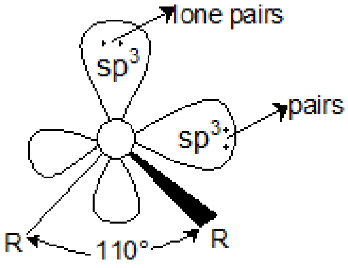
b)

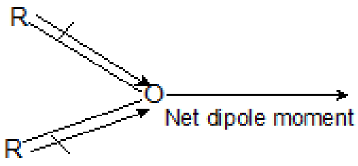


Ethers:

Physical Properties of Ethers

- **Physical state, colour and odour**: Dimethyl ether and ethyl methyl ether is gas at ordinary temperature while the other lower homologues of ethers are colourless liquid with characteristic 'ether smell'.
- **Dipole nature**: Ethers have a tetrahedral geometry i.e., oxygen is sp^3 hybridized. The C— O—C angle in ethers is 110°. Because of the greater electronegativity of oxygen than carbon, the C—O bonds are slightly polar and are inclined to each other at an angle of 110°, resulting in a net dipole moment.





Bond angle of ether is greater than that of tetrahedral bond angle of 109°28'.

- **Solubility and boiling point:** Due to the formation of less degree of hydrogen bonding, ethers have lower boiling point than their corresponding isomeric alcohols and are slightly soluble in water.

Preparation of Ethers:

a) From alcohols:

$$CH_3CH_2OH \xrightarrow[140^oC]{H_2SO_4} \underset{\text{Ether}}{CH_3CH_2-O-CH_2CH_3}$$

Order of dehydration of alcohol leading to formation of ethers: 1° > 2° > 3°

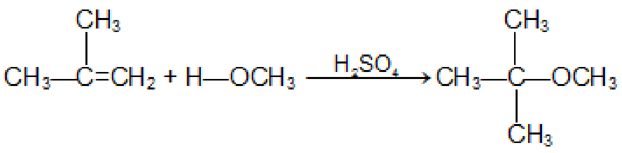
$$CH_3CH_2OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2—O—CH_3 + N_2$$

b) Williamson's synthesis:

$R\text{-}X + Na^+\ {}^-O\text{-}R' \rightarrow R\text{-}O\text{-}R' + Na^+ X^-$

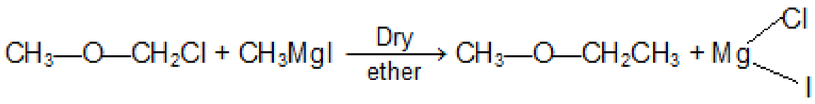
In case of tertiary substrate elimination occurs giving alkenes.

From alkenes:.



$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + H—OCH_3 \xrightarrow{H_2SO_4} CH_3—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}—OCH_3$$

From Grignard reagent: Treating a - halo ethers with suitable Grignard reagents.



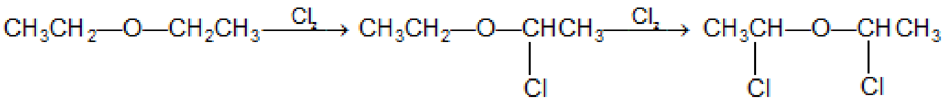
$$CH_3{-}O{-}CH_2Cl + CH_3MgI \xrightarrow[\text{ether}]{\text{Dry}} CH_3{-}O{-}CH_2CH_3 + Mg\genfrac{}{}{0pt}{}{Cl}{I}$$

On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides. The presence of peroxides is indicated by formation of a red colour when the ether is shaken with an aqueous solution of ferrous ammonium sulfate and potassium thiocyanate

?

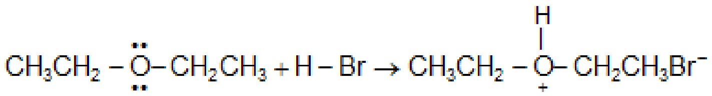
$$\text{Peroxide} + Fe^{2+} \rightarrow Fe^{3+} \xrightarrow{SCN^-} \underset{\text{Red}}{Fe(SCN)_n^{(3-n)-}} \ (n = 1 \text{ to } 6)$$

f) Halogenation of ethers:



$$CH_3CH_2{-}O{-}CH_2CH_3 \xrightarrow{Cl_2} CH_3CH_2{-}O{-}\underset{Cl}{\underset{|}{C}}HCH_3 \xrightarrow{Cl_2} CH_3\underset{Cl}{\underset{|}{C}}H{-}O{-}\underset{Cl}{\underset{|}{C}}HCH_3$$

g) Ethers as base:



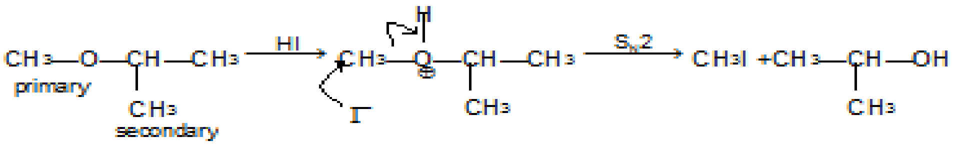
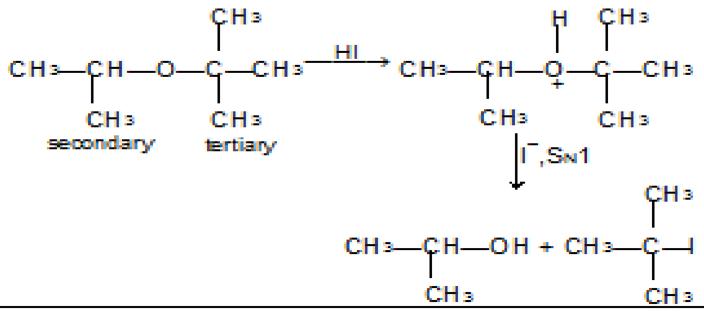
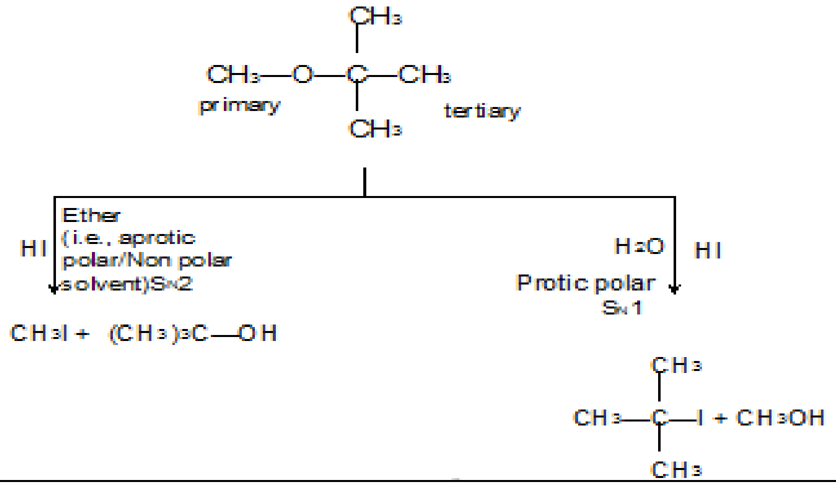
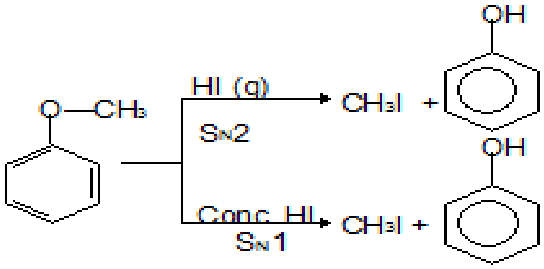
$$CH_3CH_2 - \ddot{\underset{\cdot\cdot}{O}} - CH_2CH_3 + H - Br \rightarrow CH_3CH_2 - \overset{\overset{H}{|}}{\underset{+}{O}} - CH_2CH_3 Br^-$$

h) Reaction With Cold conc. HI/HBr:

$$R{-}O{-}R' + \text{Cold HI} \longrightarrow R\text{-}OH + R'I \ (R' < R)$$

i) Hot conc. HI/HBr:

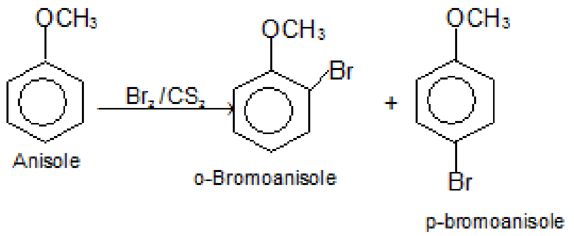
$$R{-}O{-}R' + \text{Hot HI} \longrightarrow RI + R'I + H_2O$$

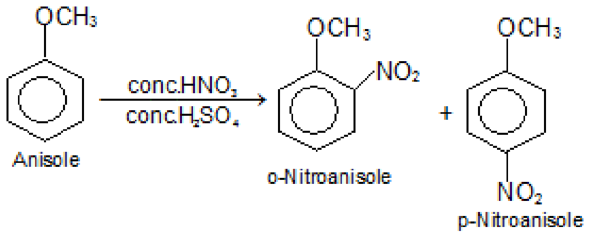
Case I:	
Case II:	
Case III:	
Case IV:	

$$C_2H_5-O-C_2H_5 \ + \ CH_3COCl \xrightarrow[Anhy\ ZnCl_2]{\Delta} C_2H_5Cl \ + \ CH_3COOC_2H_5$$

i) Reaction with acid chlorides and anhydrides:

j) Electrophilic substitution reactions

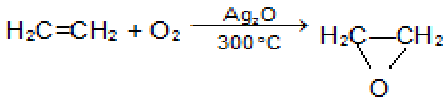




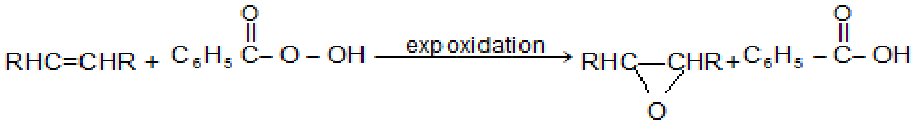
Epoxides or Oxiranes:

Preparation

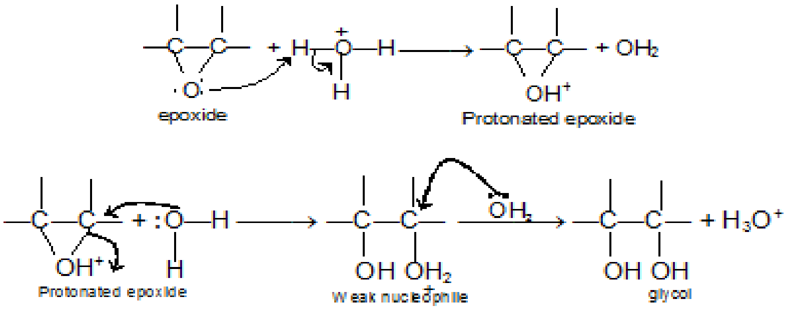
a) Oxidation of ethylene :



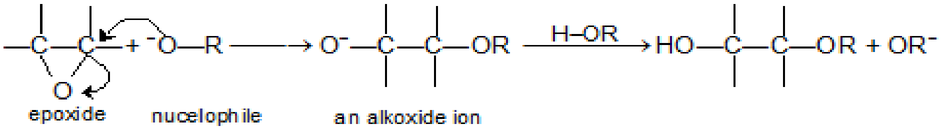
b) Expoxidation :



Acid catalysed ring opening



Base catalysed ring opening:



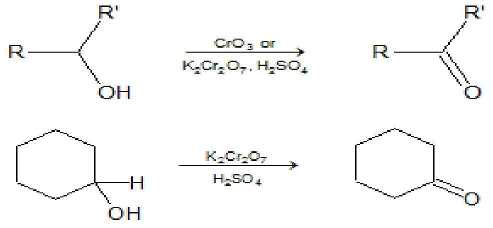
Aldehydes, Ketones & Carboxylic Acid

Aldehyde, Ketones and Carboxylic Acids

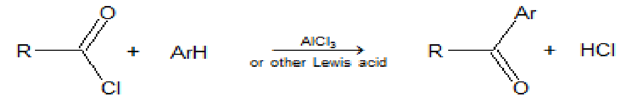
Aldehyde and Ketones

Preparation of Ketones:

a) Oxidation of Secondary alcohols:



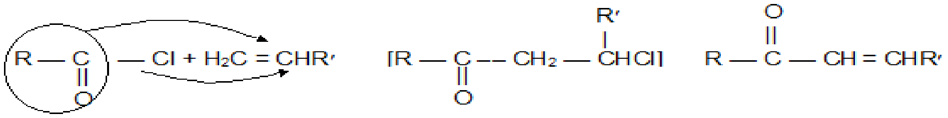
b) Friedel – Crafts acylation



acetyl chloride

ketone

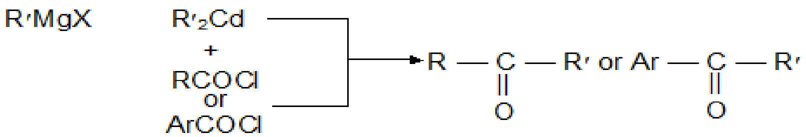
c) Acylation of Alkenes



$$R-\underset{\underset{O}{\|}}{C}-Cl + H_2C=CHR' \quad [R-\underset{\underset{O}{\|}}{C}-CH_2-\overset{\overset{R'}{|}}{C}HCl] \quad R-\overset{\overset{O}{\|}}{C}-CH=CHR'$$

This is Markovnikov addition initiated by $R-\overset{+}{C}=\ddot{O}:$, an acylium cation.

d) With Organometallics



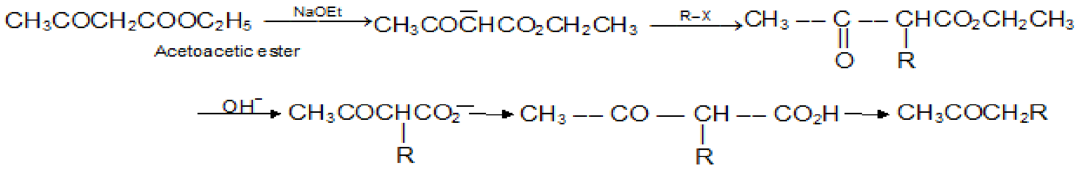
$$R'MgX \qquad R'_2Cd + RCOCl \text{ or } ArCOCl \longrightarrow R-\underset{\underset{O}{\|}}{C}-R' \text{ or } Ar-\underset{\underset{O}{\|}}{C}-R'$$

R′ must by aryl or primary alkyl

e) By heating the calcium salt of any monocarboxylic acid other than formic acid

$$(RCO_2)_2Ca + \Delta \rightarrow R_2CO + CaCO_3$$

f) Acetoacetic ester synthesis of ketones

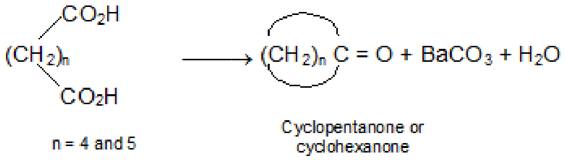


$$CH_3COCH_2COOC_2H_5 \xrightarrow{NaOEt} CH_3CO\bar{C}HCO_2CH_2CH_3 \xrightarrow{R-X} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{C}HCO_2CH_2CH_3$$

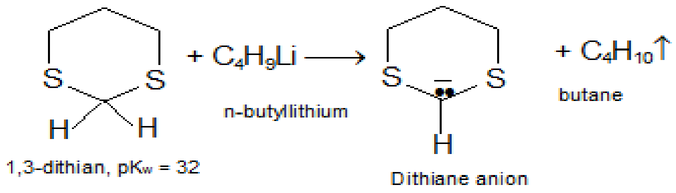
Acetoacetic ester

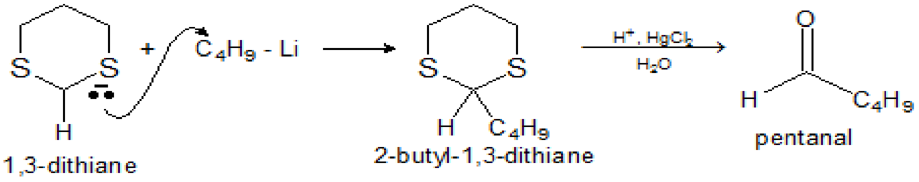
$$\xrightarrow{OH^-} CH_3CO\underset{\underset{R}{|}}{C}HCO_2^- \longrightarrow CH_3-CO-\underset{\underset{R}{|}}{C}H-CO_2H \longrightarrow CH_3COCH_2R$$

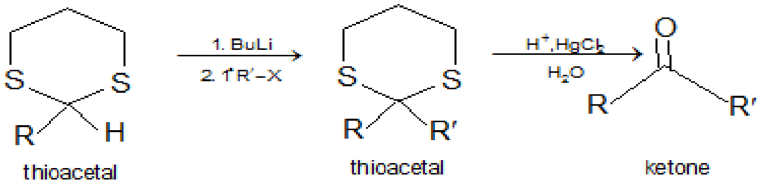
g) Ring Ketones from Dicarboxylic acids and their Derivaties:



h) Synthesis of Ketones and Aldehydes Using 1,3-Dithianes:

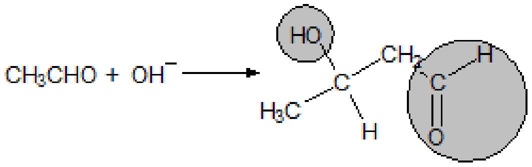






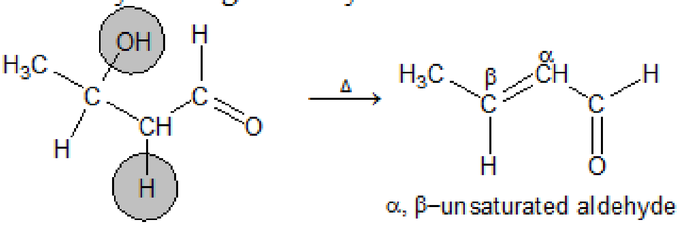
Reactions of Aldehydes and Ketones:

a) Aldol condensation



(Since it contains two functional groups aldehydes and alcohol)

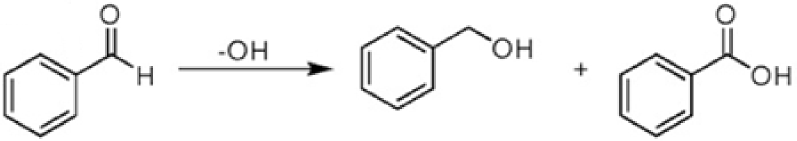
Aldol easily undergoes dehydration



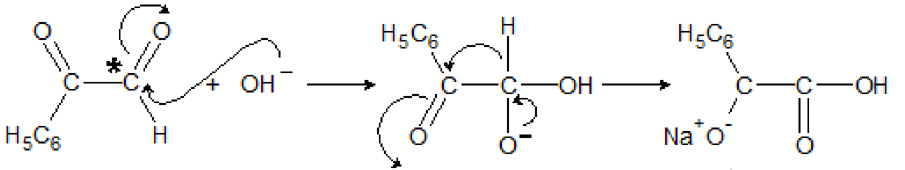
Aldehydes and ketones having alpha hydrogen atom:

b) Cannizzaro reaction:

Aldehydes and ketones having no alpha hydrogen atom:



When two carbonyl groups are present within a molecule, think of intramolecular reaction. OH$^-$ will attack more positively charged carbon. In this case, it is right >c=0 group.



Sodium salt of Mandelic acid

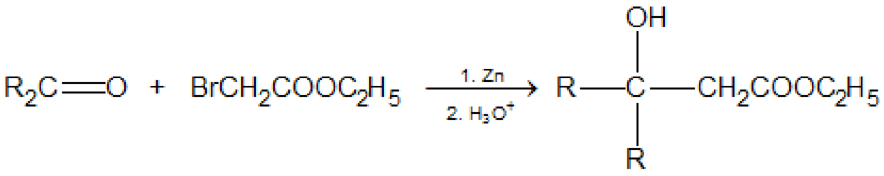
c) Formation of Keto Esters

Esters having a-hydrogen on treatment with a strong base e.g. C_2H_5ONa. Undergo self condensation to produce b-keto esters. This reaction is Claisen Condensation.

$$2CH_3COOC_2H_5 \xrightarrow[2.\ H^+]{1.\ C_2H_5ONa} CH_3COCH_2COOC_2H_5$$

d) Reformatsky Reaction

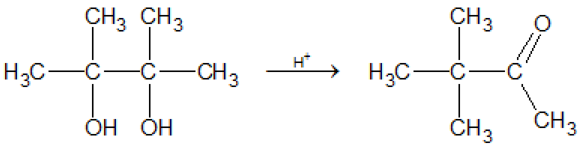
This is the reaction of a-haloester, usually an a-bromoester with an aldehyde or ketone in the presence of Zinc metal to produce b-hydroxyester.



$$R_2C{=}O + BrCH_2COOC_2H_5 \xrightarrow[2.\ H_3O^+]{1.\ Zn} R-\underset{R}{\overset{OH}{C}}-CH_2COOC_2H_5$$

e) Pinacol-pinacolone Rearrangement

The acid catalysed rearrangement of 1,2 diols (Vicinal diols) to aldehydes or ketones with the elimination of water is known as pinacol pinacolone rearrangement.



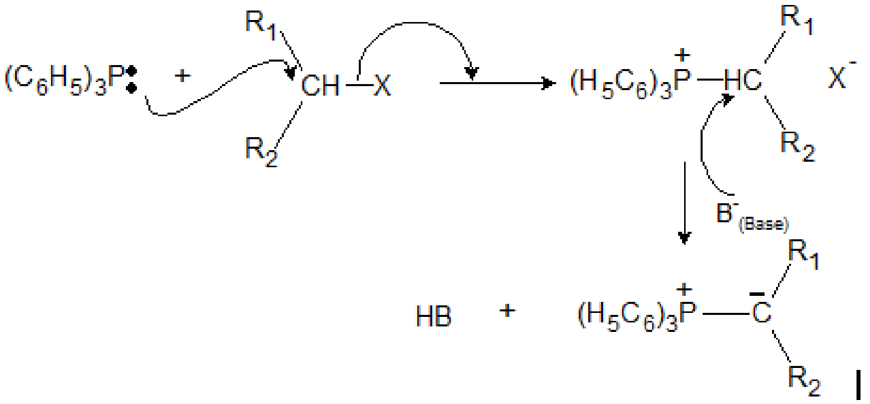
pinacol

Pinacolone
(Methyl t-butylketone)

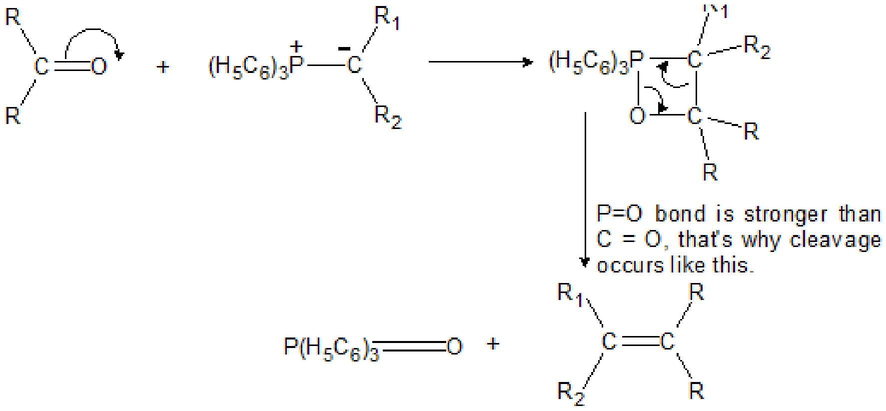
a) Wittig-Ylide Reaction

Aldehydes and Ketones react with phosphorus Ylides to yield alkenes and triphenyl phosphine oxide. An Ylide is a neutral molecule having a negative carbon adjacent to a positive hetero atom. Phosphorus ylides are also called phosphoranes.

Preparation of Ylides

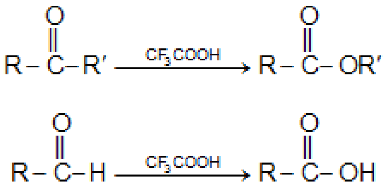


Reaction of Ylide with >C=O



P=O bond is stronger than C = O, that's why cleavage occurs like this.

d) Baeyer-Villiger Oxidation

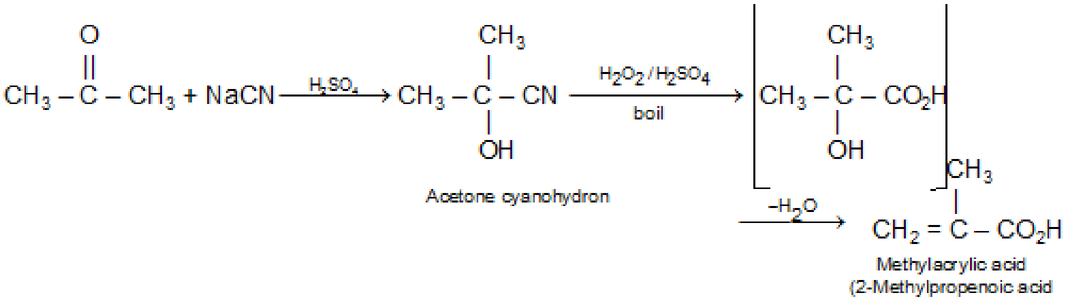


$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{CF_3COOH} R-\overset{O}{\overset{\|}{C}}-OR'$$

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{CF_3COOH} R-\overset{O}{\overset{\|}{C}}-OH$$

Above things happens in BVO (Bayer Villiger oxidation). Reagents are either per acetic acid or perbenzoic acid or pertrifluoroacetic acid or permonosulphuric acid.

e) Addition of cyanide

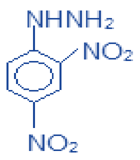
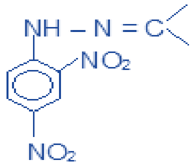


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NaCN \xrightarrow{H_2SO_4} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CN \xrightarrow[\text{boil}]{H_2O_2/H_2SO_4} \left[CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CO_2H\right] \xrightarrow{-H_2O} CH_2=\overset{CH_3}{\overset{|}{C}}-CO_2H$$

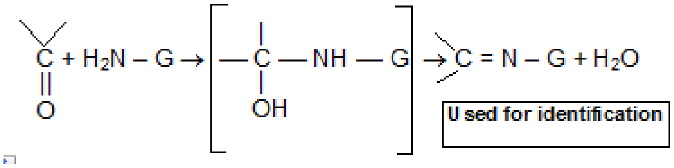
Acetone cyanohydron

Methylacrylic acid
(2-Methylpropenoic acid

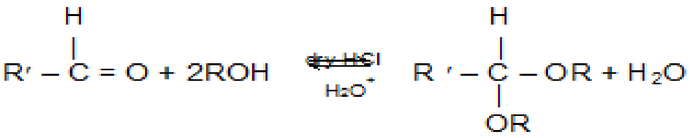
f) Addition of bisulfite:

	$H_2N - G$	Product	
H_2NOH	Hydroxylamine	$> C = N - OH$	Oxime
$H_2N - NH_2$	Hydrazine	$> C = N - NH_2$	Hydrazone
$H_2N - NH - C_6H_5$	Phenylhydrazine	$> C = N - NHC_6H_5$	Phenylhydrazone
$H_2N - NH - CO - NH_2$	Semicarbazide	$> C = N - NHCONH_2$	Semicarbazone
	2, 4-Dinitrophenyl hydrazine		2, 4-dinitrophenylhydrazone (bright orange or yellow precipitate used for identifying aldehydes and ketones

g) Addition of derivative of ammonia



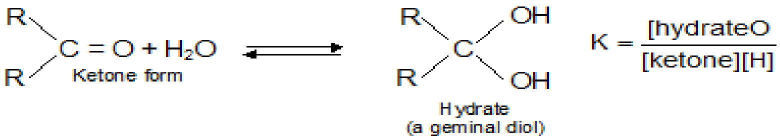
h) Addition of Alcohols; Acetal Formation



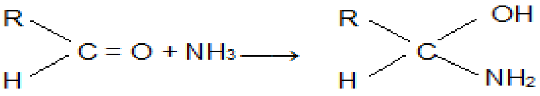
An acetal (gem-diether)

In H_3O^+, RCHO is regenerated because acetals undergo acid catalyzed cleavage much more easily than do ethers. Since acetals are stable in neutral or basic media, they are used to protect the – CH = O group.

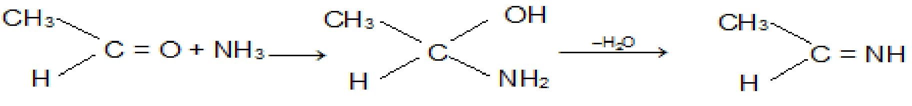
i) Addition of Water



j) Addition of Ammonia:



Aldehyde ammonia

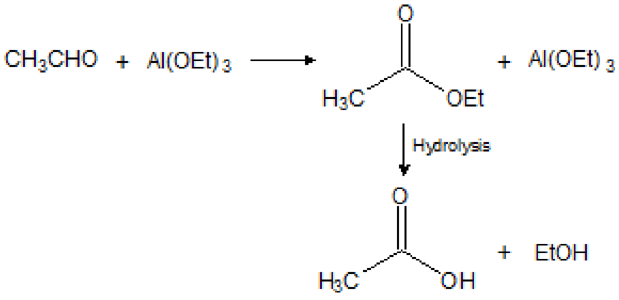


Aldehyde ammonia (unstable)

Aldimine (very reactive)

k) Tischenko reaction:

All aldehydes can be made to undergo the Cannizzaro reaction by treatment with *aluminium ethoxide.* Under these conditions the acids and alcohols are combined as the ester, and the reaction is then known as the Tischenko reaction; eg, acetaldehyde gives ethyl acetate, and propionaldehyde gives propyl propionate.



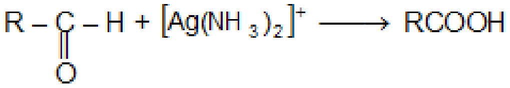
Oxidation of Aldehydes and Ketones

a)

$$R\,CH = O/\,Ar\,CH = O \xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7/H^+} R - CO_2H/\,ArCO_2H$$

b) Tollen's Reagent

A specific oxidant for RCHO is $[Ag(NH_3)_2]^+$

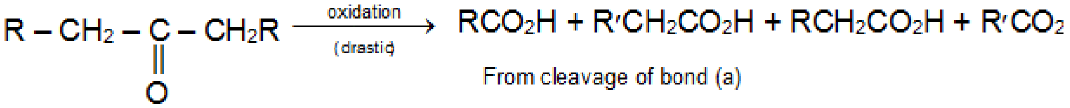


$$R - \underset{\underset{O}{\|}}{C} - H + [Ag(NH_3)_2]^+ \longrightarrow RCOOH$$

Tollen's test chiefly used for the detection of aldehydes.

Tollen's reagent doesnot attack carbon-carbon double bonds.

c) Strong Oxidants: Ketones resist mild oxidation, but with strong oxidants at high temperature they undergo cleavage of C – C bonds on either sides of the carbonyl group.



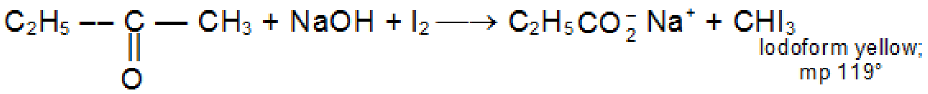
$$R - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2R \xrightarrow[\text{(drastic)}]{\text{oxidation}} RCO_2H + R'CH_2CO_2H + RCH_2CO_2H + R'CO_2$$

From cleavage of bond (a)

d) Haloform Reaction

CH_3COR are readily oxidised by NaOI (NaOH + I_2) to iodoform, CHI_3, and RCO_2Na

Example:

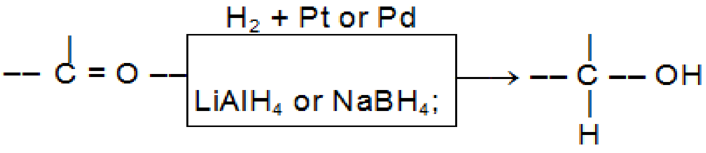


$$C_2H_5 - \underset{\underset{O}{\|}}{C} - CH_3 + NaOH + I_2 \longrightarrow C_2H_5CO_2^- Na^+ + CHI_3$$

Iodoform yellow;
mp 119°

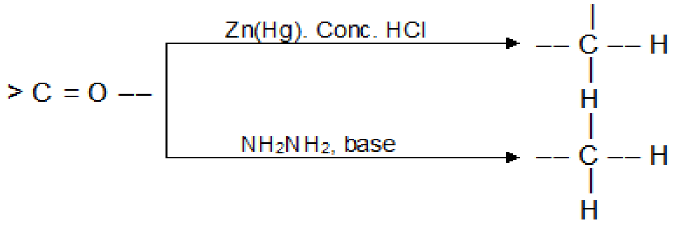
- **Reduction:**

a) Reduction to alcohols



Aldehydes → 1° alcohols; Ketones → 2°alcohols

b) Reduction to hydrocarbons



Clemmensen reduction for compounds sensitive to base

Wolff-Kishner reduction for compounds sensitive to acids

Carboxylic Acids:

Physical Properties of Carboxylic Acids

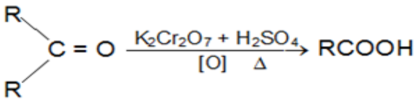
- The first three acids are colourless, pungent smelling liquids.
- First four members are miscible in water due the intermolecular hydrogen bonding whereas higher members are miscible in non – polar solvents like ether.
- Benzene or ethanol but immiscible in water due to the increase in the size of lyophobic alkyl chain.
- The b.p. of carboxylic acids are higher than alcohols because carboxylic acids exist as dimers due to the presence of intermolecular H-bonding
- Increase in the number of Halogen atoms on a-position increases the acidity, eg. $CCl_3COOH > CHCl_2COOH > ClCH_2COOH > CH_3COOH$
- Increase in the distance of Halogen from COOH decreases the acidity e.g $CH_3 – CH_2 – CH(Cl) – COOH > CH_3 – CH(Cl) – CH_2 – COOH > CH_2 – CH_2 – CH_2 – COOH$
- Increase in the electro negativity of halogen increases the acidity. $FCH_2COOH > BrCH_2COOH > ICH_2COOH$

Methods of Preparations of Carboxylic Acids

a. Oxidation of Aldehydes & Ketones

$$R - CH_2OH \xrightarrow[{[O]}]{K_2Cr_2O_7 + H_2SO_4} RCHO \xrightarrow[{[O]}]{K_2Cr_2O_7 + H_2SO_4} RCOOH$$

$$R - CHO \xrightarrow[2.\ H_3O^+]{1.\ Ag_2O \text{ or } Ag(NH_3)_2^+} RCO_2H$$



b. Oxidation of Alkanes:

$$RCH = CHR' \xrightarrow[2.\ \text{Heat},\ H_2O]{1.\ KMnO_4,\ OH^-} RCO_2H + R'CO_2H$$

c. Hydrolysis of Nitriles (Cyanides)

$$R - C \equiv N \xrightarrow[H^+,\ HOH]{\text{Acid hydrolysis}} R.COOH + NH_3$$

d. Carbonation of Grignard Reagents

$$R - X + Mg \xrightarrow{\text{Diethyl ether}} RMgX \xrightarrow{CO_2} RCO_2MgX \xrightarrow{H_3O^+} RCO_2H$$

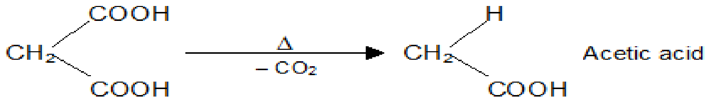
$$\text{or } Ar - Br + Mg \xrightarrow{\text{Diethyl ether}} ArMgBr \xrightarrow{CO_2} ArCO_2MgBr \xrightarrow{H_3O^+} ArCO_2H$$

e. Koch Reaction:

An olefin is heated with carbon monoxide and steam under pressure at 300-400° in the presence of a catalyst, e.g. phosphoric acid.

$$CH_2 = CH_2 + CO + H_2O \xrightarrow[\text{steam } 300-400^\circ C]{H_3PO_4} CH_3 - CH_2 - COOH$$

f. Heating Gem Dicarboxylic Acids:



Chemical Reactions of Carboxylic Acids

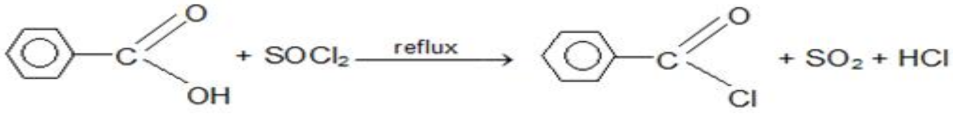
a. Salt formation:

$2CH_3COOH + 2Na \rightarrow 2CH3COO–Na^{+} + H_2$

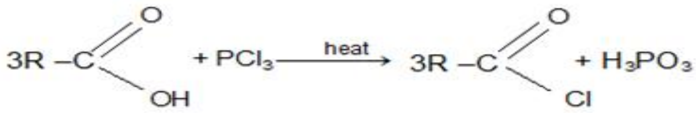
$CH_3COOH + NaOH \rightarrow CH3COO–Na^{+} + H_2O$

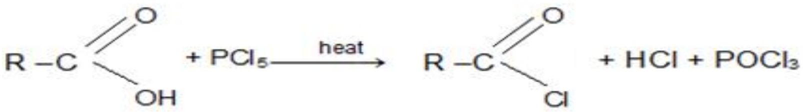
$CH_3COOH + NaHCO_3 \rightarrow CH3COO–Na^{+} + H_2O + CO_2$

b. Conversion into Acid Chlorides:

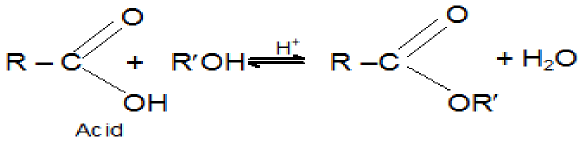


Benzoic acid Benzoyl chloride

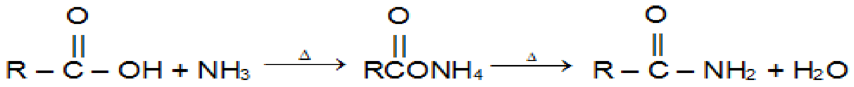




c. Conversion into Esters (Esterification)



d. Conversion into Amides



$$R-\overset{O}{\overset{||}{C}}-OH + NH_3 \xrightarrow{\Delta} R\overset{O}{\overset{||}{C}}ONH_4 \xrightarrow{\Delta} R-\overset{O}{\overset{||}{C}}-NH_2 + H_2O$$

e. Conversion into Anhydrides

$$2CH_3COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CO)_2O + H_2O$$

f. Reduction:

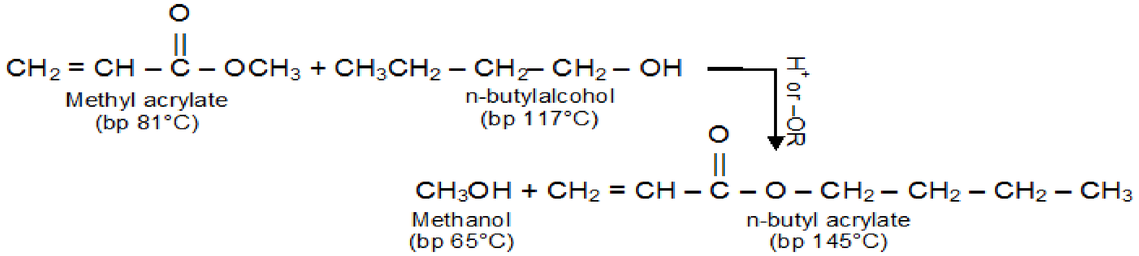
$$4R{-}COOH + 3LiAlH_4 \longrightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4\,AlLi \xrightarrow{H_2O} RCH_2OH$$

g. Halogenation:

$$CH_3-COOH \xrightarrow{Cl_2,P} Cl-CH_2-COOH \xrightarrow{Cl_2,P} Cl_2CH-COOH \xrightarrow{Cl_2,\ P} Cl_3CCOOH$$

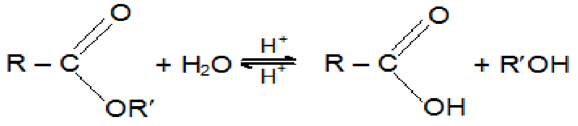
Esters

a) Transesterification :



$$\underset{\substack{\text{Methyl acrylate}\\ \text{(bp 81°C)}}}{CH_2=CH-\overset{O}{\overset{||}{C}}-OCH_3} + \underset{\substack{\text{n-butylalcohol}\\ \text{(bp 117°C)}}}{CH_3CH_2-CH_2-CH_2-OH} \xrightarrow{H^+\text{ or }-OR} \underset{\substack{\text{Methanol}\\ \text{(bp 65°C)}}}{CH_3OH} + \underset{\substack{\text{n-butyl acrylate}\\ \text{(bp 145°C)}}}{CH_2=CH-\overset{O}{\overset{||}{C}}-O-CH_2-CH_2-CH_2-CH_3}$$

b) Hydrolysis:



c) Reduction:

$$\underset{\text{Methyl laurate}}{CH_3-(CH_2)_{10}-COOCH_3} \xrightarrow[\text{150° High pressure}]{H_2,\ CuO,\ CuCr_2O_4} \underset{\text{Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} + CH_3OH$$

$$\underset{\text{Ethyl palmitate}}{CH_3-(CH_2)_{14}-COOC_2H_5} \xrightarrow{LiAlH_4} \xrightarrow{H^+} \underset{\text{1–Hexadodecanol}}{CH_3-(CH_2)_{14}-CH_2-OH}$$

Acid Chlorides:

a) Acetylation

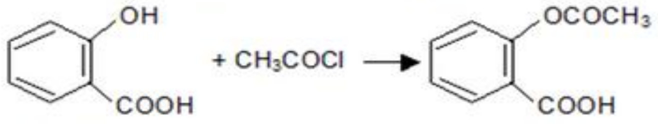
$CH_3COCl + HOH \longrightarrow CH_3COOH + HCl$

$CH_3COCl + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$

Acetyl chloride — Ethyl acetate

$CH_3COCl + H_2NC_6H_5 \longrightarrow C_6H_5NHCOCH_3 + HCl$

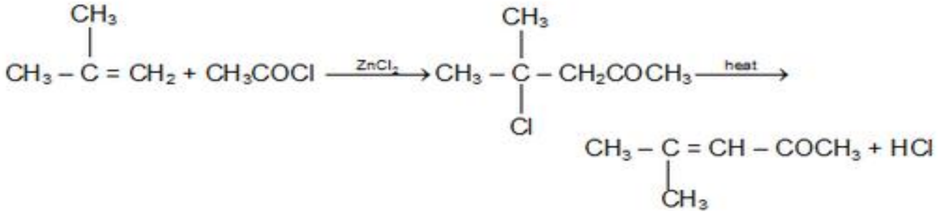
Aniline — Acetanilide



Salicylic acid

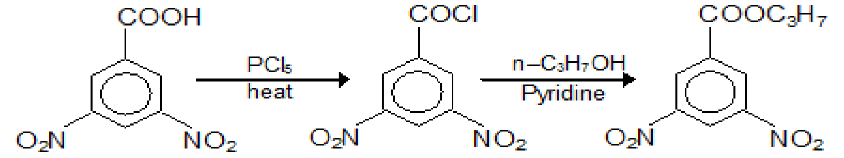
Acetyl Salicylic acid (Aspirin)

b) Reaction with Olefins:



$$CH_3-\overset{CH_3}{C}=CH_2 + CH_3COCl \xrightarrow{ZnCl_2} CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2COCH_3 \xrightarrow{heat} CH_3-\underset{CH_3}{C}=CH-COCH_3 + HCl$$

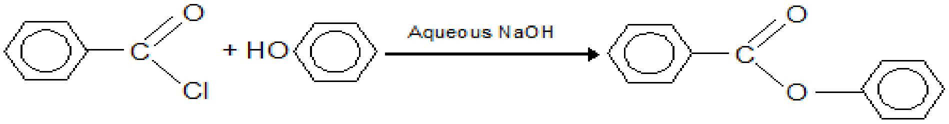
c) Conversion of Acid Chlorides into Acid Derivatives:



3-5, Dinitrobenzoic acid

3-5, Dinitrobenzoyl chloride

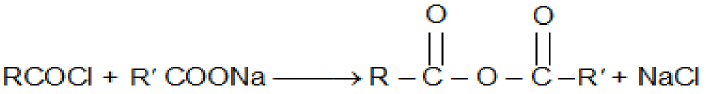
n-propyl 3, 5 – dinitrobenzoate



Benzoyl chloride

Phenol

Phenyl benzoate

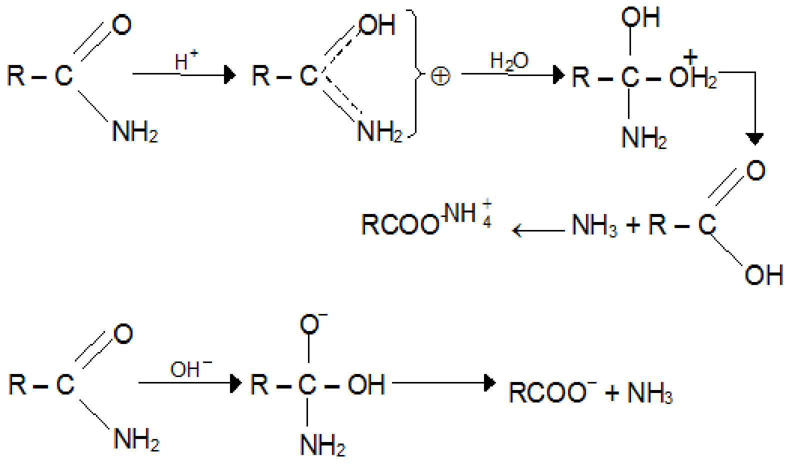


$$RCOCl + R'COONa \longrightarrow R-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-R' + NaCl$$

Acid anhydride

Amides

a. Hydrolysis:

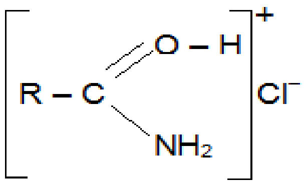


b. Acidic Character of Amides:

$2RCONH_2 + HgO \rightarrow (RCONH)_2Hg + H_2O$

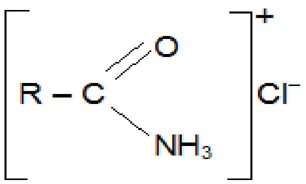
c. Basic Character of Amides:

Amides are very feebly basic and form unstable salts with strong inorganic acids. e.g. $RCONH_2HCl$. The structure of these salts may be I or II



I

or



II

d. Reduction:

$$RCONH_2 + 4H \xrightarrow{Na/C_2H_5OH} R-CH_2-NH_2 + H_2O$$

e. Reaction with Phosphorus Pentaoxide:

$$R\text{-}CONH2 + P_2O_5 \rightarrow R\text{-}CN$$

f. Reaction with Nitrous Acid:

$$RCONH_2 + HNO_2 \rightarrow RCO_2H + N_2 + H_2O$$

Nitroalkanes, Amines & Diazonium Salts

Amines

Structure of amines: Trigonal Pyramidal

Basicity of Amines

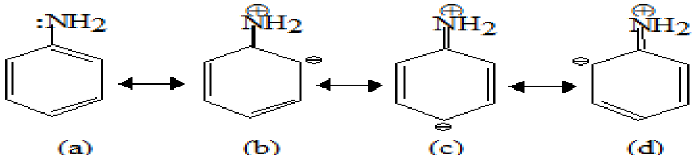
a) Aliphatic Amine:

Basic Strength: $NH_3 < RNH_2 < R_2NH < R_3N$,

b) Aromatic Amine:

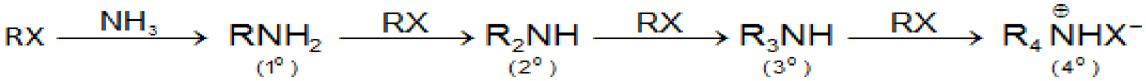
Basic Strength: $NH_3 > Ar\text{-}NH_2 > Ar_2\text{-}NH_2$

Benzene ring decreases the electron density over N atom due to resonance effect.



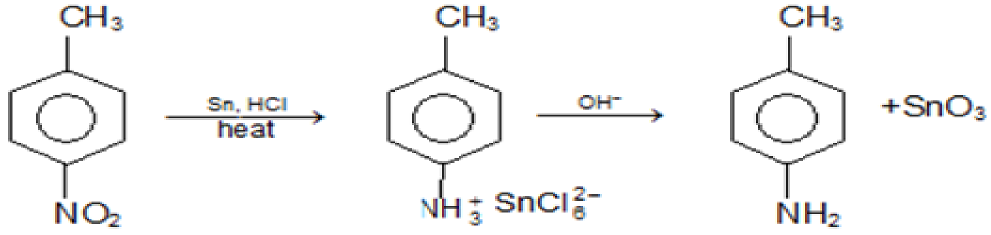
Preparation of Amines

a) From Alkyl halides:



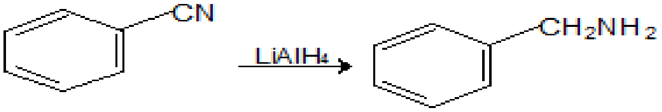
$$RX \xrightarrow{NH_3} \underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3NH} \xrightarrow{RX} \underset{(4^\circ)}{R_4\overset{\ominus}{N}HX^-}$$

b) From Nitro Compounds:



p-Nitrotoluene p-Toluidine

c) From Nitriles :



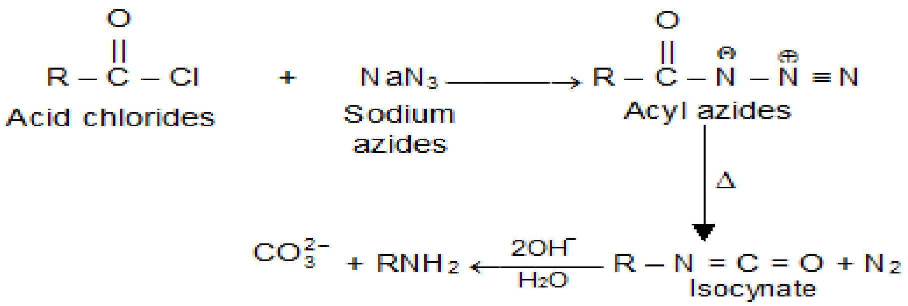
d) Hofmann Bromamide or Hofmann degradation:

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr$$

e) From carbonyl compounds (Reductive Amination)

$$CH_3CH=O + NH_3 \longrightarrow \underset{\text{(an imine)}}{CH_3CH=NH} \xrightarrow{H_2/Ni} \underset{\text{(an ami}}{CH_3CH}$$

f) Curtius reaction:



$$\underset{\text{Acid chlorides}}{R-\overset{O}{\overset{\|}{C}}-Cl} + \underset{\text{Sodium azides}}{NaN_3} \longrightarrow \underset{\text{Acyl azides}}{R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N}$$

$$\Delta$$

$$CO_3^{2-} + RNH_2 \xleftarrow[H_2O]{2OH^-} \underset{\text{Isocynate}}{R-N=C=O} + N_2$$

g) Schmidt reaction :

$$RCO_2H + HN_3 \xrightarrow{\text{conc } H_2SO_4} RNH_2 + CO_2$$

h) Reduction of Alkyl isocyanide:

$$RNC + 4[H] \rightarrow R-NH-CH_3$$

i) Preparation of tertiary amine:

$$3RX + NH_3 \text{ (In excess)} \xrightarrow{\text{Ethanolic solution}} R_3N + 2HX$$

Chemical Reactions

a) Acylation:

RNH_2 + R'COCl → R'CO NHR an N-substituted amide

R_2NH + R'COCl → $R'CO.NR_2$ an N,N disubstituted amide

b) Benzoylation (Schotten Baumann Reaction)

Primary amine reacts with benzoyl chloride to give the acylated product

c) Carbylamine Reaction (Given Only by Primary Amines):

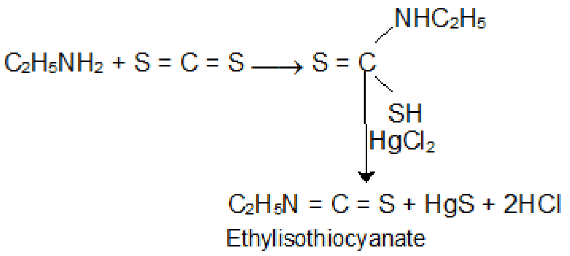
$C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$

$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$

d) Action with Aldehyde and Ketone:

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Acetaldehyde}}{CH_3CHO} \longrightarrow \underset{\substack{\text{Ethylidene ethylamine}\\ \text{(Schiff's base)}}}{C_2H_5N = CHCH_3} + H_2O$$

e) Hofmann Mustard Oil Reaction:



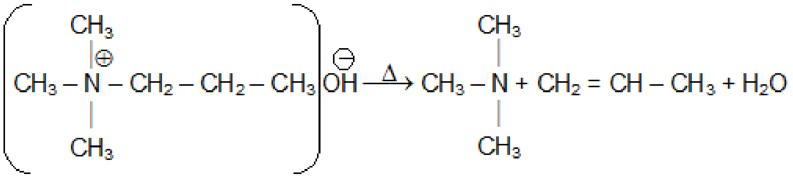
$$C_2H_5NH_2 + S = C = S \longrightarrow S = C(NHC_2H_5)(SH) \xrightarrow{HgCl_2} C_2H_5N = C = S + HgS + 2HCl$$

Ethylisothiocyanate

f) Reaction with Carbonyl Chloride: $C_2H_5 - NH_2 + COCl_2 \rightarrow C_2H_5NCO + 2HCl$

g) Hofmann Elimination:

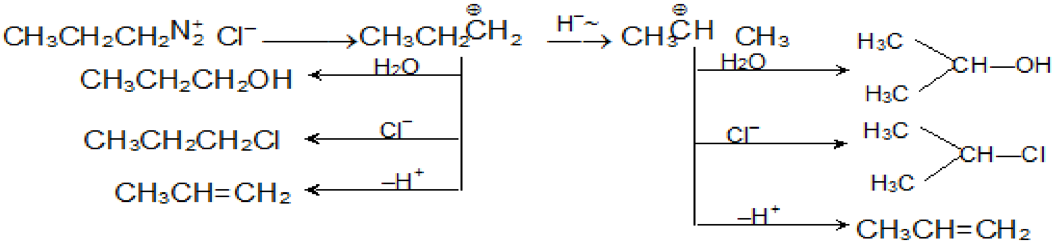
When a quaternary ammonium hydroxide is heated strongly (125° or higher) it decomposes to yield water, a tertiary amine and an alkene

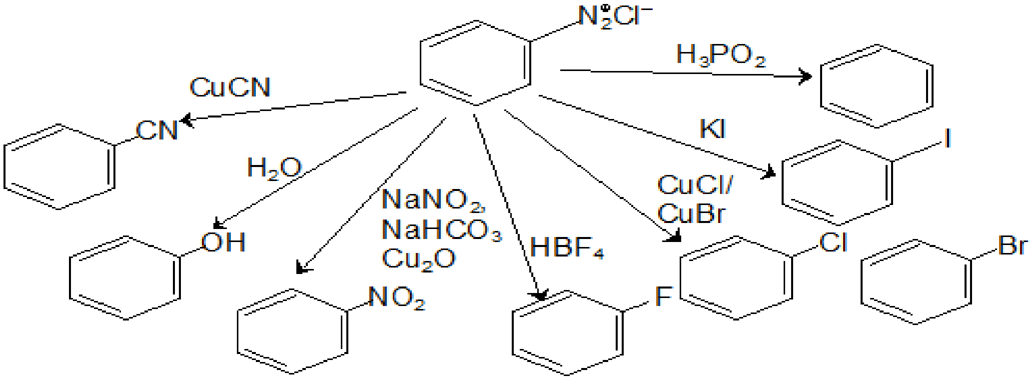


$$\left[CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}} - CH_2 - CH_2 - CH_3\right]\overset{\ominus}{OH} \xrightarrow{\Delta} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} + CH_2 = CH - CH_3 + H_2O$$

h) The diazonium salts of amines:

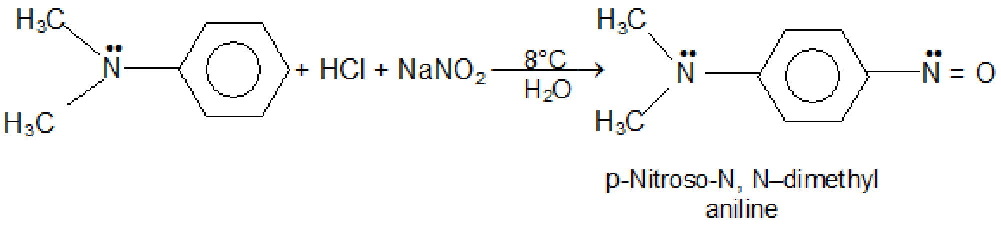
$$RNH_2/Ar\text{-}NH_2 \xrightarrow[HCl, 0°C]{HONO} RN_2^+Cl^-$$



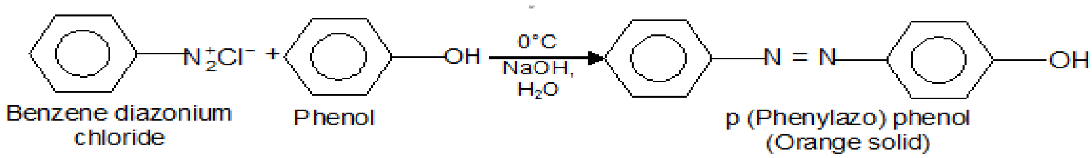


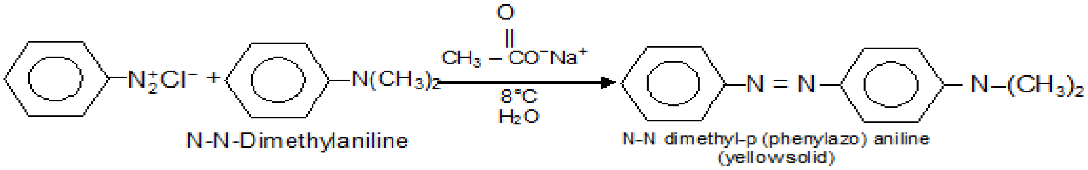
i) Reaction of Tertiary amines with Nitrous acid: When a tertiary aliphatic amine is mixed with nitrous acid, an equilibrium is established among the tertiary amine, its salt, and an N-Nitrosoammonium compound.

$$\underset{\text{Tertiary aliphatic amine}}{2R_3N} + HX + NaNO_3 \rightleftharpoons \underset{\text{Amine salt}}{R_3\overset{+}{N}H\,\overset{-}{X}} + \underset{\text{N-Nitrosoammonium compound}}{R_3\overset{+}{N}-N=OX^-}$$

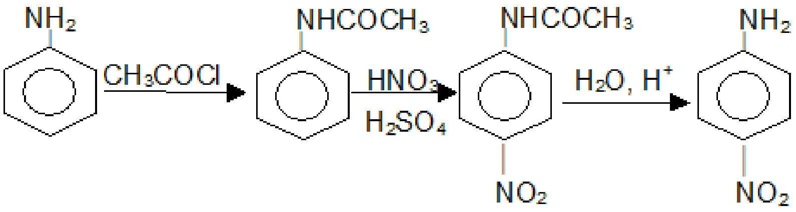


j) Coupling Reactions of Arene Diazonium Salts:

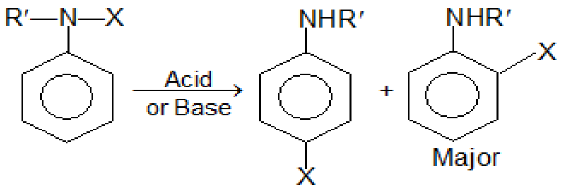




k) Ring Substitution in Aromatic Amines:

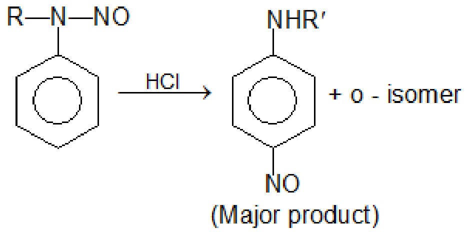


i) Aniline -X rearrangement:



Such compounds are not much stable so the group X migrates mainly at p-position.

1. Fisher-Hepp rearrangement



2. Phenylhydroxylamine - p-aminophenol rearrangement.

Separation of a Mixture of Amines:

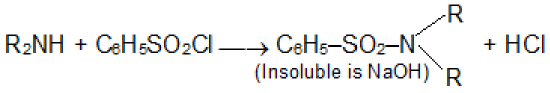
a) Hinsberg's Method

Primary amine: $RNH_2 + C_6H_5SO_2Cl$ ¾® $C_6H_5 - SO_2 - NH - R + HCl$

$C_6H_5 - SO_2 - NH - R$: N-alkyl benzene sulfonamides

Dissolves in NaOH due to acidic H-attached to Nitrogen)

Secondary Amine

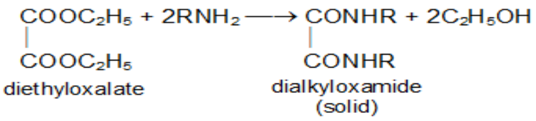


$$R_2NH + C_6H_5SO_2Cl \longrightarrow \underset{\text{(Insoluble is NaOH)}}{C_6H_5{-}SO_2{-}NR_2} + HCl$$

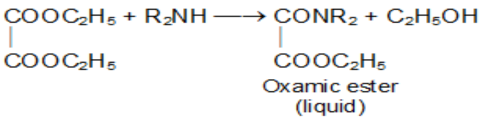
Tertiary amine : Tertiary amines do not react with Hinsberg's reagent.

a) Hofmann's Method:

The mixture of amines is treated with diethyloxalate, which forms a solid oxamide with primary amine, a liquid oxime ester with secondary amine. The tertiary amine does not react.



$$\underset{\text{diethyloxalate}}{\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix}} + 2RNH_2 \longrightarrow \underset{\substack{\text{dialkyloxamide} \\ \text{(solid)}}}{\begin{matrix} CONHR \\ | \\ CONHR \end{matrix}} + 2C_2H_5OH$$



$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + R_2NH \longrightarrow \underset{\substack{\text{Oxamic ester} \\ \text{(liquid)}}}{\begin{matrix} CONR_2 \\ | \\ COOC_2H_5 \end{matrix}} + C_2H_5OH$$

Test for Amines

Primary amine is treated with a strong base in presence in chloroform, an isocyanide is formed and this isocyanide thus formed has a very foul smell.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\substack{\text{an isocyanide} \\ \text{(foul smelling)}}}{R - \overset{+}{N} \equiv \overset{-}{C}:} + 3KCl + H_2O$$

Secondary amine is converted into nitrosoamine by treating the amine with nitrous acid. The resultant solutions warmed with phenol and concentrated H_2SO_4, a brown or red colour is formed at first soon it changes to blue and then to green. The colour changes to red on dilution and further changes to greenish blue on treating with alkali.

Tertiary arylamines react with nitrous acid to form o-nitroso aromatic compound.

Polymers

Some Important Terms

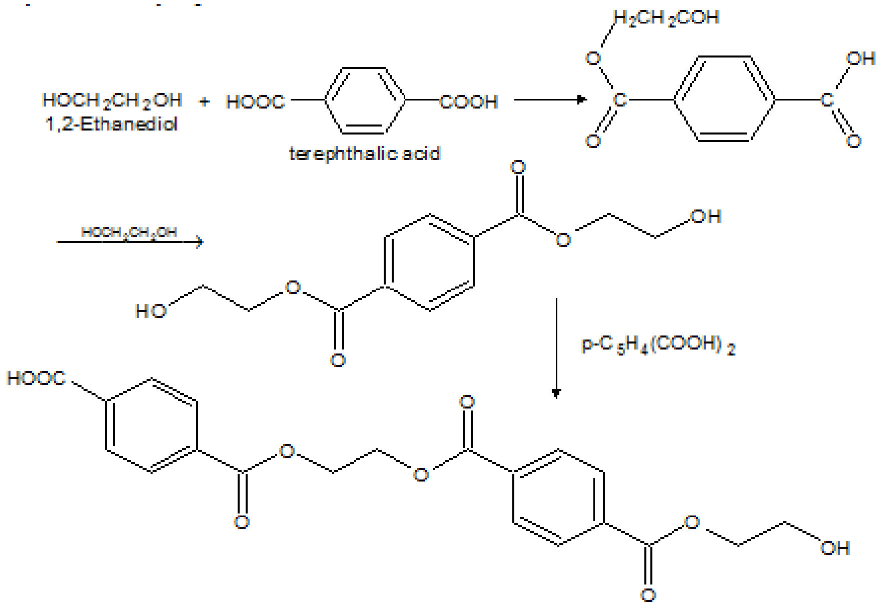
Polymer	Large molecules having high molecular mass formed by combination of number of small units called monomers.
Polymerisation	The process of formation of polymers from respective monomers.
Natural polymers	Found in plants and animals. Examples: proteins, cellulose, starch.
Synthetic polymers:	Synthesised in laboratory from natural material. Example, nylon 6, 6 , Buna-S
Addition Polymers	Formed by repeated addition of monomers having multiple bonds.
Homopolymers	Addition polymers polymers formed from single monomeric species.
Copolymers	Addition polymers formed from two different monomeric species
Condensation polymers	Formed by repeated condensation of different bi or tri-functional monomer units.
Fibres	Long thin, threadlike bits of material that are characterized by great tensile (pulling) strength in the direction of the fiber. The natural fibres – cotton, wool, silk – are typical. The lining-up is brought about by drawing – stretching — the return to random looping and coiling is overcome by strong intermolecular attractions.
Elastomers	Possesses the high degree of elasticity that is characteristic of rubber: it can be greatly deformed — stretched to eight times its original length e.g., buna N and buna S, When the stretching force is removed, the molecular chains of an elastomer do not remain extended and aligned but return to their original random conformations
Thermoplastic polymers	Soften on heating and stiffen on Cooling. e.g polythene, polystyrene, PVC
Thermosetting polymers	Do not soften on heating and cannot be remoulded. Example, bakelite

Polymers are formed in two general ways.

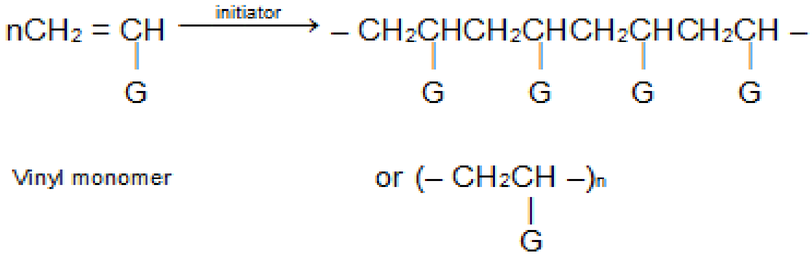
a) In chain-reaction polymerization

$\text{Rad.} + CH_2 = CH_2 \rightarrow RadCH_{2c}H_2 \rightarrow RadCH_{2c}H_{2c}H_{2c}H_{2x} \rightarrow$ etc.

b) In step reaction polymerization,



c) Free-radical vinyl polymerization:

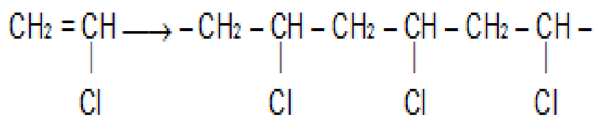


$$nCH_2=\underset{\underset{G}{|}}{CH} \xrightarrow{\text{initiator}} -CH_2\underset{\underset{G}{|}}{CH}CH_2\underset{\underset{G}{|}}{CH}CH_2\underset{\underset{G}{|}}{CH}CH_2\underset{\underset{G}{|}}{CH}- \quad \text{or} \quad (-CH_2\underset{\underset{G}{|}}{CH}-)_n$$

Vinyl monomer

Polymer

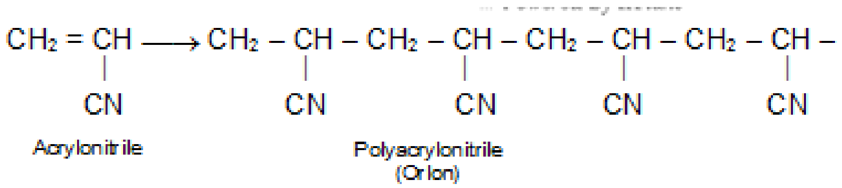
At the doubly bonded carbons — the vinyl groups — and is called *vinyl polymerization*. A wide variety of unsaturated monomers may be used, to yield polymers with different *pendant groups* (G) attached to the polymer backbone. For example.



$$CH_2=\underset{\underset{Cl}{|}}{CH} \longrightarrow -CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-$$

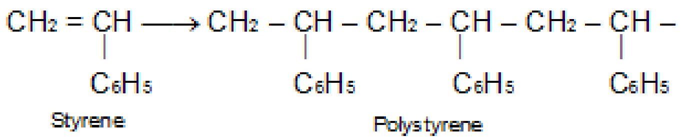
Vinyl chloride

Poly (vinyl chloride)
(PVC)



$$CH_2=\underset{\underset{CN}{|}}{CH} \longrightarrow CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-$$

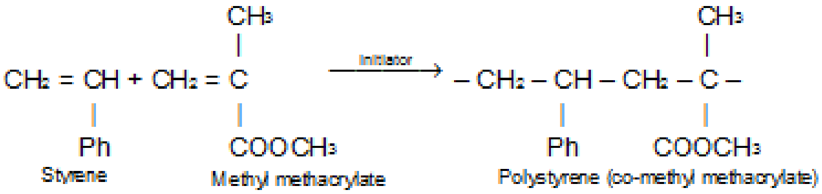
Acrylonitrile Polyacrylonitrile (Orlon)



$$CH_2=\underset{\underset{C_6H_5}{|}}{CH} \longrightarrow CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-$$

Styrene Polystyrene

d) Copolymerization:



$$CH_2=\underset{\underset{Ph}{|}}{CH}+CH_2=\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}} \xrightarrow{\text{Initiator}} -CH_2-\underset{\underset{Ph}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}-$$

Styrene Methyl methacrylate Polystyrene (co-methyl methacrylate)

Some Important Polymers:

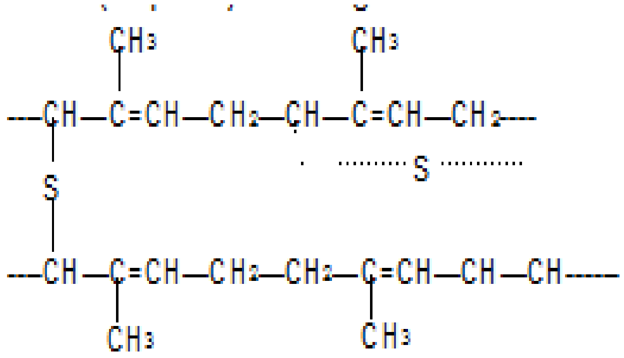
a) Natural Rubber*:*

Addition polymer of isoprene (2-methyl-1,3-butadiene)

An average chain length of 5000 monomer units of isoprene.

The rubber in which the arrangement of carbon chain is trans with respect to the double bond is known as ***Gutta Percha*** and this is the natural rubber obtained from bark of various trees.

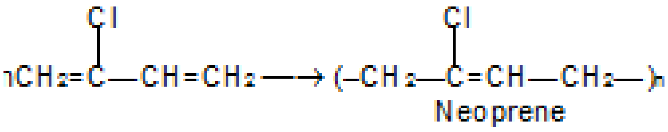
'Vulcanisation of rubber involves addition of sulphur to rubber and heating the mixture to increase the strength of natural rubber. sulphur forms short chains of sulphur atoms that link two hydrocarbon (isoprene) units together.



Vulcanised rubber is thus stronger and less sticky than the natural rubber.

b) Synthetic rubber:(Polychloroprene) or Neoprene)

It is obtained by free radical polymerisation of chloroprene in



$$nCH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2 \longrightarrow (-CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2-)_n$$

Neoprene

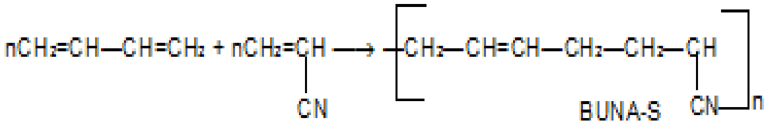
A thermoplastic and need not to be vulcanised.

It is a good general purpose rubber and superior to natural rubber as it is resistant to the reaction of aire, heat, light chemicals, alkalis and acids below 50% strength.

It is used for making transmission belts, printing rolls and flexible tubing employed for conveyence of oil and petrol.

c) **Buna rubbers**:

i) **Buna - N or GRA:** it is synthetic rubber obtained by copolymerisation of one part of acryl nitrile and two parts of butadiene.

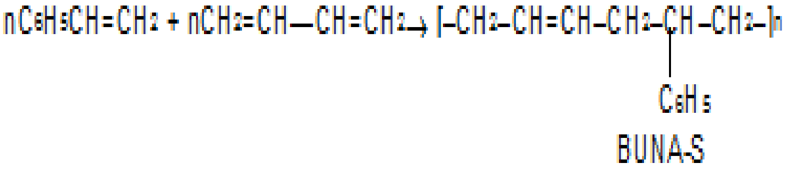


$$nCH_2=CH-CH=CH_2 + nCH_2=\underset{CN}{CH} \longrightarrow \left[CH_2-CH=CH-CH_2-CH_2-\underset{CN}{CH} \right]_n$$

BUNA-S

It is more rigid responds less to heat and very resistant to swelling action of petorol, oils and other organic solvents.

ii) **Buna -S or GRS** (General purpose Styrene rubber): It is a copolymer of three moles of butadiene and one mole of styrene and is an elastomer. It is obtained as a result of free radical copolymerisation of its monomers.



$$nC_6H_5CH=CH_2 + nCH_2=CH-CH=CH_2 \rightarrow [-CH_2-CH=CH-CH_2-\underset{C_6H_5}{CH}-CH_2-]_n$$

BUNA-S

It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and finds use in manufacture of tyres and other mechanical rubber goods.

d) **Teflon**: It is polymer of tetrafluorethylene ($F_2C=CF_2$) which on polymerisation gives Telfon.

$$nCF_2=CF_2 \xrightarrow{(NH_4)_2S_2O_8\ \ 870-1020K} (-CF_2-CF_2-)_n$$

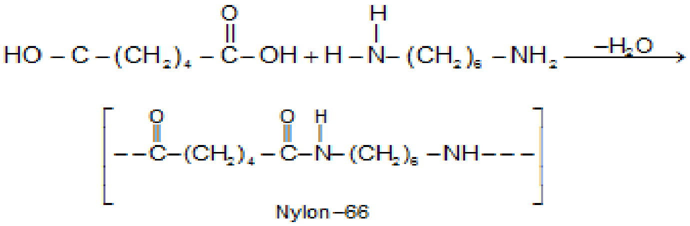
It is thermoplastic polymer with a high softening point (600K).

It is very tough and difficult to work. It is inert to most chemicals except fluorine and molten alkali metals.

It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

e) Nylon -66:

A condensation polymer formed by reaction between adipic acid and hexamethylene diamine. It is a thermoplastic polymer.

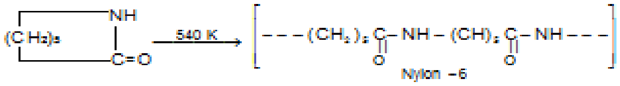


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH+H-\overset{H}{\overset{|}{N}}-(CH_2)_6-NH_2\xrightarrow{-H_2O}\left[--\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-NH---\right]$$

Nylon –66

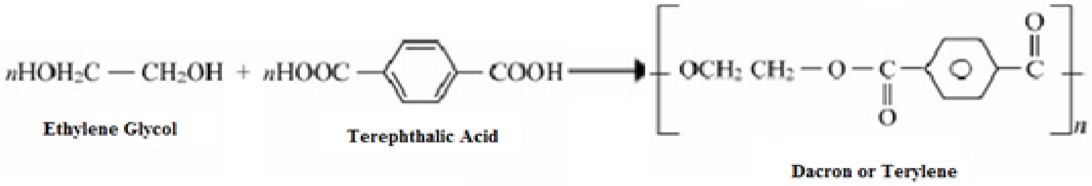
(A condensation copolymer)

f) Nylon 6 or Perolon - L: A polyamide is prepared by prolonged heating of caprolactam at 530 - 540 K.

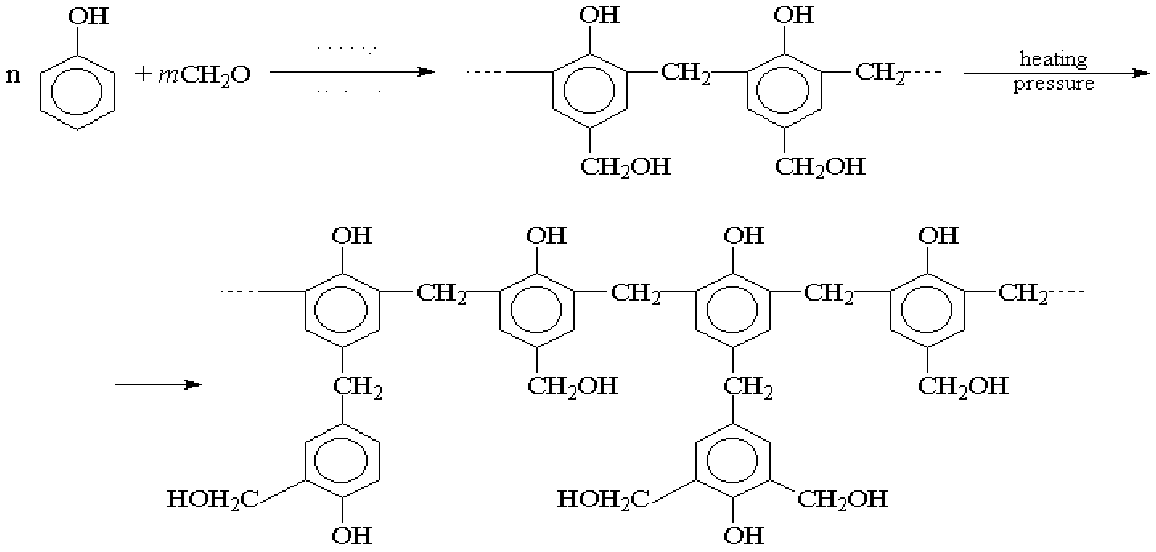


The fiber is practically identical to Nylon in properties

g) Dacron:



h) Phenol-formaldehyde polymer: E.g., Bakelite Novolac



Biomolecules

Revision Notes on Biomolecules

Carbohydrates

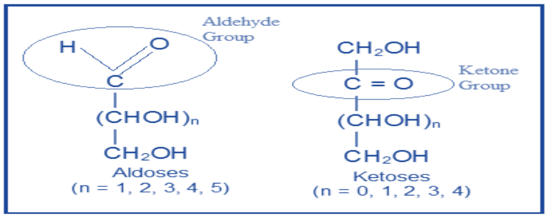
Classification of carbohydrates:

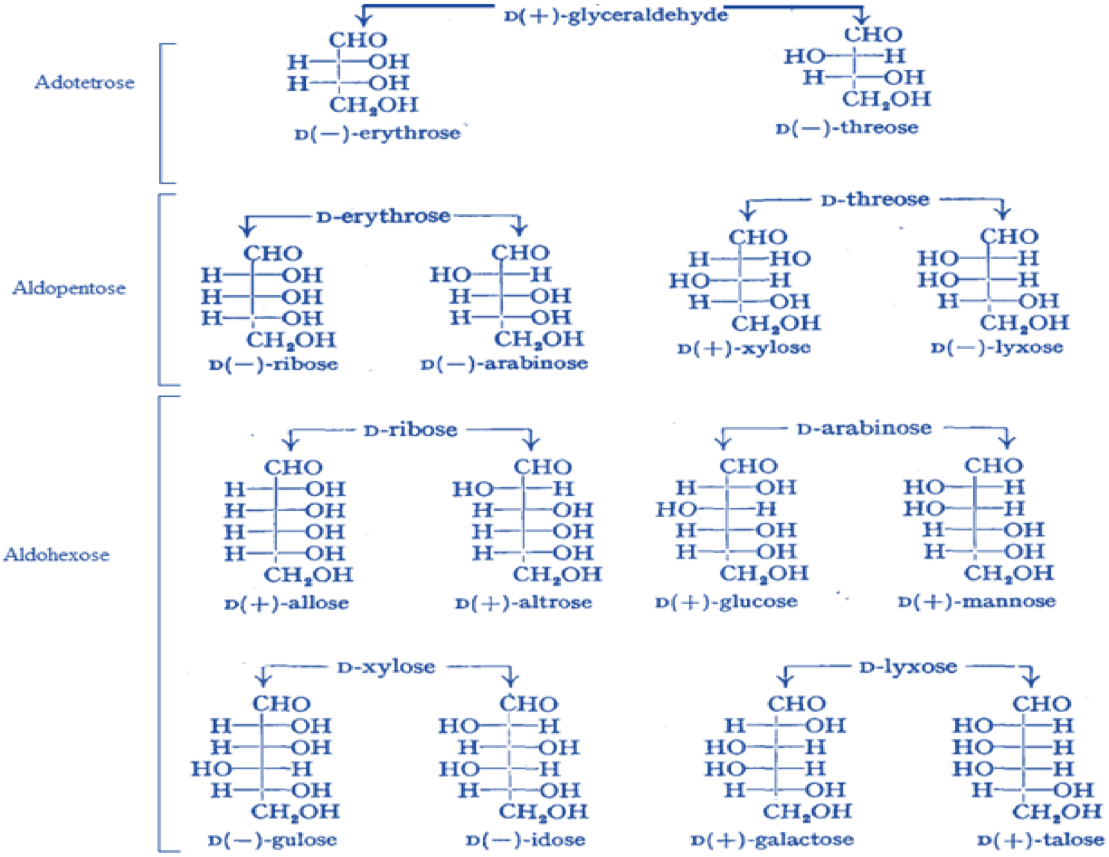
- **Monosaccharides**
- **Trisaccharides**
- **Oligosaccharides**
- **Polysaccharides**

- **Monosaccharides**

  The Aldoses, which contain an aldehyde group (-CHO).

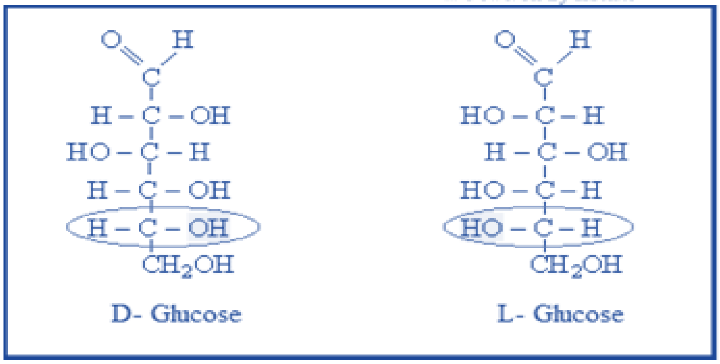
  The Ketoses, which contain a ketone group (>C=O).

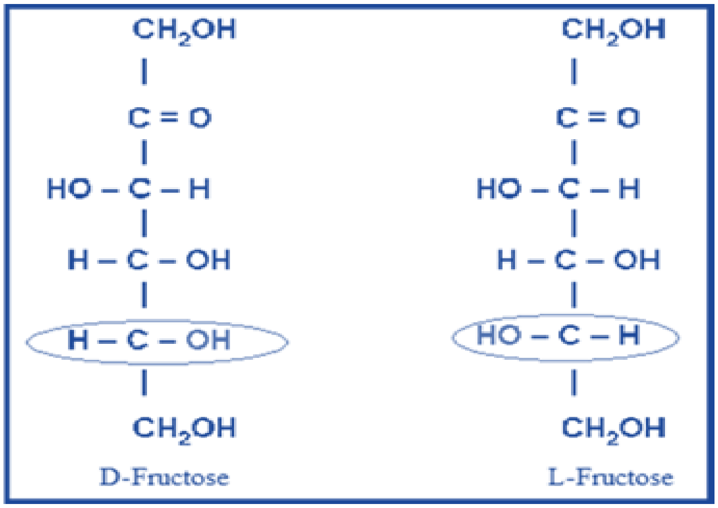




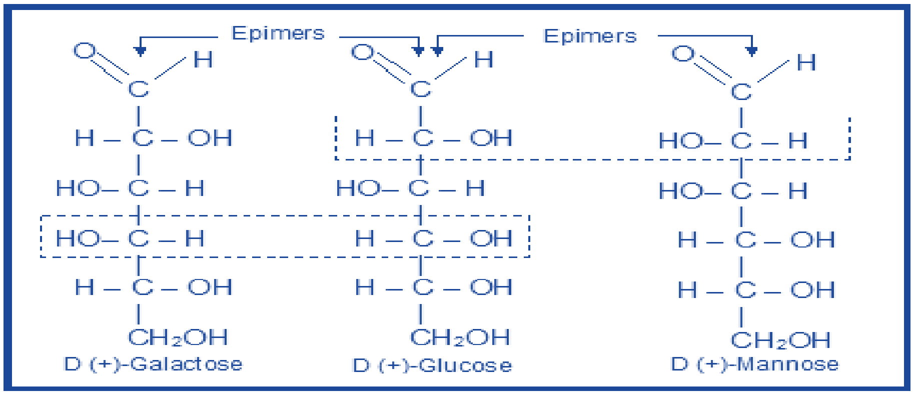
Stereo Isomerism in Carbohydrates:

- If the hydroxyl group on the asymmetric carbon atom farthest from aldehyde or ketone group projects to the right, the compound is a member of the **D-family**.
- If the hydroxyl group on the farthest asymmetric carbon projects to the left, the compound is a member of the**L-family**.



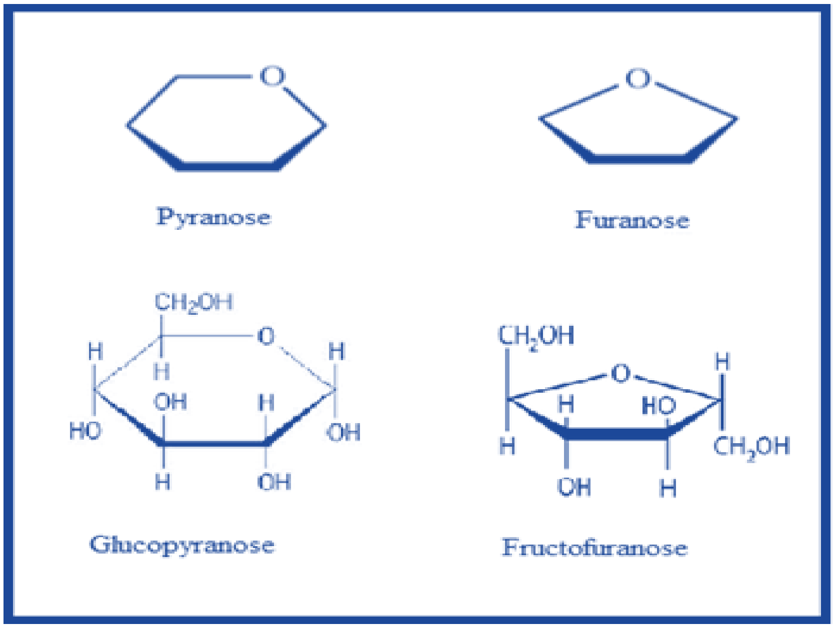


- **Maximum Number of Optical Isomers = 2^n**, where n = the number of asymmetric carbon atoms.
- **Epimer:** A pair of diastereomers that differ only in the configuration about of a single carbon atom are said to be epimers.

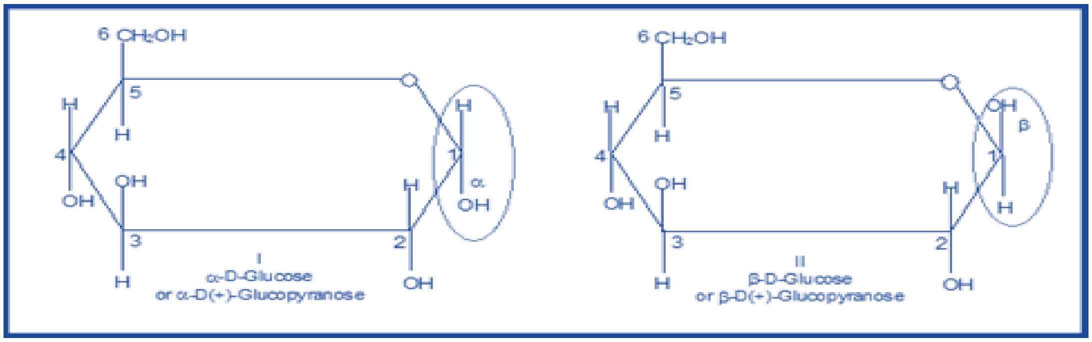


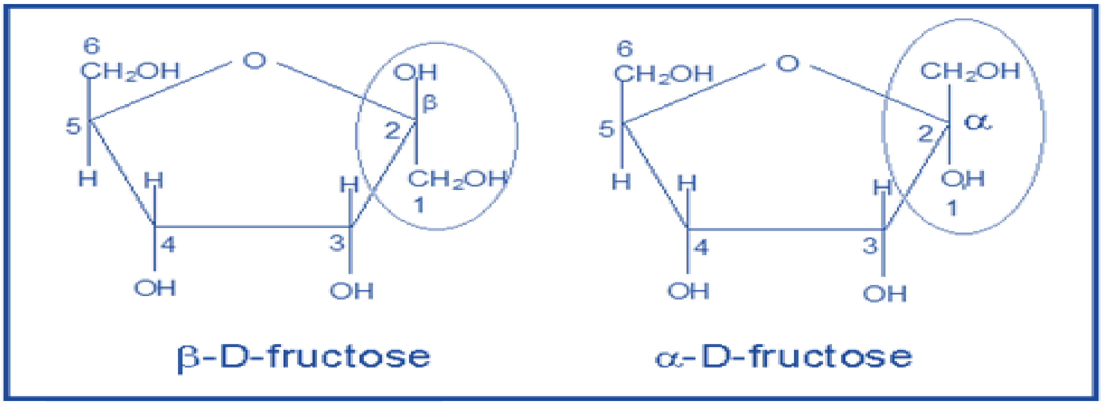
Cyclic Form of Monosaccharide:

- **Pyranose and Furanose Forms:**



- **Anomers:** Pair of stereoisomers which differ in configuration only around C_1 are called **anomers** and the C_1carbon is called Anomeric carbon.In a- anomer-, the OH group at C_1 is towards right while in b-anomer, the OH group at C_1 is toward





Mutarotation:

Change in rotation of an optically active sugar in solution with time, to an equilibrium value, is called**mutarotation**. During mutarotation, the ring opens and then recloses either in the inverted position or in the original position giving a mixture of a-and-b-forms.

Reactions of Glucose:

a) **With HI/P:** It undergoes reduction to form n-hexane while with sodium amalgam it forms orbitol.

$$\text{Glucose} \xrightarrow{HI/P} CH_3 - (CH_2)_4 - CH_3$$

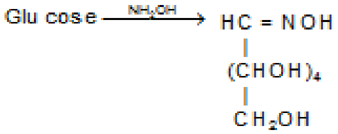
n-hexane

$$\text{Glucose} \xrightarrow{Na/Hg} CH_2OH - (CHOH)_4 - CH_2OH$$

sorbitol

b) With H_2O: It forms neutral solution

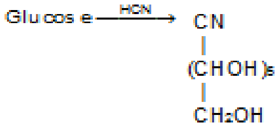
c) With Hydroxylamine (NH_2OH)



$$\text{Glucose} \xrightarrow{NH_2OH} \begin{array}{l} HC = NOH \\ \;| \\ (CHOH)_4 \\ \;| \\ CH_2OH \end{array}$$

Glucose oxime

d) With HCN: It form addition product cyanohydrin



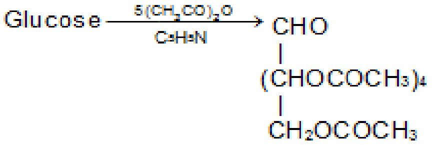
$$\text{Glucose} \xrightarrow{HCN} \begin{array}{l} CN \\ \;| \\ (CHOH)_5 \\ \;| \\ CH_2OH \end{array}$$

Glucose cyanohydrin

e) Oxidation: Glucose on oxidation with Br_2 gives gluconic acid which on further oxidation with HNO_3 gives glucaric acid

f) With Tollen reagent and Fehling solution. Glucose forms silver mirror and red ppt. of Cu_2O respectively.

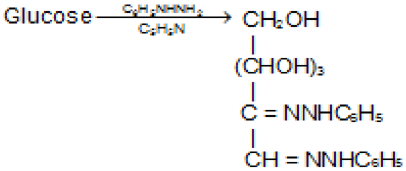
g) With acetic anhydride. In presence of pyridine glucose forms pentaacetate.



$$\text{Glucose} \xrightarrow[C_5H_5N]{5(CH_3CO)_2O} \begin{array}{l} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{array}$$

Glucose pentaacetate

h) With phenylhydrazine: it forms glucosazone



$$\text{Glucose} \xrightarrow[C_5H_5N]{C_6H_5NHNH_2} \begin{array}{l} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ C = NNHC_6H_5 \\ | \\ CH = NNHC_6H_5 \end{array}$$

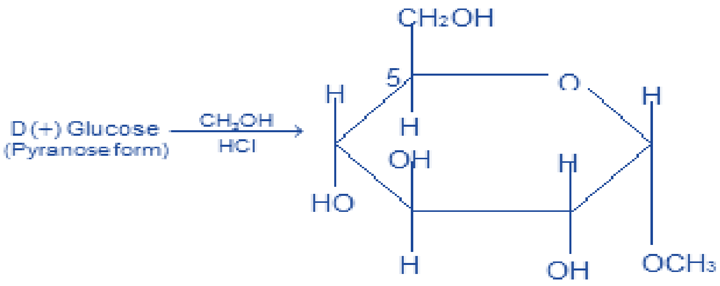
(Glucosazone)

i) With conc. HCl acid: Glucose gives laevulinic acid

$$\text{Glucose} \xrightarrow{\text{Conc. HCl}} CH_3CO \cdot CH_2CH_2 \cdot COOH + HCOOH + H_2O$$

Laevulinic acid

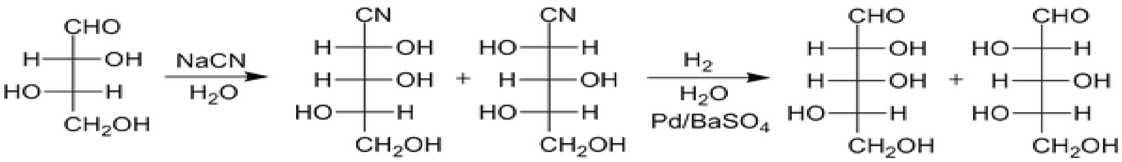
j) Glycoside formation: When a small amount of gaseous HCl is passed into a solution of D (+) glucose in methanol , a reaction takes place that results in the formation of amomeric methyl acetals.



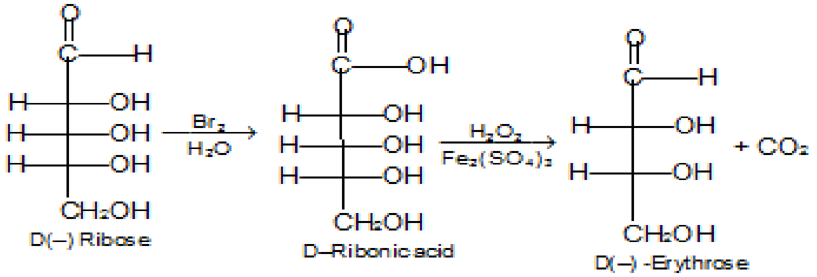
Methyl α-D-glucopyranoside
+
Methyl β-D-glucopyranoside

Carbohydrate acetals, genrally are called glycosides and an acetal of glucose is called glucoside.

k) Kiliani - Fischer Synthesis: - This is a method of lengthening the carbon chain of an aldose.



i) Ruff Degradation*:* It is opposite to Kiliani Fischer synthesis that can be used to shorten the chain by a similar unit.



- **Disaccharides:**

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Invertase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

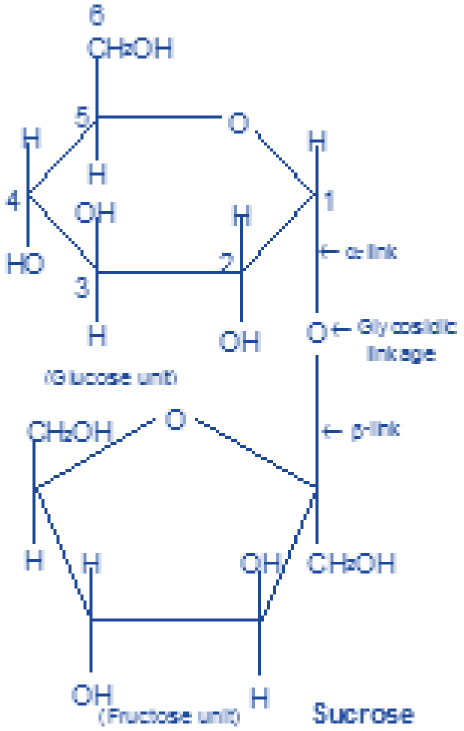
$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Maltase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Lactase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

a) Sucrose:

Non-reducing sugar.

Formed by condensation of one molecule of glucose and one molecule of fructose.

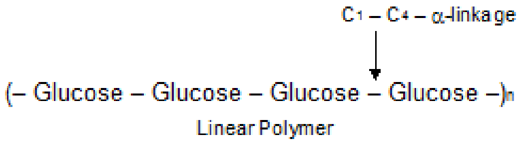


Hydrolysis: (Invert Sugar or Invertose). Hydrolysis of sucrose with hot dilute acid yields D-glucose and D-fructose.

Polysaccharides

a. Starch:

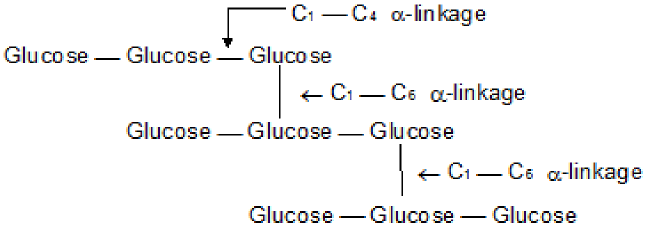
- i. A polymer of glucose.
- ii. Mixture of two components – a water soluble component called amylose (20%) and a water insoluble component called amylopectin (80%).
- iii. Both amylose and amylopectin are polymers of a-D-glucose.
- iv. Amylose is a linear polymer of a-D-glucose



$$\overset{C_1 - C_4 - \alpha\text{-linkage}}{(-\text{Glucose} - \text{Glucose} - \text{Glucose} \downarrow - \text{Glucose} -)_n}$$

Linear Polymer

- vi Amylopectin, is a highly branched polymer



Amino Acids,

Amino acids are molecules, which contain two functional groups, one is carboxylic group and another is amino group

$H_2N\ CH_2\ COOH$: Amino acetic acid, or Glycine

$CH_3\ CH\ (NH_2)\ COOH$: a - Amino propionic acid or Alanine

$H_2N\ CH_2\ CH_2COOH$: b - Amino propionic acid

Acidic Amino Acid*:* These amino acids contain a second carboxyl group or a potential carboxyl group in the form of carboxamide.

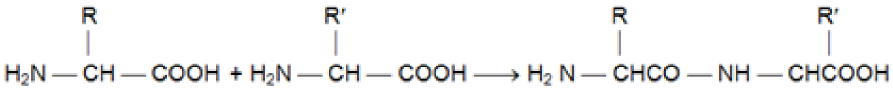
Basic Amino Acids: These contain a second basic group which may be an amino group

Iso Electric Point:

The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the ***isoelectric point*** of that amino acid.

Peptides

A peptides as the amides formed by interaction between amino groups and carboxyl groups of amino acids**.**



$$H_2N - \overset{R}{\overset{|}{C}}H - COOH + H_2N - \overset{R'}{\overset{|}{C}}H - COOH \longrightarrow H_2N - \overset{R}{\overset{|}{C}}HCO - NH - \overset{R'}{\overset{|}{C}}HCOOH$$

Depending upon the number of amino acid residues per molecule, they are known as dipeptides, tripeptides and so on and finally polypeptides.

Every two amino acids are linked by means of a –CO-NH group, which is commonly referred as **peptide bond**.

$$H_3^+N - CH_2 - COOH \rightleftharpoons H_3N^+ - CH_2 - COO^- + H^+ \qquad \ldots(1)$$

Conjugated acid (CA) Dipolar Ion (DI)

$$\text{At equilibrium } K_1 = \frac{[DI][H^+]}{[CA]}$$

$$H_3N^+ - CH_2 - COO^- \rightleftharpoons H_2N - CH_2 - COO^- + H^+ \qquad \ldots(2)$$

DI Conjugated Base (CB)

$$\text{At equilibrium } K_2 = \frac{[CB][H^+]}{[DI]}$$

$$[CA] = \frac{[DI][H^+]}{K_1}$$

$$[CB] = \frac{K_2[DI]}{[H^+]}$$

At isoelectric point [CA] = [CB]

$$\frac{[DI][[H_i^+]}{K_1} = \frac{K_2[DI]}{[H_i^+]} \text{ Where } [H_i^+] = \text{conc. of } [H^+] \text{ at isoelectric point.}$$

$$\text{or, } [H_i^+]^2 = K_1 K_2$$

$$\text{or, } 2\log [H_i^+] = \log K_1 + \log K_2$$

$$\text{or } -2 \log (H_i^+] = -\log k_1 - \log K_2$$

$$\text{or } 2pH_i = pK_1 + pK_2$$

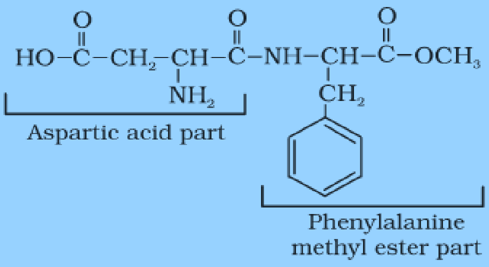
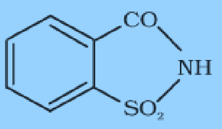
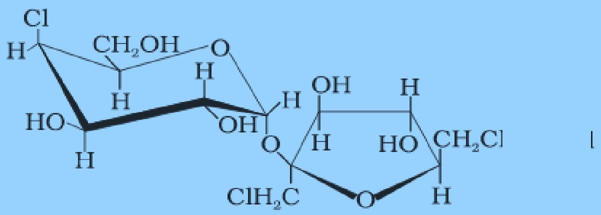
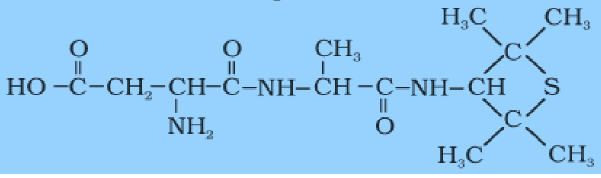
$$\text{or } pH_i = \frac{pK_1 + pK_2}{2}$$

Chemistry in Action

Drugs:

Drugs	Description	Examples
Analgesics	Relieve or decreases the pain without causing unconsciousness. These are also known as "Pain Killers".	Asprin, Analgin, seridon etc.
Tranquizers/ Antidepressants	These are used for treatment of mental diseases.	Equanil, Calmpose, Tofranil, Barbituric Acid, Cocaine and Iproniazids etc..
Antiseptics	They are applied on living tissues to kill or prevent the growth of micro-organisms.	Dettol, Savlon and Acriflavin etc.
Disinfectants	These are applied on floor, instruments or wall etc. to kill microorganisms but are not safe for application on living tissues.	Phenol
Antimicrobial	These are use to either kill (bactericidal) or stop the growth of diseases causing microorganisms. (bacteriostatic).	Salvarsan, Prontosil, Sulphanilamide, Bacteriostatic Drugs: Erythromycin, Tetracycline, Chloramphenicol Bactericidal Drugs: Ofloxacin, Aminoglycosides.
Antipyretics	These drugs bring down the body temperature during fever.	Paracetamol, Analgin and Novalgin.
Antifertility Drugs	Prevent pregnancy in women by controlling menstrual cycle and ovulation.	Norethindrone & Mestranol
Antacids	Used for the treatment of acidity. Metal hydroxides are generally used as antacids.	Eno, & Milk of magnesia [$Mg(OH)_2$]
Antibiotics	These are the chemical substances which are produced by micro –organisms like bacteria and fungi and are able to kill or stop the growth of pathogenic microorganisms.	Penicillin, Amoxicillin and Ampicillin.
Antihistamins	These drugs compete with histamine for finding sites of receptors and thus interfere with the natural action of histamine.	Brompheniramine & Terfenadine

Artificial Sweetening Agents

Artificial sweetener	Structural formula	Sweetness value in comparison to cane sugar
Aspartame		100
Saccharin		550
Sucralose		600
Alitame		2000

Food preservatives:

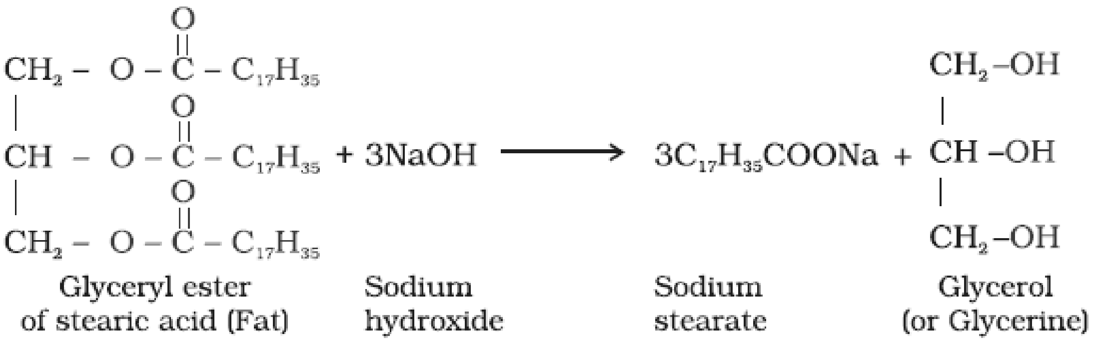
These are the chemical substances which prevent undesirable changes in flavor, colour, texture of the food during processing and storage of food.

Examples, Table salt, sugar, vegetable oils, sodium benzoate (C_6H_5COONa) etc

Cleansing Agents

Soaps:

Sodium or potassium salts of fatty acids.



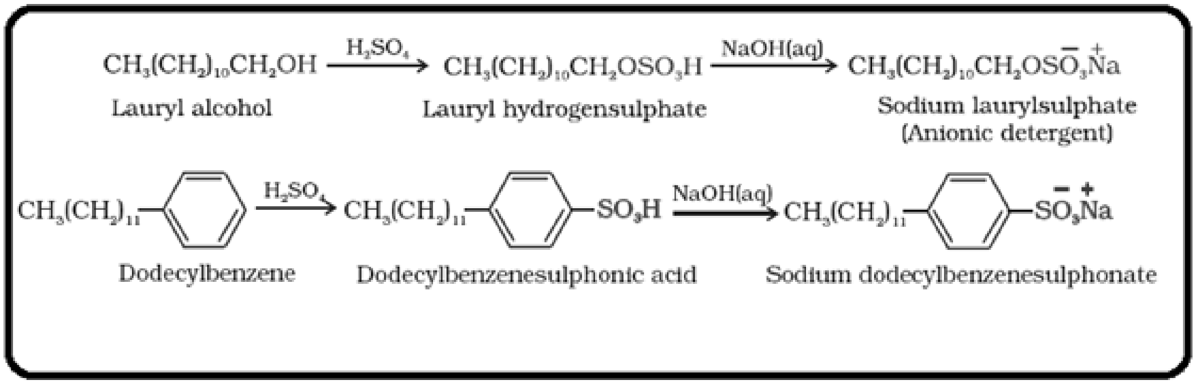
$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \end{array} + 3NaOH \longrightarrow 3C_{17}H_{35}COONa + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Soaps do not work with hard water as it forms insoluble salts with calcium and magnesium ions present in hard water.

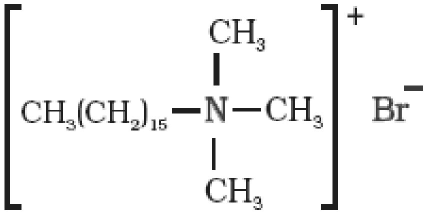
Detergents:

Sodium or potassium salts of sulphonic acids. These can work with hard water also.

Anionic Detergents: Sodium Slats of sulphonated long chain alcohols or hydrocarbons



Cationic Detergents: Quaternary ammonium salts of ammines with acetates, chlorates or bromates.



$$\left[CH_3(CH_2)_{15}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}-CH_3 \right]^+ Br^-$$

Cetyltrimethyl ammonium bromide

Non-Ionic Detergents: Do not contain any ion.

$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethyleneglycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH} \xrightarrow{-H_2O} CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

Environmental Chemistry

Components of Environment:

- **Atmosphere:** This comprises a blanket of gaseous layer around earth.
- **Hydrosphere**: This comprises about 96% of earth's surface & includes all sources of water like oceans rivers lakes, glaciers, ground water etc.
- **Lithosphere**: It refers to earth's solid crust containing the outer mineral cover. It comprises soil, minerals, organic matter etc.
- **Biosphere:** It refers to the domain of living organism in covalent with atmosphere hydrosphere as well as lithosphere.

Environmental Pollution :

Process of contamination of the environment with harmful wastes arising mainly from human activities.

- **Pollutant:** Any substance or species produced either by a natural source or by human activity, which produces adverse effect on the environment.
- **Contaminant:** A substance which does not occurs in nature but is introduced by human activity into the atmosphere affecting its composition.
- **Source:** The site from which the pollution or contaminants originate.
- **Sink:** The material or medium which consumes or interacts with a long lived pollutant is called sink.
- **Receptor** : Anything that is affected by the pollutants.
- **Threshold limit value (TLV) :** This indicates the permissible limit of a pollutant in atmosphere to which a healthy worker is exposed during hours a day or 40 hours a week for life time without any adverse effects. TLV are determined by experimentation on animals, by use of medical knowledge, epidemiology surveys & environmental studies.

Tropospheric pollution or Air pollution:

It is the atmosphere condition in which the presence of certain concentration produce harmful effects on man and his environment. These substances include:

Primary pollutants :

Particulate Matter Inorganic gases **Secondary**

Pollutant	Source	Sink	Effect
Carbon monoxide (CO)	(a) Incomplete combustion of carbonaceous matter, automobile engines & also in defective furnaces, Incomplete combustion of fossil fuels, agricultural , slash matter and other carbon $2C + O_2 \rightarrow 2CO$ (b) Dissociation of carbon dioxide. $2CO_2 \rightleftharpoons 2CO + O_2$ (c) Reaction of carbon dioxide with carbon containing compounds at high temperature. $CO_2 + C \rightleftharpoons 2CO$	Hydroxyl & perhydroxyl radicals, atomic oxygen & ozone help in the oxidation of atmospheric CO into CO_2 . Soil is major sink for CO. Some of the microorganism present in soil remove carbon monoxide from air.	Carbon monoxide is poisonous as it combines with hemoglobin of red blood cells about 300 times faster than O_2, thus forming carboxyl hemoglobin. This decreases the transport of oxygen to the body organs & cells.
Carbon dioxide (CO_2)	It is released mainly into the atmosphere by the combustion of fossil fuels (coal, oil etc) in factories & also at homes. CO_2 is also produced by biological decay of plants	Ocean is a main sink for CO_2. Green plants for photo synthesis.	CO_2 causes narcotic effect, stimulation of respiratory center & leads to asphyxiation. The increasing concentration of CO_2 also changes climatic conditions especially by raising the general temperature.
Oxides of sulphur (SO_2)	Volcanic eruptions (natural activity) & also through combustion of sulphur bearing fuels such as coal & oil (human activity). This pollutant is also produced during roasting & smelting of sulphide ores		It causes cough, shortness of breath & spasm of larynx, acute irritation to the membrane of gas resulting tears & reduces hearing ability. SO_2 irritates the respiratory system of animals &

	(human activity) A part of SO_2 undergoes photolytic & catalytic oxidation to form SO_3. The SO_3, so formed gets converted to H_2SO_4 in the presence of moisture. This acid comes down from the atmosphere in the form of sulphuric acid rain.		human, produces leaf injuries (called necrotic bloating) to board leaved plants & gases. It also causes deterioration of fabric (cotton, rayon) paper & leather.
Oxides of Nitrogen (NO_2)	NO_2 is produced in small amounts by microbiological processes in soil. However significant amount of NO & NO_2 are emitted in to the atmosphere by natural activity.	Many natural processes acts as sink for oxides of nitrogen. These oxides are inherently unstable & decompose to N_2 & O_2 after some time. Therefore, the concentration of nitrogen oxides in the atmosphere tends to remains low.	(i) NO is biologically less active & less toxic than NO_2. Like CO it binds hemoglobin & decreases oxygen transport efficiency of blood. (ii) Inhaling of nitrogen oxides by human results in pulmonary odema & hemorrhage. (iii) The oxides of nitrogen cause damage to plants. Exposure of plants to NO_2 causes leaf spotting & break down of plant tissues. (iv) The sunlight reacts with NO_2 to produce highly active oxygen atoms.

Particulate matter:

- **Soot**
- **Metal particles**
- **Metal oxides** .
- **Lead salts**
- **Fly ash**
- **Asbestos dust**
- **Solid Hydrocarbons**
- **Dust Particulates**
- **Acid mist**.

Harmful effects of particulates

- **Effect on human beings:** Affect the human respiratory system & cause several respiratory illnesses. The particles with small size are more harmful in this context. The particulates in fact, become the carriers of the toxic substances from the atmosphere to the human & cause big health hazards.
- **Effect on visibility:** Particulates in the atmosphere cause scattering & absorption of sunlight & reduce the visibility.
- **Effect on Materials :** The adverse effect of particulates on materials include corrosion of metals (when the atmosphere is humid), erosion & soiling of building, sculptures & painted surfaces & soiling of clothes & draperies.

Stratospherical Pollution: (ozone layer & its depletion):

Role of Ozone Layer: protecting earth from the UV radiation coming from the sun.

Depletion of Ozone Layer : The equilibrium between formation & destruction of ozone has been upset by influx of several substances into the atmosphere which react with ozone to destroy it.

Effect of Depletion of Ozone layer: The influx of UV radiation reaching the surface of earth would increase which would increase in risk to skin cancer due to exposure to UV radiation, UV radiations also tend to damage the immune system.

Acid Rain:

SO_2, nitrogen oxides & acidic soots. Sulphurdioxide & nitrogen dioxide interact with water vapours in presence of sunlight to form sulphuric acid & nitric acid units.

Green House Effect & Global Warming:

The green house gases (CO2, CH4, O3, CFC'S) in the atmosphere form a thick cover around the earth. About 75% of the solar energy reaching the earth is absorbed by the earth surface. The IR radiations coming from sun are not absorbed by atmospheric gases but Earth absorbs these IR radiations of short wavelength. As a result of this the temperature of earth stands rising. Eventually, earth starts emitting infrared radiations of longer wavelengths. The partially radiated infrared radiations from the earth are absorbed by the greenhouse gases. This results in excessive heating of Earth's atmosphere. Thus the greenhouse gases add to the heating of atmosphere. This causes global warming. The atmosphere traps the sun's heat near earth's surface and keeps it warm. The reemission of the earth's energy absorbed by CO2 and other greenhouse gases present near the earths surface and its radiation back to the earth is called green house effect.

Advantages of green house effect :

- It is necessary for evaporation of water, formation of clouds, rainfall etc.
- The warm atmosphere helps in rapid growth of plants, trees etc.

Harmful effects of green house effect :

- High temperature of atmosphere may melt polar ice caps which are likely to raise the level of sea thereby sinking most of the coastal areas and causing large scale destruction.
- The high temperature may reduce crop product.

- The high temperature will reduce work efficiency of human being.
- Tropical rains and hurricane will become more frequent and also stronger causing more devastation.
- The change in ocean temperature will adversely affect the warm life.

Water Pollution:

Pollutant	Source
Microorganism	Domestic sewage
Organic wastes	Domestic sewage, animal waste, decaying animals, plants and discharge from food processing factories
Plant nutrients	Chemical fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemical used for killing insects, fungi & weeds
Radioactive substances	Mining of Uranium containing minerals
Heat	Water used by industrial plants which is discharged as hot water

Biochemical Oxygen Demand (BOD) : The measure of the total contamination caused by compounds which can be oxidised in the presence of microorganisms. The BOD is taken as a realistic measure of water quality – clean water would have a BOD value of less than 5 ppm whereas highly polluted river water could have a BOD value of 17 ppm or more.

Land Pollution :

Caused by pesticides and other chemicals which are added to the soil to grow better crops.

Insecticides are the pesticides used to Control of insects by insecticides helps to curb disease and protect crops. Organo chlorines are a group of compounds which have been developed and used as insecticides.Examples: DDT (dichlorodiphenyl trichloro ethane) organo chlorines are stable in the environment, toxic to insects in small amounts, but much less go to humans, and because they are organic compounds not very soluble in water. The advantage of these insecticides is that, bring persistent

Fungicides are the pesticides used to check the growth of fungi. Fungi, are plants without chlorophyll, they cannot use solar energy for preparing their food. They live as saprophytes on decaying organic matter or as parasites at the expense of living organisms. Hence they are considered to be a threat to human interests