Rapid Revision
&
Formula Bank

CHEMISTRY

Aakash
Medical | IIT-JEE | Foundations
(Divisions of Aakash Educational Services Limited)

Contents

Chapter 1

Some Basic Concepts of Chemistry

MOLE CONCEPT

1 mole is represented in the form of atoms, molecules and ions as :

For atoms → 1 gm atom

For molecules → 1 gm molecule

For ions → 1 gm ion

Moles can be calculated in following manner :

(a) Number of moles of molecules = $\dfrac{\text{Weight of substance (in g)}}{\text{Molecular weight}}$

(b) Number of moles of atoms = $\dfrac{\text{Weight of substance (in g)}}{\text{Atomic weight}}$

(c) Number of moles of gases = $\dfrac{\text{Volume of gas at NTP (in litres)}}{22.4}$

(1 mole of any gas occupies a volume of 22.4 litres at N.T.P., N.T.P. Corresponds to 0ºC and 1 atm pressure)

(d) Number of moles of atoms/molecules/ions = $\dfrac{\text{Number of atoms / molecules / ions}}{\text{Avogadro constant}}$

(Avogadro constant is equal to 6.022×10^{23}).

LIMITING REAGENT

In the given reaction if number of quantities (either in gm/mole/molecules) are present with exact co-efficients, chemical reaction goes to completion without any reactant left unused.

However if exact proportion is not present then the one which gets totally consumed is known as **limiting reagent** (Limiting reagent decides the product quantity for given information).

e.g., $2H_2 + O_2 \rightarrow 2H_2O$

In above *e.g.* 2 moles of H_2 reacts exactly with 1 mole of O_2 to give 2 moles of H_2O. If given moles of H_2 are 4 moles and that of O_2 are 0.5, then 0.5 moles O_2 will act as limiting reagent as it is in minimum amount and product formation is given w.r.t. O_2 *i.e.*, 1 mole of H_2O.

EQUIVALENT WEIGHT

Equivalent weight of substance is defined as number of parts by weight of given substance which combines or displaces 1 part by weight of hydrogen (11.2 L of H_2 at STP), 8 parts by weight of oxygen (5.6 L of O_2 at STP), 35.5 parts by weight of chlorine (11.2 L of Cl_2 at STP).

1. Equivalent weight of element = $\dfrac{\text{Atomic weight}}{\text{Valency}}$
2. Equivalent weight of acids = $\dfrac{\text{Molecular weight of acid}}{\text{Basicity}}$
3. Equivalent weight of bases = $\dfrac{\text{Molecular weight of base}}{\text{Acidity}}$
4. Equivalent weight of salts = $\dfrac{\text{Molecular weight of salt}}{\text{Total} + \text{ve or} - \text{ve charge}}$
5. Equivalent weight of reducing agent = $\dfrac{\text{Molecular weight}}{\text{Number of } e^- \text{ lost by one molecule}}$
6. Equivalent weight of oxidising agent = $\dfrac{\text{Molecular weight}}{\text{Number of } e^- \text{ gained by one molecule}}$

n-FACTOR OR VALENCE FACTOR

n-factor is very important for both redox and non redox reactions through which we predict the following two informations:

(a) It predicts the molar ratio of the species taking part in reactions i.e. reactants. The reciprocal of n-factor's ratio of the reactants is the molar ratio of the reactants.

For example : If X (having n-factor = a) reacts with Y (having n-factor = b) then its n-factor's ratio is a : b, so molar ratio of X to Y is b : a.

It can be represented as $\underset{(nf=a)}{bX} + \underset{(nf=b)}{aY} \rightarrow \text{Products}$

(b) Equivalent weight = $\dfrac{\text{Molecular weight}}{n - \text{factor}}$ or $\dfrac{\text{Atomic weight}}{n - \text{factor}}$

LAW OF EQUIVALENCE

According to law of equivalence, for each and every reactant and product,

Equivalents of each reactant reacted = Equivalents of each product formed.

For example :

Suppose, the reaction is taking place as under

$A + B \rightarrow C + D$.

Then according to law of equivalence,

Equivalents of A reacted = Equivalents of B reacted

= Equivalents of C produced

= Equivalents of D produced

$$\text{Equivalents of any substance} = \frac{\text{Weight of substance (in g)}}{\text{Equivalent weight}}$$

$$= \text{Normality (N)} \times \text{Volume (V) (In litre)}$$

Normality (N) = n-factor × Molarity (M)

Normality and molarity are temperature dependent. Since on changing the temperature, the volume of solution changes, so normality and molarity change.

EMPIRICAL AND MOLECULAR FORMULA

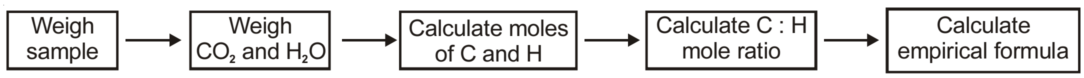
(a) **Empirical Formula of a compound** is the simplest whole number ratio of the atoms of elements constituting its one molecule. The sum of atomic masses of the atoms representing empirical formula is called **empirical** formula mass.

(b) **Molecular Formula** of a compound shows the actual number of the atoms of the elements present in its one molecule. The sum of atomic masses of the atoms representing molecule is called **molecular mass**.

(c) **Relationship between Empirical Formula and Molecular Formula**

Molecular formula = n × empirical formula where n is a simple whole number having values of 1, 2, 3... etc.

Also, n = Molecular formula mass/Empirical formula mass.



% of free SO_3 in Oleum

Strength of oleum is expressed in percentage *e.g.*, oleum sample is 109%, It means 100 g of this oleum reacts with H_2O to form 109 g of H_2SO_4

$$\underbrace{H_2SO_4 + SO_3}_{100\text{ g}} + H_2O \rightarrow \underbrace{H_2SO_4}_{109\text{ g}}$$

Actually SO_3 react with H_2O to form H_2SO_4. Here 9 g H_2O or $\frac{1}{2}$ mole H_2O react with SO_3.

So, moles of SO_3 in sample = $\frac{1}{2}$ mole

$$SO_3 + H_2O \rightarrow H_2SO_4$$

So, wt. of SO_3 = $\frac{1}{2}$ 80 (molecular weight of SO_3) = 40 g

% free SO_3 = 40%

Note : *Moles of H_2O =* $\left(\frac{\text{Percentage labelling - 100}}{18}\right)$

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Chapter 2

States of Matter (Gases, Liquids and Solids)

GASEOUS STATE

MEASURABLE PROPERTIES OF GASES

1. **Volume :** Gases have tendency to occupy all available space.

   So, volume of gas is equal to volume of container.

2. **Temperature :** It is degree of hotness and coldness.

   Conversion of °C to K

   K = °C + 273.15

3. **Pressure :** It is force exerted by gas per unit area

   $$P = \frac{F}{A} = N/m^2$$

> ***Note :** 1 atm = 760 mm of Hg = 760 torr = 1.01 $\quad 10^5$ Pa*
>
> *1 bar = 10^5 Pa*

BOYLE'S LAW

$$P \quad \frac{1}{V} \text{ at constant n and T.}$$

CHARLES' LAW

V $\quad$ T at constant n and P.

$$V_t = V_0\left(1 + \frac{t}{273}\right)$$

AVOGADRO'S LAW

V $\quad$ n (P and T constant); 1 mole of every gas at STP occupies volume = 22.4 lit.

Ideal Gas Equation

On combining the Boyle's law, Charles' law and Avogadro's law we get an equation known as ideal gas equation which correlates P, V, T, of a gas.

$\boxed{PV = nRT}$ ideal gas equation where R is a constant known as universal gas constant or molar gas constant.

Numerical value of R

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

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

$= 1.987 \quad 2$ cal K^{-1} mol^{-1}

Other form of ideal gas equation.

$$\Rightarrow \boxed{PV = \frac{W}{M}RT}$$

$$\Rightarrow \boxed{P = \frac{dRT}{M}}$$; (where M is the molecular weight)

DALTON'S LAW OF PARTIAL PRESSURE

The total pressure exerted by a mixture of two or more chemically **non-reacting gases** in a definite volume is equal to the sum of individual pressures or partial pressures where p_1, p_2 etc. are partial pressures of individual gases which each gas would exert if it occupies the same volume at a constant temperature

$P_{Total} = p_1 + p_2 + p_3 \ldots .$, where p_1, p_2 etc. are partial pressures of individual gases

$$P_{Total} = (n_1 + n_2 + \ldots\ldots.)\frac{RT}{V}$$

Partial pressure of a gas = Mole fraction of that gas × Total pressure

$$= \frac{\text{no. of moles of gas}}{\text{Total no. of moles of all gases}} \times \text{Total pressure}$$

By Dalton's law of partial pressure.

> ***Note :*** *P (moist) = P (dry gas) + P (H_2O vapours)*
>
> *P (dry gas) = P (moist) – aq. tension.*

GRAHAM'S LAW OF DIFFUSION

(a) Diffusion is the ability of gas to spread and occupy the whole volume.

(b) Under identical conditions of temperature and pressure, the rate of effusion/diffusion of a gas is inversely proportional to square root of its density.

(c) Rate of diffusion/effusion for two gases are related as

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \frac{n_1/t_1}{n_2/t_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

Effect of Pressure on Rate of Diffusion :

$$\boxed{\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}}$$ where, V = volume , t = time, M = molar mass, d = density, n = number of moles, P = pressure

KINETIC THEORY OF GASES

The postulates

(1) The gaseous molecules are considered to be point masses.

(2) The volume of a molecule is negligible as compared to total volume of the gas.

(3) There is no force of interaction among the gas molecules.

(4) The collisions are perfectly elastic i.e. there is no loss or gain of energy during the molecular collisions.

(5) The average kinetic energy of molecules is directly proportional to the absolute temperature of the gas.

(6) The effect of gravity on molecular motion is negligible.

Based on Kinetic-Molecular Theory

$$PV = \frac{1}{3}mN\overline{u^2}$$

m = Mass of one molecule

N = Number of molecules in the container

$\overline{u^2}$ = Mean square velocity

KE of n moles = $\frac{3}{2}nRT$, for n = 1 $\boxed{\overline{KE} = \frac{3}{2}RT}$

Average KE per molecule = $\frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}kT$, k = Boltzmann's constant

DISTRIBUTION OF MOLECULAR SPEEDS

(i) Root mean square velocity (u_{rms}) = $\sqrt{\frac{3RT}{M}}$

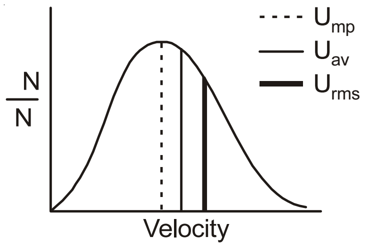
(ii) Average velocity(u_{av}) = $\sqrt{\frac{8RT}{\pi M}}$

(iii) Most probable velocity (u_{mp}) = $\sqrt{\frac{2RT}{M}}$

Note : $u_{rms} : u_{av} : u_{mp} :: 1.732 : 1.596 : 1.414 :: 1.224 : 1.128 : 1$

Hence, $u_{rms} > u_{av} > u_{mp}$

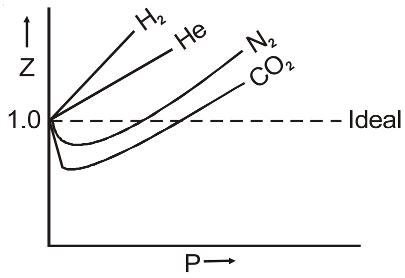
Maxwell Boltzmann's curve



DEVIATION FROM IDEALITY AND van der Waal's EQUATION

A plot of PV- P at constant temperature for a number of gases shows deviations from ideal behaviour. Therefore PV **=** nRT cannot be applied to these gases. Thus another equation must be sought in order to correlate P,V, T for these gases; which is van der waal's equation.

$$\left(P+\frac{n^2a}{V^2}\right)V \quad nb = nRT$$



Causes of Deviation

There are two objectionable postulates in kinetic theory of gases.

(1) The volume of a molecule is negligible as compared to total volume of the gas. Actually, gas molecules do posses some volume which account for the deviation. Hence total volume of gas is not equal to volume of the vessel.

(2) There is no intermolecular force of attraction between gaseous molecules.

(There exists force of attraction between gaseous molecules otherwise liquefaction of gases would be impossible).

By correcting these two postulates, we get an equation which can be applied to the gases which deviate from ideal behaviour. The deviation of a gas from ideal behaviour can also be expressed in terms of compressiblity factor (Z).

$$Z = \frac{PV}{RT} \text{ [for 1 mole]}$$

for ideal gas Z **=** 1

for real gas Z **>** 1 or Z **<** 1

LIQUID STATE

A liquid is composed of molecules that are constantly moving about at random, each undergoing billions of collisions per second. However strong attractive forces of the dipole-dipole, H-bonds, prevent them from moving as freely and as far apart as in a gas.

(a) **Vapour pressure :** It is the pressure exerted by vapours on surface of liquid at equilibrium. Vapour pressure does not depend on surface area and volume but it depend on temperature and nature of liquid. Vapour pressure increases with rise in temperature.

(b) **Viscosity :** Liquids flows as if they were divided into layers flowing over one another. Resistance offered to this flow is due to friction between two liquid layers and is called viscosity. Reciprocal of viscosity is called fluidity. Viscosity of a liquid decreases with rise of temperature.

(c) **Coefficient of viscosity :** The force in newtons per square metre required to maintain a difference of velocity of one metre per second between two parallel layers of the liquid at a distance of one metre from each other. It is expressed in kg m^{-1} s^{-1}. Liquids having stronger attractive forces are more viscous.

(d) **Surface tension :** The force that acts at right angles to an imaginary line of unit length at the surface of the liquid at rest. It is expressed in J m^{-2} or N m^{-1}. Surface tension generally decreases with the rise of temperature. Liquids exhibit capillary action and make spherical drops. This can be explained on the basis of surface tension.

IMPORTANT POINTS

(1) Critical temperature (T_c) :

It is the temperature above which a real gas cannot be liquefied whatever applied pressure may be

$$\boxed{T_c = \frac{8a}{27Rb}}$$

(2) Critical pressure (P_c) :

It is the minimum pressure required to liquefy the gas at critical temperature

$$\boxed{P_C = \frac{a}{27b^2}}$$

(3) Critical volume (V_c) :

The volume occupied by 1 mole of the gas at critical temperature and critical pressure is known as critical volume.

$$\boxed{V_C = 3b}$$

$$\boxed{V_c = 3\quad 4V_m = 12V_m}$$ (Since $b = 4V_m$)

V_m = Volume of one mole of gaseous molecule.

(4) Critical coefficient of a gas :

It is ratio of $\frac{RT_c}{P_cV_c}$ which is equal to 2.66 and remains constant for all the gases.

(5) Boyle's temperature (T_B) :

The temperature at which a real gas obeys ideal gas equation at very low pressure is known as Boyle’s temperature.

$$\boxed{T_B = \frac{a}{Rb}}$$

Boyle's temperature of a gas is always higher than its critical temperature (T_c)

(6) Inversion temperature (T_i)

If a compressed gas is allowed to pass through a fine hole, it may show cooling or heating or no change in temperature depending upon the temperature of the gas. For each gas, there exists a characteristic temperature known as inversion temperature (T_i)

If $T > T_i$ heating is produced

If $T < T_i$ cooling is produced

If $T = T_i$ neither heating nor cooling

$$\boxed{T_i = \frac{2a}{Rb} = 2T_B}$$

(7) Excluded volume (b) :

The van der Waal constant ‘b’ is known as excluded volume. It is 4 times greater than the actual volume of the gas molecule.

$b = 4N_AV$ (where V is the volume of one molecule)

SOLID STATE

ELEMENTS OF SYMMETRY

The total no. of planes, axes and centre of symmetries possessed by a crystal is termed as its elements of symmetry. A simple cubical crystal possesses a total of 23 elements of symmetry.

In a Cube

Planes of symmetry = 3 + 6 = 9

Axis of symmetry = 3 + 4 + 6 = 13

Centre of symmetry = 1

Total number of symmetry elements = 23

TYPES OF CUBIC UNIT CELL

Type of unit cell	Number of atoms			Total number of atoms per unit cubic cell	Radius of ion/atom a = edge length
	At corners	Within body	On faces		
1. Simple cube	$\frac{1}{8}\ 8 = 1$	0	0	1	$r = \frac{a}{2}$
2. Body centred cube (BCC)	$\frac{1}{8}\ 8 = 1$	1	0	2	$r = \frac{\sqrt{3}\,a}{4}$
3. Face centred cube (FCC)	$\frac{1}{8}\ 8 = 1$	0	$\frac{1}{2}\ 6 = 3$	4	$r = \frac{\sqrt{2}\,a}{4}$

Radius ratio $\left(\frac{r^+}{r^-}\right)$

r_+/r_-	Geometry	Co-ordination number	Example
$0.155\ \frac{r_+}{r_-} < 0.225$	Triangular planar	3	B_2O_3
$0.225\ \frac{r_+}{r_-} < 0.414$	Tetrahedral	4	ZnS
$0.414\ \frac{r_+}{r_-} < 0.732$	Octahedral	6	NaCl
$0.732\ \frac{r_+}{r_-} < 1$	Cubic	8	CsCl

STRUCTURE OF SIMPLE IONIC COMPOUNDS

AB type : Consisting positively and negatively charged ions in the ratio 1 : 1

These compounds can have any one of the following structures

(a) Rock salt (NaCl) type structure

Characteristics

(i) It has fcc or ccp arrangement in which Cl^- ions occupy the corners and face centres of a cube while Na^+ occupy body centres and edge centres (Octahedral voids).

(ii) This structure has 6 : 6 coordination number.

(iii) A unit cell of NaCl consist of 4Na$^+$ ion and 4Cl$^-$ ions.

i.e., Number of Cl$^-$ ions $\left(\frac{1}{8}\quad 8\right)+\left(\frac{1}{2}\quad 6\right)=4$

Number of Na$^+$ ions $\left(\frac{1}{4}\quad 12\right)+1=4$

Examples : Alkali metal halides (except Cs), Halides of Ag (except AgI).

(b) Caesium chloride (CsCl) type structure

Characteristics

(i) It has bcc arrangement

(ii) This structure has 8 : 8 coordination number

(iii) The unit cell of CsCl consists of one Cs$^+$ ion at body centre and eight Cl$^-$ ion at each corner *i.e.* one CsCl formula unit per unit cell.

Example : CsBr, CsI, CsCN, TlCl, TlBr, TlI, TICN

(c) Zinc blende (ZnS) type structure

Characteristics

(i) It has ccp arrangement in which S^{2-} ions are present at the corners as well as at the centre of each face of the cube.

(ii) Zn^{+2} ion are present at alternate tetrahedral void [50% of tetrahedral void.]

(iii) This structure has 4 : 4 coordination number.

Example : CuCl, CuBr, CuI, AgI, and BeS

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Chapter 3

Structure of Atom

BOHR'S ATOMIC MODEL

The model is based on the quantum theory of radiation and the classical concept of physics.

Postulate

(a) The path of electron is circular. The force of attraction between nucleus and electron is equal to centrifugal force of the moving electron.

(b) Electron can revolve only in those orbits whose angular momentum is an integral multiple of $\frac{h}{2\pi}$. *i.e.*, $mvr = \frac{nh}{2\pi}$. (m = mass of electron, v = velocity of electron, r = radius of orbit)

(c) Electron remains in stationary orbit where it does not lose energy.

(d) Each stationary orbit is with definite amount of energy (E) and $E_1 < E_2 < E_3$ .... Similarly $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$.

The Energy of Electron

Total energy (E) = K.E. + P.E.

$$E_n = \frac{2\pi^2 Z^2 me^4}{n^2h^2} \cdot K^2$$

where, n = 1, 2, 3 ....

E = Energy of electron in nth orbit

Z = Nuclear charge

e = Charge of electron

m = Mass of electron

h = Planck's constant

i.e., $E_n = E_1 \frac{Z^2}{n^2}$ for H-like atom

H like atoms means atom which consists of one electron.

i.e., $$E = \frac{21.79 \quad 10^{19} Z^2}{n^2} \text{ J/atom}$$

$$= \frac{13.6}{n^2} Z^2 \text{ eV per atom}$$

$$= \frac{313.6 \quad Z^2}{n^2} \text{ kcal/mol}$$

$$= \frac{1312 \quad Z^2}{n^2} \text{ kJ/mol}$$

Potential energy = 2 × E

Kinetic energy = – E

Total energy = E

***Note :** If an atom consists more than one electron, then we take shielding effect into account.*

Radii of Orbits

$$r = 0.529 \frac{n^2}{Z} \text{ Å}$$

For H-like atoms. Thus $r_n = r_1 \times n^2$

Velocity of Electron

$$v = 2.188 \times 10^8 \times \frac{Z}{n} \text{ cm/s}$$

Number of revolution per second (Frequency)

$$N = \frac{V}{2\pi r} = 6.6 \quad 10^{15} \frac{Z^2}{n^3}$$

Rydberg Equation

The wavelength ( ), wave number ($\bar{}$) for the electromagnetic radiation can be calculated by Rydberg equation.

$$\bar{} = \frac{1}{} = R_H \quad Z^2 \left[\frac{1}{n_1^2} \quad \frac{1}{n_2^2}\right]$$

Z = Atomic number

R_H = Rydberg constant = 109677 cm^{-1}

n_2 = Higher orbit

n_1 = Lower orbit

Total number of spectral lines

(i) $\frac{n(n\quad 1)}{2}$ → when electron jumps from nth level to ground level.

(ii) $\frac{(n_2\quad n_1)(n_2\quad n_1+1)}{2}$ → when electron returns from n_2 to n_1.

(iii) $n_2 - n_1$ → when electron returns from n_2 to n_1.

(iv) $n_2 - n_1$ → number of spectral line in a particular shell.

> ***Note :*** *Remember in this case n_1, n_2 are energy level or orbit number. If we have given n^{th} excited state then formula will be different.*

$\frac{n(n\quad 1)}{2}$ formula is applicable, if hydrogen sample contains several number of H atoms.

DUAL NATURE OF MATTER : de-Broglie Equation

(a) Louis de Broglie proposed that the material particles are also associated with wave nature, just as radiations.

(b) The wavelength of the wave associated with a particle mass 'm' moving with velocity 'v' as $\boxed{\ =\frac{h}{mv}}$.

where   = de-Broglie wavelength

h = Planck's constant = 6.62×10^{-34} J-s.

> ***Note :*** *The waves associated with material particles or objects in motion are called **matter waves** or **de-Broglie waves.***

(c) Number of revolutions per second by an electron in a shell may be given as = $\frac{\text{Velocity}}{2\pi r} = \frac{v}{2\pi r}$

(d) de-Broglie's equation and K.E.

Let K.E. of the particle of mass 'm' is *E*

$$E = \frac{1}{2}mv^2$$

$$2Em = m^2v^2$$

$$\sqrt{2Em} = mv = P$$

$$\ = \frac{h}{P} = \frac{h}{\sqrt{2Em}}$$

Suppose an electron makes n wave in one complete circle, then $2\pi r = n$

QUANTUM NUMBERS

The set of four integers required to define the state of electron in an atom are called **quantum numbers.** The quantum numbers are

(1) Principal quantum number (*n*)

(2) Azimuthal quantum number (*l*)

(3) Magnetic quantum number (*m*)

(4) Spin quantum number (*s*)

(1) Principal quantum number, (*n*), relates to the amplitude (*i.e.*, size) of an electron wave and also the total energy of the electron. It has integral values of 1, 2, 3, 4 ... etc., also denoted as K, L, M, N .... etc.

(2) Azimuthal quantum number, (*l*), tells us about the subenergy shell of electron. For each main energy shell there can be '*n*' number of subenergy shells. These subenergy shells are designated by different values of *l*. For each value of *n*, *l* can have values from 0, 1, 2, 3 ... $n - 1$.

(3) Magnetic quantum number, (*m*), explains the behaviour of an electron in the external magnetic field or in other words it tells us about orbitals of the electrons. The values of m gives the number of orbitals associated with a particular sub shell in shell. For each value of l, m can have values from $-l$ to $+l$ including zero.

e.g., when $l = 1$, m = –1, 0, +1; $l = 2$, m = –2, –1, 0, +1, +2

(4) Spin quantum number, (*s*), gives an idea about the electron spinning on its axis. Each spinning electron can have two values of $+\frac{1}{2}$ or $-\frac{1}{2}$.

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Chapter 4

Chemical Bonding and Molecular Structure

TYPES OF BONDS

1. Ionic Bond
2. Covalent Bond
3. Co-ordinate Bond
4. Hydrogen Bond

Ionic Bond

An ionic bond is formed by complete transfer of one or more electrons from the valency shell of one atom to the valency shell of another atom. In this way both the atoms acquire the stable electronic configurations of the noble gases. The atom losing the electrons becomes a positive ion and the atom which gains electron becomes negative ion.

FAJAN'S RULE

Covalent character in ionic bonds

When oppositely charged ions approach each other, there is not only the attraction between the positively charged cation and the negatively charged anion but also simultaneous repulsion between their nuclei. Thus there is distortion, or deformation or polarization of anions. The electronic charge of anion does not remain spherical but gets distorted.

No polarization   Polarization of anion

(1) Polarizing power of cation increases with
  (i) High charge on cation
  (ii) Small size of cation
  (iii) Pseudo (18) electronic configuration in outermost shell of cation

(2) Tendency of an anion to get polarized increases with

   (i) High charge on anion

   (ii) Large size of anion

This polarization of ion results in a electric charge concentration between the two nuclei resulting in a covalent bond with a large degree of charge separation.

The extent of polarization depends upon

(1) Polarizing power of cations.

(2) Tendency of an anion to get polarized (polarizability)

FORMAL CHARGE

$$\text{FC} = \begin{bmatrix}\text{Total number of valence}\\ e^- \text{ in free atom (v)}\end{bmatrix} - \begin{bmatrix}\text{Total number of}\\ \text{non-bonding } e^- \text{ (u)}\end{bmatrix} \frac{1}{2}\begin{bmatrix}\text{Total number of}\\ \text{bonding } e^- \text{ (s)}\end{bmatrix}$$

DIPOLE MOMENT (μ)

Dipole moment is product of the magnitude of charge developed on any one of the two atoms and the distance between the atoms. ($\mu = q \times d$), where q = charge developed and d = distance between two atoms. The unit of dipole moment is debye (D). 1 debye = 1×10^{-18} esu cm = 3.34×10^{-30} coulomb metre (Cm)

$1e^-$ charge = 4.8×10^{-10} esu = 1.6×10^{-19} coulomb

(a) Dipole moment is a vector quantity.

(b) Molecule with more than one bond will have more than one bond dipole moments. The resultant of bond dipole moments of the molecule containing two bonds is given as

$$\mu_{\text{res.}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos}$$

(c) Dipole moment predicts whether a molecule is polar or non-polar.

(d) Dipole moment is zero for symmetrical and planar species.

(e) Dipole moment helps to determine percentage ionic character and can be calculated as

$$\%\text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment assuming 100\% ionic bond}} \quad 100$$

% ionic character = $16|X_A - X_B| + 3.5\,[X_A - X_B]^2$, where X_A and X_B are the electronegativity of A and B element.

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

(a) A number of physical and chemical properties of molecules are affected by the geometry and shape of molecules.

(b) VSEPR theory gives the information of shape of molecules.

(c) The arrangement of bond pair electron and lone pair electron is done to minimize the repulsion *i.e.*,

Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.

(d) These repulsion - effects result in deviations from idealized shape and alterations in bond angles in molecules.

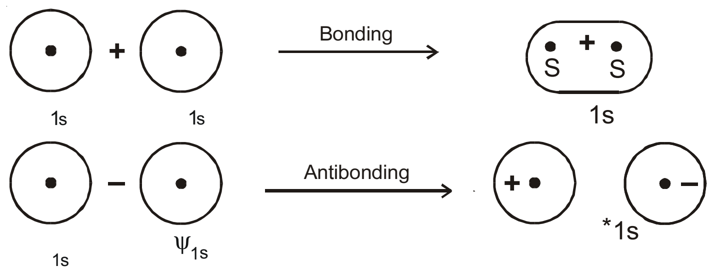
HYBRIDIZATION & SHAPES OF MOLECULES

S.No.	Type of hybridisation	No. of hybridised orbitals	Bond pair	Lone Pair	Geometry	Shape	Examples
1.	*sp*	2	2	–	Linear	Linear	CO_2, $BeCl_2$
2.	*sp^2*	3	3	–	Trigonal Planar	Trigonal Planar	BF_3
			2	1	Trigonal Planar	V-shape	SO_2
3.	*sp^3*	4	4	–	Tetrahedral	Tetrahedral	CH_4
			3	1	Tetrahedral	Pyramidal	NH_3
			2	2	Tetrahedral	V-shape	H_2O
4.	*sp^3d*	5	5	–	Trigonal bipyramidal	Trigonal bipyramidal	PCl_5
			4	1	Trigonal bipyramidal	See-saw	SF_4
			3	2	Trigonal bipyramidal	T-shape	ClF_3
			2	3	Trigonal bipyramidal	Linear	ICl_2^-
5.	*sp^3d^2*	6	6	–	Square bipyramidal	Square (octahedral) bipyramidal	SF_6
			5	1	Square bipyramidal	Square pyramidal	IF_5
			4	2	Square bipyramidal	Square Planar	XeF_4
6.	*sp^3d^3*	7	7	–	Pentagonal bipyramidal	Pentagonal bipyramidal	IF_7
			6	1	Pentagonal bipyramidal	Distorted octahedral	XeF_6

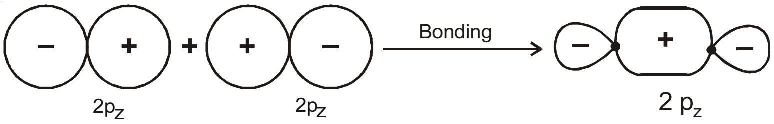
MOLECULAR ORBITAL THEORY

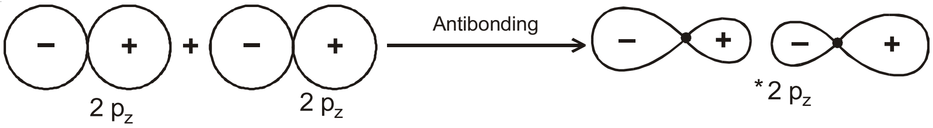
Types of Covalent Bond

***s – s overlap* (*Sigma Overlap*)**

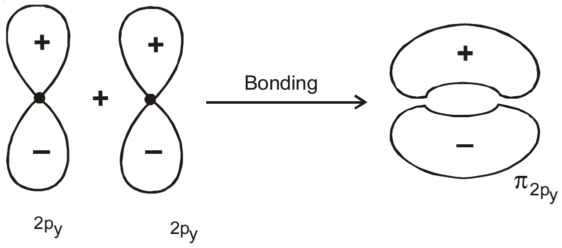


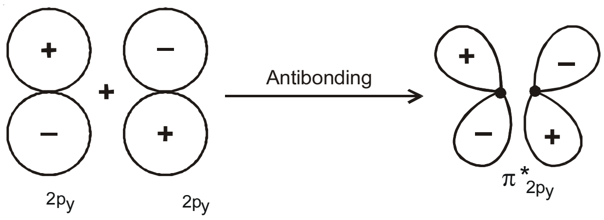
p – p overlap (Sigma Overlap)





p – p Overlap Lateral (π - overlap)





(a) Linear combination of atomic orbitals (LCAO) method is used for the formation of molecular orbitals.

(b) For two atomic orbitals A and B, whose wave function is given as $_A$ and $_B$. Then molecular orbitals (MO) are given as $_{MO} = {}_A \pm {}_B$.

(c) The molecular orbital formed by the addition of atomic orbitals is called **bonding molecular orbital**. And molecular orbital * formed by the subtraction of atomic orbitals is called **antibonding molecular orbital**.

(d) Molecular orbital configuration for diatomic molecules upto 14 electrons.

$$1s \quad *1s \quad 2s \quad *2s \ \{\pi 2p_x = \pi 2p_y\} \quad 2p_z \ \{\pi^* 2p_x = \pi^* 2p_y\} \quad *2p_z$$

(Increasing order of energy)

(e) Molecular orbital configuration for diatomic molecules with more than 14 electrons.

$$1s \quad *2s \quad 2s \quad *2s \quad 2p_z \ \{\pi 2p_x = \pi 2p_y\} \ \{\pi^* 2p_x = \pi^* 2p_y\} \quad *2p_z$$

(Increasing order of energy)

(f) Molecular orbitals are arranged with increasing order of energy level.

(g) $\pi 2p_x$ and $\pi 2p_y$ similarly $\pi^* 2p_x$ and $\pi^* 2p_y$ have same energy and follow Hund's rule.

(h) Bond order = $\frac{1}{2}$ [Bonding electrons – Antibonding electrons].

(i) Bond order Bond strength $\frac{1}{\text{Bond length}}$.

e.g., N_2 = 14 electrons

Molecular orbital configuration

$$1s^2 \quad *1s^2 \quad 2s^2. \quad *2s^2 \quad \pi 2p_x^2, \pi 2p_y^2 \quad 2p_z^2 \quad \pi * 2p_x, \pi * 2p_y \quad *2p_z$$

$$\text{B.O} = \frac{1}{2}[10 - 4] = 3$$

As no unpaired electron hence N_2 is diamagnetic.

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Chapter 5

Chemical Thermodynamics

EXTENSIVE AND INTENSIVE VARIABLES

(a) Extensive property of a system are those whose magnitude depends on the amount of matter present in the system. These are additive in nature. For example, volume, internal energy, enthalpy, entropy, mass etc. Sum, subtraction and multiplication of two extensive property is extensive.

(b) The property whose magnitude does not depend upon quantity of matter present in a system is known as intensive property of the system. It is not an additive property. Examples are : temperature, pressure, density etc. Sum, subtraction, multiplication division of two intensive properties is intensive.

INTERNAL ENERGY (U)

It is the energy associated with a system by virtue of its molecular constitution and motion of its molecule. Such motion may be translational, rotational, vibrational etc.

Internal energy is a state function and an extensive property.

Heat supplied to system is denoted by q.

(1) When $q > 0$, heat has been supplied to system.

(2) When $q < 0$, system has rejected heat.

(3) When $q = 0$, no heat exchange ; process is adiabatic.

Work done on system (W)

(1) When $W > 0$ work is done on system.

(2) When $W < 0$ work is done by system.

Processes :

When a change is observed in the properties of system, a process is said to be taking place. This may be a chemical reaction or a physical process, like crystallization. Processes are of two types.

(1) Reversible : No change in entropy of universe.

(2) Irreversible : Entropy of universe increases.

q and W for some simple processes

Table for ideal gases (only)

Reversible Process	**q**	**W**
Isothermal expansion	$nRT\ln\frac{V_f}{V_i}$ V_i = Initial volume V_f = Final volume	$nRT\ln\frac{V_f}{V_i}$
Isobaric expansion	$nC_P\ \ T$	$-P\ \ V$
Adiabatic expansion	0	$\frac{nR}{\ -1}[T_2-T_1]$
Isochoric heating	$nC_V\ \ T$	0

HESS'S LAW OF CONSTANT HEAT SUMMATION

The enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps.

If a reaction is the sum of two or more constituent reactions, then H for the overall process must be sum of the H of the constituent reactions.

$$\begin{tikzcd} A \arrow[r, "H"] \arrow[d, "H_1"'] & D \\ B \arrow[r, "H_2"'] & C \arrow[u, "H_3"'] \end{tikzcd}$$

For A → D, $H = H_1 + H_2 + H_3$.

ENTROPY AND ENTROPY CHANGE

Entropy is a measure of randomness. Higher the disorder, higher is the entropy.

Entropy for solid < liquid < gas

$$\boxed{S = \frac{q_{rev}}{T}}$$

where q_{rev} = Heat absorbed when the process is carried out reversibly and isothermally.

Entropy change is given in unit of J/K or JK^{-1}.

Example : For reversible isothermal expansion of an ideal gas $S = nR\ln\frac{V_f}{V_i}$.

GIBB'S ENERGY AND SPONTANEITY OF REACTION

Gibbs defined a function by the relation.

$G = H - TS$

Use :

(i) At a given pressure and temperature if for an anticipated change dG for system is negative, process is spontaneous and if positive, process is spontaneous in reverse direction. Also if dG = 0, system is in equilibrium with respect to the given reaction or process.

(ii) –dG = maximum work done by system on non-expansion surrounding *e.g.*, cell doing electrical work on circuit.

Spontaneity of the reaction

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Reaction Spontaneity
–	+	–	Spontaneous at all temperature
–	–	– or +	Spontaneous at low temperatures where ΔH outweighs $T\Delta S$ ($T\Delta S < \Delta H$) Non-spontaneous at high temperatures where, $T\Delta S$ outweighs ΔH
+	–	+	Non-spontaneous at all temperatures
+	+	– or +	Spontaneous at high temperatures where $T\Delta S$ outweighs ΔH ($T\Delta S > \Delta H$) Non-spontaneous at low temperatures where ΔH outweighs $T\Delta S$

IMPORTANT POINTS

(1) Relation between ΔG and $\Delta G°$

$$\Delta G = \Delta G° + 2.303RT\log Q \quad (Q = \text{reaction quotient})$$

(2) **$\Delta G°$ and equilibrium constant :**

At equilibrium, $\Delta G = 0$ and $Q = K$

$$\Delta G° = -RT\log_e K$$
$$= -2.303\,RT\log_{10} K$$

* * *

Chapter 6

Solutions

SOLUTIONS

A homogeneous mixture of two or more non-reacting substances is known as solution. Homogeneity or heterogeneity depends upon particle size and states of matter present in the solution. Every solution is made up of a solvent (present in larger quantity) and one or more solute (present in smaller quantity).

UNITS OF CONCENTRATION

(i) Molarity (M)

It is the number of moles of solute present per litre of solution.

$$\boxed{M = \frac{n}{V} = \frac{w}{M_w \quad V_{\text{in litre}}} = \frac{W \quad 1000}{M_w \quad V_{\textbf{in cc}}}}$$

$$M \times V_{\textbf{in cc}} = \frac{W}{M_w} \quad 1000$$

$\Rightarrow$ M × V (ml) = millimoles

Molarity changes with temperature of the solution. Increase in temperature generally decreases the molarity. It is the most convenient method to express concentration of the solution. On dilution, molarity decreases.

(ii) Molality (m) :

Number of moles (n) of solute present per kg of solvent

$$\boxed{m = \frac{n}{W_{\textbf{in kg}}} = \frac{w}{M \quad W_{\textbf{in kg}}} = \frac{w}{M \quad W_{\textbf{in g}}\text{ solvent}} \quad 1000}$$

It is independent of temperature since no volume factor is involved in the equation.

(iii) Mole fraction (x)

It is the ratio of number of moles of one component to the total number of moles present in the solution.

For a system having two components A and B,

$$X_A = \frac{n_A}{n_A + n_B}, X_B = \frac{n_B}{n_A + n_B}$$

$$\boxed{X_A + X_B = 1}$$

Mole fraction is also independent of temperature.

(iv) In terms of %

$$\% \text{ by weight } = \frac{\text{Wt.of solute}}{\text{Wt.of solution}} \quad 100$$

$$\% \text{ weight by volume } = \frac{\text{Wt.of solute}}{\text{Vol.of solution}} \quad 100 \text{ (In case of solid dissolved in a liquid)}$$

$$\% \text{ by volume } = \frac{\text{Volume of solute}}{\text{Volume of solution}} \quad 100 \text{ (In case of liquid dissolved in another liquid)}$$

$$\text{PPM } = \frac{\text{No. of parts of solute}}{\text{No. of parts of solution}} \quad 10^6$$

% by weight is independent of temperature while % by volume are temperature dependent.

HENRY'S LAW

Solubility of a gas at a given temperature in a solvent is directly proportional to its partial pressure. If P is the partial pressure of a gas and X_g is its mole fraction in solution. Then $P = K_H X_g$ where K_H is Henry's law constant for that gas

VAPOUR PRESSURE AND RAOULT'S LAW

The pressure exerted by the vapours at the free surface of liquid (provided system is closed) is known as its vapour pressure. The V.P. of a pure liquid is always greater than its solution (In case of non-volatile solute).

(a) Raoult's Law for a solution having non-volatile solute

$$\boxed{X_{\textbf{solute}} = \frac{P^o \quad P_s}{P^o}}$$

$$\begin{bmatrix} x_{\text{solute}} \rightarrow \text{Mole fraction of solute in solution} \\ P \quad \rightarrow \text{V.P. of pure solvent} \\ P_s \rightarrow \text{V.P. of solution} \end{bmatrix}$$

i.e., relative lowering of vapour pressure is equal to the mole fraction of solute.

(b) **Raoult's Law of miscible liquid-liquid solution**

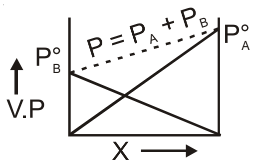
For ideal solution the partial vapour pressure is directly proportional to their mole fraction at constant temperature. For two components *A* and *B* in liquid solution.

$P_A \quad X_A$

$\Rightarrow P_A = P_A X_A$

$P_B \quad X_B$

$\Rightarrow P_B = P_B X_B$

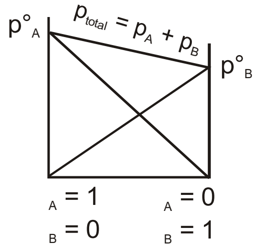
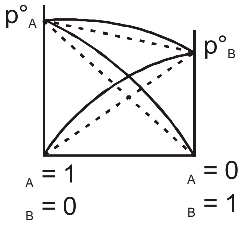
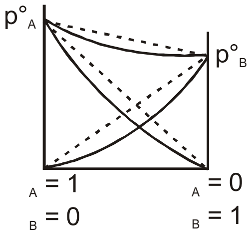


The total pressure $P = P_A + P_B = P^\circ_A X_A + P^\circ_B X_B$.

Most of the solutions show appreciable deviations from ideal behaviour known as real or non ideal solution. In some cases the deviation is +ve while in some cases deviation is –ve.

IDEAL AND NON-IDEAL SOLUTIONS

The solutions which obey Raoult's law are ideal solutions and those which do not obey Raoult's law form non-ideal solution.

Ideal Solution	Non-Ideal Solution	
	Positive Deviation	Negative Deviation
1. Obey's Raoult's law	1. Disobey Raoult's law	1. Disobey Raoult's law
2. $p_A = p^\circ_{A.}\ {}_A$ $p_B = p^\circ_B\ {}_B$ $p_{total} = p_A + p_B$	2. $p_A \quad p^\circ_{A\cdot}\ {}_A$ $p_B \quad p^\circ_{B\cdot}\ {}_B$ $p_{total} \quad p_A + p_B$ $[P_{total} > P_A + P_B]$	2. $p_A \quad p^\circ_{A\cdot}\ {}_A$ $p_B \quad p^\circ_{B\cdot}\ {}_B$ $p_{total} \quad p_A + p_B$ $[P_{total} < P_A + P_B]$
3. $H_{mix} = 0$ $G_{mix} = -ve$ $V_{mix} = 0$ $S_{mix} = +ve$	3. $H_{mix} = +ve$ $G_{mix} = -ve$ $V_{mix} = +ve$ $S_{mix} = +ve$	3. $H_{mix} = -ve$ $G_{mix} = -ve$ $V_{mix} = -ve$ $S_{mix} = +ve$
4. Interaction A – B = A – A = B – B *e.g.*, Chlorobenzene + Bromobenzene	4. Interaction A – B < A – A and B – B *e.g.*, $CH_3OH + H_2O$	4. Interaction A – B > A – A and B – B *e.g.*, $CH_3COCH_3 + CHCl_3$
		

COLLIGATIVE PROPERTIES

A colligative property of a solution is one that depends on the number of particles of solute in solution.

(a) Relative lowering of vapour pressure, $\frac{p \quad p_s}{p} = {}_{\text{solute}}$.

(b) Osmotic pressure, π = CRT.

(c) Elevation of boiling point, $T_b = k_b m$.

(d) Depression in freezing point, $T_f = k_f m$.

(a) Relative lowering of V.P. : The relative lowering in V.P. of an ideal solution is equal to the mole fraction of solute at that temperature.

$$\frac{p_A^o \quad p_A}{p_A^o} = {}_B = \frac{n_2}{n_1 + n_2} \quad \frac{n_2}{n_1} = \left(\frac{w_2}{M_2} \quad \frac{M_1}{w_1}\right) \text{ for dilute solutions.}$$

Determination of molecular masses by relative lowering in vapour pressure.

$$\frac{p^o \quad p_A}{p_A^o} \simeq \frac{w}{m} \quad \frac{M}{W}$$

w = Wt. of solute

m = Mol. wt. of solute

W = Wt. of solvent

M = Mol. wt. of solvent

(b) Osmotic pressure : The excess pressure which must be applied on a solution to prevent the passage of solvent into it through a semipermeable membrane.

Determination is done using Barkley-Hartley method:

Semipermeable membrane → egg membrane;

Chemical Semipermeable membrane → cupric ferrocyanide.

$\pi = CRT = n/V.\ RT;\ \pi V = nRT$: Van't Hoff equation for dilution solutions

$$n = \frac{w_2}{M_2};\ M_2 = \frac{w_2.RT}{\pi V}$$

For isotonic solutions $\pi_1 = \pi_2$

Molal elevation constant or ebullioscopic constant, K_b. It is the increase in boiling point when the molality of the solution is unity.

$T_b = K_b m$, when, m = 1, $T_b = K_b$

$$M_B = \frac{W_B \quad 1000}{T_b \quad W_A} \quad K_b$$

$$K_b = \frac{MRT_b^2}{1000 \quad H_{vap}}$$

Molal depression constant. or **cryoscopic constant (K_f)**. It is the decrease in freezing point when the molality of solution is unity

$T_f = K_f.m$

when, m = 1, $T_f = K_f$

$$M_B = \frac{W_B}{T_f \quad W_A} \quad 1000 \quad K_f$$

$$K_f = \frac{MRT_f^2}{1000 \quad H_{fusion}}$$

K_b and K_f are intensive properties of solvent and do not depend upon the quantity and nature of solute.

ABNORMAL MOLECULAR MASS AND Van't HOFF FACTOR (*i*)

$$i = \frac{\text{Experimental values of Colligative property}}{\text{Calculated value of colligative property}}$$

$$= \frac{\text{Observed value of Colligative property}}{\text{Normal value of the same property}}$$

$$= \frac{\text{Normal moleculer mass}}{\text{Observed moleculer mass}}$$

$$= \frac{M_{cal}}{M_{obs}}$$

Since,

$$\text{Colligative property} \quad \frac{1}{\text{Molecular mass of solute}}$$

if i = 1, no molecular association or dissociation takes place

if i < 1, molecular association takes place

if i > 1, molecular dissociation takes place.

For substances undergoing association or dissociation in the solution.

$$\boxed{\Delta T_b = iK_b \quad m}$$

$$\boxed{\Delta T_f = iK_f \quad m}$$

$$\boxed{\pi = iCRT}$$

Relation between degree of association or dissociation ( ) & Van't Hoff's factor (*i*)

For association $i = 1 + \quad \left(\frac{1}{n} \quad 1\right)$ or $\quad = \frac{n(i \quad 1)}{1 \quad n}$

where *n* = Number of particles that associate.

For dissociation $i = 1 + \quad (n - 1)$ or $\quad = \frac{i \quad 1}{n \quad 1}$

where *n* = Number of particles obtained on dissociation.

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Chapter 7

Equilibrium

RELATIONSHIP BETWEEN K_p AND K_c

$$K_p = K_c (RT)^{n_g}$$

where, $n_g = n_p - n_r$

= no of moles of gaseous product – no. of moles of gaseous reactant.

if $n_g = 0; K_p = K_c$; Example : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.

if $n_g \quad 0; K_p \quad K_c$; Example : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

if $n_g \quad 0; K_p \quad K_c$; Example : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Unit of K_p and K_c

Unit of K_p = $(atm)^{n_g}$

Unit of K_c = $(mol\ L\ ^{1})^{n_g}$

If $n_g = 0$, no unit of K_p and K_c

But now a days K_p and K_c are taken to be as unitless quantites.

Relation between degree of dissociation ( ) and Vapour density

For equilibrium reaction

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

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

For a reaction $A \rightleftharpoons nB$

or $P \rightleftharpoons aA + bB + cC + ...$

where a + b + c .... = n

$$\boxed{ = \frac{D \quad d}{(n \quad 1)d}}$$

For (i) & (ii)

n = 2

$$\boxed{\;=\frac{D}{d}\quad 1\;}$$

D = Vapour density of the gas before dissociation = Molecular weight/2

d = Vapour density of equilibrium mixture

n = Total number of moles obtained after dissociation from 1 mole of dissociating molecule.

Relation between Equilibrium Constant (K) and Standard free energy Change (G°)

$$\boxed{G \;=\; 2.303RT\log K_c}$$

$$\boxed{G \;=\; 2.303\ RT\log K_p}$$

LE-CHATELIER’S PRINCIPLE

It states that, if a system in equilibrium is disturbed by any external agency such as pressure, temperature, concentration etc. then equilibrium will get shifted to counter balance the effect of that disturbance.

Factors affecting Equilibrium

(1) Concentration

Addition of any reactant or removal of products leads to forward reaction or vice-versa.

(2) Temperature

In an endothermic reaction, (H=+ve) increase in temperature favours the forward reaction, while decrease in temperature favours backward reaction.

For exothermic reaction, (H= ve) increase in temperature favours backward reaction, while decrease in temperature favours forward reaction.

(3) Pressure

Effect of pressure is mainly applicable to gaseous reactions, since liquids & solids are incompressible in nature.

If $n_g = 0$ pressure has no effect on equilibrium constant.

$n_g \quad 0$ then on increasing pressure, equilibrium will get shifted in the backward direction.

$n_g \quad 0$ then on increasing pressure, equilibrium will shift towards forward direction.

(4) Catalyst

A catalyst has no effect on state of equilibrium but it enables the state of equilibrium to reach very quickly.

(5) Inert gas

The introduction of inert gas to any equilibrium is visualized under the condition of constant volume and constant pressure.

(a) At constant volume

$$\left.\begin{array}{l}\text{If}\quad n_g = 0\\ \qquad\; n_g \quad 0\\ \qquad\; n_g \quad 0\end{array}\right\}\text{no effect on equilibrium on addition of inert gas}$$

(b) At constant pressure

If $n_g = 0$ no effect on equilibrium

Equilibrium will get shifted in that direction where no. of moles are more.

$$\text{if} \quad \left.\begin{matrix} n_g\ \ 0 \\ n_g\ \ 0 \end{matrix}\right\} \begin{matrix}\text{In forward direction} \\ \text{In backward direction}\end{matrix}$$

IONIC EQUILIBRIUM

Dissociation of weak acids or weak bases and Ostwald's dilution law

When weak acid or weak base is dissolved in aqueous medium equilibrium exists between dissociated ions and undissociated molecules.

	CH_3COOH	$\rightleftharpoons$ CH_3COO^-	+ H^+
Initially	C	0	0
At equilibrium	C(1-)	C	C

where,   is the degree of dissociation.

$$K_a = \frac{C\ \ C\ \ }{C(1\ \ \ \ )} = C\ \ ^2 \ [\text{If} \quad << 1]$$

$$\boxed{\ \ = \sqrt{\frac{K_a}{C}}} \ \text{or} \ \boxed{\ \ = \sqrt{K_a\ \ V}} \ \text{and} \ \boxed{H^+ = C\ \ = C.\sqrt{\frac{K_a}{C}} = \sqrt{K_aC}}$$

Here V is the volume in litre containing 1 mole of electrolyte.

Similarly for weak base,

$$\boxed{\ \ = \sqrt{\frac{K_b}{C}}} \ \text{or} \ \boxed{\ \ = \sqrt{K_b x\ V}} \ \text{and} \ \boxed{[OH\ \ ] = C\ \ = C.\sqrt{\frac{K_b}{C}} = \sqrt{K_b.C}}$$

Here V is the volume in litre containing 1 mole of electrolyte.

BUFFER SOLUTIONS

Types of Buffer Solutions

Acidic buffer : A mixture of weak acid and its conjugated base form acidic buffer. *e.g.*,

$CH_3COOH + CH_3COONa$

$HCOOH + HCOONa$

$C_6H_5COOH + C_6H_5COONa$

$$\boxed{pH = pK_a + \log\frac{[Salt]}{[Acid]}}$$

Basic buffer : It is a mixture of weak base and its conjugate acid.

Ex. (1) $NH_4OH + NH_4Cl$

(2) $Cu(OH)_2 + CuCl_2$

(3) $Mg(OH)_2 + MgSO_4$

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

$$pH = 14 - pOH = 14 - \left(pK_b + \log\frac{[Salt]}{[Base]}\right)$$

$$pH = pK_w - \left(pK_b + \log\frac{[Salt]}{[Base]}\right)$$

SALT HYDROLYSIS

Consider the salt BA, which on hydrolysis will give acid and base inside the aqueous solution.

$BA + H_2O \rightleftharpoons BOH + HA$

(a) Salt made up of strong acid, strong base will not hydrolyse it will simply ionise. And pH of aqueous solution will be neutral. The pH of aqueous solution is independent with dilution *i.e.*, pH = 7. *e.g.*, NaCl, Na_2SO_4.

(b) Salt made up strong acid and weak base will hydrolyse, *e.g.*, NH_4Cl.

$$\boxed{K_h = \frac{K_w}{K_b}} \qquad pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

(c) Salt made up of weak acid and strong base, *e.g.*, CH_3COONa.

$$\boxed{K_h = \frac{K_w}{K_a}} \qquad pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

(d) Salt made up of weak acid and weak base. The pH and h of these salt solutions depend on K_a and K_b but independent with concentration, *e.g.*, CH_3COONH_4.

$$\boxed{K_h = \frac{K_w}{K_a.K_b}} \quad pH = \frac{1}{2}[pK_w - pK_b + pK_a]$$

Note : *$K_h = Ch^2$, $h = \sqrt{\frac{K_h}{C}}$, where h = degree of hydrolysis.*

SOLUBILITY PRODUCT

When a sparingly soluble salt is dissolved in water, it forms saturated solution but concentration of salt is very low. Therefore in saturated solution of such electrolytes, solid electrolyte is in equilibrium with the ions as represented below:

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

Applying Law of chemical equilibrium

$$K = \frac{[Ag^+]\,[Cl\ ]}{[AgCl]}$$

$$K[AgCl] = [Ag^+]\,[Cl^-]$$

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

where K_{sp} is a constant known as solubility product. It remains constant at constant temperature for a given salt and defined as the product of ionic concentration of a sparingly soluble electrolyte in a saturated solution.

if K_{sp} = I.P. (Ionic product) then solution is said to be saturated

if K_{sp} > I.P. then solution is said to be unsaturated

if K_{sp} < I.P. then solution is said to be supersaturated (Condition for precipitation)

Relation between Solubility and Solubility Product

For binary electrolyte; (for AB type salt)

$K_{sp} = S^2$ (AgCl, AgBr)

for ternary electrolyte; (for AB_2 or A_2B type salt)

$K_{sp} = 4S^3$ (CaF_2, $BaCl_2$)

for Quarternary Electrolyte; (for AB_3 or A_3B type salt)

$K_{sp} = 27S^4$

Solubility in presence of common ion

e.g. AgCl(s) is dissolve in xM Ag NO_3

$S = K_{sp} / x$

$x >> S$ and $x + S \quad x$

$$AgNO_3 \quad \to \underset{x}{Ag^+} + \underset{x}{NO_3}$$

$$AgCl(s) \rightleftharpoons \underset{(S+x)}{Ag^+}(aq) + \underset{(S)}{Cl}(aq)$$

$[Ag^+]_{Total} = (x + S)$

$K_{sp} = (x + S)\,S$

In general due to common ion effect solubility of salt decreases.

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Chapter 8

Redox Reactions and Electrochemistry

REDOX REACTIONS

CONCEPT OF OXIDATION & REDUCTION

Oxidation	Reduction
(i) Loss of electron	(i) Gain of electron
(ii) Loss of hydrogen	(ii) Gain of hydrogen
(iii) Gain of oxygen	(iii) Loss of oxygen
(iv) Increase in oxidation number	(iv) Decrease in oxidation number

OXIDATION NUMBER

Oxidation number change is defined as the change (real or imaginary) which an atom appears to have undergone when it is present in redox reaction. There are certain rules laid down in order to determine the oxidation number.

(a) Oxidation number of an atom in free elements is zero.

(b) Oxidation number of oxygen is –2, while in peroxides it is –1, in OF_2 it is +2.

(c) Oxidation number of hydrogen is +1, while in metal hydrides it is –1.

(d) Oxidation number of an ion is equal to the electrical charge present on it.

(e) Oxidation number of group IA elements is +1 and that of group IIA elements is +2.

(f) For complex ions, the algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.

(g) In case of neutral molecules the algebraic sum of the oxidation number of all the atoms present in the molecules is zero.

(h) Oxidation number of an atom never be greater than its valence electron. *e.g.*, valence electron for Cr is 6.

Increase in oxidation number of an element in a reaction is known as oxidation while decrease in oxidation number of an element in a reaction is known as reduction.

Besides +ve and -ve values, fractional values of oxidation number (as average) are also possible.

Balancing of H_2O can also be done as per the medium given

(1) **Acidic Medium :** Add H_2O on that side of reaction where oxygen are deficient and double number of H^+ on opposite side of reaction.

(2) **Basic Medium :** Add H_2O on that side of reaction where oxygen are excess and double number of OH^- on opposite side of reaction.

ELECTROCHEMISTRY

STANDARD ELECTRODE POTENTIAL

Standard Electrode Potential : The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 298 K is called standard electrode potential.

> ***Note :*** *Standard reduction potential = – (Standard oxidation potential)*
>
> *or Standard oxidation potential = – (Standard reduction potential)*

Standard Hydrogen Electrode – (SHE)

SHE Half Reaction	Electrode Potential
$H_2 \rightarrow 2H^+ + 2e^-$	0.0 V (anode)
$2H^+ + 2e^- \rightarrow H_2$	0.0 V (cathode)

With the help of SHE - the SRP values of all the electrodes has been determined and are placed in electrochemical series.

> ***Note :*** E_{Cell} *= O.P. of anode + R.P. of cathode.*
>
> *or* E_{Cell} *= R.P. of cathode – R.P. of anode.*

ELECTROCHEMICAL SERIES

Table in which the standard reduction potentials of various electrodes have been arranged in the increasing order is called electrochemical series or activity series or electromotive series.

Electrode	Electrode reaction	E°(volts)
Li^+/Li	$Li^+ + e^- = Li$	– 3.045 (Lowest)
Zn^{+2}/Zn	$Zn^{+2} + 2e^- = Zn$	– 0.763
H^+/H_2, Pt	$2H^+ + 2e^- = H_2$	0.0 (Standard)
Cu^{+2}/Cu	$Cu^{+2} + 2e^- = Cu$	+ 0.34
F_2/F^-, Pt	$F_2 + 2e^- = 2F^-$	+ 2.887 (Highest)

Applications of Electrochemical Series :

The important applications of electrochemical series are:

(a) Relative strength of oxidising and reducing agents. In the series, the elements are arranged in the increasing order of reduction potentials or decreasing order of oxidation potential. Therefore, the elements at the top are good reducing agents while those at the bottom are good oxidising agents.

(b) **Calculating e.m.f. of the cell :** The e.m.f. of the cell can be determined by knowing the standard electrode potentials from the series as:

$$E^\circ_{cell} = E^\circ_{(cathode)} \quad E^\circ_{(anode)} \text{ (If standard reduction potential are given)}$$

$$E^\circ_{cell} = E^\circ_{(anode)} \quad E^\circ_{(cathode)} \text{ (If standard oxidation potential are given)}$$

(c) **Predicting feasibility of a redox reaction :** In general, a redox reaction is feasible only if the species which has higher reduction potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidised i.e. loses the electrons. Otherwise, a redox reaction is not feasible. In other words, the species to release electrons must have lesser reduction potential as compared to the species which has to accept electrons.

(d) To predict whether a metal can liberate hydrogen from acid or not, only the metals which have negative reduction potentials, can liberate hydrogen from the acids.

EMF OF GALVANIC CELL

In galvanic cells, current is generated as a result of a spontaneous chemical reaction that occur in the cell. The main characteristics of galvanic cell are given below

		Cathode	**Anode**
(i)	Sign	Positive	Negative
(ii)	Half reaction	Reduction	Oxidation
(iii)	Direction of electron movement	Into the cell	Out of the cell

Note : *Flow of currrent from cathode to anode.*

GIBB'S ENERGY CHANGE AND CELL POTENTIAL

The electrical work done from the cell = nFE

$$- \quad G = nFE$$

$$G = -nFE$$

or $G^o = -\ nFE^o$

where, G = Gibb's energy change

G° = Standard Gibb's energy change

E = emf of cell/electrode potential

E° = Standard emf of cell/standard electrode potential.

Type of Electrode Potential

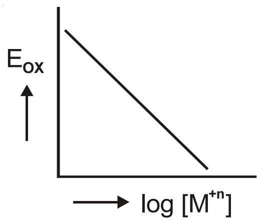
1. Oxidation Potential
2. Reduction Potential

1. **Oxidation Potential :** When electrode is negatively charged w.r.t. solution then it acts as anode, and oxidation takes place.

$$M \quad \rightarrow M^{+n} + ne^-$$

$$E_{ox} = E\ _{ox} \quad \frac{2.303RT}{nF} . \log [M^{+n}]$$

Intercept $= E^\circ_{ox}$ and Slope $= \frac{2.303RT}{nF}$



2. **Reduction Potential :** When electrode is positively charged w.r.t. solution then it acts as cathode, and reduction takes place.

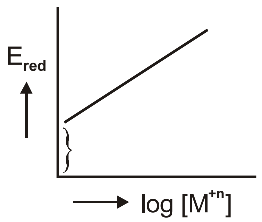
$M^{+n} + ne^- \rightarrow M$

$$E_{red} = E_{red}\ \frac{2.303RT}{nF} . \log \frac{1}{[M^{+n}]}$$

$$E_{red} = E_{red} + \frac{2.303RT}{nF} . \log [M^{+n}]$$

Intercept = E°_{red}

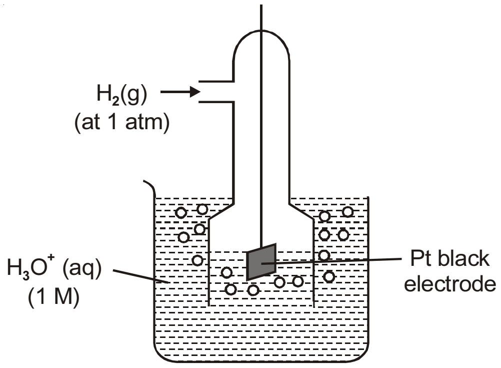
Slope = $\frac{2.303RT}{nF}$.



Various Types of electrodes

Different types of half cells are used to make complete cell with spontaneous reaction in forward direction.

1. **Hydrogen Electrode :** The standard hydrogen electrode (S.H.E.) consists of a Pt electrode coated with Pt black. The electrode dipped in a solution of 1 M and hydrogen gas bubbled through it at 1 bar.



Hydrogen electrode

$Pt, \underset{1\ bar}{H_2(gas)}|H^+(aq).\ 1M$

$H_2(g) \rightarrow 2H^+ + 2e^-$

$E^\circ_{SHE} = 0$

$$E = \frac{0.059}{1} \log H^+ = E = \frac{0.059}{1} pH$$

2. **Metal-Metal ion Half Cell** :

Ag | Ag^+(aq)

Ag(s) $\rightarrow Ag^+$(aq) + e^-

E = E° – 0.0591 log [Ag^+]

3. **Metal-Metal-Insoluble Salt anion Half Cell :**

Ag | AgCl | Cl^-(aq)

Ag + Cl^-(aq) $\rightarrow$ AgCl(s) + e^-

$$E = E^\circ - 0.0591 \log \frac{1}{[Cl\ ]}$$

E = E° + 0.0591 log [Cl^-]

4. **Calomel Electrode :**

   $Hg, Hg_2Cl_2 \mid Cl^-(aq)$

   $2Hg(l) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$

   $$E = E \quad \frac{0.0591}{2} . \log \frac{1}{[Cl^-]^2}$$

   $E = E° + 0.0591 \log [Cl^-]$.

5. **Metal-Metal Oxide Hydroxide Half Cell :**

   $Hg,HgO \mid OH^-(aq)$

   $Hg(l) + 2OH^-(aq) \rightarrow HgO(s) + H_2O(l) + 2e^-$

   $$E = E \quad \frac{0.0591}{2} . \log \frac{1}{[OH^-]^2}$$

   $E = E° + 0.0591 \log [OH^-]$.

6. **Oxidation-Reduction Half Cell :**

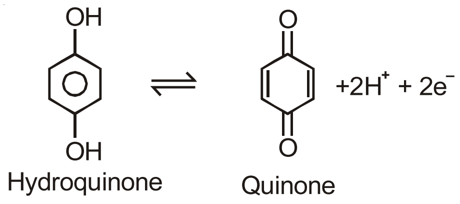
   $Pt \mid Fe^{+2}(aq), Fe^{+3}(aq)$

   $Fe^{+2}(aq) \rightarrow Fe^{+3}(aq) + 1e^-$

   $$E = E \quad \frac{0.0591}{1} . \log \frac{[Fe^{+3}]}{[Fe^{+2}]}.$$

7. **Quinhydrone Half Cell :**

   $Pt \mid Quinhydrone \mid H^+(aq)$



   $$E = E \quad \frac{0.0591}{2} . \log [H^+]^2$$

   $$E = E \quad \frac{0.0591}{1} . \log [H^+].$$

ELECTROLYSIS

(a) The decomposition of the electrolyte due to the passage of electricity is known as electrolysis.

(b) During electrolysis, electrical energy changes into chemical energy.

(c) To have electrolysis we must use direct current.

(d) Electrolysis is a redox phenomenon.

Faraday's laws of electrolysis

(a) **First Law :** The weight of substance deposited at the electrode is directly proportional to the quantity of electric charge passed through the electrolytic solution

$W \quad Q$ W = Weight in g

Q = Quantity of charge

⇒ $W = ZQ$ Z = Constant known as electrochemical equivalent

⇒ $W = ZIt$ I = Current in ampere

t = Time in second

$$Z = \frac{\text{E(equivalent mass)}}{96500}$$

(b) **Second law :** If the same quantity of current is passed through different electrolytic solutions then the weights of different substances deposited at the respective electrodes is directly proportional to their chemical equivalents.

$$\frac{\text{Weight of electrolyte (A)}}{\text{Eq. wt. of (A)}} = \frac{\text{Weight of electrolyte (B)}}{\text{Eq. wt. of (B)}}$$

ELECTROLYTIC CONDUCTION

Molten true electrolyte and the aqueous solution of electrolytes contain free ions and conduct electricity due to the movement of ions.

According to Ohm's law,

$$R \quad \frac{l}{a} \qquad \text{or} \qquad R = \quad \frac{l}{a}$$

$$= R \quad \frac{a}{l}$$

$$\frac{1}{\ } = \frac{1}{R} \quad \frac{l}{a}$$

where R = Resistance of solution

l = Length

a = Area of cross-section of the solution

= Resistivity of solution

If $l = 1$ unit of length and $a = 1$ unit of area

then $\boxed{R = \quad}$

Conductance (G) = $\frac{1}{R}$

Unit of conductance = ohm^{-1} or siemens (S)

Specific conductance (K) = $\frac{1}{} = \frac{1}{R}\ \frac{l}{a} = \frac{\text{Cell constant}}{\text{Resistance}}$ ($\frac{l}{a}$ is called cell constant)

K = Conductance if l = 1 unit (length) and a = 1 unit (area)

S.I. Unit of K = Sm^{-1}

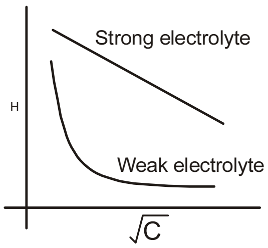
***Note :** Specific conductance is now-a-days called conductivity.*

MOLAR CONDUCTIVITY ($_{m}$)

The conducting power of all the ions furnished by one mole of an electrolyte in any solution is termed as its molar conductivity

$$_{m} = \frac{\text{Conductivity (K)}\,[\ \ ^{-1}\ \text{cm}^{-1}]}{\text{Concentration of solution in moles per unit volume (cm}^{3})}$$. Unit of $_{m}$ = $\text{ohm}^{-1}\ \text{cm}^{2}\ \text{mol}^{-1}$

Molar conductivity of weak electrolyte increases with increase in dilution or decrease in concentration due to increase in ionisation but specific conductivity decreases with increase in dilution because number of ions per cm^3 of solution decreases.



KOHLRAUSCH'S LAW

It states that at infinite dilution the molar conductivity of an electrolyte [known as limiting molar conductivity] can be expressed as the sum of the contribution from its individual ions.

$^{o}_{m} = V_{+}\ ^{o}_{+} + V\ \ ^{o}$ (where V_{+} and V_{-} are the number of cations and anions per formula unit of electrolyte respectively and $^{o}_{+}$ and $\ ^{o}$ are limiting molar conductivities of the cation and anion respectively).

Application

Some typical applications of Kohlrausch's law are

(i) Determination of $^{o}_{m}$ for weak electrolyte

(ii) Determination of degree of dissociation ( ) of a weak electrolyte

$$= \frac{^{c}_{m}}{^{o}_{m}}$$

(iii) Determination of ionisation constant of weak electrolyte of (AB) type

$$K = \frac{C(\ ^{c}_{m})^{2}}{^{o}_{m}(\ ^{o}_{m}\ \ \ ^{c}_{m})}$$

(iv) Determination of solubility of a sparingly soluble salt

Concentration of sparingly soluble salt $(C_{m}) = \frac{1000.K_{salt}}{(V_{+}\ ^{o}_{+} + V\ \ ^{o})}$

IMPORTANT POINTS

(1) Degree of dissociation ( ) can be related with conductance. *i.e.*, $= \frac{m}{\substack{o\\m}}$

(2) $G° = -nFE_{cell}$ n = Number of electrons

F = Faraday

(3) Concentration cells are made up of same electrode but dipped in different concentration of its own ion.

e.g., $Cu\,|\,Cu^{+2}_{(0.01M)}\,||\,Cu^{+2}_{(0.2M)}\,|\,Cu$

(4) For spontaneity of reaction, $E_{cell} > 0$ *i.e.*, $G < 0$.

(5) **Primary Cells :** The reaction occurs in one direction only and the cell cannot be recharged. *e.g.*, Mercury cell.

(6) **Secondary Cells :** The cells that can be recharged by passing current through it. *e.g.*, Lead storage cell.

Fuel Cell : Energy is obtained by combustion of fuels.

(7) Rusting of iron is the example of corrosion which is a electrochemical process.

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Chapter 9

Chemical Kinetics

FACTORS AFFECTING RATE OF REACTION

(i) **Nature of the reactant :** Different amount of energies are required for breaking of different bonds and different amount of energies are released in the formation of different bonds.

(ii) **Concentration of the reactant :** Greater the concentration of reactants, faster is the reaction.

(iii) **Surface area of the reactant :** Rate of reaction increases with increase in surface area.

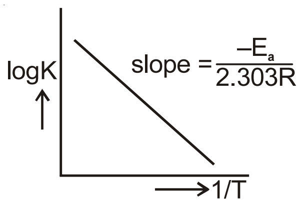
(iv) **Presence of light :** Some reactions do not take place in dark but take place in presence of light. Such reactions are called photochemical reactions.

(v) **Temperature :** The rate of reaction increases with an increase in temperature. For every 10°C rise in temperature the rate of reaction becomes twice or thrice for a homogeneous reaction. The temperature coefficient is defined as the ratio of the specific reaction rates of a reaction at two temperatures differing by 10°C.

Temp. coefficient $= \frac{K_{t+10}}{K_t} =$ between 2 or 3.

The rate constant (K) and temperature are related by **Arrhenius equation** given by

$$\boxed{K \quad e^{E_a/RT}}$$



Arrhenius equation, K = $Ae^{\frac{E_a}{RT}}$ *i.e.*, $\ln k = \ln A \quad \frac{E_a}{RT}$.

$$\log_{10} K = \log_{10} A \quad \frac{E_a}{2.303\ RT}$$

By plotting graph log K vs $\frac{1}{T}$ activation energy can be determined.

(vi) **Presence of catalyst :** The positive catalyst lowers down the activation energy. The greater the decrease in activation energy higher will be the reaction rate.

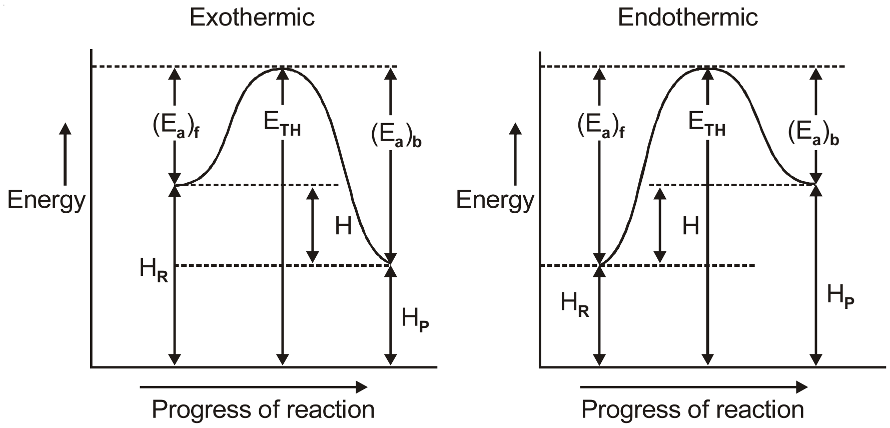
CONCEPT OF ACTIVATION ENERGY

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy

Activation energy = Threshold energy – average kinetic energy of reacting molecules

Threshold energy = Initial potential energy of reactant molecules + activation energy.

Activation Energy



E_{TH} = Threshold Energy, H_R = Enthalpy or Energy or Potential of reactants.

H_P = Enthalpy or Energy or Potential of product, $(E_a)_f$ = Activation energy for forward reaction.

$(E_a)_b$ = Activation energy for backward reaction.

ORDER OF REACTION

A. Zero order reaction : A reaction is said to be of zero order if the rate of reaction is independent of concentration of the reactant.

Rate Expression :

Let A $\rightarrow$ Product

[K is a constant called Rate Constant]

$$\boxed{K = \frac{x}{t}}$$

Characteristics :

(a) Unit of K = mol L^{-1} $time^{-1}$

(b) Half life period : Time required for the completion of half of the reaction.

Half life for zero order reaction is directly proportional to initial concentration of the reactant

$$\boxed{t_{1/2} \quad a}$$

(c) The concentration of reactant decreases linearly with time.

B. First Order Reaction :

A first order reaction is one whose rate is determined by the variation of one concentration term only.

All radioactive disintegration reactions are of the first order.

Rate Expression

Let	A	$\rightarrow$	Product
initially	a		0
after time t	(a – x)		x

$$\boxed{K = \frac{2.303}{t}\log\frac{a}{(a-x)}}$$

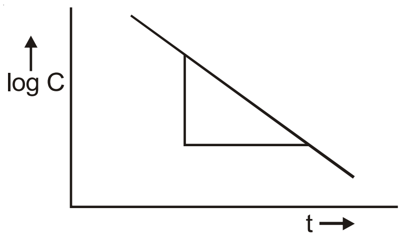
Characteristics

(a) Unit of K = time^{-1}

(b) Half-life period : The half life period is independent of initial concentration of the reactant.

$$\boxed{t_{1/2} = \frac{0.693}{K}}$$

(c) On plotting a graph between log of concentration and time we get



The slope of this line gives the value of $\frac{K}{2.303}$ from which K can be calculated.

General expression of unit of rate constant K = mole^{1-n} litre^{n-1} time^{-1}, where n is the order of reaction

RATE CONSTANTS FOR DIFFERENT ORDER OF REACTION

Reaction	Order	Rate law eqn.	Rate constant	Half life period
A $\rightarrow$ product	0	Rate = k	$k = \frac{1}{t}\left([A_0] - [A]\right)$	$t_{1/2} = \frac{[A_0]}{2k}$
A $\rightarrow$ product	1	Rate = k[A]	$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$	$t_{1/2} = \frac{0.693}{k}$
2A $\rightarrow$ product	2	Rate = k[A]^2	$k = \frac{1}{t}\left[\frac{1}{[A]} - \frac{1}{[A_0]}\right]$	$t_{1/2} = \frac{1}{[A_0]k}$

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Chapter 10

Surface Chemistry

ADSORPTION

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into higher concentration of the molecules on the surface is called adsorption.

There are two types of adsorption

(i) Physical adsorption

(ii) Chemical adsorption

Physical adsorption or Physisorption	Chemical adsorption or Chemisorption
1. Enthalpy of adsorption usually is of the order of –20 kJ mol^{-1} *i.e.* exothermic.	1. Enthalpy of adsorption is of the order of –200 kJ mol^{-1}.
2. Molecule of adsorbate and adsorbent are held by weak van der Waal's interaction.	2. Molecules of adsorbate and adsorbent are held by chemical bonds.
3. It usually takes place at low temperature and decreases with increasing temperature.	3. It takes place at relatively high temperature.
4. It is not very specific *i.e.* all gases are adsorbed on all solids to some extent.	4. It is highly specific and take place when there is some possibility of compound formation between adsorbate and adsorbent molecule.
5. Multimolecular layers may be formed on adsorbent.	5. Usually monomolecular layer is formed on the adsorbent.
6. It is reversible in nature.	6. It is usually irreversible in nature.
7. It does not require activation energy.	7. It requires activation energy.

ADSORPTION ISOTHERM

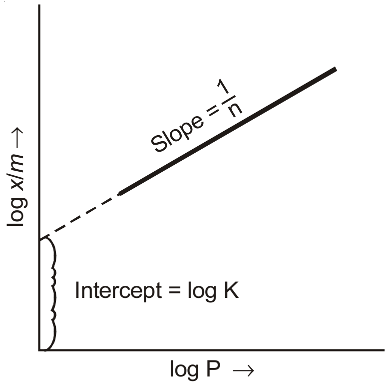
A relation or graph between x/m (x are number of moles of adsorbate and m is the mass of adsorbent) and the pressure (P) of the gas at a constant temperature is called adsorption isotherm.

A. Freundlich Adsorption Isotherm

Freundlich gave an equation $x/m = KP^{1/n}$ $(n > 1)$ to explain the effect of pressure on amount of gas adsorbed where K and n are parameters of the equations depending upon the nature of the gas and solid.

$\frac{x}{m}$ increases with increase in pressure. Since $n > 1$, so x/m does not increase, as rapidly as 'P'

$\log\frac{x}{m} = \log K + \frac{1}{n}\log P$ (Taking log on both sides)



From this graph it is possible to find out value of K and n

B. Langmuir Adsorption Isotherm

Langmuir considered that adsorption consist of the two opposing processes *i.e.*, adsorption and desorption both take place and dynamic equilibrium established between the above two processes. He also assumed that the layer of the adsorbed gas was only one molecule thick *i.e.*, unimolecular as in chemisorption.

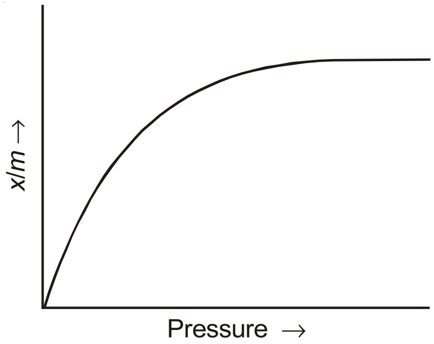
The Langmuir adsorption isotherm is represented by the relation.

$\frac{x}{m} = \frac{aP}{1+bP}$ where a and b are two Langmuir parameters.

$\frac{x}{m} = \frac{a}{b}$ (At very high pressure $1 + bP \sim bP$)

and $\frac{x}{m} = aP$ (At very low pressure $1 + bP \sim 1$)

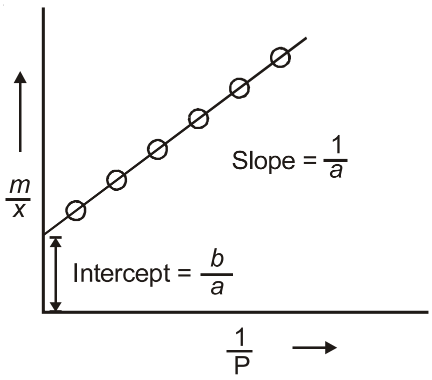
So at high pressure of the gas $\frac{x}{m}$ remains constant and nature of graph is linear at very high pressure



In order to determine the parameters a and b, we may write

$$\frac{m}{x} = \frac{1+bP}{aP} = \frac{b}{a} + \frac{1}{aP}$$

A plot of $\frac{m}{x}$ against $\frac{1}{P}$ gives a straight line with slope and intercept equal to $\frac{1}{a}$ and $\frac{b}{a}$ respectively



COLLOIDS

Colloidal state of matter is a state in which the size of particles is such (10Å – 10000Å) that they can pass through filter paper but not through animal or vegetable membrane.

CLASSIFICATION OF COLLOIDS

(i) **Based on physical state of dispersed phase and dispersion medium**–The physical state of dispersed phase and dispersion medium may be solids, liquids or gases, eight types of colloidal system are possible.

Dispersed Phase	Dispersion Medium	Name	Examples
Solid	Solid	Solid Sol	Some coloured glasses, gem stones
Solid	Liquid	Sol	Some paints, cell fluids, muddy water
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud
Gas	Solid	Solid foam	Pumice stone, foam rubber
Gas	Liquid	Foam	Whipped cream, soap lather

Note : *A gas mixed with another gas form a homogeneous mixture and not a colloidal system.*

(ii) Based on nature of interaction between dispersed phase and dispersion medium–

Divided into two types namely Lyophilic and Lyophobic Colloids

	Lyophilic Sols	Lyophobic Sols
1. Nature	Reversible	Irreversible
2. Preparation	Prepared by direct mixing with liquid dispersion medium i.e. solvent loving (greater affinity for solvent)	Cannot be prepared directly but by special method i.e. solvent hating (no affinity for solvent)

3. Stability	Quite stable and not easily precipitated or coagulated	Precipitated by adding small amount of suitable electrolyte
4. Hydration	Highly hydrated	Not much hydrated
5. Nature & substances	These sols are usually formed by the organic substances like starch, gum, proteins etc.	These are usually formed by the inorganic materials like metals, their sulphides etc.
6. Viscosity	Much higher than that of medium	Almost same as that of medium
7. Surface tension	Lower than that of dispersion medium	Nearly same as that of dispersion medium

EMULSIONS AND ITS TYPE

Emulsions are colloids in which both dispersed phase and dispersion medium are liquids and broadly classified into two types

(i) **Oil in water emulsion** – In this type of emulsion, oil acts as dispersed phase and water acts as dispersion medium. **Ex.**– Milk, vanishing cream etc.

(ii) **Water in oil emulsion –** In this type of emulsion, water acts as dispersed phase and oil acts as dispersion medium.

Ex.– Cold cream, butter, cod liver oil etc.

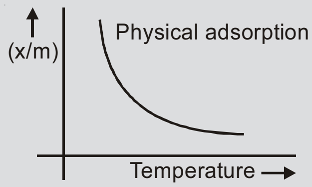
KEY POINTS

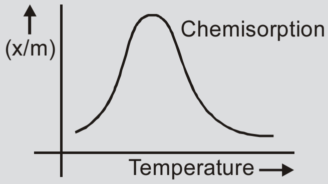
1. Colloid is not a substance, it is a state of a substance, which depends upon particle size.
2. **Emulsifier :** Long-chain hydrocarbons terminating in polar end groups are added to stabilise emulsion.
3. In **true solutions**, particle size is less than 1 nm and in **suspensions**, the particle size is more than 1000 nm.
4. The **coagulating power** of an electrolyte is inversely related to its coagulating value.
5. A phenomenon in which the molecules of dispersion medium are allowed to move under influence of electric current, whereas colloidal particles are not allowed to move, is called **electro-osmosis**.
6. The presence of electrical charge (either positive or negative) on colloidal particle is responsible for **stability of colloidal solutions**.
7. **Gold number** of a protective colloid is minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of gold sol (*i.e.*, change of colour from red to blue) take place when 1 ml of 10% NaCl solution is rapidly added to it. Obviously, smaller the gold number of a protective colloid, greater is the protective action *e.g.*, gelatin has very small value of gold number.
8. Gold number is assigend to lyophilic colloids only.
9. **Multimolecular colloids** consist of aggregated atoms or molecule *e.g.*, gold, sulphur sol.
10. **Macromolecular colloids** have dispersed phase particles as macromolecule or polymers *e.g.* protein sol.
11. Substances which possess surface activity *i.e.*, property to lower surface tensions of liquids or the tendency to increase surface area, are called **surfactants**.
12. The substances which at low concentration in a medium behave as normal strong electrolyte but at higher concentration exhibit colloidal properties due to formation of aggregated particles are called **associated colloids** or **micelles**. Their formation take place above a particular temperature called kraft temperature (T_k) and above a particular concentration (CMC – Critical Micelle Concentration), *e.g.*, soaps and detergents.

ADDITIONAL POINTS

1. SnO_2 forms a positively charged colloidal sol in acidic medium and negatively charged sol in basic medium.
2. Delta is generally formed as result of coagulation when river meets the ocean.
3. A solid metal in a finely divided state is a better catalyst.
4. H_2O is absorbed by anhydrous $CaCl_2$ whereas, it is adsorbed on **silica gel**.
5. Gases are adsorbed on solid surface (Ni, Co, Pt, Pd etc.) but absorbed in solvent phase.
6. During adsorption, H = –ve, S = –ve hence adsorption is spontaneous at low temperature, when G = –ve.

   At adsorption equilibrium G = 0 and rate of adsorption becomes equal to rate of desorption.
7. Easily liquefiable gases (*e.g.*, HCl, NH_3, CO_2) are adsorbed to greater extent than others (H_2, N_2, O_2 etc.)
8. The adsorption of gases on finely divided metal surface is also called **occlusion**.
9. As temperature increases, rate of chemisorption first increases and then decreases.





10. Freundlich adsorption isotherm is only a special case of Langmuir adsorption isotherm for intermediate pressures (Freundlich isotherm fails at high pressure of the gas).
11. Catalytic promoters increase the activity of catalyst e.g. Mo acts as promoter for Fe. (catalyst) in Haber process of formation of NH_3.
12. The potential difference set up across the surface of separation of two oppositely charged layers just in contact with each other on the surface of colloid is known as **electrokinetic** or **zeta potential**.

❑ ❑ ❑

Chapter 11

Some Basic Principles of Organic Chemistry and Purification and Characterisation of Organic Compounds

HOMOLOGOUS SERIES

It is a series of similarly constituted organic compounds in which members possess the same functional group, have a similar or almost similar characteristics, can be represented by the same general formula, and the two consecutive members differ by – CH_2 – group in their molecular formula.

e.g., General formula for saturated alcohol is C_nH_{2n+1} – OH

$$\underset{\text{Methanol}}{CH_3\ OH} \xrightarrow{+(\ CH_2\ )} \underset{\text{Ethanol}}{CH_3\ CH_2\ OH} \xrightarrow{+(\ CH_2\ )} \underset{\text{Propanol}}{CH_3\ CH_2\ CH_2\ OH}$$

ISOMERISM

Compounds having same molecular formula but different in their physical and chemical properties are called isomers. This phenomenon is called isomerism.

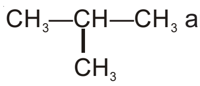
They are classified into two types

1. Structural isomerism or constitutional isomerism
2. Stereo isomerism

1. **Structural isomerism :** When same molecular formula represents two or more compounds which differ in the arrangement of atoms within the molecule, then such compounds are called structural isomers and the phenomenon is called structural isomerism. It is of the following types :

   (i) Chain isomerism : When the same molecular formula represents two or more compounds which differ in the nature of carbon chain (straight or branched), the isomers are called chain isomers and the phenomenon is known as chain isomerism.

   Example : $CH_3—CH_2—CH_2—CH_3$ and



$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}H—CH_3$ are chain isomers

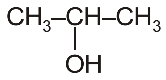
   (ii) Position isomerism : Compounds having same structural formulae but differ only in the position of the substituent atoms or groups on the carbon chain are called position isomers.

   Example : $C_3\ H_7$ OH has two position isomers

$CH_3\ CH_2\ CH_2$ –OH

propan-1-ol

and



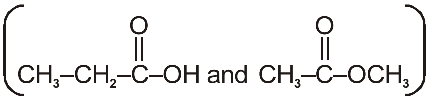
$CH_3–\underset{\displaystyle OH}{\underset{|}{C}}H–CH_3$

propan-2-ol

(iii) Functional isomerism : When any two compounds have same molecular formula but possess different functional groups, they are called functional isomers and the phenomenon is called functional isomerism. Examples of functional isomerism are

(a) Alcohol and ether ($CH_3–CH_2–CH_2–CH_2–OH$ and $CH_3–CH_2–O–CH_2–CH_3$)

(b) Carboxylic acid and ester, etc.



$$\left(CH_3–CH_2–\overset{\overset{\displaystyle O}{\|}}{C}–OH \text{ and } CH_3–\overset{\overset{\displaystyle O}{\|}}{C}–OCH_3\right)$$

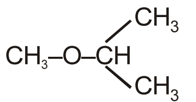
(iv) Metamerism : It arises due to different alkyl chains on either side of the functional group in the molecule. For example ethers, esters, amines, ketones etc. can exhibit metamerism.

Example :

(a) Metamers of $C_2H_5 – O – C_2H_5$ are

$CH_3CH_2CH_2–O\ CH_3$

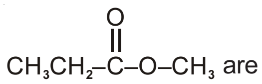
Methyl propyl ether



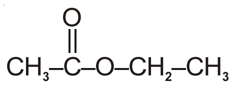
$CH_3–O–CH(CH_3)_2$

Methyl isopropyl ether

(b) Metamers of

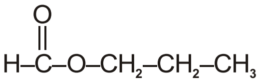


$CH_3CH_2–\overset{\overset{\displaystyle O}{\|}}{C}–O–CH_3$ are



$CH_3–\overset{\overset{\displaystyle O}{\|}}{C}–O–CH_2–CH_3$

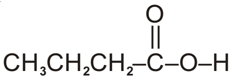
Ethyl ethanoate



$H–\overset{\overset{\displaystyle O}{\|}}{C}–O–CH_2–CH_2–CH_3$

Propyl methanoate

It is to be noted that

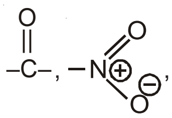


$CH_3CH_2CH_2–\overset{\overset{\displaystyle O}{\|}}{C}–O–H$ is not the metamer of above compounds. Because this compound is an acid while the above compounds are isomeric esters.

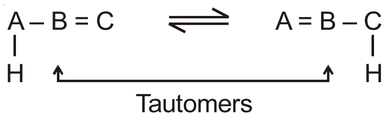
(v) Tautomerism : The phenomenon due to which two or more structurally distinct compounds are in dynamic equilibrium due to shift in the position of an atom or group in a molecule is known as tautomerism and the structural isomers are known as tautomers. Tautomerism may be catalysed by an acid, a base or traces of transition metal ions etc.

Structural Requirement for Tautomerism

When unsaturated functional group (*e.g.,*



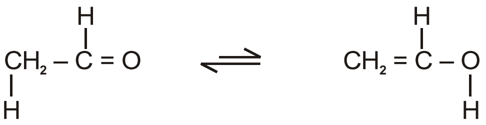
$–\overset{\overset{\displaystyle O}{\|}}{C}–$, $–\overset{\oplus}{N}(=O)–\overset{\ominus}{O}$, –N = O) have -hydrogen, the compound may exhibit tautomerism.



$$\underset{\displaystyle H}{\overset{|}{A}}–B=C \rightleftharpoons A=B–\underset{\displaystyle H}{\overset{|}{C}}$$

In simple keto-enol tautomerism generally keto form is more stable, the stability of enol form may increase due to extended conjugation, aromaticity or intramolecular hydrogen bonding.

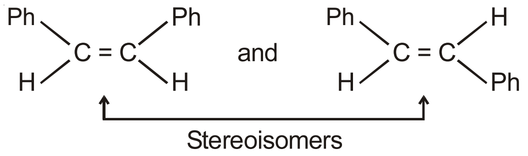
e.g.,

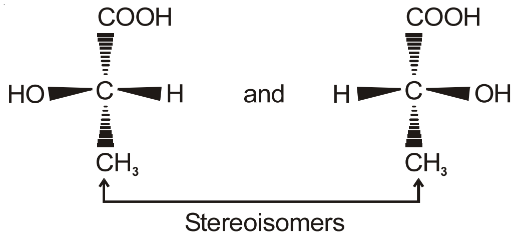


$$\underset{\displaystyle H}{\overset{|}{CH_2}}–\overset{\overset{\displaystyle H}{|}}{C}=O \rightleftharpoons CH_2=\overset{\overset{\displaystyle H}{|}}{C}–\underset{\displaystyle H}{\overset{|}{O}}$$

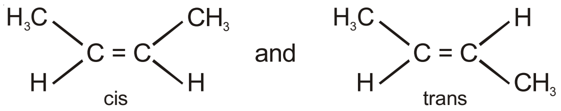
More stable > 99% Less stable < 1%

2. **Stereo isomerism :** The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers and this type of isomerism is known as stereoisomerism. This isomerism can be further classified as **geometrical isomerism** and **optical isomerism**.





Geometrical isomerism : When stereoisomerism arises due to **restricted rotation** (because of the presence of double bond or ring), then it is known as geometrical isomerism.



These are geometrical isomers because they have different spatial arrangement due to the presence of restricted rotation (due to double bond).

Note : *(i) Geometrical isomers may be named as cis-trans isomers, E-Z isomers or syn-anti isomers.*

*(ii) Geometrical isomers are also known as **diastereomers** (stereoisomers which are not the mirror images of each other). Therefore geometrical isomers have different physical properties and similar chemical properties.*

(iii) Geometrical isomers do not rotate plane polarised light (unless they also happen to be chiral).

Enantiomers : Nonsuperimposable mirror images are known as enantiomers. They have similar physical and chemical properties in symmetric environment. But they may behave differently in asymmetric environment. They also rotate plane polarised light in opposite directions but the magnitude of rotation is identical. Specific rotation of S-alanine is +8.5 while that of R-alanine is –8.5, while melting point of both the enantiomers are 297°C.

Dextrorotatory substances : Those substances which rotate the plane polarised light in clock-wise direction are known as dextrorotatory substances. The rotation is labelled as (+).

If the rotation is **counterclockwise**, the compound is called **Laevorotatory**. No relationship exists between D and L (represents relative configuration) and dextrorotatory and laevorotatory substances. A compound with D configuration may be (+) or (–). This information can be obtained only by putting the molecule in **Polarimeter** (instrument used to obtain direction and extent of rotation of plane polarised light).

Specific rotation : Specific rotation of a chiral compound is a constant at a particular temperature and wavelength (589 nm).

$$\boxed{\text{Specific rotation} = \quad _{l} = \frac{\quad}{c \quad l}}$$

= observed rotation (in degree)

c = concentration (g/ml)

l = length of sample tube (dm)

Racemic mixture : A mixture containing equal amount of two enantiomers is called racemic mixture or racemate. A racemic mixture is optically inactive due to external compensation. Racemic mixture can be resolved into optically pure form by several methods.

Percentage enantiomeric excess : It tells us how much one enantiomer is present in excess of the racemic mixture.

$$\boxed{\% \text{ ee} = \% \text{ of one enantiomer} \quad \% \text{ of the other enantiomer}}$$

Number of Possible optical isomers in Compounds having n-chiral Carbon Atoms :

Case - I : When there is no symmetry in the structure of molecule.

Number of *d* and *l* forms = 2^n

Number of meso forms = 0

Total number of optical isomers = 2^n

Case - II : When the molecule is structurally symmetric and n is even

Number of *d* and *l* forms = 2^{n-1}

Number of meso forms = $2^{n/2-1}$

Total number of optical isomers = $2^{n-1} + 2^{n/2-1}$

Case - III : When the molecule can be divided into two identical parts and n is odd

Number of *d* and *l* forms = $2^{n-1} - 2^{\frac{n-1}{2}}$

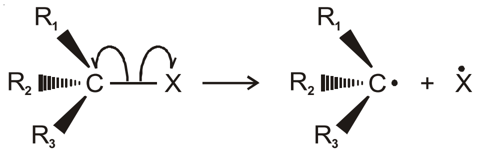
Number of meso forms = $2^{\frac{n-1}{2}}$

Total number of optical isomers = 2^{n-1}

BOND FISSION

In any reaction, bond between the reactant molecule is broken, Bond fission in organic molecules can take place in one of the two ways.

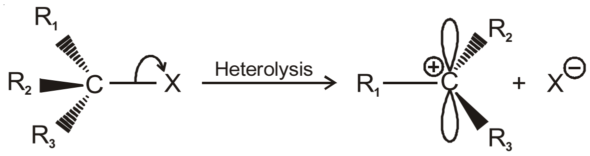
1. **Homolytic Bond Fission**



Result of homolytic fission is free radical. (Alkyl free radical may be sp^2 or sp^3 hybridised)

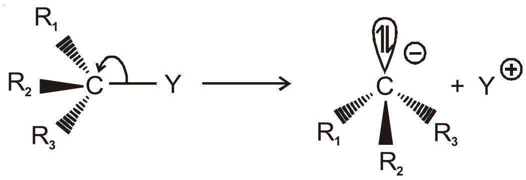
2. **Heterolytic Bond Fission**

(a) In the heterolytic bond fission bonding electron pair may move away from carbon, which results into the formation of carbocation.



[X is more electronegative than carbon]

(b) When bonding pair moves towards carbon



[Y is less electronegative than carbon]

This results in formation of carbanion. (Alkyl carbanion is sp^3 hybridised)

ELECTROPHILE

Electrophiles are electron loving species having at least one vacant orbital in valence shell.

1. Charged electrophiles X , R
2. Neutral Electrophiles : *e.g.,* BH_3, SO_3, $AlCl_3$

Note : *Electrophiles are Lewis acids.*

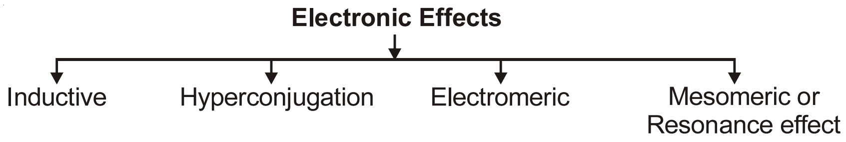
NUCLEOPHILE

Nucleophiles are nucleus loving, they are electron rich having at least one non-bonding pair of electrons in valence shell.

It can be of three types.

1. Charged Nucleophiles - $\overset{\ominus}{H}:$, $\overset{\ominus}{:\ddot{\underset{..}{O}}}-H$, $:\ddot{\underset{..}{I}}:^{\ominus}$ etc.
2. Neutral Nucleophiles - $\ddot{N}H_3$, R $\ddot{O}H$
3. Ambident Nucleophiles - $:\overset{\ominus}{C}$ N: , $\overset{\ominus}{:\ddot{\underset{..}{O}}}-C$ N: (both atoms are nucleophilic centre)

ELECTRONIC EFFECTS



1. Inductive Effect :

The permanent displacement of electrons in a bond towards the more electronegative element is called inductive effect. The effect provides polarity to the molecule. The property of electron withdrawal shown by an atom or group is its (–I) effect and that of donation is called (+I) effect. Electron donation or electron withdrawal is compared with respect to H.

$$CH_3\ \overset{\delta\delta\delta+}{CH_2}\ \overset{\delta\delta+}{CH_2}\ \overset{\delta+}{CH_2}\ \overset{\delta-}{Cl}$$

As shown above the charge decreases from to to position. Hence inductive effect decreases as number of bonds increases.

Order of –I effect : $(CH_3)_3\overset{+}{N} > -NO_2 > -CN > -F > -COOH > -Cl > -Br > -I > -OR > -OH > -NH_2 > C_6H_5- > -H$

Order of +I effect : $(CH_3)_3C- > (CH_3)_2CH- > CH_3-CH_2- > -CH_3 > -H$

Uses of Inductive Effect :

(i) Stability of ions: Stability of ions can be explained by using the concept of inductive effect and hyperconjugation.

(a) Stability of Carbocation

e.g., $(CH_3)_3C$ $(CH_3)_2\ CH$ CH_3CH_2 CH_3

(b) Stability of Carbanions

$(CH_3)_3C^{\ominus}$ $(CH_3)_2CH^{\ominus}$ $CH_3CH_2^{\ominus}$ $CH_3^{\ominus}$ (groups with +I effect decrease the stability of anion)

(ii) Acidic Properties : It is possible to compare the acidic strength of various organic compounds using the inductive effect concept, *e.g.*, in carboxylic acid

The strength of an acid depends upon the ease with which it can ionize to give proton or on the stability of the conjugate bases formed, *i.e*. if the conjugate base formed is more stable, then the acid is more acidic.

Name of Acid	Formula	K_a	Conjugate Base
Fluoroacetic acid (most acidic)	$FCH_2\,COOH$	217×10^{-5}	FCH_2COO^- (most stable)
Chloroacetic acid	$ClCH_2\,COOH$	155×10^{-5}	$ClCH_2–COO^-$
Bromoacetic acid	$BrCH_2COOH$	138×10^{-5}	$BrCH_2COO^-$
Iodoacetic acid	$ICH_2\,COOH$	75×10^{-5}	ICH_2COO^-
Acetic acid (least acidic)	CH_3COOH	1.8×10^{-5}	CH_3 COO (least stable)

Increasing stability of conjugate base increases the acidity of acids.

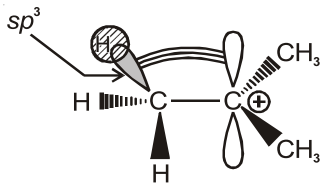
Furthermore, the inductive effect in di and trihalogenated acids is still more marked with the result they are progressively more acidic than the corresponding monohalogenated acids.

e.g., $CHCl_2 – COOH$; $K_a = 514 \times 10^{-5}$

$CCl_3 – COOH$; $K_a = 12100 \times 10^{-5}$

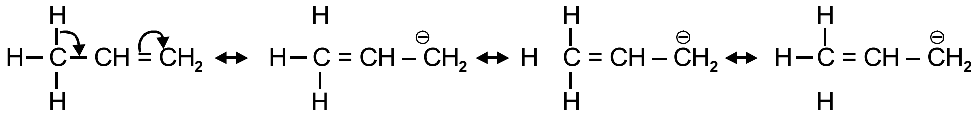
In general, dicarboxylic acids are stronger acids than monocarboxylic acids, since one of the –COOH group shows –I effect.

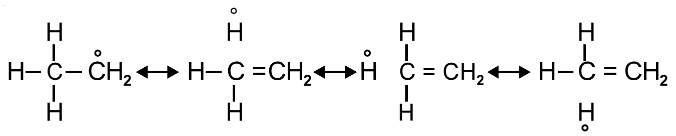
2. **Hyperconjugation :** It is also known as **no-bond resonance**. It involves delocalisation of -electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared orbital (*p* or *d* orbital). Depending on the number of -H, various hyperconjugative structures are possible. Greater the number of hyperconjugative structures, higher would be the stability of given system. It is also a permanent effect.

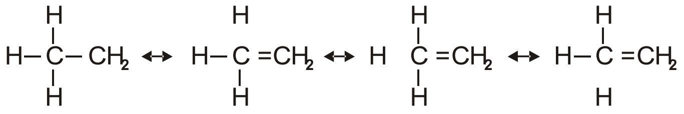


Less effective π overlap (responsible for hyperconjugative effect).

Stability of substituted alkenes, alkyl carbocations, and free radicals can be explained on the basis of hyperconjugation.



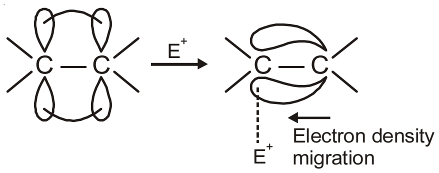




3. **Electromeric Effect :** The temporary electron density charge in substrate in presence of attacking reagent facilitate the attack of attaching reagent is called electromeric effect.

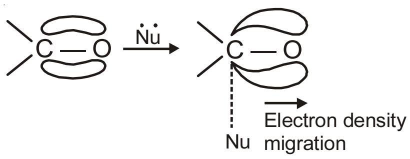
+E effect: When electron density pilled on centre to which attacking reagent attacks then electromeric effect is +E effect, observed in presence of electrophile.

e.g.,



–E effect: When electron density is removed from the centre to which attacking reagent attacks then electronic effect is –E effect, observed in presence of nucleophile.

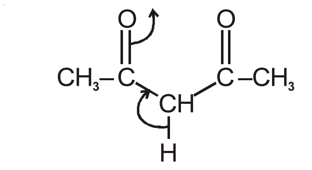
e.g.,



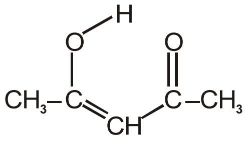
4. **Mesomeric or Resonance Effect :** The effect involves permanent delocalization of conjugated π electrons in a conjugated system. Intermediate structures formed are called resonating structures. The structure that collectively represents all resonating structures is called the resonance hybrid.

Resonating structures are imaginary having no physical significance. The average structure i.e. resonance hybrid represents the actual molecule. Resonance is also known as π-electron delocalisation, which is a permanent effect, it is distance independent effect. Normally this effect is more powerful than hyperconjugative effect.

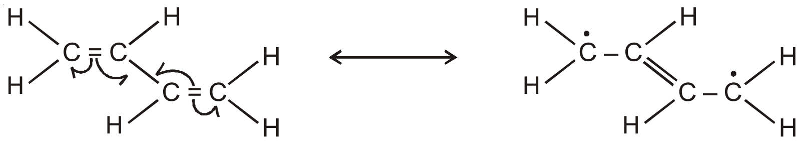
Resonating structures must be valid Lewis structures, they must have same position of atomic nuclei, same number of paired and unpaired electrons and the part of molecule taking part in resonance must be planar.



Position of H atom is changing



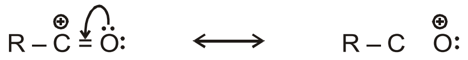
Invalid resonating structure



Invalid resonating structure
Number of unpaired
electrons is changing

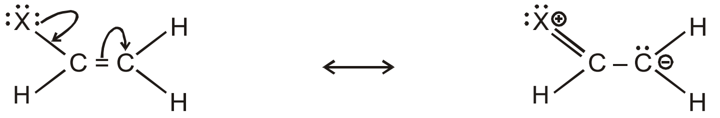
Extent of contribution of various resonating structures:

(a) Resonating structures having maximum number of covalent bonds are more contributing



Less contributing More contributing

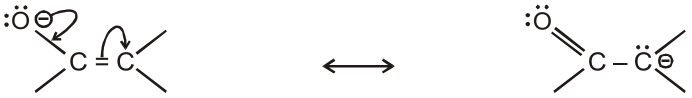
(b) Non charge separated resonating structures are more contributing than charge separated resonating structures.



More contributing

Less contributing

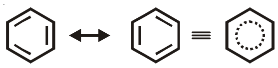
(c) Resonating structure which places negative charge on more electronegative atom is more contributing as compared to resonating structure which places negative charge on less electronegative atom.



More contributing

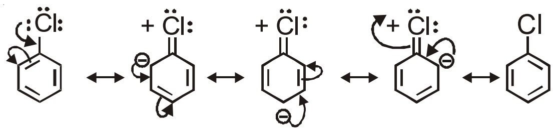
Less contributing

The difference between energies of most stable resonating structure and the resonance hybrid is called the resonance energy of the molecule.



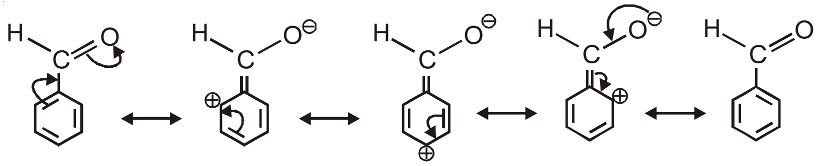
Electron Donating Mesomeric Effect (+M Effect) : Groups with +M effect releases π-electron towards unsaturated system. This effect makes certain positions in the molecule of high electron densities. This effect in chlorobenzene is shown as

+M Effect →



Electron Withdrawing Mesomeric Effect (–M Effect) : This effect is observed when the displacement of π-electrons from unsaturated system is towards the atom or group. This effect in benzaldehyde is shown as

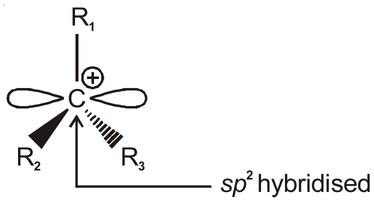
–M Effect →



REACTION INTERMEDIATES

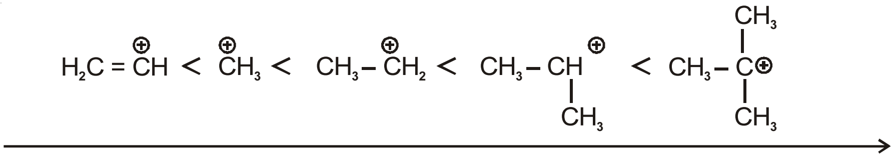
Carbocations :

Structure :

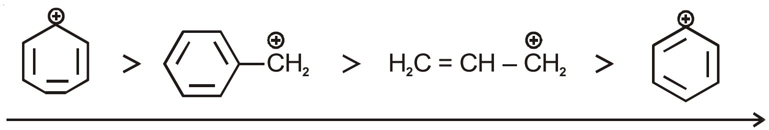


Trigonal planar

Stability: Carbocations are stabilised by electron donating groups and are destabilised by electron withdrawing groups.



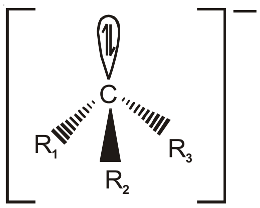
Increasing order of stability with increasing number of electron donating groups



Decreasing order of stability

Carbanions :

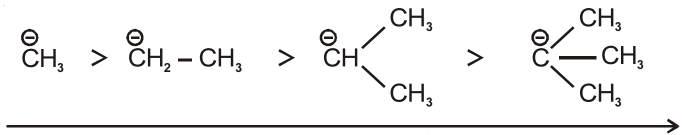
Structure :



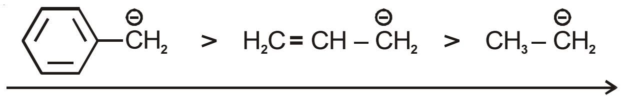
Pyramidal

Carbon bearing the negative charge is sp^3 hybridised, when lone pair on carbon not involve in resonance.

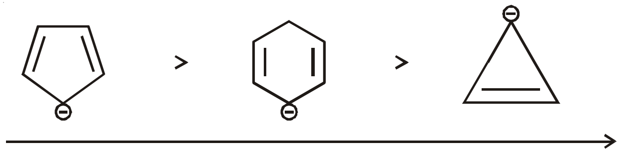
Stability: Carbanions are stabilised by electron withdrawing groups and they are destabilised by electron donating groups



Decreasing order of stability



Decreasing order of stability

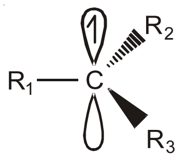


Decreasing order of stability

Carbon Free Radicals

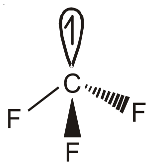
Free radicals are obtained through homolysis of a bond. They have unpaired electron associated with carbon.

Structure : The exact type of hybridisation of the carbon atom bearing an unpaired electron depends on the nature of the substituent. Generally alkyl radicals are planner and as electronegativity of bonded group increase it adopts pyramidal shape *e.g.*, CF_3 is pyramidal. In presence of resonance it surely adopts planner shape.



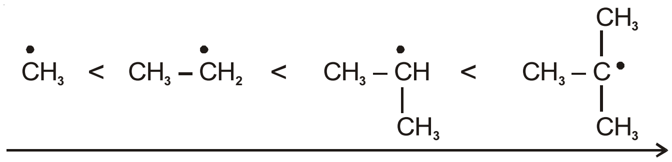
Trigonal planar

Unpaired electron is present in unhybridised p_x orbital



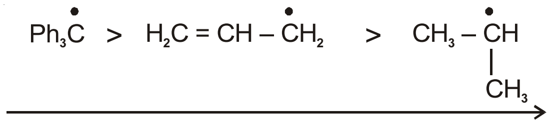
Unpaired electron is present in sp^3 hybridised orbital

Stability : Free radicals are stabilised by resonance, hyperconjugation and steric effect. Both electron donating and electron withdrawing groups stabilize free radicals.



$$\dot{C}H_3 < CH_3-\dot{C}H_2 < CH_3-\underset{\displaystyle CH_3}{\underset{|}{\dot{C}H}} < CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C^{\bullet}}}}}$$

Increasing stability



$$Ph_3\dot{C} > H_2C=CH-\dot{C}H_2 > CH_3-\underset{\displaystyle CH_3}{\underset{|}{\dot{C}H}}$$

Decreasing stability

(a) A free radical combines with other free radical

$$R + R \rightarrow R—R$$

(b) Free radicals may give disproportionation reaction

$$2CH_3\ \ CH_2 \rightarrow CH_2 = CH_2 + CH_3\ \ CH_3$$

DETECTION OF ELEMENTS (Qualitative Analysis)

Element	Sodium Fusion Extract (S.E)	Confirmed Test	Reactions
Nitrogen	$Na + C + N \longrightarrow NaCN$ (S.E)	S.E + $FeSO_4$ + NaOH, boil and cool, + $FeCl_3$ + conc. HCl → Prussian blue or green	$FeSO_4 + 6NaCN \rightarrow$ $Na_4[Fe(CN)_6] + Na_2SO_4$ $3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3$ $\rightarrow Fe_4[Fe(CN)_6]_3 + 6\,Na_2SO_4$ Prussian blue (Ferri Ferrocyanide)
Sulphur	$2Na + S \longrightarrow Na_2S$ (S.E)	(i) S.E + Sodium nitroprusside → Deep violet colour (ii) S.E + $(CH_3COO)_2Pb$ → Black ppt.	$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow$ $Na_4[Fe(CN)_5NOS]$ deep violet $Na_2S + (CH_3COO)_2Pb \rightarrow$ $\underset{\text{(black ppt)}}{PbS} + 2CH_3COONa$

Halogens	$Na + Cl \longrightarrow \underset{(S.E)}{NaCl}$	S.E + $AgNO_3 \to AgX$ (X=Cl, Br, I) (i) White ppt soluble in NH_3(liq) Cl confirms (ii) Pale yellow ppt partially soluble in NH_3(liq) Br confirms (iii) Yellow ppt, insoluble in NH_3(liq) I confirms	$NaX + AgNO_3 \to \underset{ppt}{AgX}$
Nitrogen and Sulphur together	$Na + C + N + S \longrightarrow \underset{(S.E)}{NaCNS}$	As in test for nitrogen instead of green or blue colour, blood red colouration confirms presence of N and S both	$3NaCNS + FeCl_3$ $\to Fe(CNS)_3 + 3NaCl$ blood red (Ferric thiocyanate)

QUANTITATIVE ESTIMATION OF ELEMENTS IN ORGANIC COMPOUNDS

Element	Technique	Formula
Carbon and Hydrogen	(Method) Liebig's Method	$\underset{12g}{C} \to \underset{44g}{CO_2}$ $\quad \% C = \dfrac{12 \times \text{wt. of } CO_2 \times 100}{44 \times \text{weight of organic compound}}$ $\underset{2g}{2H} \to \underset{18g}{H_2O}$ $\quad \% H = \dfrac{2 \times \text{wt. of } H_2O \times 100}{18 \times \text{wt. of organic compound}}$
Nitrogen	(i) Duma's method (ii) Kjeldahl method	(i) $2N \to N_2(g)$ 22.4 L at S.T.P. $\% N = \dfrac{28 \times V \times 100}{22.4 \times \text{wt. of organic compound}}$ where V is the volume of N_2 gas in L at S.T.P. (ii) $N \to NH_3 \quad H_2SO_4$ $\% N = \dfrac{1.4\, N_1V_1}{\text{wt. of organic compound}}$ where, N_1V_1 is the meq. of H_2SO_4 used
Sulphur	Carius method	$\underset{32g}{S} \to H_2SO_4 \to \underset{233g}{BaSO_4}$ $\quad \% S = \dfrac{32 \times \text{wt. of } BaSO_4}{233 \times \text{wt. of org. comp.}} \times 100$
Halogens	Carius method	$\underset{35.5g}{Cl} \to \underset{143.5g}{AgCl}$ $\quad \% Cl = \dfrac{35.5 \times \text{wt. of AgCl} \times 100}{143.5 \times \text{wt. of organic comp.}}$ $\underset{80g}{Br} \to \underset{188g}{AgBr}$ $\quad \% Br = \dfrac{80 \times \text{wt. of AgBr} \times 100}{188 \times \text{wt. of organic comp.}}$ $\underset{127g}{I} \to \underset{235g}{AgI}$ $\quad \% I = \dfrac{127}{235} \times \dfrac{\text{wt. of AgI}}{\text{wt. of organic comp.}} \times 100$
Oxygen		100 – (sum of % of all elements)
Phosphorus	Carius method	$\% P = \dfrac{62}{222} \times \dfrac{\text{wt. of } Mg_2P_2O_7 \text{ formed}}{\text{wt. of organic comp.}} \times 100$

EMPIRICAL AND MOLECULAR FORMULA

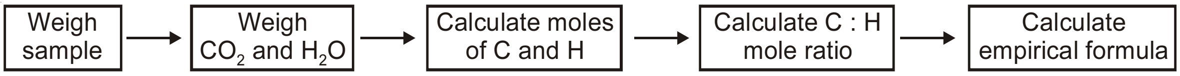
(i) **Empirical Formula of a compound** is the simplest whole number ratio of the atoms of elements constituting its one molecule. The sum of atomic masses of the atoms representing empirical formula is called **empirical** formula mass.

(ii) **Molecular Formula** of a compound shows the actual number of the atoms of the elements present in its one molecule. The sum of atomic masses of the atoms representing molecule is called **molecular mass**.

(iii) **Relationship between Empirical Formula and Molecular Formula**

Molecular formula = n × empirical formula where n is a simple whole number having values of 1, 2, 3... etc.

Also, n = Molecular formula mass/Empirical formula mass.



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Chapter 12

Hydrocarbons and Environmental Chemistry

HYDROCARBONS

ALKANES

Methods of Preparation :

I. Reactions where number of carbon atoms are increased

1. Wurtz Reaction

$$2R\quad X+2Na \xrightarrow{\text{dry ether}} R\quad R+2NaX$$

Here other metals in the finely divided state may also be used such as Cu, Ag etc.

(i) Methane cannot be prepared by this method.

(ii) Only symmetrical alkane with even number C-atoms can be prepared by this method in good yield.

(iii) The reaction fails with 3°-alkyl halides.

(iv) Alkenes are produced as by products.

2. Corey-House Synthesis:

$$R\text{-}X+2Li \quad \rightarrow RLi+LiX$$

$$2RLi+CuI \quad \rightarrow R_2LiCu+LiI$$

(i) R_2LiCu also known as Gilman reagent.

(ii) This reaction proceeds via S_N2 mechanism.

(a) $R_2LiCu+2R\quad X \quad \rightarrow 2R\quad R+LiX+CuX$ (R – X may be 1° or 2° only)

(b) $R_2LiCu+2R\quad X \quad \rightarrow 2R\quad R+LiX+CuX$ (R – X may be 1° or 2° only)

It can be used for preparing both symmetrical and unsymmetrical alkanes.

3. Kolbe's Electrolytic Decarboxylation

$$2RCOONa\ (aq) \xrightarrow{\text{electrolysis}} R\text{-}R+2NaOH+2CO_2+H_2$$

Mechanism:

$RCOONa \longrightarrow RCOO^- + Na^+$

$2H_2O \rightleftharpoons 2H^+ + 2OH^-$

Anodic Reaction

$2RCOO^- \longrightarrow 2RCOO^\bullet + 2e^-$

$2RCOO^\bullet \longrightarrow R - R + 2CO_2$

Cathodic Reaction

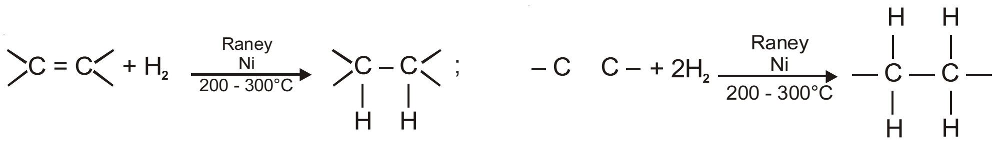
$2H^+ + 2e^- \longrightarrow H_2$

(i) Methane cannot be prepared by this method

(ii) Unsymmetrical hydrocarbon (alkane) cannot be prepared

II. Reactions where number of carbon atoms are retained

1. Sabatier-Senderen's Reduction



2. Reduction of Alkyl Halides

(a) $R \quad X + Zn \xrightarrow{HCl} R \quad H + HX$

Zn – Cu and C_2H_5OH or Na and alcohol can also be used

(b) $4R–X + LiAlH_4 \longrightarrow 4RH + LiX + AlX_3$

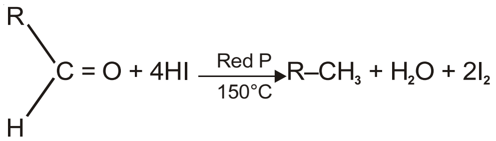
This is a nucleophilic substitution reaction with the nucleophile H^- coming from $LiAlH_4$.

(c) $R – X + (n – C_4 H_9)_3SnH \longrightarrow R – H + (n –C_4H_9)_3SnX$. (This reaction follows free radical mechanism)

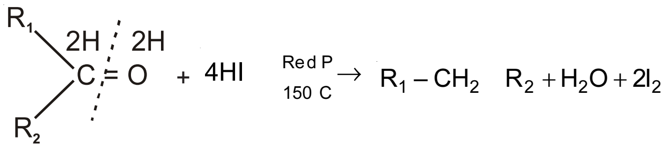
3. Reduction of Alcohols, Aldehydes, Ketones and Carboxylic Acids with HI/Red P.

(a) $ROH + 2HI \xrightarrow[150\ C]{Red\ P} R \quad H + I_2 + H_2O$

(b)

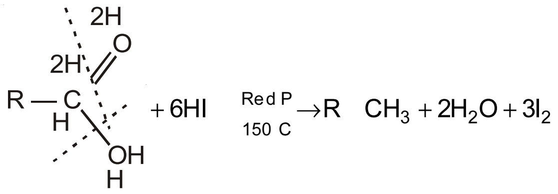


$RHC = O + 4HI \xrightarrow[150°C]{Red\ P} R–CH_3 + H_2O + 2I_2$



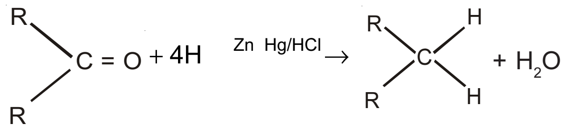
$R_1R_2C = O + 4HI \xrightarrow[150\ C]{Red\ P} R_1 - CH_2 \quad R_2 + H_2O + 2I_2$

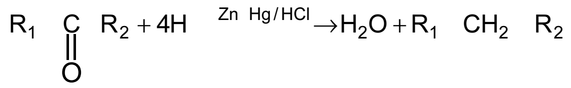
(c)



$RCOOH + 6HI \xrightarrow[150\ C]{Red\ P} R \quad CH_3 + 2H_2O + 3I_2$

(d) Clemmensen's Reduction

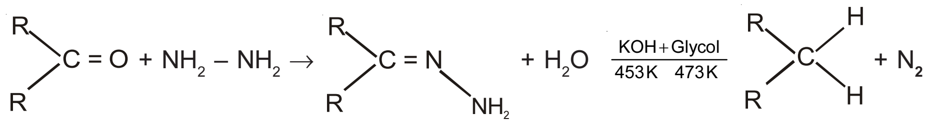




$$R_1 \underset{\underset{O}{\|}}{C} R_2 + 4H \xrightarrow{Zn\ Hg/HCl} H_2O + R_1\ CH_2\ R_2$$

When acid sensitive group is present in a compound, Clemmensen's reduction is not used.

(e) Wolff-Kishner's Reduction:



When base sensitive groups are present in the compound, Wolff-Kishner's reduction is not used.

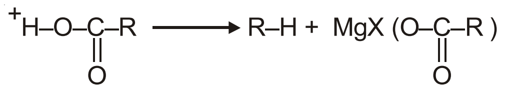
4. **(a) Using Grignard's Reagent**

$R - X + Mg \xrightarrow{ether} RMgX$

$RMgX + H - OH \longrightarrow R - H + MgX(OH)$

$+ H - NH_2 \longrightarrow R - H + MgX(NH_2)$

$+ H - OR \longrightarrow R - H + MgX(OR\ \ )$



$$+H{-}O{-}\underset{\underset{O}{\|}}{C}{-}R \longrightarrow R{-}H + MgX\,(O{-}\underset{\underset{O}{\|}}{C}{-}R\,)$$

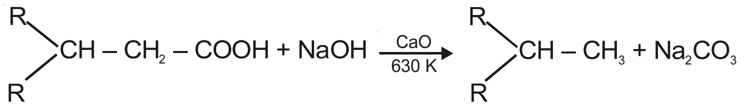
(b) Using Alkyl lithium compound

$R\ NH_2 + R{-}Li \longrightarrow (R\,NH)\,Li + R - H.$

III. Reaction where number of carbon atoms are decreased

Decarboxylation by sodalime

$$RCOONa + NaOH \xrightarrow[630k]{CaO} R - H + Na_2CO_3$$



IV. Some other methods of preparation

(1) **Methane from carbides**

(a) $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

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

(2) **Methane from carbon monoxide**

$$CO + 3H_2 \xrightarrow[250\ C]{Ni+C} CH_4 + H_2O$$

This is also called **Sabatier Senderen's** reduction

Physical Properties

Boiling Point (B.P.)

B.P. increases with the increase of molecular mass. Among the isomers, straight chain alkanes have higher b.p. than branched chain alkanes.

Melting Point (M.P.)

The melting points do not show regular variation with increase in molecular size. The even number members have higher m.p. as compared to next alkanes with odd number of carbon atoms (ALTERATION EFFECT).

Solubility

They are soluble in non-polar solvents. Hence, insoluble in polar solvents such as water.

Chemical Properties

Alkanes are generally inert towards acids, bases, oxidising and reducing agents but they give following reactions:

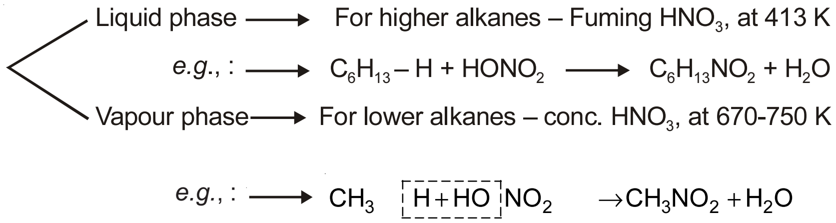
(1) Halogenation. Alkanes undergoes substitution reaction with halogen. Cl_2 and Br_2 only in presence of ultra violet light or high temperature (573 – 773K).

Decreasing order of reactivity of halogens towards alkanes.

$F_2 > Cl_2 > Br_2 > I_2$

Fluorination and chlorination are less selective as these reagents are more reactive, while bromination of alkane is more selective (less reactive).

(2) Nitration :



Liquid phase ⟶ For higher alkanes – Fuming HNO_3, at 413 K

e.g., : $\longrightarrow C_6H_{13}-H + HONO_2 \longrightarrow C_6H_{13}NO_2 + H_2O$

Vapour phase ⟶ For lower alkanes – conc. HNO_3, at 670-750 K

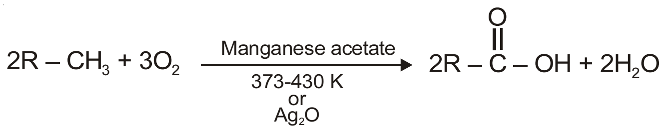
e.g., : $\longrightarrow CH_3\ \boxed{H+HO}\ NO_2 \rightarrow CH_3NO_2 + H_2O$

(3) Oxidation :

(a) $2CH_4 + O_2 \xrightarrow[573\ K/100\ atm]{Cu} 2CH_3OH$

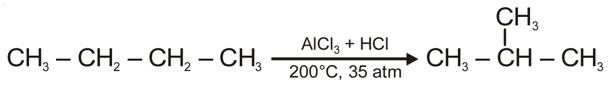
(b) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

(c)

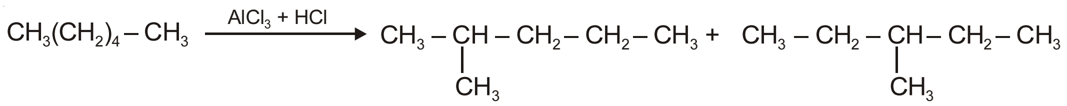


$$2R-CH_3 + 3O_2 \xrightarrow[\substack{373\text{-}430\ K \\ or \\ Ag_2O}]{\text{Manganese acetate}} 2R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 2H_2O$$

(4) Isomerization :



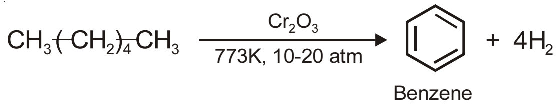
$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[200°C,\ 35\ atm]{AlCl_3 + HCl} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

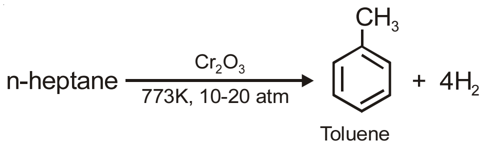


$$CH_3(CH_2)_4-CH_3 \xrightarrow{AlCl_3 + HCl} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_2-CH_3 + CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$$

2-methyl pentane 3-methyl pentane

(5) Aromatization :





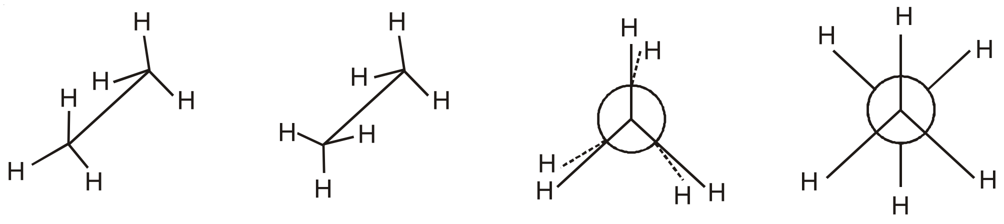
(6) Reaction with steam :

$$CH_4 + H_2O \xrightarrow{Ni} CO + 3H_2$$

Conformations of Alkanes

When different three dimensional arrangements are possible for a compound due to rotation along a single bond, then these different arrangements are known as conformers and the phenomenon is known as conformation. In fact C–C rotation is hindered by an energy barrier of **1 to 20 kJ mol^{-1}**. There are infinite number of conformers possible. Out of infinite number of conformers, extremes can be discussed as

Conformers of ethane :

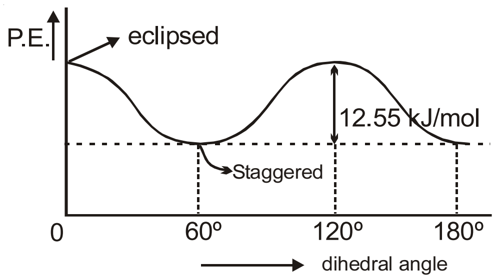


Eclipsed Staggered Eclipsed Staggered

Sawhorse projection Newmann projection

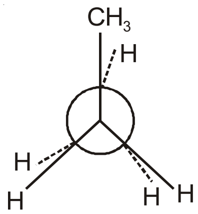
(i) It may be noted that one extreme conformation of ethane can be converted into other extreme conformer by rotation of 60° about C–C bond.

(ii) Skew conformers have energy in between staggered and eclipsed.

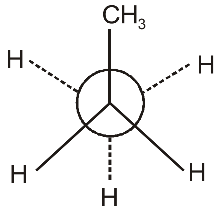


$$\xrightarrow[\text{Decreasing order of stability}]{\text{Staggered > Skew or Gauche > Eclipsed}}$$

Conformers of propane :

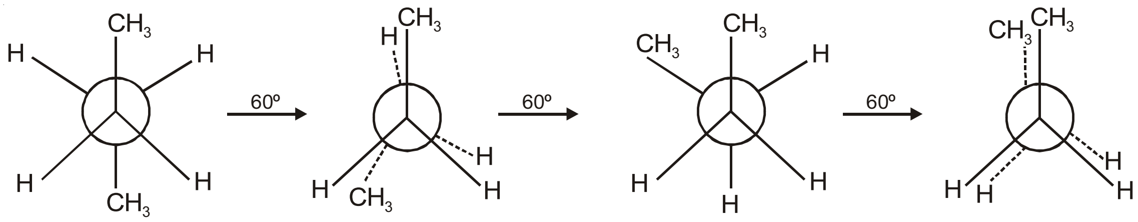


Eclipsed



Staggered

Conformers of Butane :

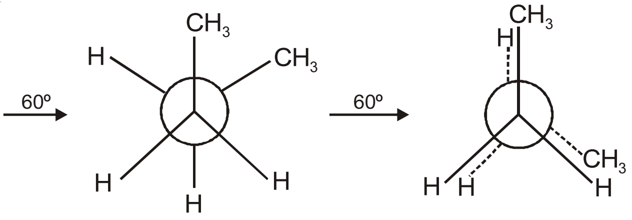


(I)
Staggered

(II)
Partially eclipsed

(III)
Gauche

(IV)
Fully eclipsed

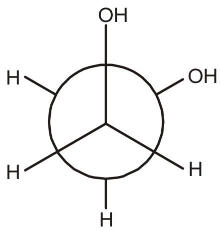


(V)
Gauche

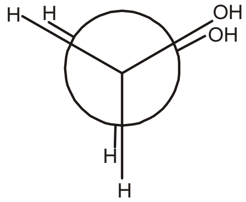
(VI)
Partially eclipsed

Stability order : I > III V > II VI > IV

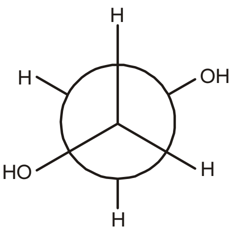
Conformers of Ethlene glycol (HO – CH_2 – CH_2 – OH):



(a)
[Gauche]
(Intramolecular
hydrogen bonding)



(b)
[Eclipsed]
(Have also intramolecular hydrogen
bonding but also have torsional strain)



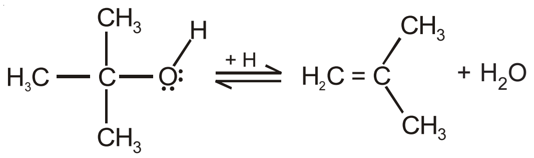
(c)
[Anti]

Stability order : Gauche > Anti > Eclipsed

ALKENES

Preparations of Alkenes

From Alcohols: When alcohol is treated with conc. acids (H_2SO_4, H_3PO_4) at higher temperature alkene is obtained.



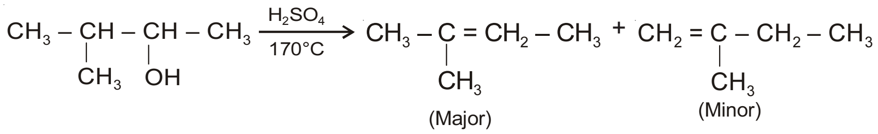
Acid catalyzed dehydration of alcohol is a reversible reaction. Alcohols can be converted to alkene in the presence of conc. H^+, while alkenes can be converted to alcohol in the presence of dilute H^+.

The ease of dehydration of alcohols depends on the stability of carbocations formed. Hence, the order of reactivity of alcohols is *ter–> sec–> pri–* because the incipient carbocation stability is *ter–> sec–> pri–*

> ***Note :*** *Since the carbocation stability is the primary criteria, so, the initially formed carbocation undergoes molecular rearrangement to give more stable carbocation.*

Hydride shift

Example (Hydride shift)



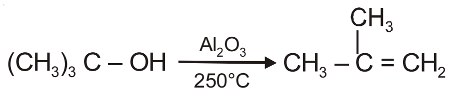
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[170^\circ C]{H_2SO_4} \underset{\text{(Major)}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2-CH_3} + \underset{\text{(Minor)}}{CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3}$$

(i) Dehydration of alcohols follow Saytzeff's rule.

Product (A) is the major product because it is more substituted alkene.

(ii) Dehydration by passing over alumina (Lewis Acid)

$$CH_3-CH_2-OH \xrightarrow[350^\circ C]{Al_2O_3} CH_2=CH_2+H_2\,O$$



$$(CH_3)_3\,C-OH \xrightarrow[250^\circ C]{Al_2O_3} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

I. Dehydrohalogenation of alkyl halides

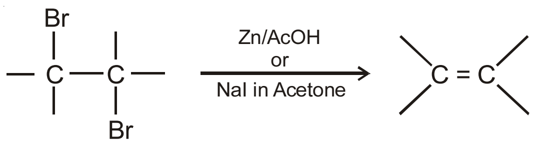
$$CH_3-CH_2-CH_2-CH_2-Br \xrightarrow{\text{alc KOH}} CH_3-CH_2-CH=CH_2$$

(i) The base used may be strongly basic anions like OH^-, RO^-, $C_2H_5O^-$.... $(CH_3)_3CO^-$ etc.)

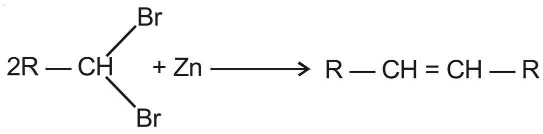
(ii) Alkyl substrates with good leaving group (X^-, etc) give good yield of elimination product.

(iii) One may also use sulphonates.

II. Dehalogenation reactions of vicinal dihalide :

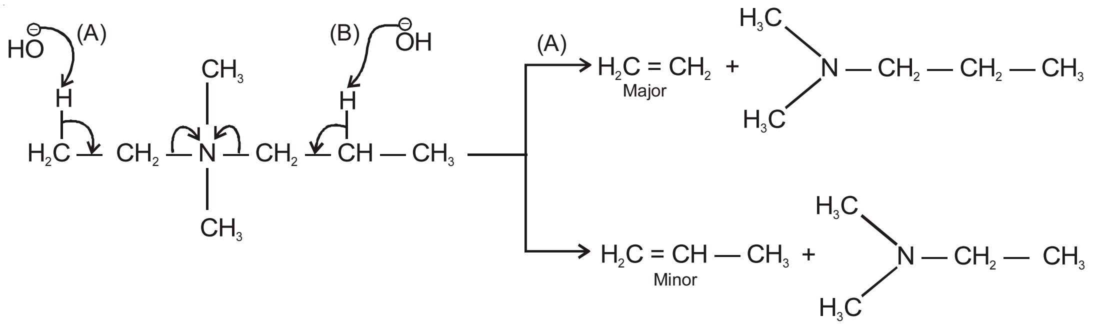


III. Dehalogenation of Geminal dihalide :

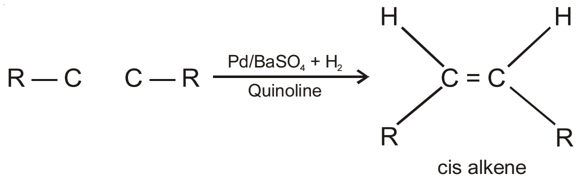


$$2R-CHBr_2 + Zn \longrightarrow R-CH=CH-R$$

IV. By heating Quaternary ammonium hydroxide again Hofmann elimination occurs and less substituted alkene is formed as the major product :



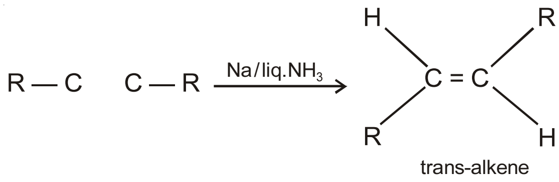
V. By catalytic hydrogenation of alkyne :



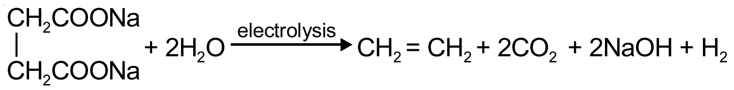
Lindlar's catalyst = Pd supported on $BaSO_4$ or $CaCO_3$ and poisoned with quinoline.

P–2-Catalyst = Nickel boride (Ni_2B) is known as P-2 catalyst.

VI. Under the presence of alkali metals in liquid ammonia, substituted alkynes are converted into trans-alkene. It is important to remember that terminal alkynes do not give this reaction.



VII. Kolbe's Electrolysis



$$\begin{array}{l} CH_2COONa \\ | \\ CH_2COONa \end{array} + 2H_2O \xrightarrow{\text{electrolysis}} CH_2=CH_2 + 2CO_2 + 2NaOH + H_2$$

Sodium succinate

Mechanism follows free radical pathway.

VIII. Pyrolysis

$CH_3CH_2CH_2CH_3 \xrightarrow[770K]{} CH_3–CH=CH_2 + CH_4$

$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow[770K]{} CH_3CH=CH_2 + CH_3CH_2CH_3$ **+ ....**

Physical Properties

Solubility

They are insoluble in water but soluble in organic solvents.

Boiling point

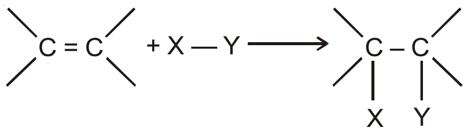
The boiling point of cis–alkenes is usually higher than corresponding trans–alkenes (More polarity).

Melting point

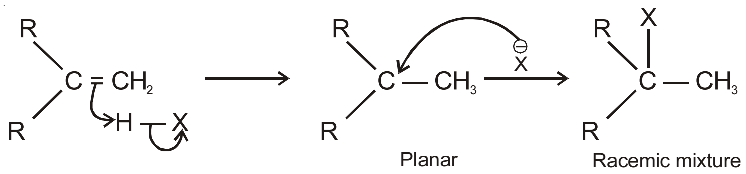
The melting point of trans-alkenes is usually greater than cis-alkene. (trans form is more symmetrical).

Chemical Properties

Electrophilic addition reaction is the most important reaction of alkenes and alkynes. Beside electrophilic addition reaction, it also gives Free radical addition, hydrogenation and oxidation reactions.



1. **Addition of Hydrogen halide (HX)**

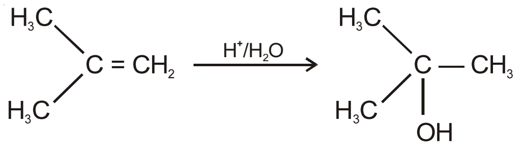


Planar Racemic mixture

As the reaction proceeds through cabocationic intermediate it results into racemization.

HI (strong acid) is most reactive while HF is least reactive.

2. **Acid catalysed hydration of alkenes :**



This reaction also involves carbocation reactive intermediate.

3. **Halogenation of alkenes :**

This reaction proceeds through cyclic halonium ion complex and hence it is a stereoselective reaction.

Note : *Trans-symmetrical alkenes give meso-dibromo product*

4. **Addition of Hypohalous Acid (HOX) :**

$$H_2O + Br_2 \quad \rightarrow HOBr$$

In this reaction, X_2 or X acts as an electrophile and H_2O acts as nucleophile

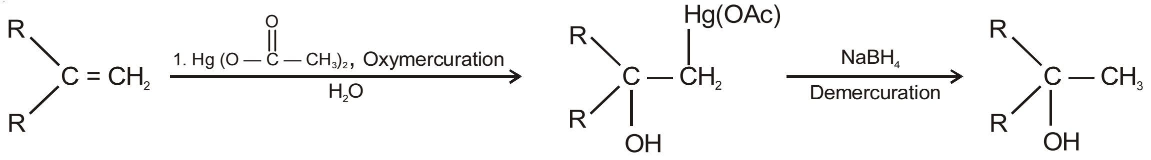
Kharasch - Mayo Effect (Anti-Markownikoff's rule)

If the above reaction is carried out in the presence of some peroxide then addition takes place contrary to Markownikoff's Rule.

$$CH_3 - CH = CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} CH_3 - CH_2 - CH_2 - Br$$

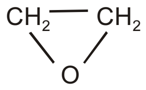
> ***Note :*** *Only HBr adds to unsymmetrical double bond according to anti-Markownikoff's rule. Other HX (HF, HCl and HI) do not give peroxide effect.*

5. **Oxy-Mercuration-Demercuration**

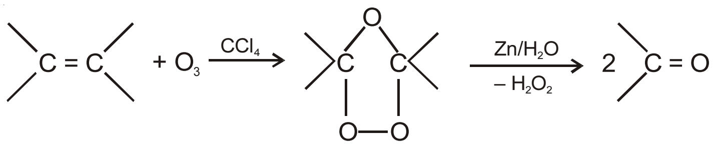


6. **Addition of Oxygen:**

$$CH_2 = CH_2 + ½\ O_2 \xrightarrow[570\ K]{Ag}$$



7. **Ozonolysis:**



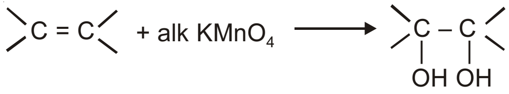
8. **Hydroboration Oxidation**

$$R \quad CH = CH_2 + B_2H_6 \xrightarrow[\text{ether}]{0°C} (R \quad CH_2 \quad CH_2)_3B \xrightarrow[OH^-]{H_2O_2} R \quad CH_2 \quad CH_2 \quad OH + H_3BO_3$$

Hydroboration oxidation reaction gives overall anti-Markownikoff's product. There is no rearrangement in this reaction.

9. **Oxidation Reactions**

(a) Reaction with Baeyer's Reagent (Cold dilute Alkaline $KMnO_4$, syn-dihydroxylation.)



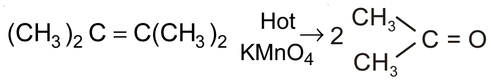
The addition is a syn addition to form vicinal dihydroxy compounds.

> ***Note :*** *Decolorization of Baeyer's reagent is also used as a test for unsaturation.*

(b) With hot $KMnO_4$ or acidic $KMnO_4$

$$CH_2 = CH_2 \xrightarrow[\text{Hot } KMnO_4]{[O]} 2HCOOH \rightarrow 2CO_2 + 2H_2O$$

$$CH_3 \quad CH = CH_2 \xrightarrow[H^+]{KMnO_4} CH_3COOH + CO_2 + H_2O$$



$$(CH_3)_2C = C(CH_3)_2 \xrightarrow[KMnO_4]{Hot} 2\ \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = O$$

10. Substitution Reaction

$$CH_3–CH = CH_2 + Cl_2 \xrightarrow{500\ \ 600\ C} Cl–CH_2–CH{=}CH_2 + HCl$$

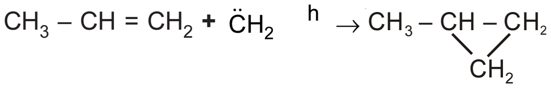
This type of reaction takes place at a carbon atom attached to double bond carbon. This is called allylic substitution.

11. Wohl Ziegler Reaction

$$CH_3 – CH = CH_2 + Br_2 \xrightarrow{\text{Low conc. of } Br_2} CH_2 = CH–CH_2–Br$$

The low concentration of Br_2 is obtained from NBS

12. Addition of Carbenes



$$CH_3 – CH = CH_2 + \ddot{C}H_2 \xrightarrow{h} CH_3 – \underset{\diagdown\ \diagup \atop CH_2}{CH – CH_2}$$

13. Isomerization :

$$CH_2 – CH_2 – CH_2 – CH = CH_2 \xrightarrow[\text{or } Al_2(SO_4)_3;\ 470\ K]{700 - 970\ atm} CH_3 – CH_2 – CH = CH – CH_3$$

14. Polymerization :

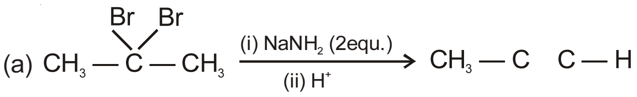
$$CH_2 = CH_2 \xrightarrow[O_2]{Pressure} –(CH_2 – CH_2)_n–$$

$$CF_2 = CF_2 \xrightarrow[O_2]{} –(F_2C – CF_2)_n–$$

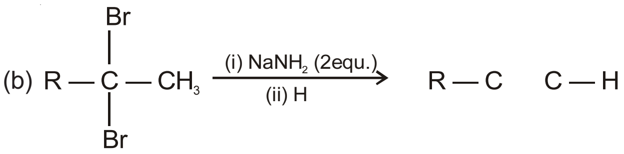
ALKYNES

Preparation of Alkynes

1. From Dehydrohalogenation of vicinal or geminal dihalides



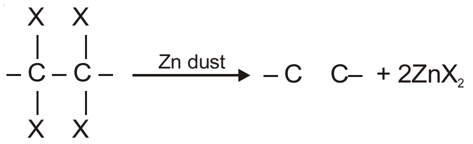
(a) $CH_3 — \overset{Br\ \ Br}{C} — CH_3 \xrightarrow[(ii)\ H^+]{(i)\ NaNH_2\ (2equ.)} CH_3 — C \quad C — H$



(b) $R — \underset{Br}{\overset{Br}{C}} — CH_3 \xrightarrow[(ii)\ H]{(i)\ NaNH_2\ (2equ.)} R — C \quad C — H$

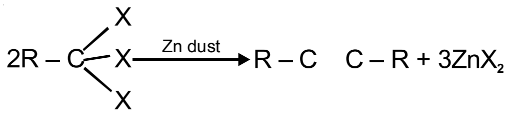
2. **Dehalogenation Reaction**

(a)



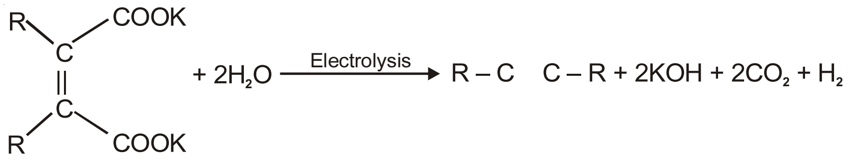
$$-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}- \xrightarrow{\text{Zn dust}} -C \quad C- + 2ZnX_2$$

(b)



$$2R-CX_3 \xrightarrow{\text{Zn dust}} R-C \quad C-R + 3ZnX_2$$

3. **Kolbe's Electrolytic Decarboxylation**



$$R(COOK)C{=}C(COOK)R + 2H_2O \xrightarrow{\text{Electrolysis}} R-C \quad C-R + 2KOH + 2CO_2 + H_2$$

cis or trans

4. **Formation of Higher alkyne**

(i) $CH \quad CH \xrightarrow{NaNH_2} CH \quad \bar{C}\overset{+}{Na} + NH_3$

$CH \quad \bar{C}\ \overset{+}{Na} + CH_3Cl \longrightarrow CH \quad C-CH_3 + NaCl$

(ii) $R{-}C \quad CH + NaNH_2 \longrightarrow RC \quad \bar{C}\overset{+}{Na} + NH_3$

$R{-}C \quad \bar{C}\ \overset{+}{Na} + R\ X \longrightarrow R{-}C \quad C{-}R + NaX$

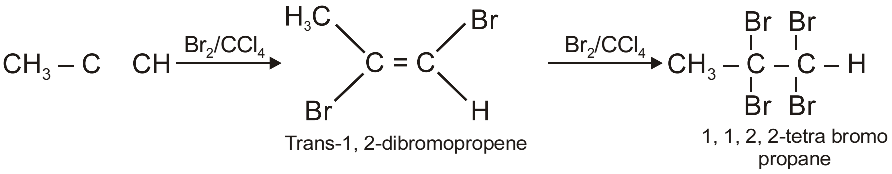
Chemical Properties

Alkynes undergo electrophilic addition generally but in the presence of salt of heavy metals which forms complexes with multiple bonds they undergo nucleophilic addition reaction.

1. **Addition Reaction**

Electrophilic addition reaction :

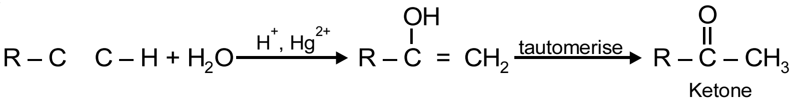
(i) Addition of halogen



(ii) Addition of halogen acids

$$HC \quad CH \xrightarrow[CH_3COOH]{HCl} \underset{\text{Vinyl chloride}}{CH_2 = CHCl} \xrightarrow[CH_3COOH]{HCl} \underset{\text{Ethylidene chloride}}{CH_3CHCl_2}$$

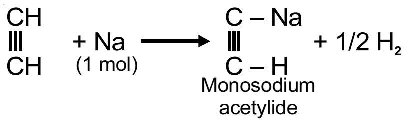
(iii) Addition of H_2O or hydration of alkyne or Kucherov reaction



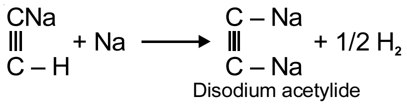
$$R-C \quad C-H + H_2O \xrightarrow{H^+,\ Hg^{2+}} R-\overset{OH}{C} = CH_2 \xrightarrow{\text{tautomerise}} \underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-CH_3}$$

2. **Reaction of Acidic H Atom**

   (i) Alkynes having acidic H atom react with metals like Na, K to evolve H_2 gas.



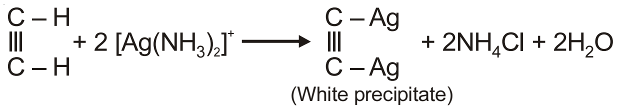
$$\begin{array}{c}CH\\ |||\\ CH\end{array} + \underset{(1\ mol)}{Na} \longrightarrow \underset{\text{Monosodium acetylide}}{\begin{array}{l}C-Na\\ |||\\ C-H\end{array}} + 1/2\ H_2$$



$$\begin{array}{l}CNa\\ |||\\ C-H\end{array} + Na \longrightarrow \underset{\text{Disodium acetylide}}{\begin{array}{l}C-Na\\ |||\\ C-Na\end{array}} + 1/2\ H_2$$

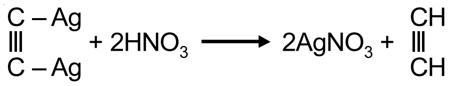
$$HC\quad C\quad H + NaNH_2 \rightarrow HC\quad \overset{\ominus}{C}Na + NH_3 \quad \xrightarrow{NaNH_2} Na\overset{\ominus}{C}\quad \overset{\ominus}{C}Na + NH_3$$

   (ii) **Reaction with Tollens reagent :** When terminal alkyne reacts with Tollen's reagent (Ammoniacal $AgNO_3$ solution) white precipitate of silver acetylide is obtained,



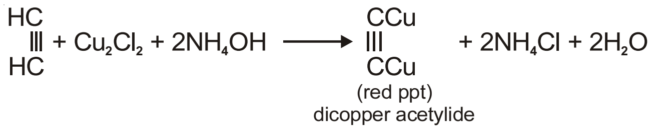
$$\begin{array}{l}C-H\\ |||\\ C-H\end{array} + 2\,[Ag(NH_3)_2]^+ \longrightarrow \underset{\text{(White precipitate)}}{\begin{array}{l}C-Ag\\ |||\\ C-Ag\end{array}} + 2NH_4Cl + 2H_2O$$

   These acetylides are not decomposed by H_2O like acetylide of Na but by mineral acids like dil HNO_3.



$$\begin{array}{l}C-Ag\\ |||\\ C-Ag\end{array} + 2HNO_3 \longrightarrow 2AgNO_3 + \begin{array}{l}CH\\ |||\\ CH\end{array}$$

   (iii) **Reaction with Ammonical Cuprous Chloride :**

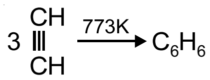


$$\begin{array}{l}HC\\ \ |||\\ HC\end{array} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{(red ppt)}\\ \text{dicopper acetylide}}}{\begin{array}{l}CCu\\ |||\\ CCu\end{array}} + 2NH_4Cl + 2H_2O$$

   These reactions are used to distinguish terminal alkynes from other alkynes.

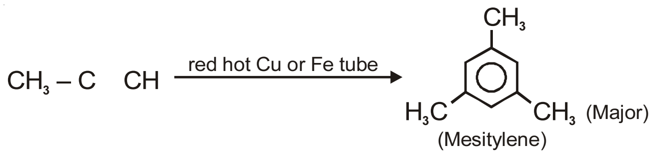
3. **Polymerization Reaction**

   (i) When acetylene is passed through red hot Cu tube, benzene is obtained.

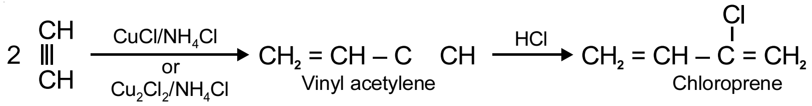


$$3\begin{array}{l}CH\\ |||\\ CH\end{array} \xrightarrow{773K} C_6H_6$$

Similarly,



   (ii)



$$2\begin{array}{l}CH\\ |||\\ CH\end{array} \xrightarrow[Cu_2Cl_2/NH_4Cl]{CuCl/NH_4Cl\ \text{or}} \underset{\text{Vinyl acetylene}}{CH_2=CH-C\quad CH} \xrightarrow{HCl} \underset{\text{Chloroprene}}{CH_2=CH-\overset{\overset{Cl}{|}}{C}=CH_2}$$

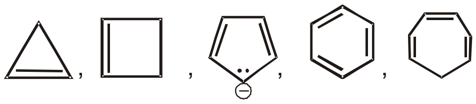
   Chloroprene on polymerization gives polymer called neoprene; used as artificial rubber.

AROMATIC HYDROCARBONS

Huckel's rule of Aromaticity : Cyclic, conjugated, planar and having (4n + 2) π electrons.

where, n = 0, 1, 2, 3 ... (Any positive integer including zero)

Few Examples of Aromatic Species :

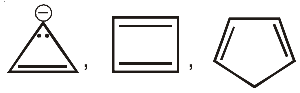


Aromatic ions are more stable than corresponding acyclic non-aromatic ions.

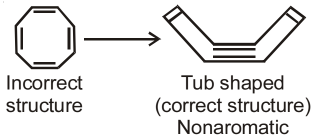
Antiaromatic Compounds :

Antiaromatic compounds are cyclic, conjugated, planar and contain 4nπ electrons (where n is a positive integer) Anti-aromatic compounds are less stable than acyclic counter part.

Examples :

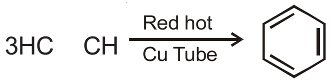


It is important to note that cyclooctatetraene is a nonaromatic compound because it is non-planar.



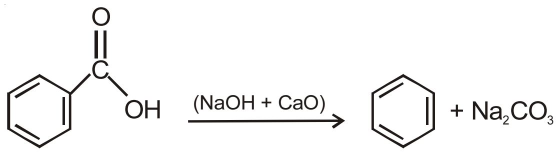
Stability order : Aromatic Non-aromatic Anti-aromatic

Preparation of Benzene :

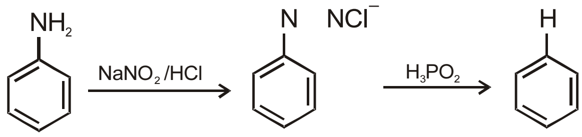
1. 

2. When phenol is treated with Zn dust, benzene is obtained :

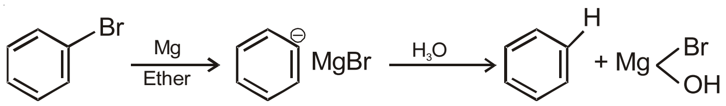
3. From the decarboxylation of benzoic acid :



4. Deamination of aniline through benzene diazonium chloride will give benzene.



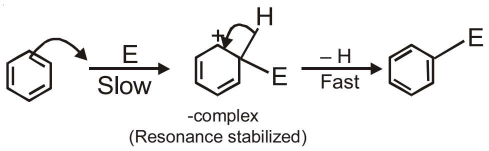
5. Through Grignard reagent.



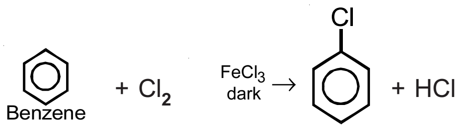
1. **Electrophilic Aromatic substitution reactions in Benzene : (EAS)**

Benzene and its homologues readily undergo EAS. As a consequence of complete delocalization of π electrons in benzene, it has π electron cloud above and below -plane allowing it to interact with electrophiles and give electrophilic substitution reaction. It resists addition because it wants to maintain its aromatic character.

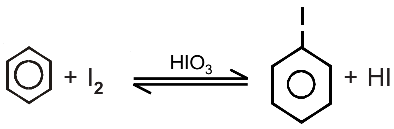
General Mechanism :



(i) Halogenation

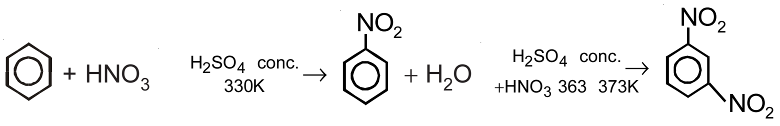


Reaction with I_2 is reversible.



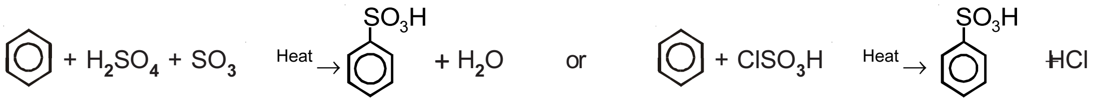
Hence, it is carried out in the presence of conc. nitric acid or HIO_3 to oxidise the Hydrogen Iodide formed.

(ii) Nitration



Nitro benzene meta-dinitrobenzene

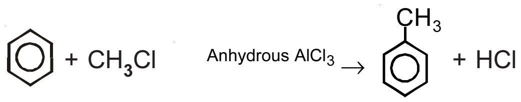
(iii) Sulphonation : Sulphonation of benzene is a reversible reaction

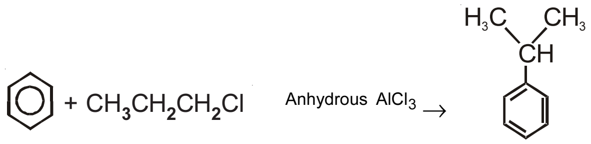


Chloro Sulphuric Acid Benzene sulphonic acid

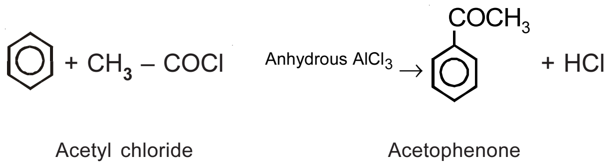
(iv) Friedel Crafts Reaction

Alkylation : Reactive intermediate is carbocation which can undergo rearrangement.





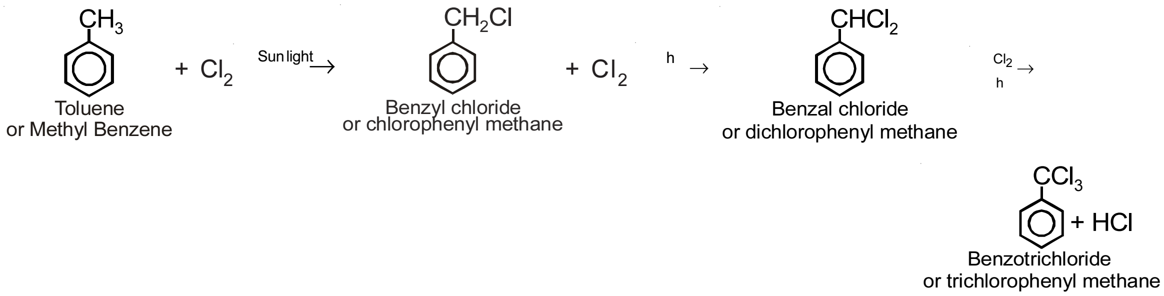
Acylation : Reactive intermediate is acylium ion $\left(\begin{array}{c} :O: \\ \| \\ R-C^+ \end{array}\right)$ which cannot undergo rearrangement.



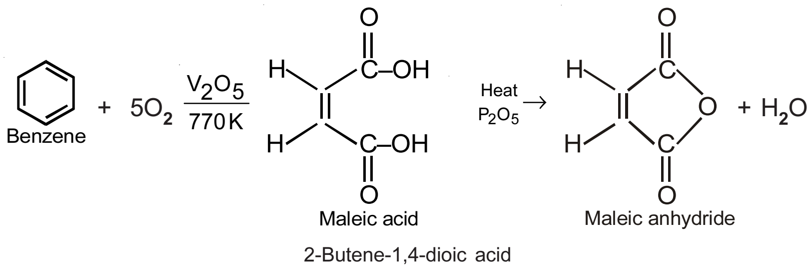
Ortho and para substitution : Electron releasing groups like - R (alkyl) $-\ddot{\underset{..}{O}}H$, $-\ddot{\underset{..}{O}}R$, $-\ddot{N}HR$, $-\ddot{N}HCOR$ are activating groups *i.e.,* they increase electron density at ortho and para position, therefore, are ortho and para directing towards electrophilic substitution reactions.

Meta substitution : Electron withdrawing groups such as $-NO_2$, – CHO, – COOH, $-COCH_3$, – CN, $-SO_3H$, – COOR are called deactivating groups. They decrease electron density at ortho and para-position, therefore, electrophilic substitution takes place at meta-position.

2. Halogenation of side chain :



3. Oxidation :



ENVIRONMENTAL CHEMISTRY

ENVIRONMENTAL POLLUTANTS

Any substance which causes pollution in the environment is known as **environmental pollutant.** It can be atmospheric, water and soil pollution.

WATER POLLUTION

The quality of drinking water is very important for human welfare. The pollution of water by sewage has been linked with the spreading of diseases such as cholera and typhoid fever.

In addition, water is also contaminated by industrial wastes, like :

(i) Heavy Metals : Such as Cd, Pb and Hg may be present.

(ii) Detergent and Fertilizers : They may contain PO_4^{-3} as additives which encourages the growth of algae that reduces the dissolved oxygen concentration of water. This process is known as Eutrophication.

(iii) Acid Polluted Water (pH < 3) : This is deadly to most forms of aquatic life.

(iv) Polychlorinated Biphenyls (PCBs) : PCBs are resistant to oxidation and their release into the environment causes skin disorders in humans. They are reported to be carcinogenic.

Determination of quality of waste water : It is done through BOD and COD.

Biological Oxygen demand (BOD) - It is the amount of oxygen required for biological oxidation by microbes in any unit volume of water. This test is done for at least 5 days. BOD values generally approximates the amount of oxidisable organic matter.

Chemical oxygen demand (COD) : BOD measurement takes few days, so another parameter called COD measurement is required. In COD measurement sample of fixed volume is treated with oxidising agent (usually $K_2Cr_2O_7$ in acidic medium). The reagent oxidises most of the polluting substances including those which are resistant to microbial oxidation.

AIR POLLUTION

Air is very essential for life, particularly oxygen which is needed for breathing. But at the same time air is polluted due to various human activities. Man made, pollutants such as gases like CO, NO, NO_2 , SO_2 , H_2SO_4, hydrocarbons and aerosols etc are being constantly released in the atmosphere leading to air pollution.

Atmospheric Pollution

Tropospheric pollution : Troposphere extends upto height of 10 km from sea level. It contains 80% of total mass of air and water vapour. Pollution is also caused by SO_2, SO_3, NO_2 etc.

Stratospheric pollution : Extends (10–50) km above sea level. It contains N_2, O_2 and ozone.

Table : Sources of Air Pollution

Sl. No.	Class	Aerosols	Gases and Vapours
1.	Combustion processes	Dust, fumes, smoke	SO_2, NO_2, CO, Organic vapours
2.	Chemical processes (cement and fertilizers)	Dust, fume, mist	Process dependent (CO_2, SO_2, CO, NH_3, NO_2 organic vapours)

3.	Petroleum operations	Dust, mist	SO_2, H_2S, NH_3, CO, hydrocarbons mercaptans
4.	Metallurgical processes (Al-refineries, steel plant)	Dust, fumes	SO_2, CO, fluorides, organic vapours
5.	Mineral processing	Dust, fumes	Process dependent
6.	Food and feed operation	Dust, mist	Odorous materials
7.	Agricultural activities crop spraying, field burning	Dust, mist, smoke, fly ash	Organic phosphates, chlorinated hydro sulphur oxide, organic vapours
8.	Nuclear energy programme (i) Fuel fabrication (ii) Ore preparation (iii) Bomb explosion	Dust	Fluorides, I-131, Ar-41 radioactive gases (Sr-90, Cs-137, C-14 etc.)

Smog

It is a combination of smoke and fog. This is the best known example of air pollution. Smog is of two types:

(1) **Classical smog :** Occurs in cool humid climate and is chemically reducing smog and has high concentration of SO_2.

(2) **Photochemical smog :** Occurs in warm, dry and sunny climate. It is an oxidising smog. Major component of photochemical smog is NO.

Acid Rain

Rain water normally has pH of 5.6 due to the formation of H^+ ions from the reaction of rain water with CO_2 present in atmosphere.

$$H_2O(l) + CO_2(g) \rightarrow 2H^+(aq) + CO_3^{-2}(aq).$$

When pH of rain water drops below 5.6 it becomes acidic. Acid rain caused by the presence of oxides of sulphur and nitrogen in the atmosphere. Oxides of sulphur are released into the environment largely because of fossil fuel combustion, ore smelting etc. Nitrogen oxides emitted into the atmosphere mainly from automobile exhausts and fossil fuel combustion. SO_2 and NO_2 after oxidation and reaction with water are major contributors to acid rain.

$$2SO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$$

$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq).$$

Acid rain is toxic to vegetation and aquatic life. It damages building and statues and dissolves heavy metals from soils, rocks etc. The heavy metals such as Cu, Pb, Hg, Al etc leached from soil enters well water and produce a variety of toxic effects.

SOIL POLLUTION

It is caused by pesticides and other chemicals which are added to the soil to grow better crops. Solid wastes are another cause of land pollution.

Pesticides are used to kill unwanted organisms. Synthetic pesticides are of great concern for us. Pesticides affect human being through eating, drinking and so on.

Insecticides : Control of insects by insecticides help to curb disease for example (malaria and yellow fever) and protects crops. *e.g.,* organochlorine like DDT.

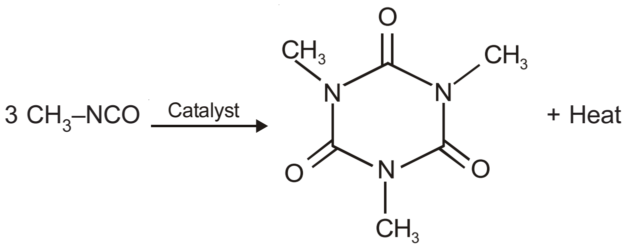
Bhopal gas tragedy occurred on 2nd Dec. 1984 in Bhopal (Union Carbide Ltd.).

Methyl iso-cyanate (MIC) was used to manufacture the insecticide called Carbyl or Sevin (commercial name). There were three tanks in the plant that stored MIC. Due to increase of pressure in one of the tanks valve was released, hence MIC escaped into atmosphere. This MIC was

(a) Hydrolysed due to presence of water in surrounding ponds.

$$\underset{\text{MIC}}{CH_3 - N = C = O} + H_2O \longrightarrow CH_3NH_2 + CO_2 \ + \text{Heat}$$

(b) Impurities of metals present in water caused polymerisation reaction



Both reactions are exothermic in nature. So escaping tendency of MIC increased and caused immense loss of life and injury to people and livestock.

❑ ❑ ❑

Chapter 13

Organic Compounds Containing Halogen

ALKYL HALIDES

General Methods of Preparation

1. **From Alcohols**

   (a) By the action of halogen acids

$$\underset{\substack{\text{Ethyl alcohol}\\ \text{(Ethanol)}}}{C_2H_5OH} + HCl(g) \xrightarrow{\text{Anhyd.ZnCl}_2} \underset{\substack{\text{Ethyl chloride}\\ \text{(Chloroethane)}}}{C_2H_5Cl} + H_2O$$

The order of rate of reaction is 3° alcohol > 2° alcohol > 1° alcohol.

   (b) By the action of phosphorus halides

(i) $$\underset{\text{Alcohol}}{ROH} + PCl_5 \rightarrow \underset{\substack{\text{Alkyl}\\ \text{chloride}}}{RCl} + HCl + \underset{\substack{\text{Phosphoryl}\\ \text{chloride or}\\ \text{Phosphorus}\\ \text{oxychloride}}}{POCl_3}$$

(ii) $$\underset{\text{Alcohol}}{3ROH} + PBr_3 \rightarrow \underset{\substack{\text{Alkyl}\\ \text{chloride}}}{3RBr} + \underset{\substack{\text{Phosphorus}\\ \text{acid}}}{H_3PO_3}$$

   (c) By the action of thionyl chloride ($SOCl_2$)- Alkyl chlorides can be prepared by heating alcohol (1° or 2°) and thionyl chloride in the presence of pyridine (base). (Darzen's Reaction)

$$\underset{\substack{\text{Alcohol}\\ (1\ \text{ or } 2\ )}}{ROH} + \underset{\substack{\text{Thionyl}\\ \text{chloride}}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\substack{\text{Alkyl}\\ \text{chloride}}}{RCl} + \underset{\substack{\text{Gaseous by}\\ \text{product}}}{SO_2 + HCl}$$

2. **From Alkenes**

$$\underset{\text{Ethylene}}{H_2C = CH_2} + HX \rightarrow \underset{\text{Ethyl halide}}{CH_3 \quad CH_2 \quad X}$$

3. **From Alkanes**

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[\text{250–400 C}]{\text{Light or}} \underset{\substack{\text{Methyl chloride}\\ \text{(Chloromethane)}}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethane}}{C_2H_6} + Br_2 \xrightarrow[\text{250 400 C}]{\text{Light or}} \underset{\substack{\text{Ethyl bromide}\\ \text{(Bromoethane)}}}{C_2H_5Br} + HBr$$

The mechanism is a free radical mechanism. The reactivity of halogen depends upon the nature of halogen used to abstract hydrogen hence $F_2 > Cl_2 > Br_2 > I_2$

4. From silver salts of fatty acids (Borodine - Hunsdiecker Reaction)

$$\underset{\text{Silver benzoate}}{C_6H_5COOAg} + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} \underset{\text{Phenyl bromide}}{C_6H_5Br} + AgBr + CO_2$$

5. By halogen exchange

(a) $$\underset{\text{Ethyl bromide}}{C_2H_5Br} + NaI \xrightarrow{CH_3OH \text{ or Acetone}} \underset{\text{Ethyl iodide}}{C_2H_5I} + NaBr$$

The reaction is possible because sodium iodide is soluble in methanol and acetone whereas sodium chloride and sodium bromide are insoluble

(b) Reaction of Grignard's reagent with I_2.

$$\underset{\text{(where, X=Cl or Br)}}{RMgX + I_2} \rightarrow R\quad I + MgXI$$

6. From Alkyl hydrogen sulphate

Alkyl iodides can be prepared by treating alkyl hydrogen sulphates with an aqueous solution of potassium iodide.

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + KI \rightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + KHSO_4$$

PHYSICAL PROPERTIES

1. Lower members such as CH_3Cl, CH_3Br, CH_3F, C_2H_5Cl etc are colourless gases at room temperature. Other alkyl halides upto C_{18} are colourless sweet smelling liquids and higher members are solids.
2. B.P. of haloalkanes decrease in order RI > RBr > RCl (for same size of alkyl group)
3. B.P. of haloalkanes with same halogen atom increase with increasing size of alkyl groups.
4. For isomeric haloalkanes, b.p. decrease with increasing branching *i.e.* 1° > 2° > 3°

   Example : n-butyl chloride > isobutyl chloride > tert butyl chloride
5. Chloroalkanes are lighter than water whereas bromides and iodides are heavier. Their densities decrease in order of RI > RBr > RCl
6. Dipole moments of halomethanes decreases in order of $\underset{1.86\text{ D}}{CH_3Cl}\quad \underset{1.847\text{ D}}{CH_3F}\quad \underset{1.83\text{ D}}{CH_3Br}\quad \underset{1.636\text{ D}}{CH_3I}$

CHEMICAL PROPERTIES

Halogen derivatives of alkanes are highly reactive as the halogen atoms are easily replaced. These derivatives especially the alkyl halides are widely used in the synthesis of many organic compounds.

The Chemical reactions of alkyl halides may be classified into three types :

(A) Nucleophilic substitution reactions.

(B) Elimination reactions.

(C) Miscellaneous reactions.

Nucleophilic substitution reactions

I. S_N2 (Nucleophilic Substitution, Bimolecular) mechanism.

II. S_N1 (Nucleophilic Substitution, Unimolecular) mechanism.

Kinetics of nucleophilic substitution S_N2

For the given Nucleophilic substitution reactions :

$$\underset{\text{Methyl bromide}}{CH_3Br} + KOH(aq) \rightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + KBr$$

rate was found to be, rate = k $[CH_3Br][KOH]$

Overall order of the reaction is two and it is one with respect to CH_3Br and one with respect to $\bar{O}H$.

> **Note :** *(i) This reaction takes place in one step without involving any reactive intermediate.*
>
> *(ii) INVERSION of CONFIGURATION takes place if leaving group* X^- *and* $\overset{\ominus}{Nu}$ *are of same priority.*
>
> *(iii) Rate of reaction of alkyl halides towards* S_N2 *reaction is governed by steric hindrance in alkyl halide.*

S_N1 Reaction

This reaction involves more than one steps.

This S_N1 reaction is independent of nature and concentration of nucleophiles.

Alkyl halides which give more stable carbocations are more reactive towards S_N1 reactions.

S_N1 reactions involve racemization with partial inversion.

Factors affecting the rate of S_N1 and S_N2 reactions :

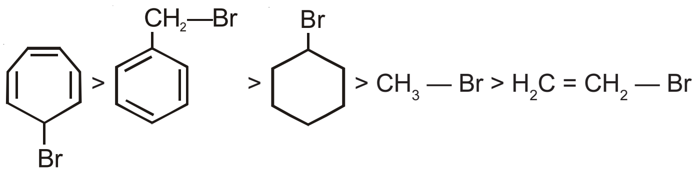
1. **Structure of substrates**

(A) For S_N1 reaction

Alkyl halides which give more stable carbocation are more reactive towards S_N1 reaction

$(CH_3)_3\,C — Br > (CH_3)_2\,CH — Br > CH_3\,CH_2\,Br > CH_3\,Br$

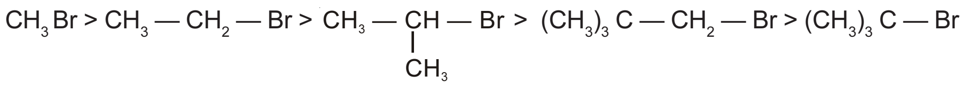
Decreasing order of reactivity



Decreasing order of reactivity

(B) For S_N2 reaction

Lesser the steric hindrance, greater the reactivity of alkyl halide towards S_N2 reactions.



$CH_3\,Br > CH_3 — CH_2 — Br > CH_3 — \underset{\displaystyle CH_3}{\underset{|}{CH}} — Br > (CH_3)_3\,C — CH_2 — Br > (CH_3)_3\,C — Br$

Decreasing reactivity towards S_N2 reaction

2. **Strength and concentration of nucleophile :**

   for S_N1 : As nucleophile does not participate in rate determining step, therefore there is no effect of concentration and strength of nucleophile on rate of reaction.

   for S_N2 : Increasing the concentration of nucleophile increases the rate for S_N2, a better nucleophile will yield better products.

3. **Solvent Effect :** Polar protic solvent favours S_N1 whereas polar aprotic solvent favours S_N2 mechanism.

4. **Nature of leaving group :** Good leaving group always increases rate of nucleophilic substitution reactions for the same reason the order of reactivity for S_N reactions of halides follow the given trend :

   RI > RBr > RCl > RF

Miscellaneous reactions

1. **Reaction with magnesium** (formation of Grignard's reagent).

$$R - X + Mg \xrightarrow{\text{Dry ether}} RMgX$$

   For a given alkyl group, the ease of formation of Grignard's reagent is of the order :

   iodide > bromide > chloride

2. **Reduction** (formation of alkanes)

   Alkyl halides are reduced to alkanes by any of the following reducing agents :

   (a) H_2 in the presence of Ni, Pt or Pd (catalytic hydrogenation).

   (b) Lithium-aluminium hydride ($LiAlH_4$).

   (c) Nascent hydrogen obtained from Zn-Cu couple and alcohol or Zn and HCl or Sn and HCl or Na and alcohol.

Friedel Craft's reaction

Formation of Alkyl benzene

$$C_6H_6 + CH_3CH_2 \quad Cl \xrightarrow{\text{Anhydrous } AlCl_3} \underset{\text{Ethyl benzene}}{C_6H_5 \quad CH_2CH_3} + HCl$$

Vinylic halides and **aryl halides** do not give a silver halide precipitate, when treated with alc. $AgNO_3$ because vinylic and phenyl cations are very unstable and therefore, do not form readily.

ARYL HALIDES

General methods of Preparation

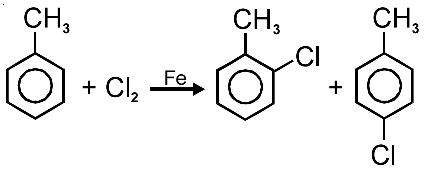
1. **From arenes by direct halogenation**

   (i) $$\underset{\text{Benzene}}{C_6H_6} + Cl_2 \xrightarrow{FeCl_3,\ 298K} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$

$$\underset{\text{Benzene}}{C_6H_6} + Br_2 \xrightarrow{FeBr_3,} \underset{\text{Bromobenzene}}{C_6H_5Br} + HBr$$

   If excess of halogen is used, dihaloderivatives are formed.

   Chlorination of toluene in the presence of iron (using equimolar quantities) gives a mixture of o- and p- chlorotoluenes.



(ii) Preparation of aryl iodides

Aryl iodides cannot be prepared by direct iodination because the reaction is reversible and hydriodic acid formed being a strong reducing agent reduces C_6H_5I to C_6H_6.

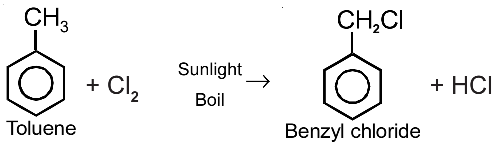
$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI$$

To overcome this difficulty, iodination is carried out in the presence of oxidizing agent such as nitric acid, mercuric oxide (HgO) or iodic acid, which oxidizes hydriodic acid to iodine and thus the reaction proceeds in the forward direction.

(iii) Aryl fluorides cannot be prepared by this method because fluorine is highly reactive and the reaction is very violent and uncontrollable.

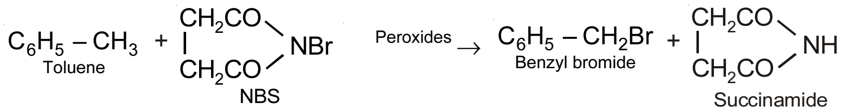
2. **Direct Halogenation**

When calculated amount of chlorine is passed through boiling toluene in presence of sunlight or ultra-violet light and in the absence of halogen carrier, benzyl chloride is formed.



3. **With NBS**

When toluene is treated with NBS (N-bromosuccinimide) in the presence of peroxides, benzyl bromide is formed.

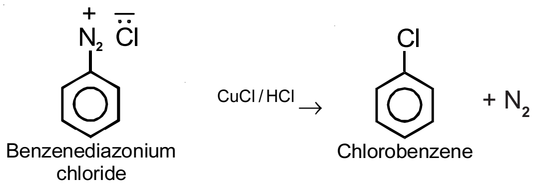


$$\underset{\text{Toluene}}{C_6H_5-CH_3} + \underset{\text{NBS}}{\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>\!NBr} \xrightarrow{\text{Peroxides}} \underset{\text{Benzyl bromide}}{C_6H_5-CH_2Br} + \underset{\text{Succinamide}}{\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>\!NH}$$

4. **From Diazonium salts**

(a) Sandmeyer's reaction

(i) Preparation of chlorobenzene



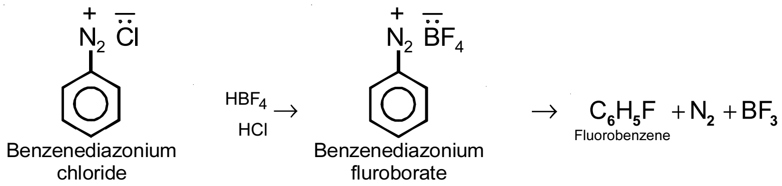
(ii) Preparation of bromobenzene

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5\overset{+}{N_2}\overset{-}{Cl}} \xrightarrow{\text{CuBr/HBr}} \underset{\text{Bromobenzene}}{C_6H_5Br} + HCl + N_2$$

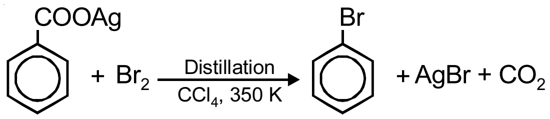
(b) Preparation of iodobenzene

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5\overset{+}{N_2}\overset{-}{Cl}} + KI \rightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + HCl + N_2$$

(c) Preparation of fluorobenzene (Balzschiemann reaction).



5. **By Hunsdiecker Reaction :**

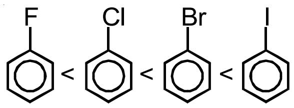


Physical Properties

(i) They are colourless stable liquids.

(ii) Insoluble in water but soluble in inorganic solvent.

(iii) Boiling and melting points : Their boiling and melting point is higher than alkyl halides. Boiling point increases with increasing size of halogen.

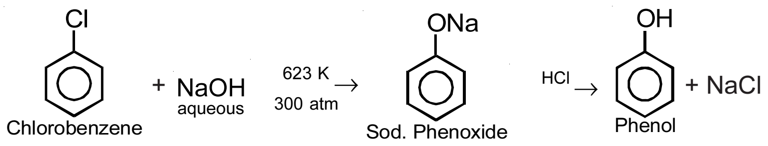


Boiling points of isomeric dihalo benzenes are very nearly the same but the melting point of para isomers is higher than ortho and meta isomer.

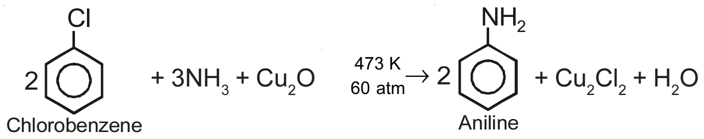
Chemical Properties

Haloarene gives S_N reaction rarely only under drastic conditions because of partial double bond character between C–X bond. i.e., at high temp. & pressure and in presence of certain catalyst.

(i) Replacement by hydroxyl group (Formation of phenols) (Dow's process)



(ii) Replacement by amino group (Formation of aryl amines)



$$\underset{\text{Bromobenzene}}{C_6H_5Cl} + \overset{+}{K}\overset{-}{\ddot{N}}H_2 \xrightarrow[240\text{ K}]{\text{Liquid NH}_3} \underset{\text{Aniline}}{C_6H_5NH_2} + KBr$$

(iii) Replacement by cyanide group (Formation of aryl cyanides)

$$\underset{\text{Bromobenzene}}{2C_6H_5Br} + Cu_2(CN)_2 \xrightarrow[470\text{ K}]{\text{Pyridine}} \underset{\substack{\text{Cyanobenzene}\\\text{(Benzonitrile)}}}{2C_6H_5CN} + 2CuBr$$

(iv) Replacement by methoxy group

$$C_6H_5Cl + \underset{\text{Sod. methoxide}}{CH_3ONa} \xrightarrow[\text{Cu salts}]{473} \underset{\text{Anisole}}{C_6H_5OCH_3} + NaCl$$

Activation of halogen atoms

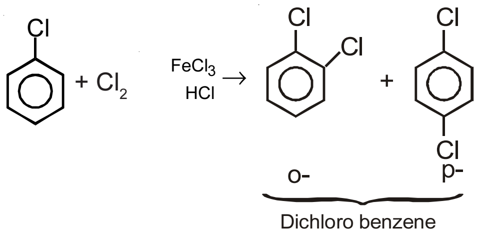
(a) Presence of electron-withdrawing groups *e.g.*, – NO_2, –CN, –SO_3H, –CHO, –COOH, etc. especially at the o- or p- position but not at m-position w.r.t. the halogen increases the ease of replacement of halogen by nucleophile.

(b) While electron donating groups like –NH_2, –OH, –OR etc. at o- or p- position with respect to halogen atom donates electron due to resonance and thus reduce positive charge on the C-atom of C–Cl bond and thus **decreases the reactivity of aryl halides.**

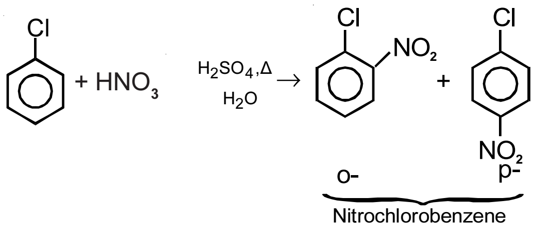
(v) Reactions due to benzene nucleus (electrophilic substitutions)

Aryl halides undergo electrophilic substitution reactions to give o- and p-substituted derivatives.

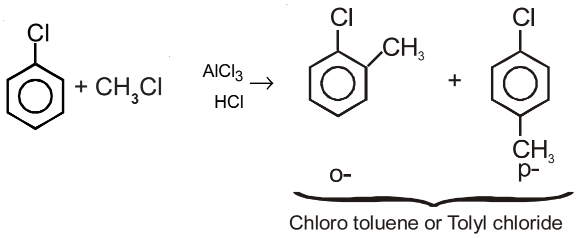
(a) Halogenation



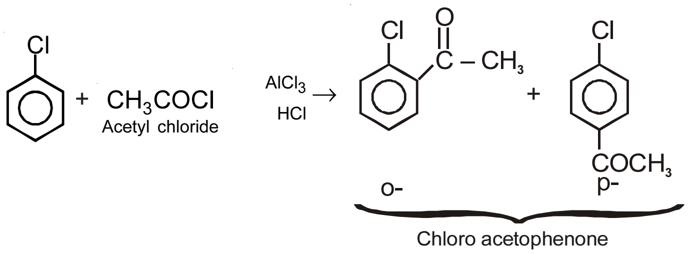
(b) Nitration



(c) Friedel - Craft alkylation reaction



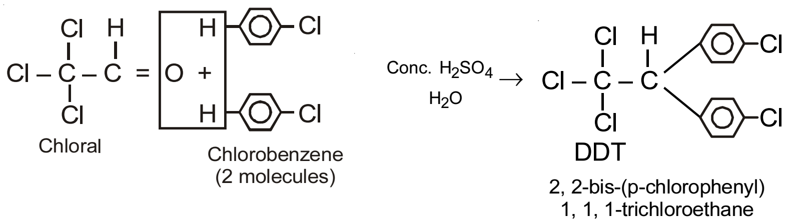
(d) Friedel Craft acylation reaction



Some Important Halogen Compounds

DDT : On heating with **chloral** in the presence of concentrated sulphuric acid, **chlorobenzene** forms (p, p' - dichlorodiphenyl trichloroethane (commonly known as DDT-a powerful insecticide.)

But it is not biodegradable because it contains halogen atoms attached to the benzene rings.



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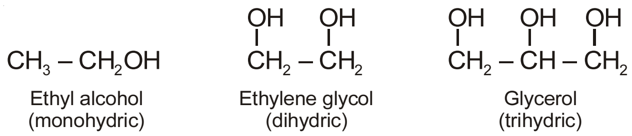
Chapter 14

Organic Compounds Containing Oxygen

ALCOHOLS

Molecules containing –OH group are termed as alcohols. Classification of alcohols they are classified as primary, secondary or tertiary alcohol according to the carbon that is bonded with –OH.

Again when any molecule contain 1, 2 or 3 –OH groups then it is called mono, di or tri hydric alcohols respectively. (as in case of alkyl halides)



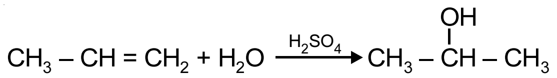
$$CH_3-CH_2OH \qquad \overset{\overset{OH}{|}}{CH_2}-\overset{\overset{OH}{|}}{CH_2} \qquad \overset{\overset{OH}{|}}{CH_2}-\overset{\overset{OH}{|}}{CH}-\overset{\overset{OH}{|}}{CH_2}$$

Ethyl alcohol (monohydric) Ethylene glycol (dihydric) Glycerol (trihydric)

GENERAL METHODS OF PREPARATION

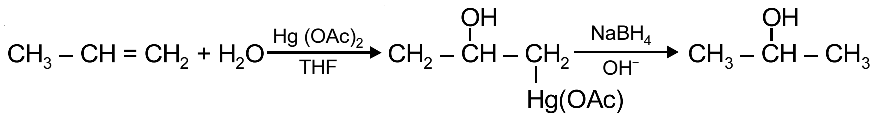
1. **From Alkenes :**

   (i) **By Acid catalyzed hydrolysis :**



$$CH_3-CH=CH_2+H_2O \xrightarrow{H_2SO_4} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

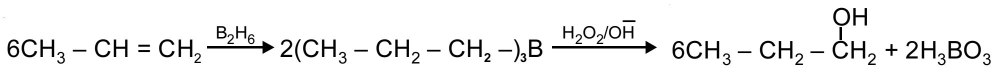
   (ii) **Oxymercuration followed by demercuration :**



$$CH_3-CH=CH_2+H_2O \xrightarrow[THF]{Hg\,(OAc)_2} CH_2-\overset{\overset{OH}{|}}{CH}-\underset{\underset{Hg(OAc)}{|}}{CH_2} \xrightarrow[OH^-]{NaBH_4} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

Overall result of above reaction is Markownikoff addition of water without rearrangement

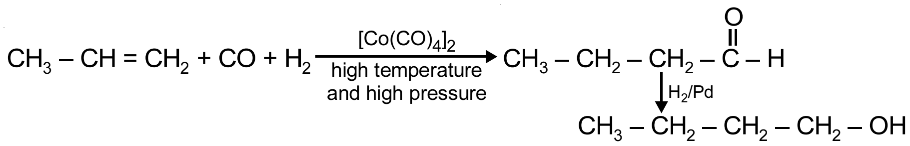
   (iii) **Hydroboration followed by oxidation :**



$$6CH_3-CH=CH_2 \xrightarrow{B_2H_6} 2(CH_3-CH_2-CH_2-)_3B \xrightarrow{H_2O_2/\overline{OH}} 6CH_3-CH_2-\overset{\overset{OH}{|}}{CH_2}+2H_3BO_3$$

Overall result of above reaction is anti Markownikoff addition of water with no rearrangement.

   (iv) **Oxo process followed by hydrogenation :**



$$CH_3-CH=CH_2+CO+H_2 \xrightarrow[\text{high temperature and high pressure}]{[Co(CO)_4]_2} CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$$

$$\downarrow H_2/Pd$$

$$CH_3-CH_2-CH_2-CH_2-OH$$

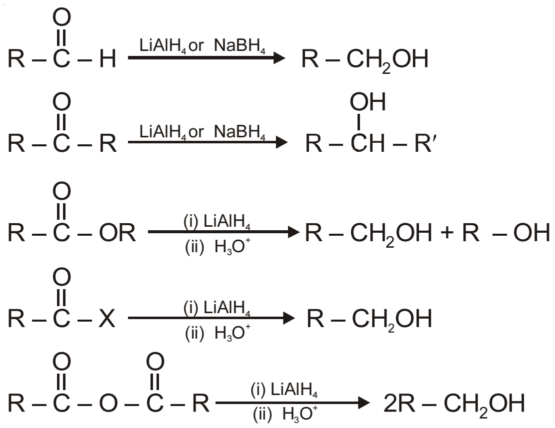
Product has one more carbon.

2. **From Alkyl Halides :**

When alkyl halides are treated with aq. KOH or aq. NaOH or moist Ag_2O, alcohols are formed.

$$R\ \ X + OH\ \ \rightarrow R\ \ OH + X^-$$

3. **Reduction of Carbonyl Compounds, Carboxylic Acids and their Derivatives :**



$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{LiAlH_4 \text{ or } NaBH_4} R-CH_2OH$$

$$R-\overset{\overset{O}{\|}}{C}-R \xrightarrow{LiAlH_4 \text{ or } NaBH_4} R-\overset{\overset{OH}{|}}{CH}-R'$$

$$R-\overset{\overset{O}{\|}}{C}-OR \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4} R-CH_2OH + R\ \ -OH$$

$$R-\overset{\overset{O}{\|}}{C}-X \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4} R-CH_2OH$$

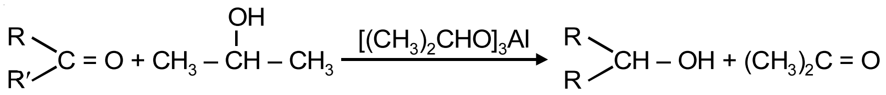
$$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4} 2R-CH_2OH$$

Table : Reducing nature of different reagents

Group	Product	$LiAlH_4/H_2O$	$NaBH_4/C_2H_5OH$	B_2H_6/THF	H_2/Pt
$-\overset{\overset{O}{\|}}{C}-H$	$-CH_2-OH$	Yes	Yes	Yes	Yes
$>C=O$	$>CH-OH$	Yes	Yes	Yes	Yes
$-COOH$	$-CH_2OH$	Yes	No	Yes	Yes
$-\overset{\overset{O}{\|}}{C}-Cl$	$-CH_2OH$	Yes	Yes	No	Yes
$(R-\overset{\overset{O}{\|}}{C}-O)_2O$	$R-CH_2OH$	Yes	No	Yes	Yes
$-\overset{\overset{O}{\|}}{C}-OR$	$-CH_2OH +$ $R-OH$	Yes	No	Yes	Yes
$>C=C<$	$>CH-CH<$	No ($LiAlH_4$ reduces) C = C only when it is conjugated with Phenylic system	No	Yes	Yes

Meerwein-Ponndorf-Verley Reduction (MPV Reduction) :

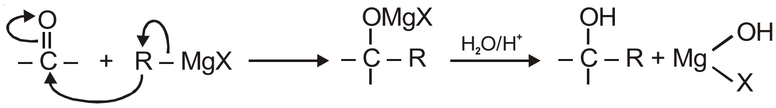
Ketones can be reduced to secondary alcohols with aluminium isopropoxide in 2-propanol solution.



$$\begin{matrix}R\\R'\end{matrix}>C=O + CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{[(CH_3)_2CHO]_3Al} \begin{matrix}R\\R\end{matrix}>CH-OH + (CH_3)_2C=O$$

4. **Using Grignard Reagent :**

   (i) **From aldehydes or ketones :**

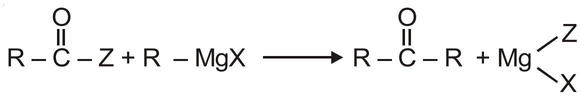


$$-\overset{O}{\overset{\|}{C}}- + R-MgX \longrightarrow -\overset{OMgX}{\overset{|}{\underset{|}{C}}}-R \xrightarrow{H_2O/H^+} -\overset{OH}{\overset{|}{\underset{|}{C}}}-R + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

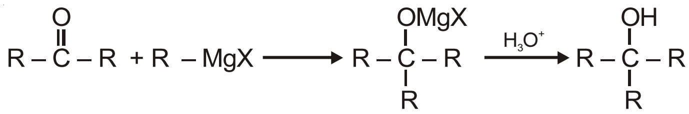
In this reaction

Formaldehyde gives	1°-alcohol
Other aldehydes give	2°-alcohol
Ketones give	3°-alcohol

   (ii) **From carboxylic acid and their derivatives :**

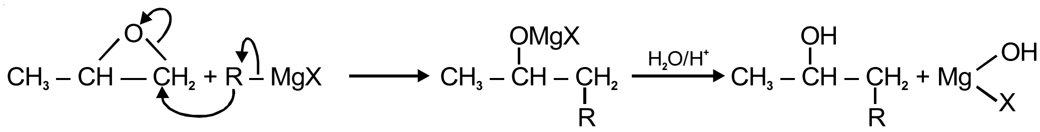


$$R-\overset{O}{\overset{\|}{C}}-Z + R-MgX \longrightarrow R-\overset{O}{\overset{\|}{C}}-R + Mg\begin{smallmatrix}Z\\X\end{smallmatrix}$$



$$R-\overset{O}{\overset{\|}{C}}-R + R-MgX \longrightarrow R-\overset{OMgX}{\overset{|}{\underset{\underset{R}{|}}{C}}}-R \xrightarrow{H_3O^+} R-\overset{OH}{\overset{|}{\underset{\underset{R}{|}}{C}}}-R$$

   (iii) **From epoxides :**



$$CH_3-CH\overset{O}{—}CH_2 + R-MgX \longrightarrow CH_3-\overset{OMgX}{\overset{|}{CH}}-\underset{\underset{R}{|}}{CH_2} \xrightarrow{H_2O/H^+} CH_3-\overset{OH}{\overset{|}{CH}}-\underset{\underset{R}{|}}{CH_2} + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

5. **Hydrolysis of Ether :**

   Ethers undergo acid hydrolysis with dilute H_2SO_4 under pressure to give corresponding alcohols.

$$R\quad O\quad R + H_2O \xrightarrow{\text{dil. } H_2SO_4} R\quad OH + R\quad OH$$

Physical Properties

(i) **Physical state :** At ordinary temperature, lower members are colourless liquids with burning taste and pleasant smell.

(ii) **Boiling Point :** The boiling point of alcohols rise regularly with the rise in the molecular weight. Amongst isomeric alcohols, the boiling point decrease in the order.

   1° > 2° > 3°

   Alcohols have high boiling point then hydrocarbons and haloalkanes of similar molecular mass due to intermolecular hydrogen bonding.

(iii) **Solubility :** The extent of solubility of any alcohol in water depends upon the capability of its molecules to form hydrogen bonds with water molecule.

(iv) Alcohols are lighter than water, however, the density increases with the increase in molecular mass.

Chemical Properties

1. **Reactions involving cleavage of O – H Bond**

   Alcohols are acidic in nature but they are less acidic than water hence they do not give H^+ in aqueous solution. They do not change the colour of litmus paper.

Their acidic strength increases by increasing–I strength of the groups attached and decreases by increasing +I strength of the groups.

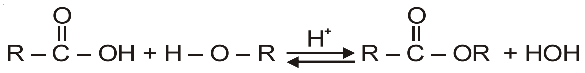
(i) Alcohols do not react with aqueous alkali, as they do not give H^+ in aqueous solution.

(ii) **Action of active metal :** When alcohols are treated with active metal they form alkoxides with the liberation of H_2 gas.

$$2ROH + 2Na \rightarrow 2R\ \ O\overset{+}{N}a + H_2$$

(iii) **Esterification :** When carboxylic acid is treated with alcohols in the presence of acid as catalyst, esters are formed.

Alcohol reactivity order 1° > 2° > 3°.



$$R-\overset{\overset{\large O}{\|}}{C}-OH + H-O-R \xrightleftharpoons{H^+} R-\overset{\overset{\large O}{\|}}{C}-OR + HOH$$

Its acid catalysed revsersible reaction.

Note : *(a) OH is removed from carboxylic acid and H is removed from alcohol.*

(b) Overall reaction is S_N2 *in which alcohol acts as nucleophile.*

(iv) **Reaction with Grignard Reagent :** When Grignard reagents are treated with alcohol (or any proton donor) they form alkanes.

$$R-MgX + H-OR \longrightarrow R-H + R\ -OMgX$$

Other proton donors can be carboxylic acids, phenols, alkynes, H_2O, Amines, NH_3 etc.

2. Reactions Involving Cleavage of C– O Bond

(i) **Reaction with HX :** Most alcohols undergo S_N1.

(a) $R\ \ OH + HCl(g) \xrightarrow{\text{Anhyd. ZnCl}_2} R\ \ Cl + H_2O$

Note : *HCl + anhyd.* $ZnCl_2$ *is called Lucas reagent. Lucas test is used to distinguish primary, secondary and tertiary alcohols.*

(b) $R\ \ OH + HBr \xrightarrow[\text{conc.}]{H^+/H_2SO_4} R\ \ Br + H_2O$

(c) $R\ \ OH + HI \xrightarrow[\text{conc.}]{H^+/H_2SO_4} R\ \ I + H_2O$

Reactivity order of HX is

HI > HBr > HCl

(ii) Alkyl chlorides can also be prepared by following methods :

$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$

$3R-OH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$

$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$ (Darzen's process)

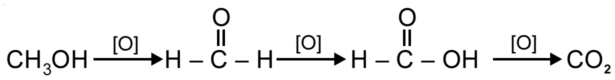
Darzen’s process is the best method as the other by-products are gases.

3. Reduction :

Alcohols are reduced to alkanes when they are treated with red P + HI.

$$R\ \ OH \xrightarrow{HI + \text{red P}} R\ \ H + ZnO$$

4. **Oxidation :**



$$CH_3OH \xrightarrow{[O]} H-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{[O]} H-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{[O]} CO_2$$

3°-alcohols can't be oxidised.

(i) Strong oxidising agent like $KMnO_4$ or $K_2Cr_2O_7$ cause maximum oxidation as above.

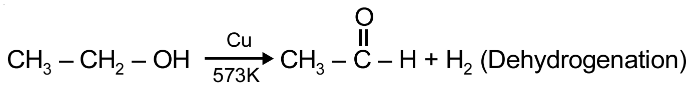
(ii) PCC (Pyridinium chlorochromate) is used to convert primary and secondary alcohol into corresponding carbonyl compound.

(iii) 2°-alcohol can be converted to ketone best by PCC + CH_2Cl_2 or CrO_3 or H_2CrO_4 in aq. acetone (Jones reagent).

(iv) MnO_2 selectively oxidises the –OH group of allylic and benzylic 1° and 2° alcohols to aldehydes and ketones respectively.

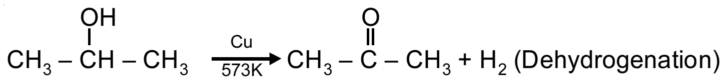
5. **Action of Heated Copper :**

(i)



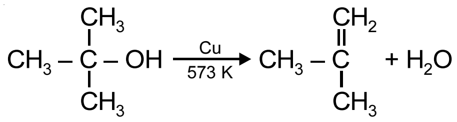
$$CH_3-CH_2-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2 \text{ (Dehydrogenation)}$$

(ii)



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[573K]{Cu} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2 \text{ (Dehydrogenation)}$$

(iii) Tertiary alcohols undergo dehydration to give alkene under similar condition.



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow[573\ K]{Cu} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_2}{\|}}{C}} + H_2O$$

Distinction Between 1°, 2° and 3° Alcohols

Lucas Test :

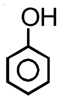
Any alcohol is treated with Lucas reagent (HCl + anhyd. $ZnCl_2$) at room temperature if

(i) Solution becomes cloudy immediately, alcohol is 3°.

(ii) Solution becomes cloudy after 5-min, alcohol is 2°.

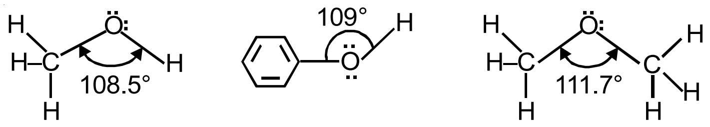
(iii) In solution cloud does not form at room temperature, alcohol is 1°.

PHENOLS



and their derivatives are called phenols. In phenol R– of alcohol is replaced by aryl ring.

Comparison of bond Angles in Phenols, Alcohols and Ethers :

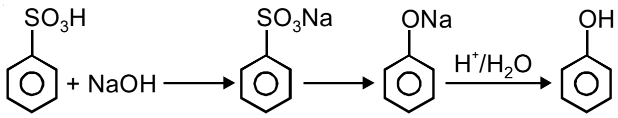


Bond angle increases with the increase in hindrance.

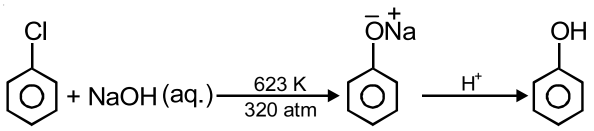
Method of Preparation

1. **From Aryl Sulphonic Acids (Industrial Method):**

When aryl sulphonic acids are fused with NaOH at 570 – 620 K followed by hydrolysis phenols are formed.

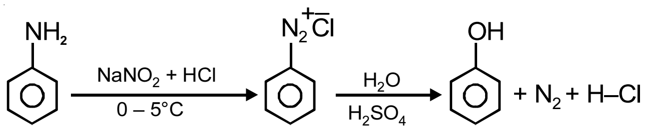


2. **From Haloarenes : (Dow's process)**

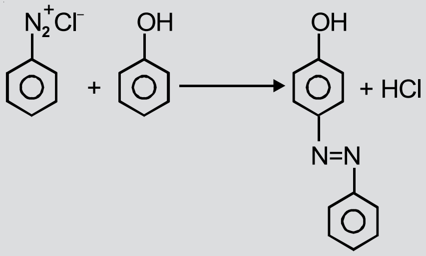


Note : *Condition of reaction become less vigorous when –M groups are present at ortho or para or both position to the chlorine atom.*

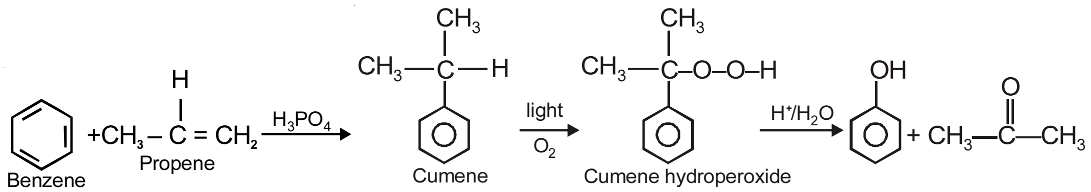
3. **From Benzene Diazonium Salts (Lab Method) :**



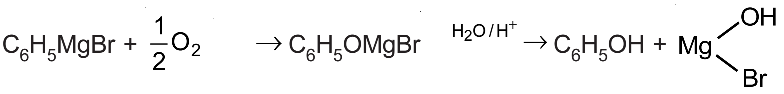
Note : *In the absence of H_2SO_4 diazocoupling will also take place.*



4. **Cumene Process :**

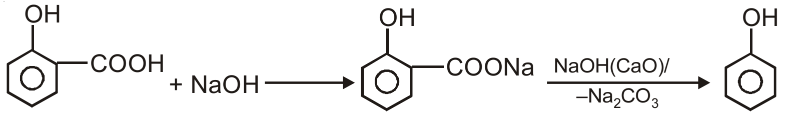


5. **Grignard's Synthesis :**

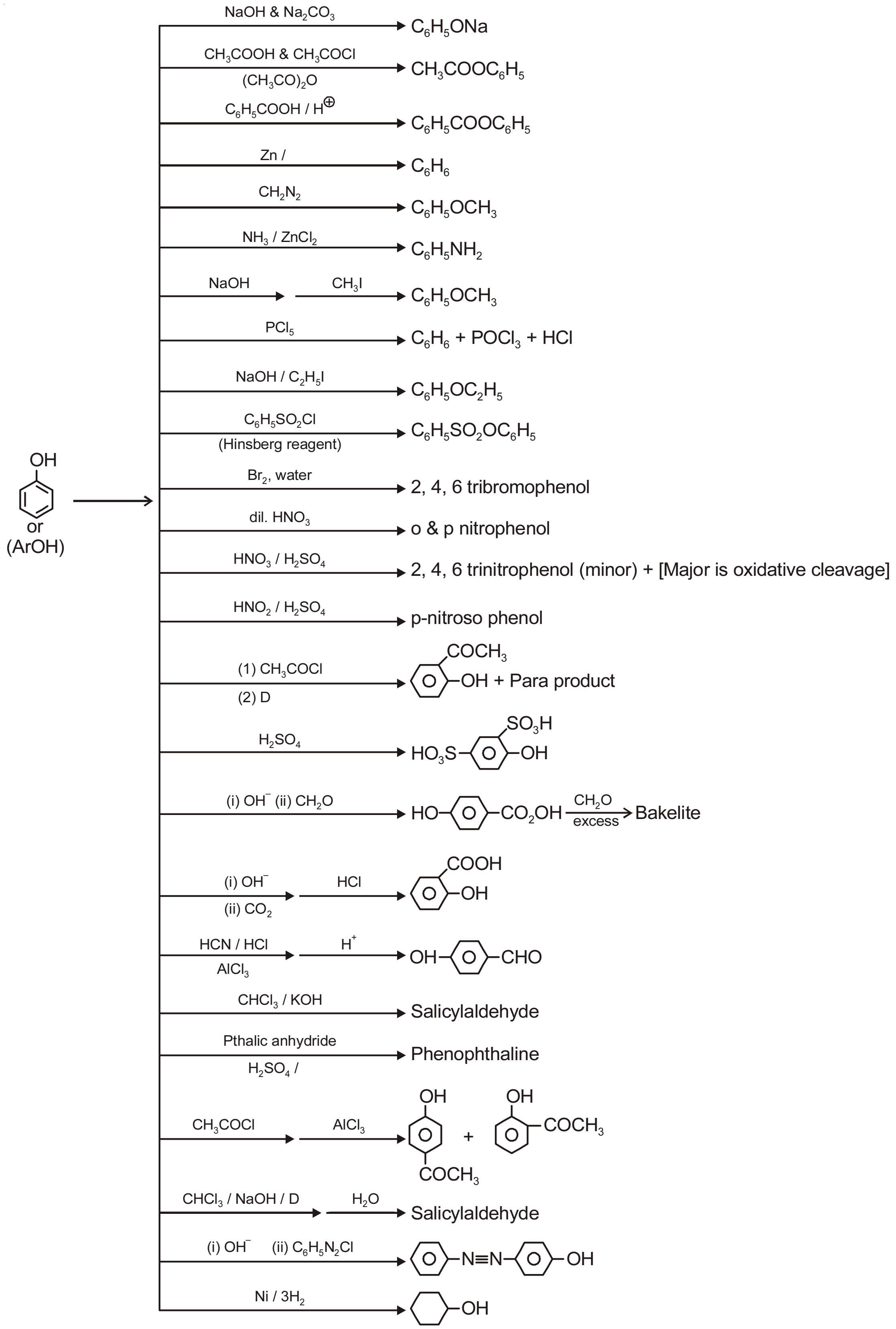


$$C_6H_5MgBr + \frac{1}{2}O_2 \rightarrow C_6H_5OMgBr \xrightarrow{H_2O/H^+} C_6H_5OH + Mg\begin{smallmatrix}OH\\Br\end{smallmatrix}$$

6. **From Salicylic Acid :**



Chemical Properties



ETHERS

Ethers are those organic compounds which contain two alkyl groups attached to an oxygen atom, *i.e.*, R–O–R. They are regarded as dialkyl derivatives of water or anhydrides of alcohols.

$$\underset{\text{Water}}{H-O-H} \xrightarrow[+\,2R]{-2H} \underset{\text{Ether}}{R-O-R} \quad H_2O \quad \underset{\text{Alcohol (2 moles)}}{R-OH + HO-R}$$

Ethers may be of two types : (i) **Symmetrical or simple ethers** are those in which both the alkyl groups are identical and (ii) **unsymmetrical or mixed ethers** are those in which the two alkyl groups are different.

$CH_3–O–CH_3$; $C_6H_5–O–C_6H_5$ $CH_3–O–C_2H_5$; $CH_3–O–C_6H_5$
Symmetrical (simple) ethers Unsymmetrical (mixed)ethers

Like water, ether has two unshared pair of electrons on oxygen atom, yet its angle is greater than normal tetrahedral (109°28′) and different from that in water (105°). This is because of the fact that in ethers the repulsion between lone pairs of electrons is overcome by the repulsion between the bulky alkyl groups.

Preparation of Ethers :

1. **By dehydrating excess of alcohols :** Simple ethers can be prepared by heating an excess of primary alcohols with conc. H_2SO_4 at 413K. Alcohol should be taken in excess so as to avoid its dehydration to alkenes.

$$\underset{\text{Ethanol (2 molecules)}}{C_2H_5-OH + HO-C_2H_5} \xrightarrow[413K]{\text{Conc. } H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + H_2O$$

Dehydration may also be done by passing alcohol vapours over heated catalyst like alumina under high pressure and temperature of 200 – 250°C.

2. **By heating alkyl halide with dry silver oxide** (only for simple ethers) :

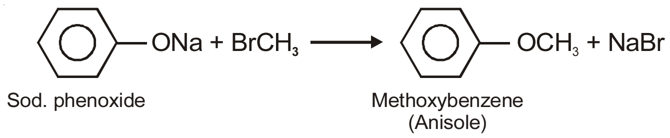
$$C_2H_5I + \underset{\text{Dry}}{Ag_2O} + IC_2H_5 \rightarrow C_2H_5OC_2H_5 + 2AgI$$

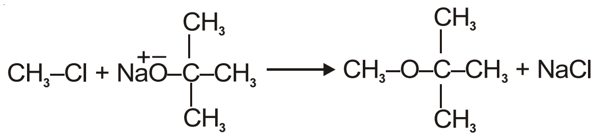
Remember that reaction of alkyl halides with moist silver oxide ($Ag_2O + 2H_2O = 2AgOH$) give alcohols

$C_2H_5I + Ag_2O$ (moist) $\rightarrow C_2H_5OH + AgI$

3. **By heating alkyl halide with sod. or pot. alkoxides** (Williamson synthesis):

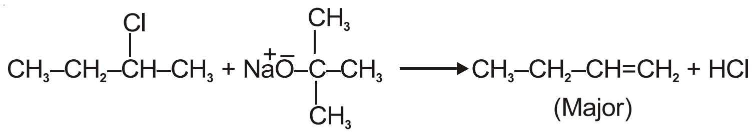
$C_2H_5ONa + ICH_3 \rightarrow C_2H_5OCH_3 + NaI$



However


$$CH_3{-}Cl + \overset{+}{Na}\overset{-}{O}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3 \longrightarrow CH_3{-}O{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3 + NaCl$$

If alkyl halide is other than methyl halide and it is treated with tertiary alkoxide ion, Hofmann elimination takes place instead of Williamson's ether synthesis.



$$CH_3{-}CH_2{-}\overset{Cl}{CH}{-}CH_3 + \overset{+}{Na}\overset{-}{O}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3 \longrightarrow \underset{\text{(Major)}}{CH_3{-}CH_2{-}CH{=}CH_2} + HCl$$

Limitations :

1. In this reaction alkoxide ion may be 1°, 2°, 3°.
2. Alkyl halide must be 1°.
3. In the case of 3° alkyl halide elimination occurs to produce alkene as major product.
4. In the case of 2° alkyl halide both elimination and substitution products are obtained.

Chemical Properties :

A. Properties due to carbon-oxygen bond :

1. Hydrolysis :

$$C_2H_5-O-C_2H_5+H_2O\xrightarrow{H_2SO_4}\underset{\text{Ethyl alcohol}}{2C_2H_5OH}$$

The hydrolysis may also be effected by boiling the ether with water or by treating it with steam.

> ***Note :*** *Ethers can never be hydrolysed in alkaline medium.*

2. Action of conc. sulphuric acid :

$$C_2H_5-O-C_2H_5+H_2SO_4\text{ (conc.)}\rightarrow\underset{\text{Ethyl alcohol}}{C_2H_5OH}+\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

$$C_2H_5OH+H_2SO_4\text{(conc.)}\rightarrow C_2H_5HSO_4+H_2O$$

3. Action of hydroiodic or hydrobromic acid :

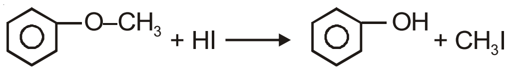
In cold, ether react with HI or HBr to give the corresponding alkyl halide and alcohol. In case of mixed ethers, the halogen atom attaches itself to the smaller alkyl group.

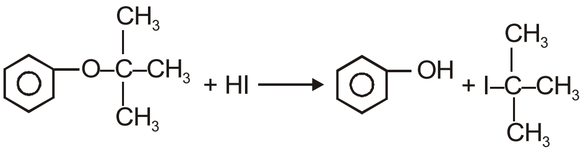
$$\underset{\text{Ethyl ether}}{C_2H_5-O-C_2H_5}+HI\rightarrow\underset{\text{Ethyl iodide}}{C_2H_5I}+\underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

The order of reactivity of halogen acids is :

HI > HBr > HCl

If one of the group around oxygen is aryl group then I^- will always attack on the group other than aryl group.

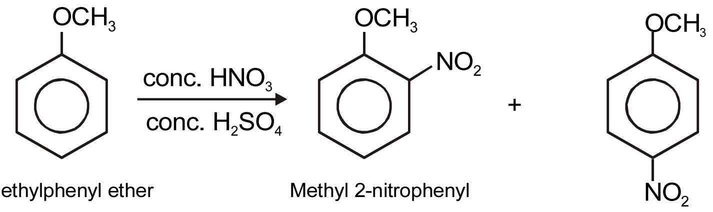




B. Properties Due to Benzene Nucleus :

Alkoxy group, being o-, p- directing, anisole undergoes substitution in o- and p- positions. However, –OR group is less activating than the phenolic group.

(i) Nitration :

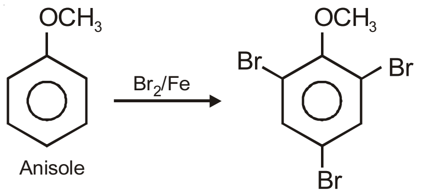


Methylphenyl ether (Anisole)

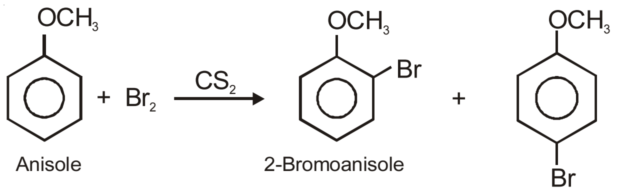
Methyl 2-nitrophenyl ether or o-Nitroanisole

Methyl 4-nitrophenyl ether or p-Nitroanisole

(ii) Bromination :

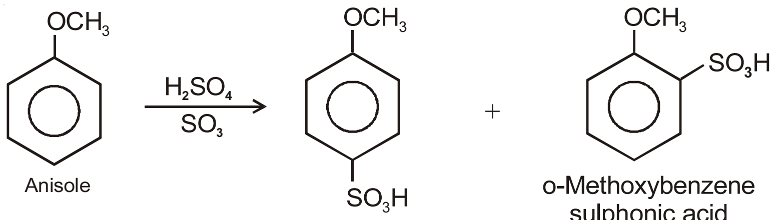


Anisole 2, 4, 6, Tribromoanisole



Anisole 2-Bromoanisole 4-Bromoanisole

(iii) Sulphonation :



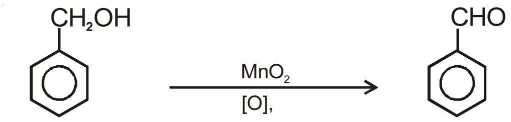
Anisole p-Methoxybenzene sulphonic acid o-Methoxybenzene sulphonic acid

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. **From Alcohols :**

(i) By Oxidation : Primary alcohols gives aldehydes, while secondary alcohols give ketones.

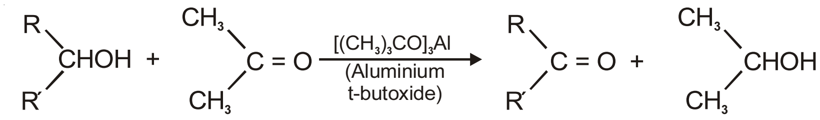
$$\underset{\substack{\text{Ethyl alcohol}\\\text{(Primary Alcohol)}}}{CH_3.CH_2OH} \xrightarrow{CrO_3\ +\text{acetone}} \underset{\text{Acetaldehyde}}{CH_3.CHO} + H_2O$$



Benzyl alcohol Benzaldehyde

Controlled oxidation of 1°- alcohol and 2° - alcohol with PCC + CH_2Cl_2 or CrO_3 forms aldehyde and ketone respectively.

Ketones in good yield can be prepared by **Oppenauer oxidation of secondary alcohols.**

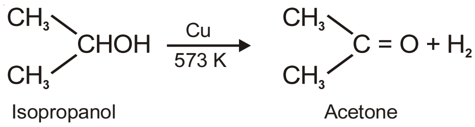


Sec. alcohol Acetone Ketone Isopropanol

(ii) By catalytic dehydrogenation of alcohols : 1° Alcohols yield aldehyde in this method.

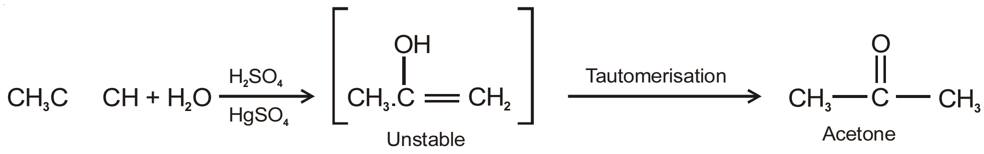
$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow[573K]{Cu} \underset{\text{Formaldehyde}}{HCHO} + H_2$$

Secondary alcohols, on similar treatment, give ketones.

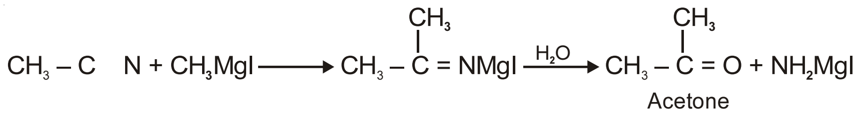


2. From Alkynes :

$$\underset{\text{Acetylene}}{CH \quad CH} + H_2O \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{\substack{\text{Vinyl alcohol}\\ \text{(Unstable)}}}{[CH_2 = CHOH]} \to \underset{\text{Acetaldehyde}}{CH_3CHO}$$



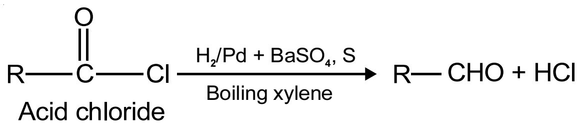
3. From Grignard Reagents :



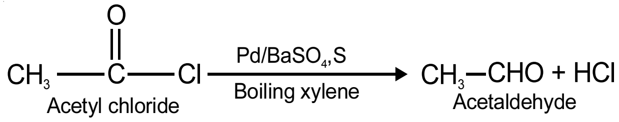
$$CH_3 - C \quad N + CH_3MgI \longrightarrow CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = NMgI \xrightarrow{H_2O} \underset{\text{Acetone}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = O} + NH_2MgI$$

4. Methods giving only Aldehydes :

(a) From Acid Chlorides (Rosenmund Reduction) :



$$\underset{\text{Acid chloride}}{R - \overset{\overset{\displaystyle O}{\|}}{C} - Cl} \xrightarrow[\text{Boiling xylene}]{H_2/Pd + BaSO_4,\ S} R - CHO + HCl$$



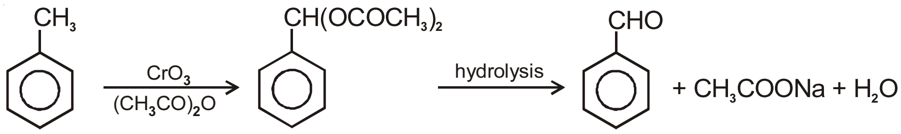
$$\underset{\text{Acetyl chloride}}{CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - Cl} \xrightarrow[\text{Boiling xylene}]{Pd/BaSO_4,S} \underset{\text{Acetaldehyde}}{CH_3 - CHO} + HCl$$

(b) From nitriles (Stephen's reduction) :

$$\underset{\text{Methyl cyanide}}{CH_3.C \quad N} \xrightarrow[2.\ OH^-]{1.\ SnCl_2 + HCl} \underset{\text{Aldimine}}{CH_3.CH = NH} \xrightarrow{H_2O/OH^-} CH_3CHO + NH_3$$

5. Methods for Aromatic Aldehydes and Ketones :

(a) Aromatic Aldehydes :



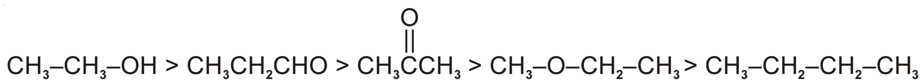
(b) Aromatic Ketones : (Friedel-Craft's acylation)

(i) $$\underset{\text{Benzene}}{C_6H_6} + CH_3COCl \xrightarrow[AlCl_3]{\text{anhy.}} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

Here instead of acid chloride we can use anhydrides also

(ii) $$C_6H_6 + C_6H_5COCl \xrightarrow[AlCl_3]{\text{anhy.}} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + HCl$$

Trend of Boiling Point



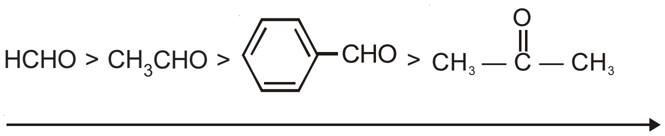
$$CH_3-CH_3-OH > CH_3CH_2CHO > CH_3\overset{O}{\overset{||}{C}}CH_3 > CH_3-O-CH_2-CH_3 > CH_3-CH_2-CH_2-CH_3$$

Chemical Properties

Both aldehydes and ketones contain a carbonyl group in the structure and hence show marked similarity in their chemical behaviour.

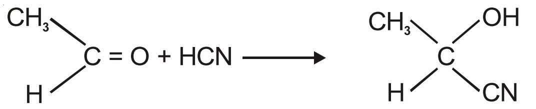
(a) Nucleophilic addition reactions

Reactivity of carbonyl compounds towards nucleophilic addition reaction is governed by ELECTRONIC FACTOR and STERIC FACTOR. Aldehydes are more reactive than ketones.

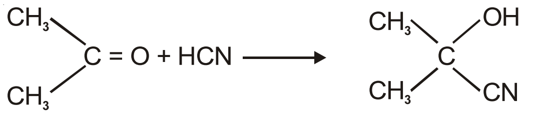


Decreasing reactivity

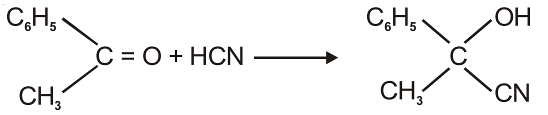
(1) Addition of hydrogen cyanide : Aldheydes and ketones react with hydrogen cyanide to form **cyanohydrins**.



Acetaldehyde Acetaldehyde cyanohydrin

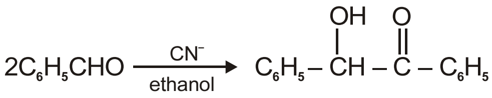


Acetone Acetone cyanohydrin



Acetophenone Acetophenone cyanohydrine

Benzophenone does not react with hydrogen cyanide because of steric hindrance. On the other hand, aromatic aldehydes (e.g., C_6H_5CHO) when refluxed with alcoholic potassium cyanide solution undergo dimerization to form benzoin.

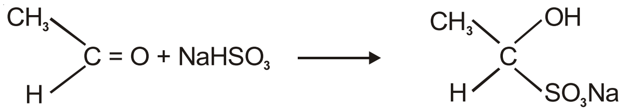


$$2C_6H_5CHO \xrightarrow[\text{ethanol}]{CN^-} C_6H_5-\overset{OH}{\overset{|}{C}}H-\overset{O}{\overset{||}{C}}-C_6H_5$$

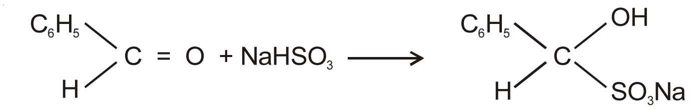
Benzaldehyde Benzoin

Above reaction is known as benzoin condensation.

(2) Addition of sodium bisulphite : Aldehydes and methyl ketones react with a saturated aqueous solution of bisulphite to form crystalline sodium bisulphite derivatives.



Acetaldehyde Sod. bisulphite Acetaldehyde sod. bisulphite

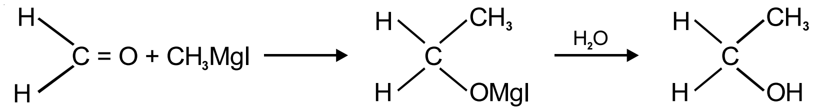


Benzaldehyde Benzaldehyde sod. bisulphite

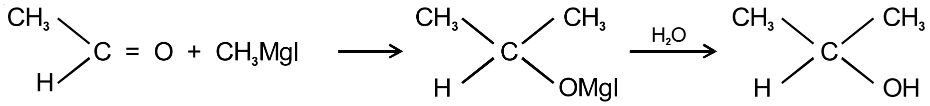
Aromatic ketones and aliphatic ketones having higher alkyl groups do not react with sodium bisulphite. This is due to the fact that the large SO_3^{2} ion cannot attack the carbonyl carbon atom when it is surrounded by larger substituents (steric hindrance).

Thus $C_2H_5COC_2H_5$, $C_6H_5COCH_3$, $C_6H_5COC_6H_5$ do not react with sodium bisulphite. Methyl ketones give this reaction.

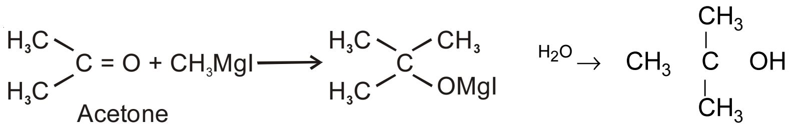
(3) Addition of Grignard reagents :



Formaldehyde Ethyl alcohol (primary alcohol)

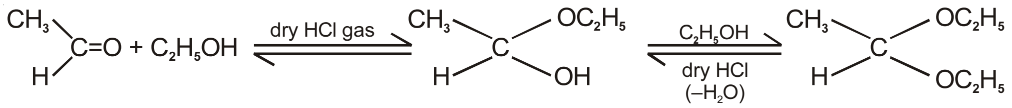


Acetaldehyde Isopropyl alcohol (Sec. alcohol)



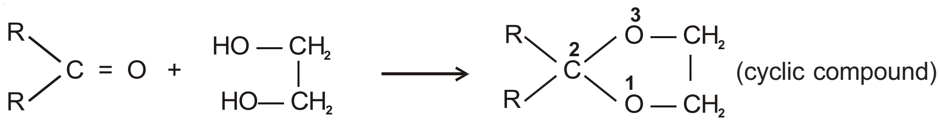
Acetone ter. butyl alcohol (ter. alcohol)

(4) Addition of alcohols (Acetal formation) : Aldehydes (not Ketones) react with alcohols in presence of dry HCl gas to form **hemi-acetals** (hemi means half) which being unstable immediately react with another molecule of alcohol to form stable acetals. For example,



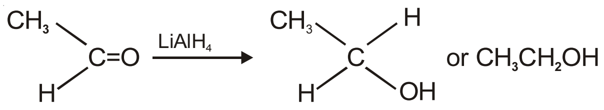
Acetaldehyde hemiacetal
(1-Ethoxyethanol)

Acetaldehyde acetal
(1, 1-diethoxyethane,
Gem diether)



Ethanol Ethylene glycol Ethylene glycol acetal

(5) Reduction by metal hydrides such as lithium aluminium hydride



Acetaldehyde Ethyl alcohol

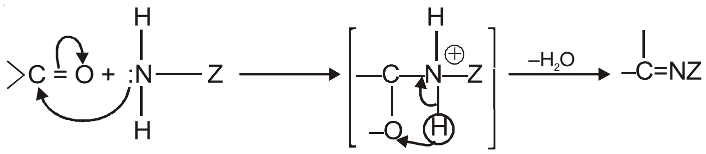
Similar product are also formed by $NaBH_4$, H_2 — Pt, H_2 — Ni or metal-acid.

However, aldehydes and ketones can be reduced to the corresponding alkanes by means of red phosphorus and hydroiodic acid, or amalgamated zinc and concentrated hydrochloric acid (**Clemmensen reduction**) or reacting hydrazine solution followed by treatment with alkaline solution of ethylene glycol (**Wolff-Kishner reduction**). The basic reaction in all these reductions is the reduction of carbonyl group to methylene group.

(1) Replacement of Carbonyl Oxygen :

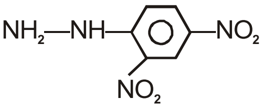
(i) Reaction with Ammonia Derivatives : Aldehydes and ketones react with a number of ammonia derivatives like NH_2OH, NH_2NH_2, $C_6H_5NHNH_2$ etc. in weakly acidic medium.

Such reactions take place in slightly acidic medium and involve nucleophilic addition of the ammonia derivative followed by dehydration.

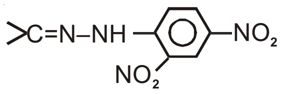


Ammonia der. Addition product

Ammonia derivatives	**Final products**
H_2N — OH Hydroxylamine	$>C = NOH$ Oximes
H_2N — NH_2 Hydrazine	$>C = NNH_2$ Hydrazones
H_2N — NHC_6H_5 Phenylhydrazine	$>C = NNHC_6H_5$ Phenylhydrazones
H_2N — $NHCONH_2$ Semicarbazide	$>C = NNHCONH_2$ Semicarbazones



2, 4 DNP (also known as Brady's reagent)

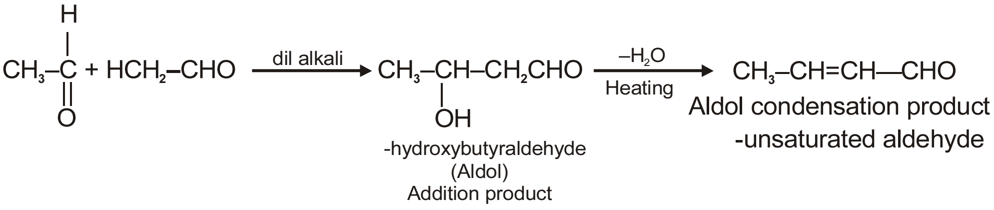


2, 4 Dinitrophenylhydrazones (These are yellow or orange or red solids)

(ii) Reaction with thioalcohols (mercaptans) : Aldehydes and ketones react with thioalcohols and form thioacetals (mercaptals) and thioketals (mercaptals) respectively.

(2) Reactions involving -hydrogen of carbonyl groups :

Aldol condensation :



-hydroxybutyraldehyde (Aldol) Addition product

Aldol condensation product -unsaturated aldehyde

Perkin reaction : Condensation of an aromatic aldehyde with acid anhydride in presence of base (sodium salt of the acid from which the anhydride is derived) to form , -unsaturated acid is known as **Perkin reaction**. For example,

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow{CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} + CH_3COOH$$

(a) Oxidation reactions :

Aldehydes are oxidised not only by strong oxidising agents like $KMnO_4$ and $K_2Cr_2O_7$ but also by much milder oxidising agents like bromine water, Tollen's reagent, Fehling's solution and Benedict's solution.

Tollen's reagent : Tollen's reagent is Ammoniacal silver nitrate solution

$$R.CHO + \underset{\text{(Tollen's reagent)}}{2[Ag(NH_3)_2]OH} \rightarrow RCO\overset{-}{O}\overset{+}{N}H_4 + \underset{\text{Silver mirror}}{2Ag} + H_2O + 3NH_3$$

Fehling solution : [Alkaline solution of copper sulphate containing sodium potassium tartarate (Rochelle salt)]

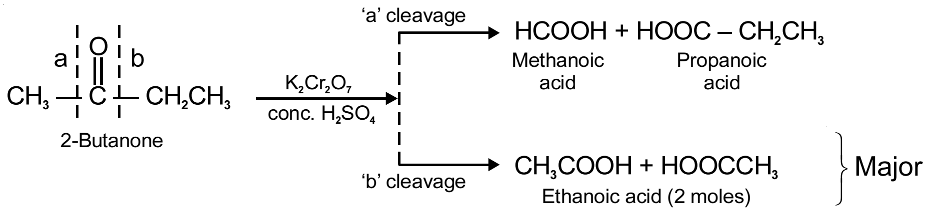
$$R\text{–}CHO + 2Cu^{2+} + 5OH^- \rightarrow R\text{–}COO^- + \underset{\text{(Reddish brown)}}{Cu_2O} + 3H_2O$$

Benedict Solution : Its a solution of $CuSO_4$, sodium citrate and sodium carbonate. When heated with aldehyde it gives a reddish brown ppt. of Cu_2O.

> ***Note :*** *Benedict solutions*

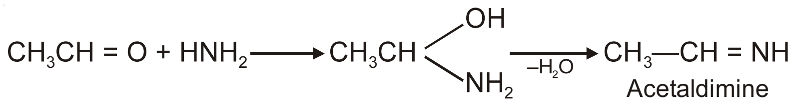
Ketones are not oxidised by mild oxidising agents.

Oxidation in drastic condition



Oxidation of mixed ketones is governed by **Popoff's rule** according to which the carbonyl group of the ketone goes with the smaller alkyl group. Thus in the above case 'b' type of cleavage will decide major products.

(b) Reaction with Ammonia :



$$CH_3CH=O + HNH_2 \longrightarrow CH_3CH\begin{cases}OH\\NH_2\end{cases} \xrightarrow{-H_2O} \underset{\text{Acetaldimine}}{CH_3\text{—}CH=NH}$$

$$6HCHO + 4NH_3 \rightarrow \underset{\substack{\text{Hexamethylene}\\\text{tetramine}\\\text{(Urotropine)}}}{(CH_2)_6N_4} + 6H_2O$$

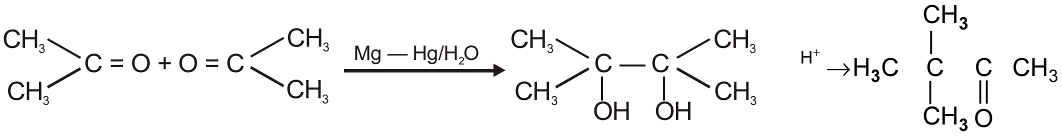
(c) Cannizzaro reaction : This reaction is preferentially given by those aldehydes which do not contain -hydrogen. In Cannizzaro reaction, one molecule of the aldehyde is oxidised to acid at the expense of the other which is reduced to alcohol *i.e.*, disproportionation reaction takes place. The reaction occurs in the presence of concentrated solution of any base.

$$\underset{\text{Formaldehyde}}{2HCHO} + NaOH \rightarrow \underset{\text{Sod. formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

(d) Reaction given only by Ketones :

(1) Reduction in Neutral or Alkaline medium :

To form Pinacol which undergoes Pinacol - Pinacolone rearrangement in acidic medium



$$(CH_3)_2C=O + O=C(CH_3)_2 \xrightarrow{Mg\text{—}Hg/H_2O} (CH_3)_2\underset{OH}{C}\text{—}\underset{OH}{C}(CH_3)_2 \xrightarrow{H^+} H_3C\underset{CH_3}{\overset{CH_3}{C}}\underset{O}{\overset{}{\underset{\|}{C}}}CH_3$$

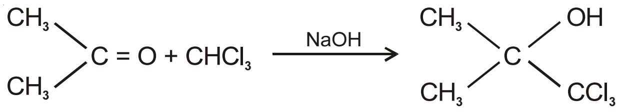
Pinacolone

Ketones can be reduced to secondary alcohols with aluminum isopropoxide in 2-propanol solution

$R_2C=O \xrightarrow[Me_2CHOH]{[Me_2CHO]_3Al} R_2CHOH$ (Meerwein Ponndorf's verley reduction)

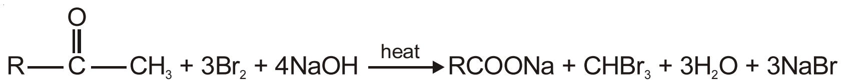
$R_2C=O \xrightarrow[Me_2CHOH]{[Me_2CHO]_3Al} R_2CHOH$

(2) Condensation with chloroform :



1, 1, 1-Trichloro-2-methylpropanol-2
(Chloretone) used as hypnotic drug

Haloform reaction : Methyl ketones or alcohols which can be oxidized to methyl ketone gives this test.

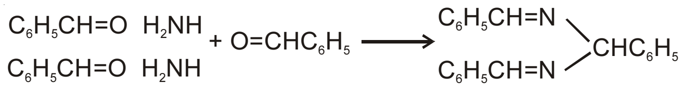
e.g., 

$$R-\overset{\overset{\large O}{\|}}{C}-CH_3 + 3Br_2 + 4NaOH \xrightarrow{heat} RCOONa + CHBr_3 + 3H_2O + 3NaBr$$

Bromoform
(reddish brown ppt.)

(e) Special Reactions of Aromatic Aldehydes and Ketones :

(i) Reaction with Ammonia :



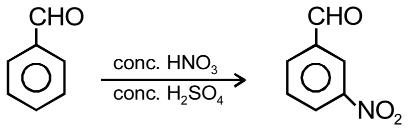
Hydrobenzamide

(ii) Reaction with amines :

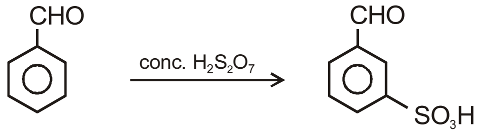
$C_6H_5CH=O + H_2NC_6H_5 \rightarrow C_6H_5CH=NC_6H_5 + H_2O$

Benzylidene aniline.
(Benzal aniline)

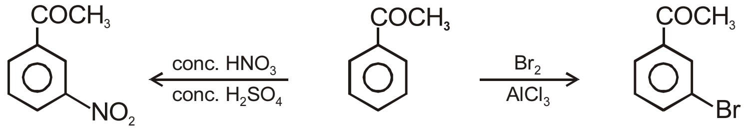
(iii) Reaction of benzene nucleus



Benzaldehyde m-Nitrobenzaldehyde



Benzaldehyde 3-Benzaldehyde sulphonic acid



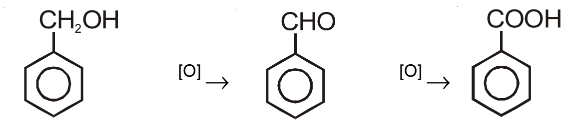
3-Nitroacetophenone Acetophenone 3-Bromoacetophenone

CARBOXYLIC ACIDS

Preparation :

1. **By the oxidation of primary alcohols and aldehydes**

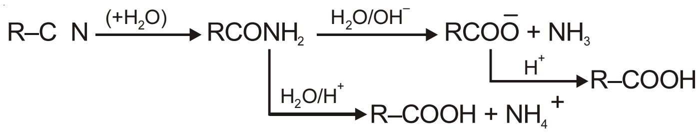
$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow{[O]} \underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{RCOOH}$$



Benzyl alcohol Benzaldehyde Benzoic acid

$$RCOCH_2R \rightarrow \underset{\text{Mixture of two carboxylic acids}}{RCOOH + R\,COOH}$$

2. **By the hydrolysis of cyanides (nitriles)**



$$R\text{–}C\ N \xrightarrow{(+H_2O)} RCONH_2 \xrightarrow{H_2O/OH^-} RCO\bar{O} + NH_3$$

$$RCO\bar{O} \xrightarrow{H^+} R\text{–}COOH$$

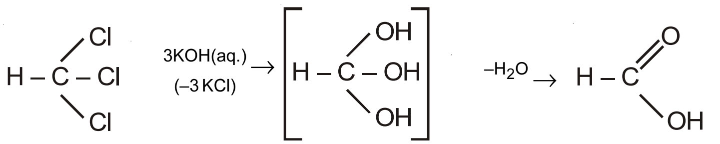
$$RCONH_2 \xrightarrow{H_2O/H^+} R\text{–}COOH + NH_4^+$$

3. **By the hydrolysis of esters**

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + KOH(aq.) \xrightarrow{heat} \underset{\text{Potassium acetate}}{CH_3COOK} + C_2H_5OH$$

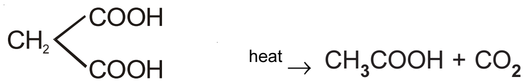
$$CH_3COOK(aq.) + HCl(aq.) \rightarrow \underset{\text{Acetic acid}}{CH_3COOH}(aq.) + KCl(aq.)$$

4. **By the hydrolysis of trihalogen derivatives of alkanes**



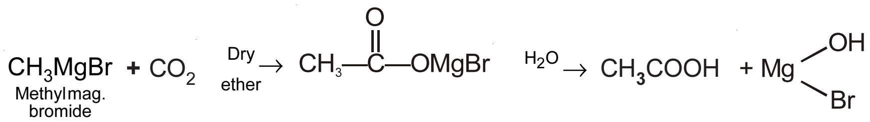
Chloroform Unstable Formic acid

5. **By heating malonic acid and their derivative acids.**

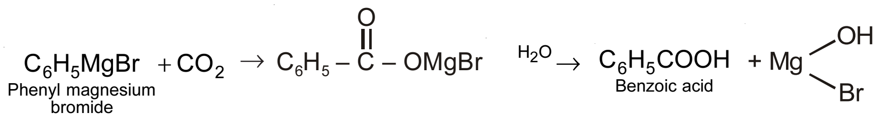


$$\underset{\text{Malonic acid}}{CH_2(COOH)_2} \xrightarrow{heat} CH_3COOH + CO_2$$

6. **By the reaction of Grignard reagent with CO_2**



$$\underset{\text{Methylmag. bromide}}{CH_3MgBr} + CO_2 \xrightarrow[\text{ether}]{\text{Dry}} CH_3\text{—}\overset{\overset{\large O}{||}}{C}\text{—}OMgBr \xrightarrow{H_2O} CH_3COOH + Mg\begin{smallmatrix}OH\\Br\end{smallmatrix}$$

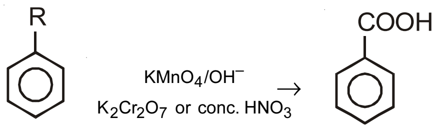


$$C_6H_5MgBr + CO_2 \rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OMgBr \xrightarrow{H_2O} C_6H_5COOH + Mg\begin{matrix}OH\\Br\end{matrix}$$

Phenyl magnesium bromide Benzoic acid

Product in above reactions have one more carbon than that in Grignard reagent taken.

7. **By oxidation of alkyl benzenes**

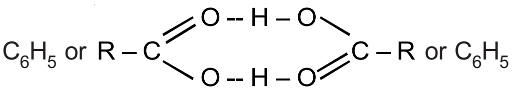


Benzoic acid

Physical properties

1. The first three members (C_1 to C_3) are colourless, pungent smelling liquids, the next three (C_4 to C_6) have unpleasant odours. Acids with 7 or more carbon atoms have no distinct smell because of low volatility.

   Two molecules of carboxylic acids are held together not by one but by two strong hydrogen bonds.



Dimers of carboxylic acids

   The behaviour of **formic acid is exceptional**. It exists as a dimer in vapour state and a polymer in liquid and solid states.

2. In normal carboxylic acids, the even members have markedly higher melting points than the odd members preceding or following it.

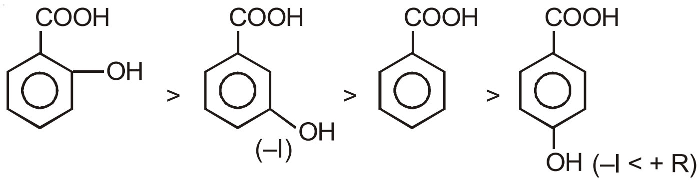
   Effect of Substituents on Acidity :

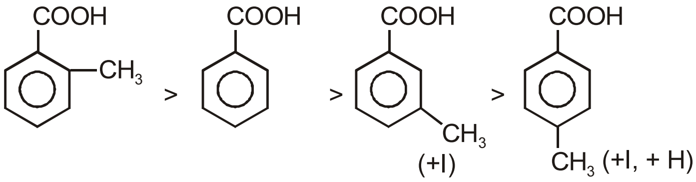
   e.g., the acidic strength of the corresponding halogen acids also follows the same order *i.e.*

FCH_2COOH	$ClCH_2COOH$	$BrCH_2COOH$	ICH_2COOH
Fluoroacetic acid	Chloroacetic acid	Bromoacetic acid	Iodoacetic acid

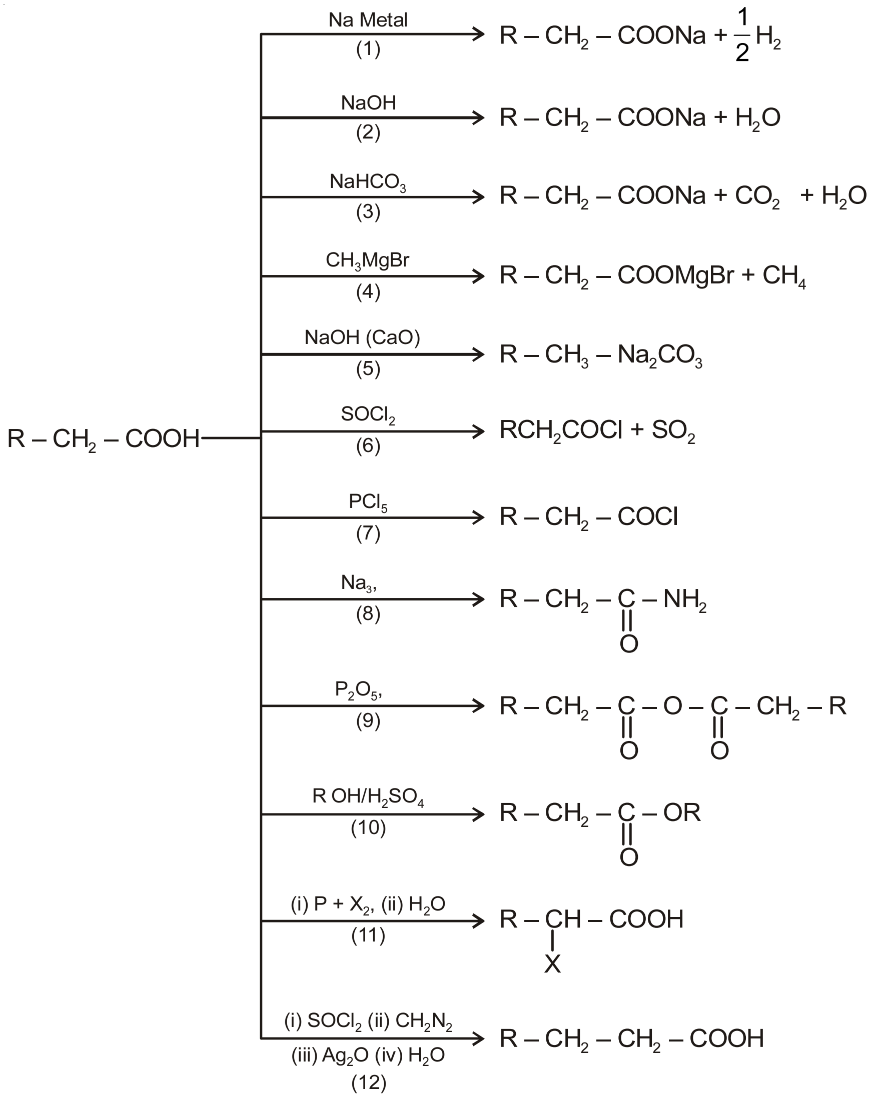
Ortho effect : Among derivative of aromatic carboxylic acid, ortho derivative is the most acidic. This effect is known as ortho effect.

e.g.,





Chemical Properties

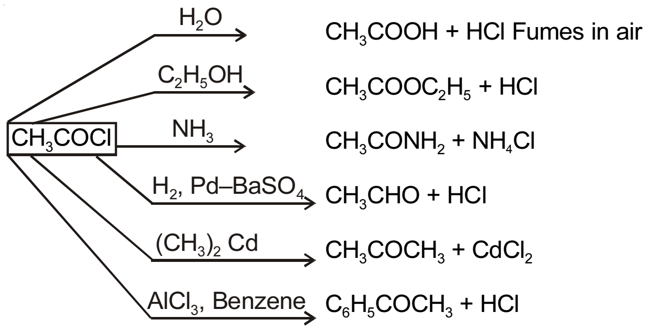


Derivatives of carboxylic acids : These are formed by the replacement of –OH group of acid by some other suitable group e.g. RCOCl, $RCONH_2$, RCOOR and $(RCO)_2O$.

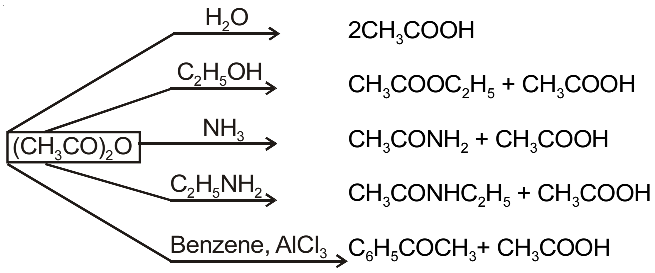
Order of Reactivity Towards Nucleophilic Substitution Reaction :

Carboxylic acid derivatives reacts with a nucleophile through addition/elimination mechanism via tetrahedral intermediate over all substitution product is obtained.

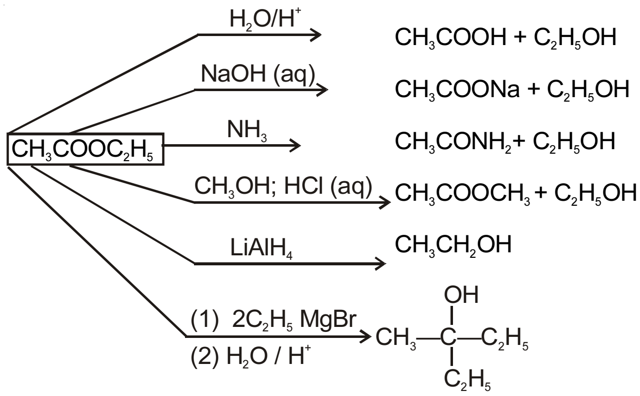
Properties :



Acid Anhydrides : $(RCO)_2O$, prepared by dehydration of carboxylic acid.

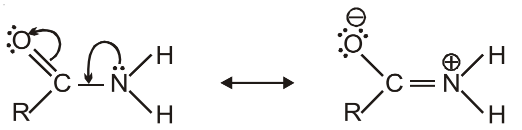


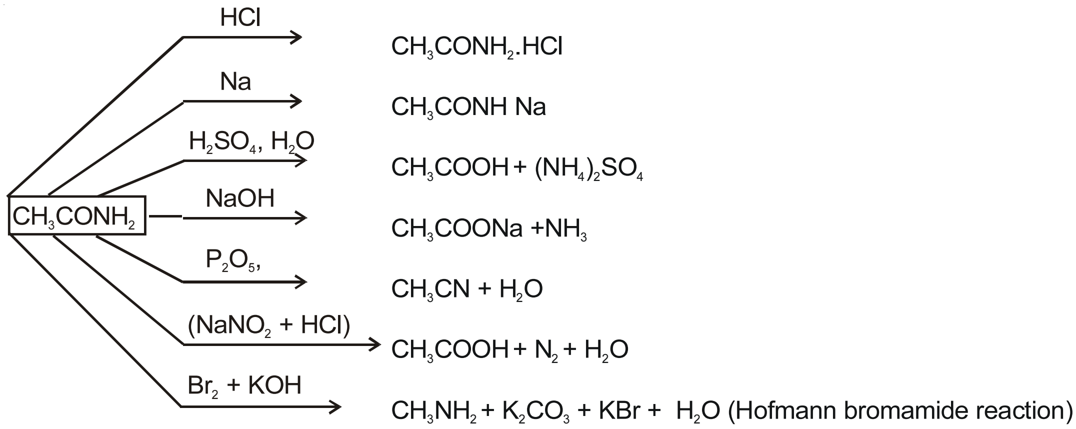
Esters : RCOOR prepared by reaction of acid with alcohol or acid chloride or anhydrides with alcohol.



Acid amides : $RCONH_2$ – It is prepared by reaction of carboxylic acid or its derivatives with NH_3. It is amphoteric in nature.

Acid amides act as weak acids as well as weak bases. Lone pair of N is delocalised with π electrons of C = O group.





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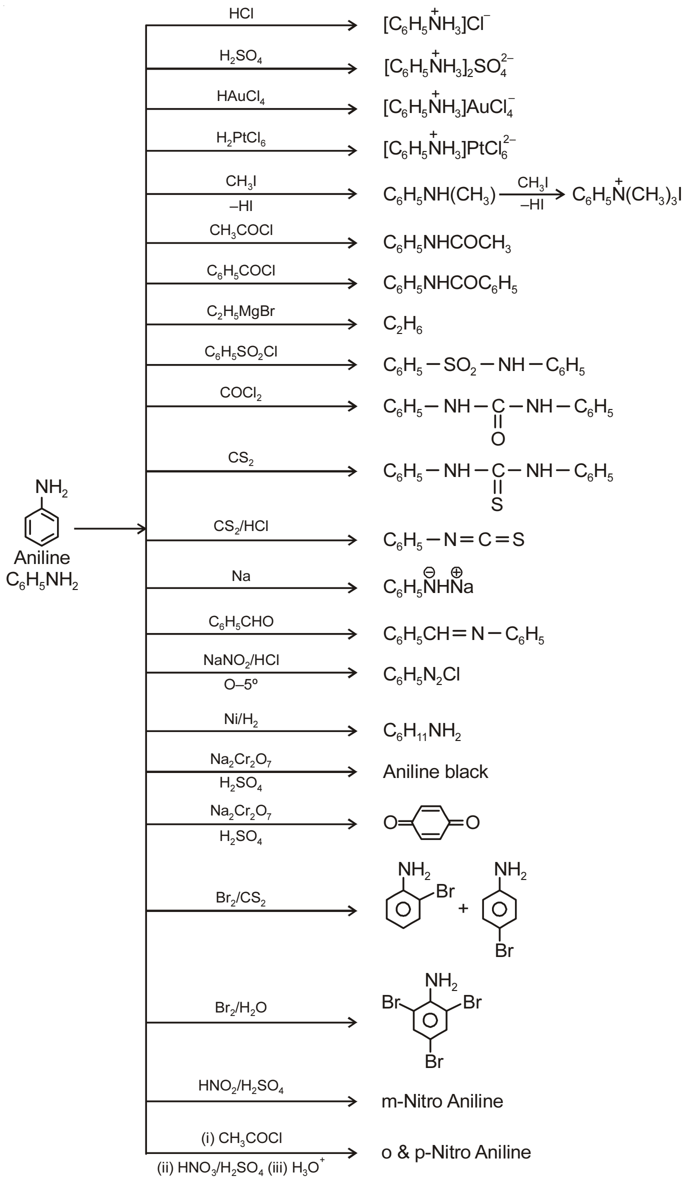
Chapter 15

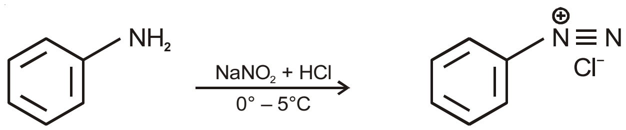
Organic Compounds Containing Nitrogen

CHEMICAL REACTIONS OF ANILINE



DIAZONIUM SALT

1. Preparation of benzene diazonium chloride

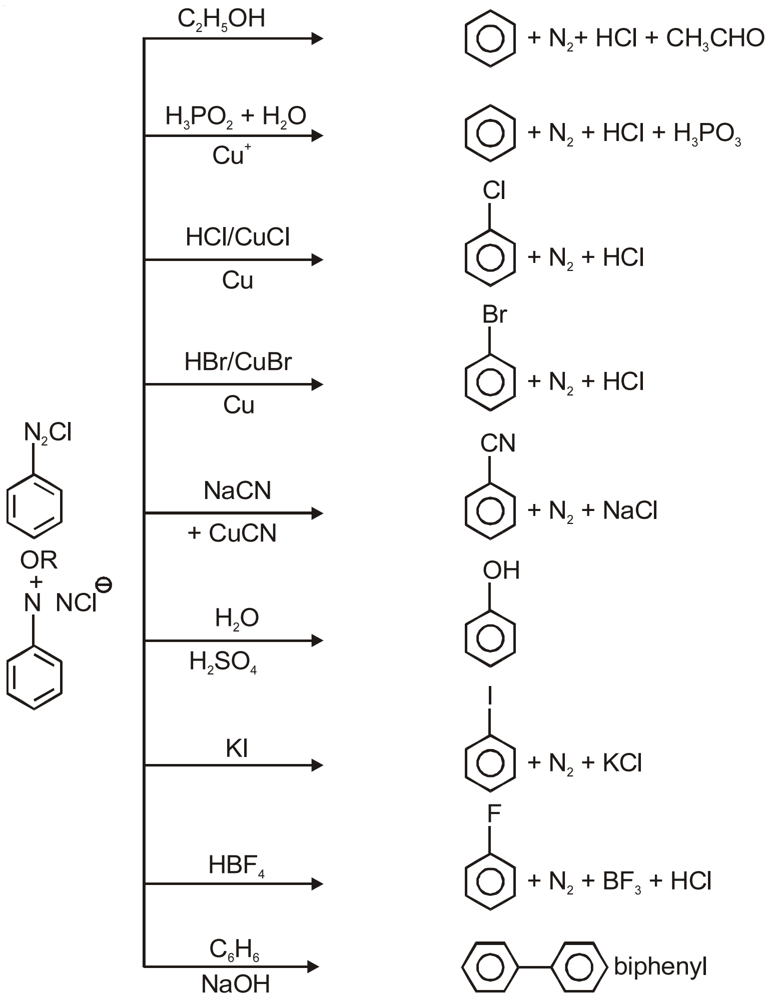


Benzene diazonium chloride
(useful reactive intermediate
in aromatic chemistry)

2. Properties of Benzene Diazonium Chloride (B.D.C.)

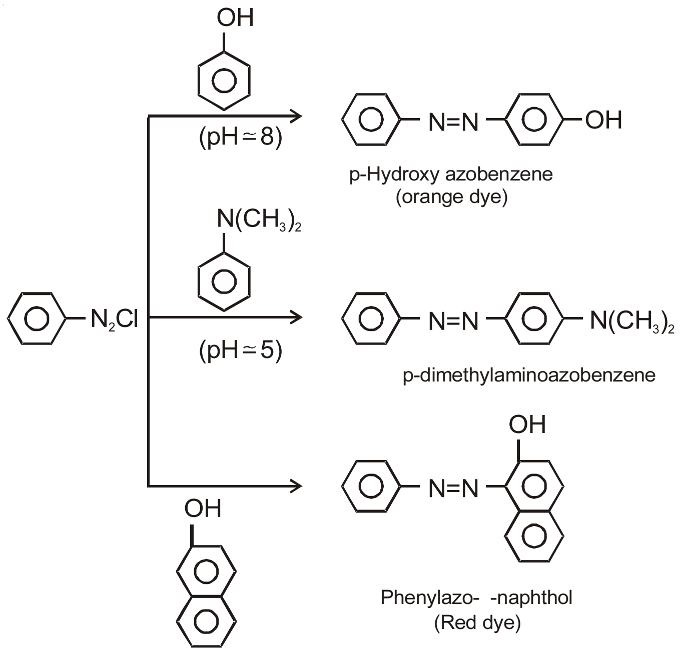
A. Substitution Reaction :

Benzene diazonium chloride is used for prepration of several organic compounds.



B. Coupling Reaction :

Coupling of benzene diazonium chloride with phenol takes place in slightly basic medium while that of aniline take place in slightly acidic medium. These compounds produce Azo dyes with benzene diazonium chloride.

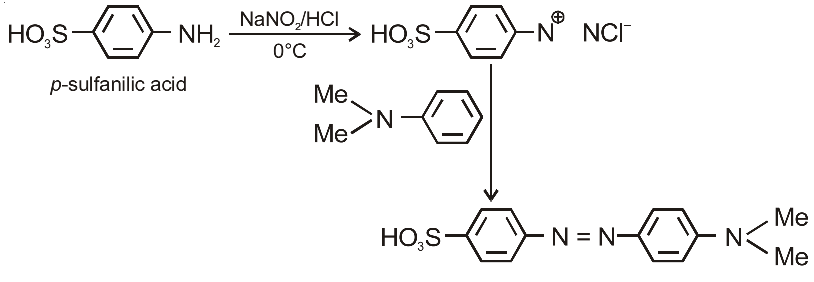


p-Hydroxy azobenzene
(orange dye)

p-dimethylaminoazobenzene

Phenylazo- -naphthol
(Red dye)

Formation of Methyl Orange



p-sulfanilic acid

Methyl orange

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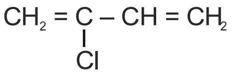
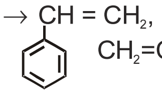
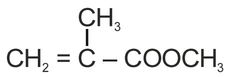
Chapter 16

Polymers, Biomolecules, Chemistry in Everyday Life

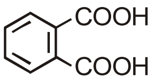
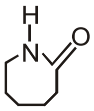
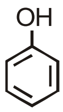
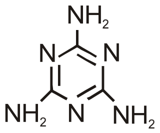
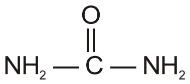
POLYMERS

SYNTHETIC POLYMERS AND THEIR APPLICATIONS

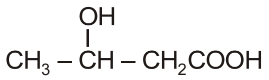
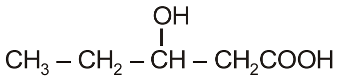
Addition Polymers

Polymer	Monomer	Application
Polyethylene	Ethene → $CH_2 = CH_2$	Packing material carry bags, insulation for electrical wires and cables... etc.
Polypropylene	Propene → $CH_3 - CH = CH_2$	Packing of textiles and foods, linears for bags, heat shrinkage wraps, carpet fibres... etc.
Polystyrene or Styron	Styrene → $C_6H_5 - CH = CH_2$	Plastic toys, house hold wares radio and television bodies
Neoprene	Chloroprene  $CH_2 = \underset{Cl}{\underset{\vert}{C}} - CH = CH_2$	shoe heels, stoppers, printing rollers
Buna-S	Styrene →  , Butadiene→ $CH_2{=}CH{-}CH{=}CH_2$	Manufacture of tyres, rubber sole, water proof shoes
Polyacrylates	Methyl methacrylate	Lenses, light covers, light shades, air craft windows... etc.
Polyethyl acrylate	 $CH_2 = \overset{CH_3}{\overset{\vert}{C}} - COOCH_3$ $CH_2 = CH - COOC_2H_5$	Latex paints adhesives
Polyacrylonitrile (PAN)(orlon)	Acrylonitrile → $CH_2 = CH - CN$	For making clothes, carpets, blankets... etc.
Polyvinyl chloride (PVC)	Vinyl chloride → $CH_2 = CH - Cl$	Good electrical insulator, hose pipes, rain coats, hand bags... etc.
Polytetrafluoro ethylene (PTFE) (Teflon)	Tetrafluoro ethylene → $CF_2 = CF_2$	For nonstick utensils coating etc.

Condensation Polymers

Polymer	Monomer	Application
Terylene or dacron	(i) Ethylene glycol– $HO-CH_2-CH_2-OH$ (ii) Terephthalic acid – 	For wash and wear fabric tyre cords, seat belts and sails
Glyptal or Alkyd resin	(i) Ethylene glycol – $HO-CH_2-CH_2-OH$ (ii) Phthalic acid – 	Paints and Lacquers
Polymer	**Monomer**	**Application**
Nylon 6, 6	Adipic acid – $HOOC-(CH_2)_4-COOH$ Hexamethylenediamine – $H_2N-(CH_2)_6-NH_2$	Textile fabrics
Nylon 6, 10	$H_2N(CH_2)_6NH_2$ Hexamethylene diamine Sebacic acid – $HOOC-(CH_2)_8COOH$	Textile fabrics, carpets, bristles for brushes
Nylon 6	Caprolactam – 	Mountaineering ropes, tyre cords fabrics
Bakelite	Phenol  Formaldehyde, HCHO	As binding glue for wood varnishes, lacquers
Melamine Formaldehyde resin	Melamine and Formaldehyde  and HCHO	Non-breakable
Urea formaldehyde resin	(i) Urea  $NH_2-\overset{\overset{O}{\|}}{C}-NH_2$ (ii) Formaldehyde HCHO	Buttons, bottle caps, surgical items

Biodegradable Polymer

Name	Monomer	Uses
Poly- -hydroxy butyrate-Co-hydroxy valerate [PHBV].	(a)  $CH_3-CH(OH)-CH_2COOH$ 3- hydroxybutanoic acid (b)  $CH_3-CH_2-CH(OH)-CH_2COOH$ 3-hydroxypentanoic acid	As packaging orthopaedic devices and in controlled drug release.

BIOMOLECULES

Carbohydrates

1. Carbohydrates are mainly compounds of carbon, hydrogen and oxygen.
2. General molecular formula initially considered was $C_x(H_2O)_y$

   e.g., glucose – $C_6H_{12}O_6$, sucrose $C_{12}H_{22}O_{11}$ etc.

   But many of the compounds which behave as carbohydrates, do not follow the general molecular formula $C_x(H_2O)_y$ formula.
3. Thus carbohydrates are the class of compounds that include polyhydroxy aldehydes or polyhydroxy ketones.
4. Carbohydrates are also known as **saccharides**.

Classification

The carbohydrates are classified into three major classes

(i) Monosaccharides

(ii) Oligosaccharides

(iii) Polysaccharides

Monosaccharides

(i) Monosaccharides are simple sugars with single unit of polyhydroxy aldehyde or polyhydroxy ketones.

(ii) General molecular formula $C_nH_{2n}O_n$ (with some exceptions).

Oligosaccharides

(i) Oligosaccharides are made up of 2-9 units of monosaccharides or simple sugars.

(ii) Oligosaccharides with two, three and four monosaccharides respectively known as disaccharides, and trisaccharides and tetrasaccharides.

(iii) Sucrose is the example of this class.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

Polysaccharides

(i) Polysaccharides are made up of 'n' number of monosaccharide units (above 10 carbon atoms).

(ii) Starch, cellulose and glycogen are the examples of this class.

(iii) $\underset{\text{starch}}{(C_6H_{10}O_5)_n} \xrightarrow[H^+]{nH_2O} \underset{\text{glucose}}{nC_6H_{12}O_6}$

(iv) Homopolysaccharides are made up of single type of monosaccharides. Heteropolysaccharide is made up of two or more different types of monosaccharides.

> **Note :** *Monosaccharides and oligosaccharides are collectively known as* ***Sugars*** *as they are soluble in water and sweet in taste. Whereas polysaccharides on other hand are known as* ***Non-sugars****.*

Monosaccharide-Glucose

Glucose is known as **dextrose** and also known as grape sugar.

Preparation

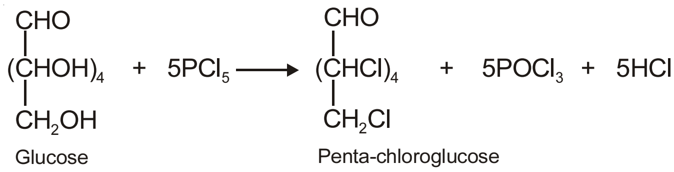
Hydrolysis of cane sugar in presence of alcohol gives glucose (along with fructose)

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Glucose and Fructose have same molecular formula but different structural formula.

Chemical Properties

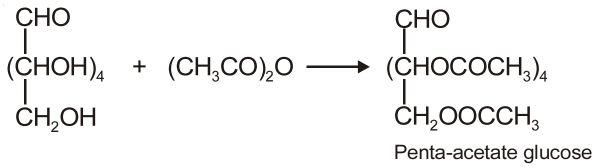
(i) **Reaction with PCl_5 :**



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 5PCl_5 \longrightarrow \begin{array}{l} CHO \\ | \\ (CHCl)_4 \\ | \\ CH_2Cl \end{array} + 5POCl_3 + 5HCl$$

Glucose Penta-chloroglucose

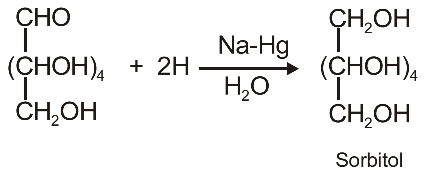
(ii) **Reaction with acetic anhydride :**



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + (CH_3CO)_2O \longrightarrow \begin{array}{l} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OOCCH_3 \end{array}$$

Penta-acetate glucose

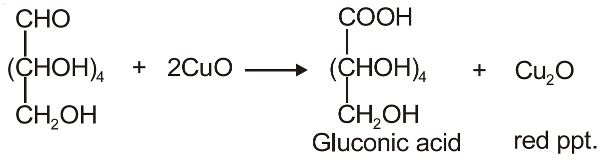
(iii) **Reduction :**



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 2H \xrightarrow[H_2O]{Na\text{-}Hg} \begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Sorbitol

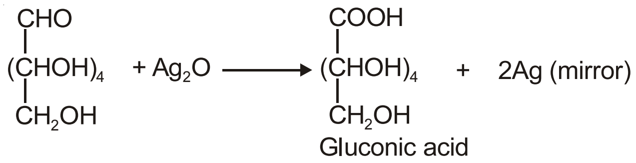
(iv) **Reaction with Fehling's solution :**



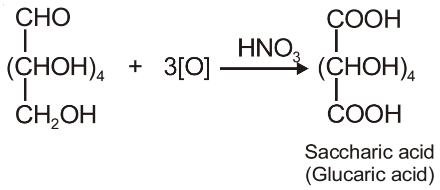
$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 2CuO \longrightarrow \begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + Cu_2O$$

Gluconic acid red ppt.

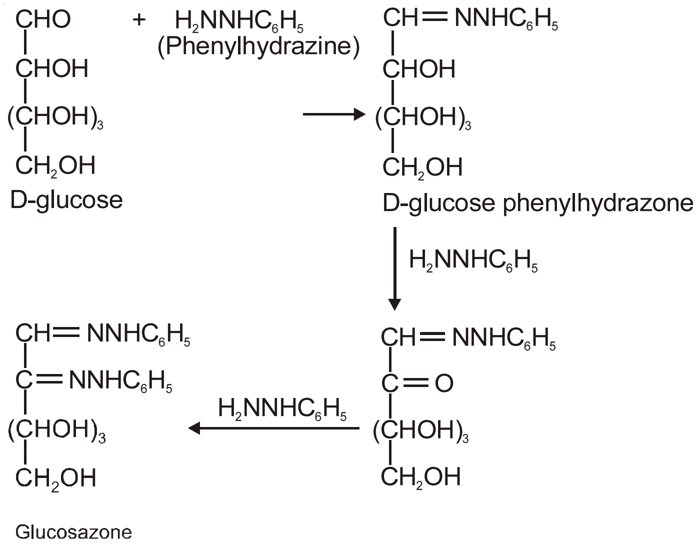
(v) **Reaction with Tollen's reagent :**



(vi) **Reaction with HNO_3 :**



(vii) **Reaction with phenylhydrazine :**



(viii) **Lobry de Bruyn-van Ekenstein rearrangement reaction :**

Glucose on reaction with dilute NaOH undergoes a reversible isomerisation and is converted into a mixture of D-Glucose, D-Mannose and D-Fructose.

D-Glucose $\rightleftharpoons$ D-Mannose $\rightleftharpoons$ D-Fructose.

Note : *Due to this isomerisation, fructose even it does not contain – CHO group reduces Fehling's solution and Tollen's reagent in alkaline medium.*

Structure of D-Glucose

(i) Open chain structure :

The reaction of glucose with

(a) HI to give hexane

(b) Hydroxylamine to form monoxime

(c) HCN to form cyanohydrin, gives the existence of the open chain structure of glucose

(ii) Cyclic structure of glucose :

The open chain structure of glucose fails to explain

(a) Any reaction with $NaHSO_3$ and NH_3 , even though – CHO group is present.

(b) The reaction of glucose with Grignard reagent.

Disaccharides

(i) Disaccharides are composed of two molecules of monosaccharides linked by **glycosidic linkage**.

(ii) The disaccharides may be reducing or non reducing in nature depending upon linkage.

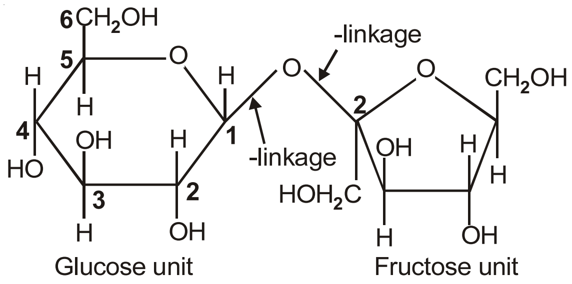
Sucrose $(C_{12}H_{22}O_{11}) \xrightarrow{H_2O/H^+} \underset{(C_1)}{\text{-D Glucose}} + \underset{(C_2)}{\text{-D Fructose}}$

Lactose $(C_{12}H_{22}O_{11}) \xrightarrow{H_2O/H^+} \underset{(C_4)}{\text{-D Glucose}} + \underset{(C_1)}{\text{-D Galactose}}$

Maltose $(C_{12}H_{22}O_{11}) \xrightarrow{H_2O/H^+} \underset{(C_1)}{\text{-D Glucose}} + \underset{(C_4)}{\text{-D Glucose}}$

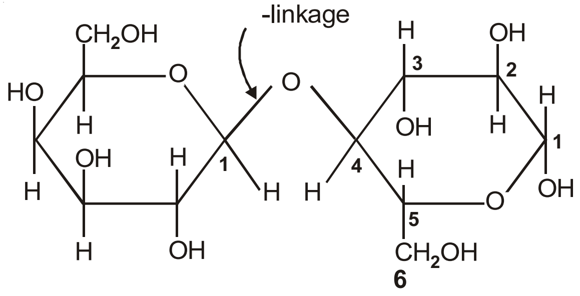
Structure of Sucrose, Lactose and Maltose

(i) Sucrose



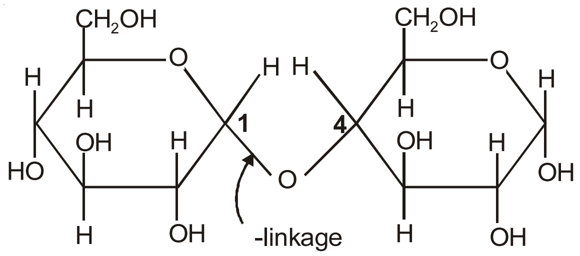
, -glycosidic linkage

(ii) Lactose



-glycosidic linkage

(iii) Maltose



-glycosidic linkage

Polysaccharides :

In polysaccharides, thousands of monosaccharide units are joined together by glycosidic linkage.

Starch : $(C_6H_{10}O_5)_n$

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow{H^+/H_2O} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{D-glucose}}{C_6H_{12}O_6}$$

(i) Starch does not reduce Fehling's solution or Tollen's reagent.

(ii) Starch does not form an Osazone.

(iii) Starch is a mixture of two polysaccharides *i.e.*, amylose (15-20%) and amylopectin (80-85%). Amylose is water soluble and amylopectin is water insoluble component of starch.

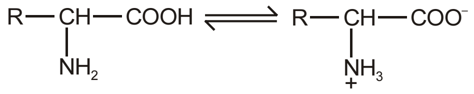
Cellulose : $(C_6H_{10}O_5)_n$

(i) Cellulose is a straight chain polysaccharide composed of only D-glucose units with 1-4 glucosidic linkage.

(ii) Cellulose does not reduce Tollen's reagent or Fehling's solution.

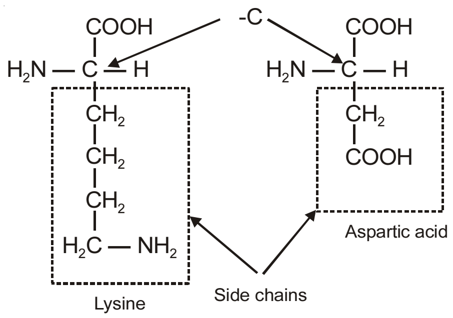
AMINO ACIDS

Proteins are made up of amino acids. All naturally occurring amino acids are -amino acids, where amine group is connected with -carbon of carboxylic acid. Amino acids have amphoteric character. A free amino group is basic, a free carboxyl group is acidic. **Lysine and Arginine** are **Basic Amino Acids** because they carry two amino groups and one carboxyl group is acidic. **Glutamic acid (glutamate) and Aspartic acid (aspartate)** contain one amino and two carboxyl groups each and are classified as **Acidic Amino Acids**. Alanine, glycine, valine and phenylalanine are **Neutral Amino Acids** as these contain one amino and one carboxyl group.

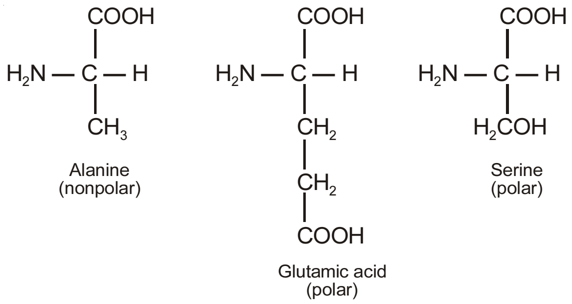


$$\underset{\substack{|\\ NH_2}}{R-CH-COOH} \rightleftharpoons \underset{\substack{|\\ \overset{+}{N}H_3}}{R-CH-COO^-}$$

Amino acid (R = side chain)



Side chain of a basic and an acidic amino acids



Examples of polar and nonpolar amino acids

Amino Acids which occur in Proteins: Glycine, alanine, serine, cysteine, aspartic acid, glutamic acid, asparagine, glutamine, methionine, threonine, valine, leucine, isoleucine, lysine, histidine, arginine, phenylalanine, tyrosine, tryptophan and proline.

PROTEINS

Proteins are polyamides formed from amino acids. The -carbon atom of the amino acids is asymmetric and show optical isomerism (stereo). Proteins consist mainly of L isomers of amino acids. There are 20 commonly occurring amino acids in proteins. Amino acids form zwitter ion. Lack of essential amino acids in diet can cause diseases such as Kwashiorkor.

Peptide Bond and Structure of Proteins: Amino acids are joined together by an amide linkage called **peptide bond**.

Proteins are long polymers of amino acids linked by peptide bonds (polypeptides). The sequence in which the amino acids are arranged in a protein is called the primary structure.

The secondary structure arises due to the regular folding of the backbone of the polypeptide chain due to intramolecular hydrogen bonding in -helix and intermolecular hydrogen bonding in -plated sheet between the carboxyl and amino groups. Lead to the formation of -helix and -pleated sheet.

Tertiary Structure of Proteins: The tertiary structure of proteins represents overall folding of the polypeptide chain *i.e.,* fruther folding of the secondary structure. It gives rise to two major molecular shapes viz fibrous and globular. The main forces which stabilises the 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

Quarternary structure of proteins : Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these sub-units with respect to each other is known as quaternary structure.

ENZYMES

Enzymes are biological catalysts which increase the rate of biochemical reactions even under mild conditions of temperature and pH without taking part in reaction.

Properties of Enzymes :

(i) They speed up reactions up to ten million times compared to the uncatalyzed reactions.

(ii) They are very specific in their action on substrates and each enzyme catalyzes only specific type of reaction.

(iii) They are active at moderate temperature and pH.

(iv) The action of enzymes are inhibited by various organic and inorganic molecules.

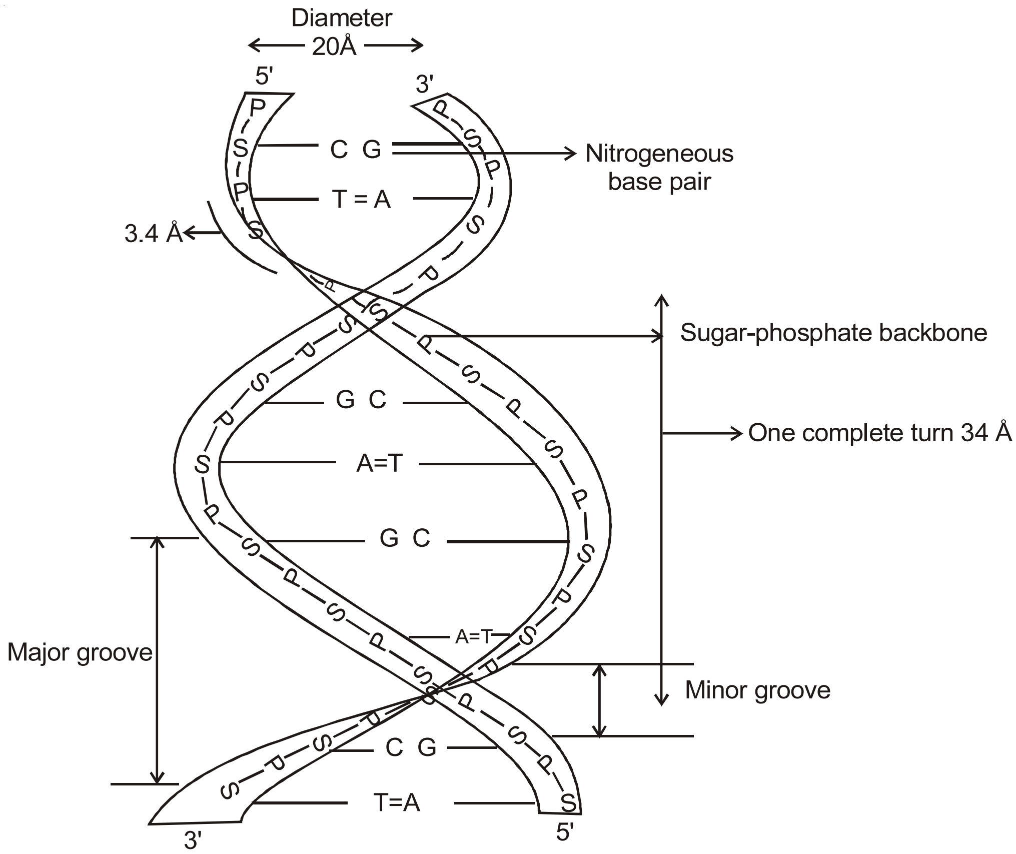
Enzymes and Diseases : Certain diseases are caused by enzyme deficiencies. The congenital disease phenylketonuria, is due to a deficiency of the enzyme phenylalanine hydroxylase. Albinism is another disease caused due to deficiency of an enzyme tyrosinase. Many heart attacks are caused by blood clot formation in a coronary artery. The enzyme streptokinase is used to dissolve the clot.

NUCLEIC ACIDS

1. Nucleic acids play an essential role in transmission of the hereditary characteristics and the biosynthesis of proteins.
2. There are two classes of nucleic acids : DNA (deoxyribonucleic acid) and RNA (ribonucleic acid). Nucleic acids are the long polymers in which the monomeric units are nucleotides. The structural units of nucleotides are made up of three essential components; a nitrogenous base, a pentose sugar (a 5-carbon sugar), and a phosphate group.
3. In nucleic acids, the individual nucleotides are linked through phosphate groups to give rise to long polynucleotide structures.

Structure of DNA

DNA consists of two strands of polynucleotides coiled around each other in the form of a double helix.



Functions of Nucleic Acids

Replication : The genetic information of the cell is contained in the sequence of the bases A, T, G and C in the DNA molecule.

The DNA sequence that codes for a specific protein or polypeptide is called a **Gene** and thus every protein in a cell has a corresponding gene. The relation between the nucleotide triplets and the amino acids is called the **GENETIC CODE**.

VITAMINS

Vitamins are organic compounds necessary for normal health but cannot be synthesised in human body. Deficiency of vitamins causes many disorders and diseases. Vitamins B and C are water soluble while vitamins A, D, K and E are fat soluble.

CHEMISTRY IN EVERYDAY LIFE

Chemicals in medicines

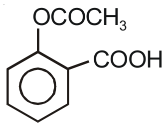
Chemical substances used for treatment of disease and for reducing the suffering from pain are called medicines or drugs. Chemotherapy is the science in which chemicals are used for the treatment of diseases.

Chemicals used in chemotherapy are frequently classified according to their action. Thus analgesics relieve pain, antipyretics reduce temperature, anti-inflammatories control inflammation and antibiotics kill bacteria and other micro-organisms.

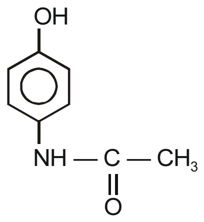
Antipyretics

Antipyretics are substances used to bring down body temperature in high fever. e.g. Aspirin, Phenacetin and Paracetamol.

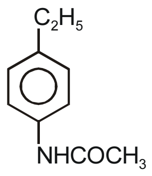
Aspirin is a common antipyretic. It should not be taken empty-stomach as it generates salicylic acid which may ulcerate stomach wall and can cause bleeding. Calcium and sodium salts of aspirin are more soluble and less harmful.



Aspirin



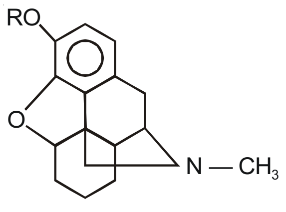
4–acetamidophenol (Paracetamol)



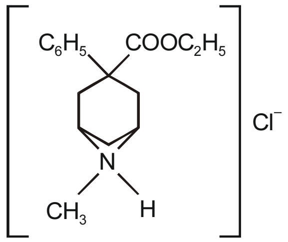
Phenacetin

Analgesics

These are drugs used for relieving pain. Aspirin and some other antipyretics act as analgesics also. Certain narcotics (which produce sleep and unconsciousness) are also used as analgesics. Examples of narcotics are morphine, marijuana, codeine, pethidine and heroin. They are known to be habit-forming.



R = H, Morphine
R = CH_3, Codeine



Pethidine hydrochloride

Antibiotics

Antibiotics are chemical substances produced by micro-organisms (bacteria, fungi and moulds) that can inhibit the growth or even destroy other micro-organisms. Penicillin is used against large number of infections caused by various bacteria. It is an effective drug for pneumonia, bronchitis, sore throat and abscesses. Other antibiotics like streptomycin and tetracycline are used against diseases caused by bacteria.

Some antibiotics are specific for certain diseases, for example, streptomycin for tuberculosis and chloramphenicol for typhoid.

Broad spectrum antibiotics are medicines effective against several different types of harmful micro-organisms, *e.g.,* tetracycline, chloramphenicol. Penicillin has a narrow spectrum. Ampicillin and amoxicillin are derivatives of penicillin.

Chloramphenicol is a broad spectrum antibiotic. It is rapidly absorbed from the gastro-intestinal tract and hence can be given orally in case of typhoid, dysentry, acute fever, certain form of urinary infections, meningitis and pneumonia.

Sulpha drugs like sulphanilamide, sulphadiazine and sulphaguanidine act against micro-organisms like antibiotics and have been used in place of them.

Tranquilizers

The chemical substances which act on the central nervous system and has a calming effect to reduce anxiety are specified as **tranquilizers**. They are used for the treatment of mental diseases they are also used for making sleeping pills. They are habit forming and should not be taken without proper prescription. They do not add any energy into the person but help to remove the emotional distress or depression and the person is able to work to his full capacity. The most commonly used tranquilizers are barbituric acid and its substituted derivatives such as luminal and seconal.

CHEMICAL IN FOOD

During processing of food, a number of chemicals are added to it to increase its life and also to make it more attractive. Some of these chemicals which are present in food are discussed below.

1. **Chemical preservatives :** Growth of micro organisms in a food material can be inhibited by adding certain chemical substances. Such chemical substances which are added to food materials to prevents their spoilage are known as chemical preservatives. The most commonly used preservatives includes table salt, sugar, vegetable oils and sodium benzoate. Sodium benzoate is used in limited quantity salts of sorbic acid and propanoic acid are also used as preservatives.
2. **Artificial sweetening agent :** Sugar is the natural sweeting agent. However, excess of sugar leads to many diseases such as obesity, diabetes. Many artificial sweetening agents have been isolated which are more sweeter than sugar. Ortho-sulphobenzimide also called saccharin is the first popular sweetening agent. Some other artificial sweetener are aspartame, sucralose, alitame etc.

CLEANSING AGENT

Two types of detergents are used as cleansing agent. These are soaps and synthesis detergents. These help in removal of fats which bind other materials to the fabric or skin.

These days detergents are much in vogue and get preference over soaps because they work even in hard water. Synthetic detergents are classified into three main categories namely anionic, cationic and non-ionic and each category has its specific use. Detergents with straight chain of hydrocarbons are preferred over branched chain as the latter are non-biodegradable and consequently cause environmental pollution.

❑ ❑ ❑

Chapter 17

Classification of Elements and Periodicity in Properties

PERIODIC TRENDS IN PROPERTIES

A. Atomic Size (or atomic radius)

Atomic radius is the size of the atom of an element. Atomic radius is defined as "the distance from the centre of the nucleus upto the centre of outermost electron." It is measured in Angstrom unit (Å). It is not possible to measure exact atomic radius as an atom is unstable and it cannot be isolated to get its radius. Moreover, the exact position of the outermost electron is uncertain. The values for radii are obtained from X-ray measurements. Following points are to be noted in this context :

(a) The size of an atom or ion decreases in a horizontal period as we move from left to right.

(b) The atomic radius increases in a group with the rise in atomic number.

(c) **A positive ion (cation) is smaller than the corresponding atom :** A positive ion or cation is formed by the loss of one or more electrons from an atom and the number of protons remains the same in the nucleus. Thus the ratio of the positive charge in the nucleus to the number of electrons *i.e.*, effective nuclear charge increases. Hence the force of attraction of nucleus to the outer electrons increases thus decreasing the size of cation. In case of alkali metals, the removal of an electron removes the entire outermost shell.

(d) **A negative ion (anion) is bigger than the corresponding atom :** In the formation of negative ion (anion) one or more electrons(s) are added to the atom. This results in the expansion of the size of the nuclear charge, which in turn decreases the force of attraction and increases the size of an anion or the pull exercised by the nucleus on the electron becomes less *i.e.*, they move a little farther resulting in an increase in the ionic size.

Note : ***Size of Iso-electronic ions :*** *These are such cations or anions which carry the same number of electrons. The size of such ions depends upon the effective nuclear charge. Greater the nuclear charge of an ion, greater will be the force of attraction for same number of electrons. As a result, the size of the ion decreases. For example :*

N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} *and* Al^{3+} *are isoelectronic ions, among these* N^{3-} *is largest* (1.71 A) *and* Al^{3+} *is smallest* (0.50 A).

B. Ionization Enthalpy

It is the amount of energy required to remove most loosely held electron from the ground state of an Avogadro number of the isolated atoms, ions or molecules in the gaseous state. The ion formed by loss of first electron may lose further electrons and thus we may have successive ionization energies for removal of 2nd, 3rd and 4th electrons in the gaseous state.

Ionization is always an endothermic process and ionization energies are therefore always assigned positive values.

Factors influencing Ionization energy

(1) Successive Ionization - Generally ionization energy increases for successive ionizations.

(2) Atomic size - Ionization energy decreases as the size of atom increases.

(3) Value of Z (atomic number) - Higher the value of Z, higher is the I.E.

(4) Distance of electron from the nucleus - Smaller the distance of the electron from the nucleus, larger is the ionization energy

(5) Shielding effect - Higher is the shielding of the electron to be removed, lower is the I.E. Shielding effect of the electrons of different orbitals follows the order $s > p > d > f$.

(6) Penetration effect - Higher the penetration power of the electron to be removed higher is the I.E. The penetration power of electrons of various orbitals follow the order $s > p > d > f$.

(7) Nature of shell - Ionization energy increases if the electron to be ionized from the species belongs to a half filled shell or a completely filled shell. The relative stability of these configurations follows the order $d^5 < p^3 < d^{10} < p^6$.

(8) Changes in the quantum shell - During the successive ionization, the electron to be ionized belongs to the lower quantum shell the I.E. therefore increases many folds. It is the combined effect of (a) effective nuclear charge (b) stability of completely filled shells (c) closer proximity of the lower shell to the positively charged nucleus.

> ***Note :*** $I.E_1$: Li < B < Be < C < O < N < F < Ne
> $I.E_1$: Na < Al < Mg < Si < S < P < Cl < Ar
> $I.E_2$: O > F > N > C.

C. Electron affinity and Electron gain Enthalpy (H_{EG})

It is defined as the energy released when electron is added to the valence shell of the one mole of isolated gaseous atoms or ions and the enthalpy change accompanying the process is defined as the electron gain enthalpy ($_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion, $X_{(g)} + e^- \rightarrow X^{\ominus}_{(g)}$. It may be considered to be same as I.E. of corresponding anion. The first E.A. of active non metals is negative. But the addition of a second electron to an already formed anion makes the reaction , ($X^- + e^- \rightarrow X^{2-}$) endothermic. At the time of formation of oxide or sulphide ion, the effect of 2nd E.A. is so much that the overall E.A. for the formation of oxide and sulphide ions is **endothermic**.

Variation of electron affinity

(1) Elements which have higher I.E. have higher E.A. also.

(2) The E.A. values of the second period elements are lower in comparison with the values of third row elements. This is due to increase in the interelectronic repulsions which are more for the smaller elements because of higher electron densities.

(3) Effective nuclear sheilding by the '*s*' electrons and the necessity of using higher energy orbitals to accept electrons turn the E.A. of group IIA elements negative.

(4) Au because of very high effective nuclear charge has higher electron affinity.

(5) The electron gain enthalpy of the elements having $d^{10}s^2$ configuration are positive as electron is to be accommodated into the higher energy *p* orbital.

> ***Note :*** EA_1 : Cl > F > Br > I
> EA_1 : S > Se > Te > Po > O
> EA_1 : C > B > Li > Be
> EA_1 : Si > Al > Na > Mg
> EA_1 : F > O > N > Ne.

D. Electronegativity

It may be defined as : "The tendency of an atom to attract shared electron pair towards itself in a molecule". The small atoms attract electrons more strongly than larger ones, hence they are more electronegative.

The numerical value of electronegativity depends upon the ionisation potential and electron affinity. Higher ionisation potential and higher electron affinity both imply higher electronegativity. To measure electronegativity, an arbitrary scale was developed by Linus Pauling which is known as electronegativity scale. On this scale fluorine has maximum electronegativity of 4.0 and Li has a value of 1.0 while inert gas have no value of electronegativity.

The value of electronegativity show periodic variations as given below

Generally, in a group electronegativity decreases from top to bottom due to increase in size of atom.

F	Cl	Br	I	At
4.0	3.0	2.8	2.5.	2.2

In a period, electronegativity increases from left to right

Li	Be	C	N	O	F
1.0	1.5	2.5	3.0	3.5	4.0

Some Important Points

1. Melting point of alkali metal halides follow following order

   M – F > M – Cl > M – Br > M – I

   NaF > NaCl > NaBr > NaI

2. The order of melting point of chlorides of alkali metals is as follows :

   LiCl < CsCl < RbCl < KCl < NaCl

3. The melting point of LiCl is lowest because it is with highest covalent character.
4. The solubility of alkali metal carbonates in water at 298 K increases down the group from Lithium to Caesium.
5. The basic character of oxides and hydroxides of group 1 and group 2 increases down the group because metallic character increases down the group *e.g.*, LiOH is least basic whereas CsOH is most basic. $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is a weak base, $Ca(OH)_2$ and $Sr(OH)_2$ are moderately strong bases, $Ba(OH)_2$ is strong base.
6. The solubility of hydroxides of Group 1 and Group 2 in water increases down the group.
7. The solubility of sulphates, carbonates and phosphates decreases down the Group 2 because lattice energy dominates over hydration energy in Group 2, for example $MgSO_4$ is soluble in water whereas $BaSO_4$ is insoluble in water.
8. Li_2CO_3 is thermally unstable whereas other alkali metal carbonates are thermally stable.
9. Thermal stability of carbonates of Group 2 increases down the group. All are thermally unstable.
10. Properties of Li almost similar to that of Mg; Be is almost similar to that of Al and B is almost similar to that of Si due to diagonal relationship.

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Chapter 18

General Principles and Processes of Isolation of Metals

IMPORTANT ORES AND MINERALS

Iron

(i) Magnetite : Fe_3O_4
(ii) Haematite : Fe_2O_3
(iii) Limonite : $Fe_2O_3.3H_2O$
(iv) Iron pyrite : FeS_2
(v) Copper pyrites : $CuFeS_2$
(vi) Siderite : $FeCO_3$

Copper

(i) Cuprite : Cu_2O
(ii) Copper pyrites : $CuFeS_2$
(iii) Copper glance : Cu_2S
(iv) Bornite : Cu_2FeS_3
(v) Malachite : $CuCO_3.Cu(OH)_2$
(vi) Azurite : $[2CuCO_3].Cu(OH)_2$

Zinc

(i) Zincite : ZnO
(ii) Calamine : $ZnCO_3$
(iii) Zinc blende : ZnS
(iv) Willemite : Zn_2SiO_4

Aluminium

(i) Corundum : Al_2O_3
(ii) Diaspore : $Al_2O_3.H_2O$
(iii) Bauxite : $Al_2O_3.2H_2O$
(iv) Cryolite : Na_3AlF_6
(v) Feldspar : $KAlSi_3O_8$
(vi) Mica : $K_2O.3Al_2O_3.6SiO_2.2H_2O$

ALUMINIUM

Al is most abundant metal in earth crust. Important ores are Bauxite $Al_2O_3.2H_2O$; Diaspore $Al_2O_3.H_2O$; Corundum Al_2O_3; Feldspar $KAlSi_3O_8$; Cryolite Na_3AlF_6. It is usually extracted from bauxite through the following steps:

Purification of Bauxite

Bayer's Process

(a) Red bauxite containing the impurity of iron oxide is concentrated by leaching with NaOH.

$$2NaOH + Al_2O_3 \rightarrow 2NaAlO_2 + H_2O$$

(b) Sodium meta aluminate thus obtained is soluble in water while impurities of iron oxides remain insoluble. The solution is diluted with water and agitated to get a precipitate of $Al(OH)_3$.

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

(c) On strong heating this precipitate gives alumina.

Hall's Process

(a) **Electrolysis of alumina (Hall Heroult's process) :** purified alumina is then mixed with cryolite to lower down its melting point, cryolite also increases, the conductance and molten cryolite acts as solvent.

$$Na_3AlF_6 \rightarrow 3NaF + AlF_3$$

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

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

At anode : $2F^{\ominus} \rightarrow F_2 + 2e^-$

(b) Aluminium thus obtained is refined by Hoope's electrolytic process using molten cryolite and BaF_2 as electrolyte.

IRON

Ores : Haematite Fe_2O_3, Magnetite Fe_3O_4; Limonite $Fe_2O_3.3H_2O$; Iron pyrites FeS_2; Siderite $FeCO_3$.

1. **Types**

   (a) Pig iron or cast iron : 2 to 4.5% C with some impurities like S, Si, P, Mn. It cannot be welded.

   (b) Wrought iron : purest form of Fe (0.2 - 0.5% C).

   (c) Steel : 0.1 to 1.5% C along with some other elements like Cr, Mn, Ni etc.

2. **Extraction from Haematite :** It is concentrated by washing with water. Then it is roasted with a little of coal in a reverberatory furnace. During roasting moisture is removed. Impurities of As, S and P are converted into their gaseous oxides. Roasted mass is then reduced by mixing with coke and limestone in a blast furnace in the ratio of 8 : 4 : 1 (Smelting).

THERMODYNAMICS OF METALLURGY

The method employed for extracting a metal from its ores depends on the nature of the metals and that of the ore may be related to the position of the metal in the electrochemical series. In general, metals with E° < – 1.5 volt yield compounds which are very difficult to reduce and electricity is usually used for the isolation of such metals. On the other hand, noble metals with E° > 0.5 volt form easily reducible compounds. A metal higher up in the electrochemical series should be more difficult to reduce to metallic form. As we move down in the electrochemical series, the reduction becomes more and more easy. E° of metal provides some idea regarding the selection of an appropriate method for extracting the metal from its compounds.

Free energy is related to standard cell potential

$$G^\circ = - nF\,E^\circ_{cell}$$

n → Number of moles electrons

F → Faraday constant 96500 C.

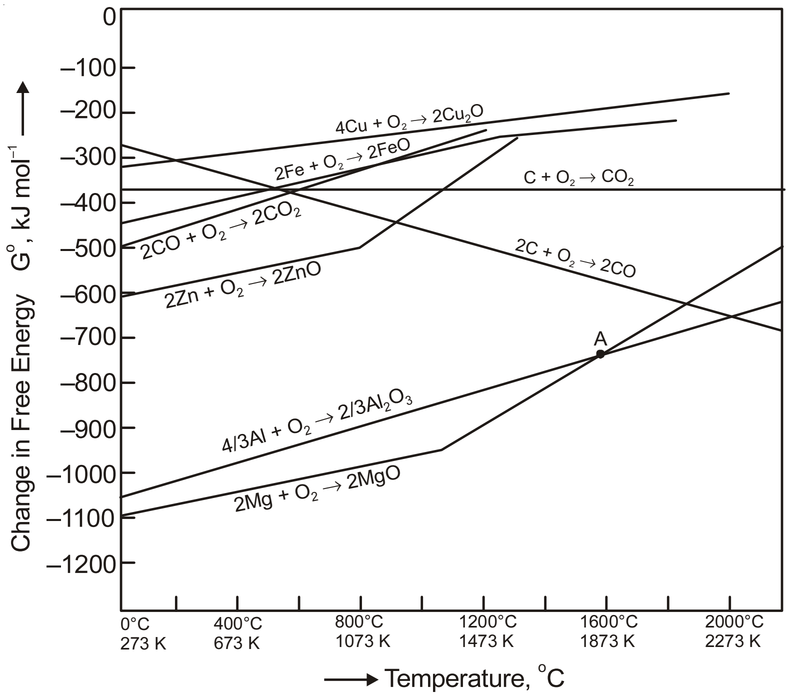
In order that the reduction of oxide, halide or sulphide ore by an element may take place simultaneously at a given temperature and pressure, there is decrease in the free energy of the system ($-\Delta G$).

More the negative value of ΔG, higher is the reducing power of an element. The free energy change (ΔG) is related to the heat change (ΔH) as well as to the product of temperature. [$\Delta G = \Delta H - T\Delta S$]

For a reaction, $2M + O_2 \rightarrow 2MO$

ΔG becomes smaller with the increase in temperature. This is because the gaseous reactant oxygen is consumed in the reaction leading to the decrease in randomness or entropy of the system hence ΔG becomes negative. With further increase in temperature, $T\Delta S$ becomes more negative value. Since the term $T\Delta S$ is high ΔG is less.

Reaction becomes more feasible.



Ellingham diagram showing the change in free energy ΔG with temperature for oxides (based on 1 g mole of dioxygen in each case)

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Chapter 19

Hydrogen and *s*-Block Elements (Alkali and Alkaline Earth Metals)

HYDROGEN

Most abundant element of the universe, which was first prepared by **Cavendish** by the action of acids on certain metals. Its name hydrogen was proposed by **Lavoisier** because it produces water when burnt in oxygen. Hydrogen is the lightest element which is found in nature both in free state and in combined state.

Position of hydrogen in the Periodic Table

The electronic configuration of hydrogen is $1s^1$, due to which it shows resemblance with alkali metals as well as halogens.

Resemblance with Alkali Metals

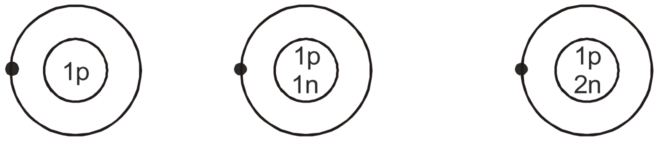
1. Its electronic configuration is similar to alkali metals.
2. It is a good reducing agent like alkali metals.
3. It can lose one electron to form H^+ ion like alkali metals.
4. It shows +1 oxidation state like alkali metals when bonded to non-metals.

Resemblance with Halogens

1. It is a non-metal.
2. It forms diatomic molecule.
3. It is gas like F_2 and Cl_2.
4. It can gain one electron to form H^- ion.
5. It is electronegative in nature.
6. Its ionisation energy is high like halogens.
7. It is liberated at anode when NaH is electrolysed.
8. It shows –1 oxidation state when bonded to metal.
9. It forms many covalent compounds like halogens.

On the basis of its marked resemblance with alkali metals and halogens, it is very difficult to place it either with the elements of group-1 or those of group-17.

Isotopes of Hydrogen : Hydrogen has three isotopes.



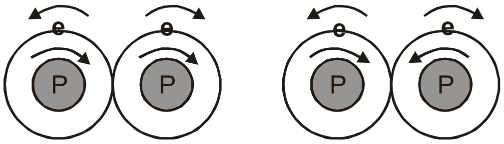
Protium (^1_1H) Deuterium (^2_1H) Tritium (^3_1H)
Non-radioactive Non-radioactive Radioactive

Physical properties of isotopes are different whereas their chemical properties are same

Physical Properties

Important physical properties of hydrogen are as follows

1. It is colourless, odourless, tasteless gas.
2. Dihydrogen has two nuclear spin isomers called **ortho** and **para**-dihydrogen.



Ortho-Hydrogen (Parallel nuclear spin) Para-Hydrogen (Antiparallel nuclear spin)

Atmosphere contains 75% ortho-H_2 and 25% para-H_2. Ortho-H_2 and Para-H_2 have 1 and 0 nuclear spin respectively. With the decrease in temperature percentage of para-form increases and it can be upto 100%.

Hard Water and Soft Water : Depending upon the behaviour of water towards soap solution. Water may be classified as soft and hard water.

The hardness of water may be

1. Temporary hardness – due to presence of bicarbonates of calcium and magnesium.
2. Permanent hardness – due to sulphates or chloride of calcium and magnesium.

Removal of Hardness : Temporary hardness of water can be removed by following methods :

1. By boiling :

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

2. By Clark's process :

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

Permanent hardness can be removed by any of the following method.

1. **Washing Soda :** It converts soluble calcium and magnesium compounds into insoluble carbonates.

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

2. **Permutit :** The sodium ions of permutit are exchanged with calcium and magnesium ions when hard water is passed through it.

$Na_2Al_2Si_2O_8 \;\; xH_2O + Ca^{2+} \rightarrow CaAl_2Si_2O_8 \;\; xH_2O + 2Na^+$, permutit can be regenerated by treatment of brine solution.

3. **Calgon :** Calcium and magnesium salts present in hard water react with calgon to give complex salt.

$$2CaSO_4 + \underset{\text{(Calgon)}}{Na_2[Na_4(PO_3)_6]} \rightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

4. **Ion exchange resins :** Ion exchange resins are giant organic molecule of high molecular masses which are of two types :

   (a) Cation exchanger [*e.g.*, RSO_3Na]

   (b) Anion exchanger [*e.g.*, $RNH_3\,^{-}OH$]

Hydrogen Peroxide (H_2O_2)

H_2O_2 is with half open book like structure with polar O–H bond and non-polar O–O bond.

Preparation : H_2O_2 is prepared by the following methods

1. By action of acid on peroxides.

   $Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$

   $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

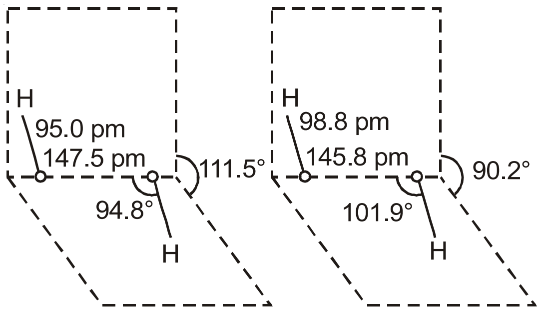
2. By electrolysis of 50% H_2SO_4 or $(NH_4)_2SO_4$

   $H_2SO_4 \rightarrow H^+ + HSO_4^-$

   At Cathode :- $2H^+ + 2e^- \rightarrow H_2$

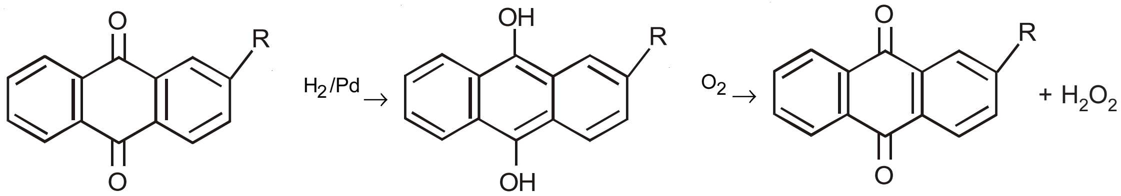
   At Anode : $2HSO_4^{\ominus} \rightarrow H_2S_2O_8 + 2e^-$

   $H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$



(a) Gas phase (b) Solid phase

3. By catalytic reduction of 2-ethyl (or butyl) anthraquinone to corresponding quinol and oxidising the latter with oxygen.



Chemical Properties

1. **Oxidising property :** Hydrogen peroxide acts as an oxidising agent both in acidic as well as in alkaline medium.

   In acidic medium

   $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$; E° = 1.77 V (slow)

   In basic medium

   $H_2O_2 + 2e^- \rightarrow 2OH^-$; E° = 0.87 V. (fast)

2. **Reducing Property :** In presence of strong oxidising agents, hydrogen peroxide behaves as a reducing agent in both the medium.

   Acidic Medium

   $H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$

   Alkaline medium

   $H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + 2e^-$

3. **Acidic property :** H_2O_2 is a weak acid ($K_a = 1.55 \times 10^{-12}$). It has two ionisable H atoms. It forms two series of salts.

4. **Decomposition :** H_2O_2 is an unstable liquid

   $2H_2O_2 \rightarrow 2H_2O + O_2$

Volume Strength of H_2O_2

Volume strength of H_2O_2 solution is defined as volumes of O_2 evolved at STP in ml that is obtained per ml of H_2O_2 solution after complete decomposition *i.e.,* if 1 litre solution of H_2O_2 gives 10 liters of oxygen at STP volume strength of H_2O_2 is 10 volume.

Volume strength of $H_2O_2 = 11.2 \times M$ or $5.6 \times N$

Reaction :- $2H_2O_2 \rightarrow 2H_2O + O_2$

s-BLOCK ELEMENTS

Group-1. Alkali Metals

Elements	Symbol	Atomic number
Lithium	Li	3
Sodium	Na	11
Potassium	K	19
Rubidium	Rb	37
Caesium	Cs	55
Francium	Fr	87

Physical Properties

Important physical properties of Alkali metals are given below :

Flame Colouration

The alkali metals and their salts impart a characteristic colour to the flame.

Li	Na	K	Rb	Cs
Crimson red	Yellow	Violet	Red violet	Blue

Reducing Power

The reducing power of a metal is related to its oxidation potential which represents the tendency of element to lose electron and get oxidised.

All alkali metals have low ionisation energy leading to a high oxidation potential.

(a) Reducing nature (in aq. solution) :

$Li > Cs > Rb > K > Na$

(b) In gaseous state

$Li < Na < K < Rb < Cs$

Solution in Liquid Ammonia

(a) The alkali metals dissolve in liquid ammonia without the evolution of hydrogen. The colour of the dilute solution is blue. The solutions are good conductors of electricity and have strong reducing properties.

(b) The dissolution of metal in NH_3 yields ammoniated cation and electron.

$$M \rightarrow M^+ + e^-$$

or $$M + (x + y)\,NH_3 \rightarrow [M(NH_3)_x]^+ + \underset{\text{solvated electron.}}{[e(NH_3)_y]^-}$$

The blue colour of solution is due to solvated ammoniated electrons.

Chemical Reactivity

Alkali metals are highly reactive due to low ionisation energy.

Metal Hydroxides

(a) Basic strength of hydroxide increases with the increasing electropositivity of metal.

CsOH > RbOH > KOH > NaOH > LiOH.

(b) Solubility of hydroxides increases with increasing ionic character.

CsOH > RbOH > KOH > NaOH > LiOH.

Nature of Carbonates and Bicarbonates

(a) Carbonates are highly stable towards heat and readily soluble in water.

(b) As the electropositive character increases from Li to Cs, the stability of carbonates also increases.

$Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$.

(c) Li_2CO_3 decomposes on heating and it is insoluble in water. $[Li_2CO_3 \rightarrow Li_2O + CO_2]$

(d) Aqueous solution of carbonates are alkaline.

(e) Bicarbonates $MHCO_3$ are known in solid state except of lithium.

GROUP-2. ALKALINE EARTH METALS

Elements	Symbol	Atomic number
Beryllium	Be	4
Magnesium	Mg	12
Calcium	Ca	20
Strontium	Sr	38
Barium	Ba	56
Radium	Ra	88

Oxidation states

All metal show a stable oxidation state of +2.

Flame Colouration

Ca, Sr, Ba, Ra impart a characteristic colour to the flame, whereas Be and Mg do not show flame colouration due to high ionisation energy.

[Ca – brick red], [Sr – crimson], [Ba – green], [Ra – crimson]

Reducing Nature

(a) The alkaline earth metals have the tendency to loose electrons and change into bivalent cation.

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

Hence they act as strong reducing agents.

(b) The reducing nature increases as the atomic number increases.

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Chapter 20

p-Block Elements

BORON FAMILY (GROUP-13 ELEMENTS)

Atomic and Physical Properties

Electropositive Nature : Less electropositive as compared to alkali metals and alkaline earth metals.

The electropositive character increases from B to Al and then decreases upto Tl. It is due to ineffective shielding caused by *d* and *f* electrons which results in the stronger nuclear pull on the electrons of outermost shell.

Compounds of Boron

1. **Orthoboric Acid : H_3BO_3**

Preparation :

(a) From Borax

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$$

(b) By hydrolysis of boron compounds

$$BN + 3H_2O \rightarrow H_3BO_3 + NH_3$$

Properties :

(a) Boric acid has layer type structure in which planar BO_3^3 units are linked to one another through Hydrogen bonds.

(b) Boric acid is a weak monobasic acid. It does not act as proton donor but acts as a lewis acid by accepting electrons from hydroxyl ion.

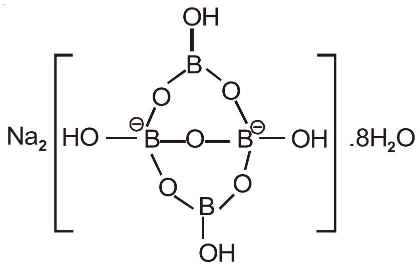
$$H_2O + H_3BO_3 \rightarrow H^+ + [B(OH_4)]^-$$

(c) $H_3BO_3 + NaOH \rightarrow NaBO_2 + 2H_2O$

(d) **Effect of heat**

$$H_3BO_3 \xrightarrow{100\ C} \underset{\text{metaboric acid}}{HBO_2 + H_2O} \xrightarrow{160\ C} \underset{\text{tetraboric acid}}{H_2B_4O_7 + H_2O} \xrightarrow{\text{Red heat}} 2B_2O_3 + H_2O$$

2. **Borax :** $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$



Preparation

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

Properties

(a) It hydrolyses in water to form alkaline solution.

(b) **Borax bead Test** (Test for Transition Elements)

Glassy bead + metal oxide → metal metaborate (coloured)

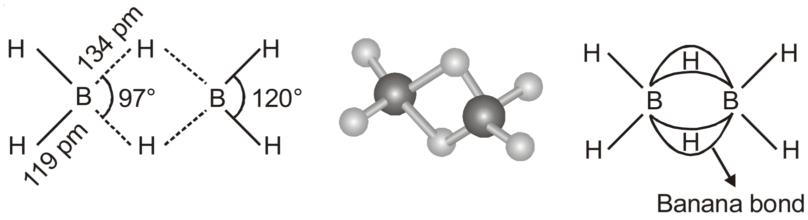
3. **Diborane: B_2H_6**

Structure of B_2H_6 (Diborane)

Boron in B_2H_6 is sp^3 hybridised.

Two bridging B – H > Terminal B – H bond

Boron is dimerised by Banana bond known as **3-centred-2electron** (3c – 2e) **bond**.



Diborane

Preparation :

(a) $3LiAlH_4 + 4BCl_3 \rightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$

(b) $2BCl_3 + 6H_2 \xrightarrow[\text{Discharge}]{\text{Silent Electric}} B_2H_6 + 6HCl$

Properties :

(a) Stable at low temperature only, colourless and highly toxic.

(b) $B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$

(c) $B_2H_6 + 6Cl_2 \xrightarrow{25\ C} 2BCl_3 + 6HCl$

(d) $B_2H_6 + 2NH_3 \rightarrow B_2H_6.2NH_3$ (white solid)

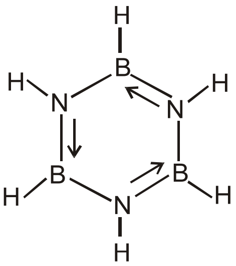
(e) $2B_2H_6 + 6NH_3 \xrightarrow{450\ K} 2B_3N_3H_6 + 12H_2$

(f) $B_2H_6 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$

4. **$B_3N_3H_6$: Borazole** also known as **Borazine** or Inorganic Benzene.

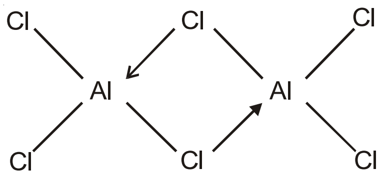
Preparation

$$B_2H_6 \xrightarrow[\text{1000 temp}]{\text{Excess of } NH_3} B_2H_6.2NH_3 \text{ or } [BH_2(NH_3)_2]^+ [BH_4]^- \xrightarrow{450\,K} B_3N_3H_6 + H_2$$



5. **Alums** : General formula, $M_2SO_4 . M'_2(SO_4)_3 24H_2O$ where M is a monovalent ion like Na^+, K^+, NH_4^+ while M' is a trivalent ion like Fe^{3+}, Cr^{3+}, Al^{3+}, $K_2SO_4. Al_2(SO_4)_3. 24H_2O$-Potash alum; $(NH_4)_2SO_4. Fe_2(SO_4)_3. 24H_2O$-Ferric alum; $K_2SO_4.Cr_2(SO_4)_3. 24H_2O$-Chrome alum. Out of all these potash alum is very common. When the crystals of potash alum are heated it swells and loses water. Anhydrous alum thus obtained is called burnt alum.

$AlCl_3$ Aluminium chloride exists as a dimer where two $AlCl_3$ units are joined together with the formation of two dative bonds (co-ordinate bonds) because $AlCl_3$ is electron-deficient (Lewis acid).



In $AlCl_3$ dimer, four bond length are larger while bond length of four bonds are small.

$AlCl_3$ is used as catalyst in Friedel Craft's reaction, where it is a Lewis acid.

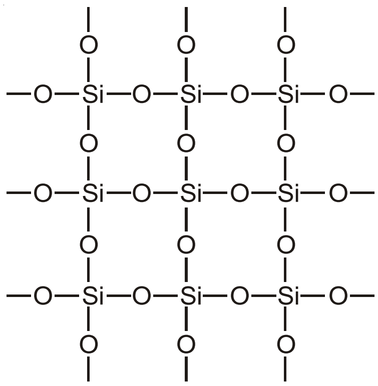
CARBON FAMILY (GROUP-14 ELEMENTS)

Element	Symbol	Atomic No.
Carbon	C	6
Silicon	Si	14
Germanium	Ge	32
Tin	Sn	50
Lead	Pb	82

Compounds of Silicon

1. **Silicon dioxide (SiO_2):**

SiO_2 is solid at room temperature and has a three dimensional network structure as shown below



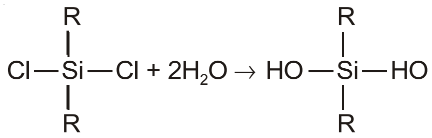
(a) In this structure, silicon atom is bonded to four oxygen atom which are tetrahedrally arranged around it.

(b) Since Si—O bonds are very strong, silica is relatively inert and has a very high melting point.

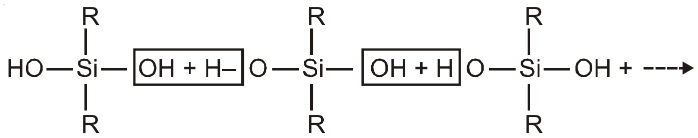
2. Silicones :

Silicones are synthetic organosilicon compounds containing repeated unit of R_2SiO held by Si–O–Si linkages.

Preparation : The silicones are prepared by the hydrolysis of dialkyl dichloro silane (R_2SiCl_2)

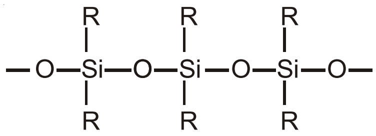


$$Cl-\underset{R}{\overset{R}{Si}}-Cl + 2H_2O \rightarrow HO-\underset{R}{\overset{R}{Si}}-HO$$



$$HO-\underset{R}{\overset{R}{Si}}-\boxed{OH + H-}O-\underset{R}{\overset{R}{Si}}-\boxed{OH + H}O-\underset{R}{\overset{R}{Si}}-OH + \dashrightarrow$$

Polymerisation :



$$-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-$$

The hydrolysis of $RSiCl_3$, gives cross linked silicones.

Properties :

(a) Silicones are chemically inert towards oxidation, thermal decomposition or attack by organic reagents.

(b) They are water repellant and heat resistant.

3. Silicates : Silicates are the compounds in which the anions present are either discrete SiO_4^{4-} tetrahedra or a number of such units joined together through corners.

Types of Silicates : Silicates are classified into different types depending upon the number of corners of SiO_4^{4-} tetrahedron shared with other tetrahedron.

		Formula
1.	**Orthosilicate** Ex. Zircon. ($ZrSiO_4$)	SiO_4^{4-}
2.	**Pyrosilicates** Ex. Thortveitite $Sc_2(Si_2O_7)$	$Si_2O_7^{6-}$
3.	**Cyclic silicates** Ex. Beryl : $Be_3Al_2Si_6O_{18}$	$(SiO_3)_n^{2n-}$
4.	**Chain Silicates** Ex. Spodumene; $LiAl(SiO_3)_2$	$(SiO_3^{2-})_n$ (Pyroxene)
5.	**Sheet silicates** Ex. Clay	$(Si_2O_5)_n^{2-}$
6.	**Three dimensional silicates** Ex. Quartz	All the four corners are shared with other tetrahedra (SiO_2)

Note : *Chain silicates are of two types*

(i) Pyroxene

(ii) Amphibole

NITROGEN FAMILY (GROUP-15 ELEMENTS)

Element	Symbol	Atomic No.
Nitrogen	N	7
Phosphorous	P	15
Arsenic	As	33
Antimony	Sb	51
Bismuth	Bi	83

Characteristics of Hydrides

(a) **Basic Strength :** All these hydrides act as Lewis bases. They can donate an electron pair to electron deficient species. (Lewis acids). **As we go down the group, the basic character of these hydrides decreases.**

(b) **Thermal Stability :** Thermal stability of the hydrides of group 15 elements decreases as we go down the group.

NH_3 PH_3 AsH_3 SbH_3 BiH_3

(c) **Reducing Character :** The reducing character of the hydrides of group 15 elements increases from NH_3 to BiH_3. Thus, increasing order of reducing character is as follows :

NH_3 PH_3 AsH_3 SbH_3 BiH_3

(d) **Boiling Points :** Ammonia (240 K) has a higher boiling point than phosphine (190 K) and then the boiling point increases down the group because of increase in size.

Thus boiling point order is $\underbrace{BiH_3 > SbH_3}_{\textbf{Mol. Mass}} > \underbrace{NH_3}_{\textbf{H–bonding}} > \underbrace{AsH_3 > PH_3}_{\textbf{Mol. Mass}}$

Nitric Acid (HNO_3) :

Preparation : Nitric acid is mostly prepared by

(a) Birkeland - Eyde Process

$N_2 + O_2 \xrightarrow[\text{3000 C}]{\text{Electric arc}} 2NO$

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

(b) Ostwald's Process

$4NH_3 + 5O_2 \xrightarrow[\text{800 C}]{\text{Pt}} 4NO + 6H_2O$

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

The important reaction of Nitric acid are given below :

Properties :

(a) Reaction with Metals

(i) $Mg + 2HNO_3$ (dil) $\rightarrow Mg(NO_3)_2 + H_2$

(ii) $Mn + 2HNO_3$ (dil) $\rightarrow Mn(NO_3)_2 + H_2$

(iii) $3Cu + 8HNO_3$ (hot and dilute) $\rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

(iv) $Cu + 4HNO_3$ (hot and Conc.) $\rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

[Ag, Pb and Bi also react as Cu]

(b) Reaction with non-metals and compounds

(i) $C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$

(ii) $6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

OXYGEN FAMILY-(GROUP-16 ELEMENTS)

Element	Symbol	Atomic No.
Oxygen	O	8
Sulphur	S	16
Selenium	Se	34
Tellurium	Te	52
Polonium	Po	84

OXYGEN

Preparation : Oxygen is mostly prepared by the following methods :

1. In laboratory it is prepared by heating $KMnO_4$ or $KClO_3$ in presence of MnO_2.

   $$2KClO_3\ (s) \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

2. It can also be prepared by reaction of H_2O on Na_2O_2

   $$2Na_2O_2 + 2H_2O\ (l) \rightarrow 4NaOH + O_2$$

Chemical properties : Oxygen reacts with metals and non-metals to form different oxides

Ozone (O_3)

Preparation : Ozone is prepared by subjecting pure oxygen to silent electric discharge

$3O_2 \rightarrow 2O_3$; H = + 284.5 kJ mole^{-1}.

Properties :

It is pale blue gas having a strong characteristic smell. It is neutral to litmus. It condenses to blue liquid (b. pt 161. 2K). It condenses to a violet- black solid (melting point 80.6 K).

The important reactions are given below:

1. $O_3 \xrightarrow{250\ C} O_2 + O$
2. $H_2S + O \rightarrow H_2O + S$
3. $2Ag + O \rightarrow Ag_2O$
4. $2Hg + [O] \rightarrow Hg_2O$ (Tailing of Mercury)
5. $I_2 + H_2O + 5[O] \rightarrow 2HIO_3$
6. It is better oxidising agent as compared to H_2O_2.

   $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$

Sulphuric Acid : (H_2SO_4)

Preparation :

It is manufactured by **Contact process**. Reaction of the process is as under :

(a) $S + O_2 \longrightarrow SO_2$ or $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(b) $2SO_2 + O_2 \underset{V_2O_5 \text{ or Pt Catalyst}}{\overset{723K - 823K\ 2\text{-}3 \text{ atmosphere}}{\rightleftharpoons}} 2SO_3$

(c) $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ (oleum)

(d) $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

Properties : The important properties are

1. It is a strong dibasic acid

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$

2. On heating it liberates oxygen and thus it acts as a strong oxidising agent

$$\underset{\text{(Conc.)}}{Cu + 2H_2SO_4} \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Oxidation of non-metals

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

It liberates iodine from KI

$$2KI + 2H_2SO_4 \rightarrow K_2SO_4 + SO_2 + I_2 + 2H_2O$$

3. H_2SO_4 is a powerful dehydrating agent

HALOGEN FAMILY-(GROUP-17 ELEMENTS)

Element	Symbol	Atomic No.
Fluorine	F	9
Chlorine	Cl	17
Bromine	Br	35
Iodine	I	53
Astatine	At	85

Atomic and Physical Properties:

1. **Atomic and Ionic Radii:** The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge.
2. **Ionization Energies:** The ionization energies of halogens are very high. It decreases from fluorine to iodine
3. **Melting and Boiling Points :** The melting and boiling points of halogens increases with increase in atomic number as we go down the group.
4. **Electron Affinity**
   (a) All these have maximum electron affinities in their respective periods.
   (b) In general, electron affinity decreases from top to bottom in a group.
   (c) Fluorine has unexpectedly low electron affinity than chlorine. Therefore, **chlorine has the highest electron affinity in this group.**

   Thus, **electron affinity** among halogens varies as : **F < Cl > Br > I**
5. **Colour :** All the halogens are coloured.

   Fluorine – Pale yellow, Chlorine – Greenish yellow, Bromine – Reddish brown liquid, Iodine – Greyish black solid (Deep violet in vapour state).
6. **Oxidation States**
   (a) They all show an oxidation state of –1.
   (b) Since fluorine is the most electronegative element, it always show an oxidation state of –1. It does not show any positive oxidation state.
   (c) The other elements also show positive oxidation state of +1, +3, +5 and +7. The higher oxidation state of chlorine, bromine and iodine are due to the presence of vacant d–orbitals in their valency shells.

7. **Low Dissociation Energies**

   All the halogen have very low dissociation energies. As a result, they can readily dissociate into atoms and react with other substance.

Molecule	**F_2**	**Cl_2**	**Br_2**	**I_2**
Dissociation energies	159	243	193	151

$\mathbf{X_2 \rightleftharpoons 2X}$ **(kJ mol^{-1})**

8. **Oxidising Power**

   (a) Halogens have high electron affinity values and therefore they have strong tendency to take up the electron :

$$\frac{1}{2}X_2 + e^- \quad \rightarrow X^-$$

   (b) As a result, they **act as powerful oxidising agents.**

   (c) The decreasing oxidising power of the halogen as we go down the group is shown by their decreasing reduction potentials.

X_2	F_2	Cl_2	Br_2	I_2
E_{RP} (volts)	2.87	1.40	1.09	0.62

OXYACIDS OF CHLORINE

Different oxyacids of chlorine are

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.

$HClO_4 > HClO_3 > HClO_2 > HOCl$

Reason : It is because the release of H^+ ion in each case would result in the formation of ClO_4^-, ClO_3^-, ClO_2^-, ClO^- ions. More is the stability of resulting ion, greater will be the ease with which the ion is formed. Therefore, the ease of formation of ions would be.

$ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$

Interhalogen Compounds

The halogens on account of the difference in their electronegativities combine with each other and form binary covalent compounds of AB_n type which are called interhalogen compounds. A is always bigger atom and B is a smaller atom. n may have value 1, 3, 5 and 7 corresponding to oxidation state of halogens.

AB type	ClF, BrF, BrCl, ICl, IBr	→ sp^3 hybridization, Linear shape
AB_3 type	ClF_3, BrF_3, ICl_3	→ sp^3d hybridization, T-shape
AB_5 type	BrF_5, IF_5	→ sp^3d^2 hybridization, distorted square pyramidal shape
AB_7 type	IF_7	→ sp^3d^3 hybridization, pentagonal bipyramidal shape

NOBLE GASES - (GROUP-18 ELEMENTS)

Element	Symbol	Atomic Number
Helium	He	2
Neon	Ne	10
Argon	Ar	18
Krypton	Kr	36
Xenon	Xe	54
Radon	Rn	86

Atomic & Physical Properties :

In general, noble gases are not very reactive. Their inertness to chemical reactivity is due to

1. The noble gases have completely filled ns^2np^6 electronic configurations in their valence shells.
2. The noble gases have very high ionisation energies.

Chemical Properties :

Among group 18 members only Xenon and Krypton show chemical reactivity. The important compounds of Xe are given below :

1. **Fluorides :** The common fluorides of xenon such as XeF_2, XeF_4 and XeF_6 can be prepared by the direct combination of xenon and fluorine under different conditions :

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

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

$$\underset{(1:20)}{Xe + 3F_2} \xrightarrow[\text{573 K, 50 60 atm}]{\text{Ni vessel}} XeF_6$$

2. **Oxides :** XeO_3 is the most common oxide and it is prepared by the hydrolysis of XeF_4 or XeF_6.

$$2XeF_4 + 3H_2O \rightarrow Xe + XeO_3 + 6HF + O_2$$

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

3. **Oxyfluorides:** The oxyfluorides of xenon are prepared by the partial hydrolysis of XeF_4 or XeF_6.

$$XeF_4 + H_2O \xrightarrow{\text{800 C}} \underset{\text{Xenon oxydifluoride}}{XeOF_2} + 2HF$$

$$XeF_6 + H_2O \rightarrow \underset{\text{Xenon oxytetrafluoride}}{XeOF_4} + 2HF$$

* * *

Chapter 21

d and *f*-Block Elements

The ***transition elements*** *may be defined as elements whose atoms or simple ions in their most common oxidation state contain partially filled d-orbitals.* This definition does not cover zinc, cadmium and mercury. However, these are studied with transition elements.

The general electronic configuration of these elements is $(n-1)d^{1-10}\,ns^{0-2}$.

ATOMIC AND PHYSICAL PROPERTIES

The important properties of the transition metals are given below :

1. Metallic Character

(a) Transition elements exhibit good mechanical properties, i.e, they are hard, malleable and ductile. They have high enthalpies of atomization, high melting and boiling points, they have high thermal and electrical conductivity as well as lustre.

(b) Their mechanical properties and high melting as well as boiling points indicate the presence of strong metallic bond.

2. Ionisation Energies

(a) The ionisation energies of transition metals increases as we move across each series though not quite regularly.

(b) It is evident that first ionisation energies of most of the 5*d* elements are higher than those of 3*d* and 4*d*-elements. This is due to the fact that the outer valence electrons of 5*d*-elements experience greater effective nuclear charge due to poor shielding of the nucleus by 4*f*-electrons.

3. Electrode Potential

In general, transition elements have low negative values of standard reduction electrode potential due to high ionisation energies, high heat of sublimation which are more than offset with large heats of hydration. Consequently, transition elements are **weak reducing agents** and are **less reactive** than *s*-block elements.

4. Variable Oxidation States

(a) Transition metals exhibit a wide range of oxidation states. When '*ns*' electrons are involved, then compounds with lower oxidation states are formed. In compounds with higher oxidation states, (*n*–1) *d* electrons are also involved.

(b) The highest oxidation state exhibited by any transition metal is +8, *i.e*, Ruthenium tetroxide (RuO_4) and Osmium tetroxide (OsO_4)

(c) The highest oxidation state are shown by transition metal when they combine with most electronegative elements such as fluorine or oxygen, *i.e.*, CrO_3, Mn_2O_7 and VF_5.

(d) Maximum number of variable oxidation states are shown by Mn (+2, +3, +4, +5, +6, +7).

(e) The most common oxidation state for first transition series is +2 which arises from the loss of 4*s* electrons (except Sc).

(f) In lower oxidation states as +2 and +3, the bonds are mostly ionic while in higher oxidation states such as +6 or +7, the bonds are essentially covalent as in MnO_4^- (Mn= +7), $Cr_2O_7^{2-}$ (Cr = +6)

5. **Formation of Complexes :**

By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant d-orbitals of suitable energy, these metals exert strong electrostatic attraction on the ligands. The species formed on interaction of metal and the ligand (or ligands) is known as a complex.

Formation of Coloured Compounds : The transition metal ions have unpaired d-electrons, which on absorbing visible light can jump from one *d*-orbital to another *i.e.*, *d-d* transitions take place. Thus when light falls certain visible wavelengths are absorbed. The reflected light appears coloured and gives the colour of compound. The ions having no *d-d* transitions are ($KMnO_4$ & $K_2Cr_2O_7$) coloured due to charge transfer spectra. Some compounds are coloured due to polarisation e.g., AgI.

6. **Catalytic Properties**

Most of the transition metals and their compounds are found to act as catalysts.

Transition Metals as Catalyst : Catalytic power of transition metals is believed to operate by the formation of interstitial compounds to adsorb and activate the reacting substances e.g. hydrogenation of alkenes in presence of palladium or platinum is thought to take place through this mechanism.

7. **Magnetic Properties**

(a) Most of the transition elements show paramagnetism. Paramagnetism arises from the presence of unpaired electrons in atoms, ions or molecules.

(b) The magnetic character is comparable in terms of magnetic moment given as $\mu = \sqrt{n(n+2)}$ Bohr magnetons. In general, more is the number of unpaired electrons greater is the magnetic character.

(c) The maximum paramagnetism is seen in d^5 cases, having the maximum unpaired electrons.

8. **Formation of Nonstoichiometric Compounds and Interstitial Compounds**

Transition metals can trap some of the small size atoms like hydrogen, boron, carbon, nitrogen, etc in the vacant spaces between the crystal lattice forming interstitial compounds.

9. **Alloy Formation**

(a) Molten transition metals are miscible with one another. Therefore, on cooling a mixture of the transition metals results in the formation of alloys.

(b) Such alloys are usually harder, have higher melting points and are more resistant to corrosion than the parent metals.

IMPORTANT COMPOUNDS OF TRANSITION METALS

Potassium Dichromate ($K_2Cr_2O_7$) :

Preparation : From Chromite ore:

The preparation is completed in the following three steps:

(a) Preparation of sodium chromate :

$$4[FeO.Cr_2O_3] + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

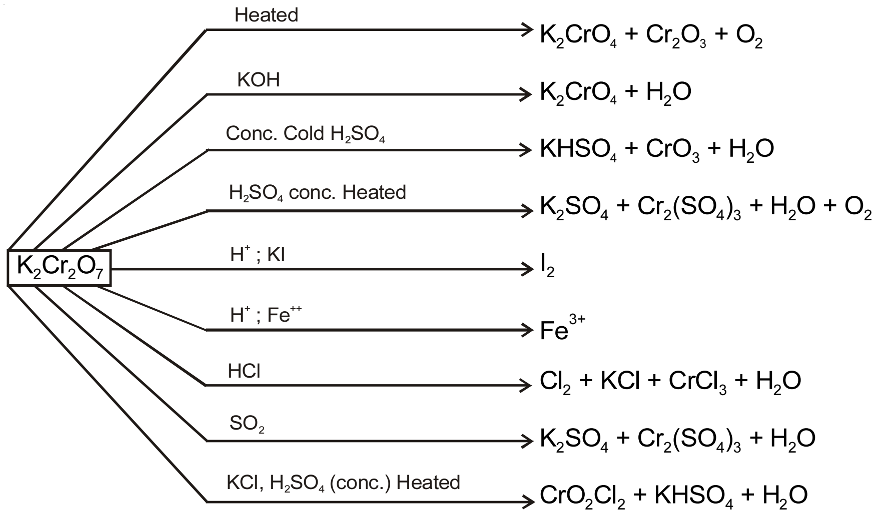
(b) Conversion of sodium chromate into sodium dichromate :

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(c) Conversion of sodium dichromate into potassium dichromate :

$$Na_2Cr_2O_7 + 2KCl \rightarrow \underset{\text{(less soluble)}}{K_2Cr_2O_7} + 2NaCl$$

Properties of $K_2Cr_2O_7$: Potassium dichromate is orange coloured compound. The important reactions are given below



Potassium Permanganate ($KMnO_4$)

Preparation :

It is prepared by fusing pyrolusite ore (MnO_2) with KOH in the presence of atmospheric oxygen or an oxidising agent like KNO_3 or $KClO_3$ to get potassium manganate K_2MnO_4, (green mass). The green mass is oxidised to potassium permanganate, electrolytically or by passing chlorine or ozone into the solution.

Step-I:

$$2MnO_2 + 4KOH + \underset{\substack{\text{(From } KNO_3 \\ \text{or } KClO_3\text{)}}}{2\,O} \xrightarrow{\text{Heat}} 2K_2MnO_4 + 2H_2O$$

Step-II:

Electrolytic Oxidation

At the cathode $2H^+ + 2e \rightarrow H_2$

At the anode $\underset{\text{(Green)}}{MnO_4^{2}} \rightarrow \underset{\text{(Purple)}}{MnO_4^-} + e^-$

Properties of $KMnO_4$: The important properties are given below:

1. **Oxidising Nature in Neutral Medium**

   [$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]$].

   In this medium $MnSO_4$ is oxidised to MnO_2 and $Na_2S_2O_3$ to Na_2SO_4.

2. **Oxidising Nature in Alkaline Medium :**

   [$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O$ + [O]].

   In this medium KI is oxidised to KIO_3 and alkenes are oxidised to glycols.

3. **Oxidising Nature in Acidic Medium :**

   [$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$].

   In this medium it oxidises

   $H_2S + [O] \rightarrow H_2O + S$

   $SO_2 + H_2O + [O] \rightarrow H_2SO_4$

   $H_2C_2O_4 + [O] \rightarrow 2CO_2 + H_2O$

   $2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$

   $2KI + [O] + H_2O \rightarrow I_2 + 2KOH$

❑ ❑ ❑

Chapter 22

Co-ordination Compounds

Different types of salt are formed due to addition of molecular compounds.

1. **Double salts** : Double salts are those molecular compounds which exists only in crystal lattice but lose their identity in solution.

   e.g., KCl. $MgCl_2.6H_2O \longrightarrow K^+ + Mg^{+2} + 3Cl^- + 6H_2O$.

   Double salts when dissolved in water ionise.

2. **Complex salts** : Complex salts are those molecular compounds which retain their identity in solid / crystal lattice as well as in the solution.

   e.g., Potassium ferrocyanide is a complex compound which is formed by adding KCN to a saturated solution of ferrous cyanide

   $4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$

   $K_4[Fe(CN)_6]$ is dissolved in water, the resulting solution does not give positive tests for ferrous or cyanide ions but we get a positive test for $[Fe(CN)_6]^{4-}$.

CO-ORDINATION COMPOUNDS

Coordination compound may be defined as a compound that results from the combination of apparently saturated molecules of different species and retain its identity in the solids as well as in dissolved state.

The formation of a coordination compound involves two components.

1. **An acceptor** : Which can accept a pair of electrons from the donor. The acceptor is usually a metal with vacant orbitals available to accept a pair of electrons from one or more neutral molecules or anions.

   In $[Fe(CN)_6]^{4-}$, Fe^{++} ion is an acceptor, which is also called as central metal ion, which acts as Lewis acid.

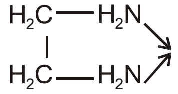
2. **A donor** : An atom or a molecule which can donate a pair of electrons is a donor. Such donor atoms or molecules are electron rich and are called **ligands**, which act as Lewis bases.

   Ligands may be neutral (NH_3, H_2O, C_6H_5N) or negatively charged species ($:CN^-, Cl^-, Br^-$) or positively charged

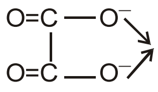
   Ligand is said to be unidentate if it has only one pair of electrons that it can donate *e.g.*, NH_3

   Ligand is said to be bidentate if it can bond from two positions

   e.g.,



ethylene diamine (en)



oxalate ion ($C_2O_4^{2-}$)

   Some ligands can be coordinated to the metal or metal ion through either of two sides, they are called "Ambident" ligands. *e.g.,* nitrite ion, if attached through 'N' ($-NO_2$), it is written as nitro (or nitrito-N), if attached through O atom (–ONO–) then Nitrito (or nitrito-O).

Some Important Points

1. Number of co-ordinate bonds formed with central metal/ion is known as co-ordination number of the central species. In case of π-complexes all the atoms of a π-ligand are counted as co-ordination number as in case of Zeise's salt $[Pt\ Cl_3C_2H_4]^{\ominus}$ co-ordination number is 5.
2. The molecules or ions bonded directly to the central ion constitute what is often termed as co-ordination sphere, written within square brackets.
3. One more important point is the oxidation state of central metal ion. It is the charge carried by a complex ion and is the algebraic sum of charges carried by central ion & the ligands co-ordinated to it.

TYPES OF COMPLEX IONS

The complex ions can be grouped into three classes depending upon the nature of charge they carry :

1. **Complex cation :** A complex ion that has a net positive charge is called a complex cation, *e.g.,* tetraamminecopper (II), $[Cu(NH_3)_4]^{2+}$.
2. **Complex anion :** A complex ion that has a net negative charge is called a complex anion, *e.g.,* hexacyanoferrate (II), $[Fe(CN)_6]^{-4}$.
3. **Neutral Complex :** A complex that has no net charge is called a neutral complex, *e.g.,* hexacarbonyl chromium(0), $[Cr(CO)_6]$.

IUPAC Nomenclature of complex compounds

In order to name these compounds certain rules have been suggested by IUPAC.

1. The positive part of a coordination compound is named first and is followed by the negative part.
2. The ligands are named first followed by the central metal. The prefixes di- tri-, tetra- etc, are used to indicate the number of each kind of ligand present. The prefixes bis (two ligands) tris (three ligands) etc. used for polydentate ligands.
3. The ligands are named in alphabetical order. Names of the anionic ligands end in O, those of cationic in **ium.** Neutral ligands have their regular names except that H_2O is named *aqua*; NH_3 *ammine*; NO *nitrosyl*; and CO *carbonyl*.
4. The oxidation state of the central metal is indicated in roman numbers in a bracket.
5. When a complex species has negative charge, the name of the central metal ends in **–ate.** For some elements, the name of ion is based on the latin name of the metal (For example, argentate for silver).

EFFECTIVE ATOMIC NUMBER

Transition metals forms coordination compounds very readily because they have vacant 'd' orbitals which can accommodate electron pairs donated by ligands. Metal ion in co-ordination compound tends to attain nearest inert gas configuration by gaining electrons from ligand.

Effective atomic number (EAN) of metal in a complex is given by :

EAN = Z–(O.N.) + 2 × Number of lone pair donated

where Z = atomic number of metal atom

O.N. = oxidation number

BONDING IN CO-ORDINATION COMPOUND

Valence Bond Theory

Important Features of Valence Bond Theory (VBT).

1. The central metal provides empty hybrid orbitals as required by the ligands *i.e.*, coordination number to form complex.

2. Each ligand should have at least one lone pair of electron.
3. The lone pair of electrons of the ligand overlap with empty hybrid orbital of metal.
4. If *d*-orbitals are involved in hybridisation that may be either inner viz (n – 1) *d*-orbital or the outer viz (n) *d*-orbital. The compounds formed by these two ways are known as inner orbital and outer orbital compounds respectively. Generally the inner orbital compounds are low spin and outer orbital compounds are high spin compounds.
5. If the compound has one or more unpaired electron, the compound is paramagnetic and if it does not contain unpaired electron, it is diamagnetic.
6. The magnetic moment of metal complex calculated by using spin only magnetic moment as $\mu = \sqrt{n(n+2)}\ \text{Bm}$, where 'n' is the number of unpaired electrons.

ISOMERISM

1. **Structural Isomerism**

   (a) **Hydrate isomerism –** Compounds which have same molecular formulae but differ in the number of water molecule as ligands and as molecules of hydration are called hydrate isomers.

   e.g., $[Co(H_2O)_6]Cl_3$ & $[Co(H_2O)_4Cl_2]Cl.2H_2O$

   (b) **Ionisation isomerism** – Compounds which give different ions in solution but have same molecular formulae are called ionization isomers.

   e.g., $[Co(NH_3)_5SO_4]Br$ & $[Co(NH_3)_5Br]SO_4$

   (c) **Linkage isomerism** – Occurs when more than one atom in a monodentate ligand functions as a donor.

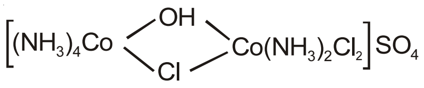
   e.g., $[Co(NH_3)_5NO_2]Cl$ & $[Co(NH_3)_5ONO]Cl$

   (d) **Co-ordination isomerism** – This isomerism is possible when both positive and negative ions of a salt are complex ion.

   e.g., $[Cr(NH_3)_6][Co(CN)_6]$

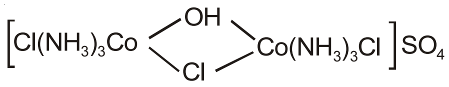
   (e) **Co-ordination position isomerism** – This type of isomerism arises in the bridged complexes due to difference in the attachment of ligands with the metal atom.

   e.g.,



$$\left[(NH_3)_4Co\overset{OH}{\underset{Cl}{\lessgtr}}Co(NH_3)_2Cl_2\right]SO_4$$

   and



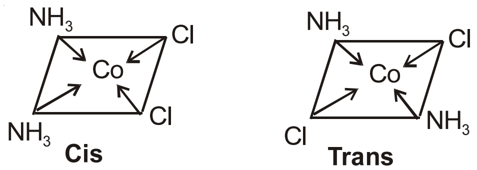
$$\left[Cl(NH_3)_3Co\overset{OH}{\underset{Cl}{\lessgtr}}Co(NH_3)_3Cl\right]SO_4$$

2. **Stereoisomerism**

   (a) **Geometrical isomerism** is common in square planar and octahedral complexes.

   Square planar complexes with general formula; $[MA_2X_2]^{\pm n}$, $[MA_2XY]^{\pm n}$, $[MABX_2]^{\pm n}$, $[MABXY]^{\pm n}$, $[M(AB)_2]^{\pm n}$ show isomerism.

   Example :



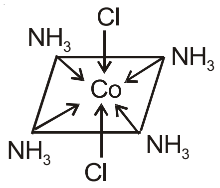
Cis **Trans**

> **Note :** *[M_{ABCD}] shows 3 geometrical isomers.*

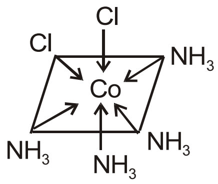
Tetrahedral complexes do not show geometrical isomerism.

(b) Octahedral complexes with general formula, $[MA_4X_2]$, $[MA_4XY]$, trans. $[M(AA)_2X_2]$ shows geometrical isomerism.

(i) *e.g.,*

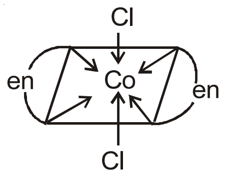


Trans-$[Co(NH_3)_4Cl_2]$

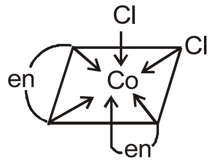


Cis-$[Co(NH_3)_4Cl_2]$

(ii)

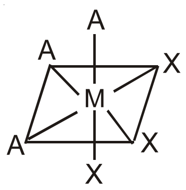


Trans-$[Co(en)_2Cl_2]$

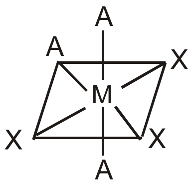


Cis-$[Co(en)_2Cl_2]$

(c) The complex with formula $[MA_3X_3]$ show facial and meridonial isomerism.



Fac-$[MA_3X_3]$



Mer-$[MA_3X_3]$

> ***Note :** Complex with general formula $[M_{(a)(b)(c)(d)(e)(f)}]$ shows 15 geometrical isomers.*

3. **Optical Isomerism**

(a) Tetrahedral complexes with formula $[M_{(a)(b)(c)(d)}]$ or $M(AB)_2$ shows optical isomerism

(b) Octahedral complexes having formula $[M_{(a)_2(b)_2(c)_2}]^{\pm n}$, $[M_{(a)(b)(c)(d)(e)(f)}]$, $[M(AA)_3]$, $[M(AA)_2b_2]$, $[M(AA)_2b_2c_2]$ containing symmetrial bidentate ligand will show optical isomerism.

> ***Note :** Square planar complexes do not show optical isomerism.*

* * *

Chapter 23

Principles Related to Practical Chemistry

ANALYSIS OF ACIDIC RADICALS

Acidic radicals are categorised into three groups. There is no such scheme which permits the separation of the common anions into major groups. The classification may be studied in two parts :

1. Those involving the identification by volatile products obtained on treatment with acids, and
2. Those dependent upon reactions in solution.

The part (1) is subdivided into

(i) Gases evolved with dilute HCl or dil H_2SO_4 and

(ii) Gases or vapours evolved with conc. H_2SO_4.

The part (2) is subdivided into

(i) Precipitation reactions and

(ii) Oxidation and reduction in solution

Group Category of Acid Radicals

Group I :

Radicals which are detected by dilute H_2SO_4 or dilute HCl, by liberating a gas/volatile material

(i) Carbonate

(ii) Sulphite

(iii) Sulphide

(iv) Nitrite

(v) Acetate

Group II :

Radicals which are detected by concentrated H_2SO_4

(i) Chloride

(ii) Bromide

(iii) Iodide

(iv) Nitrate

(v) Oxalate

Group III :

Radicals which do not give any characteristic gas with dilute and concentrated H_2SO_4

(i) Sulphate

(ii) Phosphate

(iii) Borate

(iv) Fluoride

Group	Group reagent	Group radicals	Colour & Observation
1.	Dil. H_2SO_4 or dil HCl	(i) CO_3^{2-}	Brisk effervescence in cold with evolution of colourless and odourless gas i.e. CO_2
		(ii) SO_3^{2-}	Colourless gas with suffocating odour (smell of burning sulphur) i.e. SO_2
		(iii) S^{-2}	A colourless gas with smell of rotten eggs i.e. H_2S
		(iv) NO_2^-	A light brown gas i.e. NO_2
		(v) CH_3COO^-	Colourless vapours with smell of vinegar.
2.	Conc. H_2SO_4	(i) Cl^-	Colourless gas with pungent smell which fumes in air.
		(ii) Br^-	Reddish brown fumes which intensify on addition of MnO_2.
		(iii) I^-	Violet pungent fumes evolved which intensify on addition of MnO_2 and condense as black.
		(iv) NO_3^-	Light brown vapours with pungent smell and intensify on addition of Cu turnings.
		(v) $C_2O_4^{2-}$	Colourless, odourless gas burns with blue flame at the mouth of test tube and turns lime water milky.
3.	$BaCl_2$	SO_4^{2-}	White precipitate of $BaSO_4$, insoluble in conc. HNO_3.
	C_2H_5OH and conc. H_2SO_4	BO_3^{3-}	Green edged blue flame of $(C_2H_5)_3BO_3$.
	Conc. HNO_3 and $(NH_4)_2MoO_4$	PO_4^{3-}	A canary yellow precipitate of $(NH_4)_3PO_4.12MoO_3$.
	Sand and conc. H_2SO_4	F^-	Waxy white deposit of silicic acid *i.e.* H_4SiO_4 or $Si(OH)_4$.

Identification of Acid Radicals

Group : **I**

Group acidic radicals : CO_3^{2-}, SO_3^{2-}, S^{-2}, NO_2^-

Group reagent : **dil. HCl or dil.** H_2SO_4

ANALYSIS OF BASIC RADICALS

Group - II :

Group - II is categorised as group-IIA and Group-IIB. The ions of this group do not react with HCl but precipitate with H_2S in dilute mineral acidic medium.

The Group-IIA sulphides of these cations are insoluble in ammonium polysulphide. The Group-IIB sulphides of these cations are soluble in ammonium polysulphide.

Group-IIA	**Group-IIB**
(i) Mercury (II) ion	(i) Arsenic (III) ion
(ii) Bismuth (III) ion	(ii) Antimony (III) ion
(iii) Copper (II) ion	(iii) Tin (II) ion
(iv) Cadmium (II) ion	(iv) Tin (IV) ion

Group-III :

Group-III cations do not react with dil. HCl or with H_2S in dilute acidic medium.

Group-III cations precipitate with ammonium hydroxide

(i) Iron (III) ion

(ii) Aluminium (III) ion

(iii) Chromium (III) ion

Group-IV :

Group-IV cations form sulphides with H_2S in presence of NH_4OH, these sulphides are insoluble in NH_4OH.

(i) Zinc (II) ion

(ii) Manganese (II) ion

(iii) Cobalt (II) ion

(iv) Nickel (II) ion

Group-V :

Group-V cations give precipitate with ammonium carbonate in presence of NH_4Cl in neutral or slightly alkaline medium.

(i) Barium (II) ion

(ii) Strontium (II) ion

(iii) Calcium (II) ion

Group-VI :

Group-VI cation reacts with Na_2HPO_4 to form precipitate

(i) Magnesium (II) ion

(ii) Sodium (I) ion

(iii) Potassium (I) ion

(iv) Lithium (I) ion

Group Zero :

Group zero cation *i.e.* NH_4^+ reacts with NaOH to give NH_3 gas

Group	Group Reagent	Basic Radicals	Colour and Composition of Precipitate
1.	Dil. HCl	Ag^+	AgCl — White
		Pb^{+2}	$PbCl_2$ — White
		Hg_2^{2+}	Hg_2Cl_2 — White
2.	H_2S in presence of dil. HCl	Hg^{+2}	HgS — Black
		Pb^{+2}	PbS — Black
		Bi^{+3}	Bi_2S_3 — Black
		Cu^{+2}	CuS — Black
		Cd^{+2}	CdS — Yellow
		As^{+3}	As_2S_3 — Yellow
		Sb^{+3}	Sb_2S_3 — Orange
		Sn^{+2}	SnS — Brown
		Sn^{+4}	SnS_2 — Yellow
3.	NH_4OH in presence of NH_4Cl	Fe^{+3}	$Fe(OH)_3$ — Reddish Brown
		Cr^{+3}	$Cr(OH)_3$ — Green
		Al^{+3}	$Al(OH)_3$ — White
4.	H_2S in presence of NH_4OH	Mn^{+2}	MnS — Buff
		Co^{+2}	CoS — Black
		Ni^{+2}	NiS — Black
5.	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{+2}	$BaCO_3$ — White
		Sr^{+2}	$SrCO_3$ — White
		Ca^{+2}	$CaCO_3$ — White
6.	Na_2HPO_4	Mg^{+2}	$Mg(NH_4)PO_4$ — White
Zero	NaOH	NH_4^+	NH_3 gas

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PHYSICS

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Contents

Chapter 1

Physics and Measurement

UNITS

Measurement of any physical quantity involves its comparison with a certain basic, reference standard called unit.

Measurement = nu

Here, n is numerical value and u is unit. The numerical value is inversely proportional to the size of unit.

$n \times u = \text{constant}$

$n \propto \frac{1}{u}$

DIMENSIONS OF PHYSICAL QUANTITIES

All the physical quantities represented by derived units can be expressed in terms of some combination of seven fundamental quantities. These seven fundamental quantities are called seven dimensions of the physical world. They are denoted with square brackets [ ].

S. No.	Physical quantity	Dimensional formula	Useful result
1.	Absolute permittivity (ε_0)	$M^{-1}L^{-3}T^4A^2$	$F = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r^2}$
2.	Absolute permeability (μ_0)	$MLT^{-2}A^{-2}$	$\frac{F}{l} = \frac{\mu_0 i_1 i_2}{2\pi r}$
3.	Resistance R	$MLT^{-2}A^{-2}$	$P = I^2R$
4.	Inductance L	$ML^2T^{-2}A^{-2}$	$U = \frac{1}{2}LI^2$
5.	Capacitance C	$M^{-1}L^{-2}T^4A^2$	$U = \frac{q^2}{2C}$
6.	L/R (time constant)	$[M^0L^0T^1]$	–
7.	RC (time constant)	$[M^0L^0T^1]$	–
8.	$\sqrt{LC}$	$M^0L^0T^1$	–
9.	Stress, Pressure, Energy density, $\frac{1}{2}\varepsilon_0E^2, B^2/2\mu_0$	$ML^{-1}T^{-2}$	–
10.	Heat capacity, Boltzmann constant	$ML^2T^{-2}K^{-1}$	–

DIMENSIONAL ANALYSIS AND ITS APPLICATIONS

Principle of Homogeneity of dimensions : It is based on the simple fact that length can be added to length. It states that in a correct equation, the dimensions of each term added or subtracted must be same. If two quantities are being added or subtracted, they must be of same dimensional formula. Every correct equation must have same dimensions on both sides of the equation.

> ***Note :*** *Although torque and work done by a force have same dimensional formula yet they cannot be added as their nature is different.*

Conversion of units : The numerical value of a physical quantity in a system of units can be changed to another system of units using the equation $n[u]$ = constant *i.e.*, $n_1[u_1] = n_2[u_2]$ where n is the numerical value and u is the unit.

$$n_2 = n_1\left[\frac{M_1}{M_2}\right]^a\left[\frac{L_1}{L_2}\right]^b\left[\frac{T_1}{T_2}\right]^c$$ where the dimensional formula of the physical quantity is $[M^aL^bT^c]$.

To find a relation among the physical quantities. If one knows the quantities on which a particular physical quantity depends and guesses that this dependence is of product type, method of dimensions are helpful in deducing their relation.

Suppose we want to find the relation between force, mass and acceleration. Let force depends on mass and acceleration as follows.

$F = Km^ba^c$ when K = dimensionless constant, b and c are powers of mass and acceleration.

According to principle of homogeneity,

$[F] = [K]\,[m]^b\,[a]^c$

$\Rightarrow$ $[MLT^{-2}] = [M^0L^0T^0]\,[M]^b\,[LT^{-2}]^c$

$\Rightarrow$ $[MLT^{-2}] = M^bL^c\,T^{-2c}$

Equating the dimension on both sides we get $1 = b$, $1 = c$, $-2c = -2$.

$\Rightarrow$ $b = 1$ and $c = 1$.

ACCURACY AND PRECISION

Accuracy

The closeness of the measured value to the true value of the physical quantity is known as the accuracy of the measurement.

Precision

It is the measure of the extent to which successive measurements of a physical quantity differ from one another.

Suppose the true value of a measurement is 35.75 and two measured values are 35.73 and 35.725. Here 35.73 is closest to 35.75, so its accuracy is more than 35.725 but 35.725 is more precise than 35.73 because 35.725 is measured upto 3 decimal places.

SIGNIFICANT FIGURES

The number of digits in the measured value about the correctness of which we are sure plus one more digit are called significant figures.

Rules for counting the significant figures

Rule I : All non-zero digits are significant.

Rule II : All zeros occurring between the non zero digits are significant. For example 230089 contains six significant figures.

Rule III : All zeros to the left of non zero digit are not significant. For example 0.0023 contains two significant figures.

Rule IV : If a number ends in zeros that are not to the right of a decimal, the zeros are not significant.

For example, number of significant figures in

1500 (Two)
1.5×10^3 (Two)
1.50×10^3 (Three)
1.500×10^3 (Four)

> ***Note :*** *Length of an object may be represented in many ways say 5 m, 5.0 m, 500 cm, 5.00 m, 5×10^2 cm. Here 5.00 m is most precise as it contains 3 significant figures.*

Rules for Arithmetic Operations with Significant Figures

Rule I : In addition or subtraction, the final result should retain as many decimal places as there are in the number with the least decimal places.

Rule II : In multiplication or division, the final result should retain as many significant figures as are there in the original number with the least significant figures.

Rounding Off of Uncertain Digits

Rule I : The preceding digit is raised by 1 if the insignificant digit to be removed is more than 5 and is left unchanged if the later is less than 5.

Rule II : When the insignificant digit to be removed is 5 and the uncertain digit is even, 5 is simply dropped and if it is odd, then the preceding digit is raised by 1.

ERRORS IN MEASUREMENT

1. **Mean Absolute Error :-** If a_1, a_2, a_3, ... a_n are n measurements then

$a_m = \dfrac{a_1 + a_2 + ... + a_n}{n}$ is taken as the true value of a quantity, if the same is not known.

$a_1 = a_m - a_1$
$a_2 = a_m - a_2$
....
$a_n = a_m - a_n$

Mean absolute error, $\overline{\quad a} = \dfrac{|\ \ a_1| + |\ \ a_2| + ... + |\ \ a_n|}{n}$

Final result of measurement may be written as :

$a = a_m \pm \ \ \overline{a}$

2. **Relative Error or Fractional Error :** It is given by

$$\frac{\overline{\quad a}}{a_m} = \frac{\text{Mean absolute Error}}{\text{Mean value of measurement}}$$

3. **Percentage Error** $= \dfrac{\overline{\quad a}}{a_m} \times 100\%$

4. **Combination of Errors :**

(i) In Sum : If $Z = A + B$, then maximum absolute error in Z is given by, $\ Z = \ A + \ B$, maximum fractional error in this case $\dfrac{\ Z}{Z} = \dfrac{\ A}{A+B} + \dfrac{\ B}{A+B}$ *i.e.,* when two physical quantities are added then the maximum absolute error in the result is the sum of the absolute errors of the individual quantities.

(ii) **In Difference :** If $Z = A - B$, then maximum absolute error is $\Delta Z = \Delta A + \Delta B$ and maximum fractional error in this case $\frac{\Delta Z}{Z} = \frac{\Delta A}{A-B} + \frac{\Delta B}{A-B}$.

(iii) **In Product :** If $Z = AB$, then the maximum fractional error, $\frac{\Delta Z}{Z} = \frac{\Delta A}{A} + \frac{\Delta B}{B}$ where $\frac{\Delta Z}{Z}$ is known as fractional error.

(iv) **In Division :** If $Z = A/B$, then maximum fractional error is $\frac{\Delta Z}{Z} = \frac{\Delta A}{A} + \frac{\Delta B}{B}$

(v) **In Power :** If $Z = A^n$ then $\frac{\Delta Z}{Z} = n\frac{\Delta A}{A}$

In more general form if $Z = \frac{A^p B^q}{C^r}$ then the maximum fractional error in Z is

$$\frac{\Delta Z}{Z} = p\frac{\Delta A}{A} + q\frac{\Delta B}{B} + r\frac{\Delta C}{C}$$

Applications :

1. For a simple pendulum, $T \propto l^{1/2}$ $\Rightarrow$ $\frac{\Delta T}{T} = \frac{1}{2}\frac{\Delta l}{l}$

2. For a sphere, surface area and volume are given by

$$A = 4\pi r^2, V = \frac{4}{3}\pi r^3 \quad \Rightarrow \quad \frac{\Delta A}{A} = 2.\frac{\Delta r}{r} \text{ and } \frac{\Delta V}{V} = 3.\frac{\Delta r}{r}$$

3. When two resistors R_1 and R_2 are connected

(a) In series

$$R_s = R_1 + R_2 \quad \Rightarrow \quad \Delta R_s = \Delta R_1 + \Delta R_2$$

$$\frac{\Delta R_s}{R_s} = \frac{\Delta R_1 + \Delta R_2}{R_1 + R_2}$$

(b) In parallel,

$$\frac{1}{R_P} = \frac{1}{R_1} + \frac{1}{R_2} \quad \Rightarrow \quad \frac{\Delta R_p}{R_p^2} = \frac{\Delta R_1}{R_1^2} + \frac{\Delta R_2}{R_2^2}$$

Also, $\frac{\Delta R_p}{R_p} = \frac{\Delta R_1}{R_1} + \frac{\Delta R_2}{R_2} - \frac{\Delta R_1 + \Delta R_2}{R_1 + R_2}$

4. If $x = 2a - 3b$ then, $\Delta x = 2\Delta a + 3\Delta b$

LEAST COUNT OF MEASURING INSTRUMENTS

The smallest measurement that can be taken by an instrument is equal to least count of the instrument.

For example, a meter scale has smallest division 1 mm. This represents the least count (and also the absolute error) in the measurement.

Let a length measured by the meter scale = 56.0 cm

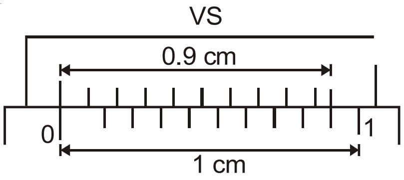
This implies that $x = 56.0$ cm

Absolute error $\Delta x = 1$ mm $= 0.1$ cm

Relative error = $\frac{\Delta x}{x} = \frac{0.1}{56.0}$

Vernier Callipers

It consists of two scales viz main scale and vernier scale. Vernier scale moves on the main scale. The least count of the instrument is the smallest distance between two consecutive divisions and it is equal to 1 MSD – 1 VSD.



In the figure shown, 1 MSD = 0.1 cm

1 VSD = 0.09 cm

Least count = 1 MSD – 1 VSD = 0.01 cm

Screw Gauge

It contains a main scale and a circular scale. The circular scale is divided into a number of divisions. In other words, the complete rotation of circular scale is divided into a number of parts. The least count of a screw gauge is pitch divided by no. of circular scale divisions.

$$\text{Least count of spherometer and Screw Gauge} = \frac{\text{Pitch}}{\text{No. of CSD}}$$

Total reading of screw gauge = Main scale reading + [(Circular scale reading) × Least count]

Table : SI Units and Dimensions of Some Important Physical Quantities

S.No.	Quantity	SI Unit	Dimensional Formula
1.	Volume	m^3	$[M^0L^3T^0]$
2.	Density	$kg\ m^{-3}$	$[M^1L^{-3}T^0]$
3.	Velocity	ms^{-1}	$[M^0L^1T^{-1}]$
4.	Acceleration	ms^{-2}	$[M^0L^1T^{-2}]$
5.	Angular Velocity	rad s^{-1}	$[M^0L^0T^{-1}]$
6.	Frequency	s^{-1} or hertz (Hz)	$[M^0L^0T^{-1}]$
7.	Momentum	$kg\ ms^{-1}$	$[M^1L^1T^{-1}]$
8.	Force	$kg\ ms^{-2}$ or newton (N)	$[M^1L^1T^{-2}]$
9.	Work, Energy	$kg\ m^2s^{-2}$ or joule (J)	$[M^1L^2T^{-2}]$
10.	Power	$kg\ m^2\ s^{-3}$ or Js^{-1} or watt (W)	$[M^1L^2T^{-3}]$
11.	Pressure, Stress	Nm^{-2} or pascal (Pa)	$[M^1L^{-1}T^{-2}]$
12.	Modulus of Elasticity	Nm^{-2}	$[M^1L^{-1}T^{-2}]$
13.	Moment of Inertia	$kg\ m^2$	$[M^1L^2T^0]$
14.	Torque	Nm	$[M^1L^2T^{-2}]$
15.	Angular Momentum	$kg\ m^2\ s^{-1}$ or J.s	$[M^1L^2T^{-1}]$
16.	Impulse	Ns	$[M^1L^1T^{-1}]$
17.	Coefficient of Viscosity	$kg\ m^{-1}\ s^{-1}$	$[M^1L^{-1}T^{-1}]$
18.	Surface Tension	Nm^{-1}	$[M^1L^0T^{-2}]$

19.	Universal Gravitational Constant	$Nm^{2}\ kg^{-2}$	$[M^{-1}L^{3}T^{-2}]$
20.	Latent Heat	$J\ kg^{-1}$	$[M^{0}L^{2}T^{-2}]$
21.	Specific Heat	$J\ kg^{-1}\ K^{-1}$	$[M^{0}L^{2}T^{-2}K^{-1}]$
22.	Thermal Conductivity	$J\ m^{-1}\ s^{-1}\ K^{-1}$	$[M^{1}L^{1}T^{-3}K^{-1}]$
23.	Electric Charge	Coulomb (C) or A.s	$[M^{0}L^{0}T^{1}A^{1}]$
24.	Electric Potential	JC^{-1} or volt (V)	$[M^{1}L^{2}T^{-3}A^{-1}]$
25.	Electric Resistance	VA^{-1} or ohm ( )	$[M^{1}L^{2}T^{-3}A^{-2}]$
26.	Electric Resistivity	m	$[M^{1}L^{3}T^{-3}A^{-2}]$
27.	Electric Conductance	$^{-1}$ or siemen (S)	$[M^{-1}L^{-2}T^{3}\ A^{2}]$
28.	Electric Conductivity	$^{-1}\ m^{-1}$ or $S\ m^{-1}$	$[M^{-1}L^{-3}T^{3}\ A^{2}]$
29.	Capacitance	CV^{-1} or farad (F)	$[M^{-1}L^{-2}T^{4}\ A^{2}]$
30.	Inductance	$Vs\ A^{-1}$ or henry (H)	$[M^{1}L^{2}T^{-2}\ A^{-2}]$
31.	Electric field	NC^{-1} or Vm^{-1}	$[M^{1}L^{1}T^{-3}\ A^{-1}]$
32.	Magnetic Induction	$NA^{-1}\ m^{-1}$ or tesla (T)	$[M^{1}L^{0}T^{-2}\ A^{-1}]$
33.	Magnetic Flux	Tm^{2} or weber (Wb)	$[M^{1}L^{2}\ T^{-2}A^{-1}]$
34.	Permittivity	$C^{2}\ N^{-1}\ m^{-2}$	$[M^{-1}\ L^{-3}\ T^{4}A^{2}]$
35.	Permeability	$Tm\ A^{-1}$ or $Wb\ A^{-1}\ m^{-1}$	$[M^{1}L^{1}T^{-2}\ A^{-2}]$
36.	Planck's Constant	Js	$[M^{1}L^{2}\ T^{-1}]$
37.	Boltzman Constant	JK^{-1}	$[M^{1}L^{2}\ T^{-2}\ K^{-1}]$
38.	Stefan’s Constant	$W\ m^{-2}K^{-4}$	$[M^{1}L^{0}T^{-3}K^{-4}]$

* * *

Chapter 2

Kinematics

DISTANCE TRAVERSED AND SPEED

Distance traversed (Path length)

1. The total length of actual path traversed by the body between initial and final positions is called distance.
2. It has no direction and is always positive.
3. Distance covered by particle never decreases.
4. Its SI unit is metre (m) and dimensional formula is $[M^0L^1T^0]$.

EQUATIONS OF MOTION

General equations of motion :

$$v = \frac{dx}{dt} \Rightarrow dx = vdt \Rightarrow \int dx = \int vdt$$ = area enclosed by velocity-time graph

$$a = \frac{dv}{dt} \Rightarrow dv = adt \Rightarrow \int dv = \int adt$$ = area enclosed by acceleration-time graph

$$a = \frac{vdv}{dx} \Rightarrow vdv = adx \Rightarrow \int vdv = \int adx$$ = area enclosed by acceleration-position graph

Equations of motion of a particle moving with uniform acceleration in straight line :

1. $v = u + at$
2. $S = ut + \frac{1}{2}at^2 = \left(\frac{v+u}{2}\right)t = vt - \frac{1}{2}at^2$
3. $v^2 = u^2 + 2aS$
4. $S_{n^{th}} = u + \frac{1}{2}a(2n-1)$
5. $x = x_0 + ut + \frac{1}{2}at^2$

Here,

u = velocity of particle at $t = 0$

S = Displacement of particle between 0 to t

$= x - x_0$ (x_0 = position of particle at $t = 0$, x = position of particle at time t)

a = uniform acceleration

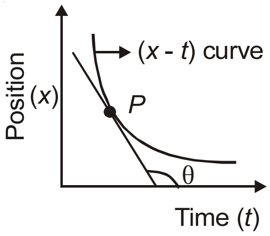
v = velocity of particle at time t

$S_{n^{th}}$ = Displacement of the particle in n^{th} second

GRAPHS

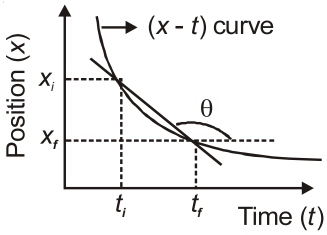
The important properties of various graphs are given below :

1. Slope of the tangent at a point on the position-time graph gives the instantaneous velocity at that point.



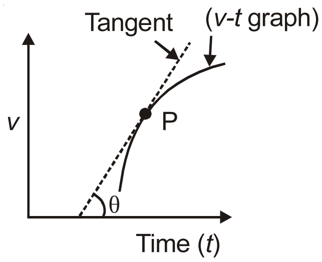
$\tan\theta = \frac{dx}{dt} = v$ (**Instantaneous Velocity** at point P)

2. Slope of a chord joining two points on the Position-time graph gives the average velocity during the time interval between those points.



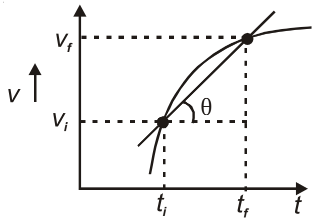
$\tan\theta = \frac{x_f - x_i}{t_f - t_i} = v_{av}$

3. Slope of the tangent at a point on the velocity-time graph gives the instantaneous acceleration at that point.



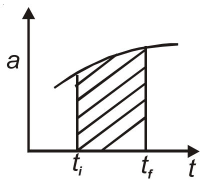
$\tan\theta = \frac{dv}{dt} = a$ (Instantaneous acceleration at P)

4. Slope of the chord joining two points on the velocity-time graph gives the average acceleration during the time interval between those points.



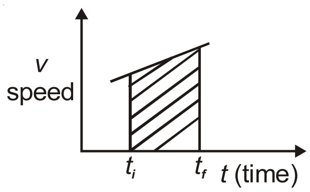
$\tan\theta = \frac{v_f - v_i}{t_f - t_i} = a_{av}$ = Average acceleration in time interval $t_f - t_i$

5. The area under the acceleration-time graph between t_i and t_f gives the change in velocity $(v_f - v_i)$ between the two instants.



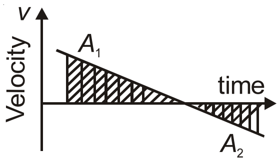
Shaded area = $v_f - v_i$ = change in velocity during interval t_i to t_f

6. The area under speed-time graph between t_i and t_f gives distance covered by particle in the interval $t_f - t_i$.



Shaded area = distance covered in time $(t_f - t_i)$

7. The area under the velocity-time graph between t_i and t_f gives the displacement $(x_f - x_i)$ between the two instants.

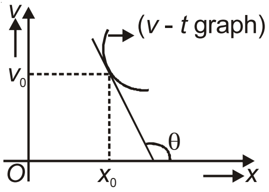


Shaded area $(A_1 - A_2)$ = Displacement in time $(t_f - t_i)$

Also, $A_1 + A_2$ = Distance covered in time $(t_f - t_i)$

8. In velocity-position graph, the acceleration of particle of any position x_0 is given as.

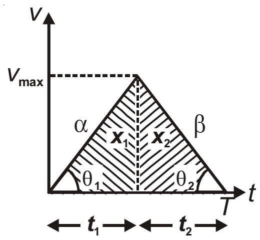
$$a = v_0 \tan\theta = v_0 \left|\frac{dv}{dx}\right|_{x=x_0}$$



9. The position-time graph cannot be symmetric about the time-axis because at an instant a particle cannot have two displacements.
10. The distance-time graph is always an increasing curve for a moving body.
11. The displacement-time graph does not show the trajectory of the particle.

Applications

1. If a particle is moving with uniform acceleration on a straight line and have velocity v_A at A and v_B at B, then velocity of particle midway on line AB is $v = \sqrt{\dfrac{v_A^2 + v_B^2}{2}}$.
2. If a body starts from rest with acceleration α and then retards to rest with retardation β, such that total time of journey is T, then



(a) Maximum velocity during the trip $v_{max.} = \left(\frac{\alpha\beta}{\alpha+\beta}\right).T$

(b) Length of the journey $L = \frac{1}{2}\left(\frac{\alpha\beta}{\alpha+\beta}\right)T^2$

(c) Average velocity of the trip = $\frac{v_{max.}}{2} = \frac{\alpha\beta T}{2(\alpha+\beta)}$

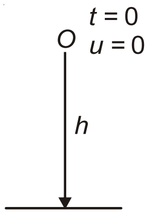
(d) $\frac{x_1}{x_2} = \frac{\beta}{\alpha} = \frac{t_1}{t_2}$.

MOTION UNDER GRAVITY

If height of object is very small as compared to radius of earth, motion of object will be uniformly accelerated. Equation of motion can be applied with proper sign convention.

Following are the important cases of interest.

1. Object is released from a height *h.*



Time taken to reach ground

$$-h = 0 - \frac{1}{2}gT^2 \text{ (taking up as positive)}$$

$$\Rightarrow T = \sqrt{\frac{2h}{g}}$$

Velocity of ball when it reaches ground

$$v = 0 - gT = -g\sqrt{\frac{2h'}{g}} = -\sqrt{2gh}$$

'–' sign indicate that velocity will be in downward direction.

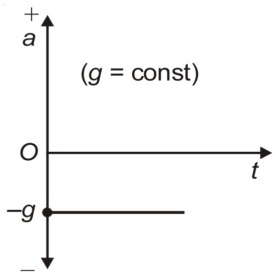
2. A particle is projected from ground with velocity *u* in vertically upward direction then

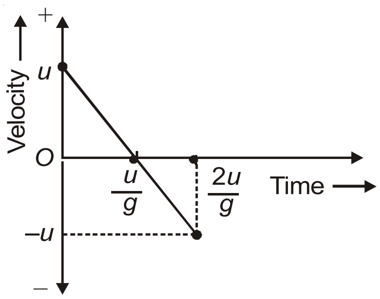
(a) Time of ascent = Time of descent = $\frac{\text{Time of flight}}{2} = \frac{T}{2} = \frac{u}{g}$

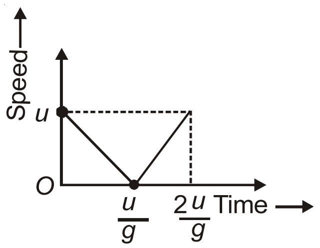
(b) Maximum height attained = $\frac{u^2}{2g}$

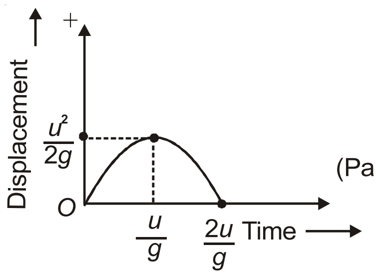
(c) Speed of particle when it hits the ground = *u*

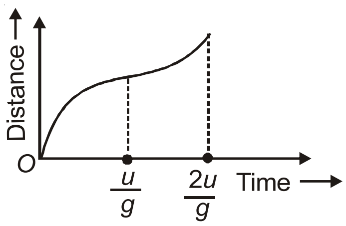
(d) Graphs











(e) Displacement of particle in complete journey = zero ⇒ average velocity $v_{av} = 0$

(f) Distance covered by particle in complete journey = $\dfrac{u^2}{g}$

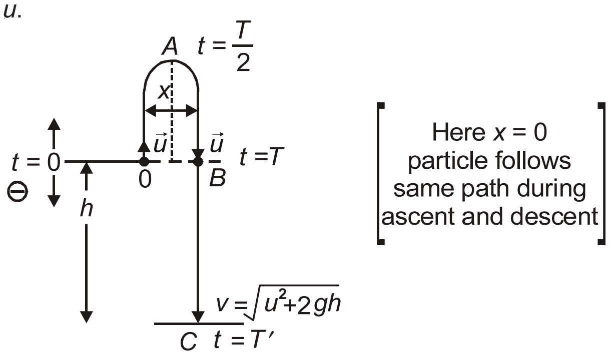
⇒ Average speed in complete journey = $\dfrac{u}{2}$

3. A body is thrown upward such that it takes t seconds to reach its highest point.
   - (a) Distance travelled in $(t)^{th}$ second = distance travelled in $(t + 1)^{th}$ second.
   - (b) Distance travelled in $(t - 1)^{th}$ second = distance travelled in $(t + 2)^{th}$ second.
   - (c) Distance travelled in $(t - r)^{th}$ second = distance travelled in $(t + r + 1)^{th}$ second.
4. A body is projected upward from certain height h with initial speed u.
   - (a) Its speed when it acquires the same level is u.
   - (b) Its speed at the ground level is

     $$v = \sqrt{u^2 + 2gh}$$
   - (c) The time required to attain same level is

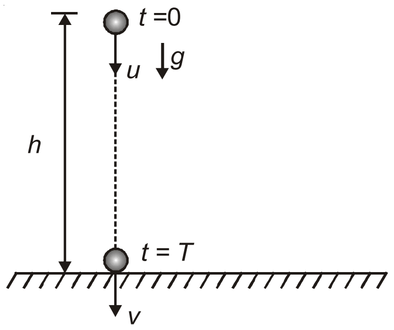
     $$T = \frac{2u}{g}$$
   - (d) Total time of flight (T') is obtained by solving

     $$\Rightarrow -h = uT' - \frac{1}{2}gT'^2 \text{ or } T' = \frac{u + \sqrt{u^2 + 2gh}}{g}$$

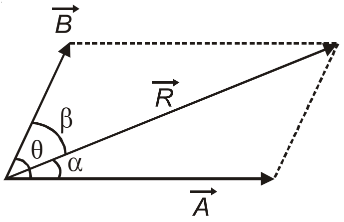


5. A body is projected from a certain height h with initial speed u downward.
   - (a) Its speed at ground level is $v = \sqrt{u^2 + 2gh}$
   - (b) Time of flight (T)

     $$T = \frac{-u + \sqrt{u^2 + 2gh}}{g}$$



Parallelogram Law of Vector Addition : If two vectors having common origin are represented both in magnitude and direction as the two adjacent sides of a parallelogram, then the diagonal which originates from the common origin represents the resultant of these two vectors. The results are listed below



(a) $\vec{R} = \vec{A} + \vec{B}$

(b) $|\vec{R}| = (A^2 + B^2 + 2AB\cos\theta)^{1/2}$

(c) $\tan\alpha = \dfrac{B\sin\theta}{A + B\cos\theta}$, $\tan\beta = \dfrac{A\sin\theta}{B + A\cos\theta}$

(d) If $|\vec{A}| = |\vec{B}| = x(\text{say})$, then $R = x\sqrt{2(1+\cos\theta)} = 2x\cos\dfrac{\theta}{2}$ and $\alpha = \beta = \dfrac{\theta}{2}$ *i.e.,* resultant bisect angle between $\vec{A}$ and $\vec{B}$.

(e) If $|\vec{A}| \quad |\vec{B}|$ then $\alpha < \beta$

(f) $R_{\text{max}} = A + B$, when $\theta = 0$ and $R_{\text{min}} = |A - B|$ when $\theta = 180°$.

(g) $R^2 = A^2 + B^2$, if $\theta = 90°$ *i.e.*, $\vec{A}$ and $\vec{B}$ are perpendicular.

(h) If $|\vec{A}| = |\vec{B}| = |\vec{R}|$, then $\theta = 120°$.

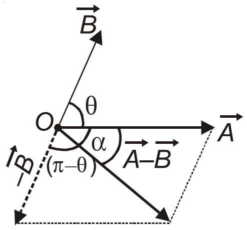
(i) If $\vec{R}$ is perpendicular to $\vec{A}$, then $\cos\theta = -\dfrac{A}{B}$ and $A^2 + R^2 = B^2$.

(j) For n coplanar vectors of same magnitude acting at a point such that angle between consecutive vectors are equal $\left(\dfrac{360}{n}\right)$, the resultant is zero.

VECTOR SUBTRACTION

Subtraction of vector $\vec{B}$ from vector $\vec{A}$ is simply addition of vector $-\vec{B}$ with $\vec{A}$ *i.e.,* $\vec{A} - \vec{B} = \vec{A} + (-\vec{B})$

Using parallelogram law,



Result : $R = |\vec{A} - \vec{B}| = \sqrt{A^2 + B^2 - 2AB\cos\theta}$, $\tan\alpha = \dfrac{B\sin\ \pi - \theta}{A + B\cos(\pi - \theta)} = \dfrac{B\sin\theta}{A - B\cos\theta}$

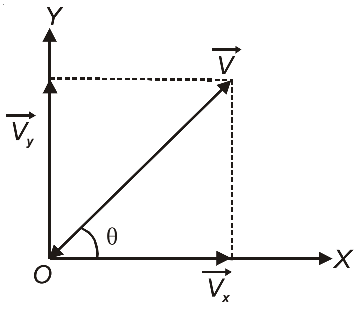
> ***Note :** If* $|\vec{A}| = |\vec{B}| = x(\text{say})$*, then* $R = x\sqrt{2(1-\cos\theta)} = 2x\sin\dfrac{\theta}{2}$.

RESOLUTION OF VECTORS

Any vector $\vec{V}$ can be represented as a sum of two vectors $\vec{P}$ and $\vec{Q}$ which are in same plane as $\vec{V} = \lambda\,\vec{P} + \mu\vec{Q}$, where λ and μ are two real numbers. We say that $\vec{V}$ has been resolved in two component vector $\lambda\vec{P}$ and $\mu\vec{Q}$ along $\vec{P}$ and $\vec{Q}$ respectively.

Rectangular components in two dimensions :

$\vec{V} = \vec{V}_x + \vec{V}_y, \vec{V} = V_x\hat{i} + V_y\hat{j},\ V = \sqrt{V_x^2 + V_y^2}$



$\vec{V}_x$ and $\vec{V}_y$ are rectangular component of vector in 2-dimension.

$V_x = V\cos\theta$

$V_y = V\sin\theta = V\cos(90 - \theta)$

V_z = zero.

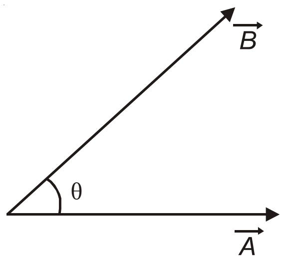
$\vec{V} = V\cos\theta\,\hat{i} + V\sin\theta\,\hat{j}$

Note : *Unit vector along* $\vec{V}$ is $\cos\theta\,\hat{i} + \sin\theta\,\hat{j}$

SCALAR AND VECTOR PRODUCTS

Scalar (dot) Product of Two Vectors : The scalar product of two vectors $\vec{A}$ and $\vec{B}$ is defined as

$\vec{A}\,.\,\vec{B} = AB\cos\theta$



$\cos\theta = \dfrac{\vec{A}\,.\,\vec{B}}{AB}$

If $\vec{A}$ and $\vec{B}$ are perpendicular, then $\vec{A}.\vec{B} = 0$

If θ < 90°, then $\vec{A}.\vec{B}\quad 0$ and if θ > 90° then $\vec{A}.\vec{B}\quad 0$.

Projection of vector $\vec{A}$ on $\vec{B}$ is $(\vec{A}.\vec{B})\dfrac{\vec{B}}{B^2}$.

$A^2 = \vec{A}.\vec{A}$

$\hat{i}.\hat{i} = \hat{j}.\hat{j} = \hat{k}.\hat{k} = 1.$

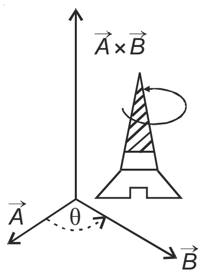
Scalar product is commutative *i.e.*, $\vec{A}.\vec{B} = \vec{B}.\vec{A}$.

Scalar product is distributive *i.e.*, $\vec{A}\ (\vec{B}\ \ +\vec{C}) = \vec{A}\ \vec{B} + \vec{A}\ \vec{C}$

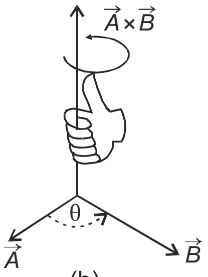
Vector Product of two Vectors :

Mathematically, if θ is the angle between vectors A and B, then

$A \times B = AB\sin\theta\,\hat{n}$ …(i)



(a)



(b)

The direction of vector $A\times B$ is the same as that of unit vector $\hat{n}$. It is decided by any of the following two rules :

(a) **Right handed screw rule :** Rotate a right handed screw from vector A to B through the smaller angle between them; then the direction of motion of screw gives the direction of vector $A\times B$ (Fig. a).

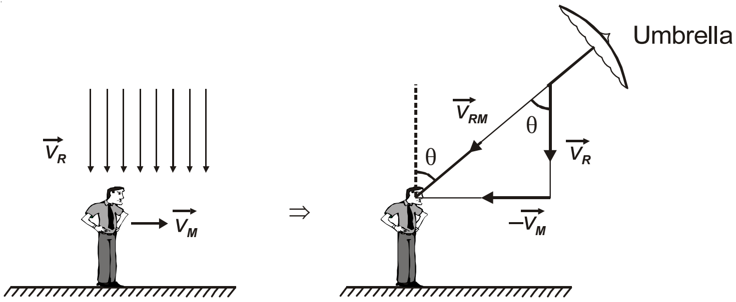
(b) **Right hand thumb rule :** Bend the finger of the right hand in such a way that they point in the direction of rotation from vector A to B through the smaller angle between them; then the thumb points in the direction of vector $A\times B$ (Fig. b).

RELATIVE MOTION IN TWO DIMENSIONS

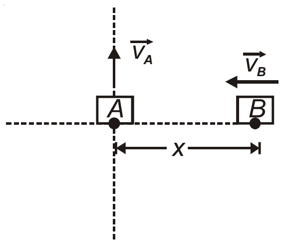
Relative velocity :

Velocity of object A w.r.t. object B is $\vec{v}_{AB}=\vec{v}_A-\vec{v}_B, \vec{v}_{BA}=\vec{v}_B-\vec{v}_A$

1. **Direction of Umbrella :** A person moving on straight road has to hold his umbrella opposite to direction of relative velocity of rain. The angle θ is given by $\tan\theta=\dfrac{v_M}{v_R}$ with vertical in forward direction.



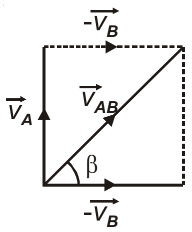
2. **Closest approach :** Two objects A and B having velocities $\vec{v}_A$ and $\vec{v}_B$ at separation x are shown in figure



The relative velocity of *A* with respect to *B* is given by

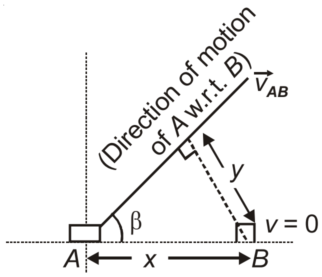
$$\vec{v}_{AB} = \vec{v}_A - \vec{v}_B$$

$$\tan\beta = \frac{v_A}{v_B}$$



The above situation is similar to figure given below.

y is the distance of closest approach.



Now, $\sin\beta = \frac{y}{x}$

$\Rightarrow$ $y = x\sin\beta$

$$y = \frac{x\tan\beta}{\sqrt{1+\tan^2\beta}} = \frac{xV_A}{\sqrt{V_B^2+V_A^2}}$$

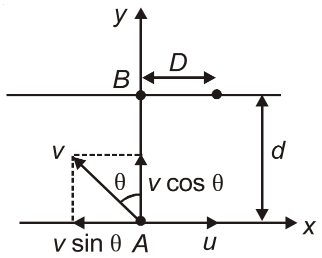
3. Crossing a river :

v = velocity of the man in still water.

θ = angle at which man swims w.r.t. normal to bank such that

$v_x = -v\sin\theta$, $v_y = v\cos\theta$

Time taken to cross the river is given by



$$t = \frac{d}{v_y} = \frac{d}{v\cos\theta}$$

Velocity along the river

$$v'_x = u - v\sin\theta$$

Distance drifted along the river $D = t\,v'_x$

$$D = \frac{d}{v\cos\theta}(u - v\sin\theta)$$

Case I : (Shortest time)

The Minimum time to cross the river is given by

$${}_{\min} = \frac{d}{v} \qquad \text{(when } \cos\theta = 1,\ \theta = 0°,\ u \quad v)$$

Distance drifted is given by

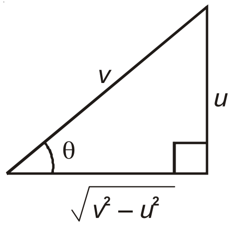
$$D = \frac{d}{v}\times u$$

Case II : (Shortest path)

To cross the river straight

drift $D = 0$ $\Rightarrow$ $u - v\sin\theta = 0$

$\sin\theta = \frac{u}{v}$ $\Rightarrow$ provided $v > u$



Time to cross the river straight across is given by

$$t = \frac{d}{v\cos\theta} = \frac{d}{\sqrt{v^2-u^2}}$$

PROJECTILE MOTION

An object moving in space under the influence of gravity is called projectile. Two important cases of interest are discussed below :

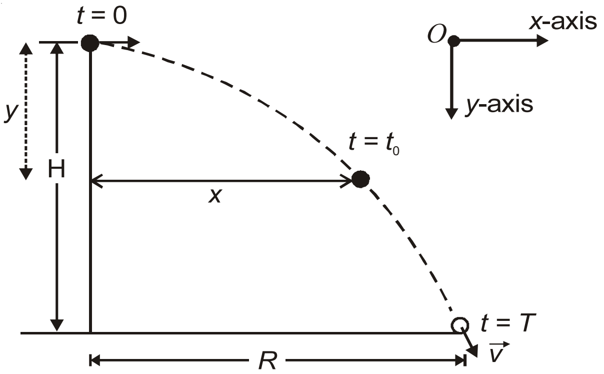
1. **Horizontal projection :**

A body of mass *m* is projected horizontally with a speed *u* from a height *h* at the moment $t = 0$. The path followed by it is a parabola.

It hits the ground at the moment $t = T$, with a velocity $\vec{v}$ such that

$$T = \sqrt{\frac{2H}{g}}$$

$$\left|\vec{v}\right| = \sqrt{u^2 + 2gH} = \left|u\hat{i} + gT\hat{j}\right|$$



The position at any instant t_0 is given by

$$x = ut_0$$

$$y = \frac{1}{2}gt_0^2$$

$$y = \frac{gx^2}{2u^2} \text{ (trajectory of particle)}$$

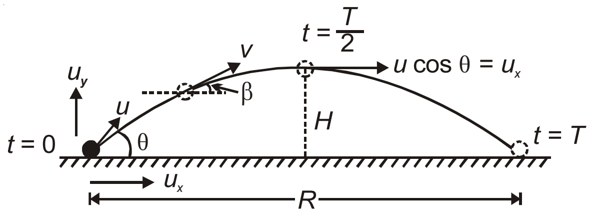
The velocity at any instant t_0 is given by

$$\overrightarrow{v_0} = u\hat{i} + gt_0\hat{j}$$

The range *R* will be given by $\boxed{R = u\sqrt{\frac{2H}{g}}}$

2. **Oblique projection :** A body of mass *m* is projected from ground with speed *u* at an angle θ above horizontal at the moment $t = 0$.

It hits the ground at a horizontal distance *R* at the moment $t = T$.

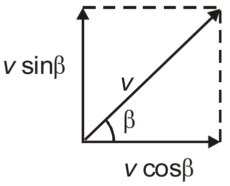


1. Time of flight $T = \frac{2u_y}{g} = \frac{2u\sin\theta}{g}$
2. Maximum height $H = \frac{u_y^2}{2g} = \frac{u^2\sin^2\theta}{2g}$
3. Horizontal range $R = u_x \times T = \frac{2u_xu_y}{g} = \frac{u^2\sin 2\theta}{g}$
4. Equation of trajectory: $y = x\tan\theta - \frac{gx^2}{2u^2\cos^2\theta}$

or $y = x\tan\theta\left(1 - \frac{x}{R}\right)$

5. Instantaneous velocity $v = \sqrt{u^2 + (gt)^2 - 2u(gt)\sin\theta}$

   and direction of motion is such that, $\tan\beta = \dfrac{u\sin\theta - gt}{u\cos\theta}$



   (a) $v = \dfrac{u\cos\theta}{\cos\beta}$ [∵ Horizontal component is same everywhere]

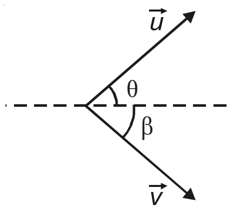
   (b) $v\sin\beta = u\sin\theta - gt$

   (c) When $\vec{v}$ (velocity at any instant 't') is perpendicular to $\vec{u}$ (initial velocity)

   $\Rightarrow \beta = -(90° - \theta)$

   (i) $v = \dfrac{u\cos\theta}{\cos(90 - \theta)} = u\cot\theta$

   (ii) $t = \dfrac{u}{g\sin\theta}$



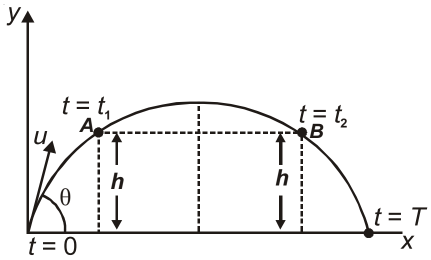
Applications :

1. The height attained by the particle is largest when θ = 90°. In this situation, time of flight is maximum and range is minimum (zero).
2. When R is range, T is time of flight and H is maximum height, then

   (a) $\tan\theta = \dfrac{gT^2}{2R}$

   (b) $\tan\theta = \dfrac{4H}{R}$

3. When horizontal range is maximum, $H = \dfrac{R_{\max}}{4}$
4. The horizontal range is same for complimentary angles like (θ, 90° – θ) or (45° + θ, 45° – θ). It is maximum for θ = 45°.
5. If A and B are two points at same level such that the object passes A at $t = t_1$ and B at $T = t_2$, then



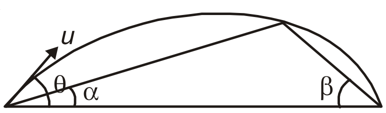
   (i) $T = \dfrac{2u\sin\theta}{g} = t_1 + t_2$

   (ii) $h = \dfrac{1}{2}gt_1t_2$

   (iii) Average velocity in the interval AB is

   $v_{av} = u\cos\theta$ [∵ vertical displacement is zero]

6. If a projectile is projected from one vertex of a triangle such that it grazes second vertex and finally fall down on 3rd vertex of the triangle on the same horizontal level, then $\boxed{\tan\theta = \tan\alpha + \tan\beta}$.



7. A projectile has same range for two angle of projection. If time of flight in two cases are T_1 and T_2, maximum height is H_1 and H_2 and the horizontal range is R. Then

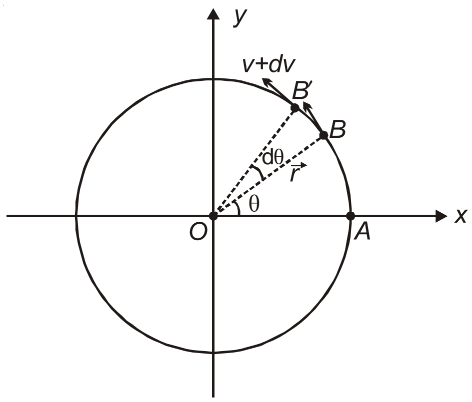
   (i) Range of projectile is $R = \frac{1}{2}gT_1T_2$

   (ii) Velocity of projection of projectile is $u = \frac{1}{2}g\left[T_1^2 + T_2^2\right]^{1/2}$

   (iii) $R = 4\sqrt{H_1H_2}$

CIRCULAR MOTION

An object of mass *m* is moving on a circular track of radius *r*. At *t* = 0, it was at *A*. At any moment of time '*t*', it has moved to *B*, such that $AOB = \theta$. Let its speed at this instant be *v* and direction is along the tangent. In a small time *dt*, it moves to *B′* such that $B'OB = d\theta$.



The angular displacement vector is $\overrightarrow{d\theta} = d\theta\hat{k}$

The angular velocity vector is $\vec{\ } = \frac{d\theta}{dt}\hat{k}$.

At *B′*, the speed of the object has become *v* + *dv*.

The tangential acceleration is $a_t = \frac{dv}{dt} = r\alpha$

The radial (centripetal acceleration) is $a_c = \frac{v^2}{r} = \ {}^2 r$

The angular acceleration is $\alpha = \frac{d}{dt}$

Relations among various quantities.

1. $\vec{v} = \vec{\ }\times\vec{r}$

2. $\vec{a} = \frac{d\vec{v}}{dt} = \vec{\ }\times\frac{d\vec{r}}{dt} + \frac{d\vec{\ }}{dt}\times\vec{r} = \overrightarrow{a_c} + \overrightarrow{a_t}$

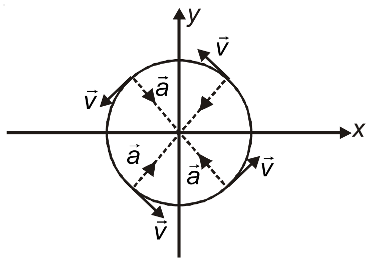
3. $\overrightarrow{a_c} = \vec{\ }\times\vec{v}$

4. $\overrightarrow{a_t} = \vec{\alpha}\times\vec{r}$

Uniform Circular Motion :

1. In uniform circular motion, the speed (v) of particle is remain constant (= constant)

2. $a_T = 0$ and $\alpha = \frac{d}{dt} = 0$



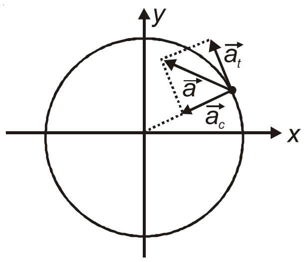
3. Only centripetal acceleration (also called normal acceleration) exists in uniform circular motion

$$a_c = r\ ^2 = \frac{v^2}{r}$$

4. In uniform circular motion $\vec{v}\quad\vec{a}$

Nonuniform Circular Motion :

1. In nonuniform circular motion the speed (v) and angular velocity ( ) change w.r.t. time.
2. Net acceleration of particle in non-uniform circular motion.



$$a = \sqrt{a_c^2 + a_t^2} = \sqrt{\left(\frac{v^2}{r}\right)^2 + r\alpha\ ^2}$$

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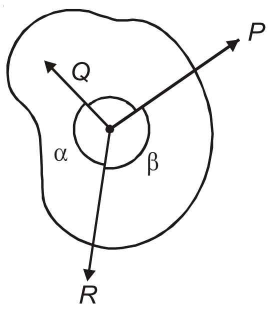
Chapter 3

Laws of Motion

Equilibrium of Concurrent Forces

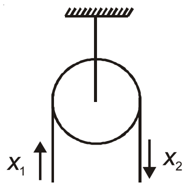
If three forces $\vec{P}$, $\vec{Q}$ and $\vec{R}$ are acting on an object such that forces are concurrent and the object is in equilibrium then $\dfrac{P}{\sin\alpha} = \dfrac{Q}{\sin\beta} = \dfrac{R}{\sin}$.



APPLICATIONS OF NEWTON'S LAWS OF MOTION

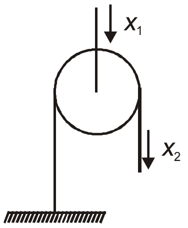
The strings connected to pulley are considered as ideal. Their length is fixed, so the ends of string follow a fixed relation between displacement velocity and acceleration. These relations are called constraint relation.

Case I **:** When the middle end is fixed

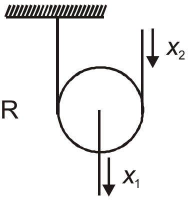


$x_1 = x_2$
$v_1 = v_2$
$a_1 = a_2$

Case II **:** When the side end is fixed

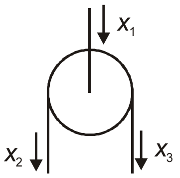


OR



$x_2 = 2x_1$
$v_2 = 2v_1$
$a_2 = 2a_1$

***Case III* :** When all the three ends are free to move



$$x_1 = \frac{x_2 + x_3}{2}$$

$$v_1 = \frac{v_2 + v_3}{2}$$

$$a_1 = \frac{a_2 + a_3}{2}$$

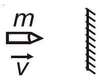
> ***Note :*** *In all the above relations downward direction is taken as positive. If any of the direction is upward in any case then –ve sign must be incorporated in the corresponding equation.*

1. A machine gun fires n bullet per second with speed u and mass of each bullet is m.

The Force required to keep the gun stationary is

$\vec{F} = nm\vec{v}$

2. Bullets moving with a speed v hit a wall normally.



(i) If the bullets come to rest in wall

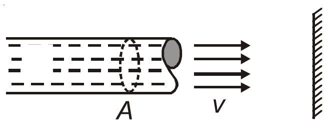
Force on wall $F_{wall} = nmv$

(Here n is number of bullets hitting the wall in one second)

(ii) If the bullets rebound elastically,

$F_{wall} = 2nmv$

3. Liquid jet of area A moving with speed v hits a wall



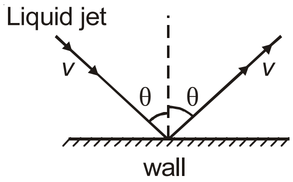
(i) Force required by a pump to move the liquid with this speed is

$$F = v\frac{dm}{dt} = v \times \quad Av = \quad Av^2$$

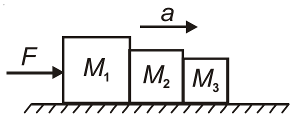
(ii) As jet hits a vertical wall and does not rebound, the force exerted by it on the wall is, $F_{wall} = \quad Av^2$

(iii) When water rebounds elastically, $F_{wall} = 2 \quad Av^2$

(iv) For oblique impact as shown, $F_{wall} = 2 \quad Av^2 \cos\theta$

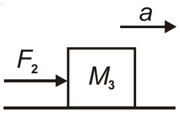


4. The blocks shown are being pushed by a force F. F_1, F_2 are contact forces between M_1 & M_2 and M_2 & M_3 respectively



$$a = \frac{F}{M_1 + M_2 + M_3}$$

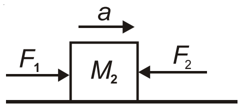
FBD of M_3



$F_2 = M_3a$

$F_1 - F_2 = M_2a \Rightarrow F_1 = (M_3 + M_2)a$

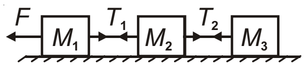
FBD of M_2



or $$F_2 = \frac{M_3}{M_1 + M_2 + M_3}F, F_1 = \left(\frac{M_2 + M_3}{M_1 + M_2 + M_3}\right)F$$

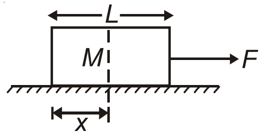
5. The strings are massless. Let T_1 and T_2 be the tensions in the two strings and 'a' be the acceleration.

$$a = \frac{F}{M_1 + M_2 + M_3}, T_1 = \frac{(M_2 + M_3)F}{M_1 + M_2 + M_3}, T_2 = \frac{M_3F}{M_1 + M_2 + M_3}$$

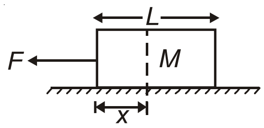


6. Tension in the block at a distance x from left end is given as

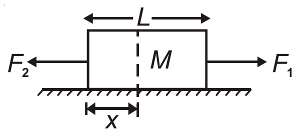
(a) $$T_x = \frac{Mx}{L} \times \frac{F}{M} = \frac{Fx}{L}$$



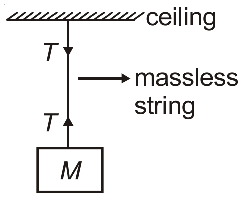
(b) $$T_x = \frac{F(L - x)}{L}$$

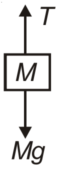


(c) $$T_x = \frac{F_1x}{L} + \frac{F_2(L - x)}{L}$$



7.





FBD of M w.r.t. ground

(a) When system is stationary

$T - Mg = 0$

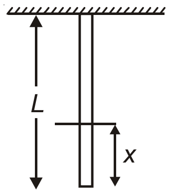
(b) System moves up with acceleration 'a'

$T = M(g + a)$

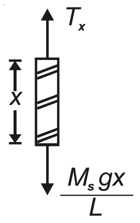
(c) System moves down with acceleration a

$T = M(g - a)$

8. Uniform rope of mass M_s.



FBD of lower portion



The tension in the rope at a distance x from free end is given below for different cases.

(a) Stationary system

$$T_x = \frac{M_s gx}{L}$$

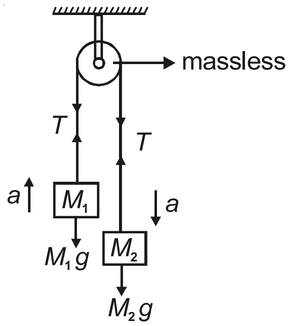
(b) If the rope is accelerating upwards, then $T_x = \frac{M_s x}{L}(g + a)$

(c) If the rope is accelerating downwards, then $T_x = \frac{M_s x}{L}(g - a)\,(g \quad a)$

IMPORTANT PROBLEMS

Pulley mass systems

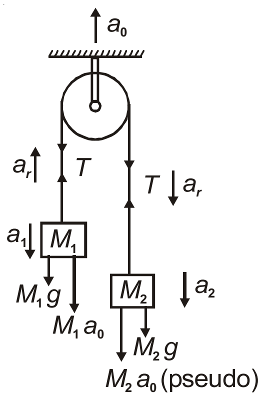
(i) Stationary pulley



$$a = \frac{M_2 - M_1}{M_2 + M_1} g$$

$$T = 2\left(\frac{M_1 M_2}{M_1 + M_2}\right) g$$

(ii) Pulley is moving upward with acceleration a_0



$$T = 2\left(\frac{M_1 M_2}{M_1 + M_2}\right)(g + a_0)$$

The acceleration of each block with respect to pulley is

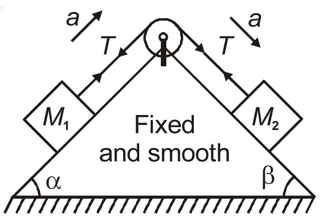
$$a_r = \left(\frac{M_2 - M_1}{M_2 + M_1}\right)(g + a_0)$$

The absolute accelerations of the two blocks are a_1 and a_2

$$a_1 = -(a_0 + a_r) \qquad \left\{a_0 = \left(\frac{a_1 + a_2}{2}\right)\right\}$$

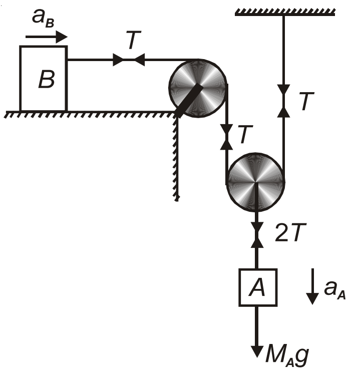
$$a_2 = a_r - a_0$$

(iii) $T = \frac{M_1 M_2 g}{M_1 + M_2}(\sin\alpha + \sin\beta)$



$$a = \left(\frac{M_2 \sin\beta - M_1 \sin\alpha}{M_2 + M_1}\right) g$$

(iv)



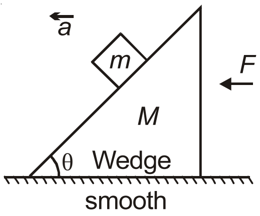
$2a_A = a_B$ ...(i)

$M_Ag - 2T = M_Aa_A$ ...(ii)

$T = M_Ba_B$ ...(iii)

Two block system :

Case - I :



Let '*m*' does not slide down relative to wedge '*M*'

The force required is given by

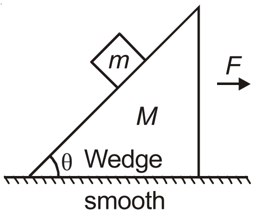
$F = (M + m)g \tan\theta$

$a = g \tan\theta$ (in horizontal direction w.r.t. ground)

Contact force *R* between *m* and *M* is

$$R = \frac{mg}{\cos\theta}$$

Case - II :



Minimum value of *F* so that '*m*' falls freely is given by

$F = Mg\cot\theta$

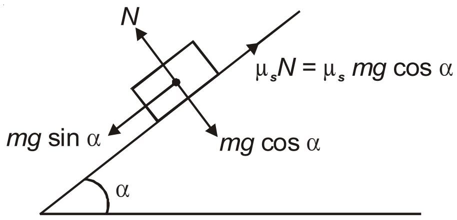
Wedge *M* moves with acceleration = $g\cot\theta$

The block falls vertically with acceleration '*g*'.

Contact force between *M* and *m* is zero.

Angle of Repose

Consider a situation in which a block is placed on an inclined plane with co-efficient of friction 'μ'. The maximum value of angle of inclined plane for which the block can remain at rest is defined as angle of repose.

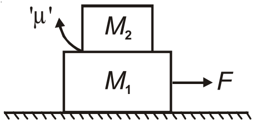


$\alpha = \tan^{-1}(\mu_s)$

Two blocks placed one above the other on smooth ground

Case - I : If a force F is applied on lower block

(a) $F \quad \mu(M_1 + M_2)g$



Smooth

Both blocks move together with same acceleration $a = \dfrac{F}{M_1 + M_2}$

$$a_{\max} = \mu g$$

(b) $F > \mu(M_1 + M_2)g$

M_2 moves with constant acceleration $a_2 = \mu g$

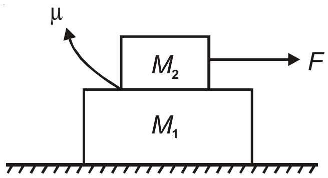
M_1 moves with acceleration $a_1 = \dfrac{F - \mu M_2 g}{M_1}$

M_2 slips backward on M_1.

Case - II : If a force F is applied on upper block

(a) $F \quad \dfrac{\mu(M_1 + M_2)M_2}{M_1}g$, both blocks move together with acceleration $a = \dfrac{F}{M_1 + M_2}$ with $a_{\max} = \dfrac{\mu M_2}{M_1}g$.

(b) If $F \quad \dfrac{\mu(M_1 + M_2)M_2 g}{M_1}$,



Smooth

M_1 moves with constant acceleration $a_1 = \dfrac{\mu M_2}{M_1}g$

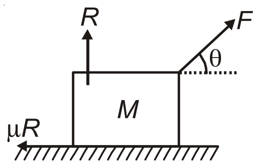
M_2 moves with acceleration $a_2 = \dfrac{F - \mu M_2 g}{M_2}$

M_2 slips forward on M_1.

Minimum force required to move a body on a rough horizontal surface

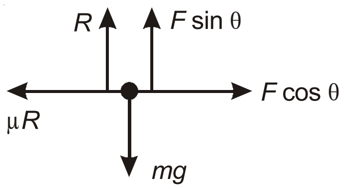
$F \cos\theta > \mu R \quad (R = mg - F \sin\theta)$

$F \quad \dfrac{\mu mg}{\cos\theta + \mu \sin\theta}$



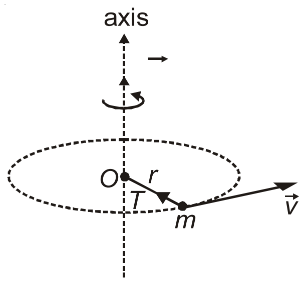
$F_{\min} = \dfrac{\mu mg}{\sqrt{1 + \mu^2}}$ at $\theta = \tan^{-1}(\mu)$

⇒



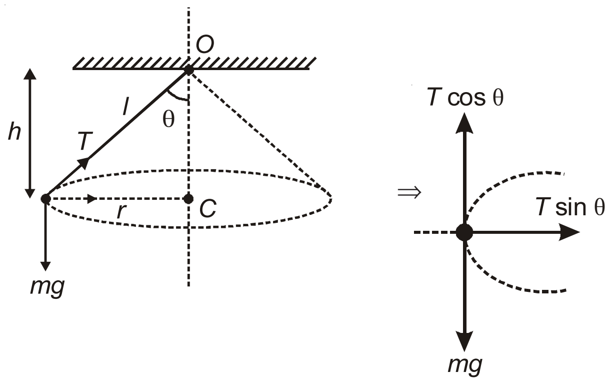
DYNAMICS OF CIRCULAR MOTION

Neglecting Gravity



T = Centripetal force = $\dfrac{mv^2}{r} = m\ {}^2r$

Considering gravity (Conical pendulum)



$T\sin\theta = m\ {}^2r$ …(1)

$T\cos\theta = mg$

$T = \dfrac{mg}{\cos\theta}$ …(2)

(a) For θ to be 90º (*i.e.*, string to be horizontal)

$T =$

∴ It is not possible.

(b) $T\sin\theta = m\ {}^2r = m\ {}^2l\sin\theta$

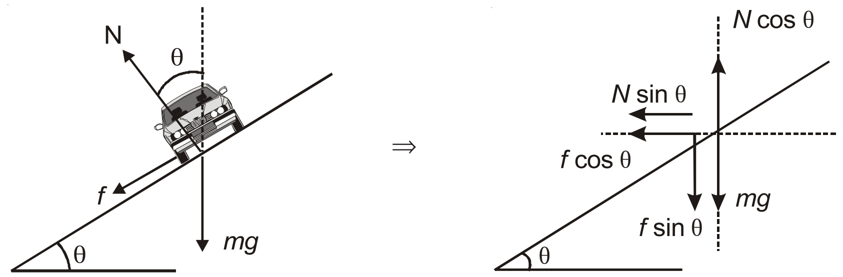
⇒ $T = m\ {}^2l$

(c) Time period = $2\pi\sqrt{\dfrac{h}{g}}$ ($h = l\cos\theta$)

Vehicle negotiating a curve on a banked road

The maximum velocity with which a vehicle can safely negotiate a curve of radius *r* on a rough inclined road is

$$V_{\max} = \sqrt{\frac{rg(\mu + \tan\theta)}{1 - \mu\tan\theta}}$$



Special Cases :

For a smooth inclined surface $\mu = 0 \Rightarrow$ $v_{max} = \sqrt{rg \tan\theta}$

For a horizontal rough surface, $\theta = 0 \Rightarrow$ $v_{max} = \sqrt{\mu rg}$

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Chapter 4

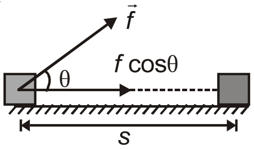
Work, Energy and Power

CONCEPT OF WORK

$$W = \vec{f}.\vec{s} \quad (\vec{s} = \vec{s}_2 - \vec{s}_1)$$

$$= fs\cos\theta$$

$$= s\,(f\cos\theta)$$



KINETIC ENERGY

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

WORK-ENERGY THEOREM

$$W_{\text{Total}} = \text{K.E.}$$

or

$$W_{\text{ext.}} + W_{\text{int.}} = \text{K.E}$$

Work Done by Spring Force

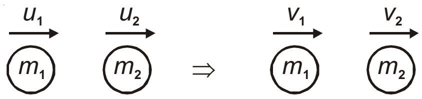
$$W = -\int_{x_1}^{x_2} kxdx = \frac{-1}{2}k(x_2^2 - x_1^2)$$

when $x_2 > x_1$, $W < 0$

when $x_2 < x_1$, $W > 0$

COLLISION

One dimension



$(u_1 > u_2$ and $v_2 > v_1)$

$$\text{KE} = \frac{1}{2}\frac{m_1m_2}{m_1 + m_2}(u_1 - u_2)^2(1 - e^2)$$

Following are the important cases

1. **Elastic collision e = 1**

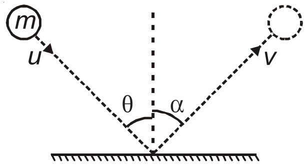
$$v_2 - v_1 = u_1 - u_2$$

$$v_1 = \frac{m_1 - m_2}{m_1 + m_2}u_1 + \frac{2m_2u_2}{m_1 + m_2}$$

$$v_2 = \frac{m_2 - m_1}{m_2 + m_1}u_2 + \frac{2m_1u_1}{m_2 + m_1}$$

KE = 0 ⇒ Final KE = Initial KE

2. **Coefficient of restitution = e**



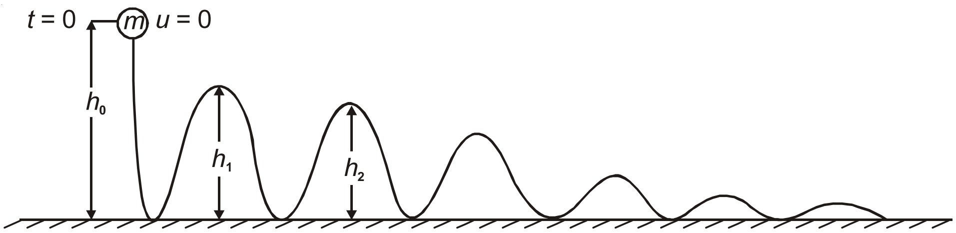
$$u \sin \theta = v \sin \alpha \qquad \text{...(1)}$$

$$eu \cos \theta = v \cos \alpha \qquad \text{...(2)}$$

$$\Rightarrow \quad v = u\sqrt{\sin^2 \theta + e^2 \cos^2 \theta}$$

$$\tan \alpha = \frac{\tan \theta}{e} \quad (i.e.\ \alpha > \theta)$$

3. **A ball of mass m is dropped from a height h_0 on an inelastic floor.**



The coefficient of restitution = e

(a) Maximum height after n^{th} bounce is $h_n = e^{2n}h_0$

(b) Speed of rebound after n^{th} bounce = $e^n\sqrt{2gh_0}$

(c) Total distance travelled before the body comes to rest

$$= h_0\left[\frac{1+e^2}{1-e^2}\right]$$

(d) The time after which the body comes to rest

$$= \sqrt{\frac{2h_0}{g}} \cdot \left[\frac{1+e}{1-e}\right]$$

(e) Average force exerted on the ground is mg

(f) Displacement of ball when it stops is h_0

4. **Oblique elastic collision**

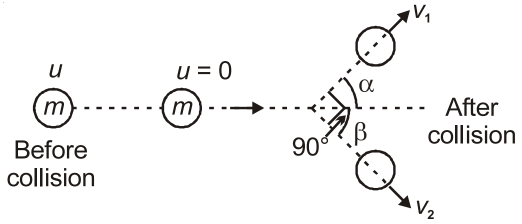
A body of mass m collides with a stationary body of same mass.

(a) $\alpha + \beta = \frac{\pi}{2}$ …(1)

(b) $v_1\cos\alpha + v_2\cos\beta = u$ …(2)

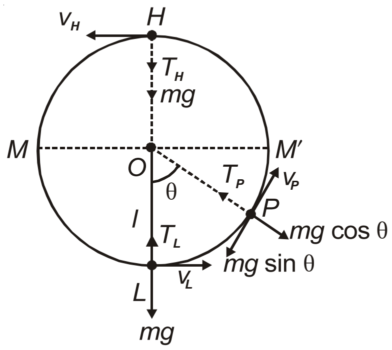
(c) $v_1\sin\alpha = v_2\sin\beta$ …(3)

(d) $u^2 = v_1^2 + v_2^2$ …(4)



MOTION IN A VERTICAL CIRCLE

A particle of mass m is tied to a string of length l whose other end is fixed. The particle can revolve about O in a vertical circle. when it is at position L (lowest point), it is given a speed V_L horizontal. Following results are useful in describing its motion.



1. $a_T = g\sin\theta$ …(1)

2. $a_C = \frac{T_p - mg\cos\theta}{m} = \frac{v_p^2}{l}$

3. $T_p = \frac{mv_p^2}{l} + mg\cos\theta$ …(2)

4. $T_L = mg + \frac{mv_L^2}{l}$

5. $v_L \quad \sqrt{2gl}$, it oscillates between M and M'

6. $\sqrt{2gl} \quad v_L \quad \sqrt{5gl}$, it will leave the circular path somewhere between M' and H.

7. When $v_L \quad \sqrt{5gl}$, it completes vertical circle (Also $v_H \quad \sqrt{gl}$)

8. $T_H = -mg + \frac{mv_H^2}{l}$

9. $T_L - T_H = 6\,mg$ (always)

❑ ❑ ❑

Chapter 5

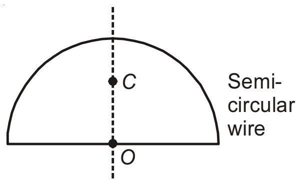
Rotational Motion

CENTRE OF MASS OF A RIGID BODY (CONTINUOUS MASS DISTRIBUTION)

Mathematically position coordinates of the centre of mass of rigid body are given by

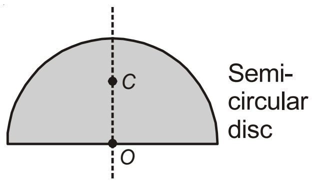
$$x_{\text{cm}} = \frac{\int x\,dm}{\int dm};\quad y_{\text{cm}} = \frac{\int y\,dm}{\int dm};\quad z_{\text{cm}} = \frac{\int z\,dm}{\int dm}$$

Centre of mass of some commonly used objects.



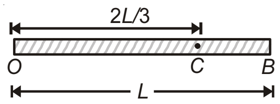
1. Semi circular wire of radius R.

$$OC = \frac{2R}{\pi}, \text{ where } C \text{ is centre of mass}$$



2. Semi circular disc of radius R

$$OC = \frac{4R}{3\pi}$$



3. Non-uniform rod of length L. The linear mass density varies linearly from zero at O to maximum at B.

$$OC = \frac{2L}{3}$$

VELOCITY AND ACCELERATION OF CENTRE OF MASS

Velocity of Centre of Mass

The instantaneous velocity of centre of mass is given by

$$\vec{v}_{\text{cm}} = \frac{m_1\vec{v}_1 + m_2\vec{v}_2 + \dots m_n\vec{v}_n}{\sum_{i=1}^{n} m_i}; \qquad \text{or} \qquad \vec{v}_{\text{cm}} = \frac{\vec{P}_{\text{system}}}{M_{\text{system}}}$$

Where $\vec{P}_{\text{system}}$ is the total linear momentum of the system of particles.

Acceleration of Centre of Mass

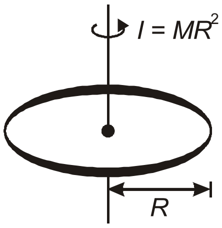
Differentiating $\vec{v}_{cm}$ w.r.t. time we get $\vec{a}_{cm}$ as

$$\vec{a}_{cm} = \frac{m_1\vec{a}_1 + m_2\vec{a}_2 + ...m_n\vec{a}_n}{\sum_{i=1}^{n} m_i}; \qquad \text{or} \qquad \vec{a}_{cm} = \frac{\vec{F}_{ext}}{M_{system}}$$

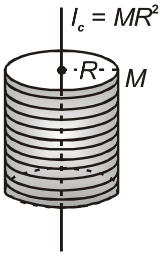
Where $\vec{F}_{ext}$ is the vector sum of forces acting on the particles of system.

MOMENT OF INERTIA OF DIFFERENT OBJECTS

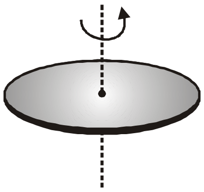
For an axis perpendicular to the plane of the ring



A hollow cylinder

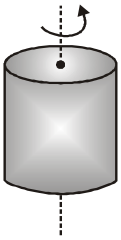


The axis perpendicular to the plane of the disc.



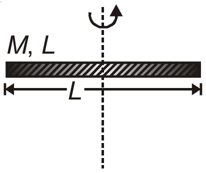
$$I_{cm} = \frac{MR^2}{2}$$

A solid cylinder



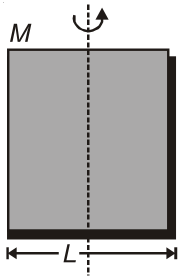
$$I_{cm} = \frac{MR^2}{2}$$

A thin rod



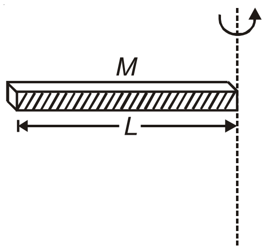
$$I_c = \frac{ML^2}{12}$$

A plate



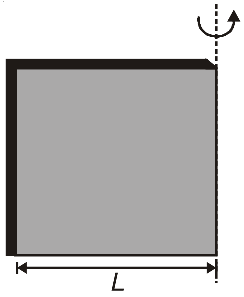
$$I_c = \frac{ML^2}{12}$$

A thin rod about a perpendicular axis through its end



$$I = \frac{ML^2}{3}$$

A plate about one edge



$$I = \frac{ML^2}{3}$$

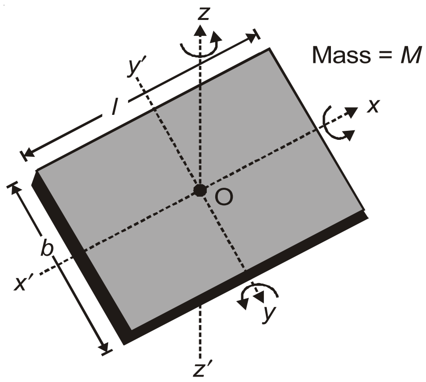
A Rectangular Plate

(a) $I_{xx'} = \frac{Mb^2}{12}$

(b) $I_{yy'} = \frac{Ml^2}{12}$

(c) $I_{zz'} = I_{xx'} + I_{yy'}$

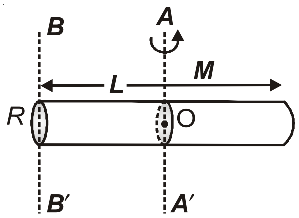
(d) $I_{zz'} = \frac{M(l^2 + b^2)}{12}$



A Thick Rod (Solid cylinder)

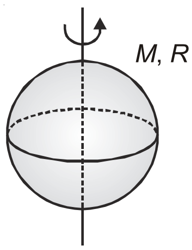
The axis is perpendicular to the rod and passing through the centre of mass

$$I_{AA'} = \frac{ML^2}{12} + \frac{MR^2}{4}; I_{BB'} = \frac{ML^2}{3} + \frac{MR^2}{4}$$



A Solid Sphere

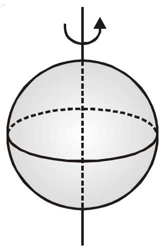
About its diameter



$$I_{\text{cm}} = \frac{2}{5}MR^2$$

A Hollow Sphere

About its diameter



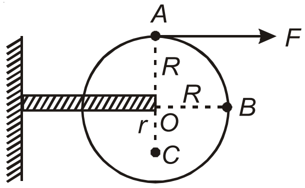
$$I_{\text{cm}} = \frac{2}{3}MR^2$$

RIGID BODY ROTATION

In this section, rotation of a body about a stationary fixed axis has been discussed

1. **Rotating Disc**

A tangential force *F* is applied at the periphery, as a result disc is rotating above an axis passing through its CM, normal to plane of disc



$= F \times R$ [about *O*]

$I = \frac{1}{2}mR^2$

$\alpha = \frac{}{I} = \frac{2F}{MR}$

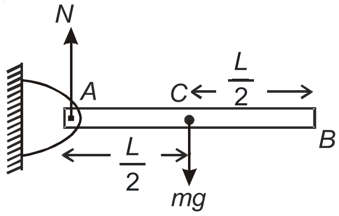
(1) Tangential acceleration of A is $a_A = R\alpha = \frac{2F}{M}$ (along horizontal)

(2) Tangential acceleration of B is $a_B = R\alpha = \frac{2F}{M}$ (vertically downwards)

(3) Tangential acceleration of C is $a_C = r\alpha = \frac{2Fr}{MR}$ (along horizontal, opposite to the direction of tangential acceleration of *A*)

2. **Hinged Rod**

The rod is released from rest from horizontal position



$= mg \times \frac{L}{2}$ (about *A*)

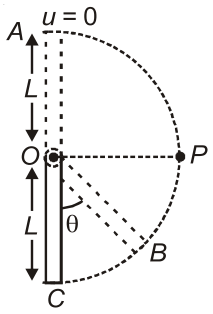
$I = \frac{ML^2}{3}$

$\alpha = \frac{}{I} = \frac{3g}{2L}$

(1) Linear acceleration of COM *C* is $a_{cm} = \frac{L}{2}\alpha = \frac{3g}{4}$. Also, $N = mg - ma_{cm} = \frac{mg}{4}$

(2) Linear acceleration of point *B* is $a_B = L\alpha = \frac{3g}{2}$

(3) The rod is released from unstable equilibrium position {from position *A*}



(a) When at *B*, $Mg\frac{L}{2}(1+\cos\theta) = \frac{1}{2}\left(\frac{ML^2}{3}\right)\ ^2$

$= \sqrt{\frac{6g}{L}}\cos\frac{\theta}{2}$

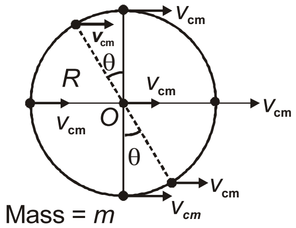
(b) at *C*, θ = 0°

$= \sqrt{\frac{6g}{l}}$

(c) at *P*, θ = 90°, $= \sqrt{\frac{3g}{l}}$

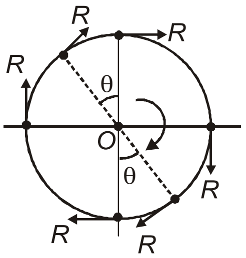
ROLLING OF A BODY

Rolling is combination of Pure Translation and Pure Rotation Motion about Centre of Mass.



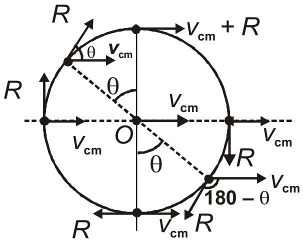
Pure translation

+



Pure rotation (about cm)

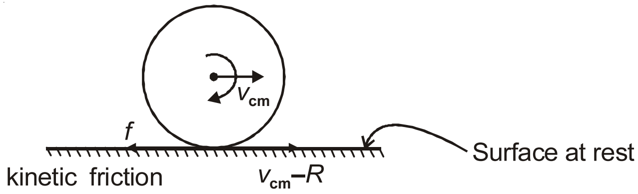
⇒



Rolling

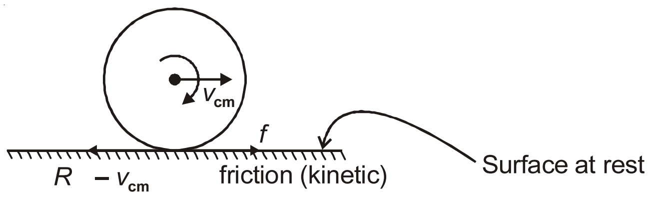
Case - I : Forward slipping

$v_{cm} > R$



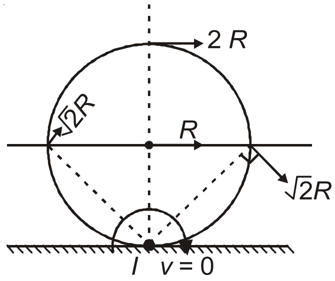
Case - II : Backward slipping

$v_{cm} < R$

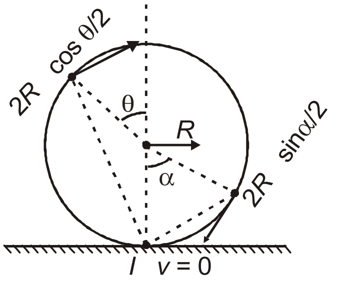


Case - III : **Pure Rolling**

$v_{cm} = R$



(instantaneous centre of rotation)



(instantaneous centre of rotation)

Note : *In this case, friction is static. It may or may not be zero.*

Kinetic energy of the body during pure rolling (E)

E = Translational KE + Rotational KE

$$= E_T + E_R$$

$$= \frac{1}{2}mv_{\text{cm}}^2 + \frac{1}{2}I_{\text{cm}} \quad ^2$$

$$= \frac{1}{2}\left(m + \frac{I_{\text{cm}}}{R^2}\right)v_{\text{cm}}^2 = \frac{1}{2}mv_{\text{cm}}^2\left(1 + \frac{K^2}{R^2}\right)$$ (where k is radius of gyration)

$$E = E_T\left(1 + \frac{K^2}{R^2}\right)$$

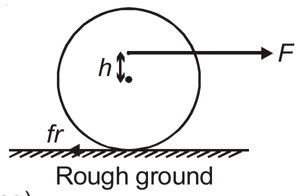
Similarly, $E = E_R\left(1 + \dfrac{R^2}{K^2}\right)$

Type of body	K	Fraction of total energy translational $X = \left(1 + \dfrac{K^2}{R^2}\right)^{-1}$	Fraction of total energy rotational $Y = \left(1 + \dfrac{R^2}{K^2}\right)^{-1}$	$\dfrac{Y}{X}$
1. Ring or hollow cylinder	R	$\frac{1}{2} = 0.5 = 50\%$	$\frac{1}{2} = 0.5 = 50\%$	$1:1$
2. Spherical Shell	$\sqrt{\frac{2}{3}}R$	$\frac{3}{5} = 0.6 = 60\%$	$\frac{2}{5} = 0.4 = 40\%$	$2:3$
3. Disc or solid cylinder	$\frac{R}{\sqrt{2}}$	$\frac{2}{3} = 0.666 = 66.67\%$	$\frac{1}{3} = 0.333 = 33.33\%$	$1:2$
4. Solid sphere	$\sqrt{\frac{2}{5}}R$	$\frac{5}{7} = 0.714 = 71.4\%$	$\frac{2}{7} = 0.286 = 28.6\%$	$2:5$

Note : *Above values X and Y are independent of mass and radius of the body. They only depend on the type of body.*

Applications

1. A force is applied at the distance h from centre of mass as shown in figure



$$a_{C.M} = \frac{F\left(1 + \frac{h}{R}\right)}{M\left(1 + \frac{K^2}{R^2}\right)}$$

$$f_r = \frac{F(K^2 - hR)}{K^2 + R^2} \quad \mu N$$ (must be less than μmg for Rolling)

If $h \quad \dfrac{K^2}{R}$ friction is backward

$h \quad \dfrac{K^2}{R}$ friction become forward

2. If force is applied at centre of mass then (h = 0)

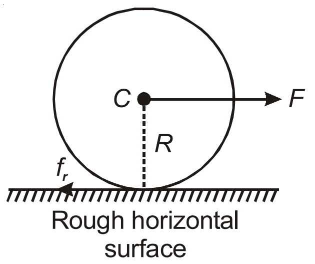
So, $a = \dfrac{F}{M\left(1 + \dfrac{K^2}{R^2}\right)}$ and $f_r = \dfrac{FK^2}{K^2 + R^2} = \dfrac{F}{\left(1 + \dfrac{R^2}{K^2}\right)}$

3. If force is applied at highest point ($h = R$)

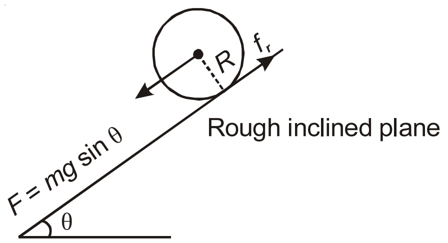
$$a_{\text{C.M.}} = \frac{2F}{M\left(1+\dfrac{K^2}{R^2}\right)}$$

$$f_r = \left(\frac{R^2 - K^2}{K^2 + R^2}\right)F \text{, forward direction}$$

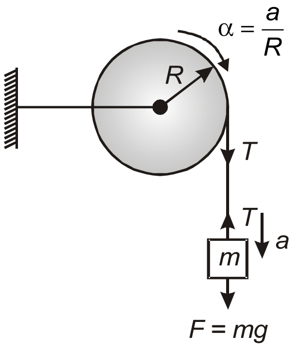
4. (i)



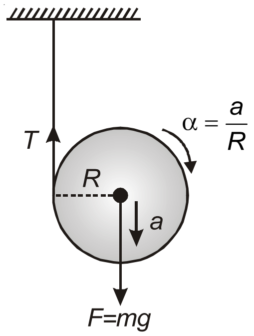
(ii)



(iii)



(iv)



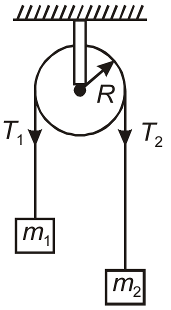
For all the four situations shown above,

$$a = \frac{F}{m + \dfrac{I_{\text{c.m.}}}{R^2}}$$

$$f_r \text{ or } T = \frac{I_{\text{c.m.}}a}{R^2}$$

In the situations described above, the linear acceleration of the moving object can be calculated by same formula, the value of F, and moment of inertia will depend on the kind of problem.

Also consider the following situation.



$$a = \frac{F}{(m_1 + m_2) + \dfrac{I}{R^2}}$$

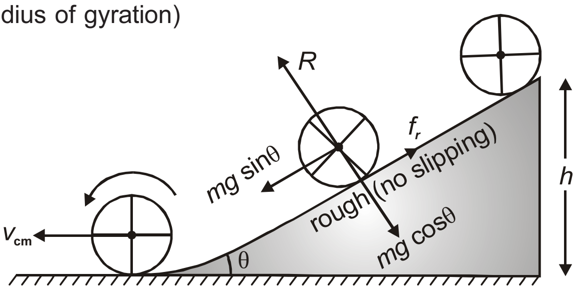
$$T_2 - T_1 = \frac{Ia}{R^2}$$

Here, $F = (m_2 - m_1)\,g$ = Net pulling force

Rolling of a Body on an Inclined Plane

By conservation of energy, $\underset{\text{(Total energy)}}{mgh} = \underset{\text{(Rotatory)}}{\frac{1}{2}I\ ^2} + \underset{\text{(Translatory)}}{\frac{1}{2}mv_{\text{cm}}^2}$

Let $\beta = 1 + \frac{I_{\text{cm}}}{MR^2} = 1 + \frac{K^2}{R^2}$ (where *k* is radius of gyration)



1. $a_{\text{cm}} = \frac{mg\sin\theta}{m + \frac{I_{\text{cm}}}{R^2}} = \frac{g\sin\theta}{1 + \frac{K^2}{R^2}} = \frac{g\sin\theta}{\beta}$

2. $v_{\text{cm}} = \sqrt{\frac{2gh}{\beta}} = \sqrt{2gh \Big/ 1 + \frac{K^2}{R^2}}$

3. $\text{Time} = \frac{1}{\sin\theta}.\sqrt{\beta\frac{2h}{g}}$ ∵ Force of friction $f_r = \frac{mg\sin\theta}{1 + \frac{R^2}{K^2}}$

   i.e., $t \propto \sqrt{\beta}$

4. Force of friction $f_r = \frac{mg\sin\theta}{1 + \frac{R^2}{K^2}}$

5. Instantaneous power $P = (mg\sin\theta)v$

6. Maximum angle of inclination for pure rolling, $\theta_{\max} = \tan^{-1}\left(\mu \times \left(1 + \frac{R^2}{K^2}\right)\right)$

Ring : $\theta_{\max} = \tan^{-1}(2\mu)$,
Spherical Shell : $\theta_{\max} = \tan^{-1}(2.5\ \mu)$
Disc : $\theta_{\max} = \tan^{-1}(3\mu)$
Solid sphere : $\theta_{\max} = \tan^{-1}(3.5\ \mu)$.

ANGULAR MOMENTUM

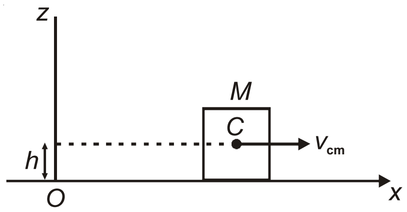
The general formula for angular momentum about any point is

$$\vec{L} = M\vec{v}_{\text{cm}}R + I\vec{\ }$$

Case - I : Pure translation

$$|\vec{L}_O| = Mv_{\text{cm}}h$$

$$L_C = 0$$



Case - II : Rolling body

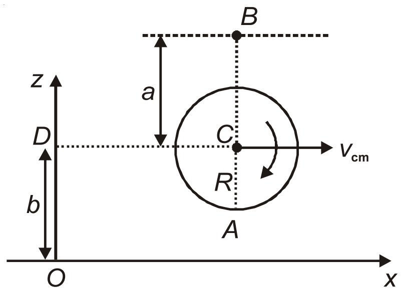
$L_c = I_c$

$L_A = I_C \quad + Mv_{cm}R$

$L_O = I_c \quad + Mv_{cm}b$

$L_B = I_c \quad - Mv_{cm}a$

$L_D = I_c$



Case - III : Centre of mass is fixed

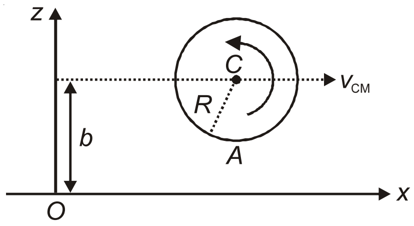
Put $v_{cm} = 0$ in the above results so $L_0 = L_A = L_C = I_C$

Case - IV

$L_c = - I_c$

$L_A = \ - I_C \quad + Mv_{cm}R$

$L_O = - I_c \quad + Mv_{cm}b$

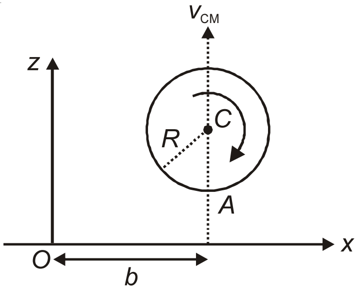


Case - V

$L_c = I_c$

$L_A = \ I_C$

$L_O = I_c \quad - Mv_{cm}b$



Note : *In all above situations, anticlockwise sense has been assigned a negative sign.*

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Chapter 6

Gravitation

VARIATION IN THE VALUE OF *g*

1. At height *h* (Above earth's surface)

$$g' = \frac{g}{\left[1+\frac{h}{R_e}\right]^2}$$

If $h = R_e$, $g' = \frac{g}{4}$

If $h << R_e$ then $g' = g\left(1-\frac{2h}{R_e}\right)$

2. At depth *"x"* (below earth's surface)

$g' = g\left\{1-\frac{x}{R_e}\right\}$, at the centre of earth $g' = 0$, weight = 0

3. **Due to Rotation of Earth :**

Apparent value of acceleration due to gravity.

$g' = g - R_e\ {}^2\cos^2\lambda$

λ angle of latitude

GRAVITATIONAL FIELD INTENSITY AND POTENTIAL (*V*)

1. Gravitational field intensity

$$\vec{I} = \frac{-GM}{r^2}\hat{r}$$

2. Gravitational potential

$$V = -\frac{W}{m} \Rightarrow V = \frac{-GM}{r} \text{ (units J/kg)}$$

Variation of Intensity and Potential

1. For a spherical shell of mass M and radius R

Case-I : $r < R$ (internal point)

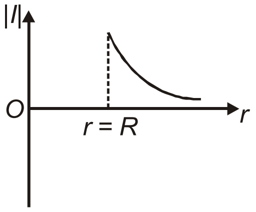
$$I_i = 0,\ V_i = -\frac{GM}{R}$$

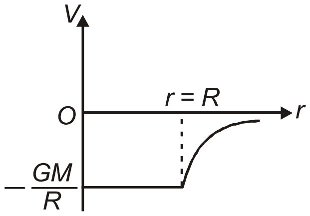
Case-II : $r = R$ (on the surface)

$$I_s = \frac{GM}{R^2}, V_s = \frac{-GM}{R}$$

Case-III : $r > R$ (outside the shell)

$$I_o = \frac{GM}{r^2}, V_o = \frac{-GM}{r}$$





2. For Uniform solid Sphere

Case-I : $r < R$ (internal point)

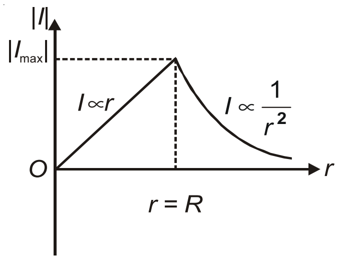
$$I_i = \frac{GMr}{R^3}, V_i = \frac{-GM}{2R^3}(3R^2 - r^2)\ \text{At centre}\ V_c = -\frac{3GM}{2R} = \frac{3}{2}V_{\text{Surface}}$$

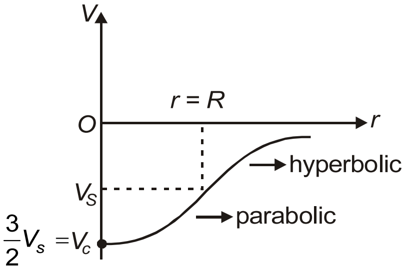
Case-II : $r = R$ (on the surface)

$$I_s = \frac{GM}{R^2},\ V_s = \frac{-GM}{R}$$

Case-III : $r > R$ (outside the surface)

$$I_o = \frac{GM}{r^2},\ V_o = \frac{-GM}{r}$$

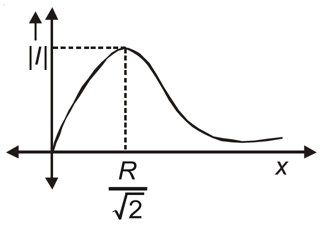


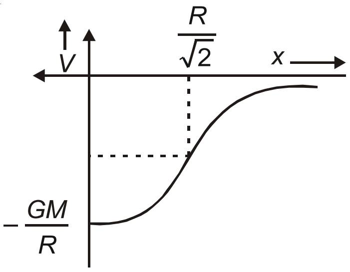


3. Gravitational intensity and potential on the axis of uniform ring of mass M radius R at distance x from centre.

$$I = \frac{GMx}{(R^2 + x^2)^{3/2}}, V = \frac{-GM}{\sqrt{R^2 + x^2}}$$

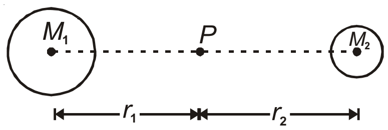
At centre $I = 0$. I is maximum at $x = \frac{R}{\sqrt{2}}$; $I_{\max} = \frac{2GM}{3\sqrt{3}R^2}$





4. **Neutral point :** The point P at which gravitational field is zero between two massive bodies, is called neutral point.

$$\boxed{\frac{M_1}{r_1^2} = \frac{M_2}{r_2^2}}$$



GRAVITATIONAL POTENTIAL ENERGY

At earth surface $U = -\frac{GM_e m}{R_e}$, At height h, $U = \frac{-GM_e m}{R_e + h}$

Energy required to escape = Escape energy = $+\frac{GM_e m}{R_e}$ = Binding energy.

ESCAPE VELOCITY

$$\Rightarrow \quad v_e = \sqrt{\frac{2GM_e}{R_e}} = \sqrt{\frac{8}{3}\pi G R_e{}^2} = \sqrt{2gR_e}$$

At earth surface, v_e = 11.2 km/s

KEPLER'S LAWS

(1) All planets revolve around the Sun in elliptical orbit having the Sun at one focus.

If e = eccentricity of ellipse then distance of the planet from the Sun at perigee is

$r_p = (1 - e)a$

and distance of the planet from the Sun at apogee is

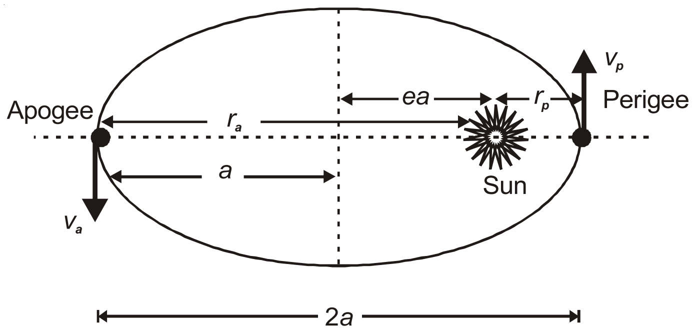
$r_a = (1 + e)a$ (a = semi major axis)

Ratio of orbital speeds at apogee and perigee is

$$\frac{v_a}{v_p} = \frac{r_p}{r_a} = \frac{1-e}{1+e}$$

Ratio of angular velocities at apogee and perigee is

$$\frac{\omega_a}{\omega_p}=\left(\frac{r_p}{r_a}\right)^2=\left(\frac{1-e}{1+e}\right)^2$$



(2) A planet sweeps out equal area in equal time interval *i.e.,* Areal speed of the planet is constant

$$\frac{dA}{dt}=\frac{1}{2}vr=\frac{L}{2m}$$ = constant (L represents angular momentum of planet about the Sun)

(3) Square of time period is proportional to cube of semi-major axis of the elliptical orbit of the planet. *i.e.*, $T^2 \propto a^3$

SATELLITES

Important results regarding satellite motion in circular orbit.

1. **Orbital Velocity (v_0) :** Gravitational attraction of planet gives necessary centripetal force.

$$\Rightarrow \quad v_0=\sqrt{\frac{GM}{r}}$$

$$v_0=\sqrt{\frac{GM}{r}}=\sqrt{\frac{gR_e^2}{R_e+h}}$$ (h = height above the surface of earth)

$$\Rightarrow \quad v_e=\sqrt{2}v_0$$

2. **Time Period :** The period of revolution of a satellite is

$$T=\frac{2\pi r}{v_0}=2\pi r\sqrt{\frac{r}{GM}}=2\pi\sqrt{\frac{r^3}{GM}}$$

For a satellite orbiting close to the earth's surface ($r \simeq R_e$), the time period is minimum and is given by

$$T_{\min}=2\pi\sqrt{\frac{R_e^3}{GM}}=2\pi\sqrt{\frac{R_e}{g}}$$

For earth R_e = 6400 km,

g = 9.8 m/s^2

T$_{\min}$ = 84.6 min.= 1.4 h

Thus, for any satellite orbiting around the earth, its time period must be more than $2\pi\sqrt{\frac{R}{g}}$ or 84.6 minutes.

3. Potential Energy (*U*), Kinetic Energy (*K*) and Total Energy (*E*) of satellite

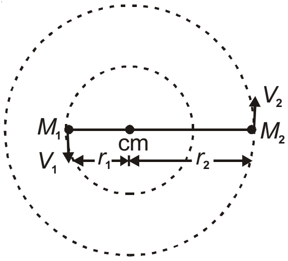
$$U = -\frac{GMm}{r}$$

$$K = \frac{GMm}{2r}$$

$$E = -\frac{GMm}{2r} \quad [K = -E \;\&\; U = 2E]$$

BINARY STAR SYSTEM

Two stars of mass M_1 and M_2 form a stable system when they move in circular orbit about their centre of mass, under their mutual gravitational attraction.



(1) $F = \frac{GM_1M_2}{r^2}$, where r is distance between them (*i.e.,* $r = r_1 + r_2$)

(2) $M_1r_1 = M_2r_2$

(3) $$\frac{GM_1M_2}{r^2} = \frac{M_1V_1^2}{r_1}$$

(4) $$\frac{GM_1M_2}{r^2} = \frac{M_2V_2^2}{r_2^2}$$

(5) $$r_1 = \frac{M_2r}{M_1 + M_2},\; r_2 = \frac{M_1r}{M_1 + M_2}$$

$$\therefore \quad V_1 = M_2\sqrt{\frac{G}{(M_1 + M_2)r}},$$

$$V_2 = M_1\sqrt{\frac{G}{(M_1 + M_2)r}}$$

when $M_1 = M_2$

$$V_1 = V_2 = \sqrt{\frac{GM}{2r}}$$

$$r_1 = r_2 = \frac{r}{2}$$

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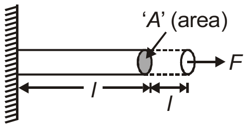
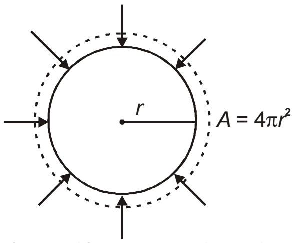
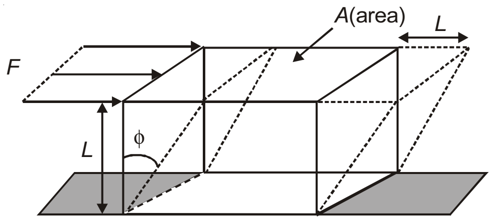
Chapter 7

Properties of Solids and Liquids

Strain	Stress
(1) Longitudinal strain = $\frac{l}{l}$	(1)  Normal Stress (Tensile) = F/A
(2) Volumetric strain = $-\frac{V}{V}$	(2)  Normal Stress (Compressive) = P (pressure)
(3) Shear strain = $\phi = \frac{L}{L}$	(3)  Tangential Stress or Shear Stress = $\frac{F}{A}$

MODULI OF ELASTICITY

(1) Young's modulus of elasticity $Y = \dfrac{\text{Tensile stress}}{\text{Longitudinal strain}} = \dfrac{Fl}{A\ l}$

(2) Bulk modulus of elasticity $\beta = \dfrac{\text{Normal or compressive stress}}{\text{Volumetric strain}} = -V\dfrac{P}{V}$ or, $\beta = -V\dfrac{dP}{dV}$

Compressibility = $\dfrac{1}{\beta}$

(3) Modulus of rigidity or shear modulus or $G = \dfrac{\text{Shear stress}}{\text{Shear strain}} = \dfrac{F}{A\phi} = \dfrac{FL}{A\ L}$

Applications :

1. For a wire $Y = \frac{Fl}{A\ \ l} \Rightarrow F = \frac{YA}{l}\ \ l$

   i.e. a wire behaves like a spring of spring constant (k)

   $$k = \frac{YA}{l} \qquad \left(i.e., k \propto \frac{1}{l}\right)$$

2. When this wire is stretched by applying an external force F, and $\ \ l$ is extension produced, then
   - (a) Work done by external force = $F\ \ l$
   - (b) Work done by restoring force = $\frac{1}{2}F\ \ l$
   - (c) Heat produced = $\frac{1}{2}F\ \ l$
   - (d) Elastic potential energy stored = $\frac{1}{2}F\ \ l$

     Energy density $U = \frac{1}{2}\frac{F\ \ l}{\text{volume}} = \frac{1}{2}\frac{F\ \ l}{Al}$

     $$= \frac{1}{2}\ \text{stress} \times \text{strain}$$

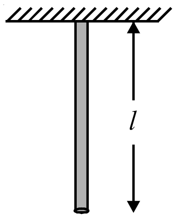
     $$= \frac{1}{2}\frac{(\text{stress})^2}{Y} = \frac{1}{2}Y(\text{strain})^2$$

3. A rod of mass m and length l hangs from a support

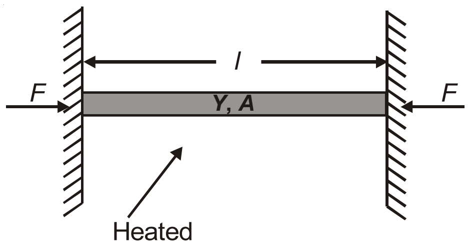
   Area of cross-section = A

   Extension produced due to its own weight,

   $$l = \frac{Mgl}{2AY} = \frac{gl^2}{2Y} \quad (\ \ = \text{density of wire})$$



Thermal Stress : Rod Fixed between Rigid Support



If $\ \theta$= Rise in temperature

Compressive strain = $\frac{\ \ l}{l} = \alpha\ \ \theta$

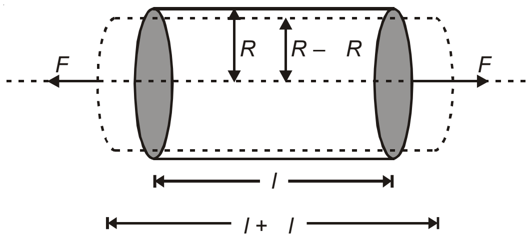
Compressive stress = Y × strain = $Y\alpha\ \ \theta$

$\Rightarrow \quad F = Y\alpha\ \ \theta \times A$

> ***Note :*** *If the rod is placed on horizontal frictionless surface, then stress developed on heating is zero.*

Poisson's Ratio

Consider a uniform bar being stretched by applying two forces at its ends.



Longitudinal strain = $\frac{l}{l}$

Lateral strain = $-\frac{R}{R}$

Poisson's ratio, $= -\frac{R/R}{l/l}$

(a) Theoretically – 1 0.5

(b) Practically 0 0.5

(c) When density of material is constant ⇒ = 0.5

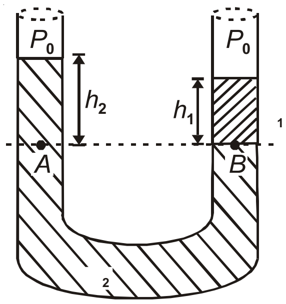
Equilibrium of Different Liquids in a U tube

1. $P_A = P_B$ (as A & B are at same level in same liquid)

 ⇒ $P_0 + h_1\ _1g = P_0 + h_2\ _2g$ (where P_0 is atmospheric pressure)

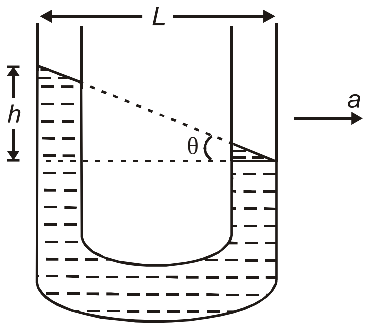
 ⇒ $h_1\ _1g = h_2\ _2g$

 ⇒ $_1h_1 = \ _2h_2$

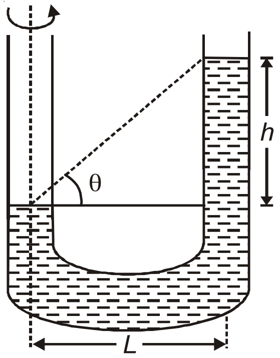


2. When the U tube accelerates horizontally, difference of levels of liquid satisfies the relation,

$$\tan\theta = \frac{a}{g} = \frac{h}{L}$$



3. When U-tube is rotated about on limb



Here $h = \frac{{}^2L^2}{2g}$ and $\tan\theta = \frac{h}{L} \Rightarrow \tan\theta = \frac{{}^2L}{2g}$.

Excess pressure

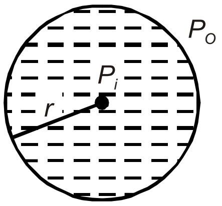
If P_o = Atmospheric pressure

P_i = Inside pressure

then $P_i - P_o$ = Excess pressure

Liquid drop

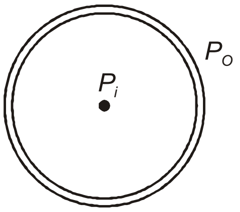
(1)



$$P_i = P_o + \frac{2T}{r}$$

Soap bubble

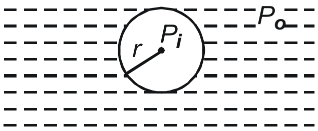
(2)



$$P_i - P_o = \frac{4T}{r}$$

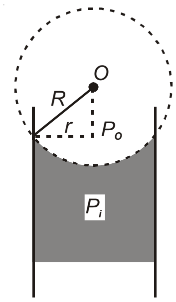
Air bubble

(3)



$$P_i = P_o + \frac{2T}{r}$$

(4) Capillary tube, concave meniscus

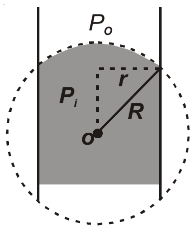


Capillary tube, Concave Meniscus

(a) $P_i = P_o - \dfrac{2T}{R}$

(b) $F_a \quad \dfrac{F_c}{\sqrt{2}}$

(5) Capillary tube, convex meniscus.



Convex Meniscus

(a) $P_i = P_o + \dfrac{2T}{R}$

(b) $F_a \quad \dfrac{F_c}{\sqrt{2}}$

Combining of Bubbles

1. If the soap bubble coalesce in vacuum, then $P_o = 0$

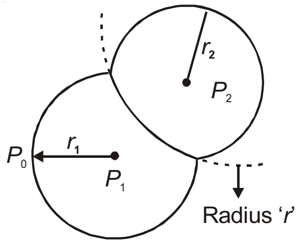
   $\Rightarrow \quad r^2 = r_1^2 + r_2^2$

2. If two soap bubbles come in contact to form a double bubble then

   r = radius of interface, $r_1 > r_2$

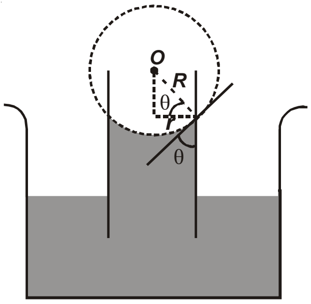
   $$\frac{1}{r} = \frac{1}{r_2} - \frac{1}{r_1}$$

   The interface will be convex towards larger bubble and concave towards smaller bubble because $P_2 > P_1 > P_0$.



CAPILLARY ACTION

Rise or fall of liquid in a tube of fine diameter.



Ascent formula

$$h = \frac{2T}{R\ \ g} = \frac{2T\cos\theta}{r\ \ g}$$

Energy of a Liquid

Various energies per unit mass :

1. Potential energy/mass = gh
2. Kinetic energy/mass = $\frac{1}{2}v^2$
3. Pressure energy/mass = $\frac{P}{\ }$

Energy Heads

Various energy heads per unit mass :

1. Gravitational head = h
2. Velocity head = $\frac{v^2}{2g}$
3. Pressure head = $\frac{P}{\ \ g}$

BERNOULLI’S THEOREM

It is based on conservation of energy.

For an ideal, non-viscous and incompressible liquid,

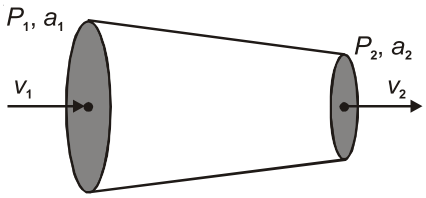
$$\frac{P_1}{\ } + \frac{v_1^2}{2} + gh_1 = \frac{P_2}{\ } + \frac{v_2^2}{2} + gh_2 = \text{constant}$$

Applications of Bernoulli’s Theorem

(1) To find rate of flow of liquid $Q = av$. Value of Q in various cases has been given below

Case - (a) :

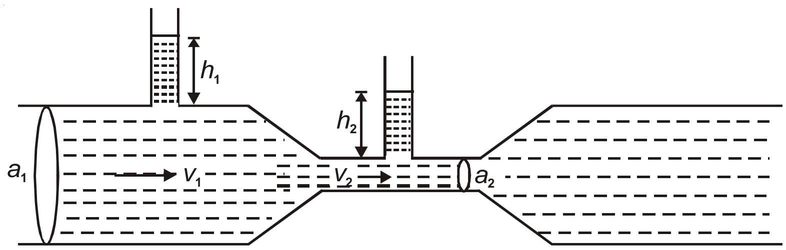
$$Q = a_1a_2\sqrt{\frac{2(P_1 - P_2)}{\ (a_1^2 - a_2^2)}}$$



Case - (b) :

Venturimeter

$$Q = a_1 a_2 \sqrt{\frac{2g(h_1 - h_2)}{a_1^2 - a_2^2}}$$

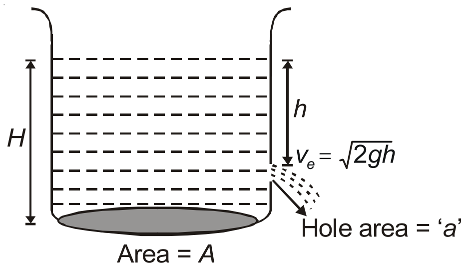


(2) Hole in a tank

(a) Speed of efflux $v_e = \sqrt{2gh}$ (If $a << A$). This is known as Toricelli's theorem.

If a is comparable to A then

$$v_e = \sqrt{2gh}\sqrt{\frac{A^2}{A^2 - a^2}}$$



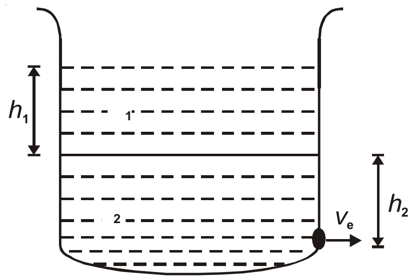
(b) Time taken by water level to fall from h_1 to h_2

$$t = \frac{A}{a}\sqrt{\frac{2}{g}}\ \sqrt{h_1} - \sqrt{h_2}$$

(c) Time taken to completely empty the container by a hole at bottom

$t \propto \sqrt{H}$ [Put $h_1 = H$, $h_2 = 0$]

(d) $v_e = \sqrt{2g\left(h_2 + \frac{{}_1h_1}{2}\right)}$ in the situation shown in figure

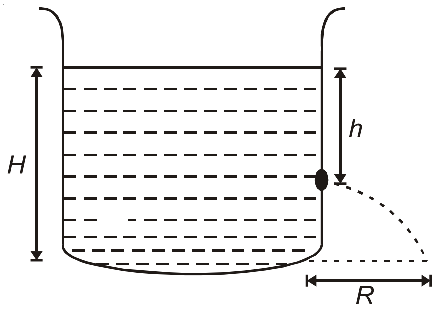


(e) Range of liquid

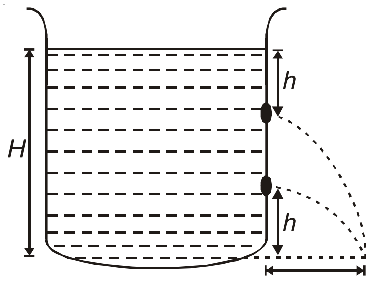
$$R = 2\sqrt{h(H-h)}$$

For a given value of total height (H)

$R_{\max} = H$ when $h = \frac{H}{2}$



(f)

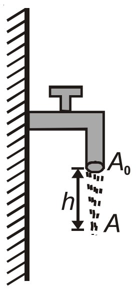


$R = 2\sqrt{h(H-h)}$ for both holes

(3) If A_0 = area of cross-section of mouth of tap

A = area of cross-section of water jet at a depth h

$A_0 v_0 = Av = Q$ [rate of flow]



By Bernoulli's theorem $\frac{v_0^2}{2} + gh = \frac{v_1^2}{2}$

[$\because$ pressure is atmospheric at both points]

Reynold's Number

$$N_R = \frac{vD}{\ } = \frac{\text{Inertial Force}}{\text{Viscous force}}$$

Value of N_R for various cases :

(1) $N_R < 2000$, flow is streamline

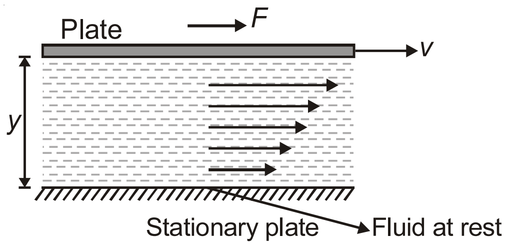
(2) $N_R > 3000$, flow is turbulent

(3) $2000 < N_R < 3000$, flow is unstable

(4) When $N_R = 2000$, flow is critical

$$\frac{vD}{\ } = 2000 \Rightarrow v_c = 2000\frac{\ }{D} \text{ (Critical velocity)}$$

Viscosity and Viscous Force



Viscous force is given in this case by,

$$F = - \ A\frac{dv}{dy}$$

Units of **:** SI 1 Pa.s = 10 poise = 1 decapoise

C.G.S 1 dyne/cm^2-s = 1 poise

Poiseuille's Equation

Volume flow rate across a tube with pressure difference between its ends is,

$$Q = \frac{dV}{dt} = \frac{\pi}{8}\frac{Pr^4}{l}$$

Series combination of two tubes

Two tubes of radius r_1, length l_1 and radius r_2, length l_2 are connected in series across a pressure difference of P. Length of a single tube that can replace the two tubes is found using,

$$\frac{l}{r^4} = \frac{l_1}{r_1^4} + \frac{l_2}{r_2^4}$$

STOKES LAW

When a small spherical body of radius r is moving with velocity v through a perfectly homogeneous medium having coefficient of viscosity , it experiences a retarding force given by

$\boldsymbol{F = 6\pi \ rv}$.

Important case :

(1) A body of radius r released from rest in a fluid

If = density of body

= density of liquid or fluid

Terminal velocity is given by,

$$v_T = \frac{2}{9}\frac{r^2 g}{\ }(\ - \ )$$

Thermal Expansion

When the temperature of a body increases, its all dimensions (length, area, volume) increase.

(1) Coefficient of linear expansion is given by

$$\alpha = \frac{L}{L \ \theta}$$

$L_\theta = L_0(1 + \alpha \ \theta)$, θ is the change in temperature in °C or K & L_0 is initial length

(2) Coefficient of superficial expansion is given by

$$\beta = \frac{A}{A\ \ \theta}$$

$$A_\theta = A_0\ (1 + \beta\ \ \theta)$$

(3) Coefficient of cubical expansion is given by

$$= \frac{V}{V\ \ \theta} \qquad \text{or} \qquad V_\theta = V_0\ (1 + \qquad \theta)$$

$$\frac{m}{_\theta} = \frac{m}{_0}(1 + \qquad \theta) \quad \Rightarrow \quad {}_\theta = {}_0(1 - \qquad)\theta$$

An Isotropic body expands equally in all directions and we can obtain the following relations

$$= 3\alpha,\ \beta = 2\alpha \ \text{ or } \ \boxed{\frac{\alpha}{1} = \frac{\beta}{2} = \frac{}{3}}, \quad = \frac{3}{2}\beta$$

CALORIMETRY

(1) Specific heat capacity or Gram specific heat (*c*) : If *Q* heat is given to a substance of mass '*m*', and rise in temperature is θ then

$$c = \frac{Q}{m\ \ \theta}\ \text{(cal/g°C)}$$

(2) Molar heat capacity (*C*) :

C = Molar mass (M) × specific heat capacity

$$\Rightarrow \quad C = Mc = \frac{M.Q}{m\ \ \theta} = \frac{Q}{n\ \ \theta}$$

$$\boxed{C = \frac{Q}{n\ \ \theta}} : n = \frac{m}{M} \text{ is number of moles}$$

(3) Heat capacity of an object is defined as product of mass and specific heat.

(4) In general if *Q* heat is given to a substance of mass '*m*' which increases its temperature by θthen

$\boxed{Q = mc\ \ \theta}$ *c* is specific heat capacity

or $\boxed{Q = nC\ \ \theta}$ *C* is molar heat capacity, *n* is number of moles of the substance.

Specific Latent heat

(1) Latent heat of fusion $L_f = \frac{Q}{m}$

(2) Latent heat of vaporisation $L_v = \frac{Q}{m}$

During phase change (liquid ⇄ solid or liquid ⇄ vapours) temperature remains constant, but internal energy changes.

Water

Specific heat C = 1 cal/gm/°C = 4.2 J/gm/°C = 4200 J/kg/°C

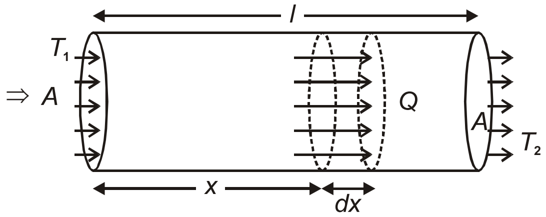
L_f = 80 cal/gm = 336 J/gm

L_v = 540 cal/gm = 2268 J/gm

For ice : C_{ice} = 0.5 cal/g °C = 2100 J/kg °C

Law of Conduction

Consider a rod of length l, cross sectional area A, with its ends maintained at temperatures T_1 & T_2 ($T_1 > T_2$). In steady state



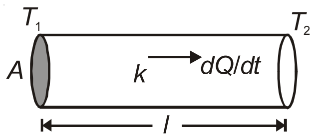
Rate of heat flow across any section is given by

$$H = \frac{dQ}{dt} = -kA\frac{dT}{dx}$$

Here k = Thermal conductivity and $\frac{dT}{dx}$ is known as temperature gradient i.e. rate of change of temperature with distance. k depends only on the nature of the material.

S.I. units of thermal conductivity is $\mathrm{Wm^{-1}K^{-1}}$

THERMAL RESISTANCE OF A ROD



In steady state $\frac{dQ}{dt} = kA\frac{(T_1 - T_2)}{l}$

Thermal resistance, $R = \frac{l}{kA}$ $\left[\text{as in current electricity } R = \frac{l}{A} = \frac{l}{A}\right]$

Weidmann – Franz law

$\frac{k}{T}$ = constant ⇒ a substance which is good conductor of heat (silver) is also a good conductor of electricity (mica & human body is exception to above law)

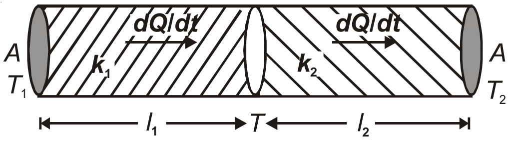
where is electrical conductivity

Composite Rod :

(1) Series

In steady state

$$R = \frac{l_1}{k_1 A} + \frac{l_2}{k_2 A} = \frac{l_1 + l_2}{kA}$$



Where k = effective thermal conductivity given by

For same area of cross section,

$$k = \frac{l_1 + l_2 + \dots\dots\dots + l_n}{\frac{l_1}{k_1} + \frac{l_2}{k_2} + \dots\dots\dots + \frac{l_n}{k_n}}$$

For two slabs of equal length

$$k = \frac{2k_1k_2}{k_1 + k_2}$$

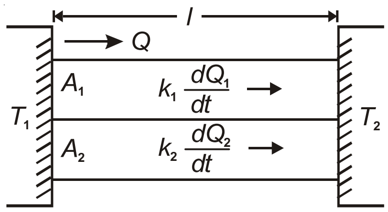
Temperature of junction

$$T = \frac{\frac{k_1}{l_1}T_1 + \frac{k_2}{l_2}T_2}{\frac{k_1}{l_1} + \frac{k_2}{l_2}}.$$

For same geometrical dimensions,

$$T = \frac{k_1T_1 + k_2T_2}{k_1 + k_2}$$

(2) In parallel



$$\frac{dQ}{dt} = \frac{dQ_1}{dt} + \frac{dQ_2}{dt}$$

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \quad \Rightarrow \frac{k(A_1 + A_2)}{l} = \frac{k_1A_1}{l} + \frac{k_2A_2}{l}$$

where k = effective coefficient of thermal conductivity given by

$$k = \frac{k_1A_1 + k_2A_2}{A_1 + A_2}$$

Example, for two slabs of equal area $k = \frac{k_1 + k_2}{2}$

STEFAN'S LAW

The radiant energy emitted by a perfectly black body per second per unit area (emissive power) is directly proportional to the fourth power of the absolute temperature of the body.

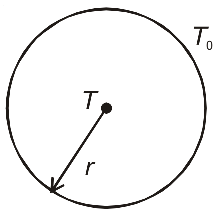
$R \propto T^4 \qquad\qquad R = \quad T^4$

$R = \frac{\text{Power}}{\text{Area}} \quad \Rightarrow \quad \text{P} = A \quad T^4 \qquad\qquad (\quad = 5.67 \times 10^{-8}\ \text{Wm}^{-2}\ \text{K}^{-4})$

For other bodies $P = \varepsilon A \quad T^4$, ε is emissivity of the body.

Rate of heat loss

For a sphere of radius r at a temperature T placed in a surrounding of temperature T_0, the rate of heat loss is $\frac{dQ}{dt} = 4\pi r^2 \varepsilon \quad (T^4 - T_0^4)$, where ε is emissivity.



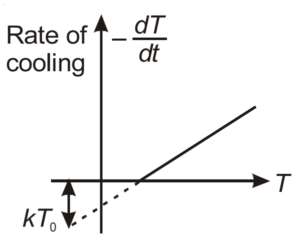
Rate of cooling

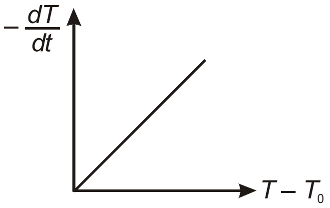
For a sphere of radius r, density and specific heat capacity s.

The rate of fall in temperature is given by $\frac{dT}{dt} = -\frac{3\varepsilon \quad (T^4 - T_0^4)}{sr}$

Newton's Law of Cooling

If the temperature T of a body is not much different from surrounding temperature T_0, then rate of cooling of a liquid is directly proportional to the difference in the temperature of liquid T and temperature of surroundings (T_0) *i.e.*





$$\text{Rate of cooling} = \left(-\frac{dT}{dt}\right) \propto (T - T_0)$$

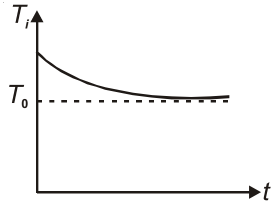
$$-\frac{dT}{dt} = \alpha(T - T_0)$$

Results

(1) $T_f = T_0 + (T_i - T_0)e^{-\alpha t}$, where T_i is initial temperature, T_f is temperature after time t.

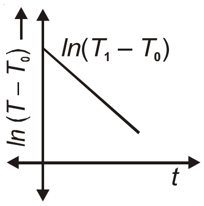
(2) Another form $\alpha t = \log\left|\frac{T_i - T_0}{T_f - T_0}\right|$

(3) $$\frac{-dT}{dt} = \frac{4\varepsilon A\ T_0^3}{mc}(T - T_0), \quad \left[\begin{array}{l} m = \text{mass of body} \\ c = \text{specific heat} \\ A = \text{surface area} \\ \varepsilon = \text{emissivity} \end{array}\right]$$



(4) Another approximate formula is

$$\frac{T_1 - T_2}{t} = \alpha\left(\frac{T_1 + T_2}{2} - T_0\right)$$



Above formula gives time 't' taken by the body to cool down from T_1 to T_2. T_0 is temperature of surrounding.

(5) If temperature of a body changes from θ_1 to θ_2 in time 't' and changes from θ_2 to θ_3 in next time then

$$\frac{\theta_2 - \theta_0}{\theta_1 - \theta_0} = \frac{\theta_3 - \theta_0}{\theta_2 - \theta_0} \quad (\theta_0 = \text{temperature of environment})$$

(6) If equal masses of two liquids having same surface area and finish, cool from same initial temperature to same final temperature with same surrounding, then

$$\frac{t_1}{t_2} = \frac{k_2}{k_1} = \frac{c_1}{c_2}; \qquad c_1 \ \&\ c_2 \text{ are specific heats}$$

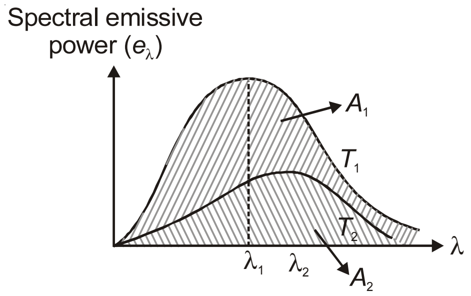
WIEN’S DISPLACEMENT LAW

This law states that the wavelength corresponding to maximum intensity for a black body is inversely proportional to the absolute temperature of the body

$$\lambda_m = \frac{b}{T}$$

where b is a constant known as Wien's constant

Results



$\boxed{\frac{\lambda_1}{\lambda_2} = \frac{T_2}{T_1}}$ $\boxed{\frac{A_1}{A_2} = \frac{T_1^4}{T_2^4}}$

(1) $\lambda_{max}\, T = b$

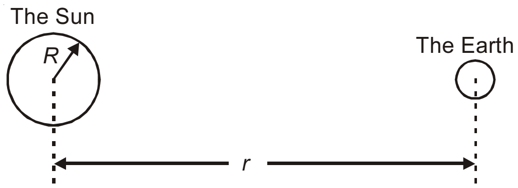
(2) $b = 2.898 \times 10^{-3}$ m-K

(3) Area under $e_\lambda - \lambda$ graph = T^4 (Total emissive power)

(4) If the temperature of the black body is made two fold, λ_{max} becomes half, while area becomes 16 times.

(5) Temperature of the Sun,

If T = temperature of sun, then total energy radiated by sun per second = $T^4\,(4\pi R^2)$



Intensity at distance r from the sun (*i.e.*, on earth)

$$I = \text{(Power radiated)(Area)} = \frac{T^4 R^2}{r^2} = S\text{, where S is called solar constant } [S = 1.4 \text{ kW / m}^2]$$

$$\text{So, } T = \left[\left(\frac{r^2}{R^2}\right)\frac{S}{}\right]^{1/4} = \left[\left(\frac{1.5\times10^8}{7\times10^5}\right)^2 \times \frac{1.4\times10^3}{5.67\times10^{-8}}\right]^{\frac{1}{4}} \quad 5800 \text{ K}$$

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Chapter 8

Kinetic Theory of Gases and Thermodynamics

Pressure Exerted by the Gas

The pressure of the gas is due to continuous bombardment of the gas molecules against the walls of the container. According to kinetic theory, the pressure exerted by an ideal gas is given by

$\boxed{P = \frac{1}{3}\frac{M}{V}\bar{v}^2}$ M = Mass of the enclosed gas

V = Volume of the container

$\bar{v}^2$ = Mean square speed of molecules

or $P = \frac{1}{3}\frac{M}{V} v_{\text{rms}}^2$ V_{rms} = Root mean square velocity

or $P = \frac{1}{3}\frac{Nm}{V}\bar{v}^2$ N = Number of molecules

$\boxed{P = \frac{}{3} v_{\text{rms}}^2}$ = density of gas

m = Mass of the molecule

$\bar{v}^2$ = Mean square speed of molecules

Speeds of gas molecules :

(i) Root mean square speed,

$$v_{rms} = \sqrt{\frac{3RT}{M_w}} = \sqrt{\frac{3P}{}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \ldots\ldots v_n^2}{n}}$$

Here, M_W is molecular weight in kg.

$$v_{rms} = \sqrt{\frac{3\,kT}{m}}$$, k = Boltzmann's constant, m = mass of one molecule in kg

(ii) Average speed $v_{avg} = \sqrt{\frac{8RT}{\pi M_w}} = \sqrt{\frac{8P}{\pi}} = \frac{v_1 + v_2 + v_3 + \ldots\ldots\ldots + v_n}{n}$

(iii) v_{mp} = Most probable speed is defined as the speed corresponding to which there are maximum number of molecules.

$$v_{mp} = \sqrt{\frac{2RT}{M_w}} = \sqrt{\frac{2P}{\ }} = \sqrt{\frac{2\,kT}{m}}$$

= Density of gas
M_w = Molecular weight
R = Gas constant
P = Pressure of gas
m = Mass of one molecule

Order of magnitude : $v_{\text{rms}} > v_{\text{avg}} > v_{\text{mp}}$

$$v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} \simeq \sqrt{3} : \sqrt{2.5} : \sqrt{2}$$

Relation between C_P & C_V :

(i) $C_P - C_V = R \qquad (C_P > C_V)$

(ii) $\frac{C_P}{C_V} =$

(iii) $C_v = \frac{f}{2}R$

Gas	Degrees of freedom (f)	$U = \frac{f}{2}nR\ T$	$C_V = \frac{U}{n\ T}$	C_P=C_V + R	$= \frac{C_P}{C_V}$
Monoatomic	3 (Translational)	$\frac{3}{2}nR\ T$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$
Diatomic	3(Trans) + 2(Rot)	$\frac{5}{2}nR\ T$	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5}$
Non-Linear Poly atomic	3 (Trans) + 3 (Rot)	$3nR\ T$	$3\,R$	$4\,R$	$\frac{4}{3}$

For a mixture of two gases A and B containing n_A and n_B number of moles.

(i) $f_{\text{mix}} = \frac{(n_A f_A + n_B f_B)}{n_A + n_B}$

(ii) $_{\text{mix}} = 1 + \frac{2}{f_{\text{mix}}}$

$$C_{v_{\text{mix}}} = \frac{f_{\text{mix}} R}{2}$$

$$C_{p_{\text{mix}}} = C_{v_{\text{mix}}} + R$$

Thermodynamic Process

(1) Melting process : (Change of state, solid to liquid)

$Q = \ U + W$

$mL_f = \ U + 0$ [W = 0 as volume remains nearly constant]

(2) Boiling process : (Change of state, liquid to vapours)

$mL_v = \ U + P[V_2 - V_1]$

V_2 = volume of vapours

V_1 = volume of liquid

When 1 g of water vapourises isobarically at atmospheric pressure. U = 2091 J, $P = 1.01 \times 10^5$ Pa, V_1 = 1 cm^3, V_2 = 1671 m^3.

(3) Isochoric process : Volume is constant

$dV = 0 \Rightarrow W = 0$ [dV = change in volume]

$Q = nC_V\ T = \ U$

$$\Rightarrow C_V = \frac{U}{n\ T}$$

(4) Isobaric process : Pressure is constant

P = constant, $dW = PdV$

$\Rightarrow W = P\ V = nR\ T$

$Q = nC_P\ T = \ U + W$

$nC_P\ T = nC_V\ T + nR\ T$

$\Rightarrow C_P = C_V + R$

$$\frac{U}{f} = \frac{W}{2} = \frac{Q}{f+2} \quad \text{or} \quad \frac{U}{1} = \frac{W}{-1} = \frac{Q}{\ }$$

Fraction of total heat converted to internal energy = $\frac{U}{Q} = \frac{1}{\ }$

Fraction of total heat converted to work is, $\frac{W}{Q} = \frac{-1}{\ }$

(5) Isothermal process : Temperature is constant

$PV = K \Rightarrow dT = 0 \Rightarrow dU = 0,\ C =$

as $PV = nRT$ (Constant)

So $P = \frac{nRT}{V}$

Work done in isothermal process

$$W = Q = nRT \log_e\left(\frac{V_2}{V_1}\right) = 2.303\ nRT \log_{10}\left(\frac{V_2}{V_1}\right) = 2.303\ nRT \log_{10}\left(\frac{P_1}{P_2}\right)$$

(6) Adiabatic process : Heat exchanged (Q) is zero

$PV\ \ = K$ [Equation of adiabatic process]

As $Q = 0$, $nC\ \ T = 0$ or $C = 0$

Also, $0 = nC_V\ \ T + W$ [by first law of thermodynamics]

Now, $\boxed{W = -\ \ U}$ i.e. $W = -\ nC_V\ \ T = -\frac{nR}{-1}(T_2 - T_1)$

(7) Polytropic Process

PV^x = Constant

$$W = \frac{nR\ T}{1-x}$$

Molar heat capacity $\boxed{C = C_V + \frac{R}{1-x}}$

(8) **Cyclic process :** System returns to its initial state (P, V & T)

For the overall process $T = 0 \Rightarrow U = 0$

$\Rightarrow Q = W$

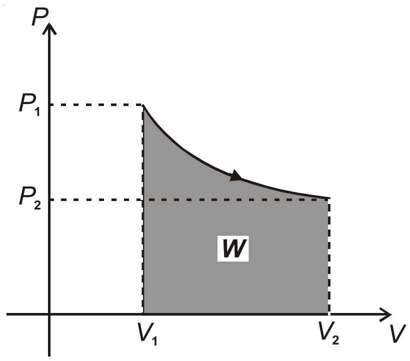
Indicator Diagram :

P-V graph of a process is called indicator diagram. Area under P-V graph represents the work done in a process.

Small work done, $dW = PdV$

Total work done, $W = \int dW = \int PdV$

= Area of curve (P – V) bounded with volume axis



CARNOT ENGINE

Heat supplied = Q_1

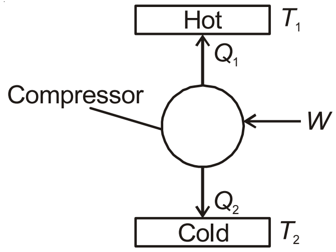
Heat rejected = Q_2 $\Rightarrow Q_1 - Q_2 = W$

% efficiency, $= \dfrac{W}{Q_{\text{supplied}}} \times 100 = \dfrac{Q_1 - Q_2}{Q_1} \times 100\%$

$$\text{Coefficient of performance, } \beta = \frac{\text{Heat Supplied}}{W_{\text{total}}} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2}$$

$$\beta = \frac{T_1}{T_1 - T_2} \text{ (for ideal pump)}$$

Refrigerator : In a refrigerator, W work is done on the working substance, Q_2 heat is absorbed from lower temperature T_2 and Q_1 heat is rejected to higher temperature T_1. ($T_1 > T_2$).



$$\text{Coefficient of performance } \beta = \frac{\text{Heat exchange from sink}}{W_{\text{total}}} = \frac{Q_2}{Q_1 - Q_2}$$

$$\Rightarrow \beta = \frac{T_2}{T_1 - T_2}$$

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Chapter 9

Oscillations and Waves

Periodic Function

If $f(t + T) = f(t)$ then function 'f' is periodic with period T.

Harmonic Motion

When oscillatory motion of a particle can be expressed in terms of sine or cosine functions, it is said to be a harmonic motion.

SIMPLE HARMONIC MOTION

When a motion can be expressed in terms of a single sine or cosine (sinusoidal) function, the motion is said to be Simple Harmonic Motion (SHM). For SHM, force ∝-(displacement)

$\Rightarrow \quad F \propto -x$

$\Rightarrow \quad F = -kx$ [Restoring Force]

$$\Rightarrow \quad a = -\frac{k}{m}x$$

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \qquad \text{or} \qquad \boxed{\frac{d^2x}{dt^2} + \quad {}^2x = 0}$$ (This equation represents the differential equation of S.H.M.)

Velocity and acceleration of a particle executing S.H.M.

If $\quad x = A \sin \ t$, A is amplitude (maximum displacement from mean position)

$$\Rightarrow \quad v = \frac{dx}{dt} = A \ \cos \ t$$

or, $\quad v = A \ \sin\left(\ t + \frac{\pi}{2}\right)$, maximum speed = A

i.e., **velocity leads displacement by** $\frac{\pi}{2}$. (This is always true in SHM)

(a) Dependence of velocity v with displacement from mean position (x)

$$v = \ \sqrt{A^2 - x^2}$$

(b) Acceleration

$$a = \frac{dv}{dt} = -A\omega^2 \sin \omega t\text{, maximum acceleration} = A\omega^2$$

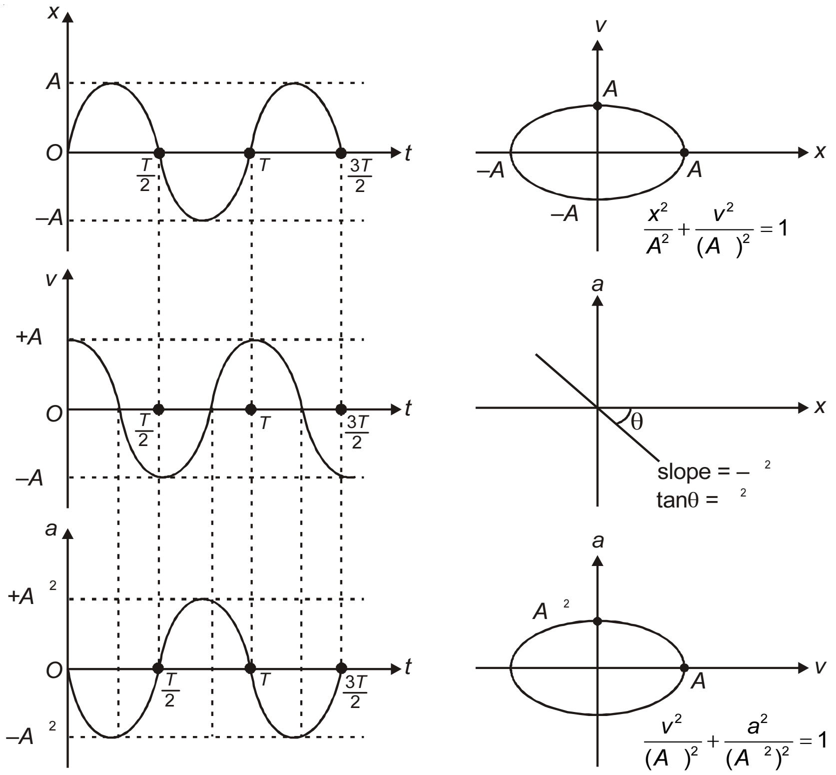
$$\Rightarrow \quad a = A\omega^2 \sin(\omega t + \pi)$$

i.e., **acceleration leads velocity by $\frac{\pi}{2}$. Acceleration and displacement are in opposite phase**.

(c) Dependence of acceleration with position, is $a = -\omega^2 x$

Graphical representation of variation of position, velocity and acceleration

(For $x = A \sin \omega t$)



Energy in SHM

Salient points regarding energy in SHM :

Oscillating quantity	Time period	Frequency
Displacement	T	f
KE	$T/2$	$2f$
PE	$T/2$	$2f$
|KE ~ PE|	$T/4$	$4f$
Total Energy		0

1. $\text{KE}_{\text{avg}} = \frac{1}{4}m\ {}^{2}A^{2}$.

2. $\text{KE}_{\text{max}} = \frac{1}{2}m\ {}^{2}A^{2}$ at mean position.

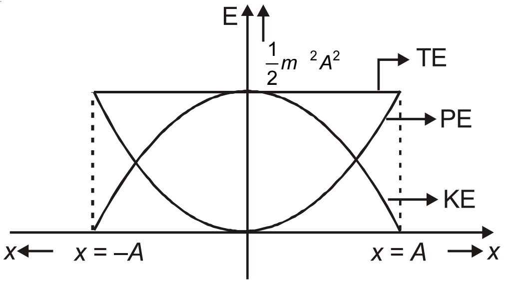
3. KE_{min} = zero at extreme position.

4. $\text{PE}_{\text{avg}} = \frac{1}{4}m\ {}^{2}A^{2}$.

5. $\text{PE}_{\text{max}} = \frac{1}{2}m\ {}^{2}A^{2}$ at extreme position.

6. Total energy, $E = \frac{1}{2}\ m\ {}^{2}A^{2}$ which is constant *i.e.* doesn't depend on x

7. Both kinetic and potential energy vary parabolically with x.



TE = Constant

TE = $(1/2)m\ {}^{2}A^{2}$

8. PE = KE at $x = \frac{A}{\sqrt{2}}$ and $t = \frac{T}{8}$. (Starting from mean position towards $+x$).

SIMPLE PENDULUM

Time period of oscillation of simple pendulum of length l for small angular amplitude is given by $T = 2\pi\sqrt{\frac{l}{g}}$

where g is the effective acceleration due to gravity, directed along the length of pendulum when it is at mean position.

SOME IMPORTANT POINTS :

On changing various factors, T changes as :

1. If length 'l' is changed, $\frac{T}{T} = \frac{1}{2}.\frac{l}{l}$

2. If gravity 'g' is changed, $\frac{T}{T} = -\frac{1}{2}.\frac{g}{g}$

Simple Pendulum in Lift

Effective $g' = |g + a|$, where $\vec{a}$ is pseudo acceleration. $T = 2\pi\sqrt{\frac{l}{g'}}$

Simple Pendulum of Length Comparable to the Radius of Earth

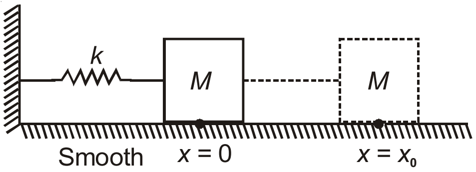
Time period of such a pendulum is given by,

$$T = 2\pi\sqrt{\frac{1}{g\left(\frac{1}{l}+\frac{1}{R_e}\right)}}$$

OSCILLATION OF SPRING

Horizontal Oscillations

The spring is pulled/pushed from $x = 0$ to $x = x_0$ and released.



The block executes SHM

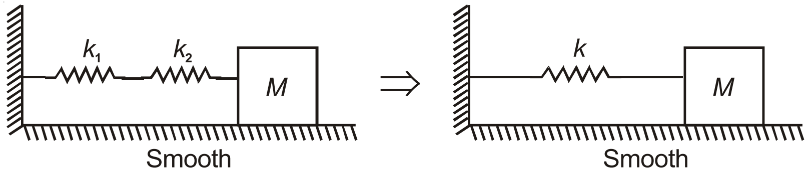
(1) Amplitude of oscillation = x_0

(2) Time period $T = 2\pi\sqrt{\frac{M}{k}}$

COMBINATIONS OF SPRINGS

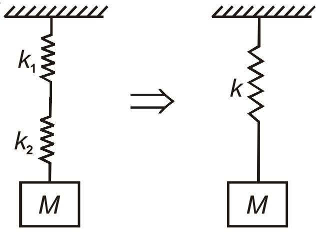
Series Combination :

(1)



$\frac{1}{k}=\frac{1}{k_1}+\frac{1}{k_2}$ or Effective spring constant, $k=\frac{k_1k_2}{k_1+k_2}$, $T=2\pi\sqrt{\frac{M}{k}}$

(2) $\frac{1}{k}=\frac{1}{k_1}+\frac{1}{k_2}$

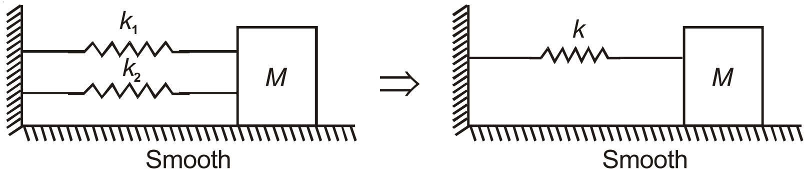


Effective spring constant, $k=\frac{k_1k_2}{k_1+k_2}$

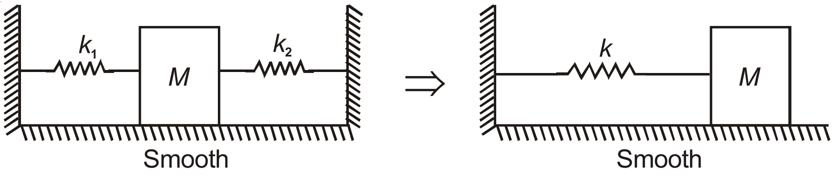
$T=2\pi\sqrt{\frac{M}{k}}$

Parallel Combination

(1) Effective spring constant, $k = k_1 + k_2$, $T = 2\pi\sqrt{\frac{M}{k}}$

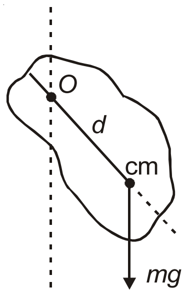


(2) Effective spring constant, $k = k_1 + k_2$ $T = 2\pi\sqrt{\frac{M}{k}}$



Physical Pendulum

Figure shows an extended body (called physical pendulum) pivoted about point *O*, which is at a distance *d* from its centre of mass.



Time period of oscillation, $T = 2\pi\sqrt{\frac{I}{mgd}}$ *I* = moment of inertia of the body about pivoted point.

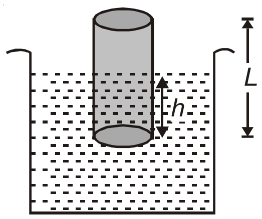
d is the distance of centre of mass from suspension point

Oscillation of a Floating Cylinder

If = density of cylinder material

= density of fluid (<)

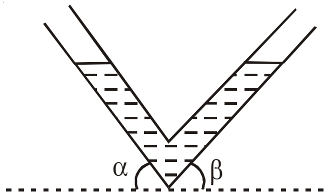
then, $T = 2\pi\sqrt{\frac{L}{g}} = 2\pi\sqrt{\frac{h}{g}}$



Oscillations of a Liquid in a Tube

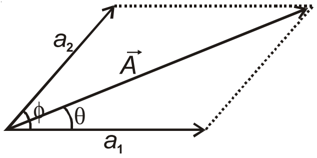
$$T = 2\pi\sqrt{\frac{l}{g(\sin\alpha + \sin\beta)}}$$

l = total length of liquid column



Superposition of SHMs

Consider two SHMs along the same line



If $y_1 = a_1 \sin \;\; t$

$y_2 = a_2 \sin (\;\; t + \phi)$

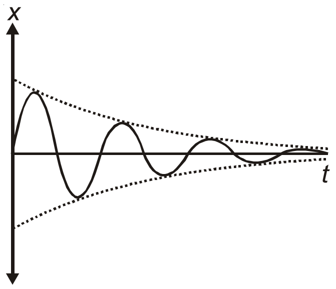
then, equation of resultant SHM is given by,

$y = y_1 + y_2 = A \sin (\;\; t + \theta)$

where, $A = \sqrt{a_1^2 + a_2^2 + 2a_1a_2\cos\phi}$ & $\theta = \tan^{-1}\left(\frac{a_2\sin\phi}{a_1 + a_2\cos\phi}\right)$

Damped Oscillations

If there is any dissipative force like viscous force in SHM, then the amplitude of the particle decreases with time such type of oscillations are known as damped oscillations.



(i) Differential equation for damped oscillation $m\frac{d^2x}{dt^2} + b\frac{dx}{dt} + kx = 0$,

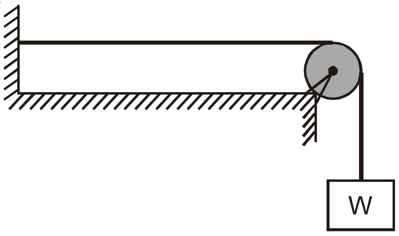
where b = Coefficient of damping.

(ii) Displacement-time equation, $x = A(t)\sin(\;\; t + \phi)$

(iii) Amplitude of damped oscillation, $A(t) = A_0 e^{-\frac{b}{2m}t}$, where A_0 = Initial amplitude.

(iv) Angular frequency of damped oscillation, $' = \sqrt{{}^{2}_{0} - \left(\frac{b}{2m}\right)^2}$, where $_0 = \sqrt{\frac{k}{m}}$ =natural frequency.

Speed of mechanical waves



(a) Transverse wave in a stretched string

T = tension in the string

μ = mass per unit length

D = diameter of string

= density

$$v = \sqrt{\frac{T}{\mu}} = \sqrt{\frac{\text{stress}}{\text{density}}} = \frac{2}{D}\sqrt{\frac{T}{\pi}}$$

$$\boxed{\mu = A \;\; = \frac{\pi D^2}{4}}$$

$$v = \sqrt{\frac{T}{A}}$$

(b) Transverse wave in a long bar is given by

$v = \sqrt{\frac{Y}{}}$ where Y = Young's modulus, = Density of material

(c) Longitudinal Waves

(i) In liquid $v = \sqrt{\frac{\beta}{}}$ β = bulk modulus of elasticity

= density

(ii) In gases $v = \sqrt{\frac{\beta}{}}$. β is bulk modulus of the gas. This value is not a fixed value for gases

Case - I : Suggested by Newton

Taking isothermal process $\beta = P \Rightarrow v = \sqrt{\frac{P}{}}$

Put P = 1 atm, = 1.23 kg/m^3 ⇒ v = 280 m/s (more than 15% error)

Case - II : Corrected by Laplace

For Adiabatic $\beta = \ P$

$\Rightarrow \quad v = \sqrt{\frac{P}{}}$. Taking = 1.4, we get, $\boxed{\text{For air } v = 20\sqrt{T}}$

v = 330 m/s

> ***Note :*** *Propagation of sound in air is adiabatic.*

Factors affecting speed of sound

$$v = \sqrt{\frac{RT}{M}} = \sqrt{\frac{P}{}}$$

(1) v is independent of pressure (If temperature is kept constant)

(2) $v \propto \frac{1}{\sqrt{}}$ or $v \propto \frac{1}{\sqrt{M}}$ (If temperature is kept constant)

(3) Velocity of a wave depends on medium, not on the frequency of source

(4) $v \propto \sqrt{T}$

(5) Velocity of sound in humid air is more because its density is less than that of dry air.

(6) Velocity of sound in humid hydrogen is less than in dry hydrogen due to similar reason.

SOUND WAVES

These are mechanical and longitudinal waves. They propagate in form of compressions and rarefactions. Particle displacements can be represented by wave function

$S = A \sin(\ t - kx)$

As particles oscillate, pressure variation takes place according to the wave function.

$P = \ P_0 \cos(\ t - kx)$, P_0 = maximum pressure variation

Characteristic of Sound

Loudness : Sensation of sound produced in human ear is due to amplitude. It depends upon intensity, density of medium, presence of surrounding bodies,

(a) Intensity of Wave

$$I = 2\pi^2 f^2 A^2 v$$

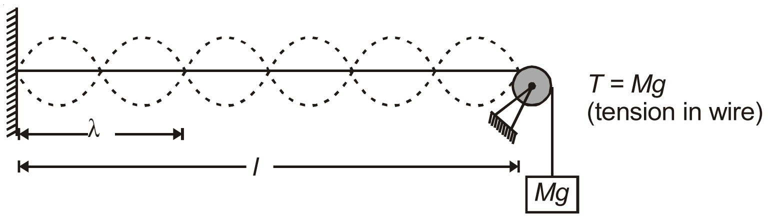
$$= \frac{1}{2}\ {}^2 A^2\ v$$

$I \propto f^2$ and $I \propto A^2$

(b) Intensity Level or (Sound Level) (β)

$$\beta = 10\log_{10}\left(\frac{I}{I_0}\right) \qquad \begin{bmatrix} I_0 = \text{minimum intensity of audible sound} = 10^{-12}\ \text{W/m}^2 \\ I = \text{measured intensity} \end{bmatrix}$$

Sonometer : In this case, transverse stationary waves are formed.



The wire vibrates in n loops, then

$$l = \frac{n\lambda}{2} \text{ or } \lambda = \frac{2l}{n}$$

Velocity $v = \sqrt{\frac{T}{\mu}}$ where 'μ' is mass per unit length of wire.

$$\Rightarrow \quad \nu_n = \frac{v}{\lambda} = \frac{nv}{2l} = \frac{n}{2l}\sqrt{\frac{T}{\mu}}$$

Pipe length l	**Fundamental Mode**	**Ist Overtone**	**$(n-1)^{\text{th}}$ overtone**	**Ratio of Successive frequency**
Open	$\nu = \frac{V}{2l}$ I^{st}Harmonic	$\nu = \frac{V}{l}$ 2^{nd}Harmonic	$\nu = n\frac{V}{2l}$ n^{th}Harmonic	1 : 2 : 3 : 4
Closed	$\nu = \frac{V}{4l}$ I^{st}Harmonic	$\nu = \frac{3V}{4l}$ 3^{rd} Harmonic	$\nu = (2n-1)\frac{V}{4l}$ $(2n-1)^{\text{th}}$ Harmonic	1 : 3 : 5 : 7

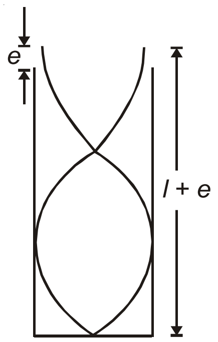
***Note :** Even numbered (i.e., 2nd, 4th .....) harmonics do not exist in close organ pipe.*

End correction (*e*) :

The antinodes are formed slightly out side the open end. The distance of antinode from open end of the pipe is called end correction. It depends on radius of pipe. ($e = 0.6\ r$)

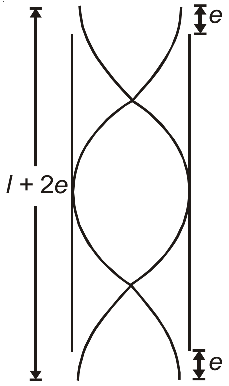
Thus, we have,

For closed organ pipe



$$\nu = \frac{(2n-1)V}{4(l+e)}$$

For open organ pipe



$$\nu = \frac{nV}{2(l+2e)}$$

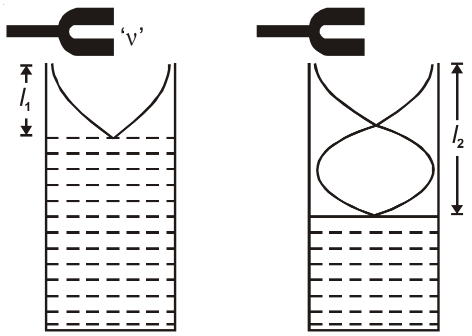
Resonance Tube:

If resonance is obtained first at length l_1.

then at length l_2, then

$\boldsymbol{\lambda = 2(l_2 - l_1)}$

⇒ distance between two successive lengths is $\frac{\lambda}{2}$



Interference

Consider two waves of same frequency and wavelength,

$y_1 = a_1 \sin(\ \ t - kx),\ I_1 = Ca_1^2$

$y_2 = a_2 \sin(\ \ t - kx + \phi),\ I_2 = Ca_2^2$

Equation of resultant wave is,

$$y = y_1 + y_2 = A\sin(\ \ t - kx + \theta), \text{ where } A = \sqrt{a_1^2 + a_2^2 + 2a_1a_2\cos\phi} \text{ and } \theta = \tan^{-1}\left(\frac{a_2\sin\phi}{a_1 + a_2\cos\phi}\right)$$

Resultant Intensity is given by

$$I = I_1 + I_2 + 2\sqrt{I_1I_2}\cos\phi$$

DOPPLER'S EFFECT

If a wave source and a observer are moving relative to each other, the frequency observed by the receiver (f) is different from the actual source frequency (f_0) given by,

$$f = f_0\left(\frac{v \quad v_0}{v \mp v_s}\right)$$

where v = speed of sound, v_0 = speed of observer, v_s = speed of source

* * *

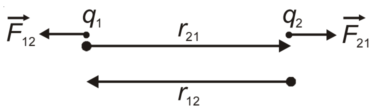
Chapter 10

Electrostatics

Coulomb's Law in Vector Form

$$\overrightarrow{F_{12}} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{|\overrightarrow{r_{12}}|^2}\hat{r}_{12} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{|\overrightarrow{r_{12}}|^3}\overrightarrow{r_{12}}$$

$$\overrightarrow{F_{21}} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{|\overrightarrow{r_{21}}|^2}\hat{r}_{21} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{|\overrightarrow{r_{21}}|^3}\overrightarrow{r_{21}}$$

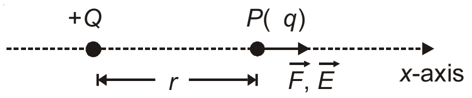


ELECTRIC FIELD

Electric Field due to a Point Charge (*Q*) :

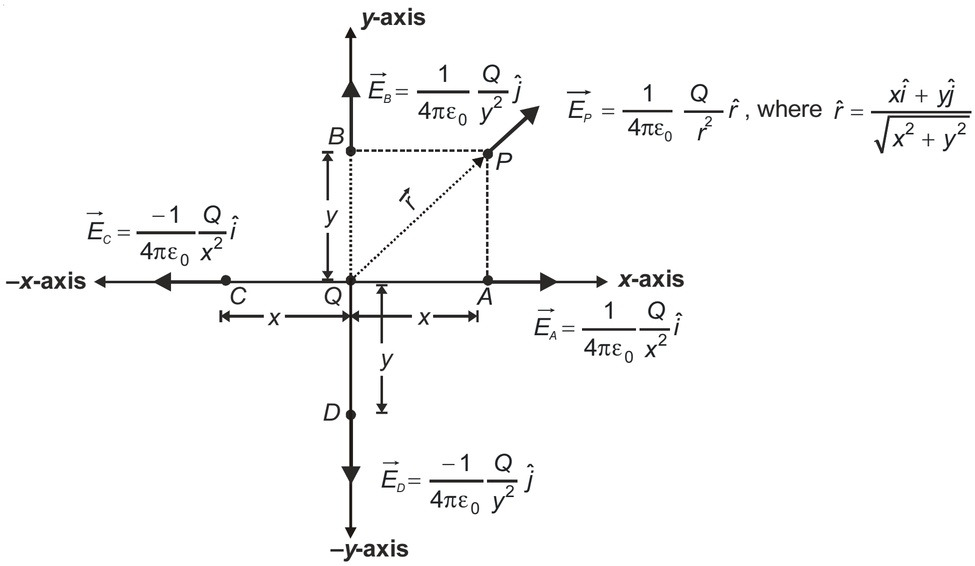
$$\vec{F} = \frac{1}{4\pi\varepsilon_0}\frac{Q\ q}{r^2}\hat{i}\ , \quad \vec{E} = \frac{\vec{F}}{q} = \frac{1}{4\pi\varepsilon_0}\frac{Q}{r^2}\hat{i}$$

$$\Rightarrow \quad \vec{E} = \frac{1}{4\pi\varepsilon_0}\frac{Q}{r^2}\hat{i}$$



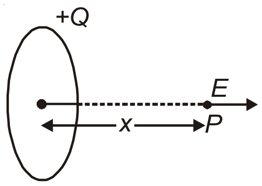
Application

(i) Direction of Electric Field at Various Points (when charge *Q* is placed at origin) :



(ii) **Electric field due to a uniformly charged ring on its axis.**

$$E_{\text{axis}} = \frac{Qx}{4\pi\varepsilon_0 (R^2 + x^2)^{3/2}}$$

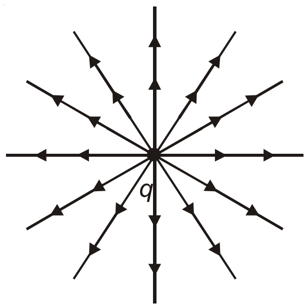


$E_{\text{centre}} = 0$

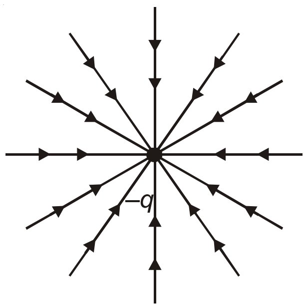
At $x = \frac{R}{\sqrt{2}}$, E is maximum.

Electric Lines of Force due to Various Configurations

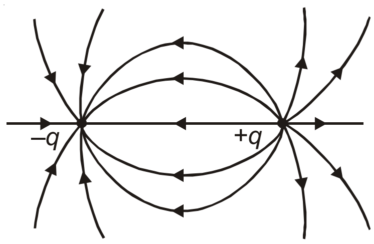
(1) Isolated point charge (+)



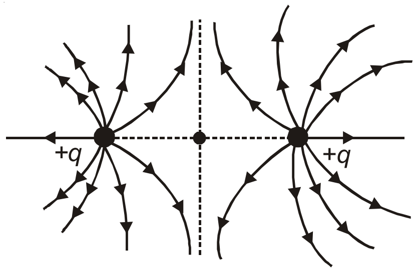
(2) Isolated point Charge (–)



(3) Electric dipole

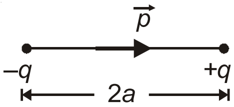


(4) Two identical charges



ELECTRIC DIPOLE

An arrangement of two equal and opposite charges separated by some distance.



Electric Field due to an Electric Dipole

1. For a point P on axial line

$$E_{\text{axial}} = \frac{2pr}{4\pi\varepsilon_0 (r^2 - a^2)^2}$$

For an ideal dipole ($r >> a \Rightarrow r^2 - a^2 \quad r^2$)

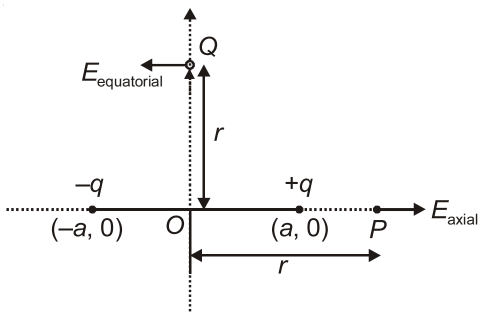
$$\Rightarrow E_{\text{axial}} = \frac{2p}{4\pi\varepsilon_0 r^3}$$

2. For a point Q on equatorial line

$$E_{\text{equatorial}} = \frac{-p}{4\pi\varepsilon_0(r^2 + a^2)^{3/2}}$$

For an ideal dipole ($r >> a \Rightarrow r^2 + a^2 \quad r^2$)

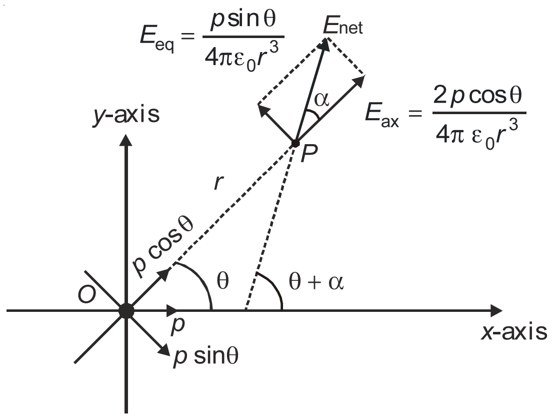
$$\Rightarrow E_{\text{equatorial}} = \frac{-p}{4\pi\varepsilon_0 r^3}$$

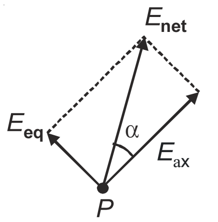


3. For an ideal dipole $E_{\text{equatorial}} = \frac{-E_{\text{axial}}}{2}$ (For same distance from centre of dipole).

4. Electric field at any point in the plane of a **short dipole**

P is a point in x-y plane at a distance r from the centre of dipole, such that OP makes an angle θ with dipole moment.





(a) $E_{\text{net}} = \frac{1}{4\pi\varepsilon_0}\frac{p}{r^3}\sqrt{1+3\cos^2\theta}$

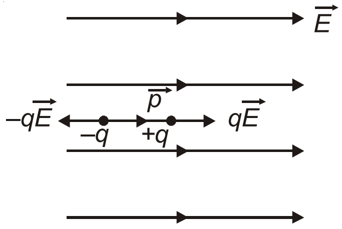
(b) $\tan\alpha = \frac{E_{eq}}{E_{ax}} = \frac{1}{2}\tan\theta \quad \Rightarrow \quad \tan\alpha = \frac{1}{2}\tan\theta$

(c) The net electric field makes an angle $\theta + \alpha$ with dipole moment.

(d) When $\vec{E} \quad \vec{p} \Rightarrow \theta + \alpha = 90° \quad \Rightarrow \quad \theta = \tan^{-1}\sqrt{2}$

Electric Dipole Placed in a Uniform Electric Field (Torque on dipole in uniform electric field)

Case-1 : $\vec{p} \parallel \vec{E}$

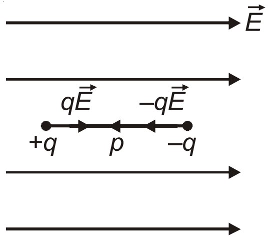


(a) Net force = $q\vec{E} - q\vec{E} = 0$

(b) Net torque = Zero

(c) Stable equilibrium

Case-2 : $\vec{p} \parallel (-\vec{E})$

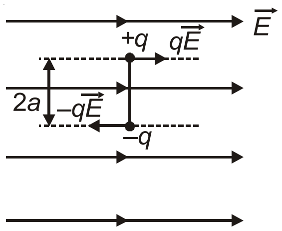


(a) Net force = $q\vec{E} - q\vec{E} = 0$

(b) Net torque = Zero

(c) Unstable equilibrium

Case-3 : $\vec{p}$ $\vec{E}$



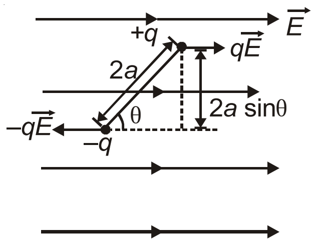
(a) Net force = Zero

(b) $= qE \times 2a = pE$ (This is the maximum value)

In vector form $\vec{\ } = \vec{p} \times \vec{E}$

(c) Translational equilibrium but not in rotational equilibrium.

Case-4 : $\vec{p}$ makes an angle θ with $\vec{E}$



(a) Net force = Zero

(b) $\vec{\ } = \vec{p} \times \vec{E}$ or $= p\ E \sin\theta$

(c) Translational equilibrium but not in rotational equilibrium.

Potential Energy of Dipole

1. The external work required to change the orientation from θ_1 to θ_2 is

   $W_{ext} = -\ pE[\cos\theta_2 - \cos\theta_1]$
2. Change in potential energy of dipole is

   $U_2 - U_1 = -pE[\cos\theta_2 - \cos\theta_1]$
3. Potential energy of dipole is

   $U = -pE\cos\theta = -\vec{p}.\vec{E}$

ELECTRIC FLUX

The number of field lines that pass through a surface is directly proportional to flux of electric field through that area.

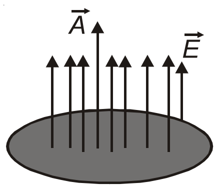
Mathematically, $\phi = \vec{E}\,.\,\vec{A}$ (If E is uniform and the surface in planar.)

In general, $\phi = \int \vec{E}\,.\,d\vec{A}$

Units : $\dfrac{\text{N m}^2}{\text{C}}$ or V-m

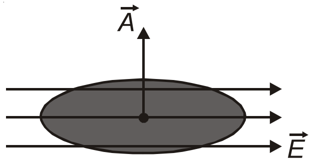
Important cases :

(1) $\vec{E} \,||\, \vec{A}$



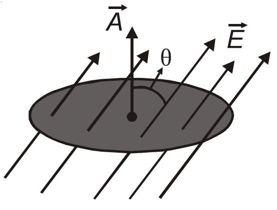
$\phi = EA$

(2) $\vec{E}$ $\vec{A}$



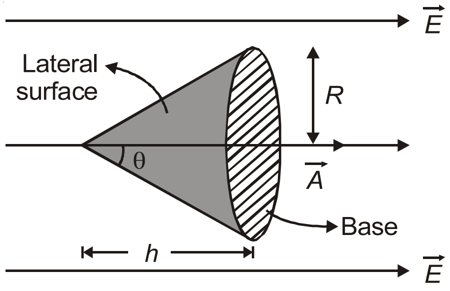
$\phi = 0$

(3) $\vec{E}$ and $\vec{A}$ make an angle θ



$\phi = EA\cos\theta$

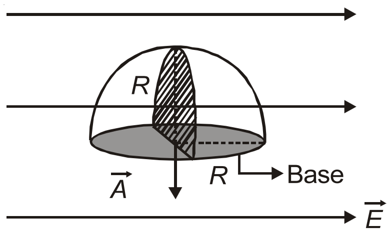
(4)



$\phi_{base} = \vec{E}\,.\,\vec{A} = E \times \pi R^2$

$\phi_{lateral} = -E \times \pi R^2$ (∵ Field lines enter through curved surface)

(5)



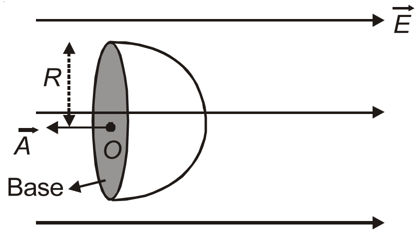
$\phi_{base} = 0$

$\phi_{curved} = 0$ (Total flux that enters = Total flux that leave)

$$\varphi_{entered} = -E \times \left(\frac{1}{2}\pi R^2\right)$$

$$\phi_{leaving} = E \times \frac{\pi R^2}{2}$$

(6)



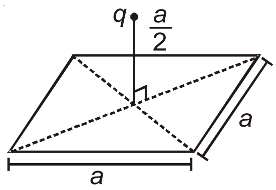
$\phi_{base} = -E \times \pi R^2$

$\phi_{curved} = +E \times \pi R^2$

Electric Flux

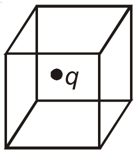
Some frequently asked cases :

1.



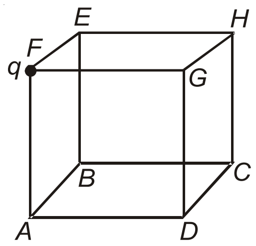
$\phi_{square} = \frac{q}{6\varepsilon_0}$

2.



$\phi_{cube} = \frac{q}{\varepsilon_0}$

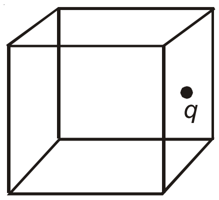
$\phi_{each\ face} = \frac{q}{6\varepsilon_0}$

3. 

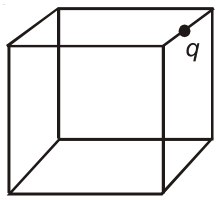
$\phi_{ABCD} = \frac{q}{24\varepsilon_0} = \phi_{DCHG} = \phi_{BCHE}$

$\phi_{ABEF} = 0 = \phi_{ADGP} = \phi_{FGHE}$

$\phi_{cube} = \frac{q}{8\varepsilon_0}$

4. 

$\phi_{cube} = \frac{q}{2\varepsilon_0}$

5. 

$\phi_{cube} = \frac{q}{4\varepsilon_0}$

Important results for fields due to different bodies (derived by Gauss Law)

1. Point charge $Q : \frac{kQ}{r^2}$.
2. Shell of charge with charge Q and radius $R : \frac{kQ}{r^2}$ (outside) and zero (inside).
3. Sphere of charge with charge Q and radius $R : \frac{kQr}{R^3}$ (inside) and $\frac{kQ}{r^2}$ (outside).
4. Infinite line of charge with linear charge density $\lambda : \frac{2k\lambda}{r}$ (perpendicular to line charge).
5. Infinite plane surface of charge with charge density $: \frac{}{2\varepsilon_0}$.
6. Infinite conducting sheet of charge with charge density $: \frac{}{\varepsilon_0}$.

Electric Potential Difference (V)

1. It is the work done against electric field in moving a unit positive charge from one point to other. That is $V_2 - V_1 = -\int_1^2 \vec{E}.d\vec{r}$.
2. V for two points at a distance r_1 and r_2 from a point charge Q

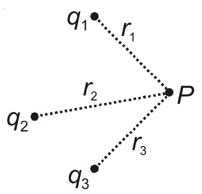
   $$V_2 - V_1 = \quad V = KQ\left[\frac{1}{r_2} - \frac{1}{r_1}\right]$$
3. Change in potential energy of a charge q when moved across V is $U = q. \; V$.
4. V between two points in electric field does not depend on path.

ELECTRIC POTENTIAL (V)

1. V at a point is work done against electric field in moving a unit positive test charge from infinity to that point is $V = -\int^r \vec{E}.dr$.

2. Potential due to a point charge Q at a distance r is $V = \frac{KQ}{r}$.

3. Potential due to a dipole at distance r at angle θ is $V = \frac{Kp\cos\theta}{r^2}$



4. Potential due to system of point charges is $V_P = \left(\frac{Kq_1}{r_1} + \frac{Kq_2}{r_2} + \frac{Kq_3}{r_3}\right)$.

   If V and E are functions of x, then $V_2 - V_1 = -\int_{x_1}^{x_2} E\,dx$.

   In general, $V_2 - V_1 = \int_{x_1}^{x_2} E_x dx - \int_{y_1}^{y_2} E_y dy - \int_{z_1}^{z_2} E_z dz$

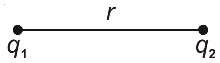
Relation between Electric Field and Potential

1. $E_x = -\frac{V}{x}$, $E_y = -\frac{V}{y}$, $E_z = -\frac{V}{z}$.

2. If V is a function of single variable r, $E = -\frac{dV}{dr}$.

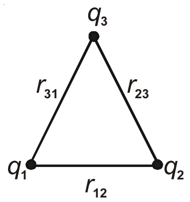
Electric Potential Energy

1. For a two point charge system



$$U = \frac{Kq_1q_2}{r}$$

2. For a three point charge system



$$U = \frac{1}{4\pi\varepsilon_0}\left[\frac{q_1q_2}{r_{12}} + \frac{q_2q_3}{r_{23}} + \frac{q_3q_1}{r_{31}}\right]$$

CAPACITOR

It is a device used to store electric energy in the form of electric field.

CAPACITANCE

Capacitance of a conductor is measure of ability of conductor to store electric charge and hence electric energy on it.

When charge is given to a conductor its potential increases. It is found that

$V \propto Q$

or, $Q \propto V$

$Q = CV$

where C is the capacitance and its unit is farad (F).

***C* depends on**

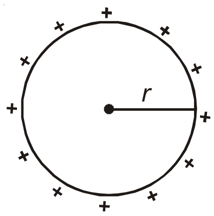
Shape and size of conductors and their relative placement w.r.t. each other.

Medium surrounding the conductor.

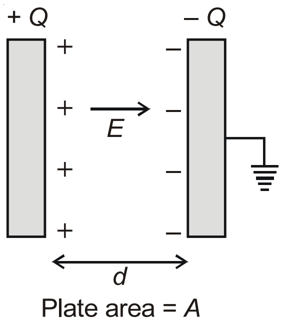
Capacitance of Isolated Spherical Conductor

$C = 4\pi\varepsilon_0 r$

Capacitance of Earth $C_e = 4\pi\varepsilon_0 R_e \ = 711\ \mu\text{F}$



Capacitance of a Parallel Plate Capacitor



1. Electric field in between plates

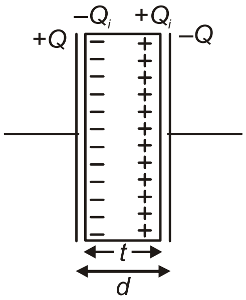
$$E = \frac{Q}{A\varepsilon_0} = \frac{}{\varepsilon_0}$$

2. Potential difference between the plates = $\frac{Qd}{A\varepsilon_0} = \frac{d}{\varepsilon_0}$

3. Capacitance = $\frac{\varepsilon_0 A}{d}$

4. Force of attraction between the plates = $\frac{Q}{2A\varepsilon_0} = \frac{{}^2A}{2\varepsilon_0} = \frac{QE}{2}$

Parallel Plate Capacitor with Dielectric Slab



(a) Induced charge $Q_i = -Q\left(1 - \frac{1}{K}\right)$, K is dielectric constant.

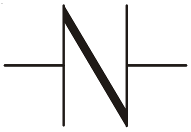
(b) Capacitance, $C = \frac{\varepsilon_0 A}{(d-t) + \frac{t}{K}}$.

(c) For conducting slab, $K =$

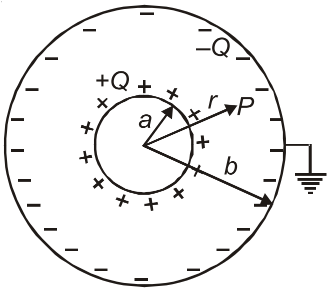
$\Rightarrow Q_i = -Q$ and $C = \frac{\varepsilon_0 A}{d-t}$

(d) The capacitance of a parallel plate capacitor is C. If its plates are connected by an inclined conducting rod, the new capacitance is infinity.

$\boxed{C = }$



Spherical Capacitor



1. Potential difference between plates

$$V = KQ\left[\frac{b-a}{ba}\right]$$

2. Electric field at any point P between plates

$$E = \frac{KQ}{r^2}$$

3. Potential at any point P between plates

$$V = \frac{KQ}{r} - \frac{KQ}{b}$$

4. Capacitance $C = \dfrac{4\pi\varepsilon_0 ab}{b-a}$

5. If the inner surface is grounded, capacitance $C = \dfrac{4\pi\varepsilon_0 b^2}{b-a}$

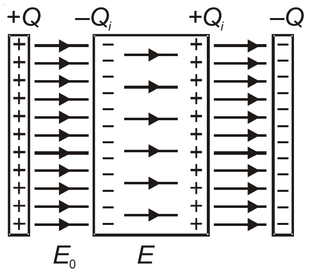
Cylindrical Capacitance of a Long Capacitor

Potential difference between plates

$$V = \frac{2KQ}{l} ln\left(\frac{b}{a}\right)$$

Dielectric Polarisation

When a dielectre slab is placed between the plates of capacitor its polarisation take place. Thus a charge $-Q_i$, appear on its left face and $+Q_i$ appears on its right face.

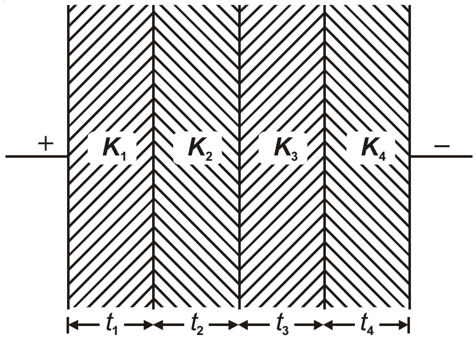


$$Q_i = Q\left(1-\frac{1}{k}\right)$$

$$E_0 = \frac{Q}{A\varepsilon_0};\ E = \frac{Q}{A\varepsilon_0 k} = \frac{E_0}{k}$$

Effective Capacitance in Some Important Cases

1. $C = \dfrac{\varepsilon_0 A}{\dfrac{t_1}{K_1}+\dfrac{t_2}{K_2}+\dfrac{t_3}{K_3}+\dfrac{t_4}{K_4}}$

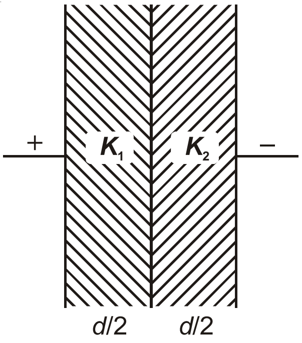


For two dielectrics,

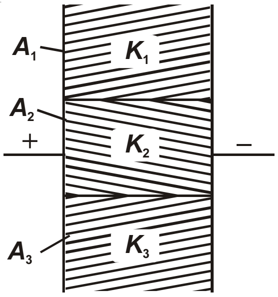
If $t_1 = t_2 = \frac{d}{2}$

$$C = \frac{\varepsilon_0 A}{\frac{d}{2K_1} + \frac{d}{2K_2}} = \frac{2\varepsilon_0 A}{d\left(\frac{1}{K_1} + \frac{1}{K_2}\right)}$$

$$\Rightarrow \quad C = \left(\frac{2K_1K_2}{K_1 + K_2}\right)\frac{\varepsilon_0 A}{d} \quad K_{eq} = \frac{2K_1K_2}{K_1 + K_2}$$



2. $C = \frac{\varepsilon_0[K_1A_1 + K_2A_2 + K_3A_3]}{d}$

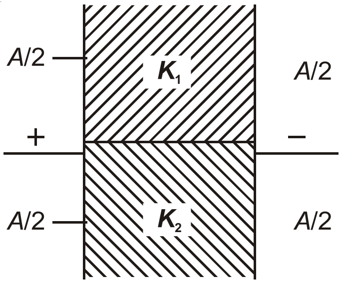


For two dielectrics,

If $A_1 = A_2 = \frac{A}{2}$

$$\Rightarrow C = \frac{\varepsilon_0\left(K_1\frac{A}{2} + K_2\frac{A}{2}\right)}{d}$$

$$\Rightarrow C = \left(\frac{K_1 + K_2}{2}\right)\frac{\varepsilon_0 A}{d} \quad K_{eq} = \frac{K_1 + K_2}{2}$$



COMBINATION OF CAPACITORS

1. **Capacitors in Series** (three capacitors)

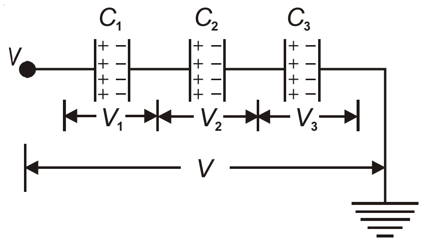
$V_1 = \frac{Q}{C_1}$, $V_2 = \frac{Q}{C_2}$ and $V_3 = \frac{Q}{C_3}$

$V = V_1 + V_2 + V_3$

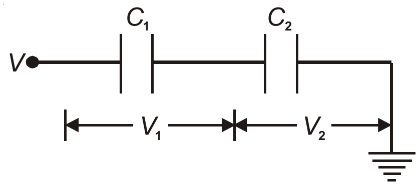
$$V = Q\left[\frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3}\right]$$

$$V = \frac{Q}{C_{eq}}$$

$$\frac{1}{C_{eq}} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3}$$



2. **Two Capacitors in Series**



$$V_1 = \frac{Q}{C_1} \qquad V_2 = \frac{Q}{C_2}$$

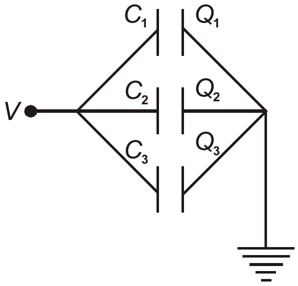
$$\frac{1}{C_{eq}} = \frac{1}{C_1} + \frac{1}{C_2}$$

$$C_{eq} = \frac{C_1C_2}{C_1 + C_2} \qquad Q = C_{eq}V$$

Potential Dividing Rule

$$V_1 = \frac{C_2}{C_1 + C_2}V \quad V_2 = \frac{C_1}{C_1 + C_2}V$$

3. **Capacitors in Parallel**



$Q_1 = C_1V$, $Q_2 = C_2V$, $Q_3 = C_3V$

$\Rightarrow Q = C_1V + C_2V + C_3V$

$\Rightarrow Q = (C_1 + C_2 + C_3)V$ and $Q = C_{eq}V$

$C_{eq} = C_1 + C_2 + C_3$

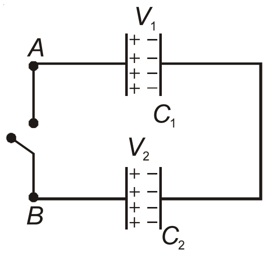
Energy Stored in a Capacitor

Energy stored in a capacitor of capacitance C, charge Q and potential difference V across it is given by

$$U = \frac{1}{2}CV^2 = \frac{Q^2}{2C} = \frac{1}{2}QV$$

Sharing of Charge

Case-1 : Two capacitors charged to potentials V_1 and V_2 are connected end to end as shown

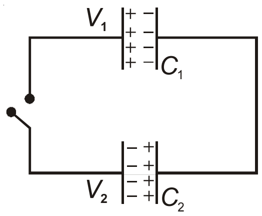


(a) Final common potential $V = \frac{C_1V_1 + C_2V_2}{C_1 + C_2}$

(b) Charge flown through key $= \frac{C_1C_2}{C_1 + C_2}(V_1 - V_2)$ in the direction A to B.

(c) Loss of energy $= \frac{C_1C_2}{2(C_1 + C_2)}(V_1 - V_2)^2$

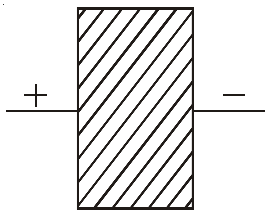
Case-2 : If positive terminal is connected to negative terminal



(a) Final common potential $V = \frac{C_1V_1 - C_2V_2}{C_1 + C_2}$

(b) Loss of energy $= \frac{C_1C_2}{2(C_1 + C_2)}(V_1 + V_2)^2$

Inserting a Dielectric Slab



1 When battery is disconnected (isolated) (charge is constant)

Q_0 = initial charge

C_0 = initial capacitance

V_0 = initial potential

E_0 = initial energy

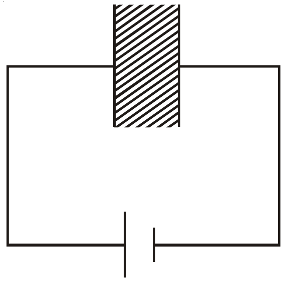
(a) New capacitance = KC_0

(b) New potential difference = $\frac{Q_0}{KC_0} = \frac{V_0}{K}$

(c) New energy stored = $\frac{1}{2}(KC_0)\left(\frac{V_0}{K}\right)^2 = \frac{E_0}{K}$

(d) Note that charge on each plate remains same.

2. When battery is connected (voltage is constant)



(a) $C = KC_0$

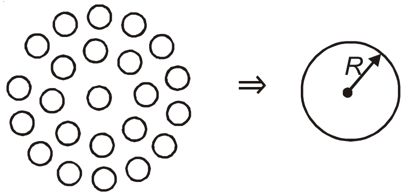
(b) $V = V_0$

(c) $Q = KQ_0$

(d) $E = \frac{1}{2}(KC_0)(V_0)^2 = KE_0$

Combining Charged Drops

When n droplets of radius r_0 having equal charge Q_0 combined to form a bigger drop of radius R.



(a) $n\frac{4}{3}\pi r_0^3 = \frac{4}{3}\pi R^3$

$\Rightarrow R = n^{1/3} r_0$

(b) $C = n^{1/3} C_0$

(c) Total charge = nQ_0

(d) $V = \frac{nQ_0}{C} = \frac{nQ_0}{n^{1/3}C_0} = n^{2/3}V_0$

(e) Total energy = $\frac{1}{2}\frac{Q^2}{C} = \frac{(nQ_0)^2}{2n^{1/3}C_0} = n^{5/3}U_0$

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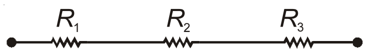
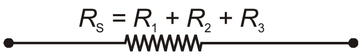
Chapter 11

Current Electricity

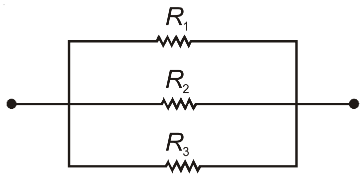
GROUPING OF RESISTORS (SERIES AND PARALLEL COMBINATION)

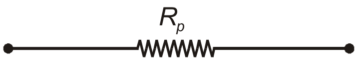
1. **Series Grouping**





2. **Parallel Grouping**

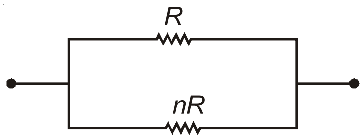


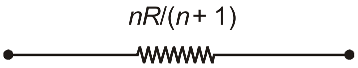


$$\frac{1}{R_p} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}$$

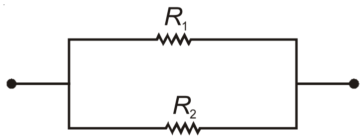
Illustrations :

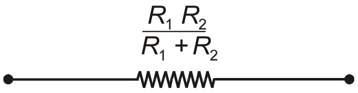
1.





2.





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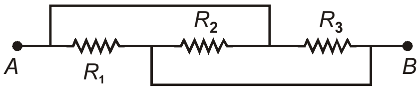
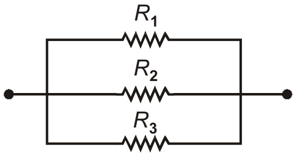
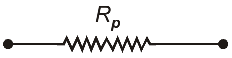






$$\frac{1}{R_p} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}$$

Cell Terminology

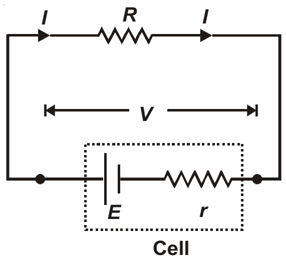
1. **EMF (*E*)**

   The potential difference across the terminals of a cell when no current is being drawn from it.

2. **Internal Resistance (*r*)**

   The opposition to flow of current inside the cell.

3. **Terminal Potential Difference**



It is the potential difference across the terminals of a cell when current is supplied by it.

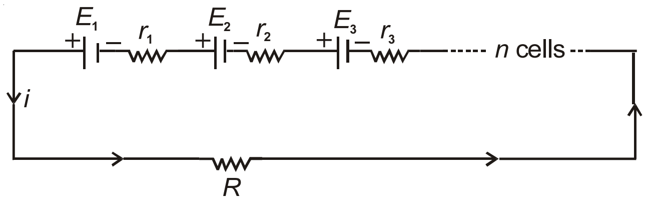
$E = IR + Ir, \quad V = IR$

$E - V = Ir \qquad \text{.... (i)}$

$$r = \left(\frac{E-V}{V}\right)R$$

Grouping of Cells (Series and Parallel Combination)

1. **Series Grouping :**



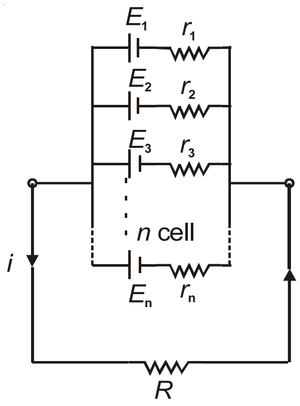
(a) $E_{\text{equivalent}} = E_1 + E_2 + E_3 + \ldots\ldots E_n$

(b) $r_{\text{equivalent}} = r_1 + r_2 + r_3 + \ldots\ldots r_n$

(c) Current $i = \dfrac{\sum E_i}{\sum r_i + R}$

> ***Note :*** *If polarity of m cells are made reverse in the series combination of n identical cells then equivalent emf $E_{equivalent} = (n - 2m)E$ and internal resistance $r_{equivalent} = nr$*

2. **Parallel Grouping :**



(a) $E_{\text{equivalent}} = \dfrac{\dfrac{E_1}{r_1} + \dfrac{E_2}{r_2} + \dfrac{E_3}{r_3} + \ldots\ldots}{\dfrac{1}{r_1} + \dfrac{1}{r_2} + \dfrac{1}{r_3} + \ldots\ldots..}$

(b) $r_{\text{equivalent}} = \dfrac{1}{\dfrac{1}{r_1} + \dfrac{1}{r_2} + \dfrac{1}{r_3} + \ldots\ldots}$

(c) If all cells have equal emf. E and internal resistance r then

$E_{\text{equivalent}} = E$

$r_{\text{equivalent}} = \dfrac{r}{n}$

$\Rightarrow$ Current $i = \dfrac{E}{\dfrac{r}{n} + R}$

3. **Mixed Grouping of Cell :**

   Let n cells be connected in series in one row and m rows of cells in parallel. If cells are identical each of emf E.

   Total number of cells = mn

   Total emf = nE

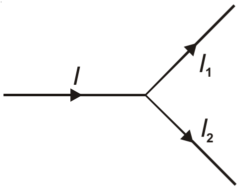
   Let i to be current through external load R.

$$i = \frac{mnE}{mR + nr}$$

   i will be maximum if $mR = nr$

KIRCHHOFF'S LAWS

1. **Junction Rule :** It is based on conservation of charge.



$I = I_1 + I_2$

2. **Loop Rule :** It is based on conservation of energy.

   (a) For any closed loop, total rise in potential + total fall in potential = 0.

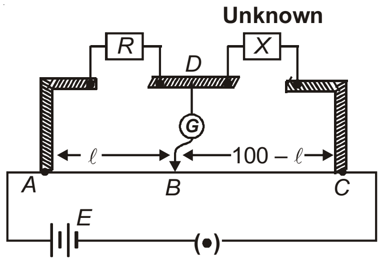
   (b) For any open part from a point A to point B, if V_A is potential at A and V_B is potential at B, then as we move from A to B.

   V_A + total rise in potential + total fall in potential = V_B.

***Note :** By convention rise in potential is taken as positive and fall in potential is taken as negative.*

METER BRIDGE

It is based on Wheatstone bridge principle. It is used to find an unknown resistance.



When there is no deflection in galvanometer then bridge is called balanced and for balanced bridge $\frac{P}{Q} = \frac{R}{S}$,

$$\frac{R}{\ell} = \frac{X}{100 - \ell} \quad \Rightarrow \quad \text{Unknown } X = R\left(\frac{100 - \ell}{\ell}\right)$$

***Note :** Location of null point is independent of resistivity or area of cross-section of wire AB.*

INSTRUMENTS

1. Ammeter

(a) Shunt resistance is added in parallel to the galvanometer coil to make it into an ammeter.

Shunt resistance $S = \left(\frac{i_g}{i - i_g}\right)G$.

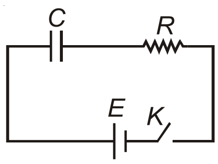
2. Voltmeter

(a) A large resistance is added in series to the galvanometer coil to make it into a voltmeter.

$$R = \frac{V}{i_g} - G$$

R-C CIRCUIT

1. Charging



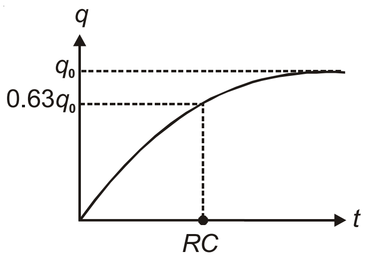
Key K is closed at $t = 0$.

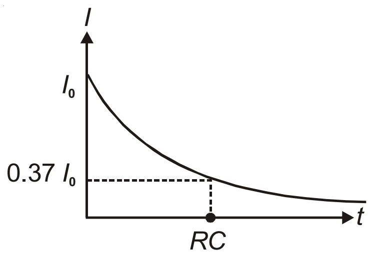
Current starts flowing and charge of capacitor starts increasing.

At any instant t, q is charge on capacitor. I is current in the circuit.

(a) $q = q_0\,[1 - e^{-t/RC}]$ where $q_0 = EC$ is maximum charge

(b) $I = \frac{E}{R}e^{-t/RC} = I_0 e^{\frac{-t}{RC}}$



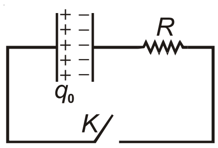


⇒ At $t = 0$, $I = E/R$

(c) RC = time constant. During charging, in $t = RC$, $q = 0.63q_0$.

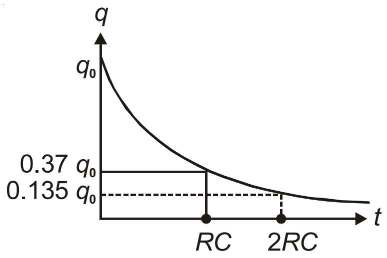
(d) In RC circuit an uncharged capacitor behaves like closed switch at $t = 0$ and open switch at $t =$.

2. Discharging RC Circuit



Key K is closed at $t = 0$

(a) $q = q_0 e^{-t/RC}$



(b) $I = -\dfrac{dq}{dt} \Rightarrow I = +I_0 e^{-t/RC}$ where, $I_0 = \dfrac{q_0}{RC}$

(c) RC = time constant ( )

at $t = 0$, $q = q_0$

at $t = RC$, $q = 0.37\ q_0$

at $t = 2RC$, $q = 0.135\ q_0$

(d) The charge and potential difference both decay exponentially like radioactive decay with half-life = 0.693 RC

HEATING EFFECT OF CURRENT

Joule's Law

When a constant current I is passed through a device having resistance R, then the amount of heat produced in time t

$H = I^2Rt$ in joules

$\Rightarrow$ $H = \dfrac{I^2Rt}{J}$ in calories, where J = mechanical equivalent of heat = 4.186 or 4.2 J/cal

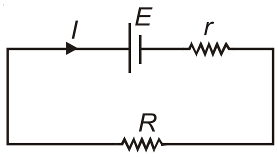
In general of a variable current I passes through a resistor, heat produced across R in time t is $H = \int_0^t I^2 R\,dt$

Maximum Power Transfer Theorem

In an electrical circuit, the maximum power can be drawn from the battery when external resistance is same as the internal resistance of the battery. Power drawn in the external resistor is

$$P = I^2R = \frac{E^2R}{(R+r)^2} \Rightarrow \frac{dP}{dR} = E^2\frac{(R+r)^2 - 2R(R+r)}{(R+r)^4} = 0$$

$\Rightarrow$ $R = r$



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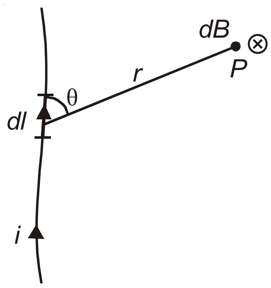
Chapter 12

Magnetic Effects of Current and Magnetism

MAGNETIC EFFECTS OF CURRENT

BIOT-SAVART LAW

Magnetic field due to current carrying element is given by



$$dB = \frac{\mu_0}{4\pi}\frac{idl\sin\theta}{r^2}$$

$$\overrightarrow{dB} = \frac{\mu_0}{4\pi}\frac{i(\vec{dl}\times\vec{r})}{r^3}$$

The direction of magnetic field due to small element dl is in the direction of $\vec{dl}\times\vec{r}$

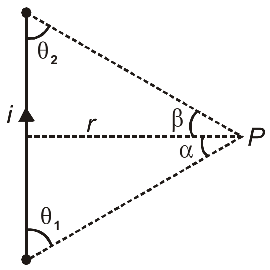
Units : 1. S.I. unit of magnetic field is tesla (T)

2. CGS unit of magnetic field is gauss.

3. 1 gauss = 10^{-4} tesla.

Magnetic Field Due to Straight Current Carrying Wire

Magnetic field at P



$$B = \frac{\mu_0 i}{4\pi r}(\cos\theta_1 + \cos\theta_2)$$

or $$B = \frac{\mu_0 i}{4\pi r}(\sin\alpha + \sin\beta)$$

1. For an infinite long wire

$\theta_1 = \theta_2 = 0$ or $\alpha = \beta = \frac{\pi}{2}$, $B = \frac{\mu_0 i}{2\pi r}$

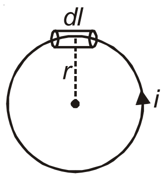
2. For semi-infinite long wire

$\theta_1 = 0°$, $\theta_2 = 90°$, or $\alpha = \frac{\pi}{2}, \beta = 0$, $B = \frac{\mu_0 i}{4\pi r}$

CIRCULAR LOOP

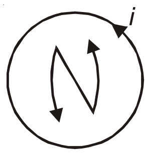
1. At the centre of a current loop

$$dB = \frac{\mu_0 i dl \sin 90}{4\pi r^2}$$

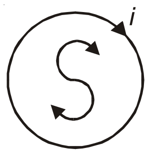


$$B = \frac{\mu_0 i}{4\pi r^2}\int dl = \frac{\mu_0 i}{4\pi r^2}\times 2\pi r$$

$$B = \frac{\mu_0 i}{2r} \text{ (Outward).}$$

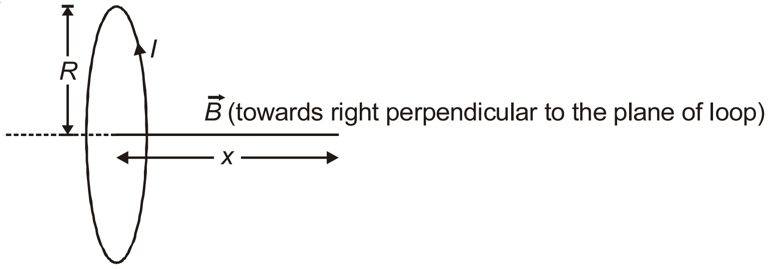


(Outward field perpendicular to the plane of loop)



(Inward field perpendicular to the plane of loop)

2. On the axis of a loop



$$B = \frac{\mu_0}{4\pi}\frac{2\times I\times \pi R^2}{(R^2+x^2)^{3/2}} = \frac{\mu_0}{4\pi}\frac{2M}{(R^2+x^2)^{3/2}}$$

For $x >> R$, $B = \frac{\mu_0}{4\pi}\frac{2M}{x^3}$ [Current carrying loop acts as an magnetic dipole]

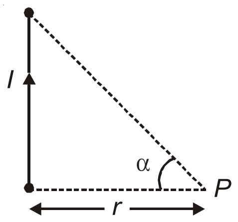
where $M = I \times \pi R^2$ is called magnetic dipole moment

$\vec{M} = I\vec{A}$

S.I. Unit : A-m^2

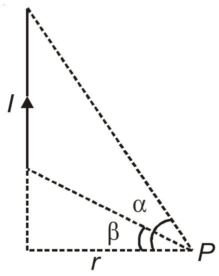
Various Cases of Magnetic Field (Straight Wire and Circular Loop)

1.



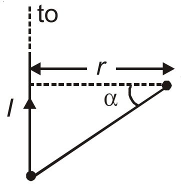
$B_P = \frac{\mu_0 I}{4\pi r}[\sin\alpha]$ ⊗

2.



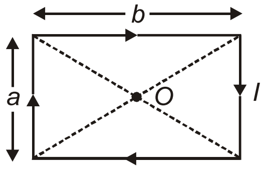
$B_P = \frac{\mu_0 I}{4\pi r}[\sin\alpha - \sin\beta]$ ⊗

3.



$$B_P = \frac{\mu_0 I}{4\pi r}[\sin\alpha + 1] \otimes$$

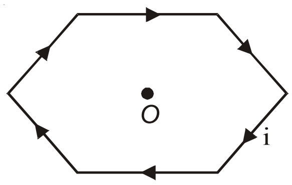
4.



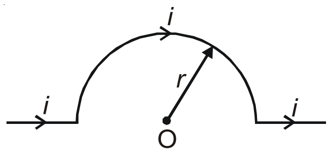
$$B_0 = \frac{8\mu_0 I}{4\pi}\frac{\sqrt{a^2+b^2}}{ab}$$

when $a = b$ $B_0 = \frac{8\sqrt{2}\mu_0 I}{4\pi a}$

5.



6.

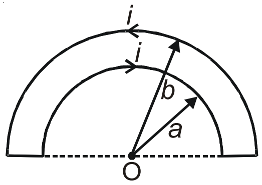


$$B_0 = \frac{\mu_0 i}{4r} \otimes$$

Magnetic field at O

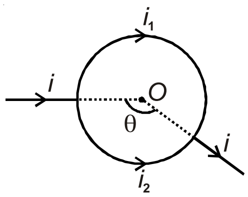
$B_0 = \frac{\sqrt{3}\mu_0 i}{\pi a}$ where 'a' is length of each side of regular hexagon

7.



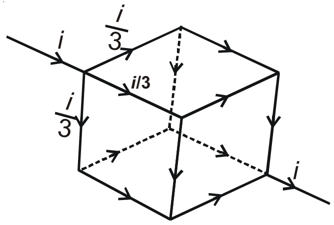
$$B_0 = \frac{\mu_0 i}{4}\left(\frac{1}{a} - \frac{1}{b}\right) \otimes$$

8.



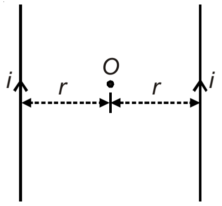
$B_0 = 0$ (for any value of θ)

9.



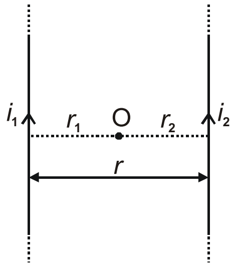
At the centre of cube, $B = 0$

10.



At O, $B = 0$

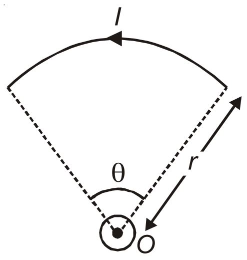
11.



At O, $B = 0$, such that

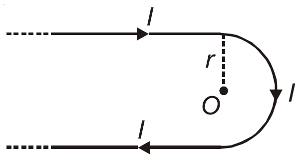
$$r_1 = \frac{i_1}{i_1 + i_2}r; r_2 = \frac{i_2 r}{i_1 + i_2}$$

12.

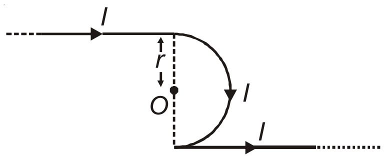


$$B_0 = \frac{\mu_0 I}{2r} \times \frac{\theta}{2\pi} \odot$$

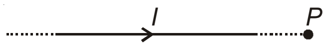
(θ is radian)

13. 

$$B_0 = \frac{\mu_0 I}{2\pi r} + \frac{\mu_0 I}{4r} \otimes$$

14. 

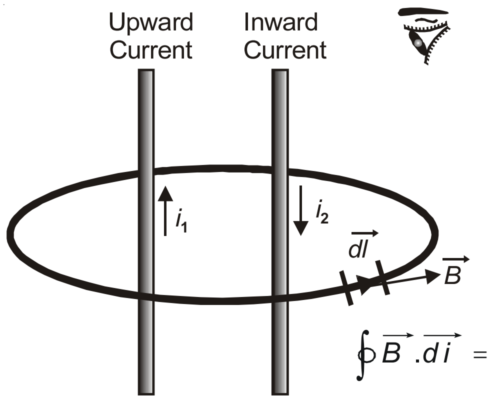
$$B_0 = \frac{\mu_0 I}{4r} \otimes$$

15. 

$B_P = 0$ (at point P)

AMPERE CIRCUITAL LAW

It states that the line integral of resultant magnetic field over a closed path is equal to μ_0 times the algebraic sum of the current threading the closed path in free space. Ampere's circuital law has the form



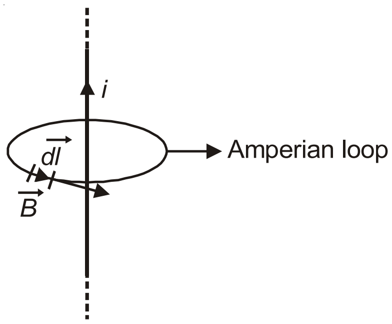
$$\oint \vec{B}.\vec{di} = \mu_0 (i_1 - i_2)$$

$$\oint \vec{B}.\vec{dl} = \mu_0 i_{enc}$$

Here $\oint \vec{B}.\vec{dl}$ implies the integration of scalar product $\vec{B}.\vec{dl}$ around a closed loop called an **Amperian loop**. The current i_{enc} is the net current encircled by the loop.

Applications of Ampere's Circuital Law

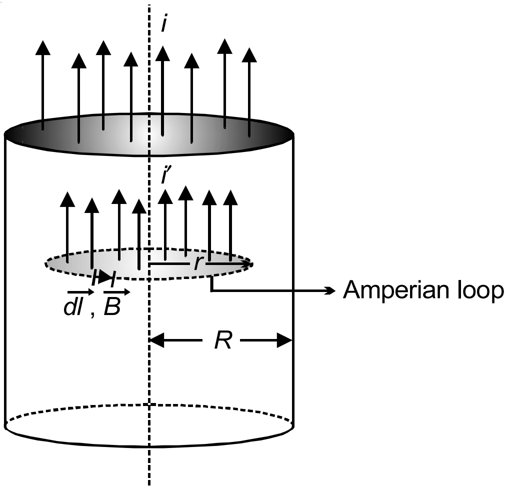
(1) Magnetic field due to a long thin current carrying wire

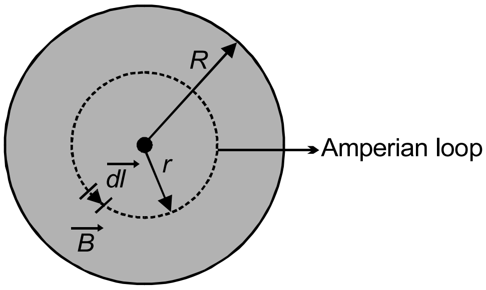


$$\oint \vec{B} \cdot \vec{dl} = \mu_0 I$$

$$B = \frac{\mu_0 I}{2\pi r}$$

(2) Magnetic field inside a long straight current carrying conductor



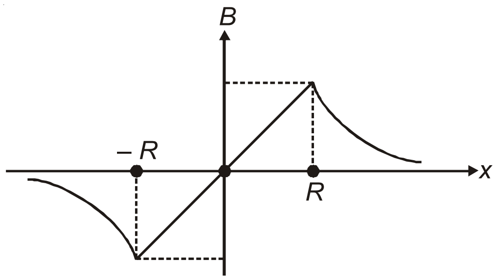


$$I' = \frac{I}{nR^2} \times \pi r^2$$

$$\oint \vec{B} \cdot d\vec{l} = \mu_0 \left(\frac{I}{nR^2} \pi r^2 \right)$$

$$B = \frac{\mu_0}{2\pi} \frac{r}{R^2} \qquad i.e.\ B_{in} \propto r$$

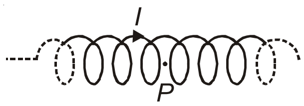
Graphical variation of magnetic field



(3) Inside a hollow tube of current, magnetic field is zero.

SOLENOID

A long solenoid having number of turns/length ‘*n*’ carries a current *I*.

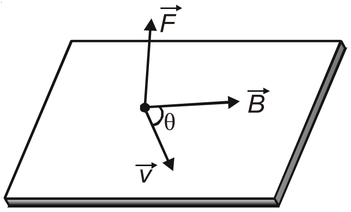


The magnetic field *B* is given by,

$B_P = \mu_0 nI$ (in between)

$B_{end} = \frac{\mu_0 nI}{2}$ (near one end)

Force on a Moving Charge in Magnetic Field



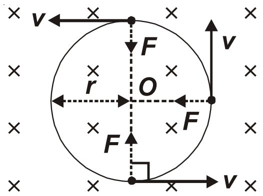
$\vec{F} = q(\vec{v} \times \vec{B})$

$F = qvB \sin\theta$

$\vec{F}$ is perpendicular to both $\vec{v}$ & $\vec{B}$ and is in the direction of $\vec{v} \times \vec{B}$ when $q > 0$ and opposite to $\vec{v} \times \vec{B}$ when $q < 0$.

MOTION OF CHARGED PARTICLE IN A UNIFORM MAGNETIC FIELD $\vec{B}$.

Case-1 : $\vec{v}$ $\vec{B}$

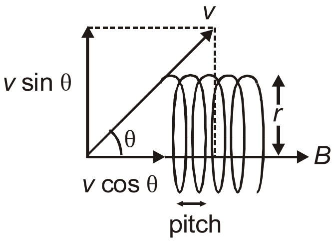


$F = qvB = \dfrac{mv^2}{r}$ $\quad \cancel{r} = \dfrac{mv}{qB} = \dfrac{p}{qB} = \dfrac{\sqrt{2km}}{qB}$ (k is kinetic energy). As $k = \dfrac{p^2}{2m}$.

Results

1. During revolution its speed is constant
2. During revolution its kinetic energy is constant
3. Work done by the magnetic force is zero
4. Velocity and momentum change continuously in direction, not in magnitude.
5. $T = \dfrac{2\pi r}{v} = \dfrac{2\pi m}{qB}$ (Independent of speed and radius)
6. Frequency $f = \dfrac{qB}{2\pi m}$ (Cyclotron frequency)

Case-2 : If $\vec{v}$ is not perpendicular to $\vec{B}$. Let θ be the angle between $\vec{v}$ and $\vec{B}$.



The particle moves in a helical path such that

$$r = \frac{mv\sin\theta}{qB}, T = \frac{2\pi m}{qB}, \text{ Pitch} = v\cos\theta \times T$$

Case-3 : If charged particle is moving parallel or anti-parallel to field $\overrightarrow{B}$ then force is zero and it moves in a straight line

Cyclotron

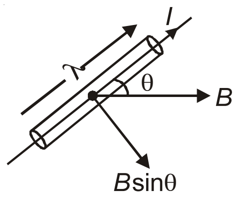
A cyclotron is a machine used to accelerate charge particle (like proton, deutron, α-particle). It uses both electric and magnetic field. Speed of particle is increased by electric field.

$$\text{Cyclotron frequency } = \frac{qB}{2\pi m}$$

$$K_{\max} = \frac{q^2B^2R_{\max}^2}{2m}$$

To accelerate electrons Betatron and Synchrotron are used. A synchrotron accounts for the variation in mass with speed. A Betatron uses the induced electric field produced by a time varying magnetic field to accelerate charged particles.

Force on a current carrying conductor in uniform field



I = Current through the conductor, ℓ = Length of the conductor

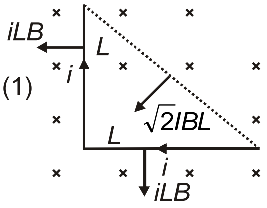
$$F = IB\ell\sin\theta$$

$$\vec{F} = I(\vec{\ell} \times \vec{B})$$

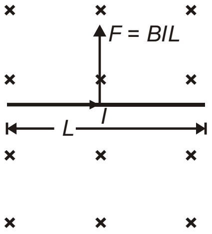
The direction of $\vec{\ell}$ is always in the direction of current.

Some Important Cases

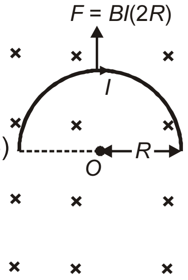
(1)



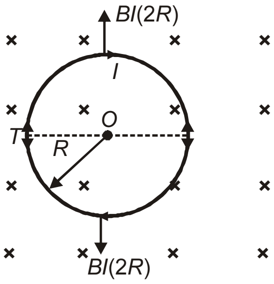
(2)



(3)



(4)

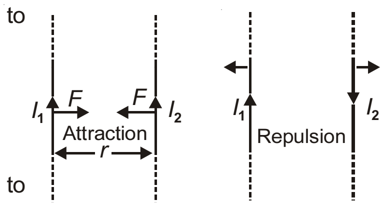


Net $F = 0$

$T = BIR$

(tension in the wire)

FORCE BETWEEN TWO CURRENT CARRYING WIRES



F (force/unit length) is given by $F = \dfrac{\mu_0 I_1 I_2}{2\pi r}$.

The force on a segment of length 'l' is $= \dfrac{\mu_0 I_1 I_2}{2\pi r} \times l$

Force on a small current carrying segment placed near long and perpendicular current carrying wire.

$$F_{PQ} = \frac{\mu_0 i_1 i_2}{2\pi} \log\left(1 + \frac{l}{d}\right)$$

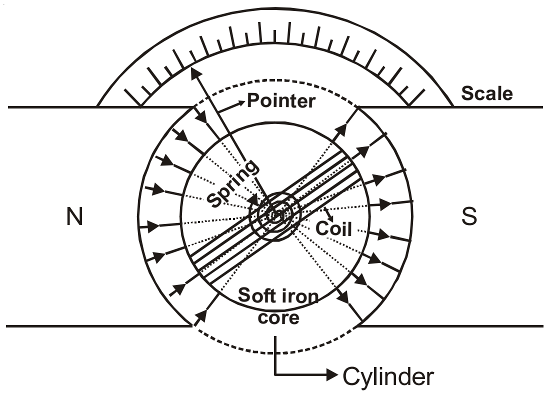
$_{PQ}$ 0

MOVING COIL GALVANOMETER

It is a device used to measure small current through the circuit.

Principle

When a current carrying coil is suitably placed in a magnetic field, torque acts on it. In moving coil galvanometer radial field is used which is obtained from magnet having concave shape poles. In this type of field plane of the coil is always parallel to the magnetic field so maximum torque acts on it.



$= NIAB$ [ϕ = 90° due to radial field] (ϕ – Angle between $\vec{M}$ and $\vec{B}$)

$= C\theta$ (θ = Angle of twist)

where θ is angle turned by the pointer and C is restoring torque/twist in the suspension wire.

$$I = \frac{C\theta}{NBA}$$

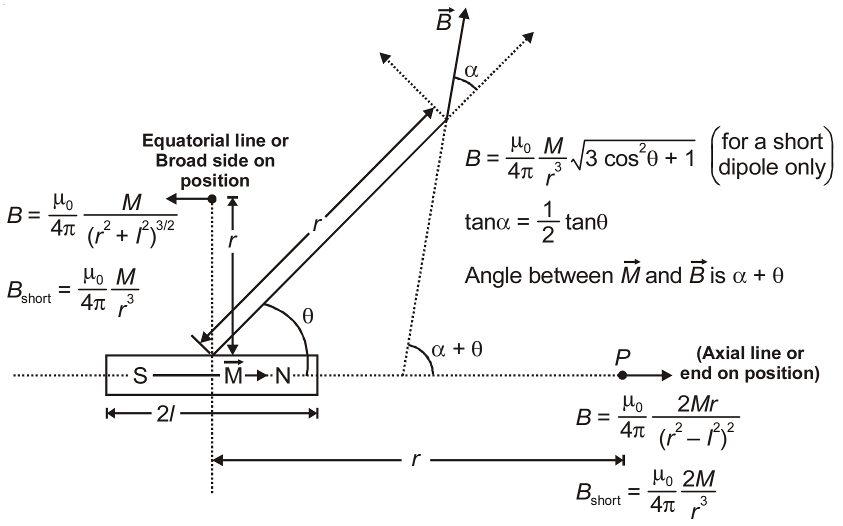
Current sensitivity = $\dfrac{\theta}{I} = \dfrac{NBA}{C}$

Voltage sensitivity = $\dfrac{\theta}{V} = \dfrac{\theta}{IR} = \dfrac{NBA}{CR}$

MAGNETISM

BAR MAGNET

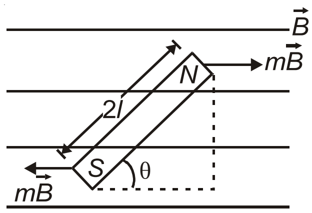
Magnetic field due to a Bar Magnet



1. $\vec{B}_{axial}$ is parallel to $\vec{M}$.
2. $\vec{B}_{equatorial}$ is antiparallel to $\vec{M}$.
3. $\vec{B}$ $\vec{M}$ when θ + α = 90° *i.e.*, θ = 90° – α

   as $\tan\alpha = \frac{1}{2}\tan\theta \Rightarrow \cot\theta = \frac{1}{2}\tan\theta$ or $\tan\theta = \sqrt{2}$.

TORQUE ON A BAR MAGNET IN MAGNETIC FIELD



$= mB \times 2l \sin\theta$

$= m \times 2l \times B \sin\theta$

$\Rightarrow \quad = MB \sin\theta$

Results :

1. $\vec{} = \vec{M} \times \vec{B}$, $_{max} = MB$ [when θ 90°],

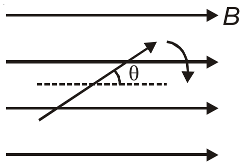
   $_{min} = 0$ [when θ = 0 or 180°]
2. Net force on dipole is zero.
3. $U = -\vec{M}.\vec{B}$ $U_{min} = -MB$ at θ = 0°

   $U_{max} = MB$ at θ = 180°
4. Work done by external agent in rotating bar magnet from angular position θ_1 to θ_2 is

   $W = MB [\cos\theta_1 - \cos\theta_2]$
5. A bar magnet kept in a non-uniform magnetic field experience a net force and may experience a torque.

Oscillations of a Bar Magnet in Magnetic Field

For small displacements from equilibrium position, bar magnet oscillates simple harmonically such that



Angular frequency $=\sqrt{\dfrac{MB}{I}}$;

Time period $T = 2\pi\sqrt{\dfrac{I}{MB}}$

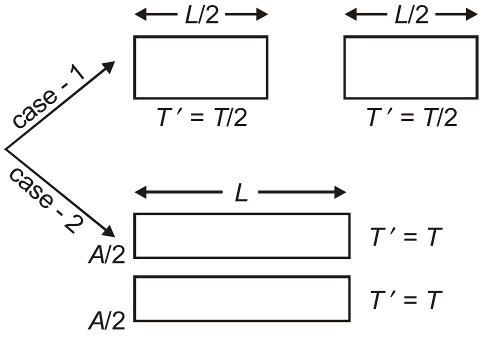
Some important cases related to time period are given below

A bar magnet of length L is,

Pole strength ∝ Area of cross-section of magnetic dipole ($m \propto A$)

$\vec{M} = m \times 2\vec{l}$

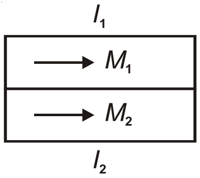
1. Cut into two halves



where $T = 2\pi\sqrt{\dfrac{I}{MB}}$

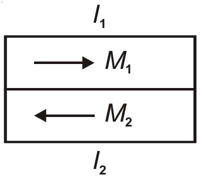
2. Two bar magnets having magnetic moments M_1, M_2 and moment of inertias I_1, I_2 are joined as shown.

(a) $T_1 = 2\pi\sqrt{\dfrac{I_1 + I_2}{(M_1 + M_2)B}}$



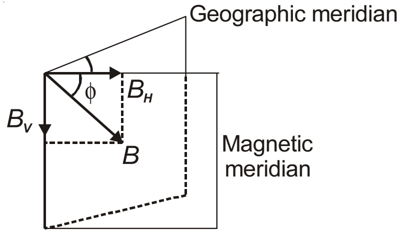
(b) $T_2 = 2\pi\sqrt{\dfrac{I_1 + I_2}{(M_1 - M_2)B}}$

$$\Rightarrow \frac{T_2^2 + T_1^2}{T_2^2 - T_1^2} = \frac{M_1}{M_2}$$



EARTH'S MAGNETIC FIELD

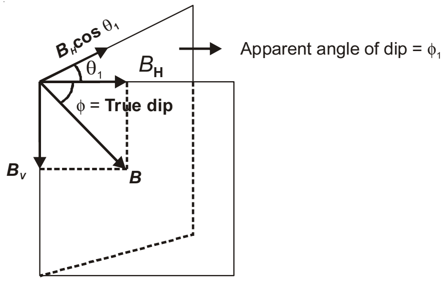
The basic components of earth's magnetic field at a place are shown



1. = Angle of declination
2. ϕ = Angle of dip/inclination
3. $B_H = B\cos\phi$
4. $B_V = B\sin\phi$
5. $B_H^2 + B_V^2 = B^2$

Note : *The needle of a vertical compass in magnetic meridian points toward B.*

6. $\tan\phi = \dfrac{B_V}{B_H}$
7. When the dip circle is not in magnetic meridian and dip circle is at an angle of θ_1 to magnetic meridian.



[ϕ = True dip angle, ϕ_1 and ϕ_2 = apparent dip angle in two arbitrary perpendicular)

$\tan\phi_1 = \dfrac{B_V}{B_H\cos\theta_1}$ (apparent dip) [Vertical component remains same]

$$\Rightarrow \quad \tan\phi_1 = \frac{\tan\phi}{\cos\theta_1}$$

8. $\cot^2\phi = \cot^2\phi_1 + \cot^2\phi_2$, plane

PARA, DIA AND FERROMAGNETIC SUBSTANCES

All the elements of the nature are studied under the action of magnetic field and classified into three parts according to following properties.

1. **Magnetic Intensity (Magnetising Force) :** $H = \dfrac{B_0}{\mu_0}$

   B_0 is magnetic field in vacuum

   SI unit = A/m

2. **Intensity of Magnetisation :** Magnetic moment developed/volume

   $I = \dfrac{M}{V}$ (Unit A/m)

$$\Rightarrow \quad I = \frac{\text{Pole strength}}{\text{area}} \qquad \begin{bmatrix} \because M = m\times l \\ \because V = A\times l \end{bmatrix}$$

3. **Magnetic Induction or Magnetic Flux Density (*B*) :** Number of magnetic field lines crossing per unit area normally through a magnetic substance.

$$B = B_0 + \mu_0 I \qquad \begin{bmatrix} B_0 = \text{applied magnetic field} \\ \mu_0 I = \text{magnetic field due to magnetisation} \end{bmatrix}$$

$$B = \mu_0 H + \mu_0 I$$

$$B = \mu_0 (H + I)$$

4. **Magnetic Susceptibility :** $_m = \frac{I}{H}$ (no unit)

5. **Magnetic Permeability :** $\mu = \frac{B}{H} \Rightarrow B = \mu H$

From above $B = \mu_0(H + I)$

$$\Rightarrow \quad \mu H = \mu_0 (H + I)$$

$$\frac{\mu}{\mu_0} = 1 + \frac{I}{H}$$

$\mu_r = 1 + {}_m$ where μ_r = relative permeability.

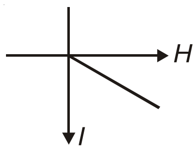
Curie Law

Magnetic susceptibility of paramagnetic material is inversely proportional to its absolute temperature.

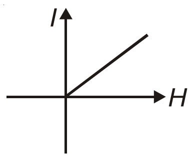
$$_m \propto \frac{1}{T}$$

Variation of *I* with *H*

1. Diamagnetic



2. Paramagnetic

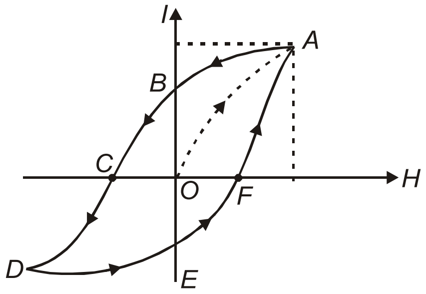


3. Ferromagnetic (Hysteresis)

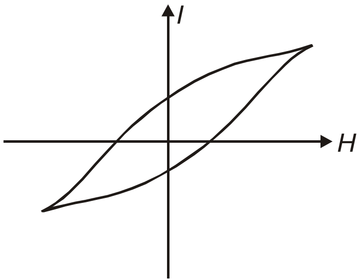
OB = Retentivity (residual magnetism even after magnetising field is reduced to zero)

OC = Coercivity (reverse magnetic field required to reduce residual magnetism to zero)

Area *ABCDEFA* = Energy loss/cycle during magnetisation and demagnetisation.



Steel
(High coercivity, high retentivity)



Soft iron
(Low coercivity, low retentivity)

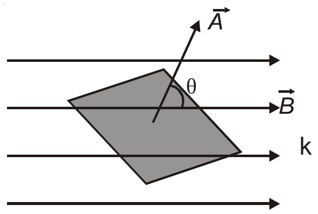
❑ ❑ ❑

Chapter 13

Electromagnetic Induction

MAGNETIC FLUX

$\phi = \vec{B}.\vec{A} = BA\cos\theta$ (θ = Angle between $\vec{B}$ and $\vec{A}$)



Faraday's Laws of Electromagnetic Induction

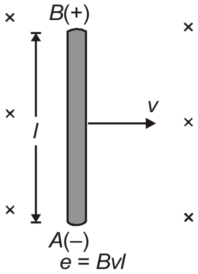
$e = -\dfrac{d\phi_B}{dt}$ (for a loop), for a plane coil having N turns

$$e = -\frac{Nd\phi_B}{dt} = -\frac{d(N\phi_B)}{dt}$$

Note : *Negative sign indicates opposition (explained by Lenz's law).*

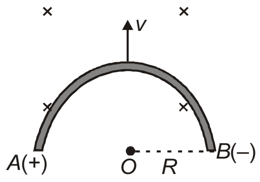
Induced EMF in different cases

1.



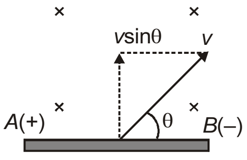
$e = Bvl$

2.



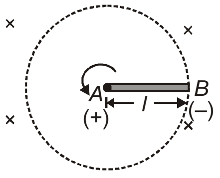
$e = Bv(2R)$

3.



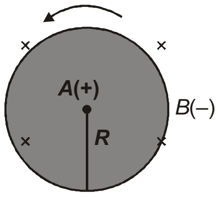
$e = Bvl\sin\theta$

4.



$e = \frac{1}{2}Bl^2$

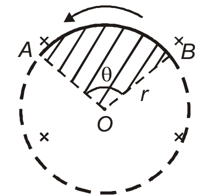
5.



$e = \frac{1}{2}BR^2$

Disc

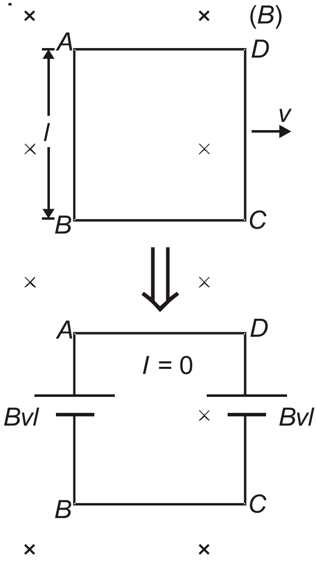
6.



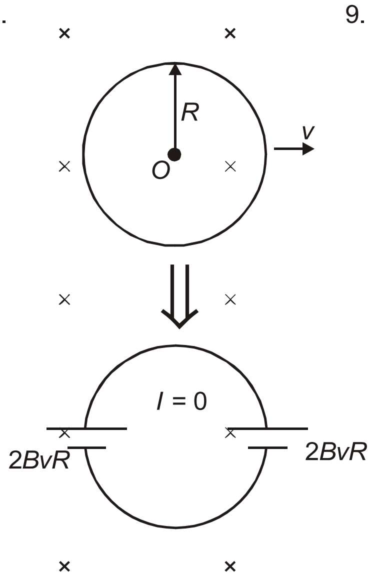
$\varepsilon_{AB} = 0$ $e_{OA} = \frac{1}{2}Br^2$

Part of Disc

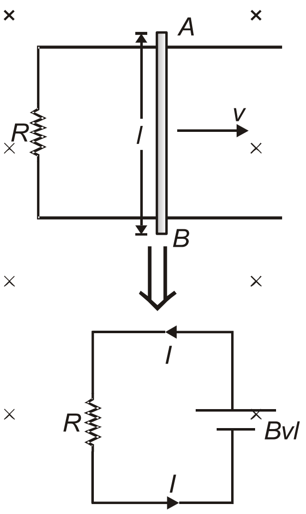
7.



8.

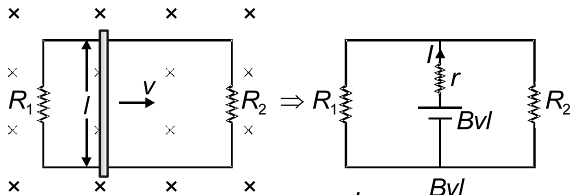


9.



$$I = \frac{Bvl}{R}$$

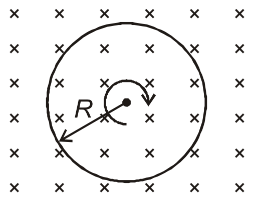
10.



Sliding rod also has a resistance '*r*'

$$I = \frac{Bvl}{r + \frac{R_1R_2}{R_1 + R_2}}$$

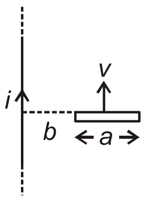
11.



$E_{\text{induced}} = 0$

Ring

12.



$$\varepsilon = \frac{\mu_0 iv}{2\pi}\ln\left(1+\frac{a}{b}\right)$$

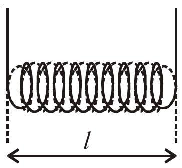
MUTUAL AND SELF INDUCTANCE

Mutual Induction

Important cases :

1. Mutual inductance of two long solenoids :

$$M = \frac{\mu_0 N_1 N_2 A}{l}$$



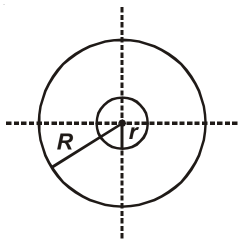
N_1 = Number of turns in one solenoid

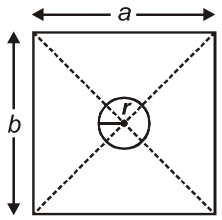
N_2 = Number of turns in other solenoid

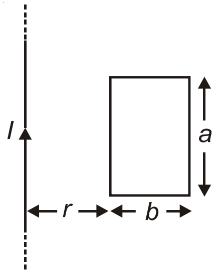
A = Area of cross-section of narrower solenoid

l = Length of solenoid

2. Two loops : $R >> r$







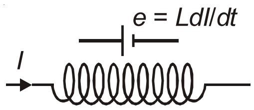
(a) $M = \frac{\mu_0 \pi r^2}{2R}$

(b) $M = \frac{\mu}{4\pi}\frac{8\sqrt{a^2+b^2}}{ab}\pi r^2$
(For r << a, r << b)

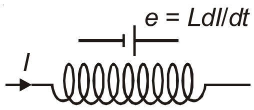
(c) $M = \frac{\mu_0}{2\pi} a \log\left(\frac{r+b}{r}\right)$

Direction of Induced emf

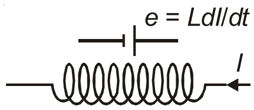
(a) I is increasing



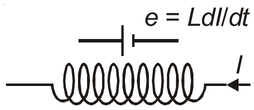
(b) I is decreasing



(c) I is increasing

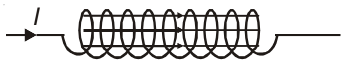


(d) I is decreasing



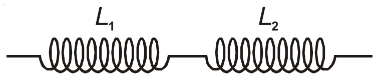
Energy in Inductor

Energy $U_B = \frac{1}{2}LI^2$, Energy density $= \frac{1}{2}\frac{B^2}{\mu_0}$



Combination of Inductors

1. Inductor in series



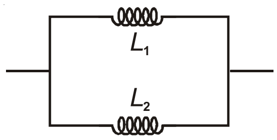
When mutual inductance is neglected $L = L_1 + L_2$

When mutual inductance is considered $L = L_1 + L_2 \pm 2M$

'+' sign is taken when flux of one coil supports the flux in other coil. '–' sign is taken when flux of one coil opposes the flux of other.

Here, $M = K\sqrt{L_1L_2}$ where K = coefficient of coupling.

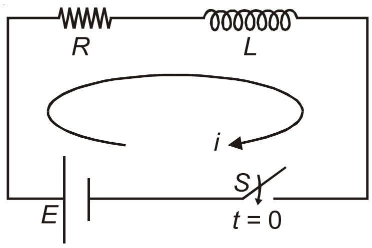
2. Inductor in parallel



$\frac{1}{L} = \frac{1}{L_1} + \frac{1}{L_2}$ (Neglecting mutual induction)

L-R- CIRCUIT WITH D.C. SOURCE

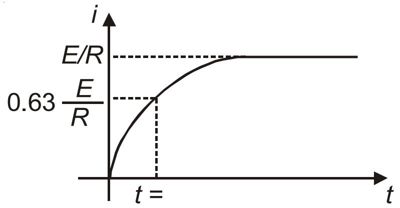
Growth of Current



At $t = 0$ the switch S is closed

$i=\frac{E}{R}\left(i-e^{-t/}\right)$. Here $=\frac{L}{R}$

Graph for variation of current (i) with time (t) is shown here.

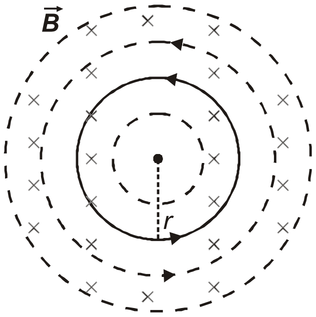


INDUCED ELECTRIC FIELD

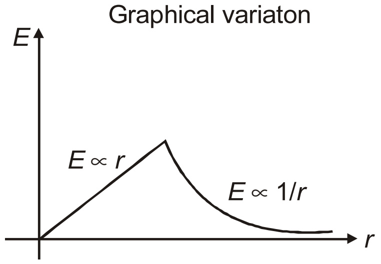
A changing magnetic field produces an electric field. This field is non-conservative and always forms closed loop. Consider a region of magnetic field. The magnetic field strength is increasing at a rate $\frac{d\vec{B}}{dt}$. This creates anticlockwise electric field lines. Electric field strength at distance r from point O is given by

$E=\frac{dB}{dt}\times\frac{r}{2}$ For inside point

$E=\frac{R^2}{2r}\frac{dB}{dt}$ For outside point

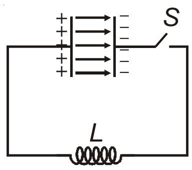


Graphical variaton



LC OSCILLATIONS

A charged capacitor is connected to an inductor and switch is closed at $t = 0$.

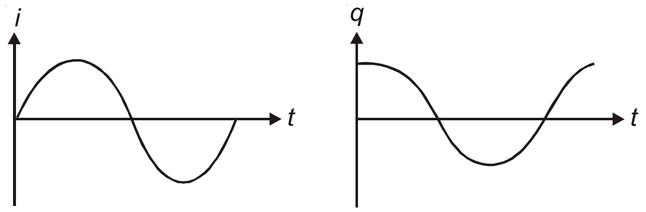


The charge and current vary sinusoidally as,

$q = q_0 \cos\ t$ [$\because$ at $t = 0$, $q = q_0$]

$i = i_0 \sin\ t$ [$\because$ at $t = 0$, $i = 0$]

Graphical representation of this variation is as shown.



$i_0 = \frac{q_0}{\sqrt{LC}}, \quad = \frac{1}{\sqrt{LC}}, \nu = \frac{1}{2\pi\sqrt{LC}}$ is frequency of *LC* oscillations

The maximum charge and maximum current in *LC* oscillation are related as $\frac{1}{2}LI_{\max}^2 = \frac{q_{\max}^2}{2C}$

$q_{\max} = I_{\max}\sqrt{LC}$

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Chapter 14

Alternating Current and Electromagnetic Waves

AVERAGE AND RMS VALUE OF AC

1. **Mean or Average value for time interval '*t*'**

$$E_{\text{mean}} = \frac{1}{t}\int_0^t E\,dt,\ I_{\text{mean}} = \frac{1}{t}\int_0^t I\,dt$$

The total charge flown in time '*t*' in a wire is $Q = I_{\text{mean}} \times t$

2. **Root Mean Square (RMS) Value**

RMS value of ac is equal to that value of dc, which when passed through a resistance for a given time interval will produce the same amount of heat as produced by the ac when passed through the same resistance for same time. RMS values are also known as **virtual or effective value.**

$$E_{\text{rms}}^2 = \frac{1}{t}\int_0^t E^2\,dt,\ I_{\text{rms}}^2 = \frac{1}{t}\int_0^t I^2\,dt$$

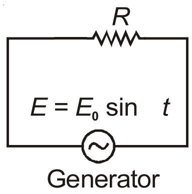
PHASOR AND AC CIRCUITS

Different ac Circuits

1. **Resistive Circuit**

$I = I_0 \sin \quad t$

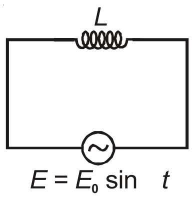
$$I_0 = \frac{E_0}{R}$$



2. **Inductive Circuit**

$I = I_0 \sin(\quad t - \pi/2)$

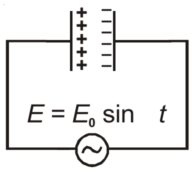
$$I_0 = \frac{E_0}{X_L},\ \text{where } X_L = \quad L = 2\pi fL$$



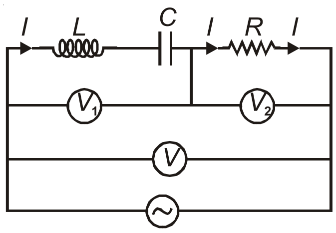
Capacitive Circuit

1. $I = I_0 \sin(\quad t + \pi/2)$

2. $I_0 = \dfrac{E_0}{X_C}$, where $X_C = \dfrac{1}{\quad C} = \dfrac{1}{2\pi fC}$



SERIES LCR CIRCUIT



$E = E_0 \sin \quad t$

$$V = \frac{E_0}{\sqrt{2}} = \text{rms value of applied voltage}$$

V_1 = rms voltage across L-C = $V_L - V_C$

V_2 = rms voltage across R = V_R

Phase Relationship

⇒ I and V_R are in same phase in case of resistance.

⇒ V_L leads I by 90° in case of inductor.

⇒ V_C lags behind I by 90° in case of capacitor.

⇒ In general, $V = \sqrt{V_R^2 + (V_L - V_C)^2}$

$$= I\sqrt{R^2 + (X_L - X_C)^2}$$

(a) Impedance = $Z = \sqrt{R^2 + (X_L - X_C)^2}$

(b) Power factor = $\cos\phi = \dfrac{R}{Z} = \dfrac{R}{\sqrt{R^2 + (X_L - X_C)^2}}$

POWER CONSUMED IN AN A.C. CIRCUIT

$$P_{\text{av}} = \frac{1}{T}\int_0^T EIdt$$

If $E = E_0 \sin \quad t$ and $I = I_0 \sin (\quad t + \phi)$

$$P_{\text{av}} = \frac{E_0 I_0}{2}\cos\phi$$

$$= \frac{E_0}{\sqrt{2}} \cdot \frac{I_0}{\sqrt{2}}\cos\phi$$

$= E_v I_v \cos\phi$ [E_v = Virtual or rms voltage, I_v = Virtual or rms current]

cos ϕ is known as power factor.

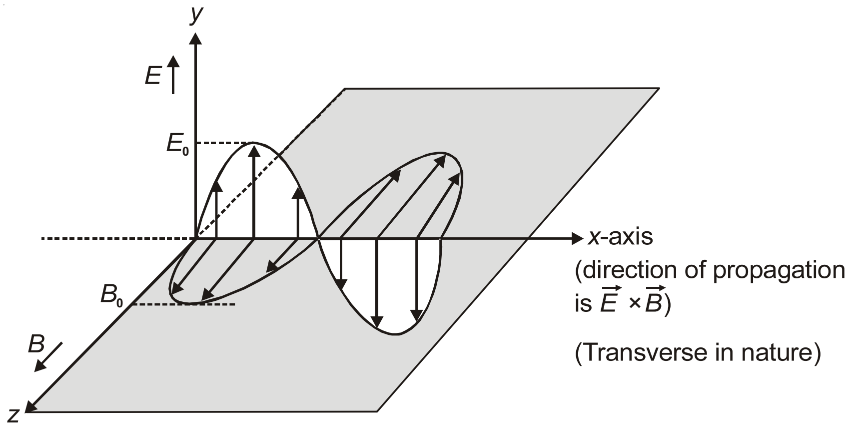
The inductor and capacitor are wattless components of ac circuit as their power consumption is zero.

ELECTROMAGNETIC WAVES

Electromagnetic waves are non-mechanical waves. They transport energy and momentum and carries information. They are transverse in nature and hence they can be polarised.

An electromagnetic wave is the one constituted by oscillating electric and magnetic fields which oscillate in two mutually perpendicular planes; the wave itself propagates in a direction, perpendicular to both the directions of oscillations of electric and magnetic fields.

Important Points Regarding Electromagnetic Waves Characteristics



1. Both electric and magnetic field vary in phase with each other.

2. $\vec{E}_y = E_0 \sin(\;t - kx)\hat{j},\ \vec{B}_z = B_0 \sin(\;t - kx)\hat{k}$, speed $v = \frac{}{k}$

3. In vacuum, $c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}$. In a medium $v = \frac{1}{\sqrt{\mu\varepsilon}}$.

   Refractive index of the medium $\mu = \frac{c}{v} = \sqrt{\mu_r \varepsilon_r}$.

4. $\frac{E}{B} = \frac{E_0}{B_0} = \frac{E_{\text{rms}}}{B_{\text{rms}}}$ = c (speed) = $\frac{}{k}$

5. Average energy density $U_{\text{av}} = \frac{1}{2}\varepsilon_0 E_0^2 = \frac{1}{2}\frac{B_0^2}{\mu_0} = \frac{1}{4}\varepsilon_0 E_0^2 + \frac{1}{4}\frac{B_0^2}{\mu_0}$

6. Poynting vector $\vec{S}$ represents instantaneous intensity at a point

   $\vec{S} = \frac{\vec{E} \times \vec{B}}{\mu_0}$ or $S = \frac{EB}{\mu_0}$. Here $\vec{E} \times \vec{B}$ represents the direction of flow of energy.

7. **Intensity :** Average rate of flow of energy per unit time per unit area in the direction of wave propagation.

   $I = S_{\text{av}} = \frac{E_{\text{rms}} B_{\text{rms}}}{\mu_0} = \frac{1}{2}\frac{E_0 B_0}{\mu_0}$

   $I = c \times U_{\text{av}}$ or $U_{\text{av}} = \frac{I}{c}$

For a point source of power P, Intensity at a distance r from the source is $I = \dfrac{P}{4\pi r^2}$.

Now $U_{\text{av}} = \dfrac{I}{c} = \dfrac{P}{4\pi r^2 c}$

$$\Rightarrow \quad \frac{1}{2}\varepsilon_0 E_0^2 = \frac{P}{4\pi r^2 c} \quad \Rightarrow \quad E_0 = \sqrt{\frac{P}{2\pi r^2 c\,\varepsilon_0}}$$

$$B_0 = \frac{E_0}{c} = \sqrt{\frac{P\mu_0}{2\pi r^2 c}}$$

8. Radiation pressure (for normal incidence)
   (a) For perfectly absorbing surface $P = I/c$
   (b) For perfectly reflecting surface $P = 2I/c$
   (c) For all other surfaces $I/c < P < 2I/c$
   (d) For a surface of reflectance r

$$P = \frac{I}{c}(1 + r)$$

9. The direction of wave propagation is always along $\vec{E} \times \vec{B}$ and E, B, c are always perpendicular.
10. Speed of electromagnetic waves only depends upon the medium. All the electromagnetic waves travels with equal speed (*i.e.* 3×10^8 m/s) in vacuum.
11. When a electromagnetic wave travels from one medium to another then its speed changes but frequency remains same.
12. Speed of electromagnetic waves in any medium = $\dfrac{c}{\mu}$ [where μ is the refractive index of the electromagnetic waves]

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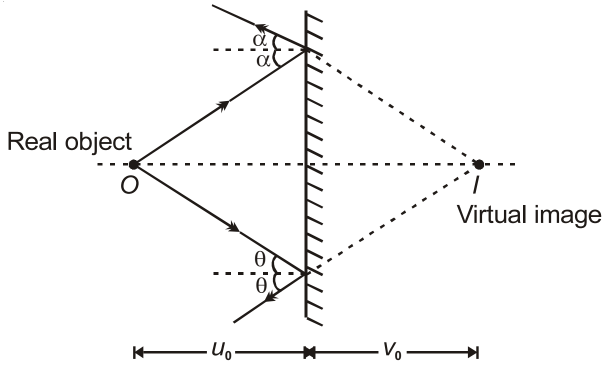
Chapter 15

Optics

PLANE MIRROR

Following are some important points regarding image formation by plane mirror :

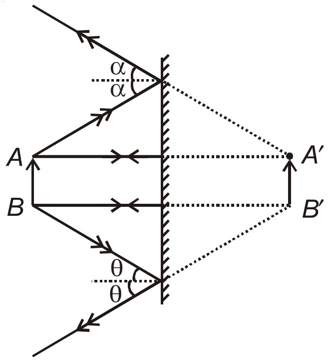


1. Object distance = Image distance, $|u_0| = |v_0|$.

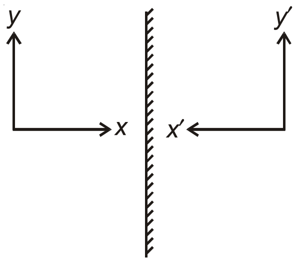
2. $\frac{du}{dt} = -\frac{dv}{dt}$, *i.e.*, speed of object w.r.t. mirror is equal to speed of image w.r.t. mirror. For example, if object is at rest and mirror is moving with velocity x towards object then velocity of image will be $2x$.

3. For extended object, it can be seen that height of object = height of image.

$$\Rightarrow \text{Magnification} = \frac{\text{Height of image}}{\text{Height of object}} = 1$$



4. Image is laterally inverted, i.e., it has front back reversed.



5. Keeping incident ray fixed, if a plane mirror is rotated by an angle θ, reflected ray rotates by an angle 2θ.

6. For two mirrors inclined at an angle ‘θ’. Number of images formed by the mirrors for a point object are

(a) $\frac{360}{\theta}-1$, if $\frac{360}{\theta}$ = even number

(b) $\frac{360}{\theta}-1$, when $\frac{360}{\theta}$ = odd and object is placed symmetrically.

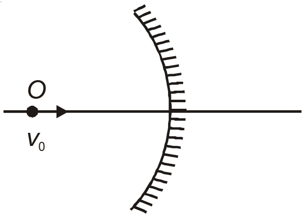
(c) $\frac{360}{\theta}$, when $\frac{360}{\theta}$ = odd and object is placed unsymmetrically.

REFLECTION FROM CURVED SURFACES

1. $f=\frac{R}{2}$
2. $\frac{1}{f}=\frac{1}{v}+\frac{1}{u}$
3. $m=\frac{I}{O}=-\frac{v}{u}=\frac{f-v}{f}=\frac{f}{f-u}$

where,
f = Focal length
u = Object distance
v = Image distance
I = Size of image
O = Size of object

4. Magnification is negative for inverted image and positive for erect image.
5. If object O is moving with velocity v_0 as shown in figure then velocity of image $v_{\text{image}}=-m^2v_0$



$$\because \quad \frac{1}{v}+\frac{1}{u}=\frac{1}{f}$$

$$\Rightarrow \quad \frac{dv}{dt}=-\frac{v^2}{u^2}\left(\frac{du}{dt}\right)$$

$$\Rightarrow \quad v_{\text{image}}=-m^2v_0$$

6. If object is moving with velocity v_0 as shown in figure then velocity of real image $v_{\text{image}} = mv_0$

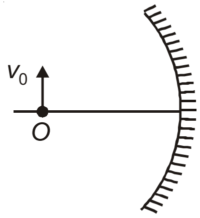
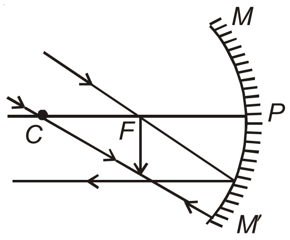
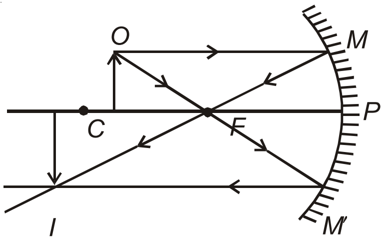
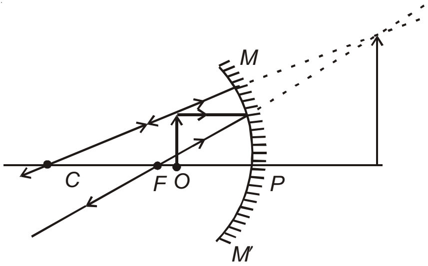


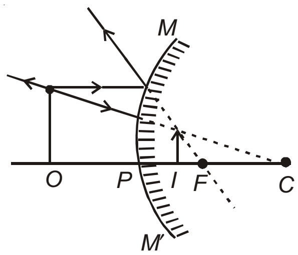
Image formation for Concave Mirror

Table : Position and nature of image for a given position of object

S.No.	Position of object	Ray diagram	Details of image
1.	At infinity		Real inverted, very small [m (0^-)]; at focus or in focal plane.
2.	Between F and C		Real, inverted, large ($m < -1$) beyond C
3.	Between F and P		Virtual, erect ($m > +1$) Behind the mirror

For Convex Mirror

Table: Position and nature of image for a given position of object

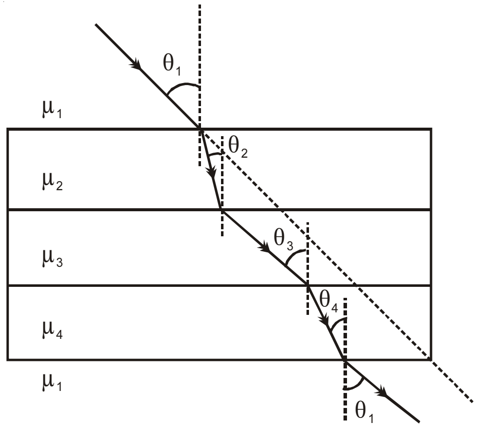
S.No.	Position of object	Ray diagram	Details of image
1.	In front of mirror		Virtual, erect, diminished ($m <\ +1$) between P and F

Laws of Refraction (Snell's Law)

Consider a light ray crossing a series of media as shown.

$\mu_1 \sin\theta_1 = \mu_2 \sin\theta_2 = \mu_3 \sin\theta_3 = \mu_4 \sin\theta_4 = \mu_1 \sin\theta_1$

$\Rightarrow$ $\mu \sin\theta$ = Constant



Incident and refracted are parallel
if they are in same medium

REAL DEPTH AND APPARENT DEPTH

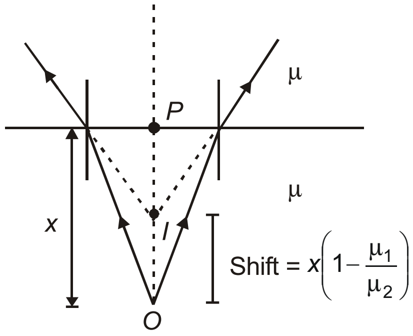
Consider that rays from object *O* are going from medium 2 to 1 ($\mu_2 > \mu_1$) and image is formed at *I*.

$\Rightarrow$ $\dfrac{OP}{\mu_2} = \dfrac{PI}{\mu_1}$ (By Snell's law)

$\Rightarrow$ $PI = \dfrac{\mu_1}{\mu_2} OP = \dfrac{\mu_1}{\mu_2} x$

$\because$ $\mu_1 < \mu_2$, $PI < OP$

$\Rightarrow$ Shift $= x\left(1 - \dfrac{\mu}{\mu}\right)$



$\Rightarrow$ Velocity of image = $\dfrac{\mu}{\mu}$ (Velocity of object)

Glass-slab

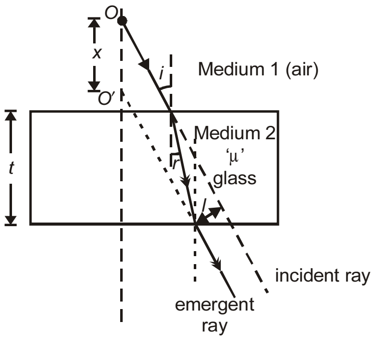
Different results for refraction by glass slab are :

1. Incident and emergent rays are parallel.

2. l = lateral displacement = $\dfrac{t \sin(i - r)}{\cos r}$

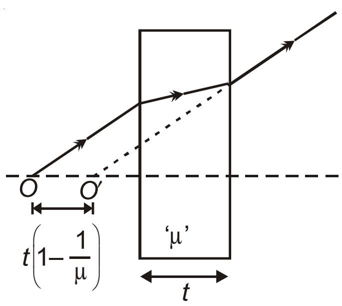
   for small values of i, $\sin(i - r) \quad i - r$ and $r \quad 0$.

   $\Rightarrow$ $l = t\left[i - \dfrac{i}{\mu}\right] = ti\left[1 - \dfrac{1}{\mu}\right]$

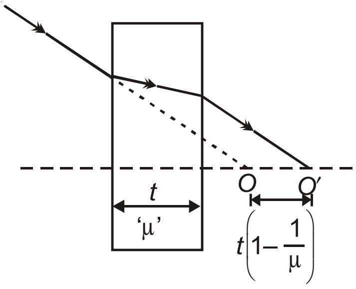


3. I I_{max}, when i 90º

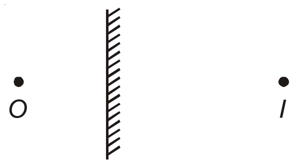
4.



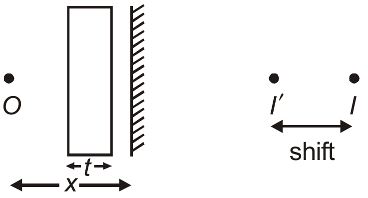
5.



If an object is placed at distance x from plane mirror then image will be formed at distance of x from mirror.



Now if a glass slab of thickness t is introduced between object and mirror then image will shift toward object by $2t\left(1-\frac{1}{\mu}\right)$



Critical Angle

If a ray is travelling from optically denser medium to optically rarer medium, then critical angle may be defined as the angle of incidence in denser medium corresponding to which angle of refraction in rarer medium is 90°.

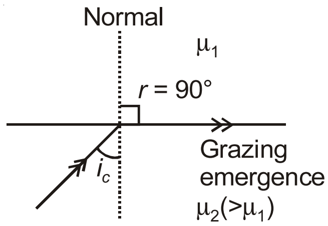
If μ_1 = refractive index of rarer medium

μ_2 = refractive index of denser medium

and i_c = critical angle

then $\mu_2 \sin i_c = \mu_1 \sin 90°$

$$\Rightarrow \quad \sin i_c = \frac{\mu_1}{\mu_2}$$

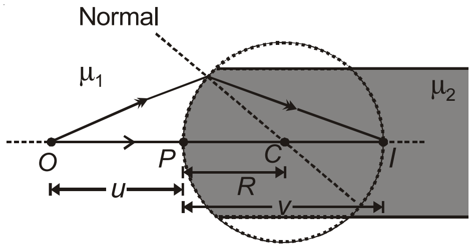


Spherical Refracting Surface

For object O, image formed by refracting surface is at I.

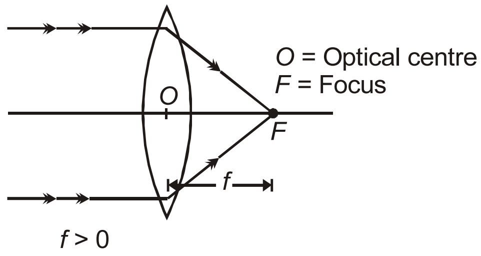
Object distance (u) and image distance (v) are related as

$$\frac{\mu_2}{v} - \frac{\mu_1}{u} = \frac{\mu_2 - \mu_1}{R}$$

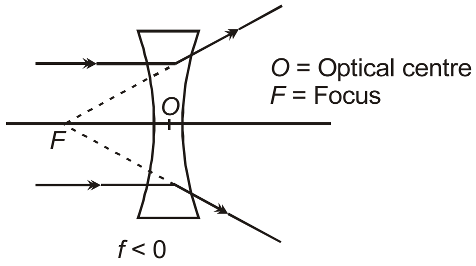


Some Important Relations for Lenses

Converging (Convex) lens



Diverging (Concave) lens

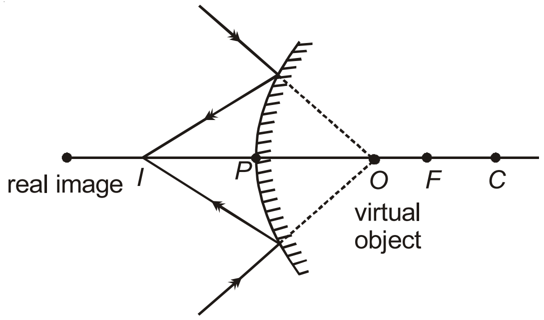


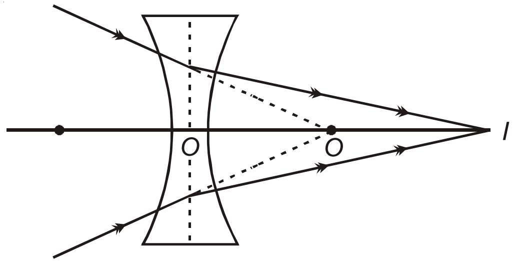
1. Lens formula $\frac{1}{v}-\frac{1}{u}=\frac{1}{f}$

2. Linear magnification $m=\frac{I}{O}$ m 0 for inverted image
   m 0 for erect image

3. In lenses, $m=\frac{v}{u}=\frac{f}{f+u}=\frac{f-v}{f}$

4. A convex mirror or a concave lens can form a real image if object is virtual as shown.





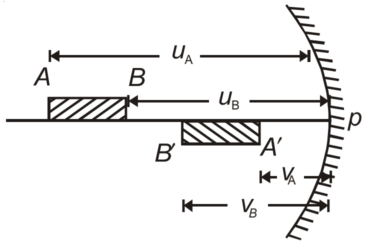
5. If an object moves along the axis of a convex lens from infinity towards its focus with a constant speed, then

   $v_i = m^2 v_0$, for a lens $v_i = \frac{v^2}{u^2}v_0$

6. If an object moves perpendicular to axis of a convex lens with a velocity v_0 then $v_i = mv_0$

LATERAL MAGNIFICATION

$$m_L=\frac{A'B'}{AB}=\frac{v_B-v_A}{u_A-u_B}$$



For short object

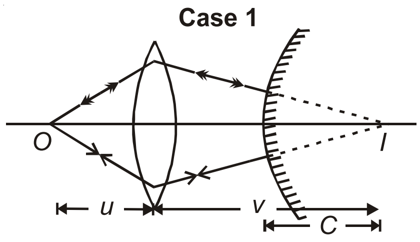
$$m_L=\frac{dv}{du}$$

For a concave mirror, $m_L=-\frac{v^2}{u^2}$

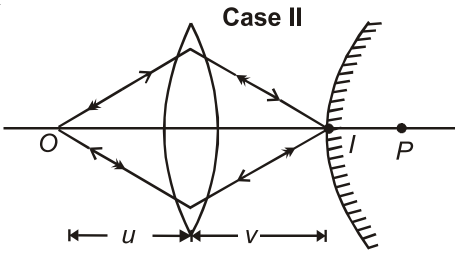
For a convex lens, $m_L=\frac{v^2}{u^2}$

Lens and Mirror

A point object is placed in front of a convex lens. A convex mirror is placed behind the lens, so that final image coincides with the object itself.



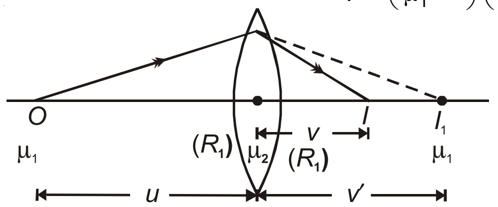
Final image is real and inverted and coincides with O



Final image is real and erect and coincides with O

Lens Maker's Formula (For thin lenses)

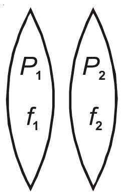
For a thin lens, $P(\text{Power}) = \frac{1}{f} = \left(\frac{\mu_2}{\mu_1} - 1\right)\left(\frac{1}{R_1} - \frac{1}{R_2}\right)$



COMBINATION OF LENSES

1. In contact :

$P = P_1 + P_2$, P is taken with sign

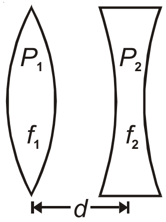


$$\Rightarrow \frac{1}{f} = \frac{1}{f_1} + \frac{1}{f_2}$$

2. $P = P_1 + P_2 - dP_1P_2$

$$\Rightarrow \frac{1}{f} = \frac{1}{f_1} + \frac{1}{f_2} - \frac{d}{f_1f_2}$$ (Applicable only for parallel rays)

where d is the separation between two lenses in air

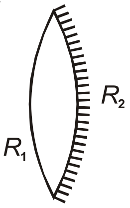


Silvering of Lenses

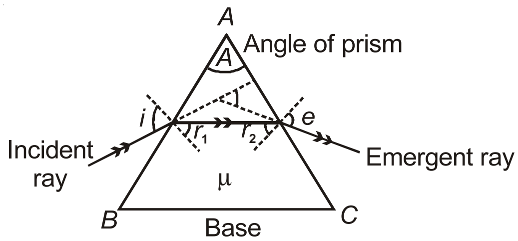
1. When a convex lens is silvered it will behave like a concave mirror.
2. When a concave lens is silvered it will behave like a convex mirror.
3. **Case-1 :** When one face (of radius of curvature R_2) of a double convex lens is silvered

$P_{eq} = 2P_l + P_m$

$$\Rightarrow \frac{1}{F_{\text{eff}}} = 2(\mu - 1)\left[\frac{1}{R_1} - \frac{1}{R_2}\right] - \frac{2}{R_2}$$

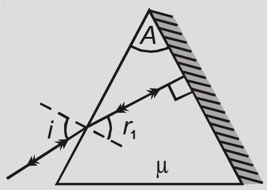


PRISM AND DISPERSION



Note :

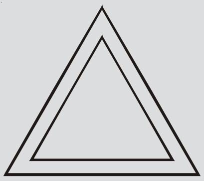
1. *The variation of with i is unsymmetrical.*
2. *Under minimum deviation, ray passes symmetrically through the prism.*
3. *If prism is isosceles or equilateral, refracted ray is parallel to base of prism under minimum deviation.*
4. *If A > 2C or* $\mu \ \ \text{cosec}\,\frac{A}{2}$*, there will be no emergent light whatever may be the angle of incidence.*
5. *A = 2C is called limiting value of angle of prism.*
6. *If A < C, total internal reflection at second face can never take place.*
7. *In case, one face is silvered, for incident ray to retrace its path after reflection from 2nd face.*



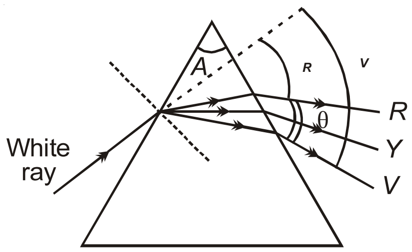
$r_2 = 0 \qquad r_1 = A$

$$\Rightarrow \qquad \mu = \frac{\sin i}{\sin A}$$

8. *Angle of deviation is maximum when angle of incidence = 90º.*
9. *A thin hollow prism as shown produces zero deviation.*



Dispersion



$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \frac{D}{\lambda^6} + \ldots \qquad \text{[Cauchy's formula]}$$

$= (\mu - 1)A$

As, $\lambda_V < \lambda_R$

$\Rightarrow \ \mu_V > \mu_R$

$\Rightarrow \ _V < \ _R$

θ = angular dispersion = $\ _V - \ _R = (\mu_V - \mu_R)A$

= Mean deviation = $(\mu - 1)A$

μ = mean refractive index = $\frac{\mu_V + \mu_R}{2}$

Dispersive power $= \frac{\theta}{\ } = \frac{(\mu_V - \mu_R)A}{(\mu - 1)A} = \frac{\mu_V - \mu_R}{\mu - 1} = \frac{d\mu}{\mu - 1}$

$d\mu$ = difference in refractive index

Combination of Prisms

$\theta = \theta_1 + \theta_2,$ $\quad = {}_1 + {}_2$

Case-1 : For dispersion without deviation

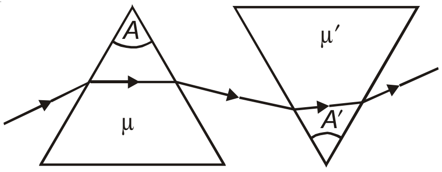
$= 0$

$\Rightarrow \quad (\mu - 1)A + (\mu' - 1)A' = 0$

Case-2 : For deviation without dispersion

$\theta = 0$

$\Rightarrow \quad (\mu_V - \mu_R)A + (\mu'_V - \mu'_R)A' = 0$



Chromatic Aberration

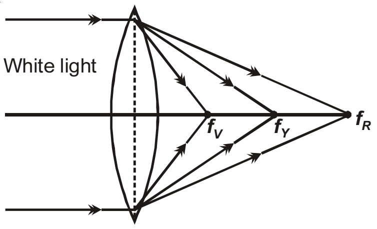
This is the phenomena observed when different colours come to focus at different points on the principal axis. This defect can be removed by using an achromatic lens combination.

As, $\mu = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4}$

and $\lambda_R > \lambda_Y > \lambda_v$

$\Rightarrow \mu_R < \mu_Y < \mu_v$

$\Rightarrow f_R > f_Y > f_v \qquad \left[\text{as } \frac{1}{f} = (\mu - 1)\left(\frac{1}{R_1} - \frac{1}{R_2}\right)\right]$



Achromatic Combination

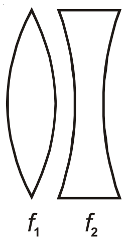
A combination free from chromatic aberration is achromatic combination.

1. Lenses in contact

Power $P = \frac{1}{f_1} + \frac{1}{f_2} = P_1 + P_2$

Condition for achromatism

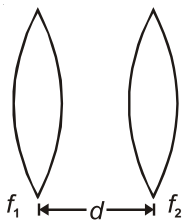
$\frac{{}_1}{f_1} + \frac{{}_2}{f_2} = 0$ or ${}_1P_1 + {}_2P_2 = 0$



$\Rightarrow$ P_1 and P_2 or f_1 and f_2 should be opposite sign also ${}_1$ ${}_2$ as P will become zero.

2. $P = \frac{1}{f_1} + \frac{1}{f_2} - \frac{d}{f_1 f_2} = P_1 + P_2 - dP_1P_2$

Condition for achromatism $d = \frac{{}_1f_2 + {}_2f_1}{{}_1 + {}_2}$.



Note : *(a) f_1 and f_2 can be of same or opposite sign*

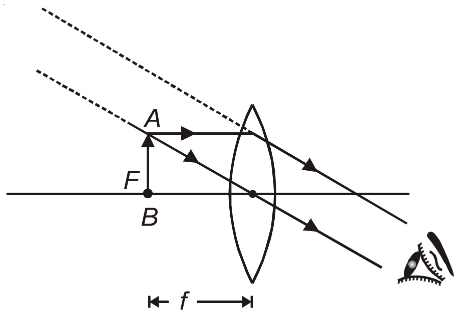
(b) ${}_1 = {}_2 \Rightarrow d = \frac{f_1 + f_2}{2}$

OPTICAL INSTRUMENTS

1. **Simple Microscope / Magnifying Glass :** It uses a single convex lens of focal length f

$m = \frac{D}{u}$, where u is distance of object

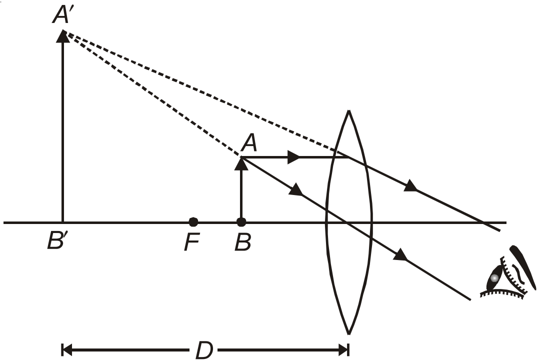
Case-1 :



(Final image at infinity)

For relaxed eye, $u = f$, image at $\Rightarrow m = \frac{D}{f} > 0$

Case-2 :



(Final image at least distance of distinct vision)

For strained eye, image is at $D \Rightarrow m = 1+\frac{D}{f} > 0$

2. **Compound Microscope**

It uses two convex lens objective (f_o) and eyepiece (f_e)

u_o = object distance from objective (u_o is close to f_o)

v_o = image distance from objective (close to length of tube)

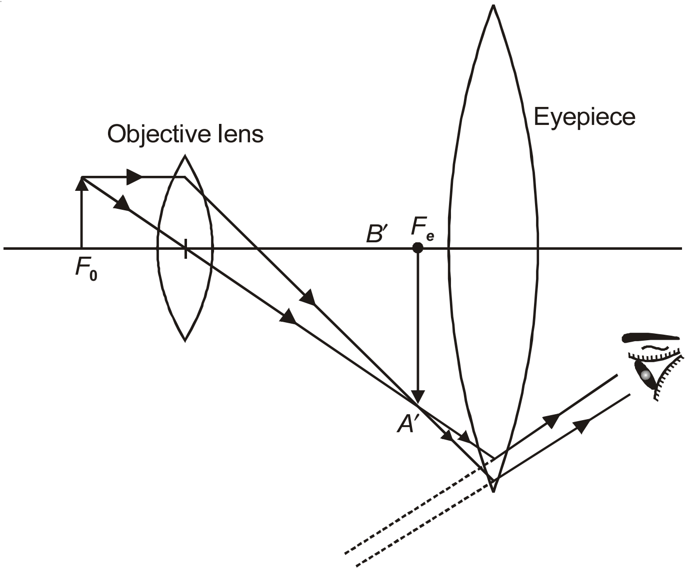
Magnification by objective $m_o = -\frac{v_o}{u_o}$ (–ve)

Magnification by eyepiece $m_e = \frac{D}{u_e}$

Magnification for microscope

$$m = m_o \times m_e = \frac{-v_o}{u_o} \times \frac{D}{u_e}$$

Case-1 :

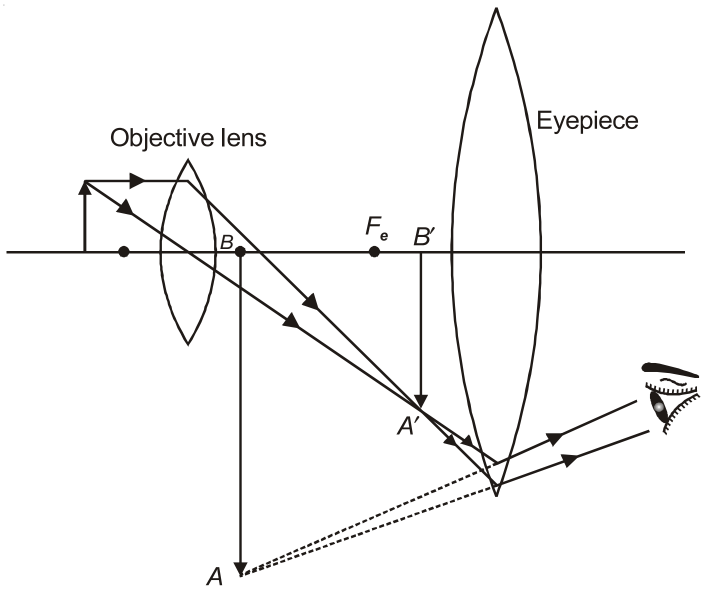


(Final image at infinity)

Relaxed eye : $m = \frac{-v_o}{uo} \times \frac{D}{f_e} \quad \frac{-L}{f_o}\left(\frac{D}{f_e}\right)$

Length of tube $L = V_0 + f_e$

Case-2 :



(Final image at least distance of distinct vision)

Strained eye : $m = \frac{-v_o}{u_o}\left(1+\frac{D}{f_e}\right) \quad -\frac{L}{f_o}\left(1+\frac{D}{f_e}\right)$

Length of tube $V_0 + \frac{f_e D}{f_e + D}$

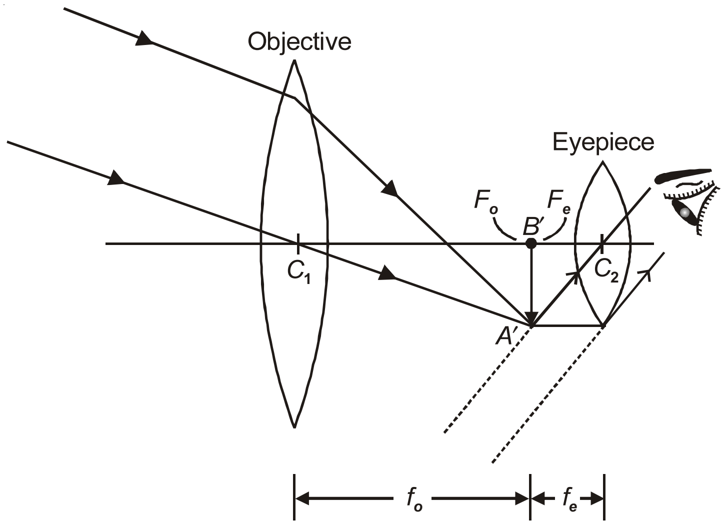
3. **Astronomical Telescope :** f_o is focal length of objective and f_e is focal length of eye-piece.

$m = m_o \times m_e$ here $m_o < 0$, $m_e > 0.$, $m < 0$

Case-1 :

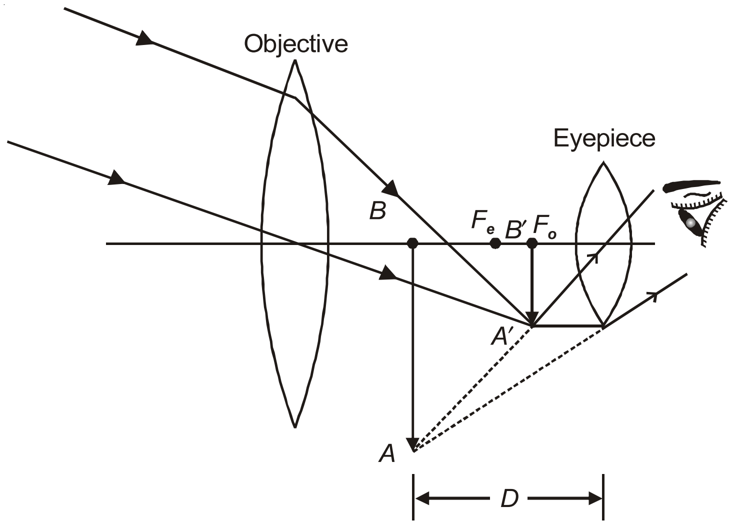
For relaxed eye *i.e.,* normal adjustment. $m = -\frac{f_o}{f_e}$

Length of tube $L = f_o + f_e$



(Final image at infinity)

Case-2 :



(Final image at least distance of distinct vision)

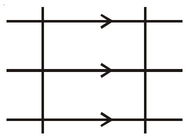
For strained eye : $m = \frac{-f_o}{f_e}\left(1 + \frac{f_e}{D}\right)$

length of tube $L < f_o + f_e$

WAVE OPTICS

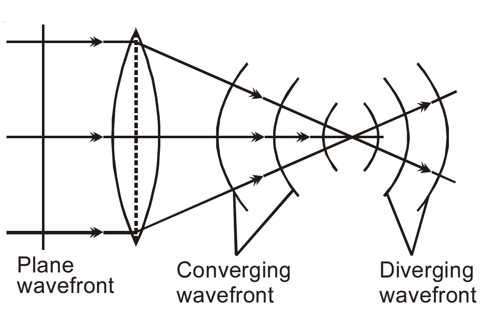
Plane Wavefront (Plane sheet source)

1. Amplitude = constant $\Rightarrow$ $A \propto r^0$
2. Intensity = constant $\Rightarrow$ $I \propto r^0$

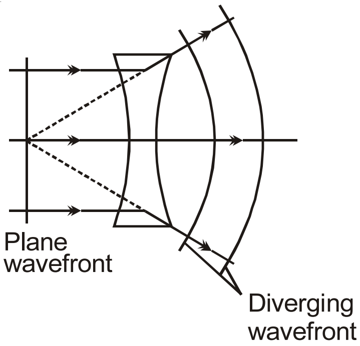


Refraction in form of Wavefronts

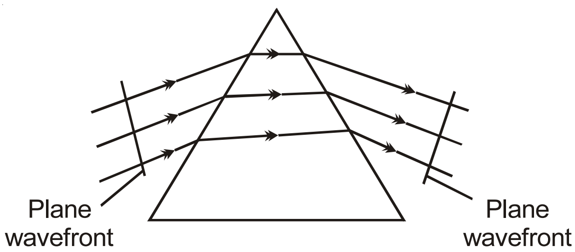
1.



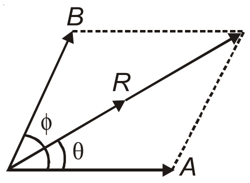
2.



3.



SUPERPOSITION OF WAVES



Wave-1 : $y_1 = A \sin\ \ t$

Wave-2 : $y_2 = B \sin(\ \ t + \phi)$

Resultant wave : $y = y_1 + y_2$ $\Rightarrow$ $y = A \sin\ \ t + B \sin(\ \ t + \phi)$

$\Rightarrow$ $y = R \sin(\ \ t + \theta)$

where $\tan\theta = \dfrac{B\sin\phi}{A + B\cos\phi}$

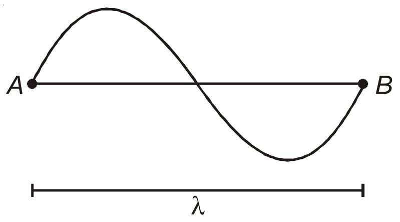
and $R = \sqrt{A^2 + B^2 + 2AB\cos\phi}$

Intensity $\propto$ (Amp)^2 $\therefore$ $I_1 \propto A^2$, $I_2 \propto B^2$, $I \propto R^2$

As, $R^2 = A^2 + B^2 + 2AB\cos\phi$ $\Rightarrow$ $I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\phi$

Relation between phase difference and path difference

For the two points *A* and *B* on a wave,



$\phi_{AB} = 2\pi$

$X_{AB} = \lambda$

$$\boxed{\phi = \frac{2\pi}{\lambda}\; x}$$

Condition for Maxima

When $\cos\phi = 1$ or $\phi = 2n\pi$ or $x = n\lambda$ (path difference)

$R_{\max} = A + B$, $I_{\max} = \sqrt{I_1} + \sqrt{I_2}\;^{2}$

Condition for Minima

When $\cos\phi = -1$ or $\phi = (2n-1)\pi$ or $x = (2n-1)\dfrac{\lambda}{2}$

$R_{\min} = A - B$, $I_{\min} = (\sqrt{I_1} - \sqrt{I_2})^2$

$$\Rightarrow \frac{R_{\max}}{R_{\min}} = \frac{A+B}{A-B} \qquad \frac{I_{\max}}{I_{\min}} = \left(\frac{\sqrt{I_1}+\sqrt{I_2}}{\sqrt{I_1}-\sqrt{I_2}}\right)^2 = \left(\frac{\sqrt{\beta}+1}{\sqrt{\beta}-1}\right)^2, \text{ where } \beta = \frac{I_1}{I_2}$$

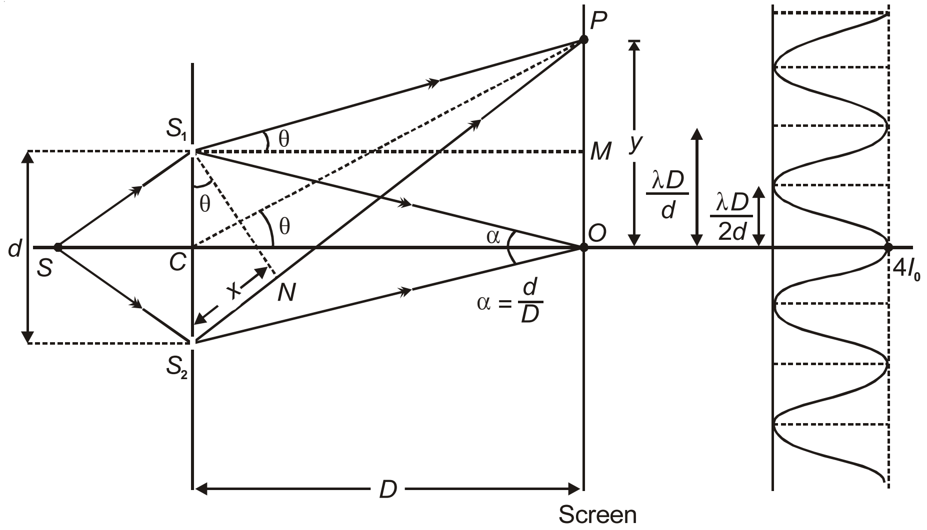
Interference

Phenomenon of redistribution of energy on account of superposition of waves is known as interference.

Coherent Sources

Condition for sustained interference-Sources must be coherent *i.e.*, phase difference between them must be constant.

Young's Double Slit Experiment



For waves reaching *P* from S_1 and S_2, path difference $x = d\sin\theta$.

For small θ $\quad x = \dfrac{yd}{D} \qquad \left[\because\ \sin\theta \quad \tan\theta = \dfrac{y}{D}\right]$

Condition for Maxima

For maxima $x = n\lambda \Rightarrow y = n\dfrac{\lambda D}{d}$ $(n = 0, 1, 2, \ldots)$

or $d \sin\theta = n\lambda$

$\Rightarrow$ $\sin\theta = \dfrac{n\lambda}{d}$

Condition for Minima

For minima $x = (2n-1)\dfrac{\lambda}{2}$ $\Rightarrow$ $y = \dfrac{(2n-1)\lambda D}{2d}$ $(n = 1, 2, \ldots)$

or $d\sin\theta = \dfrac{(2n-1)\lambda}{2}$

$\Rightarrow$ $\sin\theta = \dfrac{(2n-1)\lambda}{2d}$

If λ and d are comparable then, as $-1 \quad \sin\theta \quad 1$

$$-1 \quad \frac{(2n-1)\lambda}{2d} \quad 1$$

$$\Rightarrow \quad \frac{-2d+\lambda}{2\lambda} \quad n \quad \frac{2d+\lambda}{2\lambda}$$

From here you can find maximum number of dark fringes observed on the screen.

For example, if $d = 2\lambda$, then

$$\frac{-4\lambda+\lambda}{2\lambda} \quad n \quad \frac{4\lambda+\lambda}{2\lambda}$$

$-\dfrac{3}{2} \quad n \quad \dfrac{5}{2}$ so, n can have four values *i.e.*, –1, 0, 1, 2.

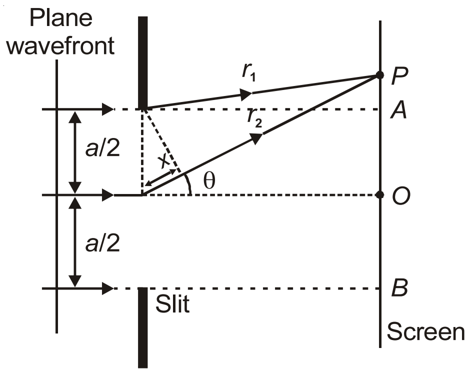
This means that only four minima are observed on the screen.

DIFFRACTION

Diffraction is the phenomenon of light observed due to superposition of secondary wavelets starting from different points of a wavefront which is not blocked by an obstacle or which are allowed by an aperture (of size comparable to the wavelength of light).

In other words you can say diffraction is the phenomena of entering of light in the region of geometrical shadow, due to bending around obstacle edges.

Diffraction by Single Slit



1. $x = \frac{a}{2}\sin\theta$
2. For '*O*' waves from all points in the slit travel about the same distance and are in phase.
3. At *P*, waves r_1 and r_2 have a phase difference $x = \frac{a}{2}\sin\theta$.
4. When $\frac{a}{2}\sin\theta_1 = \frac{\lambda}{2}$, there will be destructive interference.

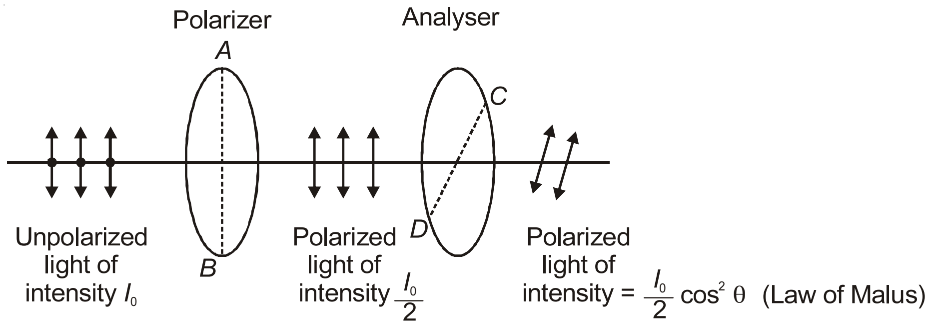
   ∴ when $a \sin \theta_1 = \lambda$, first minima will be formed at *P*.
5. In general $a \sin \theta_n = n\lambda$ is position of n^{th} minima.
6. Angular position of first minima $\theta_1 = \sin^{-1}\left(\frac{\lambda}{a}\right)$
7. Angular spread of central maximum is $2\theta_1 = 2\sin^{-1}\left(\frac{\lambda}{a}\right)$. If $\lambda << a$, then angular spread = $\frac{2\lambda}{a}$.
8. When $\lambda > a \Rightarrow \sin\theta > 1$ which is not possible

   ∴ diffraction cannot be observed.
9. $\lambda < < a$, then $\sin\theta \quad \theta = \frac{\lambda}{a}$ (in radians)
10. Width of central maximum = $\frac{2\lambda D}{a}$
11. Width of other fringes = $\frac{\lambda D}{a}$.
12. If I_0 is the intensity of central maximum, then intensity of n^{th} maxima is $I_n = \frac{4I_0}{(2n+1)^2\pi^2}$

    ∴ $I_0 : I_1 : I_2 : : 1 : 0.045 : 0 : 016$.
13. The intensity of fringe goes on decreasing in case of diffraction while it remain nearly same in the interference.

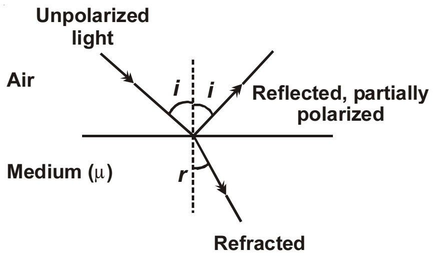
Polarization

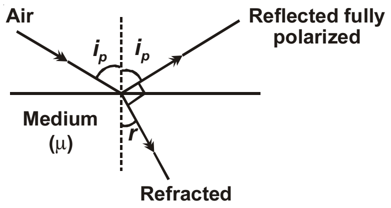
Polarization is a phenomenon exhibited by transverse waves only.



where θ = angle between the transmission (*i.e.*, *AB* and *CD*) axis of the two polaroids

Polarization by Reflection





SOME IMPORTANT POINTS :

1. Reflected light is partially polarized.
2. When $i = i_p$ (polarizing angle), reflected light is completely polarized, i_p is also called Brewster's angle.
3. When reflected light is completely polarized, reflected and refracted light are perpendicular to each other.
4. This was found experimentally by **Sir David Brewster**.

   At this situation $i_p + r = 90°$

   $\Rightarrow$ $\mu = \tan i_p$. This is called Brewster's law.

   $$\Rightarrow \tan i_p = \frac{1}{\sin i_c}$$

   $\Rightarrow$ $\sin i_c . \tan i_p = 1$ [Here i_c is critical angle]

❑ ❑ ❑

Chapter 16

Dual Nature of Matter and Radiation, Atoms and Nuclei

DUAL NATURE OF MATTER AND RADIATION

WAVE NATURE OF PARTICLES

The following points should be kept in mind :

1. Any particle in motion can act like a wave. Wave associated with a particle is called Matter wave or de-Broglie wave.
2. de-Broglie wavelength of a particle $\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2mE_k}}$.

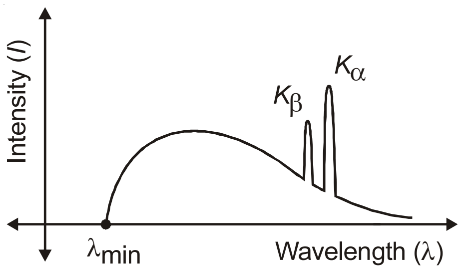
   where $p = mv$ is momentum of particle

   E_k = kinetic energy.
3. For an electron accelerated through V volts.

   $$E_k = eV \therefore \lambda = \frac{h}{\sqrt{2meV}} = \frac{12.27}{\sqrt{V}} \text{Å} \quad \text{or} \quad \lambda = \sqrt{\frac{150}{V}} \text{ Å}$$
4. For a proton accelerated through V volts, $\lambda = \frac{0.286}{\sqrt{V}} \text{Å}$
5. For an α-particle accelerated through V volts, $\lambda = \frac{0.101}{\sqrt{V}} \text{Å}$
6. For an electron revolving in n^{th} orbit of Bohr's Hydrogen atom, $mvr = \frac{nh}{2\pi}$, $\lambda = \frac{h}{mv} = \frac{2\pi r}{n}$.

X-RAYS

Variation of intensity (I) of X-rays with wavelength λ :



Important points related to the above curve :

1. At certain sharply defined wavelength, the intensity of X-rays is very large as marked K_α and K_β. These are known as **characteristic X-rays**.
2. At other wavelengths intensity varies continuously. These are known as **continuous X-rays**.
3. Minimum wavelength or cut off wavelength or threshold wavelength of continuous X-rays,

   $\lambda_{\text{min}} = \frac{hc}{eV} = \frac{12400\,\text{Å}}{V}$, where V is applied voltage in volts.

4. The minimum wavelength does not depend on the material of target. It depends only on the accelerating potential.
5. Continuous X-rays are due to continuous loss of energy of electrons striking the target through successive collisions.
6. Characteristic X-rays are due to the transition of electrons from higher energy level to the vacant space present in the lower energy level.
7. Wavelength of K_α, $\lambda = \frac{hc}{E_L - E_K}$ (transition from L to K)
8. Wavelength of K_β, $\lambda = \frac{hc}{E_M - E_K}$ (transition from M to K)

Moseley's law : Applicable to characteristic X-rays only.

Mathematically $\boxed{\sqrt{\nu} = a(Z-b)}$ a and b are Moseley's constants, ν is frequency of X-rays.

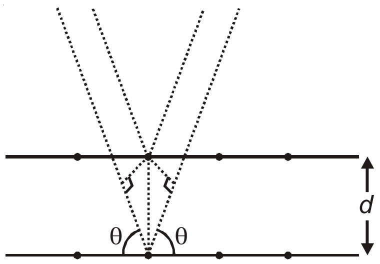
Z is atomic number of the target atom.

For K_α X-ray,

$$a = \sqrt{\frac{3Rc}{4}}$$

$$b = 1$$

Diffraction of X-Rays



Bragg's Law : $2d\sin\theta = n\lambda$ [condition for constructive interference]

where, λ = wavelength of X-ray.

d = separation between crystal planes.

θ = angle between X-ray beam and crystal plane.

$2d\sin\theta$: Path difference

Davisson and Germer's accidental discovery of the diffraction of electrons was the first direct evidence confirming de Broglie's hypothesis that particles have wave properties as well.

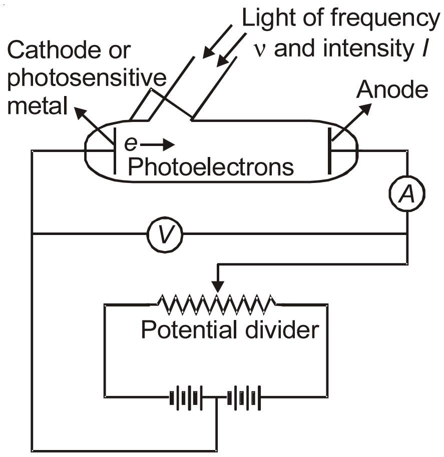
PHOTOELECTRIC EFFECT

The emission of electrons from a metallic surface when illuminated with light of appropriate wavelength (or frequency) is known as photoelectric effect. It was discovered by Hertz in 1887.

Einstein's Theory of Photoelectric Effect

Light of frequency ν consists of stream of packets or quanta of energy $E = h\nu$. These are called photons.

In the process of photoemission, a single photon gives up all its energy to a single electron. As a result, the electron can be ejected instantaneously.



Exp. set up photoelectric effect

Work Function (ϕ) : It is the minimum energy of photon required to liberate an electron from a metal surface.

Threshold Frequency (ν_0) : The frequency of incident radiation below which photoelectric effect does not take place. $h\nu_0 = \phi$.

Stopping Potential (V_0) : The smallest negative value of anode potential which just stops the photocurrent is called the stopping potential.

If the stopping potential is V_0 then $eV_0 = \text{KE}_{\text{max}}$ = Maximum kinetic energy of photoelectrons emitted.

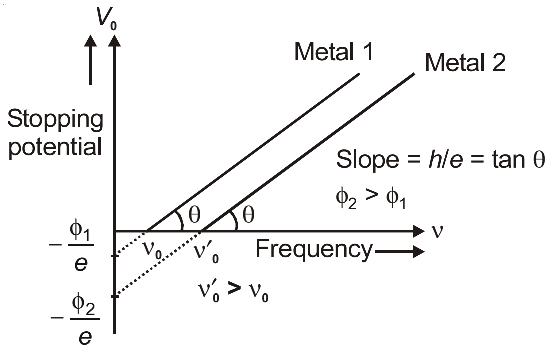
The following important points should be kept in mind :

1. The kinetic energy of photoelectrons varies between zero to KE_{max}.
2. If ν (> ν_0) is frequency of incident photon, $h\nu_0$ is work function then $h\nu - h\nu_0 = \text{KE}_{\text{max}}$. This is Einstein's photoelectric equation. Here h is Planck's constant.
3. Efficiency of photoelectric emission is less than 1%. It means it is not necessary that if the energy of incident photon is greater than work function electrons will definitely be ejected out.
4. If frequency of incident radiation (ν) is doubled, stopping potential (V_0) or kinetic energy maximum (K.E._{max}) gets more than doubled.
5. If on a neutral ball made up of metal of work function ϕ, radiation of frequency ν (greater than threshold frequency) is incident, number of photoelectrons emitted from the ball before the photoelectric emission stops is given by $n = \frac{(h\nu - \phi)4\pi\varepsilon_0 R}{e^2}$.
6. Saturation current depends upon intensity of incident light whereas stopping potential depends upon frequency of light as mentioned in graphs also.

Graphs for Photoelectric Effect (Lenard's Observations)

Following graphs are important :

1.



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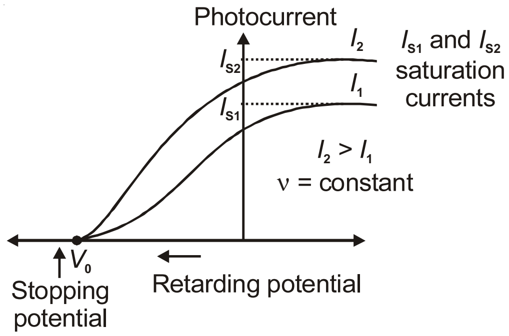

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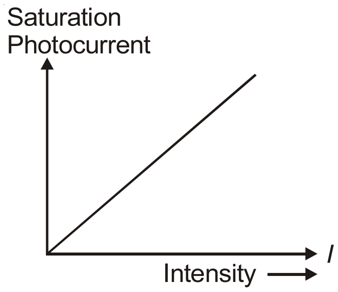

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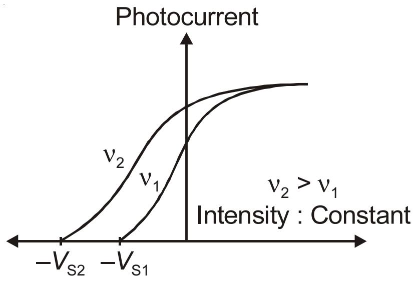


ATOMS AND NUCLEI

BOHR'S ATOMIC MODEL

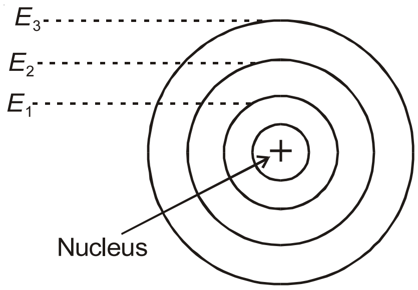
In 1913 Niels Bohr, a Danish physicist, introduced a revolutionary concept *i.e.*, the quantum concept to explain the stability of an atom. He made a simple but bold statement that "The old classical laws which are applicable to bigger bodies cannot be directly applied to the sub-atomic particles such as electrons or protons".

Postulates of Bohr's Theory

1. Electron revolves round the nucleus in circular orbits.
2. Electron can revolve only in those orbits in which angular momentum of the electron about the nucleus is an integral multiple of $\frac{h}{2\pi}$

   i.e., $mvr = \frac{nh}{2\pi}$

   n = principal quantum number of the orbit in which electron is revolving.
3. Electrons in an atom can revolve only in discrete circular orbits called stationary energy levels (shells). An electron in such a shell is characterised by a definite energy, angular momentum and orbit number. While an electron is in any of these orbits it does not radiate energy although it is accelerated.
4. Electrons can jump from one stationary orbit to another stationary orbit. Electrons in outer orbits have greater energy than those in inner orbits. The orbiting electron emits energy when it jumps from a higher energy state to a lower energy state and absorbs energy when it makes a jump from lower orbits to higher orbits. This energy (emitted or absorbed) is in form of photons.



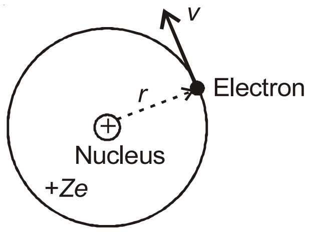
$E_2 - E_1 = h\nu$

where, E_2 = higher energy state

E_1 = lower energy state

and ν = frequency of photons of radiation/emitted absorbed.

Mathematical Analysis of Bohr's Theory



Electric force of attraction provides the centripetal force

$$\Rightarrow \frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{mv^2}{r} \qquad \text{...(i)}$$

where, m = mass of electron

v = velocity (linear) of electron

r = radius of the orbit in which electron is revolving

Z = atomic number of hydrogen like atom

Angular momentum about the nucleus, $mvr = \frac{nh}{2\pi}$ ...(ii)

(a) Velocity of electron in *n*th orbit

Putting value of *mvr* from equation (ii) into equation (i),

$$\frac{1}{4\pi\varepsilon_0}Ze^2 = \left(\frac{nh}{2\pi}\right)v$$

$$\Rightarrow v = \frac{Z}{n}\left[\frac{e^2}{2\varepsilon_0 h}\right] = \frac{Z}{n}.v_0 \qquad \text{...(iii)}$$

where,

$$v_0 = \frac{c}{137} = 2.2 \times 10^6 \text{ m/s}$$

where $c = 3 \times 10^8$ m/s = speed of light in vacuum, $\frac{v_0}{c} = \frac{1}{137}$ = fine structure constant

(b) Radius of the *n*th orbit

Putting value of *v* from equation (iii) in equation (ii), we get,

$$m\left(\frac{Z}{n}\times\frac{e^2}{2\varepsilon_0 h}\right)r=\frac{nh}{2\pi}$$

$$\Rightarrow \quad r=\frac{n^2}{Z}\left[\frac{\varepsilon_0 h^2}{\pi me^2}\right]=\frac{n^2}{Z}.r_0 \qquad \text{...(iv)}$$

where,

$r_0 = 0.53$ Å.

(c) Total energy of electron in n^{th} orbit

From equation (i)

$$\text{K.E.}=\frac{1}{2}mv^2=\frac{Ze^2}{8\pi\varepsilon_0 r}$$

$$\text{and P.E.}=\frac{1}{4\pi\varepsilon_0}\frac{(Ze)(-e)}{r}=-2\text{K.E.}$$

P.E. = – 2 K.E.

Total energy, E = K.E. + P.E. = –K.E.

$$E=\frac{Z^2}{n^2}\left(-\frac{me^4}{8\varepsilon_0^2 h^2}\right)=\frac{Z^2}{n^2}.E_0$$

where, $E_0 = -13.6$ eV.

(d) Time period of revolution of electron in *n*th orbit

$$T=\frac{2\pi r}{v}=\frac{n^3}{Z^2}.T_0$$

where,

$T_0 = 1.51 \times 10^{-16}$ s.

(e) Frequency of revolution in *n*th orbit

$$f=\frac{1}{T}=\frac{Z^2}{n^3}.f_0$$

where,

$f_0 = 6.6 \times 10^{15}$ Hz.

(f) Magnetic field at the centre due to revolution of electron

$$B=\frac{\mu_0 I}{2r}=\frac{\mu_0 e}{2r\,T}=\frac{\mu_0 e}{2r}\times\frac{v}{2\pi r}$$

$$B\propto\frac{v}{r^2} \quad\Rightarrow\quad B\propto\frac{Z}{n}\times\left(\frac{Z}{n^2}\right)^2 \quad\Rightarrow\quad B\propto\frac{Z^3}{n^5}$$

(g) Wavelength of photon

$$\frac{1}{\lambda} = \bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]Z^2$$

where,

$\bar{\nu}$ is called wave number.

R = Rydberg constant

$= 1.09677 \times 10^7\ \text{m}^{-1}$

$= 1.09677 \times 10^{-3}\ \text{Å}^{-1}$ (for stationary nucleus)

$$= \left(\frac{1}{912}\right)\text{Å}^{-1}$$

BINDING ENERGY

The amount of energy needed to separate the constituent nucleons to large distances is called binding energy.

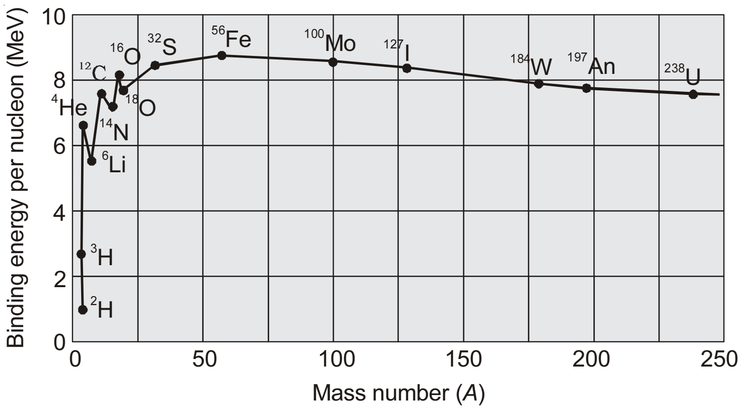
If the nucleons are initially well separated and are brought to form the nucleus, this much energy is released.

$\boxed{\text{BE} = (ZM_p + NM_n - M)c^2}$ (Where M = mass of nucleus and $N = A - Z$)

M_p = Mass of proton, M_n = Mass of neutron.

Binding Energy Curve

B.E./nucleon is very low for light nuclei. This means energy will be released if two nuclei combine to form a single middle mass nucleus. The release of energy in a fusion process is based on this fact.



Likewise, the low B.E. per nucleon for heavy nuclei indicates that if a single heavy nucleus breaks up into middle mass nuclei, energy will be released. Release of energy in fission process is based on this fact.

Note : *1. Binding energy per nucleon is practically constant for 30 < A < 170.*

2. B.E. per nucleon is lower for both light nuclei (A < 30) and heavy nuclei (A > 170).

RADIOACTIVITY

Law of Radioactive Disintegration

$$-\frac{dN}{dt} \propto N$$

$$-\frac{dN}{dt} = \lambda N \text{ (}\lambda\text{ is decay constant)}$$

$$\Rightarrow \quad \boxed{N = N_0 e^{-\lambda t}}$$

Activity $A = -\frac{dN}{dt} = \lambda N_0 e^{-\lambda t}$

$$\boxed{A = A_0 e^{-\lambda t}}$$

Half Life ($T_{1/2}$)

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

Let N_0 be the initial number of active nuclei and N be the number of active nuclei remaining after n half lives then $N = \frac{\mu_0}{2^n}$.

Application : Let R_1 be activity of radioactive substance at $t = T_1$ and R_2 be the activity at $t = T_2$, then
$R_1 = \lambda N_1$ and $R_2 = \lambda N_2$
Number of nuclei disintegrated in $(T_2 - T_1)$ is

$$N_1 - N_2 = \frac{R_1 - R_2}{\lambda} = \frac{(R_1 - R_2)T}{\ln 2}$$

where T is the half life of radioactive substance.

Average Life (T_{av})

$$\boxed{T_{av} = \frac{1}{\lambda} = \frac{T_{1/2}}{\ln 2}} \text{ or } T_{av} = 1.44\ T_{1/2} \text{ or } T_{1/2} = 0.693\ T_{av}$$

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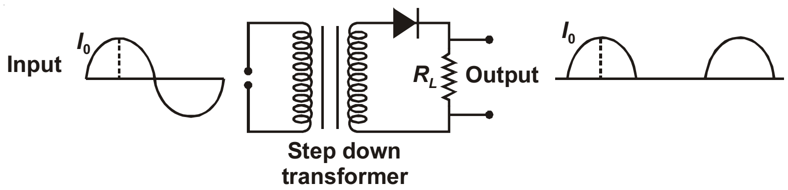
Chapter 17

Electronic Devices and Communication Systems

DIODE AS RECTIFIER

A device to convert ac into dc.

1. Half Wave Rectifier



$I_{\text{rms}} = \frac{I_0}{2}$

$I_{\text{mean}} = \frac{I_0}{\pi}$

form factor $= \frac{I_{\text{rms}}}{I_{\text{mean}}} = 1.57$

Important points :

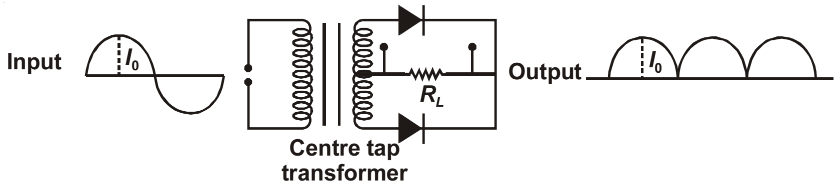
a. Input frequency = Out put frequency.

b. Maximum Efficiency = 40.6%

c. Ripple factor $r = \frac{\text{ac component}}{\text{dc component}} = \sqrt{\frac{I_{\text{rms}}^2}{I_{\text{mean}}^2} - 1} = 1.21$.

d. Efficiency of half wave rectifier $= \frac{0.406 R_L}{r_f + R_L}$

2. Full Wave Rectifier



$I_{\text{rms}} = \frac{I_0}{\sqrt{2}}$

$I_{\text{mean}} = \frac{2I_0}{\pi}$

a. Out put frequency = 2 × input frequency

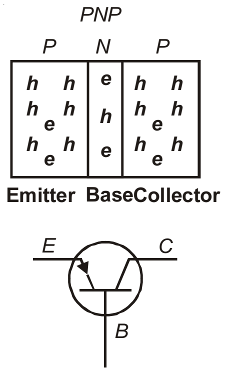
b. Maximum Efficiency = 81.2%.

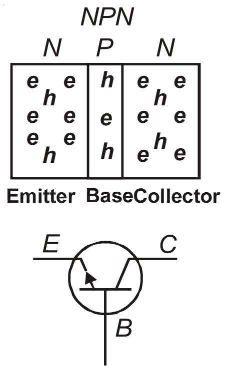
c. Ripple factor r = 0.48.

d. Efficiency of full wave rectifier $= \frac{0.812 R_L}{r_f + R_L}$

JUNCTION TRANSISTOR

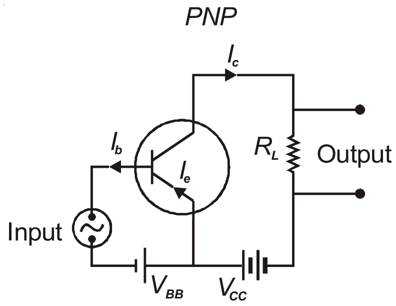
Symbols used for transistors are shown here :

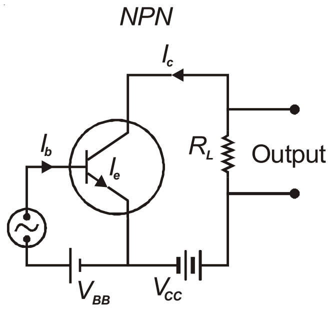




Common-Emitter (CE) Amplifier

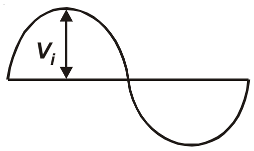
$$\boxed{I_e = I_b + I_c}$$

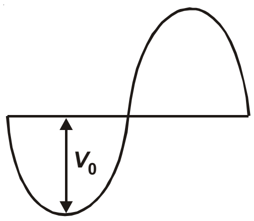




Input $v_i = V_i \sin\ t$

Output $v_0 = V_0 \sin(\ t \pm \pi)$





Important Points related to CE-Amplifier

1. There is phase reversal of 180°.
2. DC current gain $\beta = \frac{I_c}{I_b}$.
3. AC current gain $\beta_{ac} = \frac{I_c}{I_b}$.
4. AC voltage gain $A_v = \frac{V_0}{V_i}$.
5. AC power gain = $\beta_{ac} \times A_v$ [maximum in *CE* mode]

6. Resistance gain $R_g = \frac{R_L}{R_i}$ (R_i = input resistance).

7. $\frac{1}{\alpha} - \frac{1}{\beta} = 1$

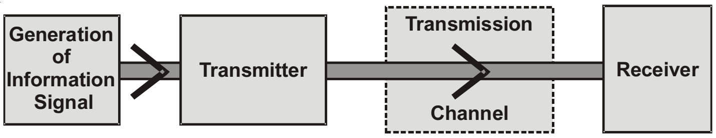
8. $\alpha < 1, \beta > 1$

9. Transconductance $g_m = \frac{I_c}{V_i}$

COMMUNICATION SYSTEMS

Communication of information to each other is a basic human activity. For example, one person wishes to tell something or give a message to another person sitting near him. Then he speaks and transmits sound waves through air medium or channel. The other person receives the message by listening through his/her ears. In modern communication systems the information is first converted into electrical signals or electromagnetic waves and then sent electronically. This has the advantage of speed, reliability and possibility of communicating over long distances.

The key to communication system is to obtain an electrical signal voltage or current which contains the information. For example, a microphone can convert speech signals into electrical signals. Similarly, pressure can be sensed by **piezoelectric** sensor which gives pressure in terms of electrical signal. A signal is defined as **a single-valued function of time (that conveys the information) and which, at every instant of time has a unique value.**



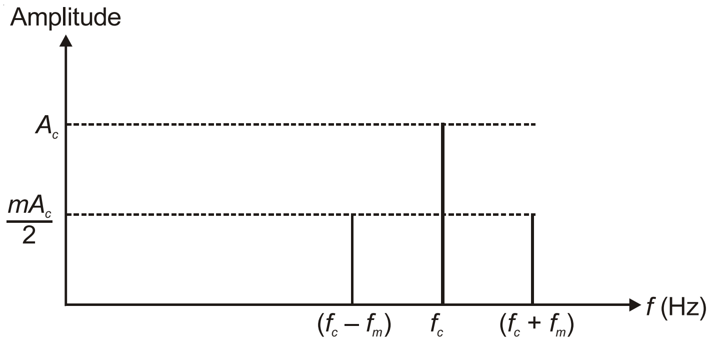
Basic units of all communication systems

1. An AM-wave is equivalent to the summation of three sinusoidal waves whose frequencies are $_c$, $(_c + _m)$ and $(_c - _m)$ and the amplitudes are respectively V_c, $\frac{mV_c}{2}$ and $\frac{mV_c}{2}$

2. The frequency f_c is known as **carrier frequency** and $(f_c + f_m)$ and $(f_c - f_m)$ are known as **Upper side band** and **Lower side band** respectively.

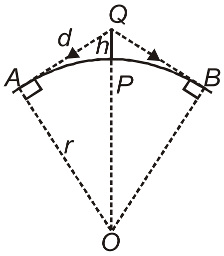
> ***Note :*** *In an AM-wave the difference between upper side band and lower side band (which is equal to* $2f_m$*) is known as the* ***band width****.*

Graphically, the carrier frequency and the side bands can be shown as :



Space Wave Propagation or Tropospheric Wave Propagation

The transmitted waves, travelling in a straight line, directly reach the receiver end and are then picked up by the receiving antenna. This mode of communication is termed as **Line of sight communication.**



Ray path of transmitted waves following space-wave (or line of sight) mode of propagation. The transmitter is located at the ground on a tall lower.

Range

$$d = \sqrt{2rh} \qquad \begin{bmatrix} r : \text{Radius of earth} \\ h : \text{Height of transmitting antenna} \end{bmatrix}$$

This distance is of the order of 40 km.

* * *