General Elective I

ATOMIC STRUCTURE

Bohr's Theory :-

i) According to this theory electron revolves in definite circular orbit around the nucleus and these orbits are designated by letter K, L, M, N for 1, 2, 3.

i) As long as the electron revolves in particular orbit they can neither gain energy and lose energy such orbit are called stationary orbit or state.

ii) When an electron moves from lower state to higher state obserption takes place.

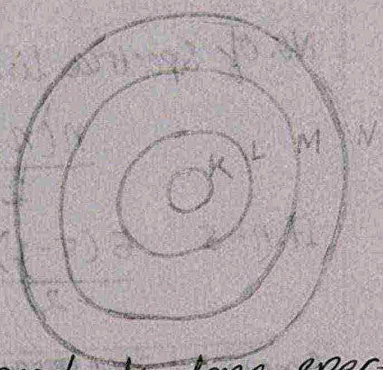
iii) When an electron moves from higher state to lower state emission of energy takes place.

iv) When an electron trasition takes place between two state that differ in energy by.

$$\Delta E = h\nu = E_2 - E_1$$

The angular momentum of an electron is given by

$$mvr = \frac{nh}{2\pi}$$



It explains stability of atom and also line spectrum of hydrogen atom.

Limitation of Bohr's Theory :-

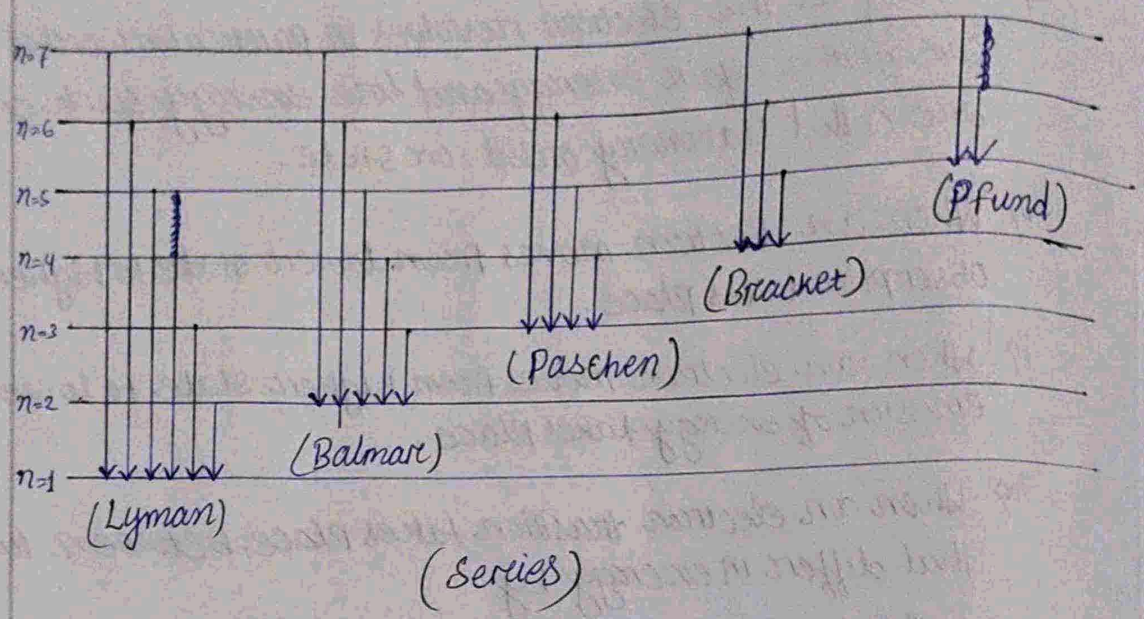
i) It works only to single electron atom like He^+, Li^{2+} etc.

ii) It fails to explain the fine structure of hydrogen atom.

iii) It could not explain the stability of atom to find molecules by chemical bond.

Spectral Series Of H-atom :-

In hydrogen spectrum each group of spectral lines corresponding to electron transition to a perticular state.



No. of Spectra lines (transition) protons :-

$$\frac{n(n-1)}{2}$$

If $n=5$ $\quad \frac{5(5-1)}{2} = \frac{5\times4}{2} = \frac{20}{2} = 10$

Spectral Series	Low energy level	High energy level	Longest wavelength $n=p+1$	Shortest wave length	$\frac{\lambda \text{ longest}}{\lambda \text{ shortest}}$
Lymen series	1	∞	2	∞	$\frac{n^2}{n^2p^2} = 4:3$
Balmar series	2	∞	3	∞	9:5
Paschen Series	3	∞	4	∞	16:7
Bracket Series	4	∞	5	∞	25:9
Pfund Series	5	∞	6	∞	36:11

~~Summerfield atomic theory~~ :-

Debroglie wavelength = λ

$$\lambda = \frac{h}{mv}$$

Where, m = mass of the particle
v = velocity
h = Planck's constant

we know that $mv = p$ (momentum)

$$\lambda = h/p$$

p = linear momentum of the particle.

Kinetic energy $= \frac{1}{2}mv^2$

$$= \frac{1}{2} \times m \times (p/m)^2 \quad \left(\because mv = p \Rightarrow v = p/m\right)$$

$$\Rightarrow E = \frac{1}{2} \times \frac{p^2}{m}$$

$$\Rightarrow 2mE = p^2$$

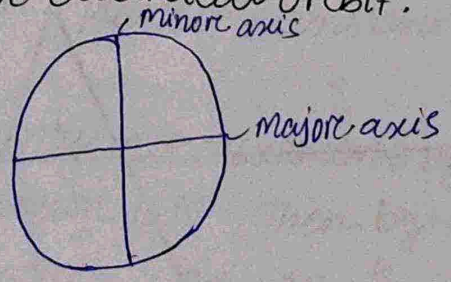
$$\Rightarrow p = \sqrt{2mE}$$

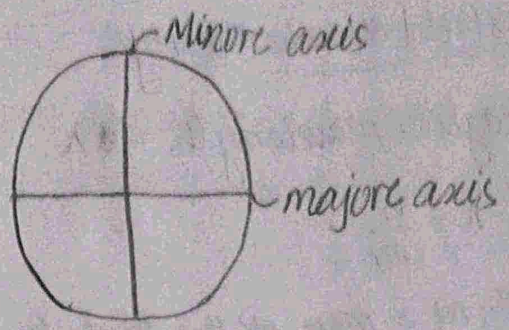
$$\lambda = \frac{h}{\sqrt{2mE}}$$

Summerfield atomic theory :-

→ Atomic spectrum studied with high resolution spectroscope. Each line was found to have a no. of closely spaced line.

→ Extended bohrs model by proposing that electrons in an atom have electrical orbit.





Majore axis → Principal quantum no. (n)
Minore axis → ~~Azumi~~ Azimuthal quantum no. (k)

$$\frac{n}{k} = \frac{\text{length of majore axis}}{\text{length of minore axis}}$$

When, $n = 3$
$k = 1, 2, 3$

$n = 4$
$k = 1, 2, 3, 4$

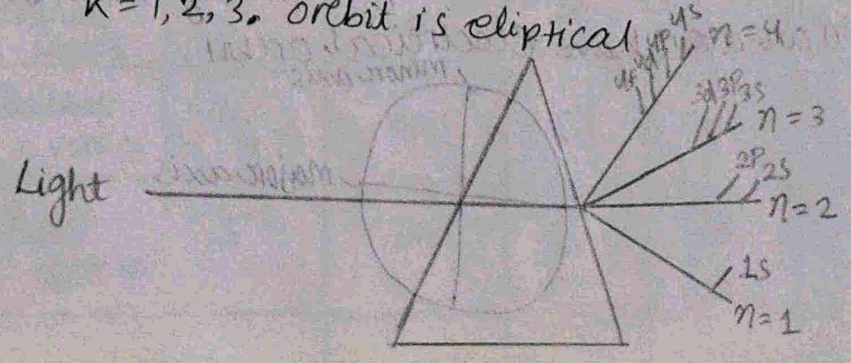
$n = 5$
$k = 1, 2, 3, 4, 5$

When, $n = 3$
$k = 3$ orbit is ~~cic~~ Circulare.

$n = 3$
$k = 1$ ore 2 orbit is eliptical

$n = 4$
$k = 4$ orbit is circulare

$n = 4$
$k = 1, 2, 3.$ orbit is eliptical



~~Heig~~ Heisenberg's Uncertainty Principle :-

According to this Principle microscopically it is Possible to exactly measure the position of a moving Particle of any instant and momentum of particle at that position. But microscopically it is not possible to measure exactly the position of the particle and its momentum simultaniously.

→ The reason is that behaviour of a moving particle is expressed by a wave packet any where of a group velocity.

→ According to maxburn, Particle can be found any-where within the wave packet. That is position of the Particle is uncertainity within the limit of wave packet.

→ For an extended wave packet the momentum of the Particle can be exactly measure but its position cannot be determined.

→ Exactly on other word if a wave packet is small the momentum of the particle cannot be determined.

→ According to Heisenberg's uncertainty principle the Product of uncertainty in the measurement of momentum and position of particle is of orderc $\frac{h}{2\pi}$ where, h = planck's constant.

If the uncertainty in measurement of position is Δx while the momentum is ΔP. Then by Heisenberg's uncertainty principle is $\Delta x \times \Delta P = \frac{h}{2\pi} = \hbar$

→ The exact form of the product of uncertainty in position and momentum of particles cannot be less than $\frac{1}{2}\hbar$

$$\Delta x \times \Delta P \geq \frac{\hbar}{2}$$

$$\Rightarrow \Delta x \times \Delta P \geq \frac{h}{2\pi} \times \frac{\hbar}{2}$$

$$\Rightarrow \boxed{\Delta x \times \Delta P = \frac{h^2}{4\pi}}$$

Schrodinger wave equation for hydrogen atom:-

Schrodinger equation is established to explain the behaviour of electronic wave in an atom and molecule.

→ In schrodinger equation the stationary ~~to~~ energy level proposed by Bohr's was replaced by electronic function (ψ).

The classical wave equation for a particle moving along x-axis is given by,

$$\psi = A \sin 2\pi \frac{x}{\lambda} \quad \text{—— (1)}$$

Where, ψ = wave function of the amplitude

λ = wavelength of the standing wave travelling along x-axis.

x = distance of the particle from the nucleous.

Differentiating eq^n(1) with respect to x.

$$\frac{d\psi}{dx} = A \cos 2\pi \frac{x}{\lambda} \left(\frac{2\pi}{\lambda}\right)$$

Differentiating again w.r.t. x

$$\frac{d^2\psi}{dx^2} = \frac{2\pi A}{\lambda} - \sin\frac{2\pi x}{\lambda}\left(\frac{2\pi}{\lambda}\right)$$

$$= -\frac{4\pi^2 A}{\lambda^2}\sin\frac{2\pi x}{\lambda}$$

$$= \frac{-4\pi^2}{\lambda^2}\left[A\sin 2\pi\left(\frac{x}{\lambda}\right)\right]$$

$$= \frac{-4\pi^2\psi}{\lambda^2}\left[\because \psi = A\sin 2\pi\left(\frac{x}{\lambda}\right)\right]$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2\psi}{\lambda^2} = 0 \quad \text{——— (2)}$$

Eq^n(2) represent wave motion of any particle in x-axis.

Since, electron is considered along x, y, z axis Eq^n(2) will be

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{4\pi^2}{\lambda^2} = 0$$

(When particles move in 3D)

$$= \nabla^2\psi + \frac{4\pi^2\psi}{\lambda^2} = 0$$

$$\lambda = \frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2}$$ (This is laplace's equation)

$$\Rightarrow \frac{4\pi^2\psi}{\lambda^2} = \nabla^2\psi$$

$$\Rightarrow \frac{1}{\lambda^2} = \frac{\nabla^2\psi}{4\pi^2\psi} \quad \text{——— (3)}$$

According to de-broglie equation

$$\lambda = \frac{h}{mv}$$

$$\Rightarrow \lambda^2 = \frac{h^2}{m^2v^2}$$

$$\Rightarrow \frac{1}{\lambda^2} = \frac{m^2v^2}{h^2}$$

$$\Rightarrow \frac{m^2v^2}{h^2} = \frac{-\nabla^2\psi}{4\pi^2\psi}$$

$$\Rightarrow m^2v^2 = -\nabla^2\psi \times \frac{h^2}{4\pi^2\psi}$$

$$\Rightarrow mv^2 = -\nabla^2\psi \times \frac{h^2}{4\pi^2\psi m}$$

$$\Rightarrow \frac{1}{2}mv^2 = -\frac{1}{2}\Delta\psi^2 \times \frac{h^2}{4\pi^2\psi m}$$

$$K.E = -\Delta^2\psi \times \frac{h^2}{8\pi^2\psi m}$$

$$\Rightarrow \Delta^2\psi + K.E \cdot \frac{8\pi^2\psi m}{h^2} = 0 \quad \text{——(4)}$$

Since total energy of the system = sum of total of Potential and K.E energy

$$E = P.E + K.E$$

$$\Rightarrow E - PE = K.E$$

$$\Rightarrow K.E = E - P.E$$

Substituting the value of K.E in eq^n(4)

$$\Delta^2\psi + (E - PE) \cdot \frac{8\pi^2\psi m}{h^2} = 0$$

$$\Rightarrow \Delta^2\psi + (E - V) \cdot \frac{8\pi^2\psi m h^2}{h^2} = 0$$

This Schrodinger equation for the particle moving in three dimension.

→ For H-atom having nuclear charge.

→ Ze and electronic charge -e.

→ The potential energy is given by

$$V = \frac{-Ze \times e}{r} = \frac{-Ze^2}{r}$$

→ Substituting value of V is schrodinger value equation.

$$\nabla^2\psi + \left(E + \frac{Ze^2}{r}\right) \cdot \frac{8\pi^2 \psi m}{h^2} = 0$$

$$\Rightarrow \nabla^2\psi + \left(E + \frac{Ze^2}{r}\right) \cdot \frac{8\pi^2 \psi m}{h^2} = 0$$

∴ This schrodinger wave equation for H-atom.

Significance of schrodinger wave equation :-

→ Schrodinger wave equation is second order differentiated equation, hence it was many solution for ψ.

→ Most of the solution may be imaginary has no significant, only those value of ψ will be significant which satisfy the following condition.

→ The wave function must definite and continuous.

→ The solution must be single value.

→ $\frac{d\psi}{dx}, \frac{d\psi}{dy}, \frac{d\psi}{dz}$ must be continous function of x, y, z respectively.

→ The probability of finding an e^- over the entire space must to be equal to 1.

$\int d\psi^2 . dx . dy . dz = 1$

Where ψ^2 = probability density of e^- arround the nucleous.

→ Schrodinger wave equation for H-atom when solve the energy of e in H-atom is round to be.

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

$$= -13.\frac{6}{m^2}$$ ~~P/atom~~ electron ~~volt~~ Volt / atom.

→ During the solution of schrodinger wave equation three constant (n, l, m) are involved. This three constant most be signify three quantum no. of an electron.

'n' represents for principal quantum no.
'l' represents for ~~Azumithal~~ Azumithal quantum no.
'm' represents for magnetic quantum no.

→ It helps to calculate the probability of finding electron around nucleus in different energy state.

Significane of shy (ψ) :-

→ It is a wave function which solution to schrodinger wave equation.

→ It is represent the amplitude of the wave describe how this amplitude varies with distance of direction.

→ Schrodinger wave equation have different value of ψ.

→ All values may not be significant.

→ The significant value of the wave function is known as Eigen value and the wave function is called Eigen function.

Significant of ψ^2 :-

ψ^2 = density of electron

→ For light wave ψ^2 represents intensity of light.

→ For electronic wave ψ^2 represents intensity of e^- at any point namely it represent probable density of electron around the nucleous.

→ ψ^2 is always more significant than ψ because a wave function ψ may be real may be imaginary.

→ But ψ^2 is always real

$\psi = a + ib$ imaginary number

$\psi^* = a - ib$

Hence $\psi^2 = \psi \times \psi^*$

$= (a+ib)(a-ib)$

$= a^2 - (ib)^2$

$= a^2 + b^2$ is a real no.

→ Schrodinger wave equation in polar coordinates :-

Quantum number :-

Quantum numbers are physical constants use to solve Schrodinger wave equation and to explain the orbital concept of atomic number.

i) Principal quantum number (n)

ii) Azimuthal quantum number (l)

iii) Magnetic quantum number (m)

iv) Spin quantum number

i) Principal quantum number (n) :-

→ It represents measure the energy level which e^- belongs

Where, $n = 1$ (K shell)

$n = 2$ (L shell)

$n = 3$ (M Shell)
$n = 4$ (N Shell)

→ It also gives the average distance of the electron from the nucleus.

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 Z}$$

Where, h = planck's constant
Z = Atomic number
n = Number of shell
m = mass
e = electron.

→ It also determine the energy of an electron in an orbits.

$$E_n = \frac{-2\pi^2 m e^4 Z^2}{n^2 h^2}$$

For hydrogen atom $E_n = \frac{-13.6}{h^2}$ e.v/atom

→ The ~~Maximum~~ maximum number of e^- that can present in a shell is equal to $2n^2$

For, K Shell = 2 electron
L Shell = 8 electron
M Shell = 18 electron
N Shell = 32 electron

→ The number of orbitals that can present in a shell is equal to n^2.

→ The number of sub-shell than can present in a shell is equal to the shell ~~no~~ number.

Azimuthal quantum number :-

→ It represent the measure sub-shell present in a shell.

→ The value of azimuthal quantum number varies from to (n-1).

K shell (n=1)	$l = 0$	s - Subshell
L shell (n=2)	$l = 0$ $l = 1$	p - Sub shell
M shell (n=3)	$l = 0$ $l = 1$ $l = 2$	d - Sub shell
N shell (n=4)	$l = 0$ $l = 1$ $l = 2$ $l = 3$	f - Sub shell

→ The number of electron that can present in a sub-shell is given by $4l+2$.

→ s - subshell max. electron = $2e^-$

p - Subshell max. electron = $6e^-$

d - subshell max. electron = $10e^-$

f - subshell max. electron = $14e^-$

→ The number of orbital that can be present in a subshell is given by $2l+1$.

For s - subshell $(2 \times 0 + 1 = 1)$

→ It also represents orbitals angular momentum & sub-shell and given by $\frac{h}{2\pi}\sqrt{l(l+1)}$

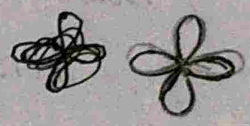
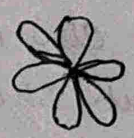
Magnetic quantum number:

→ It represents the number of orbitals present in a shell.

→ The value of magnetic quantum number m from $-l$ to l.

K Shell ($n=1$)	$l=0$	$m=0$	
L Shell ($n=2$)	$l=0$ $l=1$	$m=0$ $m=-1,0,1$	(4 orbits)
M Shell ($n=3$)	$l=0$ $l=1$ $l=2$	$m=0$ $m=-1,0,1$ $m=-2,-1,0,1,2$	(9 orbits)
N Shell ($n=4$)	$l=0$ $l=1$ $l=2$ $l=3$	$m=0$ $m=-1,0,1$ $m=-2,-1,0,1,2$ $m=-3,-2,-1,0,1,2,3$	(16 orbits)

→ It also signify the shape of orbital.

	Shape	Structure
s- orbital → 1	Spherical	
P- orbital → 3	Dumbell	
d- orbital → 5	Double dumbell	
f-orbital → 7	Difuse	

Spin quantum number :-

→ It represent the orientation or spin of electron around its own axis.

→ When the spin of electron is clockwise $s = +1/2$ and When the spin of electron is anti-clockwise $s = -1/2$

Pauli's exclusion Principle :-

→ According to this Principle two electrons in the orbitals of an atom can have all 4 quantum number are not alive.

→ For any two electrons of value of 3 quantum number (n, l, m) may be the same.

Ex :- For 1st orbit of K - shell

we have $n = 1$, $l = 0$, $m = 0$, $s = +1/2$

$n = 1$, $l = 0$, $m = 0$, $s = -1/2$

From the above we see that :-

i) an orbital can not have more than 2 electrons

ii) the electrons which occupy the same have opposite spin.

iii) the ~~electron~~ maximum number of e^- present in a given shell is equal to $2n^2$. Thus the 2nd, 3rd and 4th shell we have maximum number of electron are 8, 18, 32 respectively.

→ This principle is called exclusion principle because it excludes the probality of accumadating more than $2n^2$ electrons in an orbits.

Hund's rule :-

Hund's rule of maximum multiplicity :-

According to this rule no electron pairing takes place in the orbital of P, d, f sub-shell each orbitals single filled with electrons having parallel spin.

Explanation of Hund's rule:

Consider the electron configuration of carbon atom

$_6C - 1s^2 2s^2 2p^2$

Carbon atom has two orbitals in its 2p sub-shell. This two electrons can be distributed in P_x, P_y, P_z orbitals of same energy as follow.

$_6C - 1s^2 2s^2 2p^2$

↑↓	↑↓	1	1	
		P_x	P_y	P_z

$_7N - 1s^2 2s^2 2p^3$

↑↓	↑↓	1	1	1
		P_x	P_y	P_z

$_8O - 1s^2 2s^2 2p^4$

↑↓	↑↓	↑↓	1	1
		P_x	P_y	P_z

$_9F - 1s^2 2s^2 2p^5$

↑↓	↑↓	↑↓	↑↓	1
		P_x	P_y	P_z

$_{10}Ne - 1s^2 2s^2 2p^6$

↑↓	↑↓	↑↓	↑↓	↑↓
		P_x	P_y	P_z

→ No pairing of electrons in orbitals of same energy takes place unless each orbital is single filled.

→ When different orbitals of same energy ½ filled or less than ½ filled the electron should have parallel spin. It is because the parallel arrangement spin is more stable than ~~and~~ antiparallel arrangement.

→ Exactly ½ filled and fulfilled orbitals are more stable.

Ex:- ns^2, np^3, np^6, nd^5, nd^{10}, nf^7, nf^{14} configuration are ~~more~~ most stable.

Aufbau Principle :-

According to this principle the electron are filled in various orbitals in the order of there increasing energy.

→ An orbital with lowest energy will be filled first. The energy content of the two sub-shell can be compared by means of $(n+l)$ rule.

→ The sub-shell with lower $(n+l)$ value will posess lower energy and will be filled first.

Ex:- 4s subshell is filled first than 3d

a) For 4s sub-shell $n+l = 4+0 = 4$

b) For 3d sub-shell $n+l = 3+2 = 5$

→ The sub-shell with lower value of n posess lower energy, if $(n+l)$ value of both the sub-shell are equal.

Ex:- 3p subshell is filled first than 4s

a) For 3p sub-shell $n+l = 3+1 = 4$

b) For 4s sub-shell $n+l = 4+0 = 4$

→ 3p sub-shell has lower energy than 4s sub-shell and is filled first.

→ The increasing order of energy of various ~~en~~ energy sub-shell is as follow.

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d$

Limitation :-

→ In 3rd, 4th, 5th subshell $(n-1)d$ subshell & ns subshell are very closed to energy but $(n-1)d$ subshell has some higher energy.

→ Hence electronic configuration of

$_{29}Cu - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

$_{24}Cr - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

→ $_{29}Cu$ is $3d^9 4s^2$ not ..... $3d^{10}, 4s^1$

→ According to Aufbau Principle the outer electronic configuration of 43 (Tc) should be $5s^2 4d^5$ but not $5s^1 4d^6$.

→ According to Aufbau Principle the outer electronic configuration of Paladium (Pd) should be $5s^2 3d^8$ but not $5s^0 3d^{10}$.

UNIT - II

Chemical Bonding

Ionic Bond :-

Electrovalent or Ionic bond lattice energy.

i) This type of bond is formed between two dissimilar atom A and B.

ii) The atom A has one or more electrons more than nearest inert gas configuration and has low ionisation potential.

iii) The atom B has one or more electrons less than nearest inert gas configuration and high electron affinity.

iv) The atom A that looses n electrons is said to be oxidised to A^{+n}

v) Atom B that gain n electrons is said to be reduce to B^{-n}.

vi) Thus the formation of Ionic bond from elements involves an oxidation reduction reaction.

vii) Ionic bond is non directional. Such compounds which are formed by the transference of one or more electrons from one atoms to other atoms are called electrovalent or Ionic compound and this type of linkage is called electrovalent linkage.

$$\underset{(2,8,1)}{Na^{\times}} \longrightarrow \cdot\underset{\cdot\cdot}{\ddot{Cl}}: \longrightarrow \underset{(2,8)}{Na^{+}} \longrightarrow :\underset{\cdot\cdot}{\ddot{Cl}}^{-}$$

General characteristics of Ionic compounds :-

Hard and rigid :-

Ionic compounds are hard and rigid.

High density :-

→ The cations and anions are held together by strong electrostatic force of attraction in an Ionic compounds.

→ The volume of the system thus decreases and density increase.

High melting points and boiling points :-

→ The cations and anions are held together in an ionic compound.

→ A large amount of energy is needed to overcome this forces to cause breaking down of crystal lattics.

Conductivity :-

→ This compounds are good conductors of electricity.

Non directional nature :-

These ions will attract oppositely charged ion from all direction hence ionic bond is non directional.

High solubility in water :-

Due to high dielectric constant the force of attraction between cations and anions of the ionic compound decreases.

→ Thus the ion separate the ionic compound dissolves in water.

Highly Breittle :-

→ Ionic solids are generally very breittle.

→ The cations and anions are inter locked alternatively to form compact mass.

→ When a little stress is applied the ions which similar charged come together and began triple each other.

→ This tendency makes the solid break easily.

→ Hence ionic solid are highly breittle.

Types of Ions :-

→ Ions with no outer electrons

→ Ions with Irregular configuration.

Ex:- Pb^{-4}, Ge_2^{+2}

Poly atomic Ions :-

→ Ions with nobel gas configuration.

→ 18 electron cell ions.

Radius ratio :-

→ In an ionic crystal A^+, B^- the radius ratio means the ratio of size of cation to that anion.

→ Radius ratio = $\frac{\text{Size of cation}}{\text{Size of anion}} = \frac{r^+}{r^-}$

→ Shape of an ionic solid, solid depends on the limiting radius ratio values and the corresponding coordination number of cation.

r^+/r^-	Coordination no. of cation	Shape
0 to 0.155	2	Linear
0.155 to 0.225	3	Triangular
0.225 to 0.414	4	Tetrahedral
0.414 to 0.732	6	Octahedral
0.732 to 1.	8	Cubic
1	12	Close packing

Radius ratio rule :-

→ In an ionic crystal A, B^-, A^+ ion, ion is surrounded by a definite number of B^- ion. This is called coordination number of A^+ ion. similarly, B^- ion are surrounded by a definite number A^+ ion in an ionic crystal (A^+B^-). This number is called the coordination number of B^- ion.

→ In a binary compound AB, the coordination number of A^+ ion = The coordination number of B^- ion.

→ In a AB type ~~compound~~ compound, the coordination number of A^+ ion = 2 × coordination number of B^- ion.

→ The coordination number which provides most stable structure, any pair of A^+B and B^- ion depends upon the value of radius ratio.

Packing of ion in crystal :-

In an ionic crystal the +ve and -ve ions arrangeed themselve in such a way that the compound attain, minimum potential energy or maximum stability.

→ Ionic compounds are following type

(i) AB type ionic compounds

(ii) AB_2 type ionic compounds

(iii) AB_3 type ionic compounds

AB type ionic compound :-

NaCl, CsCl, ZnS, having which symmetry ionic compound.

having hexagonal structure.

Structure of NaCl :-

Radius ~~ratio~~ cation in NaCl

Radius ratio ~~ro~~ is $= \frac{Na^+}{Cl^-} = \frac{0.95 Å}{1.81 Å}$

$= 0.524 Å$

This value is less 0.732. Hence the coordination number should be 6 or 4.

→ Thus Na^+, Cl^- should have square planner or octahedral structure.

Structure of CsCl :-

Radius ratio of CsCl $= \frac{Cs^+}{Cl^-} = \frac{1.69}{1.81}$

$= 0.93 Å$

CsCl has body center cubic structure.

→ CsCl lattice is more stable stable than NaCl because higher the coordination number greater will be the number of ions of opposite charges surround its centerion and greater the force of attraction.

→ CsCl lattice has actually even found, one or more stable than that of NaCl structure.

Application of Born Equation :-

Consider NaCl crystal.

On a crystal there are many $Na^{\oplus}$ and $Cl^{\ominus}$ ion.

Each $Na^{\oplus}$ ion is surrounded by

(i) 6 $Cl^{\ominus}$ ions at a distance (r).

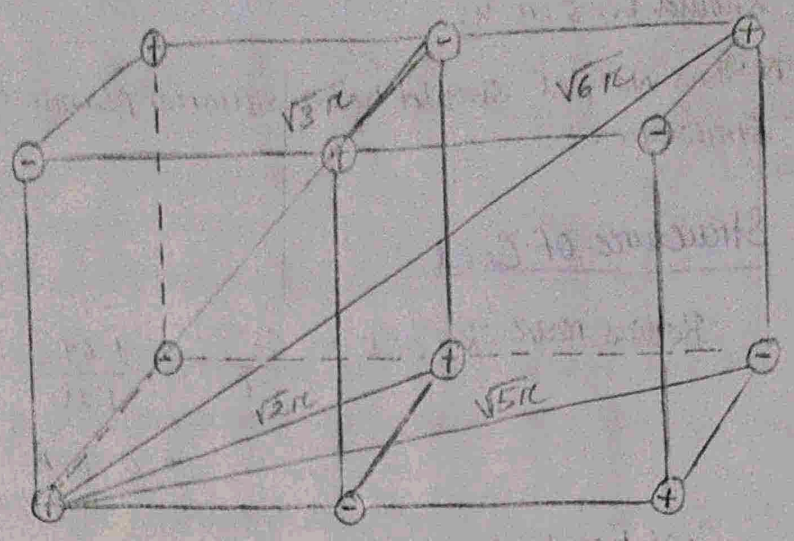
(ii) 8 $Cl^{\ominus}$ more at a distance $\sqrt{3}r$

(iii) 24 more $Cl^{\ominus}$ ions at a distance $\sqrt{5}r$

(iv) 6 more $Na^{\oplus}$ ions at a distance $2r$

(v) 12 more $Na^{\oplus}$ ions at a distance $\sqrt{2}r$

(vi) 24 more $Na^{\oplus}$ ions at a distance $\sqrt{6}r$



Lattice Energy :-

The amount of energy released when 1 mole of ionic Solid is prepared from its constituent gaseous ion is called lattice energy.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) + L.E$$

Amount of energy required to break 1 mole of ionic Solids into its constituent gaseous ion is called lattice energy.

$$NaCl(s) \xrightarrow{L.E} Na^+(g) + Cl^-(g)$$

Charge on ions :-

→ Greater the charge on the ions, greater is the force of attraction and higher is the value of lattice energy.

Lattice energy $\propto$ charge on ion.

Size of ion :-

→ Smaller the size of ion less with the inter-nuclear distance and greater will be the force of attraction. Hence higher will be the value of lattice energy.

→ Greater the lattice energy of a compound lesser will be its solubility.

Q: Which of the following is more soluble and why?

Ans. **NaCl and KCl :-**

KCl is more soluble than NaCl due to largest size of K^+ ion in comparision of Na^+ ion, which in term possess lower lattice energy.

NaCl and MgCl :-

MgCl is soluble than NaCl due to the more charge on magnesium than sodium which takes ~~Pla~~ low lattice energy.

NaCl and NH_4Cl :-

NH_4Cl is more soluble than NaCl due to inter molecular hydrogen bonding with water molecule.

Born-Haber cycle :-

It is used to calculated the amount of lattice energy released during the formation of an ionic solid.

$$
\begin{array}{ccc}
Na(s) + \frac{1}{2}Cl(g) & \longrightarrow & NaCl(s) + \Delta H \\
\Delta H \downarrow & \downarrow \Delta H & \\
Na(g) & Cl(g) & \\
I.E \downarrow & \downarrow I.E & \\
Na^+(g) + Cl^-(g) & \longrightarrow & \uparrow L.E
\end{array}
$$

$\Delta H_{Formation} = \Delta H_{sublimation} + I.E + 1H + E.A + L.E$

(Ionisation energy) (Electron affinity)

The formation of ionic solid can be described by following two process.

i) Direct Process :-

In this process $Na(s)$ & $\frac{1}{2} Cl_2(g)$ combine directly to form 1 mole of NaCl the amount of energy released in this process is called enthalpy of formation.

ii) Indirect Process :-

The Sublimation of $Na(s)$ to $Na(g)$:-

In this step 1 mole of $Na(s)$ is converted into 1 mole of $Na(g)$. The energy require for this process is enthalpy of sublimation.

Dissociation :-

In this step $\frac{1}{2}$ mole of $Cl_2(g)$ is disociated into $Cl(g)$. The energy required for this process is enthalpy of disociation.

Ionisation :-

In this step $Na(g)$ is converted into $Na^+(g)$. The enthalpy required is ionization energy and ionisation potential.

Conversion of $Cl(g)$ to $Cl^-(g)$:-

In this step the amount of energy released is called electron affinity.

Combination of Na^+ and Cl^- to form $NaCl(s)$:-

The amount of energy released in this process is called lattice energy.

According to Hesses's law the amount of energy evolved or absorbed during a chemical process whether it takes place in one step or multiple step the energy is always constant.

$\Delta H_{form^n} = \Delta H_{sub} + I.E + 1H_{dis^n} + E.A + L.E$

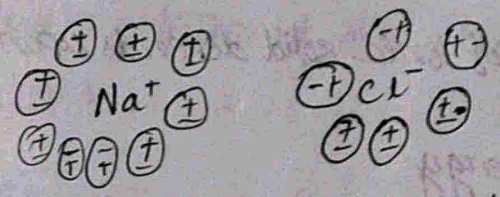
Solvation Energy :-

When an ionic solid is dissolved in the solvent the cation and anion present in the solid get surrounded by the negative and ~~posst~~ positive and the solvent molecule, this phenomenon is called Solvation or Hydration.

→ The amount of energy released when 1 molecule of anion is completely solvated by the solvent molecule.

$$K^+_{(aq)} + H_2O \longrightarrow K^+Ca_2 + S.E$$

$$NaCl + solvent \longrightarrow Na^+ + Cl^- + solvation\ energy$$



Hydration → Addition of H_2O remain as single unit.

Hydrolysis → Addition of H_2O break as H^+ and OH^- ion.

Factors

Size of ion

Smaller the size of ion greater is the degree of solvation and greater is the solvation energy,

$$\text{Size of ion} \propto \frac{1}{\text{Hydration energy}}$$

Charge on ion:-

Greater the charge of the ion smaller is the size and greater is the value of Hydration energy.

Which of the following compound has greater degree of conductance comparison between Nacl and Kcl.

Ans. The conductivity power of Nacl and Kcl due to large size of K^+ ion in comparision to Na^+ ion.

→ Since greater the size of ion lesser is the value of solvation and greater is its mobility.

→ Due to the greater mobility of K^+ ion in comparison to Na^+ ion hence Kcl possess greater value of conductance.

→ Greater is the value of solvation energy greater is the value of solubility of ionic solid.

→ The overal dissolution of ionic solid depends upon the two factor

(i) Hydration energy

(ii) Lattice energy

Again the degree of dissociation depends upon the enthalpy of solution.

$$\Delta H_{(sol^n)} = \text{Hydration energy} - \text{Lattice energy}$$

Greater the value of Lattice energy greater is the -ve value of ΔH solution and lesser is the solution.

→ Between Nacl and MgO:-

Nacl is more soluble due to greater size at

Na^+ ion in ~~Comparis~~ Compairision Mg^{+2} ion as a result of which NaCl posses lower lattice energy and greater solubility than MgO.

→ High charge ⟶ Small size ⟶ high lattice energy ⟶ lesser solubility.

NaCl, NH_4Cl
more soluble NH_4Cl than NaCl.

Fajan's Rule :-

Fajan's rule deals with co-valent character in an ionic compound.

(a) Unlike co-valent compound or co-valent bond or ionic bond also develop some co-valent character due to different on electronegative of the bonded atoms.

(b) According to Fajan's rule the power of an ion to distoted the electron cloud of another atom is called ~~as~~ it's polarizing power and the tendency of an ion to get polarised is called it's polarisibility. Thus greater the polarization, greater is the co-valent character in an ionic bond.

(c) The polarisation of ion depends upon two factors.

(1) High Charge :-

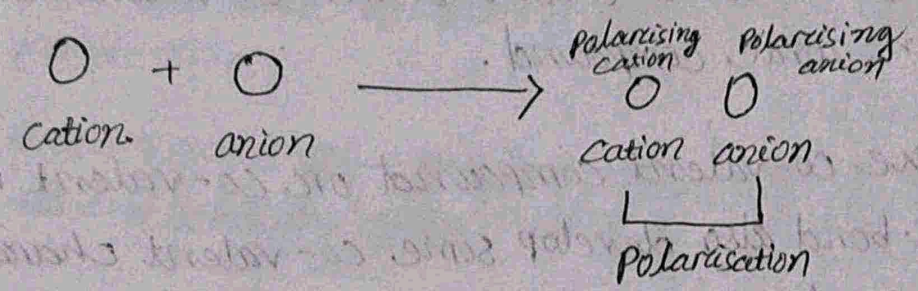
Greater the charge on a cation smaller will be it's size and greater will be it's polarising power.

Similarly higher the charge on anion large will be it's size greater will be it's polarisibility.

(2) Size :-

Small the size of cation greater will be the force of attraction hence greater will be it's polarising power similarly larger the size of ion lesser will be the force of attraction and greater will be it's polarisibility.

cation → Polarising power
anion → Polarisebility



Between NaCl and NaI which posses higher B.P or M.P, Why?

Ans. NaI is predominatly co-valent due to Fajani rule while NaCl Predominatly ionic on character. Due to greater ionic character greater Lattice energy NaCl posses higher M.P and B.P NaI.

Co-valent Bond :-

① This type of bond is formed between two similar atoms (A-A) or two disimilar atom (A-B).

② Here both the atoms are short of one or more electron pairs from the nearest inert gas configuration.

③ When the atoms are similar the bond formed between them is called non-polar covalent bond.

Ex H_2, O_2, N_2, Cl_2 etc.

④ When the atoms are disimilar the bond formed between them is called polar co-valent bond.

Ex HF, HCl, H_2O etc.

Hence the bond formed between two similar or disimilar atoms by m during of electrons is called co-valent bond.

V.S.E.P.R Theory:-

Valence shell electron pair repulsion theory:-

This theory was proposed by Sidgwick and Pool to establish the shape of the molecule. The various postulates of this theory are.

① The unpaired electron in the valence shell of the central atom forms bond pair with the unpaired electron with surrounding atoms while the paired electron remain as lone pairs.

② Being similar charge, the bond pair as well as the lone pair tend to repell one another.

③ The electron pairs around the central atom adjust themselve in such a way that the force of repulsion between the electrons pairs is minimum.

④ The source of repulsion between the bond pairs and lone pairs is not same the order of repulsion is

L.P − L.P > L.P − B.P > B.P − B.P

Types of molecules	No. of B.P	No. of L.P	Total stereo active pairs	Most expected Hybridisation	Shape of molecule	Examples
AX_2	2	0	2	sp	Linear	$BeCl_2$
AX_3	3	0	3	sp^2	Trigonal Planar	BF_3
	2	1	3	sp^2	V-shape	$SnCl_2$
AX_4	4	0	4	sp^3	Tetrahedral	CH_4
	3	1	4	sp^3	Pyramid	NH_3
	2	2	4	sp^3	V-shaped	H_2O
AX_5	5	0	5	sp^3d	Trigonal bipyramidal	PCl_5
	4	1	5	sp^3d	Irregular tetrahedral or see saw structure	SF_4
	3	2	5	sp^3d	T-shape	ClF_3
	2	3	5	sp^3d	Linear	$ICl_2^{\ominus}$
AX_6	6	0	6	sp^3d^2	Octahedral	SF_6
	5	1	6	sp^3d^2	Square pyramidal	IF_5
	4	2	6	sp^3d^2	Square planner	XeF_4
AX_7	7	0	7	sp^3d^3	Pentagonal Bipyramidal	IF_7
	6	1	7	sp^3d^3	Distoneted Pentagonal bipyramidal	XeF_6

CH_4

The central atom is C

No. of valence electron = 4

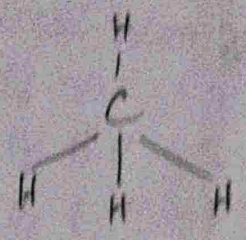
No. of Bond pair = 4

$$\text{No. of lone pair} = \frac{\text{Valence electron} - \text{Bond pair}}{2}$$

$$= \frac{4-4}{2} = 0$$

Total stercio active pairs = 4 + 0 = (B.P + L.P) = 4

Geometry of molecules is tetrahedral



ICl_2^-

The central atom is I

No. of valence electron = 7+1=8

No. of Bond pairs = 2

No. of lone pair = $\frac{8-2}{2} = 3$

Total Sterio active pairs = 2+3 = 5

Expected hybridisation is sp^3d

Since there 5 sterio active pairs hence geometry of the molecule should be linear. Has even due to presence of 3 L.P of electron there is substancial L.P. - L.P as well as L.P - B.P repulsion. Hence the original geometry is distorted to linear shape.

Cl - I - Cl

ICl_4^-

The central atom is I

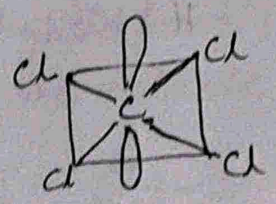
No. of valence electron = 7+1=8

No. of Bond pair = 4

No. of Lone pair = $\frac{8-4}{2} = 2$

Total sterioactive pairs = 4+2 = 6

Expected hybridisation is sp^3d^2



SF_4

Central atom is S

No. of V.E = 6

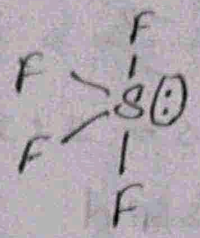
No. of B.P = 4

No. of L.P = $\frac{6-4}{2}$ = 1

Total Stereo active pairs = 4 + 1 = 5

Expected hybridisation is sp^3d

Geometry of the molecule



H_2O

Central atom = O

No. of V.E = 6

No. of B.P = 2

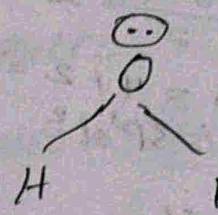
No. of L.P = $\frac{6-2}{2}$ = 2

Total Stereo active pairs = 2 + 2 = 4

Expected hybridisation = sp^3

Due to 2 lone pair geometry changed

So it is V-Shape



$SnCl_2$

Central atom is Sn

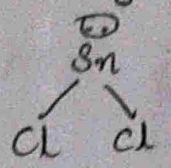
No. of V.E = 4

No. of B.P = 2

No. of L.P = $\frac{4-2}{2} = 1$

Total sterio active pair = 2 + 1 = 3

~~Exp~~ Expected hybridisation = sp^2



It is V-shape

IF_7

Central atom is I

No. of V.E = 7

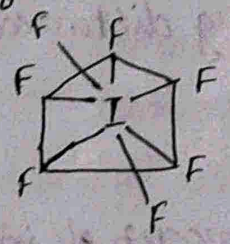
No. of B.P = 7

No. of L.P = 0

Total sterio active pair = 7

Expected hybridisation sp^3d^3

Geometry of the molecule is pentagonal bipyramidal



I_3^-

Central atom is I

No. of V.E. = 7 + 1 = 8

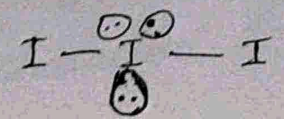
No. of B.P. = 2

No. of L.P. = 3

Total no. of sterio active pairs = 5

Expected hybridisation sp^3d

Geometry of the molecule is linear.



SO_4^{-2}

Limitations

① V.S.E.P.R theory is applicable to only simple co-valent molecules and does not covere ionic species.

② It ~~does~~ does not make any distington between the electrons Present in different type of orbital s, p, d, f of the valence Shell.

③ It is unable to predict the exact bond angle in molecule Such as H_2O and NH_3 having distorted geometry.

Hybridisation :-

→ Hybridisation is the concept of intermixing of the orbitals of an atoms having same and nearly same energy to give exactly equivalent orbital with same energy, identical shape and symmetrical orientation in space.

→ The atomic orbitals which combines are called hybridising orbitals and the new orbital form are called hybrid orbitals.

Condition for Hybrid orbital :-

→ Only the orbital of the central atom participate in hybridisation.

→ It is only the orbitals and not the electrons which get hybridised.

→ The hybridising orbital must differ slightly in energy.

Characteristics of hybridisation :-

→ The number of hybrid orbitals form is equals to no. of hybridising orbital.

→ The hybrid orbital formed are equivalent in shape and energy.

→ The hybrid orbital which takes part in bond formation must contain one electron it.

→ A hybrid orbital like atomic orbital cannot have more than two electrons with opposite spin.

→ Due to inter electronic repulsion the hybrid orbitals tends to remain maximum distance apart.

→ The hybrid orbital are more effective in forming stable bonds then the pure atomic orbital.

Types of Hybridisation :-

① SP Hybridisation :-

→ Here one 'S' orbital and one 'P' orbital of central atom get hybridised to form two SP hybrid orbitals.

→ The hybrid orbitals are linear in shape and bond angle 180°.

→ Each SP hybrid orbital contain 50% S character and 50% P character.

$BeCl_2$

Central atom is Be

$_4Be_{G.S}$ – $1s^2 2s^2$

$_4Be_{E.S}$ – $1s^2 2s^1 2p_x^1 2p_y^0 2p_z^0$

$_{17}Cl_{G.S}$ – $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$

→ Here one 2s orbital and one 2p orbital of berillium atom containing unpaired electron each get hybridised to form 2 sp hybrid orbital.

→ Each sp hybrid orbital overlap with p_z orbital of Chlorin containing unpaired electron $sp - p_z$ σ bond.

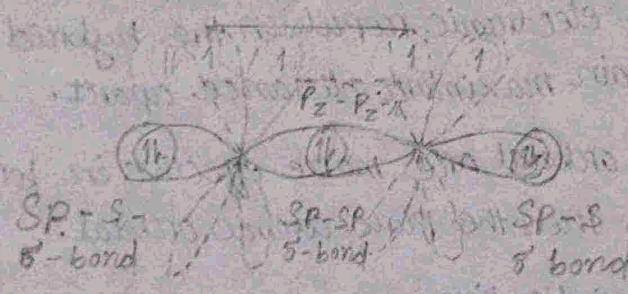
→ The shape of molecule in linear with bond angle 180°.

C_2H_2

$CH \equiv CH$

$_6C$ – $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$

$_{E.S}C$ – $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$



② sp^2 hybridisation :-

→ Here one - s orbital and 2 - p orbital of central atom get hybridised to form 3 - sp^2 hybrid orbitals.

→ The shape of the hybrid orbital is trigonal planner with B.A. 120°

→ ~~The shape of the hybrid orbital is trigonal.~~

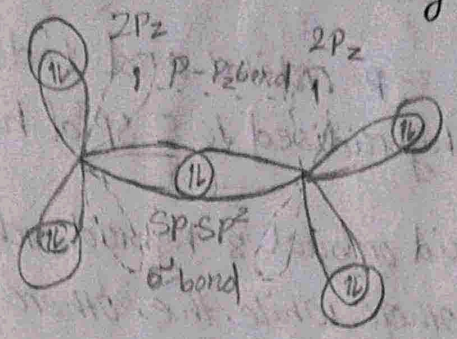
→ Each sp^2 hybrid orbital contain 33.3% character 66.6% 3p character.

Ex :- $CH_2 = CH_2$, BF_3

$CH_2 = CH_2$:-

$$_6C_{G.S} - 1s^2\, 2s^2\, 2p_x^1\, 2p_y^1\, 2p_z^0$$

$$_6C_{E.S} - 1s^2\, 2s^1\, 2p_x^1\, 2p_y^1\, 2p_z^1$$



→ Here both the carbons are sp^2 hybridised namely 1s-orbital and 2p-orbitals intermix to form 3 sp^2 hybrid orbitals each containing one-unpaired electron.

→ One sp^2 hybrid orbital of each C-atom overlap ~~axially~~ axialy forming sp^2-sp^2 σ-bond.

→ The other two hybrid orbital of each C-atom overlap with H-atom forming sp^2-s σ bond

→ The unhybridised P_z-orbital of each C-atom overlap sidewise forming π-bond.

→ The shape of molecule is trigonal.

③ Sp^3 Hybridisation :-

→ Here one s-orbital and 3p-orbital of central atom get hybridised to form 4 sp^3 hybrid orbitals.

→ The hybrid orbitals are tetrahedral in shape with bond angle 109°.28'

→ Each sp^3 hybrid orbital contain 25% s-character and 25% P-character.

Ex:- CH_3-CH_3, H_2O, NH_3

$_6C_{G.S} = 1s^2\ 2s^2\ 2p^2$

$= 1s^2 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$

$_6C_{E.S} = 1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

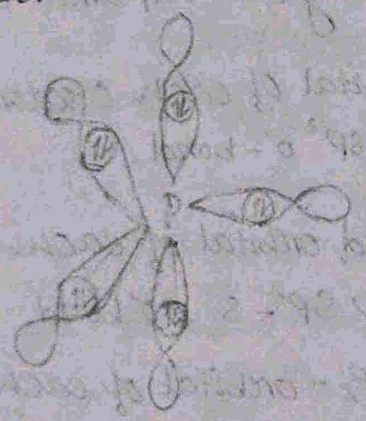
$_1H_{G.S} = 1s^1$

(4) sp^3d Hybridisation :-

→ Here 1s-orbital, 3-p-orbital and 1-d-orbital of the central atom get hybridised to 5 sp^3d hybrid orbital.

→ Out of this 5-hybrid orbital 3-hybrid orbitals directed at 120° to one another while the other two hybrid orbitals remains 180° one another.

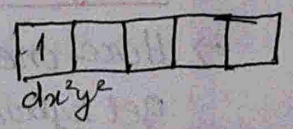
→ The shape of the hybrid orbital is trigonal biplanner.



Ex:- PCl_5

$_{15}P_{G.S} - 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$

$P_{E.S} - 1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1$



$_{17}Cl_{G.S} - 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

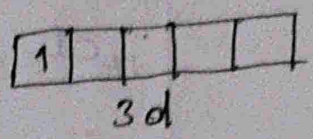
$- 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$

sp^3d (SF_4)

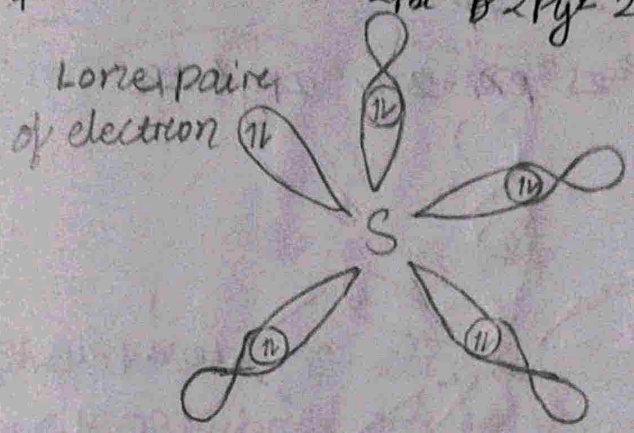
$_{16}S_{G.S} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^4$

$\rightarrow 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$

$_{16}S_{E.S} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$



$_9F_{G.S} \rightarrow 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$



sp^3d - P — σ-bond

→ The central sulphur atom is sp^3d hybridised

→ 4 - sp^3d hybrid orbital containing one - unpaired electron each overlap axially with p- orbital of Florine atom forming sp^3d - P - σ - bond.

→ The 5th sp^3d hybrid orbital of S-atom contain a lone pair of electron.

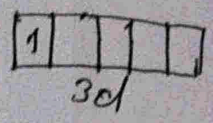
→ Due to presence of lone pair there ~~sub~~ Sub - staincial lone pair - bond pair repulsion. as a result of which the original trigonal bipyramidal geometry is distorted to see-saw shaped.

ClF_3

$_{17}Cl_{G.S} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5$

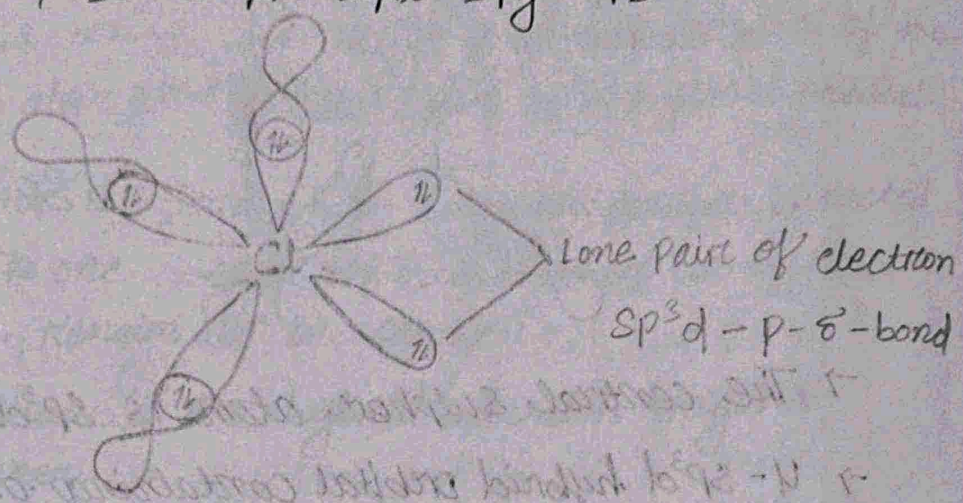
$\rightarrow 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$

$_{17}Cl_{E.S} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$



$_9F_{G.S} \rightarrow 1s^2 2s^2 2p^5$

$\rightarrow 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$



→ The central atom 'Cl' is sp^3d hybridised.

→ Out of 5 sp^3d - hybrid orbital 3 sp^3d orbital contain one unpaired electron each overlap axially with $2p_z$ orbital of florine atom forming sp^3d - p - σ - bond.

→ The other 2 sp^3d hybrid - orbital of Cl - atom contain 2 - lone pair of electron.

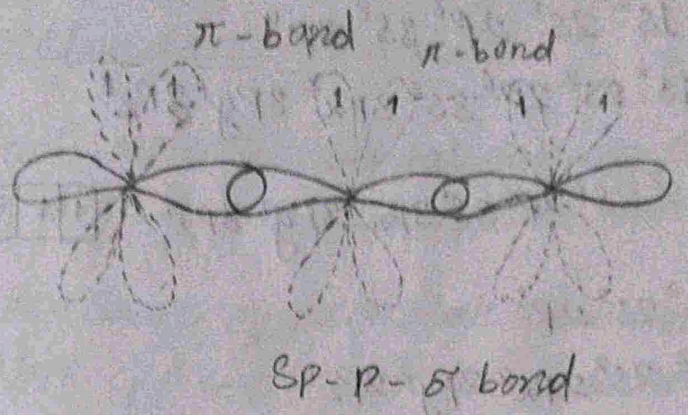
→ Due to ~~prten~~ presence of 2 - lone pair of electron original structure distorted.

→ Shape of molecule is T - shape.

CO_2

$_6C_{E.S} \rightarrow 1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$

$_8O \rightarrow 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$



→ The central C-atom is sp-hybridised. Both the sp-hybrid orbital containing one-unpaired electron each overlap axially with $2p_z$ orbital of oxygen atom forming sp-p-σ-bond.

→ The unhybridised $2p_y$ orbital of C-atom overlap side wise with p-orbital of oxygen atom forming π-bond.

→ The unhybridised $2p_z$ orbital of C-atom overlap side wise with another oxygen atom forming π-bond.

→ Shape of molecule linear and B.A. 180°.

sp^3d^2 hybridisation :-

→ Here one s-orbital, 3p orbital and 2d-orbital of the central atom inter mix to give 6-sp^3d^2 hybrid orbital.

→ The hybridisation result in formation of 6-sp^3d^2 hybrid orbital directed at 90° to each other.

→ The shape of the molecule is octahedral.

Ex:- SF_6 ; IF_5^- , XeF_4

SF_6 :

$_{16}S_{GS} \rightarrow 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^4$

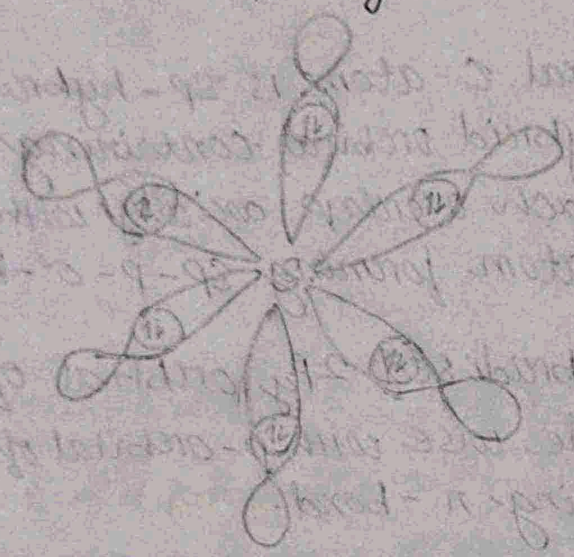
$\rightarrow 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p_x^2\, 3p_y^1\, 3p_z^1$

$_{16}S \rightarrow 1s^2\, 2s^2\, 2p^6\, 3s^1\, 3p_x^1\, 3p_y^1\, 3p_z^1$

1	1			

$_9F \rightarrow 1s^2\, 2s^2\, 2p^5$

$\rightarrow 1s^2\, 2s^2\, 2p_x^2\, 2p_y^2\, 2p_z^1$



$sp^3d^2 - p_z$, σ-bond

XeF_4, IF_7

Molecular orbital Theory (MOT):-

① Molecular orbitals may be defined as the region in space in which finding of electron is maximum.

② Molecular orbital are formed by linear combination of atomic orbital (LCAO)

③ When a set of atomic orbital atomic orbital combine to form molecular orbital the no. of molecular orbitals equals to the no. of atomic orbitals combine.

(4) When two atomic orbital combines two molecular orbital are formed one of these molecular orbital posses lower energy called bonding molecular orbital and the molecular orbital posses higher energy called anti-bonding molecular orbital.

(5) Each molecular orbital can accomodation maximum of two electrons with opposite spin.

(6) The shape of molecular orbital depends upon the shape of the atomic orbital combine.

(7) The molecular orbitals are arranged in increasing order of their energy.

(8) Electron pairing in degenerate molecular orbital cann't takes place unless each molecular orbital is single occupied by electrons by same spin.

Bond Order:-

The no. of co-valent bond present in a molecular is called it's bond order.

$$\text{Bond order} = \frac{1}{2}\left[N_b - N_a\right]$$

$N_b \rightarrow$ No. of bonding electron

$N_a \rightarrow$ No. of anti-bonding electron.

Stability:-

(1) When the bond order is greater than zero the molecule is stable.

(2) When the bond order is less than equal to zero it is unstable.

Bond length:-

Greater the bond order smallest is the bond length.

$$\text{Bond ordered} \propto \frac{1}{\text{bond length}}$$

Bond energy:-

Greater the bond order smallest is the bond length.

$$\text{Bond ordered} \propto \frac{1}{\text{bond length}}$$

Magnetic behaviour:-

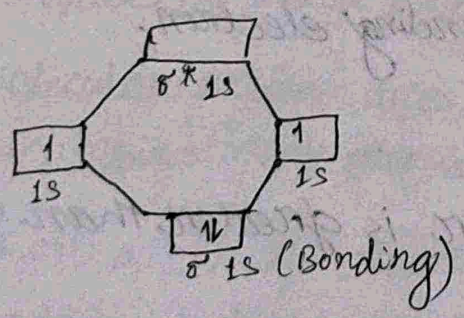
① **Para magnetic:-**

When one of the molecular orbital containing an unpaired electron the molecule is para magnetic.

② **Diamagnetic:-**

If all the molecular orbital containing an unpaired electron the molecules are paired the molecule is diamagnetic.

H_2 $H_2 \rightarrow H - H$

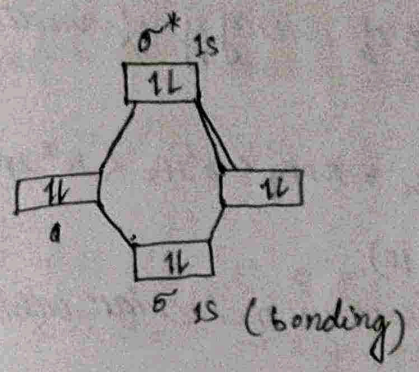


$$\text{Bond ordere} = \frac{2-0}{2} = 1$$

Stability = more stable

Magnetic = Diamagnetic

$He_2 \rightarrow He - He$



Bond order $= \frac{2-2}{2} = 0$

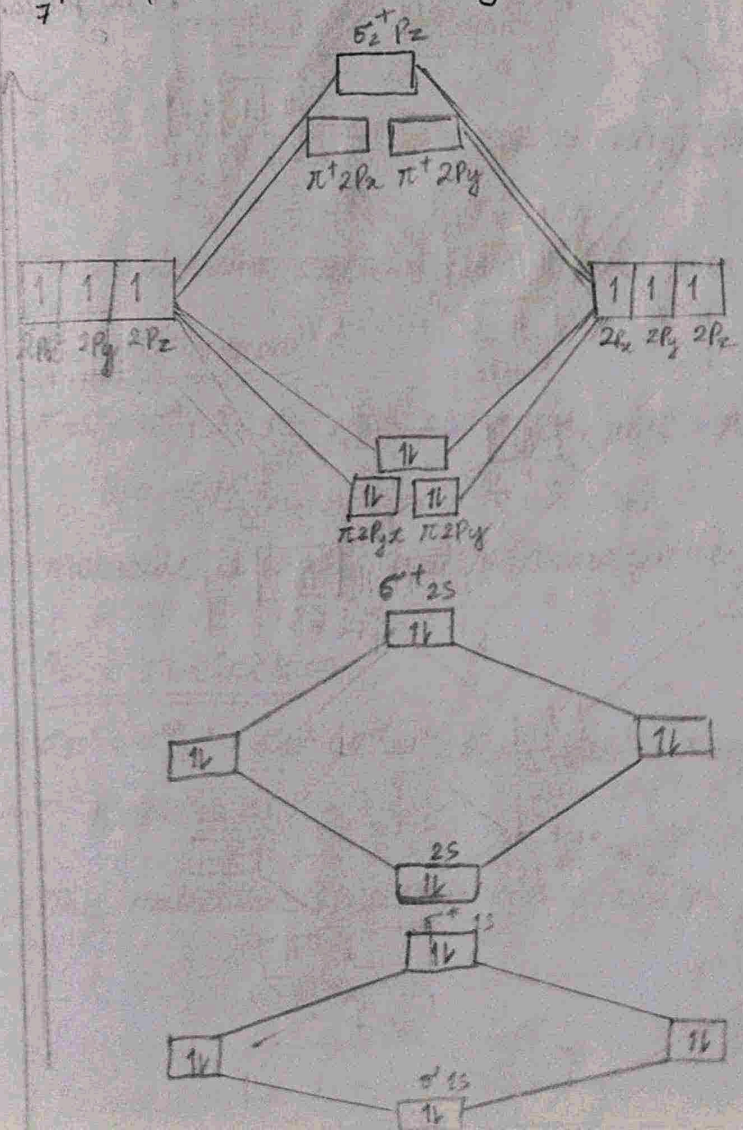
molecule is unstable.

N_2 $N_2 \rightarrow N - N$

N_2 molecule is forms by linear combination of atomic orbitals of 2N atom.

$_7N \rightarrow 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

$_7N \rightarrow 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$



B.O $= \frac{10-4}{2} = 3$

molecule is stable

Diamagnetic

HO_1

The increasing order of energy of various molecular orbital up to nitrogen.

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

Beyond Nitrogen :- (8 to 10)

The energy order of various molecular orbitals beyond nitrogen.

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

O_2

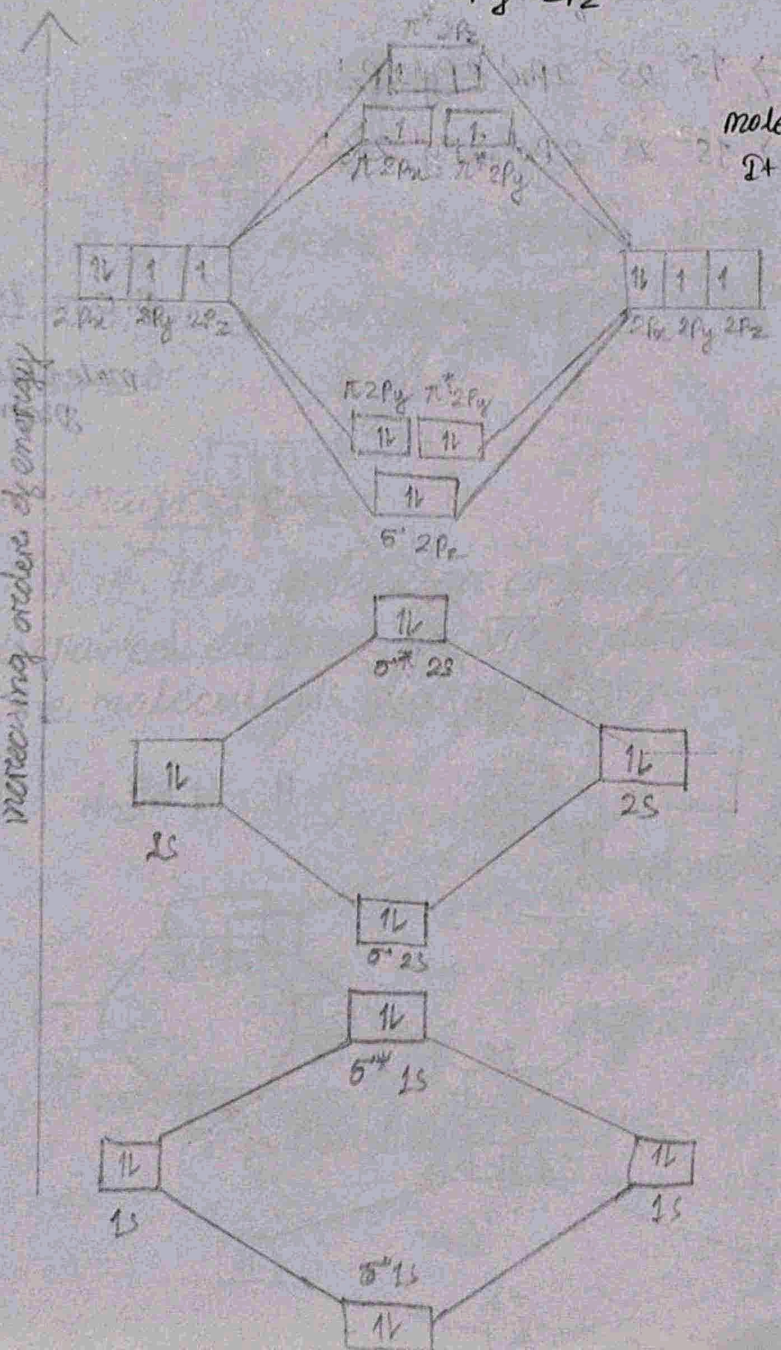
$_8O_2 \rightarrow 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

$_8O_2 \rightarrow 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

$B.O = \frac{10-6}{2} = 2$

molecule is stable

It is paramagnetic



2. Arrange the following compounds in the increasing order of their energy, bond length, bond order and establish their stability and magnetic behaviour

$N_2^+, N_2^-, O_2, O_2^{-2}, O_2^+, O_2^-$

Ans. $N = \sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma_2 p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

$N_2^+ = 13$ electrons.

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 = \pi 2p_y^2 < \sigma 2p_z^2 < \pi^+ 2p_x = \pi^* 2p_x < \sigma^* 2p_z$

$B.O = \frac{1}{2}(9-4) = \frac{5}{2} = 2.5$

Molecular species is stable and paramagnetic.

$N_2^- \rightarrow 15$ electrons.

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 = \pi 2p_y^2 < \sigma 2p_z^2 < \pi^* 2p_x^1 = \pi^* 2p_y < \sigma^* 2p_z$

$B.O = \frac{10-5}{2} = \frac{5}{2} = 2.5$

The molecular species is stable and para magnetic.

$O_2 = 16$ electron

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2 = \pi 2p_y^2 < \pi^* 2p_x = \pi^* 2p_y^1 < \sigma^* 2p_z$

$B.O = \frac{10-6}{2} = \frac{4}{2} = 2$

molecule is stable and paramagnetic.

$O_2^- = 17$ electron

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 1s^2 < \sigma^* 2s^2 < \sigma_2 p_z^2 < \pi 2p_x^2 = \pi 2p_y^2 < \pi^* 2p_x^2 = \pi^* 2p_y^1 < \sigma^* 2p_z$

$B.O = \frac{10-7}{2} = \frac{3}{2} = 1.5$

The molecular species is stable and paramagnetic.

O_2^{-2} = 18 electron

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2 = \pi_2 p_y^2 < \pi^*_{2p_x^2}$
$= \pi^*_2 p_y^2 < \sigma^*_2 p_z$

$$B.O = \frac{10-8}{2} = \frac{2}{2} = 1$$

O_2^+ = 15 electron

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi_2 p_x^2 = \pi 2p_y^2$
$< \pi^*_2 p_x^2 = \pi^*_2 p_y < \sigma^*_2 p_z$

$$B.O = \frac{10-5}{2} = \frac{5}{2} = 2.5$$

Molecular species is stabe and paramagnetic
increasing order = $O_2^{-2} < O_2^- < N_2^- = O_2^+ \neq O_2^+$
increasing order of bond energy is

$$O_2^{-2} < O_2^- < N_2^- = N_2^+ = O_2^+$$

Because greater is the bond order greater is the bond energy.
Increasing order of bond length is

$$N_2^- = N_2^+ = O_2^+ < O_2^- < O_2^{-2}$$

Molecular orbital or heteronuclear diatomic molecule :

① In case of heteromolecular diatomic molecule the atomic orbital of both the atoms are not placed in same energy level rather bonding molecular orbitals are nearer to highly electronegative atom.

CO

carbon monoxide is formed by the linear combination of atomic orbitals of carbon and ~~oxy~~ oxygen.

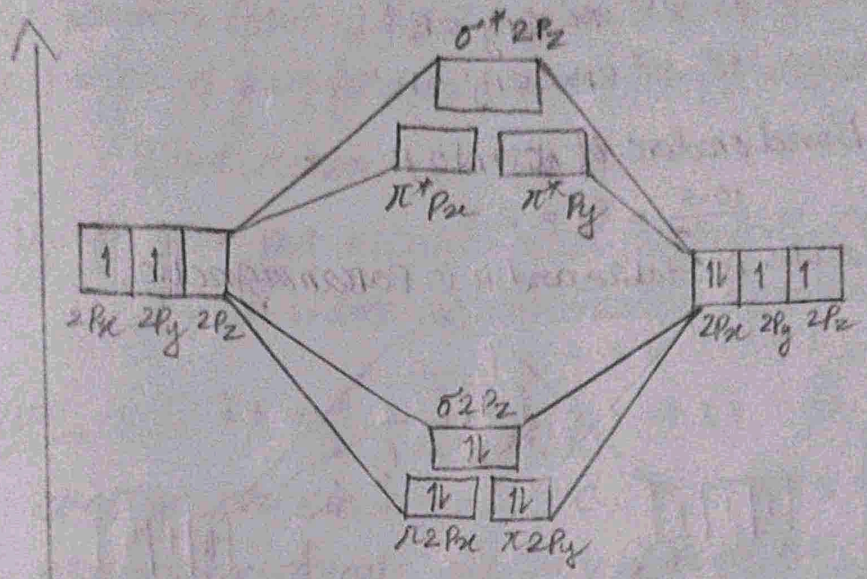
* Since oxygen is more electronegative than carbon it's atomic orbital ~~while that of carbon~~, remain closer to bonding molecular orbital while that of carbon remain closer to anti-bonding molecular orbital.

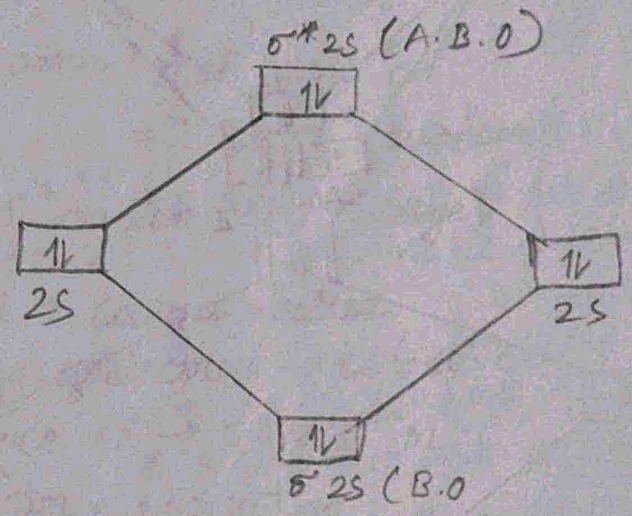
$_6C = 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$

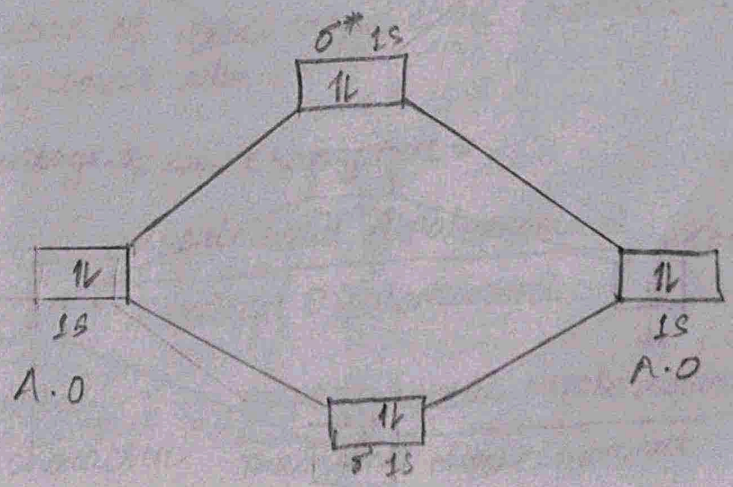
$_8O = 1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$

Bond order of CO is $\frac{10-4}{2} = \frac{6}{2} = 3$

Molecule is stable and it is diamagnetic because all the electrons are paired.







NO

Nitric oxide is formed by the linear combination of atomic orbitals of nitrogen.

* Since oxygen is more electronegative it's atomic orbital remain close to bonding molecular orbital and that of nitrogen remain closer to antibonding m.o.

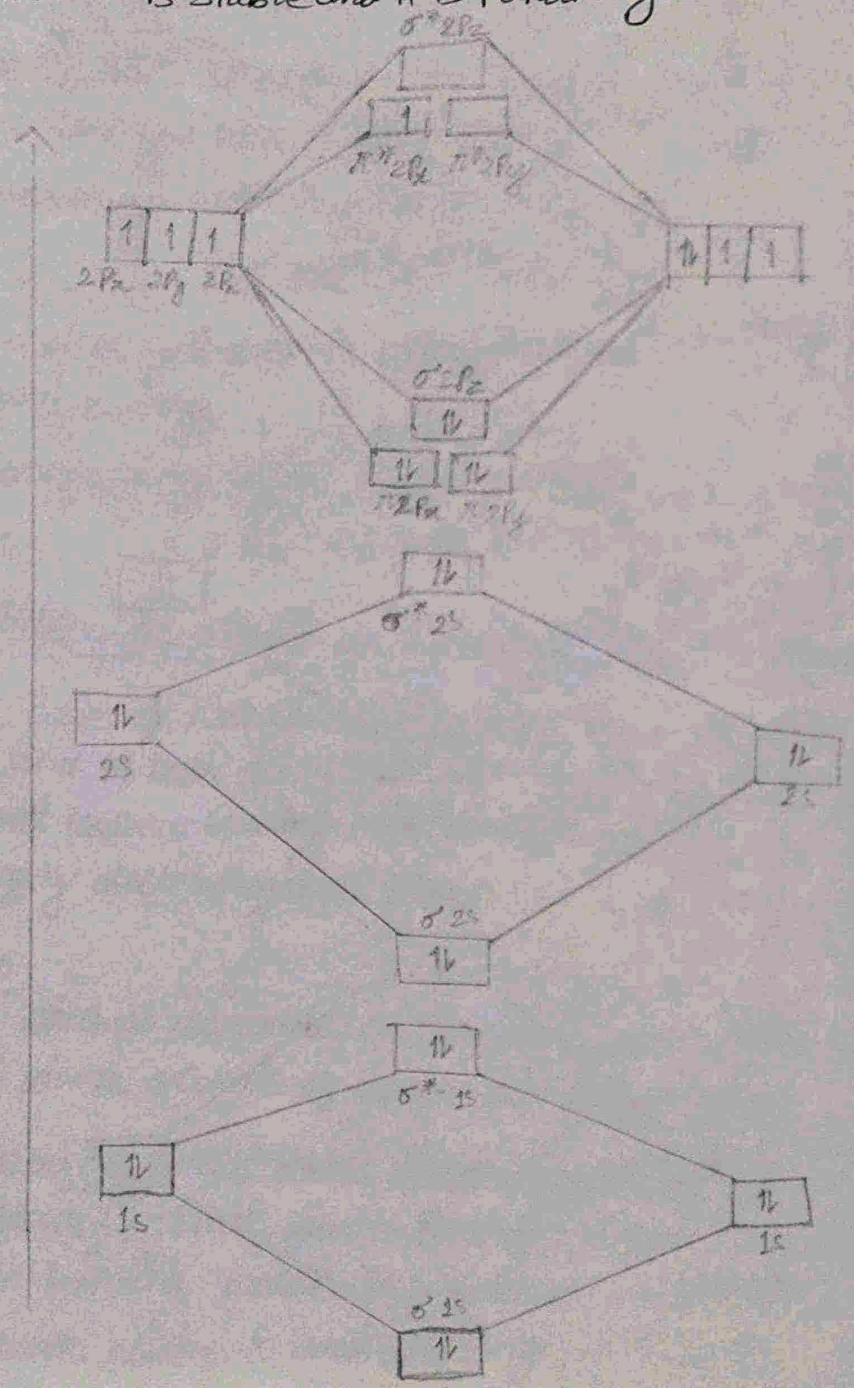
$_7N_2 \rightarrow 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

$_8O_2 \rightarrow 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

Bond order of NO is

$$\frac{10-5}{2} = \frac{5}{2} = 2.5$$

Molecule is stable and it is paramagnetic.



Dipolemoment :

In case of heteronuclear molecules the more electro-negative atom withdraw co-valent electron towards itself and develop partially negative charge. This type of molecule thus posses dipolement.

* Dipolemoment is ~~defined as~~ defind as the product of net ~~position~~ positive and negative charge and the distance of separation between the charges.

Dipolemoment $(\mu e) = e \times d$.

Where, e = net positive and negative charge

d = distance of separation between the charges.

unit → C.G.S →

charge on electron is C.G.S → 4.8×10^{-10} esu

esu → Electrostatic unit of charge.

Distance → 1Å → 10^{-8} cm

$= 4.8 \times 10^{-18}$ esu × cm

10^{-18} esu × cm = 1D (debye)

S.I → Coulmn × meter

Charge of electron → 1.6×10^{-19} c

Distance 1Å → 1.6×10^{-10} m

Dm = 1.6×10^{-29} cm.

Calculation of percentage ionic character from Dipole moment value →

Percentage of ionic character =

$$= \frac{\text{experimental dipolemoment}}{\text{Theoritical Dipolemoment}} \times 100$$

$$\text{Functional Ionic character} = \frac{\text{experimental dipole moment}}{\text{Theoritical dipole moment}}$$

Ques

The D.M. of HCl is 1.03D and inter atomic distance between H and Cl is 1.27 Å. What is the percentage ionic character in HCl.

Ans HCl → Net charge on HCl = 1.6×10^{-19} C

$= 4.8 \times 10^{-10}$ esu

Distance of separation = 1.27×10^{-8} cm.

Theoritical D.M. = $4.8 \times 10^{-10} \times 1.27 \times 10^{-8}$

$= 4.8 \times 1.27 \times 10^{-8}$

$= 6.1 \times 10^{-18}$ esu

$= 6.1$ D

Experimental D.M = 1.03D

% of ionic character of HCl = $\frac{1.03}{6.1} \times 100$

$= 16.9$

% of covalent character = $100 - 16.9 = 83.1$

Ques

~~The DM of LiH is 1.96D~~

The DM of LiH is 1.964×10^{-29} cm and the inter atomic distance between Li and H is 1.596 Å. calculate % ionic character.

Ans Net charge on LiH = 1.6×10^{-19} cm

Distance separation = 1.59 Å $\times 10^{-10}$ m

Theoritical D.M. = $1.6 \times 10^{-19} \times 1.596 \times 10^{-10}$

$= 1.6 \times 1.596 \times 10^{-29}$ cm

$= 2.557 \times 10^{-29}$ cm

Experimental D.M. = 1.964×10^{-29} cm

$= \frac{1.964 \times 10^{-29}}{2.557 \times 10^{-29}} \times 100$

$= \frac{1.964}{2.557} \times 10^{2} = 76.80$

Valence Bond Theory :

This theory was put forward by Hitler and London and was later modified by Pauli and Slater to explain the nature of co-valent bond it's directional characteristics.

① A co-valent bond is formed when half filled atomic orbitals (one unpaired electron) of one atom overlaps with half filled orbital of another atom.

② The ~~combinge~~ combining half filled ~~Atom~~ Atomic orbital merged together to form a co-valent bonds or bond orbitals in which both the electrons occupies their space.

③ Two types of co-valent bonds generally exist. namely 'σ' bond and π bond. σ-bond is formed due to axial overlaps of atomic orbitals while π-bonds are formed by the sidewise overlapping as atomic orbitals.

④ The two electrons which occupy the same molecular orbital must have opposite spin.

⑤ The localised molecular orbital is considered to belong to the electrons of both the combing atom.

⑥ Maximum electron is found near overlapped region, The force that beyonds co-valent bonded atom is due to electrostatic force of attraction between a nucleous of one atom and electron of another atom.

FUNDAMENTALS OF ORGANIC CHEMISTRY

Electron Displacements In Organic Compounds :-

There are four types of electron displacement mechanisms generally observed in organic molecules.

i) Inductive effect
ii) Resonance effect
iii) Electromeric effect
iv) Hyperconjugation

Inductive effect :- (I effect)

The permanent displacement of the shared pair of electron in a carbon chain towards the more electro negative group is known as the Inductive effect.

Types :-

i) -I effect :- If a group is more electronegative than carbon, then the group withdraws electrons from the carbon chain, towards itself. It is then said to have -I effect.

$$-\overset{\delta^+}{C} \longrightarrow \overset{\delta^-}{X}$$ X is more electronegative.

In a carbon chain, the electron displacements progressively decreases as the distance from the carbon atom directly attached to the more electronegative element increases. It is almost negligible after three carbon atoms.

$$\overset{\delta_3^+}{C} - \overset{\delta_2^+}{C} - \overset{\delta_1^+}{C} - \overset{\delta^-}{X}$$

$$\delta^- = \delta_1^+ + \delta_2^+ + \delta_3^+$$

$$\delta_1^+ > \delta_2^+ > \delta_3^+$$

The various groups with -I effect are given in decreasing order.

$\overset{+}{N}R_3 > \overset{+}{N}H_3 > NO_2 > CN > COOH > F > Cl > Br > I > OC_6H_5 >$
$> COOR > OR > OH > C_6H_5$

ii) <u>+I effect</u>:-

If a group attached to the carbon is less electronegative than carbon, it donates electrons to the carbon chain. It is then said to have +I effect.

$$-\overset{\delta^-}{\underset{|}{\overset{|}{C}}} \longleftarrow \overset{\delta^+}{Y}$$ Y is less electronegative.

$$\overset{\delta_3^-}{C} - \overset{\delta_2^-}{C} - \overset{\delta_1^-}{C} \longrightarrow \overset{\delta^+}{Y}$$

$$\delta^+ = \delta_1^- + \delta_2^- + \delta_3^-$$

$$\delta_1^- > \delta_2^- > \delta_3^-$$

The various groups with +I effect are given in decreasing order.

$$(CH_3)_3C- > (CH_3)_2CH- > CH_3-CH_2- > \cancel{CH_3-}$$

<u>Application of Inductive effect</u>:-

① It explains the relative strength of acid :-

i) The presence of electron withdrawing groups (-I effect) attached to -COOH group make the acid stronger.

ii) The presence of electron donating groups (+I effect) attached to COOH group make the acid weaker.

Ex:- 1) Chloroacetic acid is a stronger acid than acetic acid

$Cl-CH_2-COOH$	CH_3-COOH
Chloro acetic acid	Acetic acid
-I effect	+I effect
(stronger acid)	(weaker acid)

② It explains the relative strength of bases :-

i) The presence of +I group attached to $-NH_2$ group make the base stronger.

ii) The presence of -I group attached to $-NH_2$ group make the base weaker.

Ex:- Methyl amine is a stronger base than chloramine

$CH_3-\ddot{N}H_2$	$Cl-\ddot{N}H_2$
(Methyl amine)	(chloramine)
+I effect ~~stronger~~	-I effect
~~st base~~ stronger base	Weaker base

Electromeric Effect :- [E effect]

Complete transfer of a shared pair of electrons of a multiple bond to one of the bonded atoms under the influence of the attacking reagent is known as electromeric Effect.

Types :-

i) +E effect

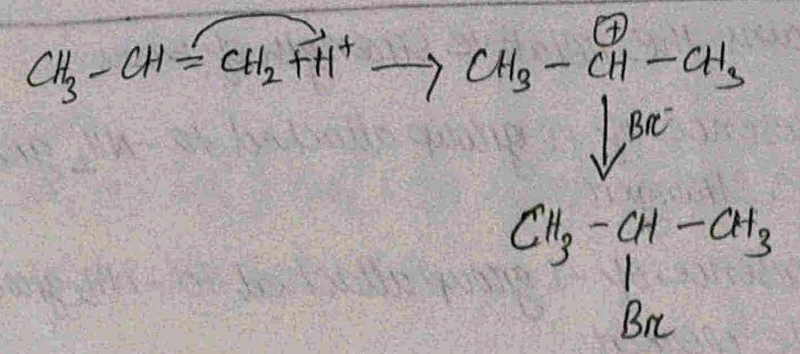
ii) -E effect

+E effect :-

When the transfer of π electrons takes place towards the attacking reagent (electrophile) then the effect is called +E effect.

Ex:- Addition of HBr to Propene

$$HBr \longrightarrow H^+ + Br^-$$

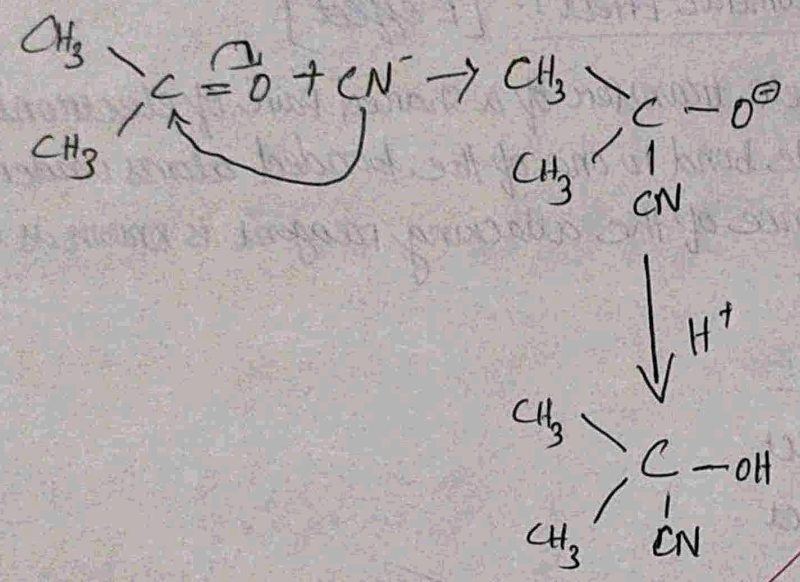


-E effect :-

When the transfer of π electrons takes place away from the attacking reagent (nucleophile) the effect is called -E effect.

Ex:- Addition of HCN to acetone

$$HCN \rightarrow H^+ + CN^-$$



Resonance:-

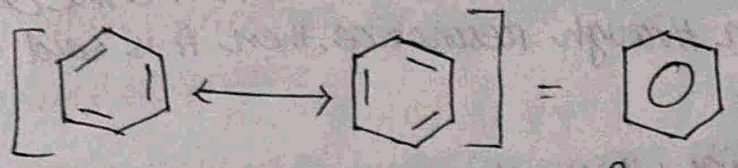
When more than one structure can be written for a compound but none of them is able to explain the known properties of the compound completely, then the different structures written are known as the resonating or contributing or canonical structures. The actual structure of that compound is the resonance hybrid of these resonating structures. This phenomenon is known as Resonance.

Ex:- Benzene

Benzene can be represented by following two structures given by Kekate

Structure-1 Structure-2

It has been found that neither St-1 ~~are~~ nor St-2 explain all the known properties of benzene so actual structure of benzene is the Resonance hybrid of the above two structures.



Resonance hybrid structure of benzene

* A resonance hybrid is always more stable than any of the resonating structures.

* Greater the number of resonating structures for a molecule, greater will be the stability.

Resonance effect :- (R-effect) or Mesomeric effect (M-effect)

The flow of electrons from one part of conjugated π-system to the other, caused by phenomenon of resonance is called Resonance effect or Mesomeric effect.

Types :-

i) +R or +M effect

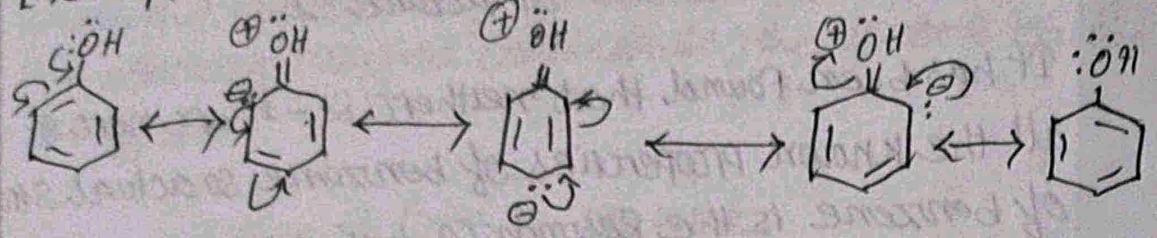
ii) -R or -M effect

+R effect:-

If a group ~~deno~~ donates electrons to the conjugation π-system through resonance, then it is said to have +R effect.

The groups which shows +R effect are F, Cl, Br, I, OH, SH, NH_2, OR, R etc.

Ex:- Phenol

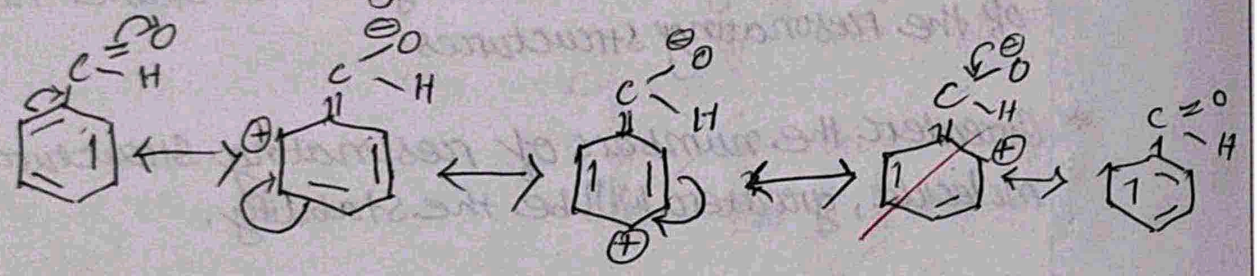


-R effect:-

If a group withdraw electrons from the conjugated π system through resonance, then it is said to have -R effect.

The groups which shows -R effect are -CHO, -COOH, -COR, -COOR, -CN, $-NO_2$ and $-SO_3H$ etc.

Ex:- Benzaldehyde :-



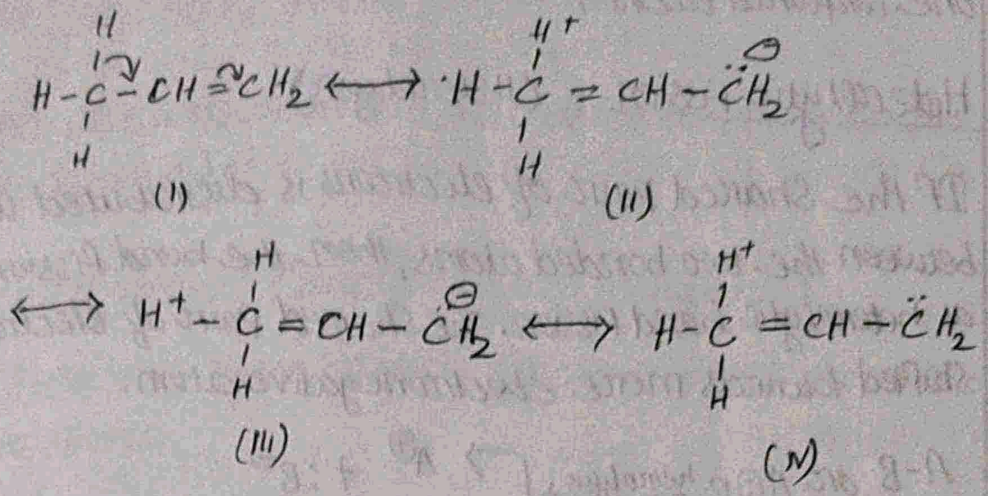
Hyperconjugation:-

When α hydrogen atoms attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of the H-C bond enter into conjugation with the unsaturated system. Such conjugation between electrons of single (H-C) bond with multiple ~~or~~ bond called hyperconjugation

According to the concept of hyperconjugation, if an alkyl group carrying at least one hydrogen atom is attached to an unsaturated carbon atom ~~is attached to~~

an unsaturated it releases electrons of H-C single bond towards the multiple bond.

Ex:- The hyperconjugative structure of propene are



AS there is no bond between the α-carbon atom and one of the hydrogen atoms, the hyperconjugation is also called no-bond resonance.

* More the number of hyperconjugative structures, more is the stability.

Bond Fission (Bond Cleavage) :-

The breaking of covalent bond in organic reactions is known as Bond Fission, which can take place in two ways.

i) Homolytic fission

ii) Heterolytic fission

Homolytic Fission :- (Homolysis)

If the shared pair of electrons is distributed equally between two bonded atoms, the bond fission is known as the homolytic bond fission.

$$A-B \text{ or } A:B \xrightarrow{\text{homolysis}} \dot{A} + \dot{B}$$

(Free radicals)

$Cl-Cl$ or $Cl:Cl \xrightarrow{\text{UV light}} Cl^{\cdot} + Cl^{\cdot}$

The two fragments formed by the homolysis ~~or~~ are known as free radicals. Free radicals are neutral species containing one unpaired electron.

Heterolytic Fission :- (Heterolysis)

If the shared pair of electrons is distributed unequally between the two bonded atoms, then the bond fission is known as heterolytic bond fission. The shared pair of electron is shifted towards more electronegative atom.

$$A-B \text{ or } A:B \xrightarrow{\text{hetrolysis}} \begin{cases} A^{\oplus} + :B^{\ominus} \\ A^{\ominus}: + B^{\oplus} \end{cases}$$

Ex:- $CH_3-Cl \longrightarrow CH_3^{\oplus} + :Cl^{\ominus}$

During heterolysis, +ve and -ve ions formed. Positive charge on carbon is known as carbonium ion while -ve charge on carbon is known as carbanions.

Electrophiles (Electron Loving reagent) :-

These are the reagents having an atom which is deficient in electrons. So they try to seek electrons from other sources

Types :- i) Positive electrophiles
ii) Neutral electrophiles

i) Positive Electrophiles (E^+)

These are deficient in electrons and carry positive charge. These have sextet of electrons in their outershell.

Ex:- H^+, H_3O^+, NO_2^+, NO^+, $Cl^{\oplus}$, $Br^{\oplus}$, $CH_3^{\oplus}$ etc.

ii) Neutral Electrophiles (E)

These do not carry any charge but are electron deficient.

Ex:- BF_3, $AlCl_3$, $FeCl_3$, SO_3 etc

* An electrophile is a Lewis acid and it accepts an electron pair.

Nucleophiles :- (Nucleus loving reagents)

These are electron rich species so they donates electrons to others.

Types:- 1) Negative Nucleophiles
2) Neutral Nucleophiles

1) Negative Nucleophiles :- ($Nu^{\ominus}$)

These have an excess electron pair and carry a negative charge.

Ex:- $\overset{\ominus}{C}H_3$, $CH_3-\overset{\ominus}{C}H_2$, $Cl^{\ominus}$, $\overset{\ominus}{B}$, $\overset{\ominus}{O}H$, $\overset{\ominus}{C}N$ etc.

2) Neutral Nucleophiles :- (Nu)

These have an unshared pair of electrons but carry no charge.

Ex:- $\ddot{N}H_3$, $R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$, $H_2\ddot{O}$

$R-\ddot{O}-H$, $R-\ddot{O}-R$ etc.

* A nucleophile is a Lewis base and it donates an electron pair.

Reactive intermediates :-

In most of the organic reactions, reactants first change into intermediate substances known as the reactive intermediates. These intermediates ultimately give the products.

These reaction intermediates are extremely short lived. They get formed during one step in a reaction and then immediately get consumed in the next step.

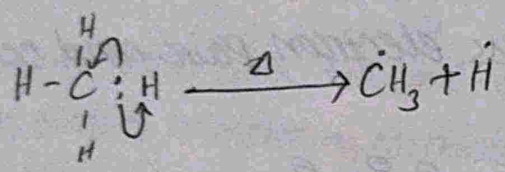
Some of the reaction intermediates are i) Free radicals ii) carbonium ions iii) carbanions.

Free radicals :-

It is a neutral species having an unpaired electron. It is formed by the homolytic bond fission of a covalent bond.

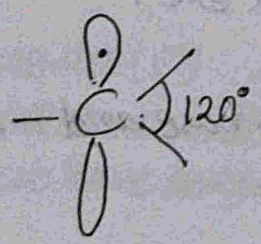
Ex:- $Cl:Cl \xrightarrow{\text{U.V light}} \dot{Cl} + \dot{Cl}$

Free radicals



Structure :-

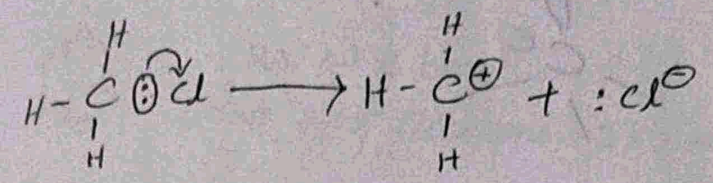
The alkyl radicals such as methyl radicals have sp^2 hybridisation having trigonal planar shape. The three hybrid orbitals form three single bonds with other atoms while the unhybridised orbital carries the unpaired electron



ii) Carbonium ions (carbocations):-

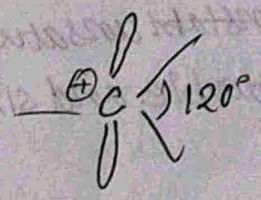
An organic ion having the positive charge on carbon and six electrons in its valence shell is known as the carbonium ion.

It is formed by the heterolytic cleavage of C-X bond where X is more electronegative than carbon.



Structure :-

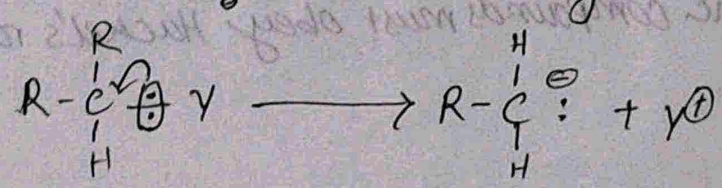
The positively charged carbon of the carbocation is sp^2 hybridised. The three sp^2 hybrid orbitals are used in making three bonds with other atoms while the unhybridised p orbital remain vacant.



iii) Carbanions:-

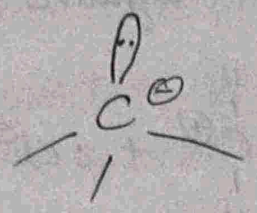
An organic ion with an unshared pair of electrons and a negative charge on the central carbon atom is called a carbanion.

It is formed by the heterolytic bond cleavage of C-Y bond where Y is less electronegative then carbon.



Structure :-

The negatively charged carbon atom in carbanions is sp^3 hybridised giving a pyramidal structure. The three sp^3 hybrid orbitals are used ~~with~~ in making three bonds with other atoms while the fourth sp^3 hybrid orbital is occupied by a lone pair of electrons.



Aromaticity :-

The common characteristics of Aromatic compounds are

1) They are sweet smelling compounds containing high percentage of carbon so they produce sooty flame.

2) They are highly ~~unstabl~~ unsaturated compounds and contain alternate double and single bonds in a cyclic structure.

3) They undergo substitution reaction rather than addition reaction.

4) They are cyclic compounds having planar rings.

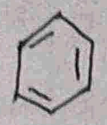
5) These compounds must have cyclic delocalised π electron cloud lying above and below the plane of the ring.

6) The Aromatic compounds must obey Huckel's rule.

Huckel's rule :-

A cyclic compound is said to aromatic if it contain $(4n+2)$ π electrons where $n = 0, 1, 2, 3 \ldots$ etc. i.e they contains $2, 6, 10, 14, \ldots \pi$ electrons.

Ex :- Benzene

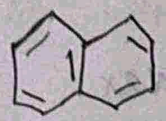


No. of π bonds = 3

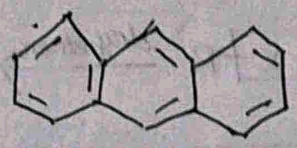
No. of π Electrons = $3 \times 2 = 6$

It satisfy Huckel's rule. So it is Aromatic compound.

Other examples of Aromatic compounds are

i) 

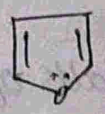
Napthalene
(10π)

ii) 

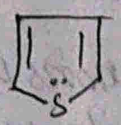
Anthracene
(14π)

iii)

Pyridine
(6π)

iv) 

Furan
(6π)

v) 

Thiophene
(6π)

vi)

Pyrrole
(6π)

Aliphatic Hydrocarbon

Alkanes :-

Preparation :-

① **Hydrogenation of alkenes and alkynes :-** (Sabatier and Senderens reaction)

When Alkene or Alkyne reacts with hydrogen in presence of Ni at 523 - 573K it gives Alkane.

Ex:- $CH_2 = CH_2 + H_2 \xrightarrow[523-575K]{Ni} CH_3 - CH_3$

$CH_2 \equiv CH + 2H_2 \xrightarrow{Ni} CH_3 - CH_3$

② **Wurtz reaction :-**

When Alkyl halide reacts with sodium in presence of dry ether it gives Alkane.

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

Ex:- $CH_3 - \boxed{Br + 2Na + Br} - CH_3 \xrightarrow{\text{dry ether}} CH_3 - CH_3 + 2NaBr$
ethane

③ **Kolbe's Electrolytic reaction :-**

When aqueous solutions of sodium salts of Carboxylic acid undergo electrolysis it gives alkane at anode.

$R - COONa \longrightarrow R - COO^{\ominus} + Na^{\oplus}$

At anode :-

$R - COO^{\ominus} - e^{\ominus} \longrightarrow R - COO$

$2R - COO \longrightarrow R - R + 2CO_2$
Alkane

At cathode :-

$Na^{+} + e^{-} \longrightarrow Na$

$2Na + 2H_2O \longrightarrow 2NaOH + H_2$

Ex:- $CH_3COONa \longrightarrow CH_3COO^- + Na^+$

At ~~catho~~ anode:-

$$CH_3-COO^- - e^- \longrightarrow CH_3-COO$$

$$2(CH_3-COO) \longrightarrow CH_3-CH_3 + 2CO_2$$

ethane

④ From Greignard's reagent :-

When Greignard's reagent treated with water or alcohol it gives Alkane.

$$R-MgX + H_2O \longrightarrow R-H + Mg(OH)X$$

Ex:- $CH_3-MgBr + H_2O \longrightarrow CH_4 + Mg(OH)Br$

⑤ Decarboxylation of carboxylic acids :-

When sodium salt of carboxylic acid is heated with sodalime (NaOH + CaO) it gives Alkane.

$$R-COONa + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

Alkane

Ex:- $CH_3-COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

Methane

Chemical properties:-

Free reddical substitution reaction:-

Halogenation:-

Alkanes react with halogens in presence of UV light or on heating gives halo alkane.

$$R-H + X_2 \longrightarrow R-X + HX$$

i) Chlorination:-

$$CH_4 + Cl_2 \xrightarrow[\text{sunlight}]{\text{diffused}} CH_3Cl + HCl$$

Chloromethane

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

dichloromethane

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

Trichloro methane

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Tetrachloromethane

ii) Bromination:-

It is similar to chlorination but takes place less readily.

$$C_2H_6 + Br_2 \xrightarrow{\Delta} C_2H_5-Br + HBr$$

iii) Iodination:-

It can not be carried out directly because the reaction is extremely slow and reversible, due to reducing nature of HI.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

Iodo methane

In order to check the reversibility of the reaction, the reaction is carried out in presence of an oxidising agent like Iodic acid (HIO_3) or nitric acid (HNO_3)

The oxidising agent oxidises the HI into Iodine.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

iv) Fluorination :-

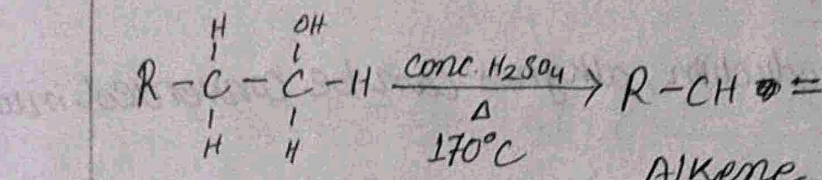
Direct fluorination is not possible because of the explosive nature of the reaction

Alkene :-

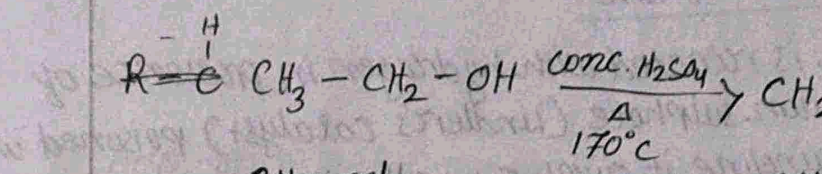
Preparation :-

① Dehydration of alcohols :-

On heating with concentrated sulphuric acid or phosphoric acid or Al_2O_3. Alcohols lose a water molecule to form alkenes.



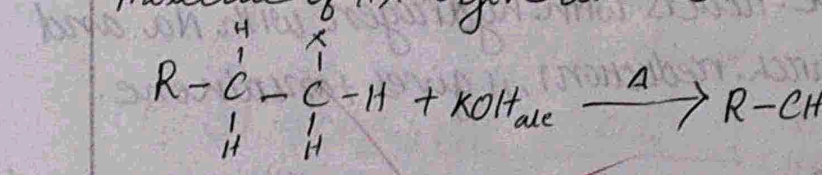
Alcohol Alkene



ethanol ethene

② Dehydrogenation of Alkyl halides :-

Alkyl halides on treatment with alcoholic KOH, lose a molecule of HX to give alkenes.



Ex :- $CH_3-CH_2-Br + KOH_{alc} \xrightarrow{\Delta} CH_2=CH_2 + KBr + H_2O$

Bromo ethane ethene

Saytzev Rule:-

According to this rule, In the α, β - elimination reaction, the most substituted alkene is the predominent product.

Ex:- $CH_3-\underset{}{\overset{CH_3}{CH}}-\underset{Cl}{CH}-CH_3 \xrightarrow{alc\ KOH}$ i) $CH_3-\overset{CH_3}{C}=CH-CH_3$ (major product)

ii) $CH_3-\underset{CH_3}{CH}-CH=CH_2$ (minor product)

③ From Alkynes:-

By partial reduction, alkynes can be converted into Alkenes.

a) Formation of cis- Alkene:-

When alkyne is reacted with hydrogen in presence of Pd and Barium sulphate (Lindler's catalyst) poisoned with sulphur or quinoline it gives cis-alkene.

$$CH_3-C\equiv C-CH_3 + H_2 \xrightarrow[S]{Pd/BaSO_4} \begin{matrix} CH_3 \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} CH_3 \\ H \end{matrix}$$

b) Formation of trans-alkene:-

When alkyne reacts with hydrogen with Na and liquid NH_3 (Birch reduction), it gives transalkene.

Ex:- $CH_3-C\equiv C-CH_3 + H_2 \xrightarrow{Na\ liq\ NH_3} \begin{matrix} CH_3 \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} H \\ CH_3 \end{matrix}$

trans-but-2-ene

Chemical Properties of Alkene :-

① Electrophilic Addition reaction :-

a) Action with dilute alkaline $KMnO_4$ (Baeyer's reagent) :-
(Cis - Addition)

When alkene treated with Baeyer's reagent, a vicinal glycol is formed.

Ex:- $CH_2 = CH_2 + H_2O + O \xrightarrow[KMnO_4]{\text{dil. alkaline}} CH_2(OH) - CH_2(OH)$
(cis)

Ex:- $CH_3 - CH = CH_2 + H_2O + O \xrightarrow[KMnO_4]{\text{dil. alkaline}} CH_3 - CH(OH) - CH_2(OH)$

Propate-1,2-diol
(Cis)

b) Addition of Br_2 (Trans Addition) :-

Bromine or Chlorine add to alkene to form vicinal dihalide.

$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} CH_2(Br) - CH_2(Br)$
(trans)

1,2 - dibromo ethane

$CH_3 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3 - CH(Br) - CH_2(Br)$

1,2 - dibromo propane
(trans)

c) Addition of halogen acid (HX) :-

i) Addition to symmetrical alkenes :-

HX adds to symmetrical alkenes to form alkyl halides.

$$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2 - Br$$

ii) Addition to unsymmetrical alkenes :- (Markownikoff's rule)

Addition of HX to unsymmetrical alkene takes place according to markownikoff's rule.

Markownikoff's rule :-

When addition reaction takes place in an unsymmetrical alkene (or alkyne) across C=C (or C≡C) the negative part of the addendum is attached to that carbon atom which carries the least number of hydrogen atoms.

Ex :- $CH_3 - CH = CH_2 + HBr \longrightarrow CH_3 - \underset{\underset{Br}{|}}{CH} - CH_3$

2-bromo propane

Anti-Markownikoff's addition :- (Khrash peroxide effect)

The addition of HBr to unsymmetrical alkenes in presence of organic peroxides takes place against the Markownikoff's rule. This is called as peroxide effect.

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-bromo propane}}{CH_3 - CH_2 - CH_2 - Br}$$

Hydration :-

A water molecule gets added to alkenes in presence of acids to form alcohol.

$$\underset{\text{ethene}}{CH_2 = CH_2} + H_2O \xrightarrow{H^+} \underset{\text{ethanol}}{CH_3 - CH_2 - OH}$$

Addition to unsymmetrical alkenes follows markownikoff's rule.

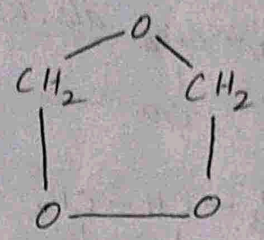
$$CH_3-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propene — Propan-2-ol

Ozonolysis :- (Addition of ozone)

Ozone is passed through a solution of alkene in CCl_4 to form an alkene ozonide. This ozonide is quite unstable and can be decomposed by hydrolysis in presence of Zn dust to give aldehydes or ketones or both.

Ex:- $CH_2=CH_2 + O_3 \longrightarrow$

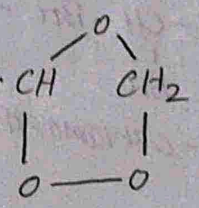


ethene — ethene ozonide

$$\xrightarrow{Zn \mid H_2O} 2H-\overset{O}{\overset{\|}{C}}-H + H_2O_2$$

formaldehyde

Ex:- $CH_3-CH=CH_2 + O_3 \longrightarrow$



propene — propene ozonide

$$\xrightarrow{Zn \mid H_2O} CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H + H_2O_2$$

Acetaldehyde — formaldehyde

Alkynes:

Methods of preparation:-

① Preparation of Acetylene by hydrolysis of calcium carbide:-

When calcium carbide (CaC_2) is treated with water it gives Acetylene

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{Acetylene}}{C_2H_2} + Ca(OH)_2$$

② By dehydrohalogenation of vicinal or gem dihalides:-

i) When vicinal dihalide is treated with alcoholic KOH it gives alkyne.

Ex:- $\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}} \xrightarrow{\text{alc. KOH}} CH \equiv CH + 2HBr$

Ex:- $CH_3 - \underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_2}} \xrightarrow{\text{alc. KOH}} \underset{\text{propyne}}{CH_3 - C \equiv CH} + 2HBr$

1, 2 - dibromo propane

ii) When gem dihalide is treated with ~~alcohol~~ alcoholic KOH it gives alkyne.

$CH_3 - \underset{Br}{\underset{|}{CH}} - Br \xrightarrow{\text{alc. KOH}} CH \equiv CH + 2HBr$

1, 1 - dibromo ethane

③ By dehalogenation of tetrahalides:-

When tetra halo alkane is heated with Zn dust it gives alkyne.

$$\underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH}} + 2Zn \xrightarrow{\Delta} CH \equiv CH + 2ZnBr$$

$$CH_3-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{CH}} + 2Zn \xrightarrow{\Delta} CH_3-C\equiv CH + 2ZnBr$$

1,1,2,2 - tetrabromo Propane Propyne

④ Preparation of higher alkyne :-

When Acetylene reacts with Sodamide in presence of liquid NH_3 it gives sodium acetylide, which reacts with alkyl halide to give higher alkyne.

$$\underset{\text{Acetylene}}{CH\equiv CH} + NaNH_2 \xrightarrow{liq\ NH_3} \underset{\text{Sodium Acetylide}}{CH\equiv C.Na} + NH_3$$

$$CH\equiv C.Na + CH_3-Br \longrightarrow \underset{\text{Propyne}}{CH\equiv C-CH_3} + NaBr$$

⑤ From Iodoform :-

When Iodoform is heated with Silver powdere it gives acetylene

$$H-C\boxed{\begin{matrix} I \\ I \\ I \end{matrix} + 6Ag + \begin{matrix} I \\ I \\ I \end{matrix}}C-H \xrightarrow{\Delta} \underset{\text{Acetylene}}{CH\equiv CH} + 6AgI$$

Chemical Properties :-

① Acidic nature of Alkynes :-

Acetylene and 1-alkynes are weakly acidic in nature.

The following reactions show the acidic nature of alkynes.

i) Reaction with Na :-

$$\underset{\text{Acetylene}}{2CH\equiv CH} + 2Na \xrightarrow{liq.\ NH_3} \underset{\text{Sodium Acetylide}}{2CH\equiv C.Na} + H_2$$

$$2R-C\equiv CH + 2Na \longrightarrow 2R-C\equiv C\cdot Na + H_2$$

Alkyne — Sodium alkynide

ii) Reaction with Cu_2Cl_2 :-

$$CH\equiv CH + Cu_2Cl_2 \xrightarrow{NH_4OH} Cu.C\equiv C.Cu + 2HCl$$

dicopper acetylide (Red ppt.)

$$R-C\equiv CH + Cu_2Cl_2 \xrightarrow{NH_4OH} R-C\equiv C.Cu + HCl$$

iii) Reaction with $AgNO_3$:-

$$CH\equiv CH + 2AgNO_3 \xrightarrow{NH_4OH} Ag.C\equiv C.Ag + 2HNO_3$$

disilver Acetylide (white ppt.)

$$R-C\equiv CH + AgNO_3 \xrightarrow{NH_4OH} R-C\equiv C.Ag + HNO_3$$

② Electrophilic Addition Reaction :-

a) Addition of halogen :-

Alkynes add two molecules of halogen in presence of CCl_4 to form tetrahaloalkanes.

$$CH\equiv CH + Br_2 \xrightarrow{CCl_4} \underset{Br}{\underset{|}{CH}} = \underset{Br}{\underset{|}{CH}} \xrightarrow[CCl_4]{Br_2} \overset{Br}{\overset{|}{CH}} - \overset{Br}{\overset{|}{CH}}$$

$$\underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH}}$$

ethyne — (tetrabromo ethane)

b) Addition of HX :-

Alkyles add two molecules of halogen acids to give Alkyl dihalide.

$$CH\equiv CH + HBr \longrightarrow CH_2 = CH - Br \xrightarrow{HBr} CH_3 - \underset{Br}{\underset{|}{CH}} - Br$$

(1,1 - dibromo ethane)

c) Addition of H_2O :-

When alkyne reacts with water in presence of dil. sulphuric acid containing $HgSO_4$, it gives aldehydes or ketone.

$$CH \equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_2 = CH - OH \xrightarrow{\text{tautomerisation}} CH_3 - CHO$$

Acetaldehyde

Ex :- $$CH_3 - C \equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3 - \underset{\underset{CH}{|}}{C} - CH_2 \xrightarrow{\text{Tautomerise}} CH_3 - \overset{O}{\overset{\|}{C}} - CH_3$$

Acetone

③ Oxidation :- (with Potassium Permanganate)

a) Alkynes on treatment with $KMnO_4$ gives 1,2 -diketone.

$$CH_3 - C \equiv C - CH_3 + 2H_2O + O_2 \xrightarrow{KMnO_4} CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}} - \underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}} - CH_3 \longrightarrow$$

But-2-yne

$$CH_3 - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - CH_3 + 2H_2O$$

Butane-1,2-dione

b) When Alkyne reacts with hot alkaline $KMnO_4$, the diketone formed undergoes oxidation to form carboxylic acids on acidification.

Ex:- $$CH_3 - C \equiv C - CH_3 \xrightarrow[\text{ii) } H_3O^+]{\text{i) } KMnO_4/OH^-/\Delta} 2CH_3COOH$$

But-2-yne

Acetic acid

④ Ozonolysis :-

Alkyne forms an ozonide with ozone. The ozonide gets decomposed with water to give glyoxal.

$$CH \equiv CH + O_3 \longrightarrow \begin{matrix} CH & O & CH \\ | & & | \\ O & — & O \end{matrix} \xrightarrow{H_2O} \begin{matrix} CHO \\ | \\ CHO \end{matrix} + H_2O_2$$

Glyoxal

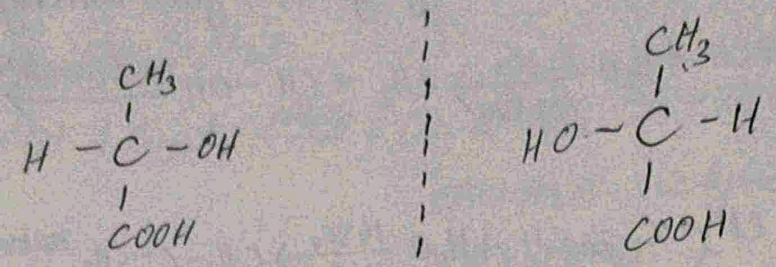
14/12/24

$$CH_3 - C \equiv C - CH_3 + O_3 \rightarrow CH_3 - \underset{\underset{O}{|}}{C} \overset{O}{\diagup\diagdown} \underset{\underset{O}{|}}{C} - CH_3 \xrightarrow{H_2O} CH_3 - \underset{\underset{O}{\|}}{C} - \underset{\underset{O}{\|}}{C} - CH_3 + H_2O_2$$

STEREO CHEMISTRY

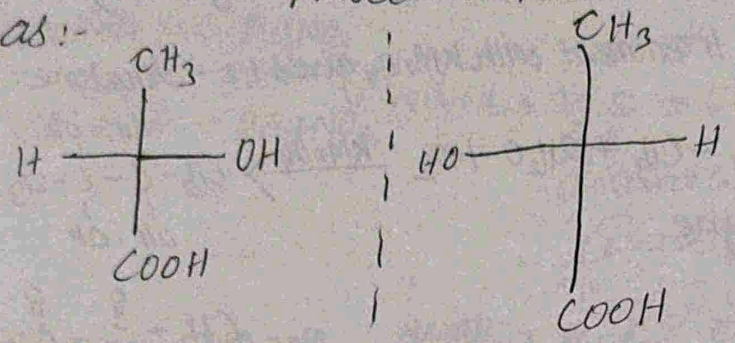
a) Fischer Projection:-

Ex:- Lactic acid:-



(d-Latic acid) (l-Latic acid)

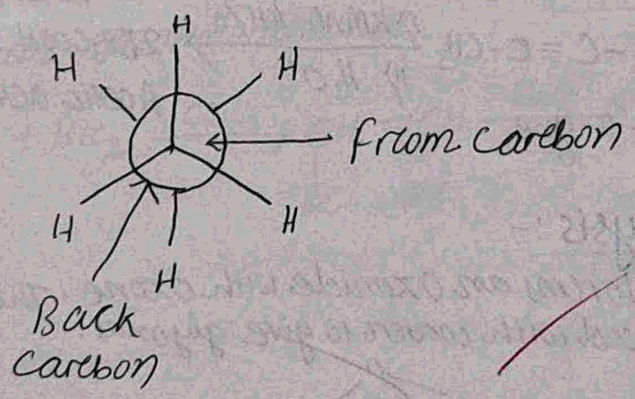
The fischer projection formula can be represented as:-

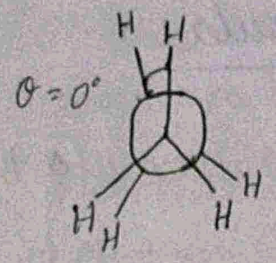


b) Newman Projections:-

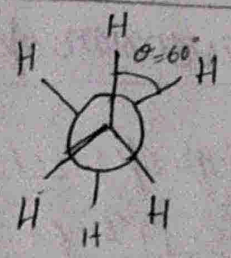
Consider the example of ethane

$CH_3 - CH_3$

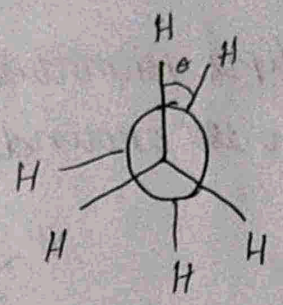




Eclipsed (θ = 0)



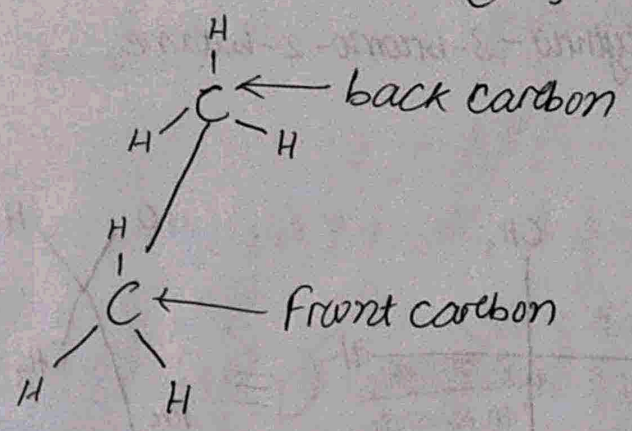
Staggered (θ = 60°)

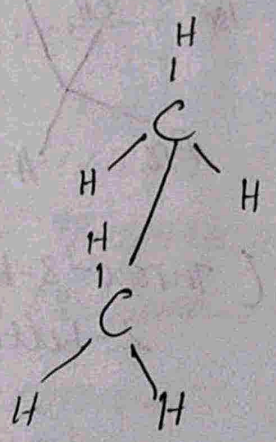


Skew (θ = ~~60°~~ 0° - 60°)

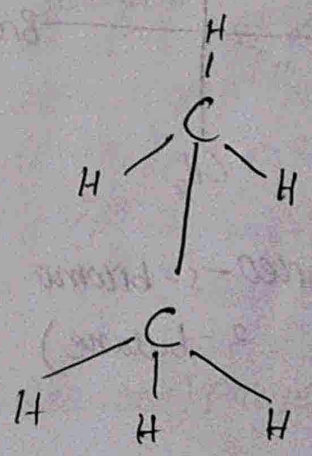
Sawhorse Projection :-

Consider the example of ethane ($C^1H_3 - C^2H_3$)





Eclipsed (θ = 0°)



Staggered (θ = 60°)

Interconversion of wedge formula :-

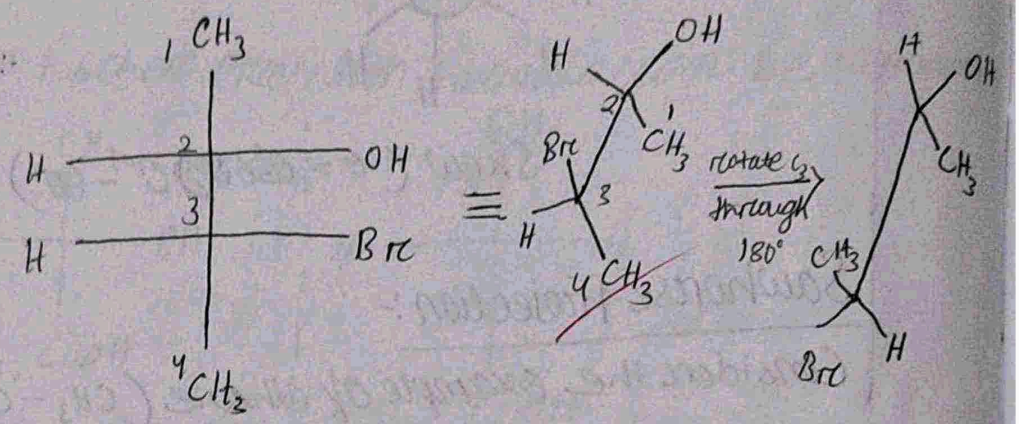
① Conversion of Fischer projection formula to Sawhorse projection formula :-

The Fischer projection formula can be transformed into sawhorse by

i) First making the eclipse form and

ii) then rotating through 180° around C_2-C_3 bond.

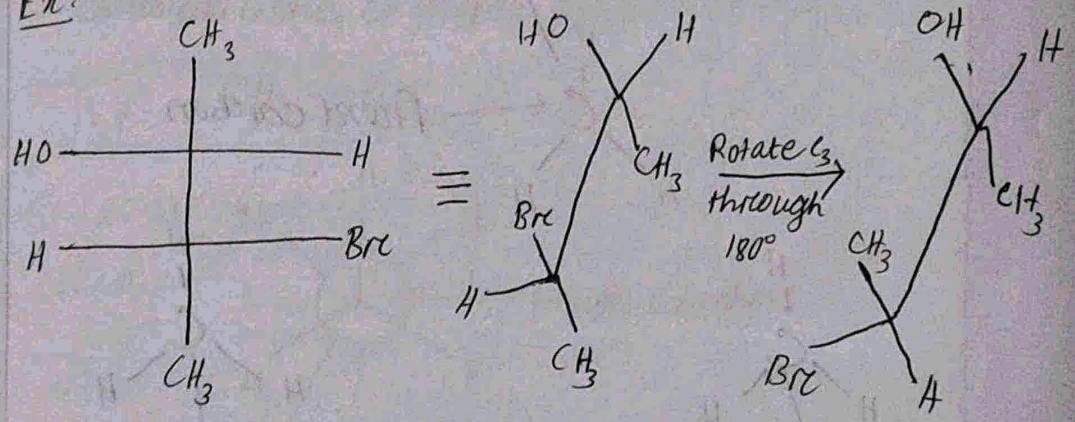
Ex :-



Erythro - 3-bromo- 2 - butane

Erythro-3-bromo 2-butane

Ex :-



(Threo-3-bromo 2-butane)

(Threo-3-bromo-2-butane)

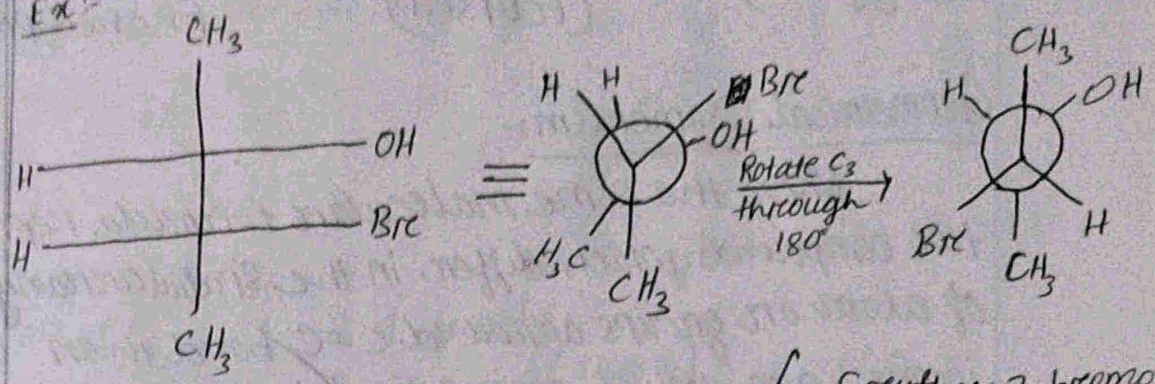
② Conversion of Fischer Projection Formula to Newman Projection Formulae:-

The Fischer Projection formulae can be transformed to Newman Projection formulae by

i) First making the eclipsed from and

ii) then rotating through 180° around $C_2 - C_3$ bond.

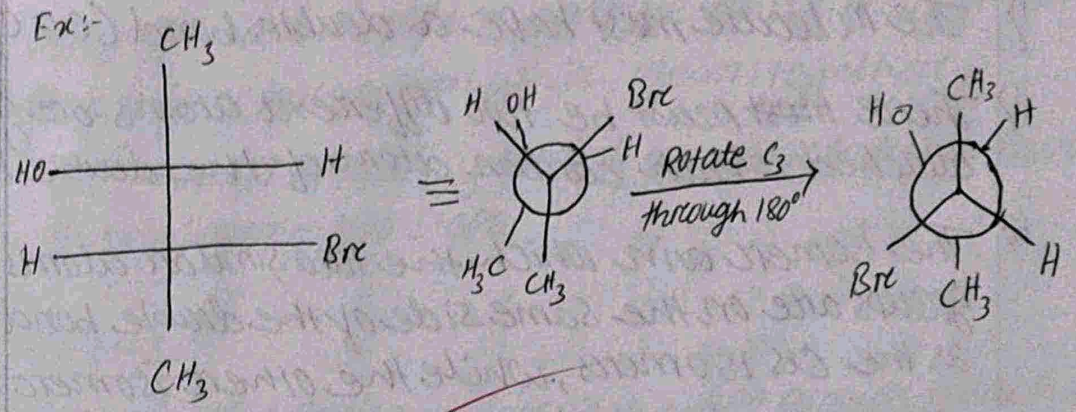
Ex:-



Erythro form
(3-bromo-2-butanol)

(Erythro 3-bromo-2-butanol)

Ex:-



Threo form
(3-bromo-2-butanol)

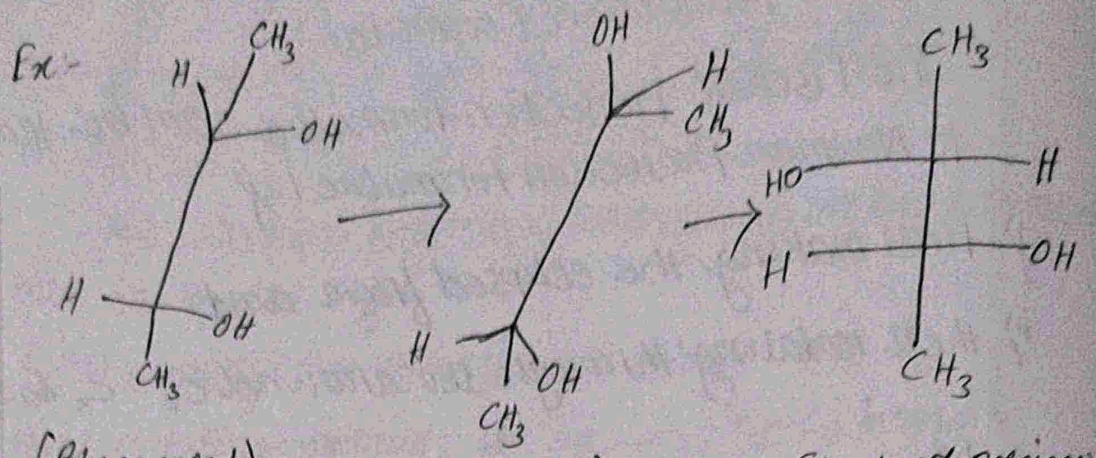
③ Conversion of Sawhorse (or Newman) Projection to Fischer projection formulae:-

Following steps are involved.

i) Convert staggered form of sawhorse projection to the eclipsed form and

ii) Then to the Fischer projection.

Ex:-



(Staggered) (Eclipsed) Fischer projection.

Geometrical Isomerism:-

When the same molecular formula represents two compounds which differ in the spatial arrangement of atom or groups arround C=C bond then isomers are called geometrical isomers and the phenomenon is called geometrical Isomerism.

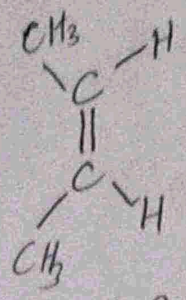
Conditions for Geometrical isomerism:-

i) The molecule must have a double bond (C=C)

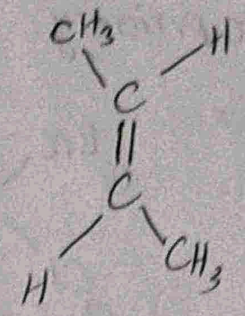
ii) There ~~must~~ must be two different atoms or groups attached to each carbon atom of the double bond.

iii) The isomer in which the two similar atoms or groups are on the same side of the double bond is known as the cis isomers, while the other isomer in which the two similar atoms or groups are present on the opposite sides of the double bond is known as trans-isomers.

Ex:- But-2-ene

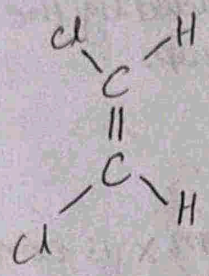


cis-but-2-ene

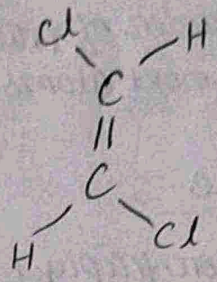


trans-but-2-ene

Ex:- 1,2-dichloroethene



(cis)



(trans)

The E and Z Nomenclature of Geometrical Isomers:-

The symbol E stands for the German word entgegen which means 'opposite' while the symbol Z stands for zusammen which means together.

The proposed system of nomenclature involves the following two steps.

Step-1 :-

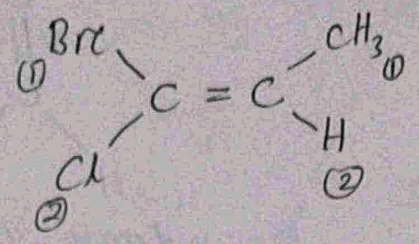
Assign the priority order to the two groups attached to each of the doubly bonded carbon in accordance with the following sequence rules.

i) Sequence rule 1:-

If the two atoms attached to C=C bond are different. Priority depends on atomic number. The atom having higher atomic number gets higher priority and

the atom with lower atomic number gets the lower priority.

Ex:-

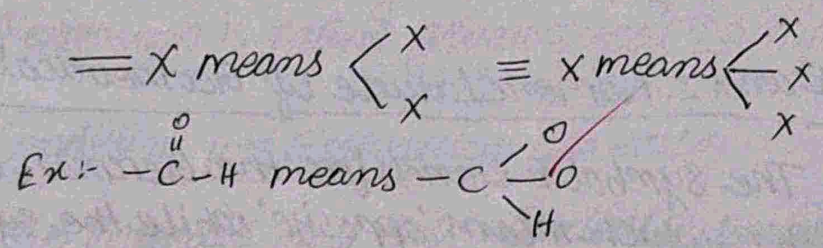


ii) Sequence rule-2:-

If two atoms directly attached to the C=C bond are the same, the order of priority is decided by the atomic number of the next atoms in the group.

iii) Sequence rule-3:-

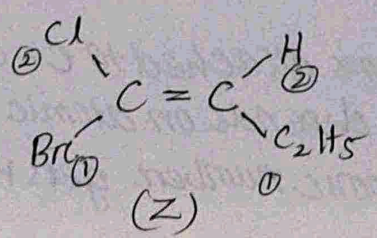
A doubly or triply bonded atom X is considered to be equivalent to two three X's.



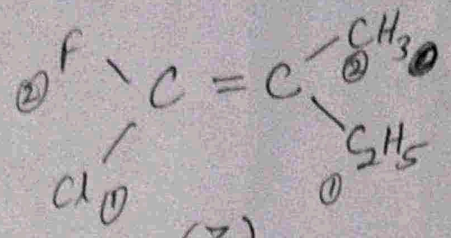
Step-2:-

After deciding the sequence of priority of two groups attached to each carbon of C=C bond, the compound is assigned Z configuration if the atoms or groups of higher priority are on the same side of double bond. On the other hand, if the atoms or groups of higher priority on each carbon are on the opposite sides of the double bond, the isomer is assigned the configuration E.

Ex:- 1)

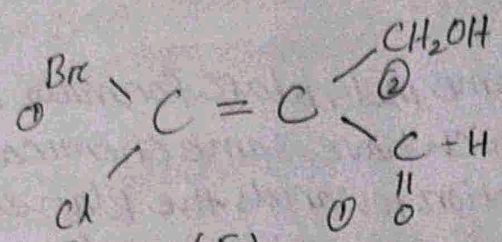


2)



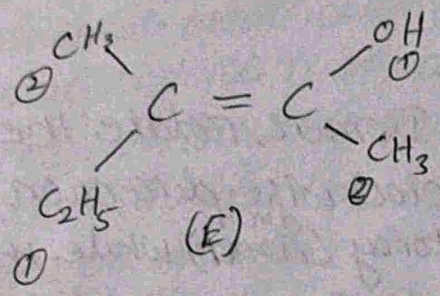
(Z)

3)



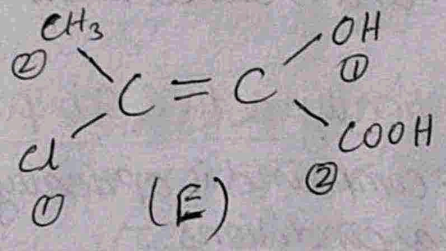
(E)

4)



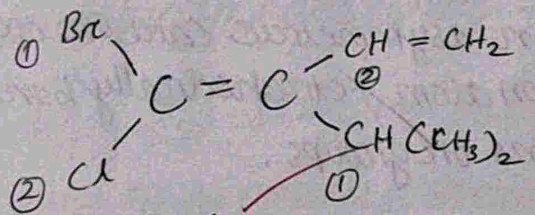
(E)

5)



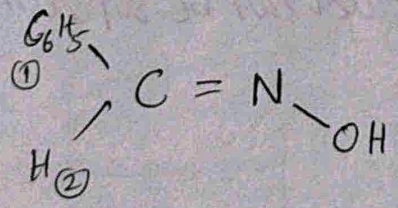
(E)

6)

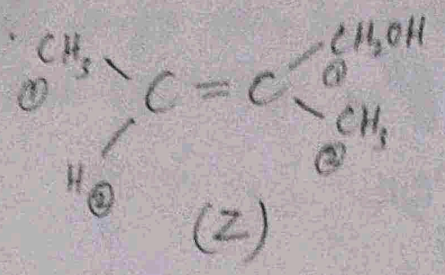


(E)

7)



(E)



(Z)

Optical Isomerism:-

When the same molecular formula represents two compounds which have same chemical properties but different action towards the plane polarised light then such compounds are called optical Isomers and the phenomenon is called optical Isomerism.

One of the Isomer, rotate the plane polarised light in clockwise direction and is called dextrorotatory (d or +) while the other isomer, rotate the plane polarised light in anticlockwise direction and is called laevorotatory (l or -)

Identification of optically active compounds:-

An organic compound is optically active if it satisfies the following conditions.

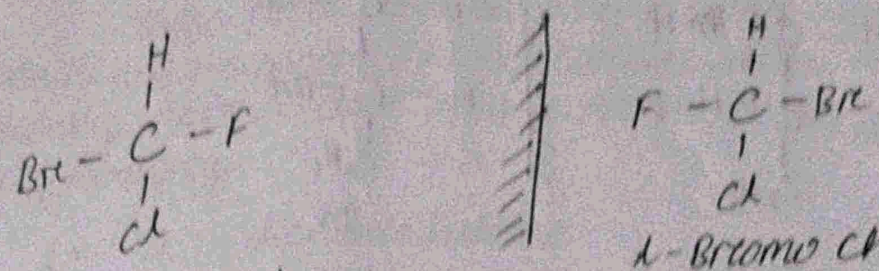
a) It should contain an asymmetric carbon or chiral carbon i.e a carbon atom tetrahedrally bonded to four different atoms or groups.

b) It should not have any plane of symmetry i.e compound and its mirror image should not be superimposable on each other.

Enantiomers:-

Enantiomers are defined as the isomers where molecular structures are mirror images of each other and which rotate the plane of the

Polarised light equally but in opposite directions.



d - Bromo chloro Fluoro methane

l - Bromo chloro Fluoro methane.

Recemic Mixture :-

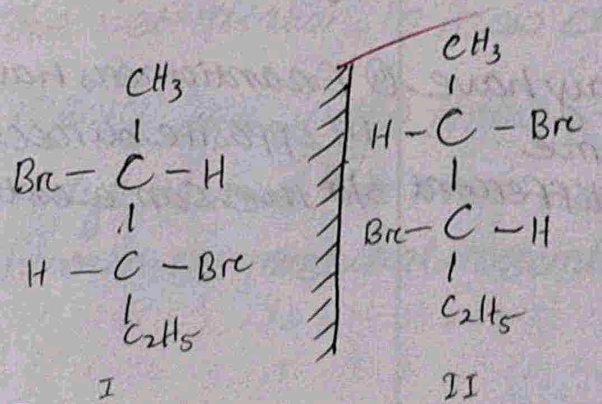
A mixture of two enantiomers in equimolar proportions (1:1 ratio) is called a racemic mixture, or racemic modification or dl-mixture (±). Ratemic mixture is optically inactive because the dextrorotatory property of one isomer is compensated by the Laevo-rotatory property of the other isomer. This is called External compensation.

Diastero-Isomers :-

These are defined as the pair of molecules with two or more different chiral carbon atoms which are neither identical nor non-superimposable mirror images of each other.

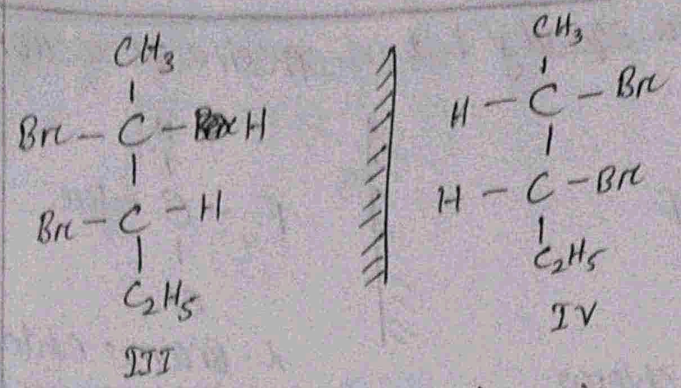
Ex :- 2,3-Dibromo pentane

The possible Steoisomers are



I II

(Pair of Enantimorces)



(Pair of Enantiomers)

Structure I and II, III & IV are mirror images to each other and are called Enantiomers. While Structure I and III, II and IV are not mirror images of each other and are called diastereo-isomers.

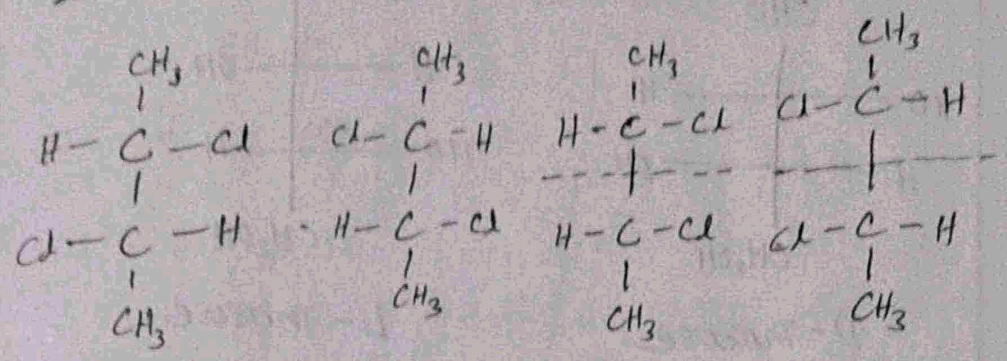
Diastereomers	Enantiomers
① These are stereoisomers that do not have a mirror image relationship.	① These are stereo-isomers that have a mirror image relationship.
② These have different physical properties.	② These have similar physical properties.
③ These can be separated by physical methods like fractional distillation, fractional crystallisation etc.	③ These can not be separated by physical methods like fractional distillation and fractional crystallisation etc.
④ Diastereomers may have rotation in the same direction but to different extent.	④ Enantiomers have rotation in opposite direction but to the same extent.

Meso Compounds :-

These are defined as the compounds which contain two or more chiral carbon atoms and are optically inactive due to the presence of the plane of symmetry.

Ex :- 2, 3 - dichloro butane :-

It has two chiral carbon atoms so it has $2^2 = 4$ number of stereo isomers. These are :-



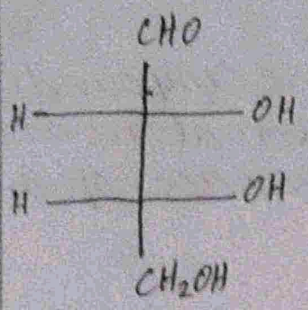
(I) (II) (III) (IV)

Structure I and II are optically active because they are the non-superimposable mirror images and are Enantiomers.

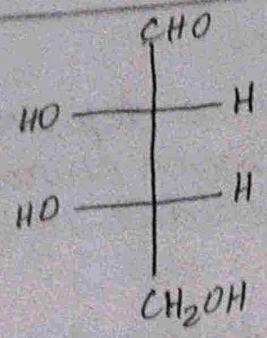
But structure III and IV are optically inactive and are called Meso compounds. The optical inactivity in meso compounds is due to the presence of plane of symmetry. In such compounds, the rotation due to one half of the molecule is cancelled by the rotation due to other half of the molecule in the opposite direction. This is called Internal compensation. The net rotation in meso compounds is zero.

Erythro and Threo Nomenclature :-

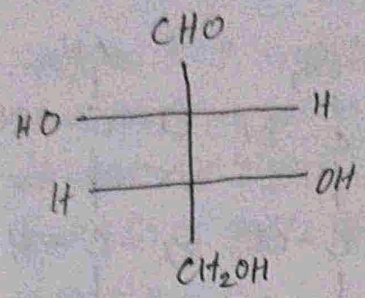
Erythro and ~~the~~ threo notations are derived from the structural resemblance to two sugars.



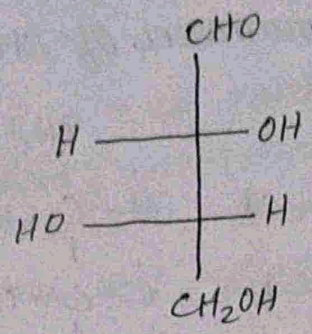
D- Erythrose



L- Erythrose



D - Threose



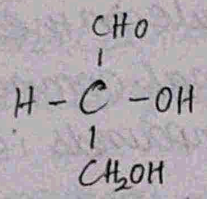
L- Threose

a) The Isomers with identical groups on the same side are called erythro forms.

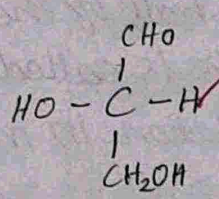
b) The Isomers with identical groups on the opposite side are threose forms.

D and L system of Nomenclature :-

The simplest monosaccharide Glyceraldehyde exist in the following two forms.



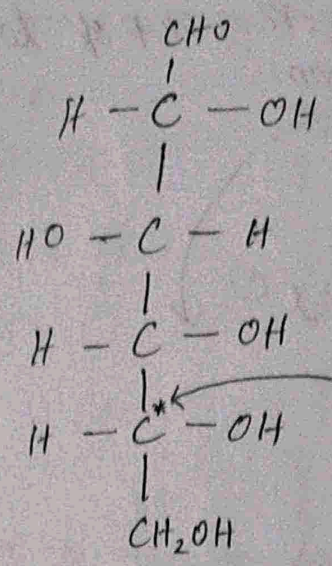
D- Glyceraldehyde



L- Glyceraldehyde

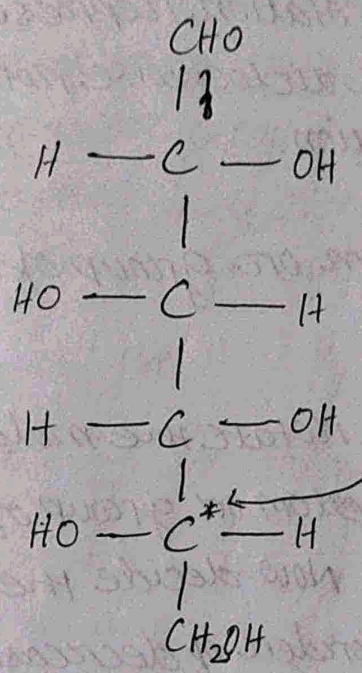
A monosaccharide is said to be in D family if it's highest numbered chiral carbon has the same configuration as D-glyceraldehyde. While if it resembles with L-glyceraldehyde then it is said to be in L-family.

Ex:-



Highest number chiral carbon.

D - Glucose

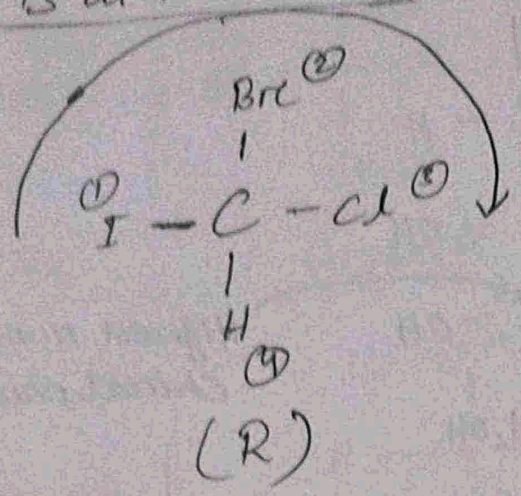


L-Glucose

R and S configuration from planar formulae (Fischer projection) :-

In case of a planar structure, give priority numbers to all the four atoms or groups attached to chiral carbon and then decide the configuration as follows.

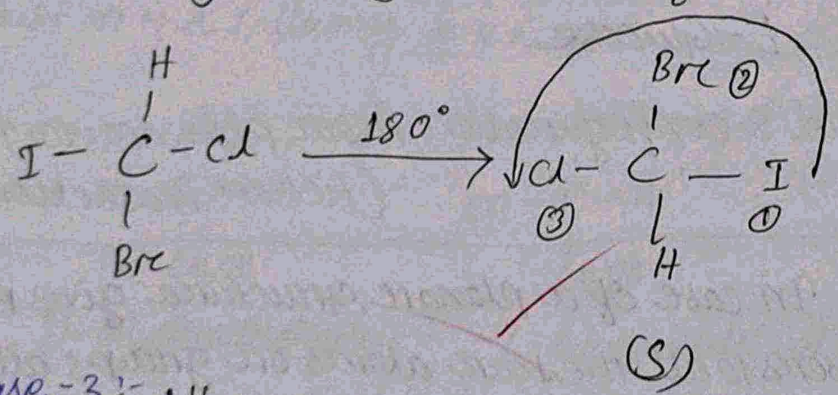
Case-1:- When the atom or group of lowest priority is at the bottom:



Simply rotate the eye in order of decreasing priority. Clockwise rotation represents R-configuration and anticlockwise rotation represents S-configuration.

Case-2:- When the atom or group of lowest priority is at the top:-

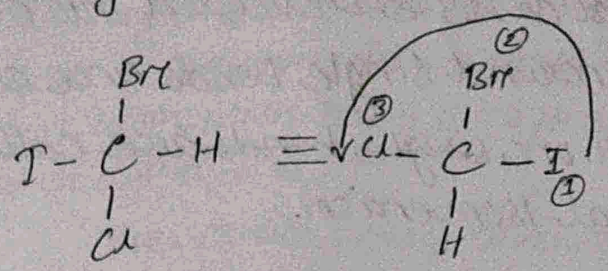
In such a case, rotate the molecule by 180°, so as to bring the atom or group of lowest priority at the bottom. Now decide the configuration by rotating the eye in order of decreasing priority.



Case-3:- When the atom or group of lowest priority is at the right hand side:-

~~In such~~ In such a case, keep the top position fixed and change the position of

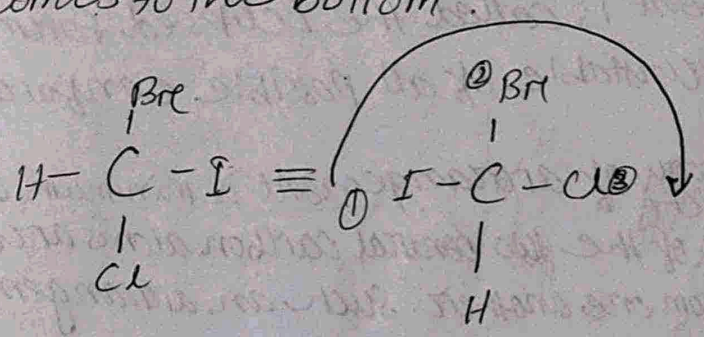
other atoms or groups in ~~clos~~ clockwise direction so that the atom or group of lowest priority comes to the bottom.



(S)

Case-4:- When the atom or group of lowest priority is at the left hand side:-

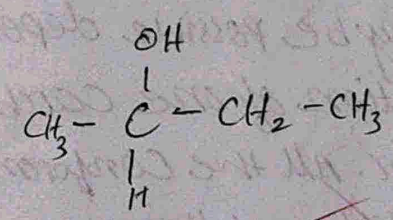
In such a case keep the top position fixed and change the position of the remaining atoms or groups in the anti clock-wise direction so that the atom or group of lowest priority comes to the bottom.



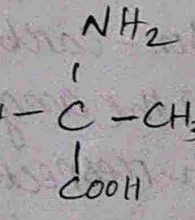
(R)

Problem:- Give R and S configurations to the following compounds.

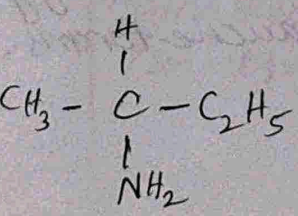
i)



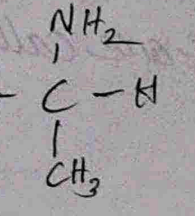
iii)



ii)



iv)



Conformational Isomerism:-

Different spatial arrangements of atoms or groups that can be converted into one another by rotation around single bonds are called conformations or ~~single bonds are called~~ Conformational Isomerism.

Characteristics of conformations:-

① The various conformations of the same compound differ slightly in their energy contents.

② The energy of an arrangements is maximum when the bond paires of the two central carbon atoms are very close to each other. Such an arrangement is called the Eclipsed form. This is the most unstable of all possible conformations.

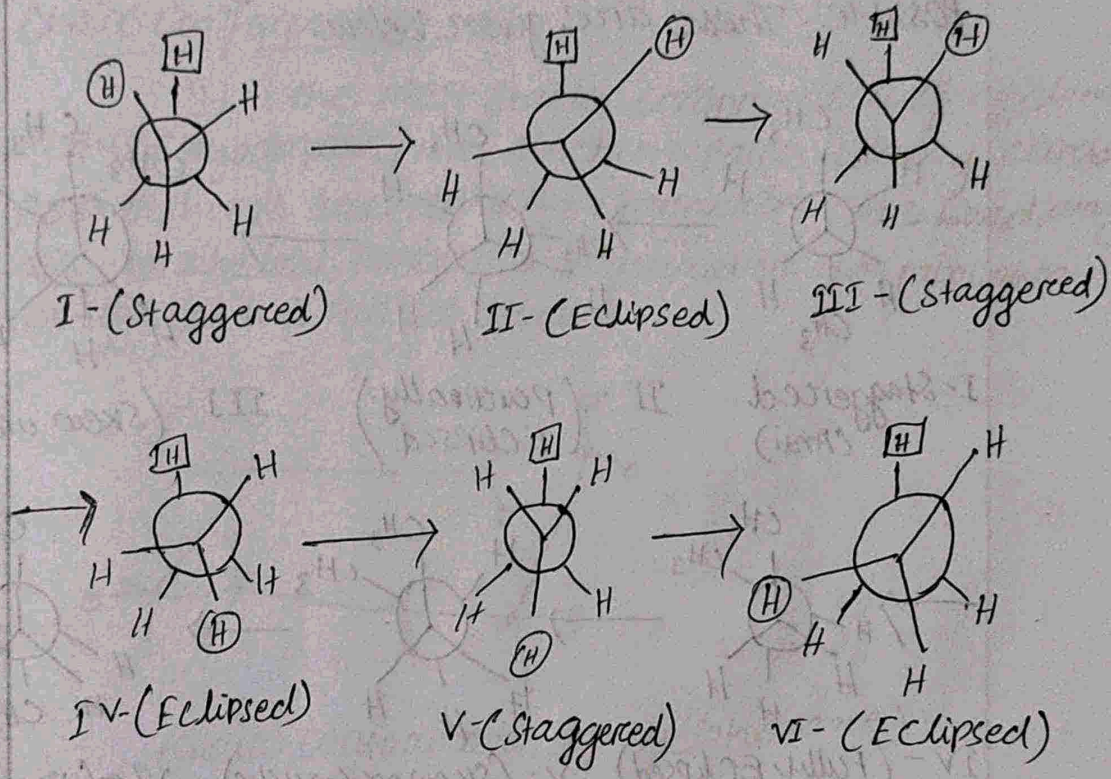
③ The energy of arrangement is minimum when the bond paires of the two central carbon atoms are very far off from one another. Such an arrangement is called the Staggered form. This is the stablest of all possible conformations ~~of a molecule~~.

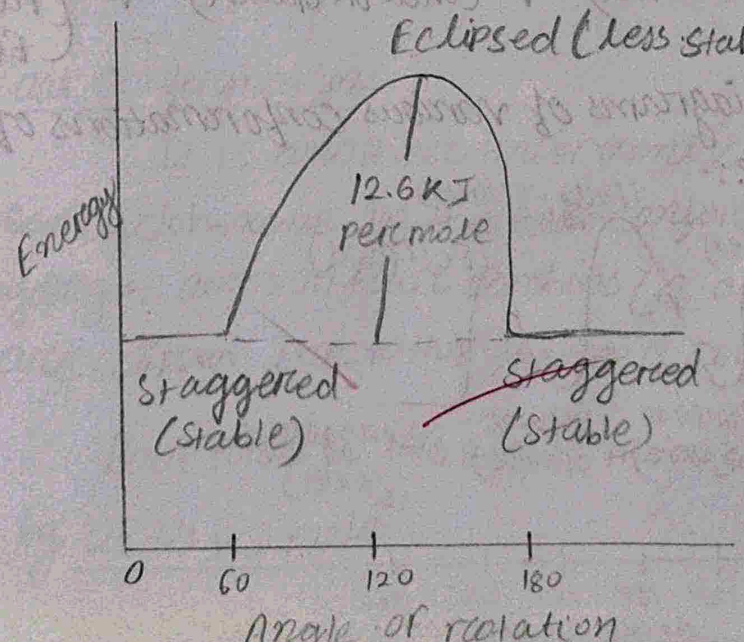
④ A number of conformations of a molecule involving carbon - carbon bond may be possible depending upon the angle of rotation of one carbon atom with respect to the other. All the conformations other than the eclipsed and the staggered one are called Skew or Gauche forms.

Conformations of Ethane :- ($CH_3 - CH_3$)

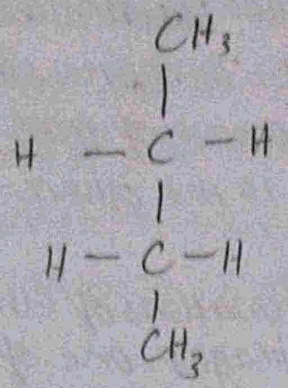
In this molecule, two ~~carbon~~ carbon atoms are bonded by a single bond. Therefore ethane exists a number of conformations because of free rotation of one carbon atom with respect to the other about the central sigma bond.

The various conformations of ethane can be clearly understood if we imagine one of its carbon atoms to be fixed and the other one is rotated through an angle of 60° at a time.

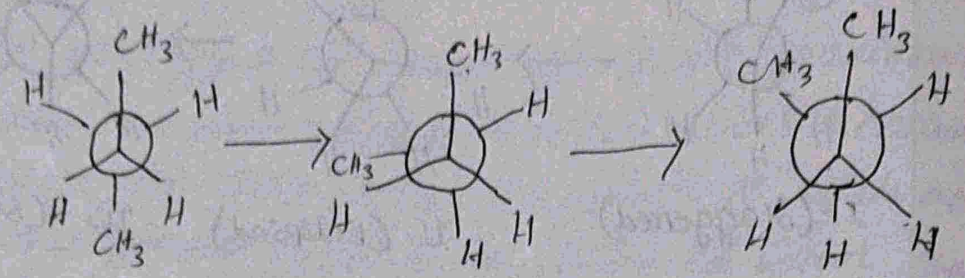




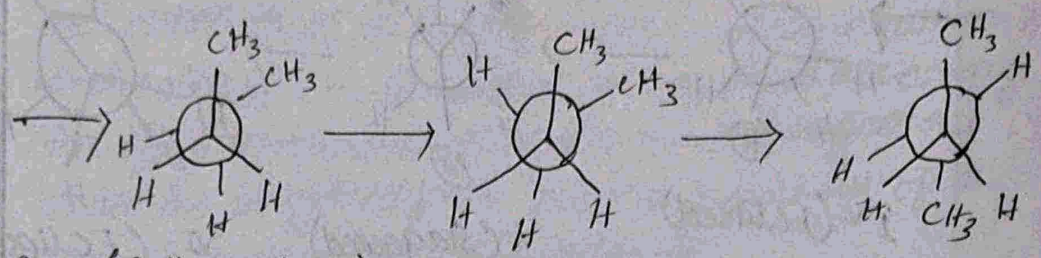
Conformations of n-Butane:-



By fixing rear carbon atom and rotating the front one, different conformations of n-butane are possible. These are given below.

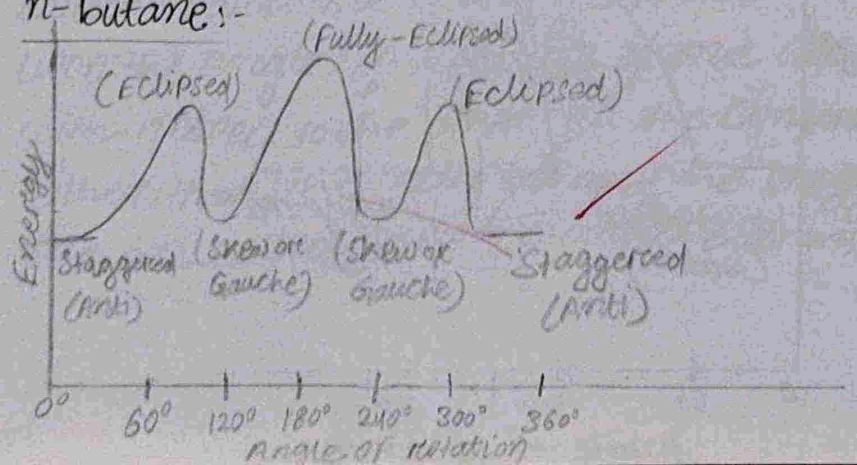


I- Staggered (Anti) II - (Partially Eclipsed) III - (Skew or Gauche)



IV - (Fully Eclipsed) V - (Skew or Gauche) VI - (Partially Eclipsed)

Energy diagrams of various conformations of n-butane:-



~~Angle of rotation~~:-

The order of stability of different conformations of n-butane is :-

Staggered (anti) > Skew > partially eclipsed > fully eclipsed

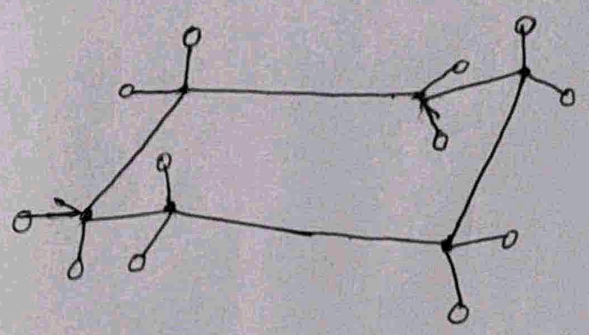
Conformational Analysis of cyclohexane :-

Two Important conformations of cyclohexane are.

i) Chair conformation ii) Boat conformation.

Chair conformation :-

It is the most stable conformation of cyclohexane. In this conformation, the electron pairs forming carbon carbon bonds are perfectly staggered. The bond angles are tetrahedral. Hence this conformation has minimum energy, as it is free of strain.

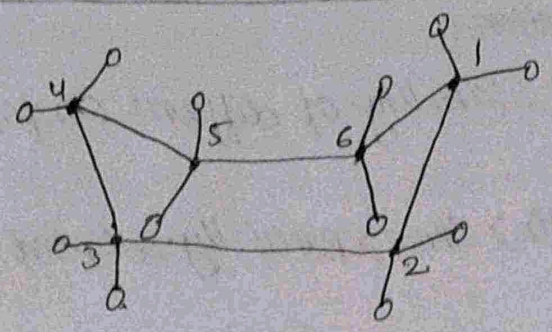


(Chair conformation of cyclohexane)

Boat conformation :-

It is another important conformation of ~~cyc~~ cyclohexane. In the boat conformation, the hydrogen atoms on four carbons (C_2 and C_3, C_5 and C_6) are eclipsed. Due to this there is considerable strain.

Boat form is ~~less~~ stable than chair conformation by 28.84 kJ mole^{-1}.



(Boat conformations of cyclohexane)

In addition to chair and boat conformations, cyclohexane also exists in several other conformations such as half chair, twist boat forms etc.

24/2/22

G.E-II (Chemistry)

UNIT-I

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May 11, 2022.

Chemical Energetics:

1. Thermodynamics:

It is the branch of Science which deals with changes in Energy (Heat) that accompany physical or chemical changes in matter.

2. Objectives of Thermodynamics:

(a) To predict the physibility of a process.
(b) To predict the extent of a reaction.
(c) To deduce certain laws of physical chemistry

3. Limitations of Thermodynamics:

(a) Laws of thermodynamics apply only to matter involve and not to individual atoms or molecule.
(b) It predict only the physibility of a process, but not it's success.
(c) It doesn't predict the rate of a reaction.
(d) It doesn't tell anything about the mechanism of the reaction.

4. System:

System is defined as any part of universe enclosed by some boundary through which exchange of Heat or energy takes place.

5. Surrounding:

The mass or region outside the System is called the surroundings.

6. Boundary:

The realor imaginary Surface that Separates the System from its Sourrounding is called Boundary, the boundary of a System can be fixed or movable.

7. Types of System:

It is of 3 types;

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(a) Open System - allows exchange of matter & energy betn System & Surroundings.
(b) Closed System - allows only exchange of energy betn System & Surroundings.
(c) Isolated system - Doesn't allow matter & energy exchange.

8. Homogenous system :
The System which is uniform throughout reaction is called Homogenous system.
Ex:

9. Heterogenous system :
The System which is not uniform throughout reaction is called Heterogenous System.
Ex:

10. Macroscopic properties :
These are the properties associated with the bulk of matter.

11. State of a System :
It is the condition of existance of a System when it's macroscopic properties have a definite value.

12. State variables :
These are those macroscopic properties which when changed cause a change in the State of a System.
Ex: Composition, pressure, Temperature & Volume

13. State function :
It is a property of a System that depends only on the State of the System & independent of path followed.
Ex: ΔU, ΔP, ΔT & ΔV etc.

14. Path function :
It is a property of a System that depends on the path by which the System acheived a particular State & Dependent on the path taken to product.
Ex: Work, Heat etc.

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THERMODYNAMIC PROCESSES:

May, 18, 2022

Isothermal process:

It is a thermodynamic process, in which temperature remains constant throughout the process. i.e. $\Delta T = 0$

Ex: Refrigerator, Boiling etc.

Isobaric process:

It is a thermodynamic process, in which pressure remains constant throughout the process i.e. $\Delta P = 0$

Ex: Boiling of water to steam & freezing of water to ice etc.

Isochoric process:

It is a thermodynamic process in which volume remains constant throughout the process i.e. $\Delta V = 0$

Ex: Ideal otto cycle etc.

Adiabatic process:

It is a type of thermodynamic process that occurs without transferring heat or mass between the thermodynamic system and its environment.

Ex: turbine & evaporation etc.

Cyclic & Acyclic processes:

If a system goes back to its initial stage after the end of a sequence of processes, then it is cyclic process otherwise acyclic process.

Ex: cyclic: Refrigerator, AC & acyclic: boiling of water

Reversible & Irreversible processes:

A reversible process is one in which both the system and its environment can return to exactly the states they were in by following the reverse path. An irreversible process is one in which they can't return together.

Ex: R: Expansion, melting of ice & IR: burning of fuel.

Exothermic & Endothermic processes:

An Exothermic process releases heat, causing the temp. of the immediate surroundings to rise.

Ex: $CaO + H_2O \longrightarrow Ca(OH)_2 + Heat$

An Endothermic process absorbs heat and cools the surroundings.

Ex: [illegible]

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Internal (or) Intrinsic Energy (U):

It is the total Energy stored in a system under a given set of conditions. It is a state function. Absolute value of internal energy can not be determined. However internal energy change (ΔU) can be determine by measuring the heat evolved or absorbed in a process. (constant temperature and volume)

It may be denoted as, $\boxed{\Delta U = U_P - U_R}$

where, ΔU = change in internal energy.
U_P = internal energy of product.
U_R = internal energy of reactant.

Enthalpy:

It is the total heat content of the system at constant pressure.

Mathematically, $\boxed{H = U + PV}$

where, H = Enthalpy of a system.
U = Internal energy of the system
P = pressure of system
V = volume

It is also a state property and it's absolute value can't be determined. However, enthalpy change can be determined easily.

So, $\boxed{\Delta H = H_P - H_R}$

where, ΔH = Enthalpy change
H_P = Enthalpy of product
H_R = Enthalpy of reactant.

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Enthalpy of reaction : (Heat of the Reaction)

It is the total amount of heat energy evolved or absorbed when the number of moles of reactants react completely to give the products as given in balanced chemical Equation.

As most of the reactions are takes place at Constant pressure, There fore Enthalpy change (ΔH) is heat of the reactions.

Types :

ⓐ **Enthalpy of Solution :**

It is defined as the change in enthalpy that results when 1 mol of Solute is dissolved in a Solvent to form infinitely dilute Solution.

Ex: $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$ $\quad \Delta H^{\ominus}_{Soln} = +4\ KJ/mol$

ⓑ **Enthalpy of fussion : (H_f)**

The energy required to change an amount of Substance from the Solid to the liquid State. The temp. during this phase change remains Constant. unit: J/g or J/mol.

ⓒ **Enthalpy of vaporisation : (H_v)**

The energy required to change an amount of Substance from liquid to gas State. The temp. during this phase change remains constant.

unit: J/g or J/mol

ⓓ **Enthalpy of formation :**

It is the enthalpy change for the reaction that forms one mole of compound from its element, with all Substances in their standard states.

$2C(s) + \frac{1}{2}O_2(s) + 3H_2(g) \longrightarrow C_2H_5OH(l)$ $\quad \Delta H_f^{\circ} = -277.69\ KJ$

ⓔ **Enthalpy of Combustion :**

When 1 mole of Substance undergoes Combustion. It is a exothermic reaction. Hence energy is always evolved. So also called as Heat energy evolved.

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

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(f) Enthalpy of Neutralisation :

It is the heat energy released when 1 mole of water is formed from neutralisation of an acid with a base.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Extensive properties :

These are the properties like mass, volume, heat capacity, internal energy, entropy, Gibb's free energy, enthalpy etc. which depend upon the quantity of matter present in that system.

Intensive properties :

These are the properties like ~~mass, volume, heat capacity~~ pressure, temperature, density, viscosity, surface tension, refractive index, chemical potential, electromotive force, which are independent of the amount of the substances present in the system.

LAWS OF THERMODYNAMICS :

Hess's Law of Constant Heat Summation :

It states that the enthalpy change during a chemical reaction is the same, whether the reaction takes place in one step or in several steps.

First law of Thermodynamics :

(i) In a system of constant mass, energy can neither be created nor be destroyed by any physical or chemical change.

(ii) The sum of all the form of energy in an isolated system is constant.

(iii) When one form of energy disappears exactly the same ammount of energy appears in some other form.

(iv) The total sum of mass and energy in the universe is constant, called as law of conservation of energy.

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Mathematically, $\Delta U = q + W$

where, ΔU is increase in internal energy.

q is the heat absorbed.

and W is the workdone on the system.

Second law of Thermodynamics:

(i) According to kelvin-planck; "It is impossible for a cyclic process to take heat from a cold reservoir and convert it into work without at the same time transferring heat from a hot to cold reservoir."

(ii) According to Claussius, "It is impossible to construct a machine which is able to convey heat by a cyclic process from one reservoir at a lower temperature to another at higher temperature unless work is done on the machine by some outside agency.

(iii) Entropy 'S' is a state function and the entropy of the universe remains constant for a reversible process and increases for a irreversible process. The entropy on universe never decreases.

IMPORTANT PRINCIPLES AND DEFINITIONS OF THERMO-CHEMISTRY:

Concept of Standard State:

The molar enthalpy of a substance is a function of temperature and pressure. In thermodynamics the pressure dependance is removed by defining the standard state of substance as follows;

(i) For a pure gaseous substance, the standard state at a given temperature is the ideal gas at one bar pressure.

(ii) for a pure liquid the standard state at a given temperature is pure liquid at one bar pressure.

(iii) for a pure crystalline substance the standard state at a given temperature is the pure crystalline substance at one bar pressure.

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The Standard Molar enthalpy of a Substance is represented by placing the Subscript degree to the Symbol 'H', i.e. H°.

Standard Enthalpies of Formation:

Enthalpy of formation is defined as the enthalpy change when One mole of Substance is formed from its Constituent elements. It is denoted as $\Delta_f H$.

Heat formation of $H_2O(l)$ i.e. $\Delta_f H = -286$ kJ

" " of CO_2 is -393.5 kJ

→ Standard Enthalpy of formation is defined as the Enthalpy change when 1 mole of a Substance is formed from its Constituent elements in their standard states.

It is denoted as $\Delta_f H^\circ$.

NOTE:

In Calculating $\Delta_f H^\circ$ values, it is assume that the standard enthalpies of elements are Zero.

- The Compounds having +ve value of ΔH_f° are Endothermic Compounds.
- The Compounds having -ve value of ΔH_f° are Exothermic Compounds.

The heat of formation values Can be used to Calculate the heat of reactions in general the Standard enthalpy of reaction is equals to the difference between ΔH_f° values of all the products and reactants.

$$\boxed{\Delta_r H^\circ = \Sigma \Delta_f H^\circ_{(product)} - \Sigma \Delta_f H^\circ_{(Reactant)}}$$

where, $\Delta_r H^\circ$ = Standard enthalpy of reaction.

$\Delta_f H^\circ_p$ = Standard enthalpy of formation of all product

$\Delta_f H^\circ_R$ = Standard enthalpy of formation of all reactants.

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for a general reaction, $aA + bB \longrightarrow cC + dD$

$$\boxed{\Delta_r H^\circ = \{c\Delta_f H^\circ(C) + d\Delta_f H^\circ(D)\} - \{a\Delta_f H^\circ(A) + b\Delta_f H^\circ(B)\}}$$

Questions:

① from the data given below at 298K, for the reaction, $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$. Calculate the enthalpy of formation of CH_4 at 298 K.

Enthalpy of reaction = -890.5 KJ

Enthalpy of formation of $CO_2(g)$ = -393.5 KJ/mol

Enthalpy of formation of $H_2O(l)$ = -286.0 KJ/mol

Ans: Given, $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta_r H^\circ = -890.5$ KJ

$\Delta_f H^\circ(CO_2) = -393.5$ KJ/mol

$\Delta_f H^\circ(H_2O) = -286$ KJ/mol

let, $\Delta_f H^\circ(O_2) = 0$

We know, $\Delta_r H^\circ = \Delta_f H^\circ(CO_2) + 2\times\Delta_f H^\circ(H_2O) - \Delta_f H^\circ(CH_4) - 2\Delta_f H^\circ(O_2)$

$\Rightarrow -890.5 = -393.5 + 2\times(-286) - \Delta_f H^\circ(CH_4) - 2\times 0$

$\Rightarrow -890.5 + 393.5 + 572 = -\Delta_f H^\circ(CH_4)$

$\Rightarrow 75 = -\Delta_f H^\circ(CH_4)$

So, $\Delta_f H^\circ(CH_4) = -75.0$ KJ/mol

② Calculate the standard internal energy change for the following reaction at 25°C.

$C(graphite) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

Given that $\Delta_r H^\circ$ at 25°C for $H_2O(g) = -241.8$ KJ/mol; for $CO(g) = -110.5$ KJ/mol and gas Constant (R) = 8.314 $\frac{J}{K.M}$

Ans: Given, $C(Graphite) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

$\Delta_f H^\circ(H_2O) = -241.8$ KJ/mol

$\Delta_f H^\circ(CO) = -110.5$ KJ/mol

$R = 8.314$ J/kmol, $T = 25°C = 298K$,

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We know, $\Delta_r H^\circ = \Delta_f H^\circ(CO) + \Delta_f H^\circ(H_2) - \Delta_f H^\circ(C) - \Delta_f H^\circ(H_2O)$

$= -110.5 + 0 - 0 + 241.8$

$= 131.3 \text{ kJ/mol} = 131300 \text{ J/mol}$

$\Delta n_{(g)} = (1+1) - (0+1) = 1$

But, $\Delta U^\circ = \Delta H^\circ - \Delta nRT$

$\Rightarrow \Delta U^\circ = 131300 - 1 \times 8.314 \times 298 = 128822.4 \text{ J/mol}$

$= 128.822 \text{ kJ/mol}$

③ Calculate the value of ΔH° for the reaction:

$2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(l) + 2SO_2(g)$

$\Delta_f H^\circ(H_2S) = -20.6 \text{ kJ/mol}$, $\Delta_f H^\circ(H_2O) = -285.8 \text{ kJ/mol}$ and $\Delta_f H^\circ(SO_2) = -296.8 \text{ kJ/mol}$

Ans: Given, $2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(l) + 2SO_2(g)$

$\Delta_f H^\circ(H_2S) = -20.6 \text{ kJ/mol}$

$\Delta_f H^\circ(H_2O) = -285.8 \text{ kJ/mol}$

$\Delta_f H^\circ(SO_2) = -296.8 \text{ kJ/mol}$

We know, $\Delta_r H^\circ = 2\Delta_f H^\circ(H_2O) + 2\Delta_f H^\circ(SO_2) - 2\Delta_f H^\circ(H_2S) - 3\Delta_f H^\circ(O_2)$

$= 2\times(-285.8) + 2\times(-296.8) - 2(-20.6) - 3\times 0$

$= -571.6 - 593.6 + 41.2$

$= -1124 \text{ kJ/mol}$

④ The molar heat of formation of NH_4NO_3 is -367.50 kJ and those of $N_2O(g)$ and $H_2O(l)$ are 81.5 kJ and -285.8 kJ respectively at 25°C and 1 atm pressure. Calculate ΔH for the reaction:

$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$

Ans: Given, $NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$

We know, $\Delta_r H^\circ = \Delta_f H^\circ(N_2O) + \Delta_f H^\circ(H_2O) - \Delta_f H^\circ(NH_4NO_3)$

$= 81.5 - 285.8 + 367.50$

$= -122.6 \text{ kJ}$

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May. 25, 2022

Bond Energy and Bond Dissociation Energy :-

Bond Dissociation Energy :

The amount of energy required to break a bond between the atoms in the gaseous state in a specific compound is called bond dissociation energy.

→ The bond dissociation energy of H_2 and Cl_2 are 435.4 kJ/mol and 242.8 kJ/mol respectively.

→ Bond dissociation energy is a definite quantity and depends on the presence of other groups in a molecule.

e.g: the bond dissociation energies of the two 'O-H' in water are different. The energy required to break the O-H bond in hydroxyl groups is 430 kJ/mol.

$$H-O-H(g) \rightarrow H(g) + O-H(g) \quad ; \Delta_{O-H}H^\circ = 498 \text{ kJ/mol}$$

$$O-H(g) \rightarrow O(g) + H(g) \quad ; \Delta_{O-H}H^\circ = 430 \text{ kJ/mol}$$

Bond Energy :

Bond Energy of a given bond is defined as the average of energies required to dissociate one mole of said bond present in different gaseous compounds into free atoms or radicals in the gaseous state.

e.g; The O-H bond energy in water molecule is the average of two bond dissociation energies.

$$\Delta_{O-H}H^\circ = \frac{498+430}{2} = \frac{928}{2} = 464 \text{ kJ/mol}$$

The word 'Average' in the definition of bond energy of a particular bond is not the same when present in different compounds.

Calculation of Bond Enthalpies:

The values of bond energies can be calculated by using spectroscopic data, electron impact studies and thermochemical data.

In the case of diatomic molecule (H_2, N_2, Cl_2, O_2 etc.) the bond energy of a bond may be taken equal to its bond dissociation energy, but for polyatomic molecules the bond energy of a particular bond can be calculated from the values of heats of formation. The heat of formation in turn can be calculated from the heats of combustion, dissociation, sublimation etc.

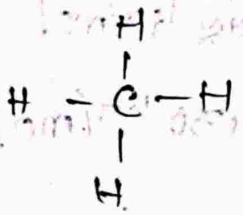
e.g: for the bond energy of C-H bond in methane, can be calculated as follows:

Given,

$$C(s) \xrightarrow{\text{Sublimation}} C(g) \quad \Delta H^\circ = 716.68\ kJ$$

$$\frac{1}{2}H_2(g) \xrightarrow{\text{Dissociation}} H(g) \quad \Delta H^\circ = 217.97\ kJ$$

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \quad \Delta H^\circ = -74.75\ kJ$$



$$CH_4(g) \longrightarrow C(g) + 4H(g)$$

(Methane)

Now,

$$2H_2(g) \longrightarrow 4H(g)$$

$$CH_4(g) \longrightarrow C(s) + 2H_2(g)$$

$$C(s) \longrightarrow C(g)$$

$$CH_4(g) \longrightarrow C(g) + 4H(g) \quad \Delta H^\circ = 1663.37\ kJ$$

The C-H bond energy is, $\frac{1663.31}{4} = 415.82\ kJ/mol$

The actual value is 413 kJ.

Questions:

① Calculate the bond energy of C-C bond from the following data: C-H bond energy = 413 kJ/mol. Enthalpy of formation for: $C_2H_6(g) = -85$ kJ/mol; $C(g) = 716.7$ kJ/mol and $H(g) = 216.5$ kJ/mol.

Ans: $2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$ — ① $\Delta H = -85$ kJ

$C(s) \longrightarrow C(g)$ — ② $\Delta H = 716.7$ kJ

$\frac{1}{2}H_2(g) \longrightarrow H(g)$ — ③ $\Delta H = 216.5$ kJ

Required Eq^n is $C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$ $\Delta H = ?$

Eq^n ② × 2 + Eq^n ③ × 6 ⇒ $2C(s) + 3H_2(g) \longrightarrow 2C(g) + 6H(g)$ — ④

$\Delta H = 2 \times 716.7 + 6 \times 216.5$

$= 2732.4$ kJ

Eq^n ④ − Eq^n ① ⇒ $C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$ $\Delta H = 2817.4$ kJ.

The above reaction involves the breaking of one C–C & six C–H bonds.

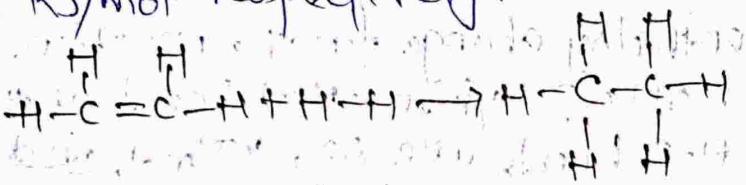
Bond energy of 6 C–H bonds = 413 × 6 = 2478 kJ

∴ Bond energy of C–C bond = 2817.4 − 2478 = 339.4 kJ

② Calculate the bond energy of C=C from the following reaction $H_2C=CH_2(g) + H_2(g) \longrightarrow CH_3-CH_3(g)$. $\Delta H = -125.5$ kJ

The bond energies of C–C, C–H & H–H are 347.3, 414.2 & 435.1 kJ/mol respectively.

Ans:



4 C–H bonds are not affected. One H–H bond is broken, $\Delta H = 435.1$ kJ, one C=C bond is broken, $\Delta H = ?$

Two C–H bonds are formed, $\Delta H = -2 \times 414.2$ kJ $= 848.4$ kJ

one C–C bond is formed $\Delta H = 347.3$ kJ

Enthalpy change for the reaⁿ will be

$\Delta H = (\Delta H_{C=C} + \Delta H_{H-H}) - (\Delta H_{C-C} + 2\Delta H_{C-H})$

$\Rightarrow -125.5 = (\Delta H_{C=C} + 435.1) - (347.3 - 848.4)$

$\Rightarrow \Delta H_{C=C} = -125.5 - 435.1 + 347.3 + 848.4$

$= 615.1$ kJ

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Calculation of Heats of Reaction from bond Energy data:

Bond energy values are very useful in calculating the heats of gaseous reactions involving substances having only covalent bonds. In using bond energy data, a plus sign is affixed to the bond enthalpies when a bond is broken, since heat is absorbed under such conditions and minus sign when a bond is formed and heat is evolved. It is general convention to take the enthalpies of pure elements in their standard states as zero and then enthalpy of pure compounds is taken as its enthalpy of formation ($\Delta_f H^\circ$) from it elements in standard state. The enthalpy change of a reaction ΔH° is given by,

$$\boxed{\Delta_R H^\circ = \Sigma H^\circ_P - \Sigma H^\circ_R} \quad \text{(or)} \quad \boxed{\Delta_R H^\circ = \Sigma \Delta_f H^\circ (\text{products}) + \Sigma \Delta_f H^\circ (\text{Reat})}$$

Questions:

① Calculate the enthalpy change for the reaction, $H_2 + F_2 \longrightarrow 2HF$: $\Delta H = ?$ Given that bond enthalpies of H-H, F-F & H-F bonds are 434 kJ/mol, 158 kJ/mol & 565 kJ/mol respectively.

Ans:

Since, breaking of bonds involves absorption of energy and formation of bonds involve release of energy. We have,

$\Delta_R H^\circ$ = (Sum of bond enthalpies of reactions) − (Sum of bond enthalpies of products)

= Bond enthalpy of H-H bond + bond enthalpy of F-F bond − 2 × bond enthalpy of H-F bond

= 434 + 158 − 2 × 565

= 592 − 1130

= −538 kJ

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Calculation of Resonance Energy from Thermochemical Data:

When a Compound shows resonance, there is Considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

Thus,

Resonance energy = [Experimental or actual heat of formation] - [calculated heat of formation]

Agreement between the calculated values of heat of formation obtained by using the bond energy Concept and the experimental method is usually good. However, large deviations are observed in case of Compounds which show the phenomenon of resonance

e.g: $C_6H_6(g) \longrightarrow 6C(g) + 6H(g)$

the energy required to break six C-H bonds and six C-C bonds should be

$= 6 \times \Delta H^\circ(C-H) + 3\Delta H^\circ(C-C) + 3\Delta H^\circ(C=C)$

$= 6 \times 413 + 3 \times 348 \times 3 \times 610 = 5352$ kJ/mol

However, the experimental value is 5525 kJ/mol. Thus benzene is more stable by 173 kJ/mol. This is due to resonance i.e. in benzene, there is no localisation of single and double bonds, but the electrons involved are delocalised. The extra stability of the molecule arises from the delocalisation of the π-bonds in the ring.

Question:

① Calculate the resonance energy of N_2O from the following data: $\Delta_f H^\circ$ of N_2O = 82 kJ/mol. Bond energy of N≡N, N=N, O=O & N≡O bonds is 946, 418, 498 and 607 kJ/mol respectively.

Ans: $N \equiv N(g) + \frac{1}{2}(O=O) \longrightarrow N=N=O(g)$

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$$\Delta H_f(N_2O) = (\Delta H_{N\equiv N}) + \frac{1}{2}(\Delta H_{O=O}) - (\Delta H_{N=O} + \Delta H_{N=N})$$

$$= 946 + \frac{1}{2} \times 498 - (607 + 418)$$

$$= 946 + 249 - 607 - 418$$

$$= 107 \text{ kJ/mol}$$

Resonance energy = Observed heat of formation − calculated heat of formation

$$= 82 - 170 = -88 \text{ kJ/mol}$$

Thus, N_2O is more stable by 88 kJ/mol.

Imp (LQ)

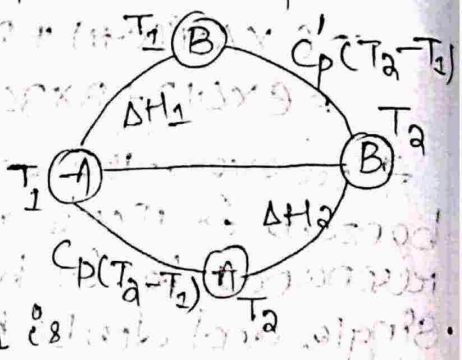
Variation of enthalpy of a reaction with temp.

KIRCHOFF'S EQUATION (Temp. dependance of Enthalpy):

The heat change of any physical or chemical process changes with temperature. The exact influence of temperature can be work out by applying first law of thermodynamics.

Consider a hypothetical reaction at constant pressure,

A (reactant) ⟶ B (product)



STEP-1:

Let the heat change = ΔH_1

(reaction proceed at temp. T_1)

Now the product B formed at T_1 is brought to temp. T_2 that the amount of heat absorbed be $C_p'(T_2-T_1)$:

where, C_p' = Mean molar heat capacity of the product between T_1 to T_2 at constant pressure

So the heat change in the whole process, $= \Delta H_1 + C_p'(T_2-T_1)$ — (1)

STEP-2:

In the second experiment, let the temperature of the reactant A be rised from T_1 to T_2. Thus the heat observed $= C_p(T_2-T_1)$

where C_p = Mean molar heat capacity of the reactant A between T_1 & T_2 at constant pressure.

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Now the reaction occurs at temp. T_2 and let the heat of reaction be ΔH_2.

Thus net heat change during the whole process is

$$= \Delta H_2 + C_p(T_2 - T_1) \quad \text{——— (2)}$$

Thus we see that the reactant A at temp. T_1 has changed to product B at temp. T_2.

According to first law of thermodynamics, the two energy changes should be equal.

$$\Delta H_1 + C_p'(T_2 - T_1) = \Delta H_2 + C_p(T_2 - T_1)$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = C_p'(T_2 - T_1) - C_p(T_2 - T_1)$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = (T_2 - T_1)(C_p' - C_p)$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = (T_2 - T_1)\Delta C_p$$

$$\Rightarrow \boxed{\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}} \quad \text{——— (1)}$$

This is called Kirchoff's equation of constant pressure. The change in the heat of reaction at constant pressure with the temperature depends upon the sign of ΔC_p. Kirchoff's equation of constant volume is given by,

$$\boxed{\Delta C_v = \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1}} \quad \text{——— (2)}$$

from Eq (1) & (2) it is clear that, the heat of reaction will not change with temp. in case ΔC_p or ΔC_v is zero. The heats of reaction involving solids only do not appreciably change with temp. as the molar capacities are equal to one another.

Mathematical derivation of Kirchoff's Equation:

Consider a process. A (reactant) $\longrightarrow$ B (product)

Let H_A & H_B be the enthalpies of reactants & products at same temp. & pressure.

Then enthalpy change, $\Delta H = H_B - H_A$ —— (1)

Differentiating eq (1) w.r.t T at P constant.

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left(\frac{\partial H_B}{\partial T}\right)_P - \left(\frac{\partial H_A}{\partial T}\right)_P$$

$$\Rightarrow \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = (C_p)_B - (C_p)_A = \Delta C_p$$

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As ΔH is heat of reaction at constant pressure,

$$\frac{\partial(\Delta H)}{\partial T} = \Delta C_p \quad \text{—— (2)}$$

$\Rightarrow \partial(\Delta H) = \Delta C_p \partial T$ (for a small difference in T)

$\Rightarrow d(\Delta H) = \Delta C_p dT$ (for a large difference in T)

$$\Rightarrow \int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p dT$$

$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$.

$$\Rightarrow \boxed{\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p} \quad \text{—— (3)}$$

Here, H_1 = Heat of reaⁿ at T_1
H_2 = " " " at T_2

This relation is applicable if ΔC_p is independent of temp.
If C_p is not independent of temp.

So, $C_p = \alpha + \beta T + \gamma T^2 + \cdots$

$\Rightarrow \Delta C_p = \Delta\alpha + (\Delta\beta)T + (\Delta\gamma)T^2 + \cdots$

put this value in Eqⁿ (3) we get,

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p dT$$

$$\Rightarrow \Delta H_2 = \Delta H_1 + \Delta\alpha T + \frac{1}{2}\Delta\beta T^2 + \frac{1}{3}\Delta\gamma T^3 + \cdots$$

Questions:

① The heat of the reaction, $2A + B \rightarrow 2C$ is -99.764 kcal at 298 K. Calculate the heat of reaction at 398 K. The mean values of molar heat capacities of A, B and C at constant pressure between the given temp. range are 5.51, 8.4 & 10.89 cal/kmole respectively.

Ans: Given, $2A + B \rightarrow 2C$ & $\Delta H_1 = -99.764$ kcal at 298 K.

ΔC_p = (Molar capacities of products) − (Molar capacities of reactants)

= (2 × Molar capacity of C) − (2 × Molar capacity of A + Molar capacity of B)

$= (2 \times 10.89) - (2 \times 5.51 + 8.4) = 21.78 - (11.02 + 8.4) = 21.78 - 19.42$

$= 2.36$ cal $= 2.36 \times 10^{-3}$ kcal

Applying reaⁿ, $\Delta H_2 - \Delta H_1 = C_p(T_2 - T_1)$

$\Rightarrow \Delta H_2 = \Delta H_1 + C_p(T_2 - T_1) = -99.764 + 2.36 \times 10^{-3}$ [illegible]

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② The standard enthalpy of formation of gaseous water at 298 K is −241.82 kJ/mol. Estimate the value at 373K. Given the value of molar heat capacities at constant pressure.

$H_2O(g) = 35.58$ J/K.mol, $H_2(g) = 28.84$ J/K.mol, $O_2(g) = 29.37$ J/K.mol.

Ans: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

from Kirchoff's Eqn, $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

Here, $\Delta H_1 = -241.82$ kJ/mol $= -241820$ J/mol, $T_1 = 298$K, $T_2 = 373$K

ΔC_p = (Heat Capacity of product − Heat capacity of reactant)

$\Rightarrow \Delta C_p = C_p(H_2O) - [C_p(H_2) + \frac{1}{2}C_p(O_2)] = 35.58 - 28.84 - \frac{1}{2} \times 29.37$

$= -7.945$ J/K.mol.

So, $\Delta H_2 - (-241820) = -7.945 \times (373 - 298)$

$\Rightarrow \Delta H_2 + 241820 = -7.945 \times 75 = -595.875$

$\Rightarrow \Delta H_2 = -242415.8$ J/mol $= -242.415$ kJ/mol

③ The standard heat of formation of HCl at 298K is −92.30 kJ/mol. What would be its value at 373K? Given the following values of molar heat capacities of constant pressure.

Ans: C_p of $H_2(g) = 28.53$ J/K.mol, C_p of $Cl_2(g) = 32.26$ J/K.mol & C_p of $HCl(g) = 28.5$ J/K.mol.

Also, $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$, $\Delta H = -92.30$ J/K.mol

$\therefore \Delta C_p$ = Sum of heat capacities of products − Sum of the heat capacities of reactants.

$= 28.5 - \frac{1}{2}(28.53 + 32.26) = -1.895$ J/K.mol.

using Kirchoff's Eqn,

$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$ here, $T_1 = 298$K & $T_2 = 373$K.

So, $\Delta H_2 + 92.3 = -\frac{1.895 \times 75}{1000} = 0.1421$ kJ

$\Rightarrow \Delta H_2 = -92.3 + 0.1421 = -92.1579$ kJ/mol

Hence, heat of formation of HCl at 373K,

K = −92.1579 kJ/mol.

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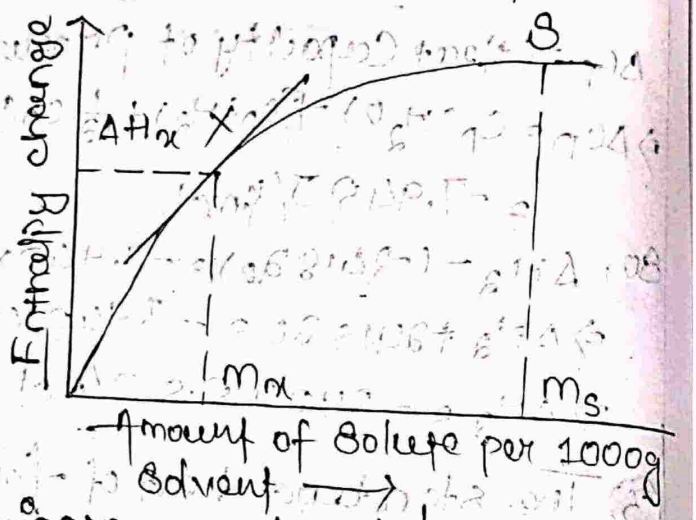
Integral & Differential enthalpies of Solution & Dilution:

* INTEGRAL ENTHALPY OF SOLUTION:

It is known that when a solute is dissolved in solvent generally heat is either evolved or absorbed. The enthalpy change per mole of solute dissolved isn't constant. Usually it changes with conc. of the solution.

Suppose,
ΔH = Enthalpy change when amount m of the solute is dissolved in a definite quantity of the solvent.
Let, the process of dissociation is endothermic.



→ The curve between ΔH against m:

→ It is observed that ΔH increases almost linearly with amount 'm' but later the increase is not as fast as m. finally, it reaches a constant value when the solution becomes saturated w.r.t solute.

Hence The Integral enthalpy of solution at a given conc is the enthalpy change (ΔH) when one mole of the solute (m) is dissolved in a definite quantity of solvent to produce a solution of a desired conc. (or)

$$\text{Integral enthalpy of solution} = \frac{\text{observed value of enthalpy change}}{\text{amount of solute dissolved for a particular conc. of solution}}$$

i.e.

$$\boxed{\text{Integral enthalpy of solution} = \frac{\Delta H}{m}}$$

* DIFFERENTIAL ENTHALPY OF SOLUTION:

It is the enthalpy change when 1 mole of the solute is dissolved in a very large volume of solution of known conc so that there occurs no appreciable change in conc. of the solution.

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→ It can be calculate from the slope of the curve between ΔH & m at a given conc.

→ It may be represented as, $\frac{d(\Delta H)}{dm}$.

where, $d(\Delta H)$ = change in the value of ΔH when an infinitesimal amount of solute i.e. dm is added to a solution of definite composition.

→ It may also defined as the change in ΔH per mole of solute when an infinitesimal amount of the solute is added to a solution of definite conc.

⇒ From the slope of the curve, we concluded that;

① For smaller values of m, the curve is almost linear, its slope will have a constant value and will be equal to $\Delta H/m$. It also represents integral enthalpy of solution. Thus, integral enthalpy & differential enthalpy of solution are essentially equal for very dilute solutions.

② As the conc. of the solution increases, the curve no longer remains linear. The reason is that ΔH does not increase as fast as m. Thus the slope of the curve decreases as the value of m increases. Hence, we say that the differential enthalpy of solution decreases as the conc. of the solution increases. It becomes zero when the solution is saturated.

* INTEGRAL ENTHALPY OF DILUTION:

It is known that the enthalpy of solution of a solute varies with its conc. It means that there must be a change in enthalpy when a solution is diluted by adding more of solvent.

" The integral enthalpy of dilution is the change in enthalpy when a solution containing one mole of solute is diluted from one conc. to another.

→ By Hess's law; it can be said that integral enthalpy of dilution is the difference between the integral enthalpies of solution at two concentrations

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DIFFERENTIAL ENTHALPY OF DILUTION:

It is the enthalpy change when 1 mole of solvent is added to a large volume of the solution of known conc. so that there occurs no appreciable change in the conc. of the solution. The value of differential enthalpy of dilution can be obtained by plotting ΔH of the solution at various conc. against the amount of the solvent associated with definite quantity of solute.

Reversible process	Irreversible process
→ It returns to its initial stage without disturbing surrounding.	→ It doesn't return to its initial stage.
→ It carried out infinitesimally slowly.	→ It carried out rapidly.
→ At any stage, the equilibrium is not disturbed.	→ Equilibrium may exist only after the completion of the process.
→ It takes infinite time for completion.	→ It takes a finite time for completion.
→ Work obtained in this process is maximum.	→ Work obtained in this process is not maximum.
→ The reactants cannot be converted completely into products.	→ The reactants can be completely converted into products.
→ Both forward & backward reactions take place simultaneously.	→ It is unidirectional. proceed only in forward direction.

Bond Energy

→

Bond dissociation energy:

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THIRD LAW OF THERMODYNAMICS:

Statement: (By Nernst)

According to this law, "The entropy of a perfectly crystalline substance at absolute zero is taken as zero". As the temp. is raised, the entropy of the pure substances increases. This definition is valid for perfectly crystalline solids.

Lewis & Randall gives modified version i.e. "Every substance has a finite value of positive entropy but at absolute zero temp. the entropy may become zero and it does become zero in case of perfectly crystalline solids.

Testing the validity of Third law:

Relation between standard free energy (ΔG°) & equilibrium constant is. $-\Delta G^\circ = RT \ln K$ —— (1)

Also the relation between standard free energy change & standard enthalpy is, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ —— (2)

Substituting the experimental value of ΔH° & calculated value of ΔS° & applying the relation.

$\Delta S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{Reactants}$

ΔG° can be calculated for a reaction. When value of ΔG° is substituted in Eq (1), the value of equilibrium constant (K) can be calculated.

If the value of K comes close to the experimental value, the validity of third law of thermodynamics is proved.

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G.E-II

UNIT-II

Ionic Equilibrium:

May 12, 2022

The equilibrium between ions and unionized molecules in the solution is called as ionic Equilibria in an electrolyte.

Electrolytes:

It can be defined as the substances through which electricity can pass in its aqueous solution or fused state.

Ex: Acid, bases & all water soluble salts.

It is of three types; Strong Electrolytes
Weak Electrolytes
Moderate Electrolytes

1. Strong Electrolytes:

These are the substances which are almost completely ionised when dissolved in water.

Ex: Strong acids (HCl, H_2SO_4, HNO_3 etc)
Strong alkalies ($NaOH$, KOH etc.)
Water soluble salts ($NaCl$, KCl, $CuHSO_4$ etc)

2. Weak Electrolytes:

These are the substances which are ionised to a very small extents when dissolved in water.

Ex: Weak acids ($HCOOH$, CH_3COOH, oxalic acid)
Weak alkalies ($Al(OH)_3$, NH_4OH, etc...)

3. Moderate Electrolytes:

These are the electrolytes which ionised to a little extent & their degree of ionisation lie in between weak & strong electrolytes.

Degree of Ionisation (or) Degree of Dissociation:

Degree of ionisation or dissociation can be defined as "the ratio between the total number of electrolytes dissociated into ions to the total number of molecules of the electrolytes".

$$\text{Degree of Ionisation} = \frac{\text{Total no. of electrolytes dissociated into ions}}{\text{Total no. of molecules of the electrolytes.}}$$

In case of strong electrolytes 'α' is almost equal to '1' as the electrolyte is completely ionised. But, in case of weak electrolytes 'α' has very low value as the electrolyte is poorly ionised.

→ The ionisation of strong electrolytes is shown by single arrows,

$$NaCl + H_2O \rightarrow Na^+(aq) + Cl^-(aq)$$

$$HCl + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$$

So, Equilibrium exists for strong electrolytes.

→ But equilibrium exists between un-ionised molecules & the ions in case of weak electrolytes. It is called ionic equilibrium & is shown by two arrows,

$$NH_4OH + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Ostwald's dilution law:

The degree of ionisation of a weak electrolyte can be found by the application of Ostwald dilution law. Consider that a weak electrolyte (AB) is dissolved in water. Its ionisation is given by

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

Let initial conc. of undissociated 'AB' = C mol/lit.

Degree of dissociation of 'AB' at equilibrium = α

Thus, Conc. of different species at equilibrium will be given as

	AB	$\rightleftharpoons$	A^+	+	B^-
initial conc.	C		0		0
Conc. at equilibrium	$C(1-\alpha)$		$C\alpha$		$C\alpha$

Applying law of chemical equilibrium,

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$$K_i = \frac{[A^+][B^-]}{[AB]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

Where, K_i = Dissociation or Ionisation Constant

For electrolytes having α is extremely small as compared to unity, α can be neglected.

For such case, $1-\alpha = 1$

Hence, $K_i = c\alpha^2$

$$\Rightarrow \alpha^2 = \frac{K}{c} \text{ (or) } \alpha = \sqrt{\frac{K}{c}} = \sqrt{KV}$$

Limitations of Ostwald's dilution law:

This law holds only for weak electrolytes.

(i) For weak acids, at a given temp., $\alpha = \sqrt{\frac{K_a}{c}}$

(ii) For weak bases, at a given temp., $\alpha = \sqrt{\frac{K_b}{c}}$

Where K_a & K_b are ionisation constants of acid & base respectively.

Questions:

1. A solution of 0.10M acetic acid is found to be dissociated to the extent of 1.43%. Calculate the dissociation constant of the acid.

Ans: Molar Concentration $C_1 = 0.1M$

percentage dissociation = 1.43%

Degree of dissociation, $\alpha = \frac{1.43}{100} = 0.01413$

The dissociation of acetic acid is represented as;

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Conc. at eq. $c(1-\alpha)$ $\quad c\alpha \quad c\alpha$

$$K_a = \frac{[CH_3COO^-(aq)][H_3O^+(aq)]}{[CH_3COOH(aq)]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Since, α is very small,

$$K_a = c\alpha^2 = 0.1 \times (0.01413)^2 = 2.09 \times 10^{-5}$$

2. The dissociation constant of 0.05 M acetic acid is 1.74×10^{-5} at 298 K. Calculate its degree of ionisation and hydrogen ion concentration at the same temperature.

Ans: Assuming that degree of ionisation is very small, $\alpha = \sqrt{\frac{K_a}{c}}$

Now, $K_a = 1.74 \times 10^{-5}$; $c = 0.05$ M

$$\therefore \alpha = \sqrt{\frac{1.74 \times 10^{-5}}{5 \times 10^{-2}}} = 0.01865$$

If, α is the degree of ionisation, then equilibrium conc. may be expressed as;

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^{\ominus} + H_3O^{\oplus}$$
$$c(1-\alpha) \qquad c\alpha \qquad c\alpha$$

Thus, $[H_3O^{\oplus}] = [H^{\oplus}] = c\alpha = 0.05 \times 0.01865 = 9.32 \times 10^{-4}$ gmol/L

Factors affecting Degree of Ionisation :

1. Dilution :

On diluting the degree of dissociation or ionisation of weak electrolyte increases. This value becomes maximum at infinite dilution. But incase of strong electrolyte dilution has very little effect on the degree of ionisation.

2. Temperature :

In case of endothermic substances like NH_4Cl, KNO_3 etc., the degree of ionisation increases with increase in temperature. But, in case of exothermic substances like $Ca(OH)_2$, the degree of dissociation decreases with increase in temperature.

3. Addition of Salt Containing Common ion :

In case of weak electrolyte the degree of ionisation decreases when a salt having common ion is added to it. e.g. Degree of ionisation of NH_4OH decreases when a little amount of NH_4Cl is added to it.

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Ionic Product of Water:

As pure water is a weak electrolyte, it is slightly dissociated into H^+ & OH^- ions.

$$H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$$

Applying law of equilibrium to dissociation equation,

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$$\Rightarrow K[H_2O] = [H^+][OH^-] \quad \text{--- (1)}$$

Where, K = Ionisation constant

$[H_2O]$ = Constant at Constant temperature.

$[H^+]$ = Molar Conc. of H^+ ion

$[OH^-]$ = Molar Conc. of OH^- ion

from Eq (1), $K_W = [H^+][OH^-]$ where, $K_W = K \times [H_2O]$

= dissociation constant of water (or) ionic product of water.

At room temperature i.e. 298 K.

$[H^+] = [OH^-] = 10^{-7}$ mol/litre

So, $K_W = 10^{-7} \times 10^{-7} = 10^{-14}$ moles/litre.

So, $\boxed{K_W = 10^{-14} \text{ moles/litre}}$

Effect of Temperature On 'K_W':

Degree of ionisation increases with increase in temperature. So, the molar concentration of H^+ ions and OH^- ions increases. As a result, the value of 'K_W' increases with increase in temperature.

Ionisation Constant:

It depends upon the equilibrium between ions and molecules that are not ionized in a solution or liquid. It is the ratio of products and reactants raised to appropriate stoichiometric powers or the ratio of the product of concentration and reactant.

→ It is denoted by 'K'.

for weak acid soln, $K = K_a$ & for weak base soln, $K = K_b$.

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Ionisation of Weak Acids:

A weak acid is a weak electrolyte that doesn't completely ionize when mixed with water to form H^+.

→ The ionisation constant for weak acid is denoted as 'K_a'.

→ The stronger the acid the larger the K_a.

General formula: $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

$$K_a = \frac{[H_3O^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

Ex: $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Ionisation of Weak bases:

A weak base is a base that ionizes only slightly in an aqueous solution.

→ The ionisation constant for weak base is denoted as 'K_b'.

→ The stronger the base the larger the K_b.

General formula: $B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$

$$K_b = \frac{[BH^+_{(aq)}][OH^-_{(aq)}]}{[B_{(aq)}]}$$

Ex: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

PH SCALE:

PH of a solution can be defined as the negative logarithm of H^+ concentration $\{-\log[H^+]\}$ in mol/lit.

→ It can also be defined as; "the pH of a solution is numerically equal to the negative power to which 10 must be released in order to express the hydrogen ion concentration $[H^+]$ in a solution.

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Mathematically; $P_H = -\log[H^+]$

→ P_H values of the solution ranges from 0-14.

for, acidic solution pH < 7

Basic solution pH > 7

Neutral solution pH = 7

for pure water, $[H^+] = [OH^-] = 1 \times 10^{-7}$

pH of pure water $= -\log(10^{-7}) = -(-7) = 7$

Thus, the pH value of pure water is equals to 7.

→ Also, pH values of boiling water is neutral.

pOH: It is defined as the negative logarithm of hydroxyl ion conc.

$pOH = -\log[OH^-]$

Since, the ionic product, $[H^+][OH^-]$ is always equal to 10^{-14}.

∴ The sum of pH & pOH is always equal to 14.

i.e. $pH + pOH = 14$

(or) $pOH = 14 - pH$

Importance of pH:

1. In agriculture pH has great importance. Soil is tested to determined whether acidic or basic fertilizers are required is decided from pH value.
2. It has great importance in biochemical reactions such as digestion of food.
3. preservation of food requires a definite pH value.
4. Large no. of qualitative & quantitative analysis are done by using pH values.
5. pH decreases with increase in temperature.

Questions:

1. Calculate the pH of 0.001 N of HCl solution.

Ans: $[H^+] = 0.001$

$pH = -\log[0.001] = -\log[10^{-3}] = (-3) \times (-\log 10) = (-3) \times (-1)$

$= 3$

2. Calculate the pH of 0.01N of NaOH solution.

Ans: $[OH^-] = [0.01] = [10^{-2}]$

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$pOH = -\log[OH^-] = -\log[10^{-2}] = (-2)\times(-\log 10) = (-2)\times(-1) = 2$

$pH = 14 - pOH = 14 - 2 = 12$

3. Calculate the pH of a solution containing 0.0315 gm. of nitric acid in 500 ml of solution.

Ans: HNO_3 in 500 ml. of solⁿ contain = 0.0315 gm
" " 1000 ml " " " = 0.63 gm

$N = \frac{0.63}{63} = 10^{-2} N$

$HNO_3 = [H^+] = 10^{-2} N$

So, $pH = -\log[H^+] = -\log[10^{-2}] = (-2)(-\log 10) = (-2)(-1) = 2$

4. Calculate the pH of HCl solution.

Ans: In HCl, $[H^+] = 1$

So, $pH = -\log[1] = 0$

5. How many gms of KOH must be dissolved in 1 litr. of the solution to give it a pH value of 12.

Ans: $pH = 14 - pOH = 14 - 12 = 2$

$[OH^-] = 10^{-2} = 0.01 N$

$N = \frac{gm/lit}{Eq. Mass}$

$\Rightarrow gm/lit = N \times Eq. mass = 0.01 \times 56 = 0.56 gm/lit$.

Relationship betⁿ K_a & K_b for an acid & its Conjugate base:

for a weak acid HA:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{—(1)}$$

where, A^- is the Conjugate base of HA.

Similarly for base $A^-(aq)$:

$$A^-(aq) + H_2O \rightleftharpoons HA(aq) + OH^-(aq) \quad \therefore K_b = \frac{[HA][OH^-]}{[A^-]} \quad \text{—(2)}$$

Eqⁿ (1) & (2) we get,

$$K_a(HA) \times K_b(A^-) = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-]$$
$$= K_w$$

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(or) $K_a(HA) \times K_b(A^-) = K_w$

(or) $K_a(\text{Acid}) \times K_b(\text{conjugate base}) = K_w = 1 \times 10^{-14}\ mol^2/l^2$

$\Rightarrow \log K_a(\text{Acid}) + \log K_b(\text{conjugate base}) = \log K_w$

$\Rightarrow -\log K_a - \log K_b = -\log K_w$

$\Rightarrow pK_a + pK_b = pK_w = 14$

(or) $pK_a(\text{acid}) + pK_b(\text{conjugate base}) = 14$ at $22^\circ C$

Common Ion Effect:

Sometimes, it is desirable to lower the solubility of a sparingly soluble salt still further. This is done by adding a soluble salt having the same cation or the same anion to the suspension of sparingly soluble salt in water.

When solution of strong electrolyte having common ion is added to the solution of weak electrolyte or vice-versa, the ionisation of weak electrolyte is suppressed. This effect is called common ion effect.

(or)

The common ion effect is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances.

Ex: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

NH_4Cl provides the common ion NH_4^+ ions hence dissociation of NH_4OH is suppressed in accordance with Le-chatlier's principle.

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

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

The increase in conc. of Cl^- ions shifts the equilibrium towards left & more of AgCl is formed.

Applications:

1. Recovery of pure NaCl from sea water.
2. Salting out of soap.
3. It explains the precipitation of sulphides, hydroxides & carbonates under controlled conditions in qualitative analysis.

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HYDROLYSIS OF SALT:

When a salt is dissolved in water, it undergoes ionization. The ions of salt interact with opposite ions of water to form acidic, basic or neutral solutions. This process is called hydrolysis. Thus hydrolysis may be defined as the interaction of ions of a salt with oppositely charged ions of water to give acidic or basic solution.

Let, AB be a general salt.

Dissociation of salt: $AB + H_2O \longrightarrow A^+ + B^-$

" of water: $H_2O \rightleftharpoons H^+ + OH^-$

$\downarrow$ on mixing

$AOH + HB$ (Base) (Acid)

→ It is a reverse of neutralisation.

→ The equilibrium constant of hydrolysis reaction is called hydrolysis constant i.e. K_h.

where, 'h' is the degree of hydrolysis and it is the fraction of the total salt that gets hydrolysed at equilibrium.

→ The ions of a strong electrolyte remain as such where as ions of weak electrolyte combine immediately.

Let us consider different types of hydrolysis of salts;

(a) Salt of strong acid & strong base:

The examples of salts of strong acid & strong base are NaCl, KNO_3, Na_2SO_4, $NaNO_3$, KCl etc...

Let, $NaCl \longrightarrow Na^+ + Cl^-$

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

$\xrightarrow[\text{dissociation}]{\text{on}} Na^+ + Cl^- + H_2O$

As, the final solution contains equal number or same concentration of H^+ & OH^- ions. It is neutral having pH 7. Hence the salt of strong acid & strong base donot under go hydrolysis. So, there is no degree of hydrolysis and hydrolysis constant.

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(b) Salt of weak acids & strong bases:

The examples of such salts are CH_3COONa & K_2CO_3. the hydrolysis of CH_3COONa is,

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + OH^- + Na^+$$

(or) $$CH_3COO^- + H_2O \rightleftharpoons \underset{\text{(free acid)}}{CH_3COOH} + \underset{\text{(free base)}}{OH^-}$$

According to law of chemical equilibrium,

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \text{—— (1)}$$

But, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ & $H_2O \rightleftharpoons H^+ + OH^-$

Dissociation constant of acid

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad \text{—— (2)}$$

& $K_w = [H^+][OH^-]$ —— (3) (from ionic product of water)

Now, $\frac{Eq(3)}{Eq(2)} \Rightarrow \frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$ —— (4)

using Eq (4) in Eq (1) we get, $\boxed{K_h = \frac{K_w}{K_a}}$

where, K_w = Constant

So, K_h depends on the K_a.

Degree of Hydrolysis:

Let 'c' mol/lit be the initial conc. of CH_3COONa & 'h' is the degree of hydrolysis,

initial conc.	c	$CH_3COO^- + H_2O$	$\rightleftharpoons$ CH_3COOH	OH^-
			0	0
at equilibrium.	$c(1-h)$		ch	ch

$$K_h = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{1-h}$$

If h is too small as compared to unity, $K_h = ch^2$

$\Rightarrow h = \sqrt{\frac{K_h}{c}}$

(or) $\boxed{h = \sqrt{\frac{K_w}{K_a \cdot c}}}$

* $pH = \frac{1}{2}(pK_w + pK_a + \log c)$

(or) $\boxed{pH = 7 + \frac{1}{2}(pK_a + \log c)}$ at 298K

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(c) Salt of strong acids & weak bases:

The examples of such type of salts are, NH_4Cl and $Ca(NO_3)_2$.

the hydrolysis of NH_4Cl is,

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

(or) $NH_4^+ + H_2O \rightleftharpoons \underset{\text{(free base)}}{NH_4OH} + \underset{\text{(free acid)}}{H^+}$

According to law of equilibrium, $K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$ —— (1)

But, $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Dissociation constant of base, $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$ —— (2)

from ionic product of water, $K_w = [H^+][OH^-]$ —— (3)

$\frac{Eq^n (3)}{Eq^n (2)}$, $\Rightarrow \frac{K_w}{K_b} = \frac{[H^+][NH_4OH]}{[NH_4^+]}$ —— (4)

using Eq^n (4) in Eq^n (1) we get, $\boxed{K_h = \frac{K_w}{K_b}}$

Degree of hydrolysis:

let c mol/lit be the inital conc. of NH_4Cl and h be the degree of hydrolysis.

	c		0	0
initial conc.	NH_4^+	$+ H_2O \rightleftharpoons$	NH_4OH	$+ H^+$ —— (5)
at equilibrium,	$c(1-h)$		ch	ch

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]} = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)}$$

If, h is too small as compared to unity, $K_h = ch^2$

$\Rightarrow h = \sqrt{\frac{K_h}{c}}$ (or) $\boxed{h = \sqrt{\frac{K_w}{K_b \cdot c}}}$

pH: from Eq^n (5), $[H^+] = ch = c \cdot \sqrt{\frac{K_w}{K_b \cdot c}} = \sqrt{\frac{K_w \cdot c}{K_b}}$

$\therefore pH = -\log_{10}[H^+] = -\log_{10}\left[\sqrt{\frac{K_w \cdot c}{K_b}}\right] = \frac{1}{2}(pK_w - pK_b - \log_{10} c)$

(or) $\boxed{pH = 7 - \frac{1}{2}(pK_b + \log c)}$ at 298 K

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(d) Salt of Weak acids & Weak bases:

The examples of such salt is CH_3COONH_4.

the hydrolysis of CH_3COONH_4 is,

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons \underset{\text{(free acid)}}{CH_3COOH} + \underset{\text{(free base)}}{NH_4OH}$$

According to law of equilibrium, $K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$ —— (1)

But, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ & $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Dissociation constant of acid, $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ —— (2)

Dissociation Constant of base, $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$ —— (3)

from ionic product of water, $K_w = [H^+][OH^-]$ —— (4)

$$\frac{Eq^n (1)}{Eq^n (2) \times Eq^n (3)} \Rightarrow \frac{K_w}{K_a \cdot K_b} = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \quad \text{—— (5)}$$

using Eq^n (5) in Eq^n (1) we get, $\boxed{K_h = \frac{K_w}{K_a \cdot K_b}}$

Degree of Hydrolysis:

Let c mol/lit is the initial Conc. of CH_3COONH_4 & h is its degree of hydrolysis.

$$\begin{array}{lcccccc} \text{initial conc.} & c & & c & & 0 & 0 \\ & CH_3COO^- & + & NH_4^+ & + H_2O \rightleftharpoons & CH_3COOH & + NH_4OH \\ \text{at equilibrium,} & c(1-h) & & c(1-h) & & ch & ch \end{array}$$

$$K_h = \frac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \frac{h^2}{(1-h)^2}$$

If, h is too small as compared to unity,

$K_h = h^2$ (or) $h = \sqrt{K_h}$ (or) $\boxed{h = \sqrt{\frac{K_w}{K_a \cdot K_b}}}$ —— (5)

from the above relation, the weaker acid & base greater is the degree of hydrolysis of salt. Here, the degree of hydrolysis doesn't depend upon the conc. of the solution. As K_w increases with temp, the degree of hydrolysis increases with increase in temperature.

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pH : from Eq (2), $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$\Rightarrow \frac{[CH_3COOH]}{[CH_3COO^-]} = \frac{[H^+]}{K_a} = \sqrt{\frac{K_w}{K_a \cdot K_b}}$

$\Rightarrow K_a = [H^+] \times \frac{1}{\sqrt{\frac{K_w}{K_a \cdot K_b}}} = \sqrt{\frac{K_a K_b}{K_w}} \times [H^+]$

$\Rightarrow [H^+] = \sqrt{\frac{K_a K_w}{K_b}}$

$pH = -\log_{10}[H^+] = -\log_{10}\sqrt{\frac{K_a K_w}{K_b}} = \frac{1}{2}(pK_w + pK_a - pK_b)$

(or) $\boxed{pH = 7 + \frac{1}{2}(pK_a - pK_b)}$ at 298 K

Buffer Solution :

It can be defined as a System which maintains its hydrogen ion or hydroxyl ion Concentration at an approximately constant table & which doesnot change by adding water or small amount of any acid or alcohol to it.

(or)

It is defined as a Solution whose pH value does not change appreciably upon the addition of small amounts of acids, bases & water externally.

→ The mechanism through which buffer Solutions resist the changes in pH value is called BUFFER ACTION.

→ Buffer Solutions is of following 2 types;

(i) Acidic Buffer

(ii) Basic Buffer.

(i) Acidic Buffer :

It is an equimolar mixture of weak acid & salt of it from strong base.

Ex: Mixture of 1 mole CH_3COOH & 1 mole CH_3COONa is acidic buffer. (pH = 4.74)

Mixture of 1 mole CH_3COOH & 1 mole CH_3COOK is acidic buffer. (pH = 4.49)

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Buffer action for Acidic buffer:

Let us Consider an weak acid having equimolar quantity of CH_3COOH & CH_3COONa.

→ Inside the Solution there will be larger Concentration of CH_3COO^-, Na^+ & undissociated CH_3COOH.

→ When few drops of HCl is added to the buffer solution than most of the H^+ ions will combine with CH_3COO^- to form CH_3COOH molecules as a result negligible change in pH value occurs.

→ When a few drops of water is added it will produce equal number of H^+ ions and OH^- ions. So there will be no change in pH value.

→ Thus, the dilution of buffer doesnot result in the change in pH because the products formed by dilution are very weakly ionised.

Basic Buffer:

It is an equimolar mixture of a weak base and a Salt of it from strong acid.

Ex: Mixture of 1 mole NH_4OH & 1 mole NHCl is basic buffer: (pH = 20.25)

Buffer action for Basic Buffer:

Let us consider a weak base NH_4OH & equimolar quantity of it's Salt from strong acid NHCl.

→ Inside the Solution there will be a larger conc. of NH_4^+, Cl^- and undissociated NH_4OH molecules.

→ When few drops of HCl are added to the buffer then H^+ ions will combine with OH^- ions of NH_4OH to form weakly ionised water molecule. As a result there will be no change in pH value.

→ When a few drops of NaOH are added to the buffer than the OH^- ions will combine with NH_4^+ ions of buffer to form weakly ionised NH_4OH molecules. As a result no appreciable change in pH value occurs.

→ When few drops of water is added then it will produce equal number of H^+ ions & OH^- ions. As

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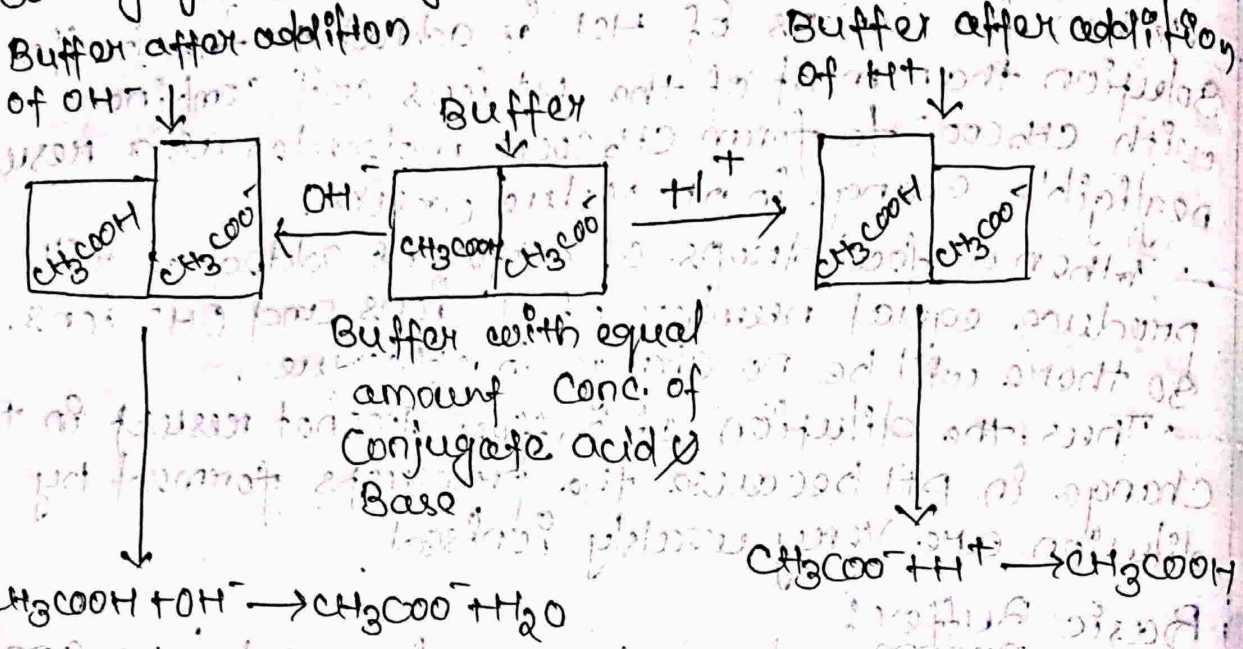
a result the pH value remains unchanged.

→ When a few drops of NaOH are added then the OH^- ions are neutralised by H^+ ions from buffer solution to form weakly ionised water molecular so negligible change in pH value occurs.



Numerical problems On Calculation of pH of Buffer Solution:

(a) for an acidic buffer solution,

$$pH = pKa + \log_{10}\frac{[Salt]}{[Base]}$$

(b) for a basic buffer solution,

$$pH = 14 - pOH \quad \text{where, } pOH = pK_b + \log_{10}\frac{[Salt]}{[Base]}$$

Buffer Capacity: (β)

Buffer capacity is also called as "Magnitude of the buffer action". It is defined as the number of moles (x) of acid or base which when added to 1 litre of buffer solution change its pH by unity.

$$\text{Buffer capacity} = \frac{\text{No. of moles added per litre}}{\text{change in pH}}$$

(or) $$\boxed{\beta = \frac{\Delta A / \Delta B}{\Delta pH}}$$

Where, ΔA & ΔB are small increment or litre of strong acid & base respectively added to buffer to bring about a pH change of ΔpH.

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Buffer Range:

A given weak acid proves useful in preparing a buffer if its pH lies within the range pK_a+1 and pK_a-1.

Ex: Glycine + Glycine HCl (pH range → 1.0–3.7)
Boric acid + Borax (pH range → 6.8–9.8)
$CH_3COOH + CH_3COONa$ (pH range → 3.7–5.6)

Applications of Buffer:

1. Blood is the best example of buffer solution. It contains PO_4^{3-}, HCO_3^- & proteins (bases) and has a pH = 7.39 to 7.45.
   Tears (pH = 7.4)
   Saliva (pH = 6.35–6.85)
   Urine (pH = 4.8–7.5)
   Milk (pH = 6.6–6.9)
2. Helps in manufacture of paper, dyes, inks, paints.
3. For healthy seeding & growth of crops, the soil needs to be maintained at a particular pH by means of suitable buffer solutions.

Solubility Product:

→ The substances, which dissolve in water to an extremely small extent are known as sparingly soluble.

Ex: AgCl, $PbSO_4$, $BaSO_4$ etc.

Let us consider, $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

Applying law of chemical equilibrium, we have,

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

(or) $K \times [AgCl] = [Ag^+][Cl^-]$

$\Rightarrow [Ag^+][Cl^-] = K \times$ Constant

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

Where, K_{sp} = Solubility product & [AgCl] is always constant as conc. of solid is always constant.

$[Ag^+][Cl^-]$ = Ionic product.

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Let us consider general case of a sparingly soluble salt: A_aB_b.

$$A_aB_b(s) \longrightarrow aA^{b+} + bB^{a-}$$

Solubility product will be, $\boxed{K_{sp} = [A^{b+}]^a [B^{a-}]^b}$

Where, A^{b+} & B^{a-} denote the +ve & -ve ions respectively and a & b represent the number of these ions in the formula of electrolyte.

Thus, solubility product of a salt at a given temp. is defined as, the product of molar conc. of the ions each raised to the power equal to the no. of times each ion occurs in the equation for solubility equilibrium at constant temp.

Hence, solubility product varies with temp.

$BaSO_4$: $K_{sp} = [Ba^{2+}][SO_4^{2-}]$, PbI_2 : $K_{sp} = [Pb^{2+}][I^-]^2$

Ag_2CrO_4 : $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

Solubility:

It is defined as the max^m amount of a substance that will dissolve in a given amount of solvent at a specified temperature.

Solubility	Solubility Product
(i) It is applicable for all solutes.	(i) It is only significant in case of electrolytes.
(ii) It has a constant value at a given temp.	(ii) It varies with temp.
(iii) It depends on temp., pressure, pH etc.	(iii) It depends on temp.

Relation between Solubility and Solubility product:

Let solubility of sparingly soluble salt A_aB_b is S mol/lit

$$A_aB_b \rightleftharpoons aA^{b+} + bB^{a-}$$

S moles aS bS

Thus, $[A^{b+}] = aS$ & $[B^{a-}] = bS$

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$\therefore K_{sp} = [A^{b+}]^a [B^{a-}]^b = [as]^a [bs]^b = a^a s^a \cdot b^b \cdot s^b$

$\Rightarrow \boxed{K_{sp} = a^a b^b \cdot s^{a+b}}$

Ex: for, $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$; $a = 2$ & $b = 1$

$K_{sp} = 2^2 \cdot 1^1 \cdot s^{2+1} = 4s^3$

where, s is solubility of Ag_2CrO_4.

Ionic product	Solubility product
(i) It calculate for all solution.	(i) It calculate only for conc. solution.
(ii) value of it changes, when conc. of solution changes.	(ii) Value remains constant at const. temp. for given salt.

Relation between Ionic product & Solubility product:

Let, Ionic product = Q_{IP}

& Solubility product = K_{sp}

(i) If, $Q_{IP} = K_{sp}$, then solution is just saturated & no precipitation takes place.

(ii) If, $Q_{IP} > K_{sp}$, then solution is super saturated & precipitation takes place.

(iii) If, $Q_{IP} < K_{sp}$, then solution is unsaturated and more of the solute can dissolve.

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G.E-II

UNIT-III

May 7, 22

Aromatic Hydrocarbon :

(i) Aromatic hydrocarbon are those closed chain alkenes, which are planar in nature and obey Huckels rule. These are also known as Arenes or Aromatic Compounds.

(ii) Most of the Aromatic Compound contain benzene ring and are known as benzoids. And all other Compounds those not contain benzene ring are known as Non-benzoide aromatic compounds.

(iii) Aromatic Compounds may exist in their merge form or bicyclic form.

(De-merge) (Merge) (Bicyclic)

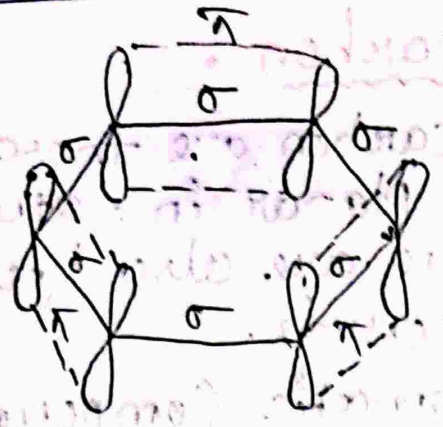
Structure of Benzene :

Benzene is a resonance stabilised aromatic structure in which all the carbons are involved during resonance of pi-electron.

→ Depending upon the resonating structure of benzene there are two stable resonating structure exist for benzene & two canonical structures represent benzene.

(Canonical Structure) (Hybrid structure)

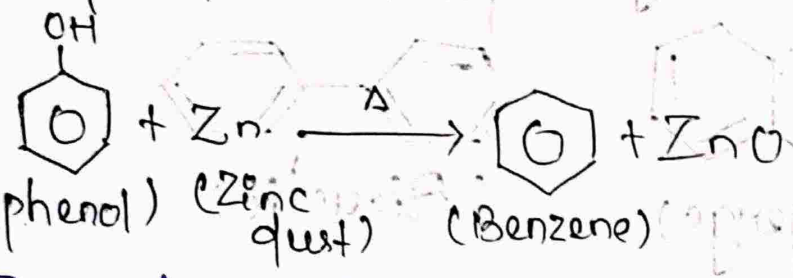
from one of the canonical structure if we consider valency bond theory to discuss bonding structure of benzene then we get all the carbon atoms on benzene are sp^2 hybridisation.



Preparation of Benzene :

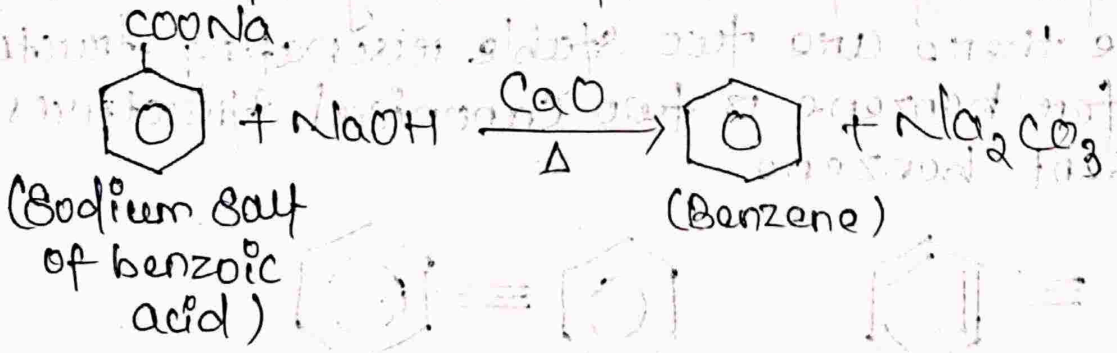
1. From phenol :

When phenol is heated in presence of Zinc dust it will readily reduce to produce benzene as the final product.



2. From Aromatic acid :

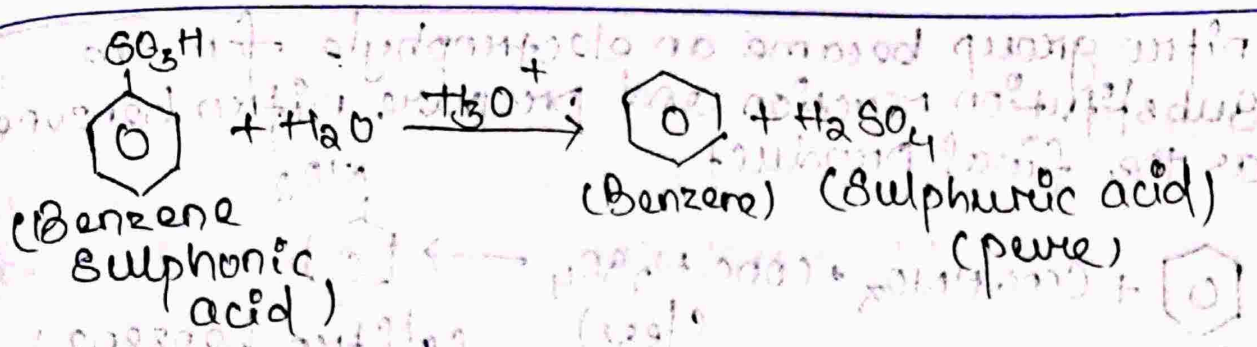
When Sodium Salt of aromatic acid heated in presence of Sodalime, it will produce benzene as final product & the process through which the reaction carried out is known as Decarbonylation of Salt of benzoic acid.



3. From Benzene Sulphonic acid :

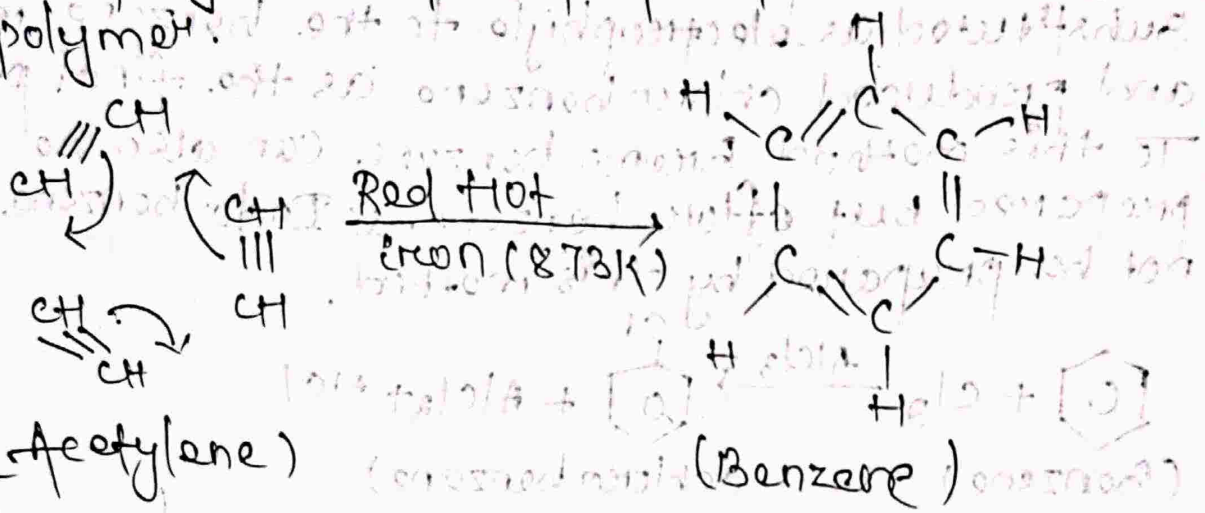
When benzene Sulphonic acid is exposed to Superheated Steam it will produce benzene as the major product.

** Super heated Steam is H_2O vapours due to process Hydrolysis.



4. From Acetylene (Cyclic polymerization):

When acetylene or ethyne passed through Red hot iron tube at 873K it will undergo cyclic polymerization to produce benzene as a polymer.



Chemical property of Benzene:

(1) Due to availability of maximum π-electrons in its resonating structure, benzene always under goes electrophylic substitution reaction, in which a positive charge containing species carry out π-electrons of benzene throughout the mechanism of benzene chemical reactions.

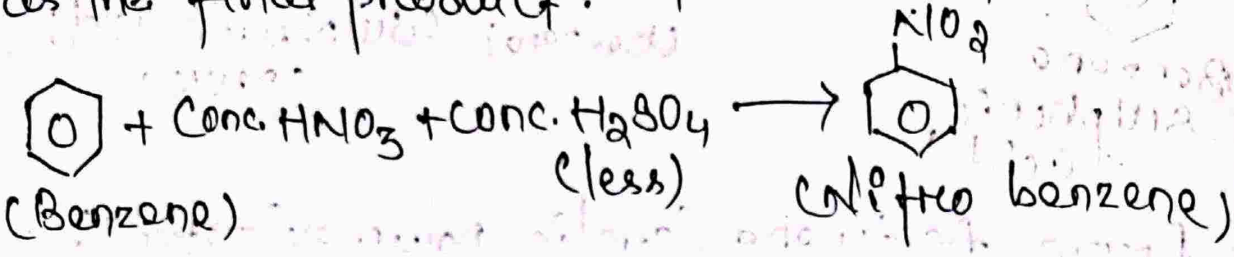
Electrophylic substitution reaction:

Electrophilic substitution reactions are nitration, sulphonation, Freidel kaft alkylation and acylation.

*) **Nitration:**

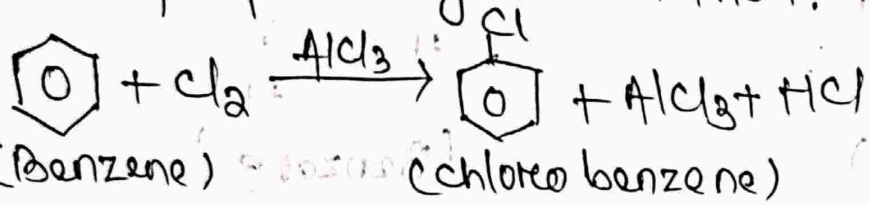
When a nitro group is introduced into benzene ring by heating of benzene with concentrated nitric acid and conc. sulphuric acid in less amount

nitro group became an electrophyle for the substitution reaction and prepare nitro benzene as the final product.



(*) Halogenation :

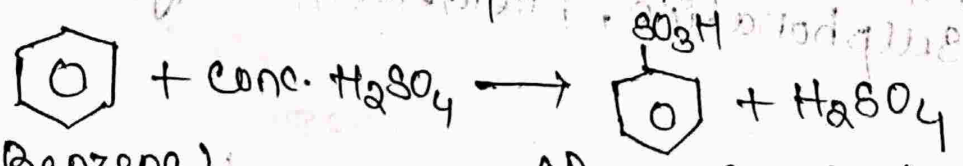
When chlorin gas passed through benzene chloride ion in presence of reducing agent $AlCl_3$ substituted as electrophyle to the benzene ring and produced chloro benzene as the final product. To this method Bromo benzene can also be prepared but floro benzene & Iodo benzene can not be prepared by this method.



→ florine & Iodine are not in gas form due to highly electronegative & small size of florine and highly sensitive to sunlight of Iodine. so floro benzene & Iodo benzene can't be prepared.

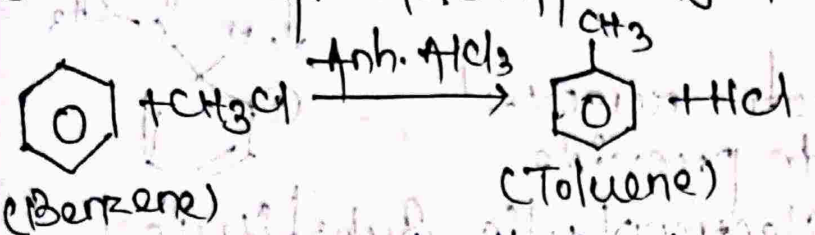
(*) Sulphonation :

When benzene react with Conc. Sulphuric acid, sulphonic acid as the electrophile substituted to benzene ring and benzene sulphonic acid prepared as the substituted product.



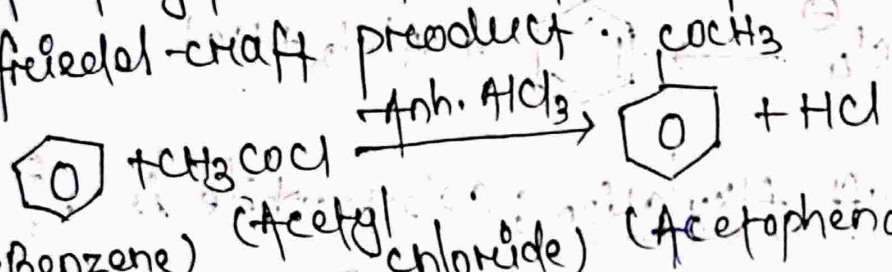
Friedelcraft Alkylation :

When benzene treated with alkyl halide in presence of reducing agent $AlCl_3$ it will produce alkylated benzene as friedelcraft alkylated product.



Friedelcraft Acylation :

When benzene react with Acyl halide in presence of Anhydrous $AlCl_3$ it will prepare Acylated friedel-craft product.



Mechanism :

for electrophylic substitution reaction mechanism carried out in three steps;

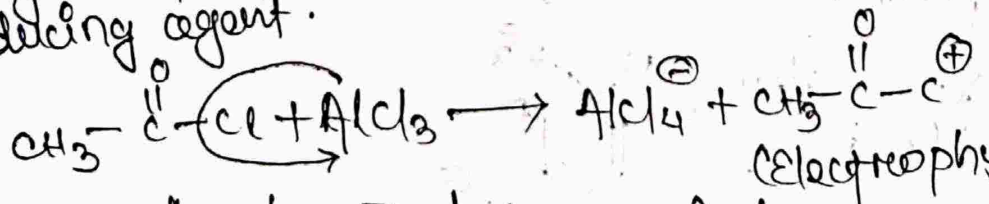
(i) Generation of electrophyle

(ii) Attack from benzene to electrophyle

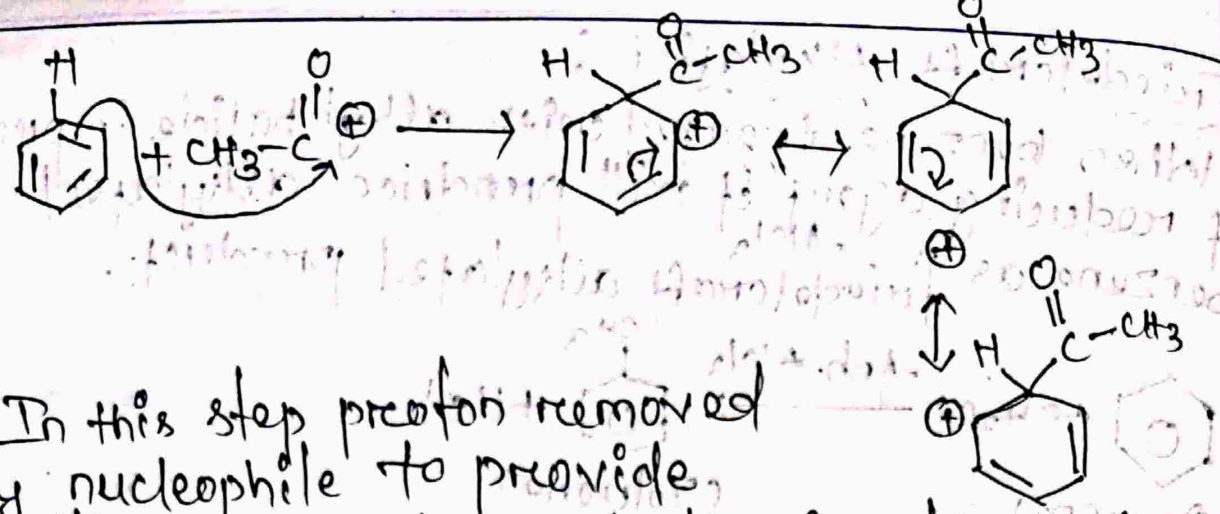
(iii) Removal of proton

In friedelcraft Acylation :

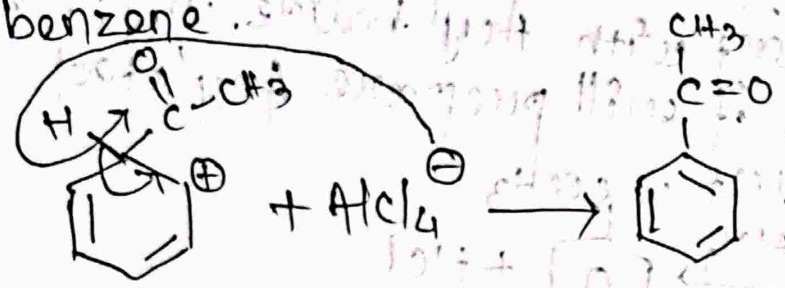
(i) An electrophyle in electrophylic substitution reaction is generated either by heating or in the presence of reducing agent.



(ii) In this step π-electrons of benzene attack electrophyle to make it stabilised or neutral, in this process the electrophyle easily substituted it self at sp^2 hybridised carbon of benzene ring.



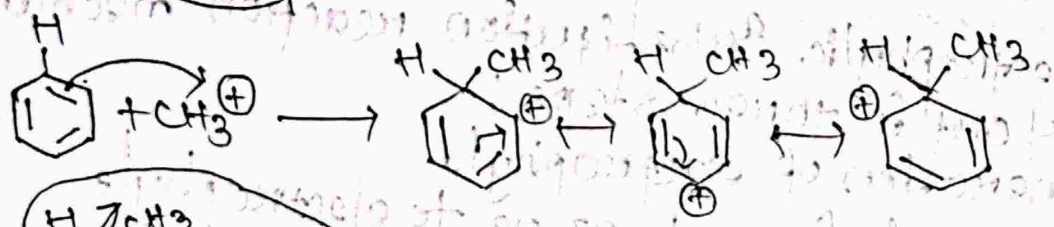
(iii) In this step proton removed by nucleophile to provide stability to the electrophylic substituted benzene.



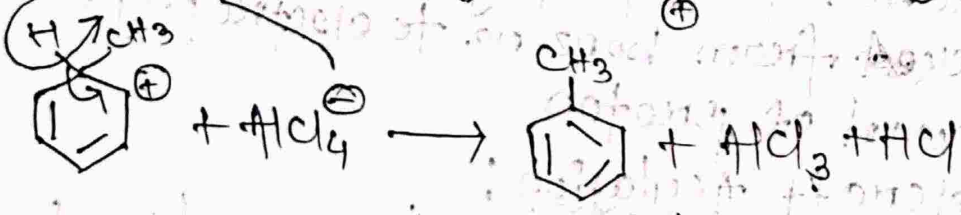
(*) In friedel craft Alkylation : (Electrophile is $CH_3^{\oplus}$)

(i) $CH_3-Cl + AlCl_3 \longrightarrow AlCl_4^{\ominus} + CH_3^{\oplus}$

(ii)



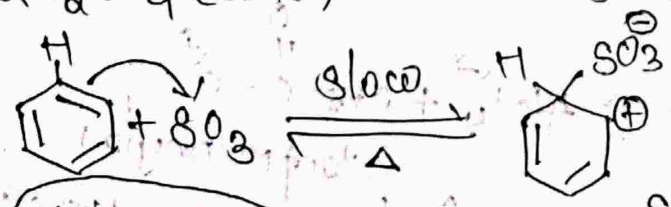
(iii)



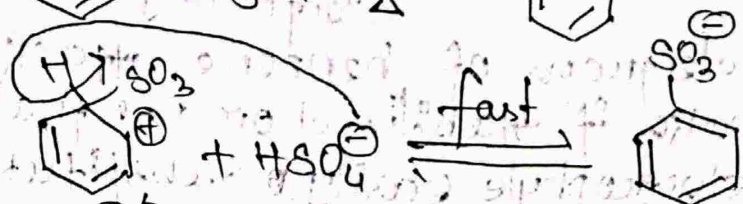
(*) In Sulphonation : (Electrophile is SO_3, electron deficient specie)

(i) $2H_2SO_4\,(conc.) \rightleftharpoons SO_3 + H_3O^{\oplus} + HSO_4^{\ominus}$

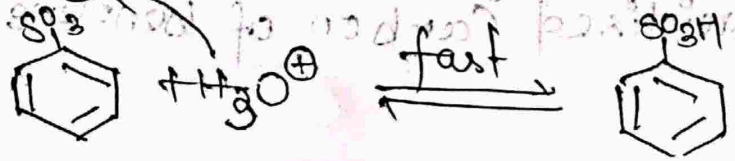
(ii)



(iii)

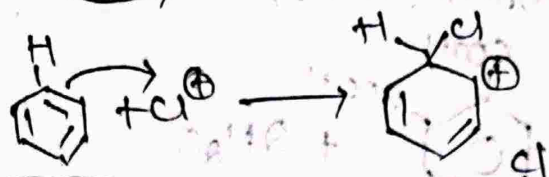


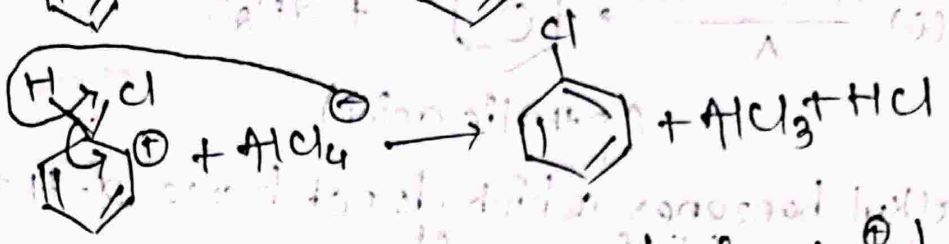
(iv)



(*) In Halogenation : (Electrophile is $Cl^{\oplus}$)

(i) $Cl-Cl + AlCl_3 \longrightarrow AlCl_4^{\ominus} + Cl^{\oplus}$

(ii) 

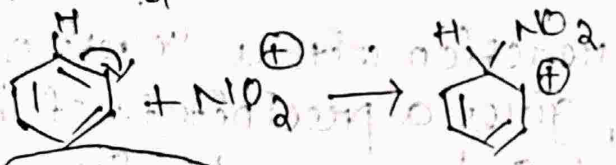
(iii) 

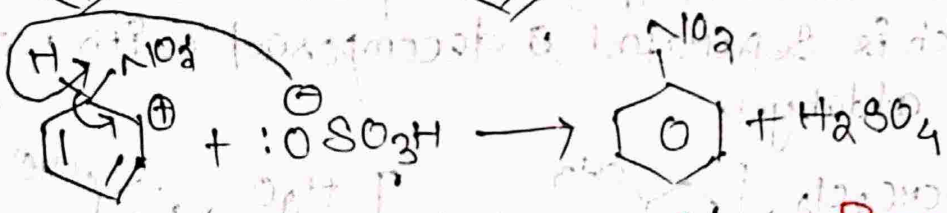
(*) In Nitration : (Electrophile is $NO_2^{\oplus}$)

(i) $H-NO_2 + HOSO_3H \rightleftharpoons H-\underset{H}{O}-NO_2 + O^{\ominus}SO_3H$

$H-\underset{H}{O}-NO_2 + H_2SO_4 \rightleftharpoons NO_2^{\oplus} + :OSO_3H + H_3O^{\oplus}$

$HONO_2 + 2H_2SO_4 \rightleftharpoons NO_2^{\oplus} + H_3O^{\oplus} + O^{\ominus}SO_3H$

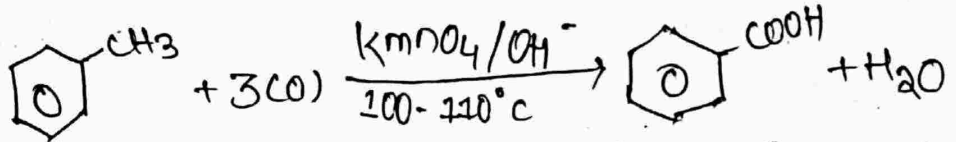
(ii) 

(iii) 

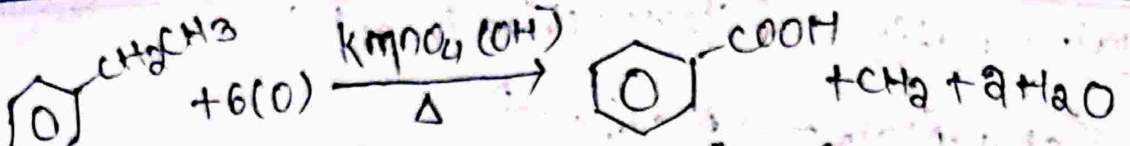
SIDE CHAIN OXIDATION OF ALKYL BENZENES :

It is known that benzene & Alkanes are quite stable towards oxidising agents. The presence of benzene ring makes the side chain susceptible to oxidation. The alkyl benzene can be easily oxidised to benzoic acid with alkaline potassium permanganate. Due to the oxidation, only the side chain is oxidised to carboxylic acid & the ring remains intact.

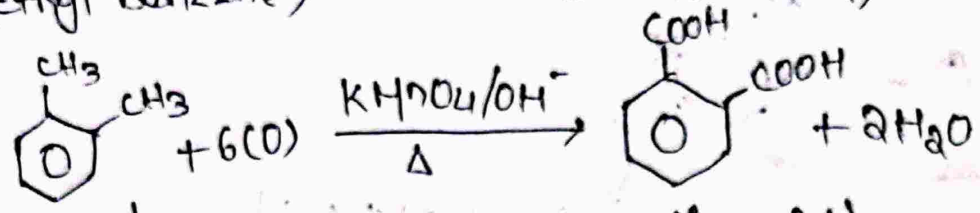
The position of the $-COOH$ group after oxidation indicate the position of the alkyl group.



(Toluene) (Benzoic acid)

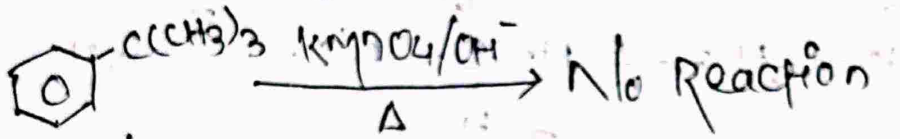


(Ethyl benzene) (Benzoic acid)



(o-xylene) (pthalic acid)

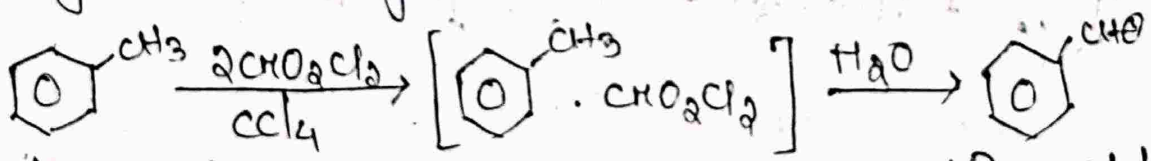
→ The alkyl benzenes which do not have α-H atom do not undergo oxidation easily.



(t-butyl benzene)
(no α-Hydrogen)

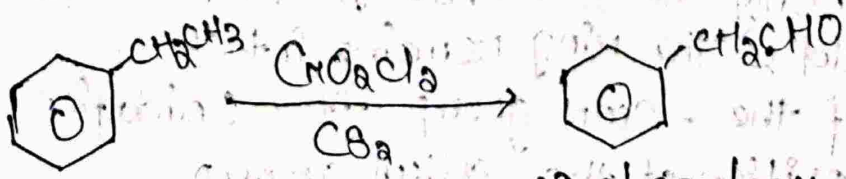
ETARD'S REACTION:

When Toluene undergo reaction with a solution of chromyl chloride in CCl_4 gives a precipitate of brown complex which is separated & decomposed with water to give an aldehyde.



(Toluene) (Brown Complex) (Benzaldehyde)

→ Mild oxidising agent like chromyl chloride oxidise the terminal methyl group of the side chain into aldehyde group without decreasing the number of carbon atoms of the chain.



(Ethyl benzene) (2-phenyl ethanal)

ALKYL HALIDE :

Alkyl Halides are the derivatives of alkanes which can be obtained by replacing one hydrogen atom by halogen atom.

Ex: CH_3Cl (Methyl chloride)

CH_2Cl_2 (Dichloromethane)

$CHCl_3$ (Trichloro methane) (Chloroform)

CH_2Cl-CH_2Cl (Ethylene dichloride)

$CH_3-C(CH_3)_2-Cl$ (2-Methyl-2-chloropropane)

PHYSICAL PROPERTIES :

1. Physical State : Some of the lower members are colourless gases. Higher members are solids.
2. Boiling points : keeping the alkyl group same, the B.P. increase with the increase in the size of the halogen atom. $CH_3F < CH_3Cl < CH_3Br < CH_3I$

   keeping the halogen atom same, the B.P. increases with the increase in the size of the alkyl group.

   $CH_3Cl < C_2H_5Cl < n\text{-}C_3H_7Cl < C_4H_9Cl$
3. Solubility : Inspite of the polarity of molecule, alkyl halides are insoluble in water.
4. Density : The alkyl iodides & bromides are heavier than water, while the chlorides and fluorides are lighter than water.

CHEMICAL PROPERTIES :

Alkyl halides are highly reactive because a halogen atom is a source of polarity. In some reaction, the halogen atom is removed along with a H-atom from the molecule to form alkenes. The H-atoms in an alkyl halide can be further replaced by halogens to give polyhalogen derivatives.

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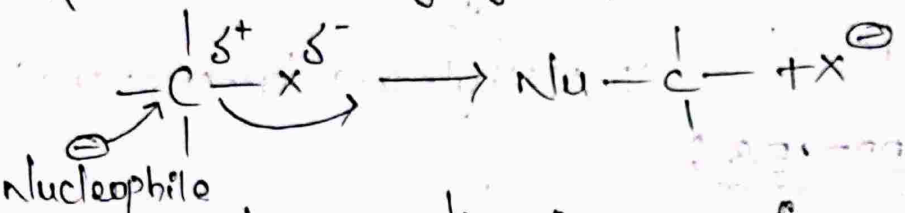
Nucleophilic Substitution Reaction :

In alkyl halide Carbon attached to halogen group which is more electronegative than Carbon

→ Carbon halogen bond is a polar bond with partial charges on carbon and halogen due to this polarity and partial positive character of Carbon, alkyl halide undergoes nucleophillic substitution reaction and halogen groups are known as leaving group.



Nucleophilic substitution reaction are of two types;

(i) Substitution nucleophilic unimolecular (SN_1)

(ii) Substitution nucleophilic bimolecular (SN_2)

Depending upon rate of the reaction and rate determining state. Nucleophilic substitutions are subdivided into above categories.

SN_2 Mechanism :

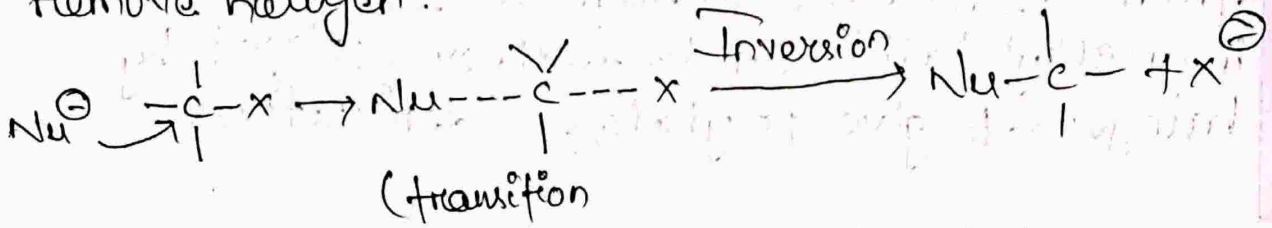
→ When alkyl halide hydrolised in presence of Sodium hydroxide undergo substitution reaction to produce alcohol and Sodium Salt of Corresponding halogen.

$$R-X + NaOH \xrightarrow{SN_2} R-OH + NaX$$

→ Rate of this reaction depends upon the concentration of halide as well as hydroxide.

$$Rate = [R-X][OH^-]$$

→ In this type of substitution reaction, Complete reaction, Carried out in a single state and the nucleophile must be more negative than the leaving group so that alkyl halide can easily remove halogen.



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→ When more electronegative electrophile attack partially positive carbon centre from opposite side of leaving group. the transition state formed between nucleophile, carbon and halogen and the hybridisation become sp^3 to sp^2 for transition state.

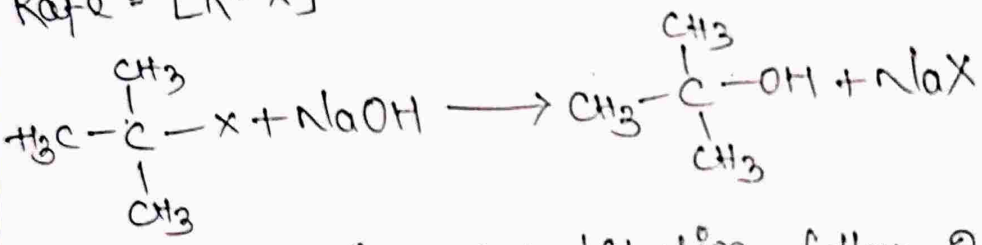
→ With the removal of leaving group from carbon centre, C–H bonds get inverted. Which is known as Walden inversion and the hybridisation of carbon changes from sp^2 to sp^3.

SN_1 Mechanism:

When alkyl halide react with sodium hydroxide in the absence of excess alcohol, it undergo SN_1 mechanism in which rate of the reaction completely depends upon concentration of alkyl halide only provided the alkyl hallide is a tertiary bond.

$$R-X + NaOH \xrightarrow{SN_1} R-OH + NaX$$

Rate = [R–X]

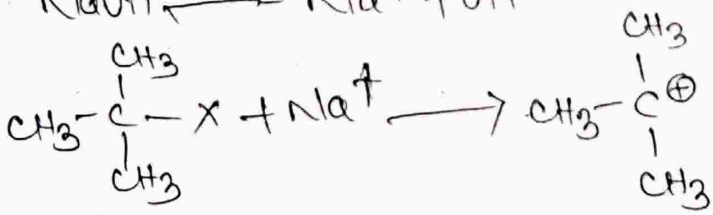


In this mechanism substitution follow 2 step reaction.

(i) Generation of Nucleophile & formation of Carbocation:

When sodium hydroxide dissociate, it produce nucleophile OH^- and electrophile Na^+. This electrophile remove leaving group from tertiary carbon, produce tertiary carbocation.

$$NaOH \rightleftharpoons Na^+ + OH^-$$



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(ii) Substitution of Nucleophile :

Now the nucleophile can easily substituted at the carbocation forming tertiary alcohol.

→ In SN_1 Mechanism. No transition state
No back attack
No change in hybridisation
No inversion

(Unit-4)) ((Part-1)) -:((Alcohols)):-

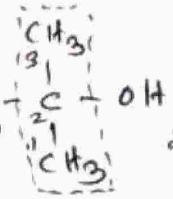
Introduction:- The organic compands with contain 'OH' group are called alcohols.

- Alcohols are hydroxy derivative of alkane.

$$\underset{\text{alkane}}{R-H} \xrightarrow[-H]{+OH} \underset{\text{alcohol}}{R-OH}$$

Ex: CH_3-CH_2-OH
Ethanol
or
Ethyl alcohol

monohydric alcohol



2 methyl propan 2 ol.

Dihydric alcohol:-

CH_2-CH_2 (OH, OH) Ethane 1,2 diol (Glycol)

Trihydric alcohol:-

$CH_2-CH-CH_2$ (OH, OH, OH)
propane 1,2,3 triol
(Glycerol)

Classification of alcohol:-

(I) Primary alcohol:-

CH_3-CH_2-OH
Ethanol
(1° alcohol)

$CH_3-CH(CH_3)-CH_2-OH$ Iso butyl alcohol

(II) secondary:-

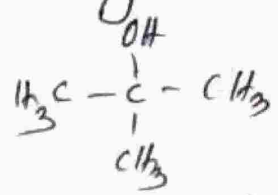
$CH_3-CH(OH)-CH_3$
Iso propyl alcohol

$CH_3-CH_2-CH(OH)-CH_3$
butan-2-ol
Secondary butyl alcohol.

(III) Tertiary alcohol:-

The alcohol in which OH group attached to tertiary carbon atom is called tertiary ~~alc~~ alcohol.

Ex:



(Tertiary butyl alcol)

2 methyl propan 2 ol

(A) Method of preparation of alcohol :-

1. From Grignard's reagent ($R-mgx$)
2. Ester hydrolysis
3. Reduction of aldehyde, ketone, carboxilic acid and ester.

1. From Grignard's reagent ($R-mgx$) :-

Grignard reagent is a strong nucleophile and base. The most important method for the preparation of primary (1°), secondary (2°) and tertiary (3°) alcohol is by the reaction between a ~~gri~~ Grignard reagent and a carbonyl compound such as an ~~ald~~ aldehyde & a ketone.

- Aldehydes and ketones form addition products with grignard's reagent. The addition products on hydrolysis with the water or aqueous acid form different types of alcohol.
- (i) Formaldehyde and ~~ex~~ epoxides yield primary alcohol (1°).
  (ii) All other aldehyde yield secondary alcohol (2°).
  (iii) All ketone yield tertiary alcohol.

(i) $R-mgx + HCHO \longrightarrow R-\underset{H}{\overset{H}{C}}-O\,mgx \xrightarrow{H_2O} R-CH_2-OH + mg(OH)X$

Grignard reagent, formaldehyde, (1° alcohol)

$H-CHO + CH_3-mgI \longrightarrow CH_3-CH_2-omgI \xrightarrow{H_2O} CH_3-CH_2-OH + mg(OH)I$

formaldehyde, methyl magnesium Iodide, Ethanol

(ii) $R-CHO + Rmgx \longrightarrow (R)_2CHO\,mgx \xrightarrow{H_2O} (R)_2CH-OH + mg(OH)X$

(aldehyde), (2° alcohol)

$CH_3-CHO + CH_3-mg-I \longrightarrow (CH_3)_2CHO\,mgI \xrightarrow{H_2O} (CH_3)_2CH-OH + mg(OH)I$

acetaldehyde, (Iso propyl alcohol)

(iii) $R-\overset{O}{\overset{\|}{C}}-R + R-mgx \longrightarrow (R)_3C-omgx \xrightarrow{H_2O} (R)_3C-OH + mg(OH)X$

(ketone), (3° alcohol)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-mg\,Br \longrightarrow (CH_3)_3C-omgBr \xrightarrow{H_2O} (CH_3)_3C-OH$

Acetone, methyl magnesium Bromide, tertiary butyl alcohol

2. From Ester hydrolysis :- when esters are heated with aqueous alkali KOH or NaOH, hydrolysis takes place resulting in the formation of the original alcohol and potassium or sodium salt of the acid. The alkaline hydrolysis of these esters is called as ~~Sap~~ saponification.

$$R-COOR' + KOH \xrightarrow{\Delta} RCOOK + R'-OH$$

$$CH_3-COOC_2H_5 + KOH \xrightarrow{\Delta} CH_3-COOK + C_2H_5-OH$$

Ethyl acetate — Ethyl alcohol

3. Reduction of aldehyde, ketone, carboxylic acid & Ester :-

(i) Reduction of aldehyde & ketone :- when aldehyde and ketones are heated with H_2 in the presence of a catalyst such as Ni or Pt ~~and~~ at 473 – 673 K temperature then they form primary and secondary alcohol respectively.

(i) $R-CHO + H_2 \xrightarrow[473K]{Ni} R-CH_2-OH$

aldehyde — alcohol (1°)

$CH_3-CHO + H_2 \xrightarrow[473K]{Ni} CH_3CH_2-OH$

Acetaldehyde — Ethyl alcohol

(ii) $\begin{matrix} R \\ R \end{matrix}\!>C=O + H_2 \xrightarrow[473K]{Ni} \begin{matrix} R \\ R \end{matrix}\!>CH-OH$

(Sec-alcohol) (2°)

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>C=O + H_2 \xrightarrow[473K]{Ni} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>CH-OH$

Acetone — Iso propyl alcohol

(ii) Reduction of carboxilic acid :-

when carboxilic acid undergoes reduction in the presence of lithium-aluminium hydride ($LiAlH_4$) then primary alcohol is formed.

$$R-COOH + 4H \xrightarrow{LiAlH_4} RCH_2-OH + H_2O$$

Carboxylic acid — 1°-alcohol

$$CH_3-COOH + 4H \xrightarrow{LiAlH_4} CH_3-CH_2-OH + H_2O$$

Acetic acid. — Ethyl alcohol

(iii) Reduction of Ester :- Lithium aluminium hydroxide reduces ester to primary alcohol.

$$CH_3-C(=O)-OC_2H_5 + 4H \xrightarrow{LiAlH_4} CH_3-CH_2-OH + C_2H_5-OH$$

Ethyl acetate — Ethyl alcohol

$$R-C(=O)-OR' + 4H \xrightarrow{LiAlH_4} R-CH_2-OH + R'-OH$$

(Ester) — alcohol (1°)

(b) Reaction :- (i) Reaction with Sodium :- when alcohol reacts with alkali Sodium (Na) then Sodium alcoxide is formed.

$$2\,R\text{-}OH + 2\,Na \longrightarrow 2\,RONa + H_2\uparrow$$

alcohol (alk) — Sodium alcoxide

$$2\,CH_3\text{-}OH + 2\,Na \longrightarrow 2\,CH_3\text{-}ONa + H_2\uparrow$$

methyl alcohol — Sodium methoxide

$$2\,(CH_3)_2CH\text{-}OH + 2\,Na \rightarrow 2\,[(CH_3)_2CH\text{-}ONa] + H_2\uparrow$$

iso propyl alcohol — Sodium iso propoxide

$$2\,(CH_3)_3C\text{-}OH + 2\,Na \longrightarrow 2\,[(CH_3)_3C\text{-}ONa] + H_2$$

tertiary butyl alcohol — Sodium tertiary butoxide

(ii) Reaction with lucas Reagent :- (Lucas Test)

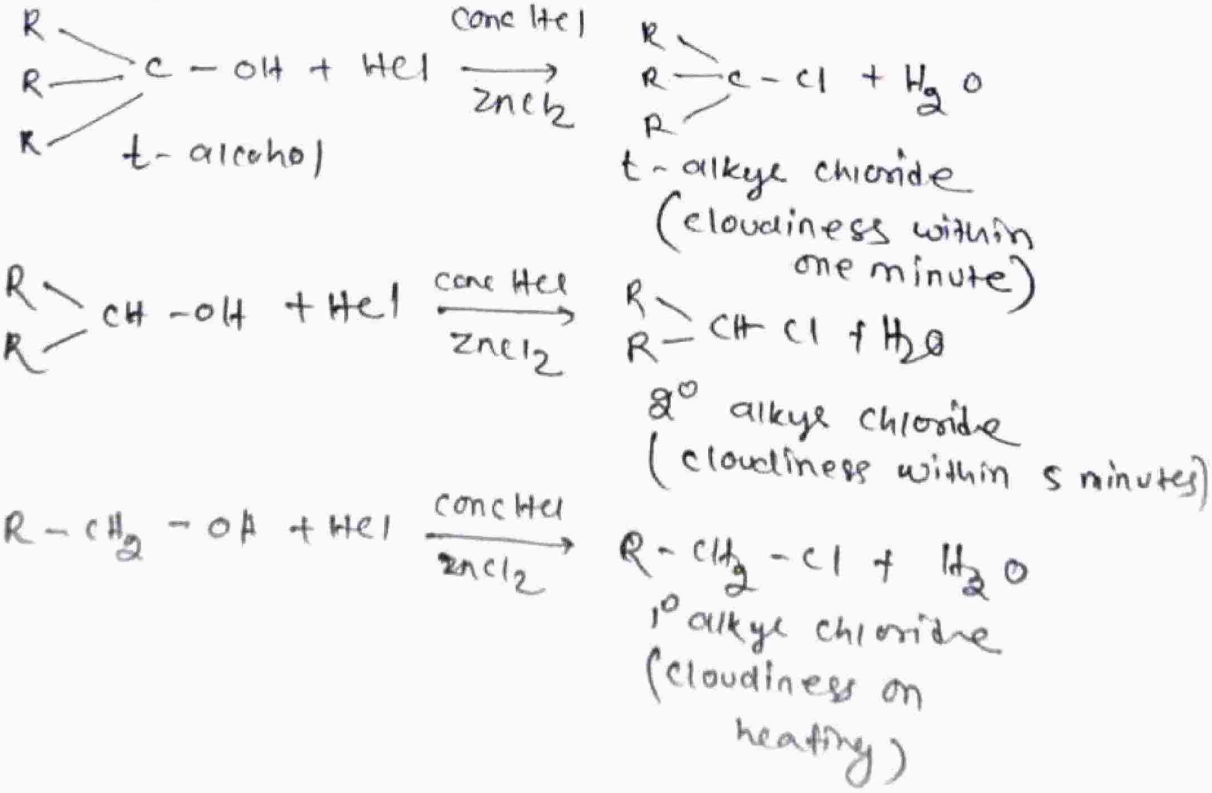
This test is based upon the difference in reactivity of three classes of alcohol with lucas reagent (a mixture of concentrated hydrochloric acid (HCl) an $ZnCl_2$). The formation of corresponding alkyl chloride, being immiscible, is indicated by the cloudiness which appears in the reaction mixture.

In case of,

(a) tertiary alcoho, cloudiness appears immediately

(b) secondary alcohol, cloudiness appears within five minutes.

(c) primary alcohols, cloudiness appears upon heating.



(iii) Esterification :- when an alcohol reacts with a carboxylic acid in the presence of concentrated sulphuric acid (H_2SO_4) or dry hydrochloric acid (HCl) then ester is formed. This is a reversible process and is known as "Esterification".

$$\underset{\text{m.c.A}}{R-COOH} + \underset{\text{Alcohol}}{HOR'} \underset{H_2SO_4}{\overset{H^+}{\rightleftharpoons}} \underset{\text{Ester}}{R-COOR'} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3-COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[H^+]{H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3-COOC_2H_5} + H_2O$$

(iv) Oxidation of alcohol :- primary and secondary alcohol are easily oxidized by a variety of reagent including chromate reagent, permanganate, nitric acid and NaOCl sodium hypochlorid.

(a) Oxidation of primary alcohol :- on oxidation with oxidising agents like acidified dichromate, it gets readily oxidised to aldehydes having the same number of carbon atoms as the parent alcohol. The aldehyde formed gets further oxidised to carboxylic acid having the same number of carbon atoms.

- Howevers, if the oxidation is carried out by passing the vapours of alcohol over copper turnings heated to 475 - 575 K, the reaction stops at the aldehyde stage.

$$\underset{\substack{\text{(alcohol)}\\(1^\circ)}}{R-CH_2-OH} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-CHO + H_2$$

$$R-CHO \xrightarrow{[O]} \underset{\text{m.c.A}}{R-COOH}$$

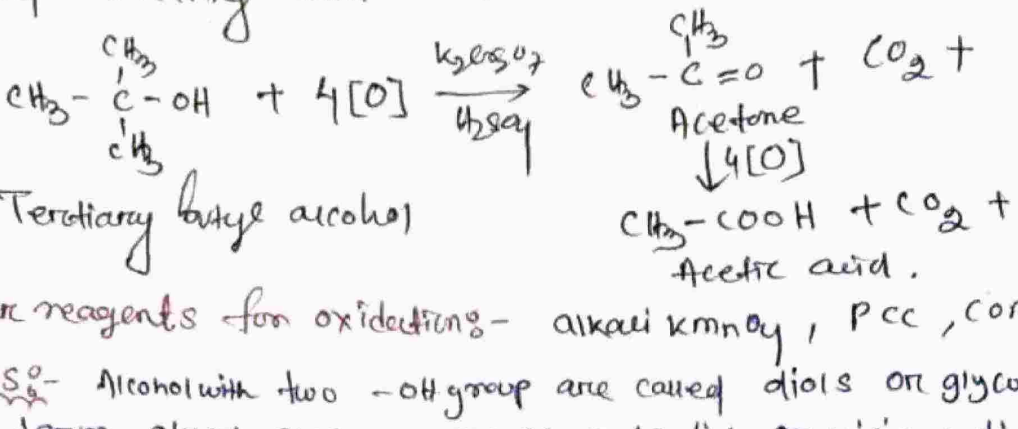
$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3-CHO} + H_2O \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3-COOH}$$

(b) Oxidation of secondary alcohol :- Secondary alcohol on oxidation with oxidising agent like acidified dicromate or on passing their vapours over heated Cu, yield ketones having the same number of carbon as the parent alcohol.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O + H_2O$$

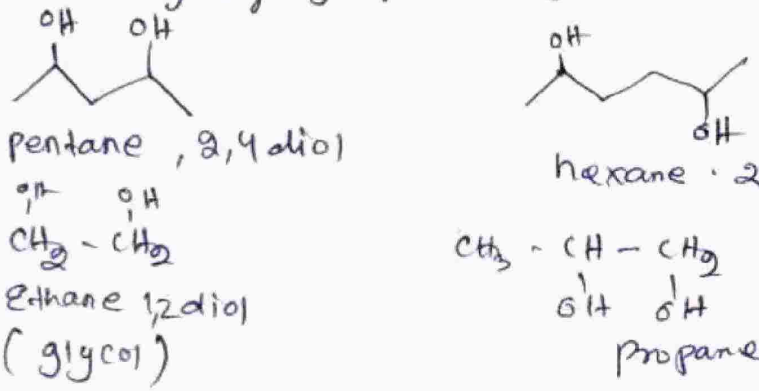
* ketones formed do not get further oxidised easily. They yield acids having lesser number of carbon atom under quite vigorous condition. It is because the oxidation involves the braking of a strong carbon carbon bond.

- For the same reason, tertiary alcohols are not easily oxidised. But on oxidation under vigorous conditions, they yield ketones having fewer number of carbon atoms than alcohols. ketones formed on prolonged oxidation with strong oxidising agent give carboxylic acid having still fewer number of carbon atoms.



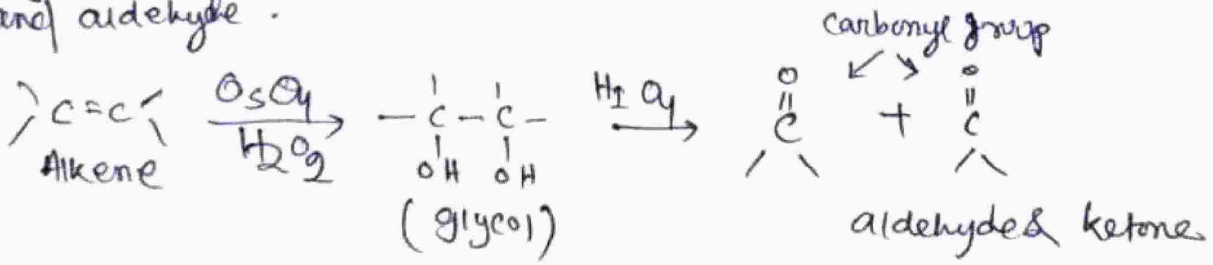
Other reagents for oxidation:- alkali $KMnO_4$, PCC, conc HNO_3

Diols:- Alcohol with two -OH group are called diols or glycols. The term glycol generally means a 1,2 diol or vicinal diol, with its two hydroxyl groups on adjacent carbon atoms.

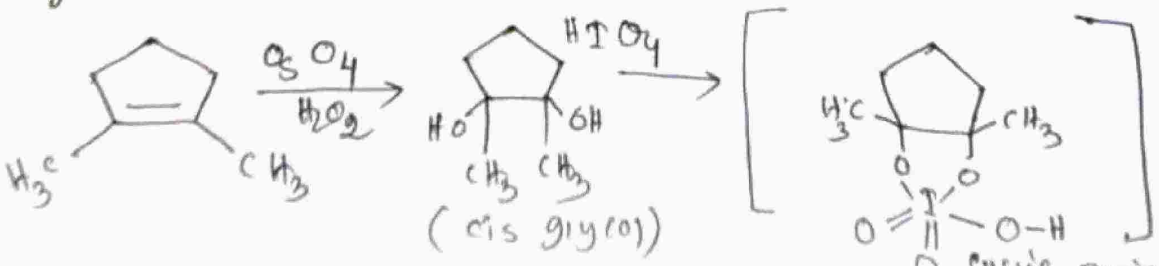


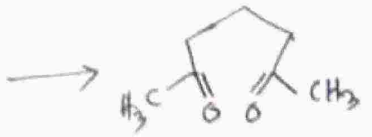
Oxidative cleavage of Diols:-

Alkene can be converted in to 1,2 Diols by hydroxylation (in the presence of H_2O_2 or OsO_4. The 1,2 Diols are cleaved by periodic acid (HIO_4). The products are the ketones and aldehyde.



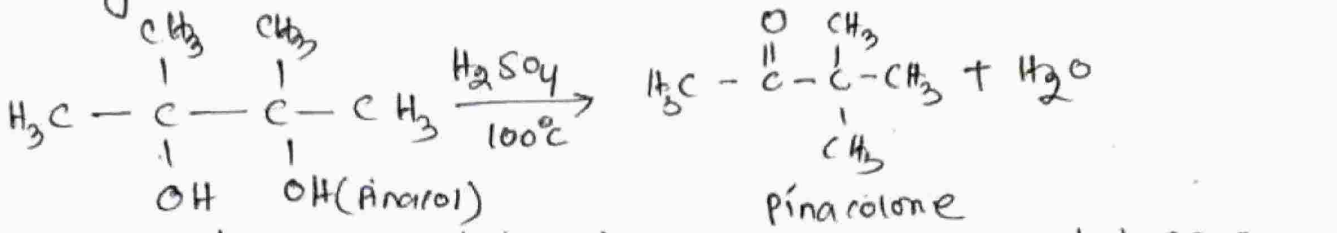
* Periodic acid (HIO_4) cleavage of a glycol probably involves a cyclic periodat intermediate.





Ketone

Pinacol - pinacolone Rearrangement :- conversion of an alcohol having two adjacent alcohol groups (pinacol) to a ketone (pinacolone) by the action of an acid (catalyst) is known as pinacol - pinacolone rearrangement.

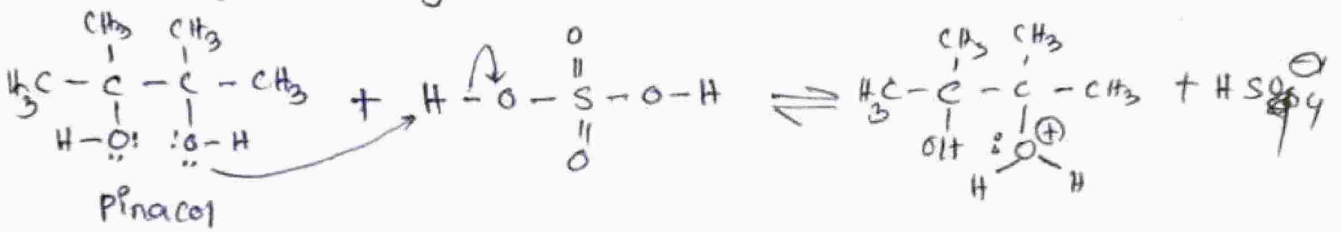


2,3 - dimethyl - 2,3 butanediol Pinacolone 3,3 - dimethyl - 2 - butanone

- The pinacol - pinacolon rearrangement is formally a dehydration.

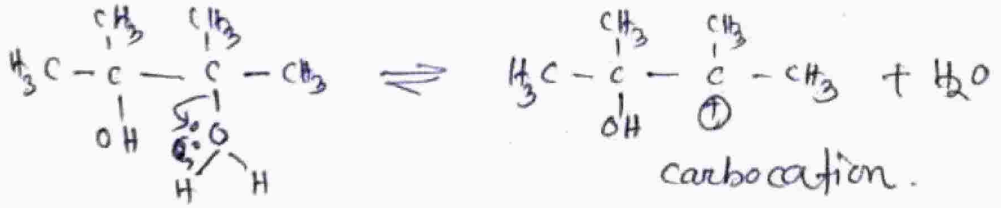
mechanism :-

① protonation of a hydroxyl group :-



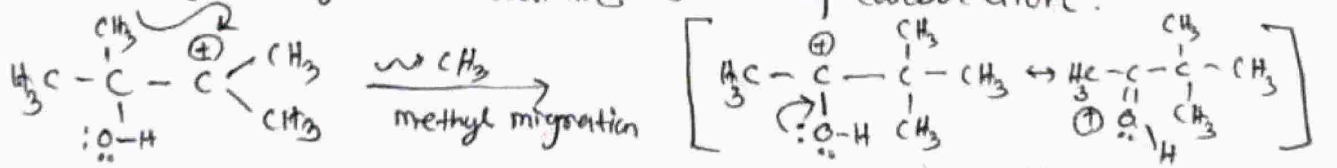
Pinacol

② Loss of water give a carbocation :



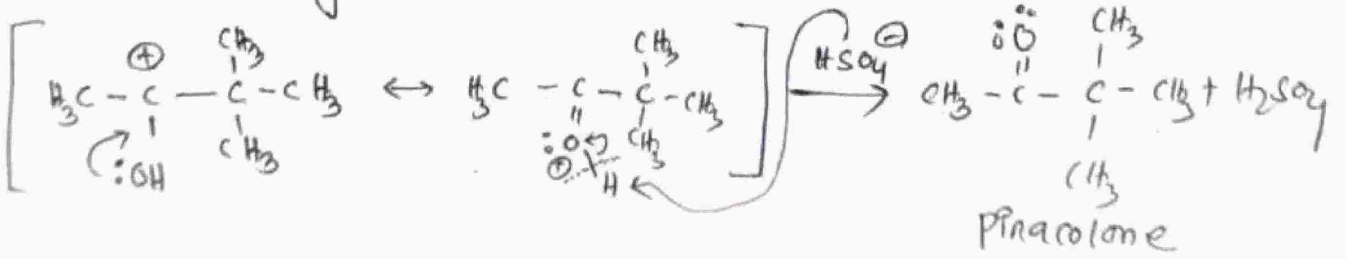
carbocation.

③ methyl migration forms a resonance - stabilized carbocation.



resonance - stabilized carbocation

④ Deprotonation gives the product :



Pinacolone

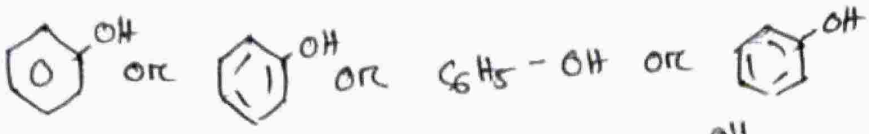
((Part-2)) :- ((Phenol)) :-

- Phenol is hydroxy derivative of ~~phenol~~ Benzene.

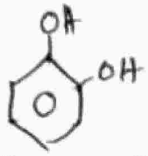
$$C_6H_6 \xrightarrow[-H]{+OH} C_6H_5-OH$$

Benzen — phenol, hydroxy benzene

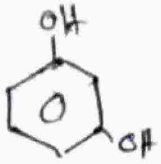
- General formula of phenol :



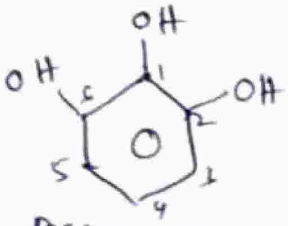
(monohydric phenol)



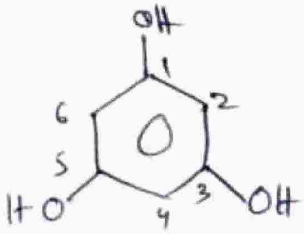
(Dihydric phenol) Benzene 1,2-diol



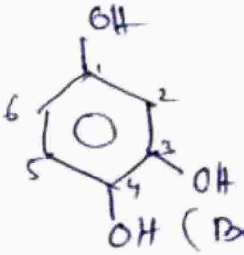
(Benzene 1,3 diol)



(Benzene 1,2,3 triol)



(Benzene 1,3,5 triol)

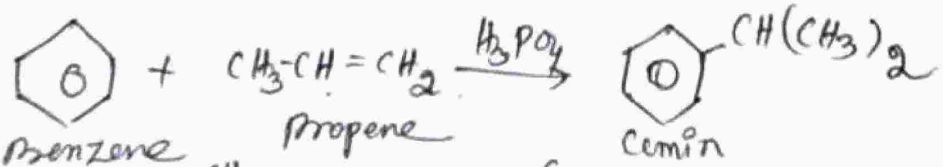


(Benzene 134 triol)

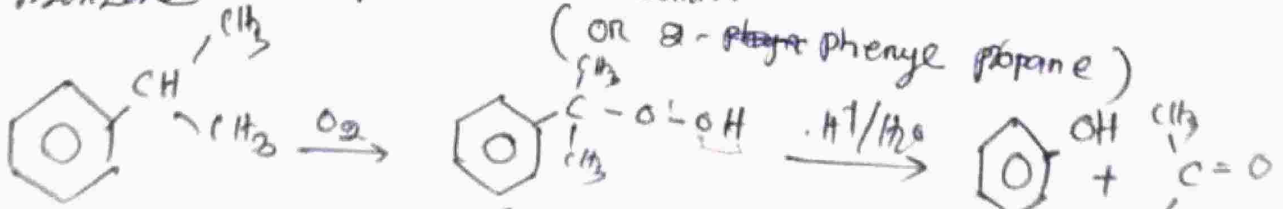
(Tri hydric phenol)

(A) Method of preparation of Phenol :-

(1) From Cumene hydroperoxide method :- Cumin is isopropyl benzene. propene is a petroleum product. It is treated with benzene in presence of phosphoric acid (H_3PO_4) to get cumin. cumin is oxidised with oxygen or air into cumin hydroperoxide in the presence of a catalyst. It is then decomposed by dilute sulphuric acid into phenol & acetone.



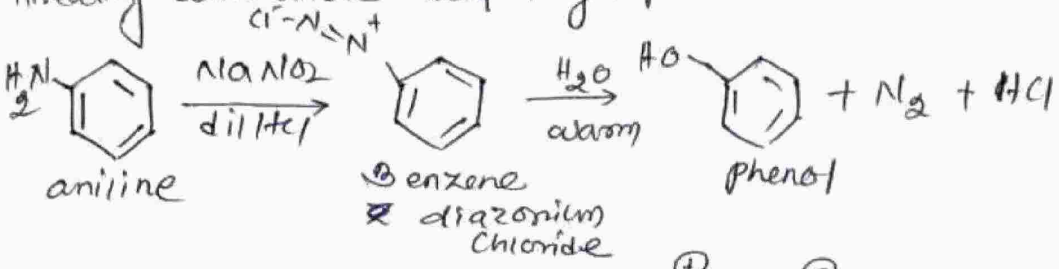
Benzene — Propene — Cumin (OR 2-~~phen~~ phenyl propane)

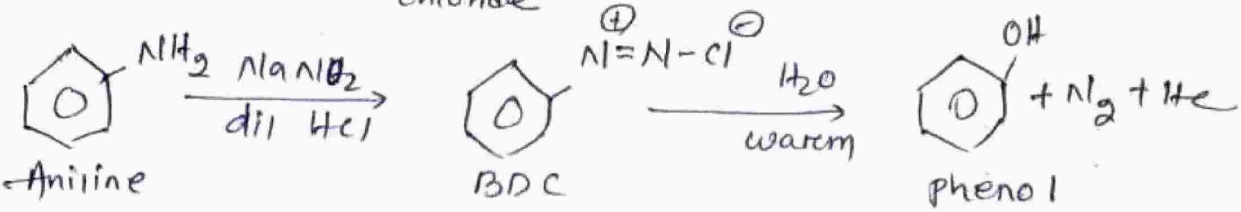


Cumene — Cumene — Cumene hydroperoxide — Phenol — acetone

(ii) From Benzene diazonium chloride (BDC) :-

Benzen diazonium chloride is formed by ~~tot~~ treating an aromatic primary amine (say aniline) with nitrous acid ($NaNO_2$ + dil. HCl) at 0-5°C. Diazonium salt so formed is then hydrolysed with warm water or treating with dilute acid to get phenol.



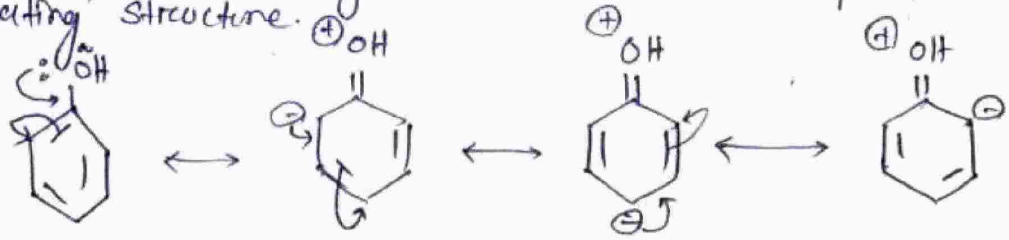


(B) Reaction of phenol :- (1) Electrophilic substitution reaction :-

Phenol undergo electrophilic substitution reaction. The -OH group (phenolic) is an activating group. Therefore phenol undergoes electrophilic substitution at a faster rate than benzene.

- Phenol shows ortho and para directing because OH group is activating group due to +I or +R character. So the incoming electrophile occupies ortho and para position with respect to phenolic (-OH) group.

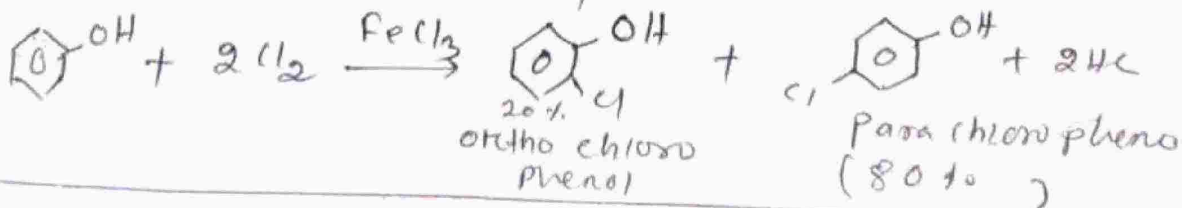
- Ortho and para directing nature can be explained by the following resonating structure.



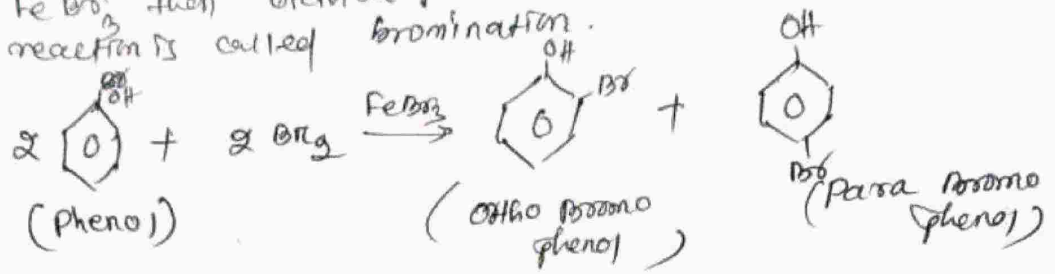
- From the above resonating structure, it is clear that the negative charge arises at the ortho and para position & it makes more electron density so the incoming electrophile can attack at ortho & para position.

(1) Halogenation of phenol :-

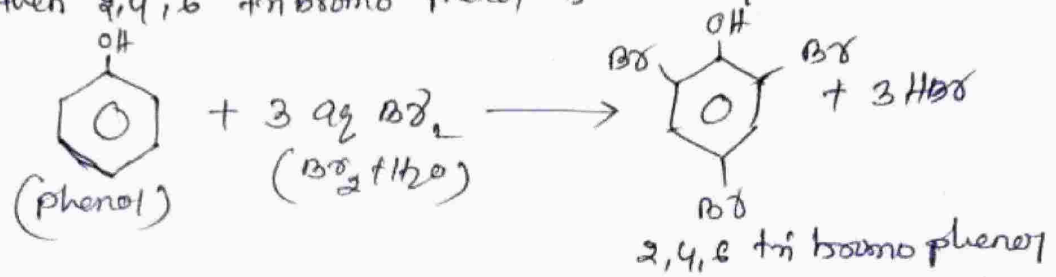
(a) Chlorination :- when phenol reacts with chlorine in presence of $FeCl_3$ or $AlCl_3$ the ortho chloro phenol or para chloro phenol is formed. This reaction is called chlorination of phenol.



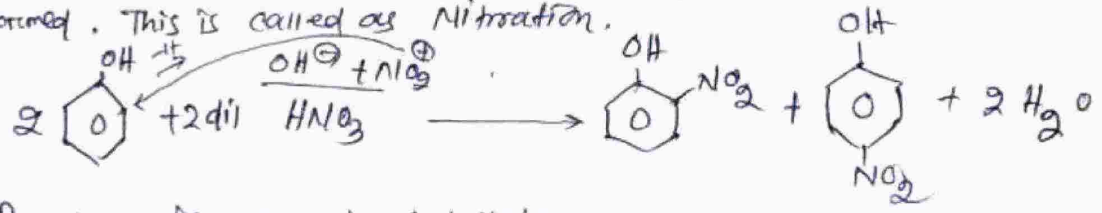
(b) bromination :- when phenol reacts with bromin in the presence of $FeBr_3$ then ortho or para bromo phenol is formed this reaction is called bromination.



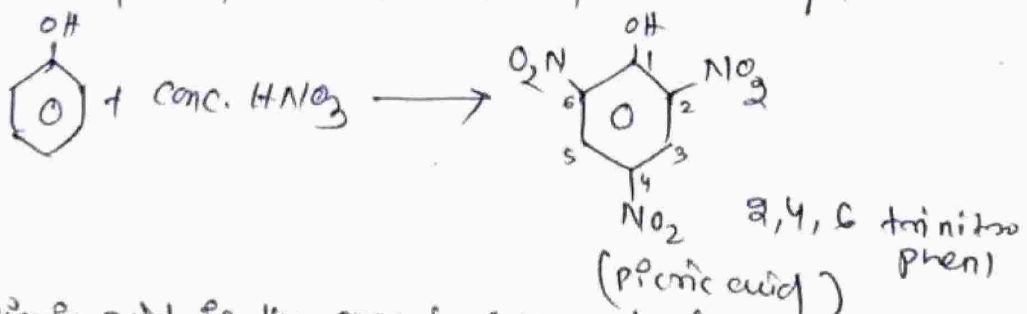
* Reaction with aqueous bromin :
when phenol reacts with aqueous bromin or bromin water then 2,4,6 tribromo phenol is formed.



(ii) Nitration :- when phenol ~~reacts~~ reacts with dilute nitric acid at low temperature then a mixture of ortho & para nitro phenol is formed. This is called as Nitration.

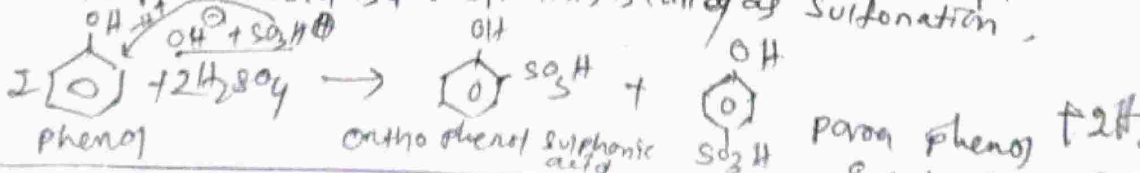


. Reaction with concentrated HNO_3 :
when ~~phen~~ phenol reacts with concentrated HNO_3 then 2,4,6 tri nitro phenol or picric acid is formed.

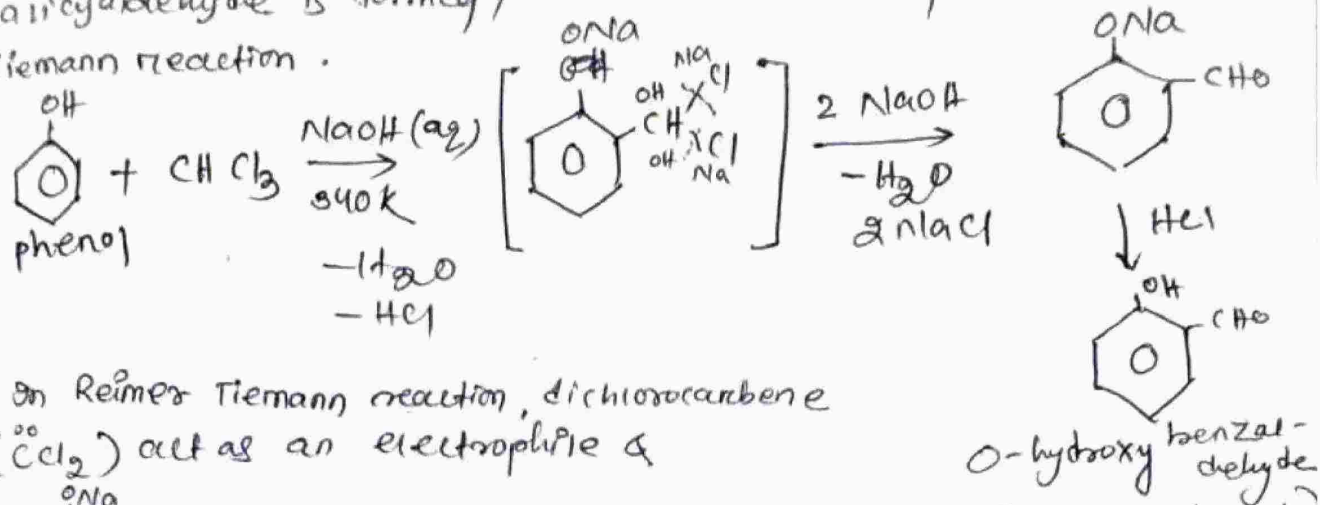


- picric acid is the organic compound which is acidic but do not contain -COOH group.

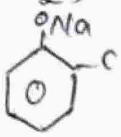
(iii) Sulphonation :- when phenol reacts with sulphuric acid the ortho and para hydroxy benzene sulphonic acid or ortho and para phenol sulphonic acid is formed. This is called as Sulfonation.



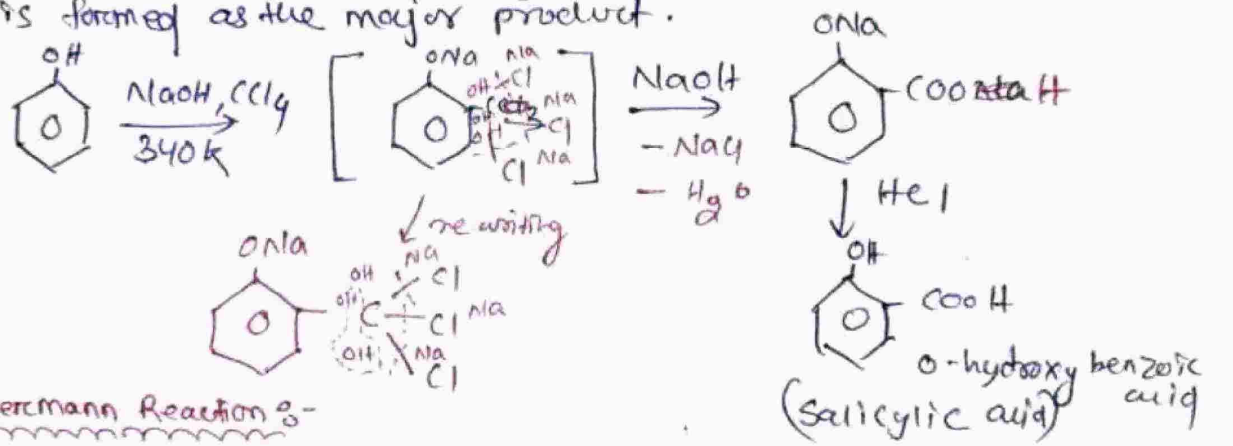
② **Reimer Tiemann reaction :-** when phenol reacts with chloroform ($CHCl_3$) in the presence of an aqueous alkali (NaOH or KOH) at 340 K then ortho hydroxy benzaldehyde or salicylaldehyde is formed, this reaction is called as Reimer Tiemann reaction.



* In Reimer Tiemann reaction, dichlorocarbene ($:CCl_2$) act as an electrophile & $CHCl_2$ is an intermediate.

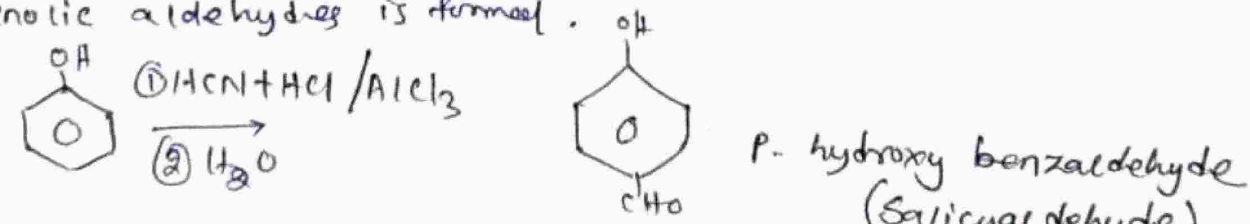


* If carbon tetrachloride is employed in place of chloroform, salicylic acid is formed as the major product.



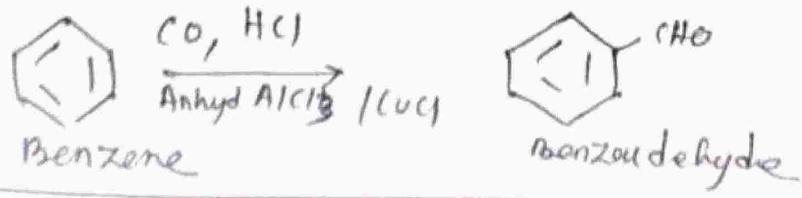
③ **Gattermann Reaction :-**

when phenol treated with a mixture of hydrogen cyanide and hydrogen chloride in the presence of an hydrous aluminium chloride then phenolic aldehydes is formed.



④ The aldehyde group gets attached preferably to para position.

Gattermann koch reaction :- In Gattermann - koch reaction benzene is treated with carbon monoxide in acidic medium in presence of anhydrous aluminium chloride to give benzaldehyde.



* Phenol & Phenol ether substrates are not applicable for Gattermann koch Reaction.

((Part-3)) :- :((Ethers)) :-

- The general formula of ether is R-O-R.
- Ethers are dialkyl derivative of water.

$$\underset{\text{waters.}}{H-O-H} \xrightarrow[-2H]{+2R} \underset{\text{Ether}}{R-O-R}$$

alkyl alkyl ether.

- The IUPAC Name of the Ether is alcoxy alkane. (lower alkyl group corresponds to alcoxy group)
- Ex

	IUPAC	common name
CH_3-O-CH_3	methoxy methane	dimethyl ether.
$C_2H_5-O-C_2H_5$	Ethoxy Ethane	diethyl ether
$C_2H_5-O-CH_3$	methoxy Ethane	Ethyl methyl ether
$C_3H_7-O-C_2H_5$	Ethoxy propane	Ethyl propyl ether
$C_4H_9-O-C_3H_7$	propoxy Butane	Butyl propyl Ether.

(A) Method of preparation :-

(1) Williamson's Synthesis :-

$$\underset{\text{alkyl halide}}{R-X} + R-O-Na \longrightarrow \underset{\text{Ether}}{R-O-R} + NaX$$

$$\underset{\text{methyl chloride}}{CH_3-Cl} + CH_3-O-Na \longrightarrow \underset{\text{dimethyl ether.}}{CH_3-O-CH_3} + NaCl$$

(B) Reaction of Ether :-

Cleavage of Ethers by HI :- Ether are not commonly used as synthetic intermediates because they do not undergo many reactions. This unreactivity makes ethers attractive as solvents. Even so, ethers do undergo limited number of characteristics reaction.

- Ether are cleaved by heating (100°c) with H-Br or HI to give alkyl bromides or alkyl iodides.

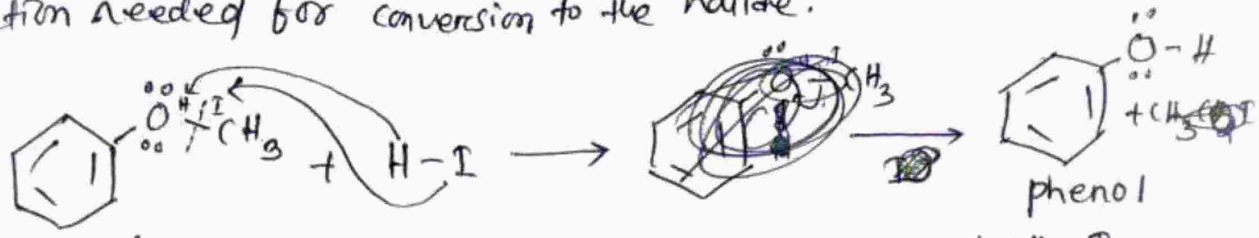
$$\underset{\text{Ether}}{R-O-R'} \xrightarrow[100°c]{HI \text{ excess}} \underset{\text{Alkyl Iodides.}}{R'-I + R-I} + H_2O$$

$$\underset{\text{dimethyl ether}}{CH_3-O-CH_3} \xrightarrow[100°c]{2HI} \underset{\text{methyl Iodide}}{CH_3-I + CH_3-I} + H_2O$$

$$\underset{\text{ethyl methyl ether}}{C_2H_5-O-CH_3} \xrightarrow{2HI} \underset{\text{methyl iodide}}{CH_3-I} + \underset{\text{Ethyl Iodide}}{C_2H_5-I} + H_2O$$

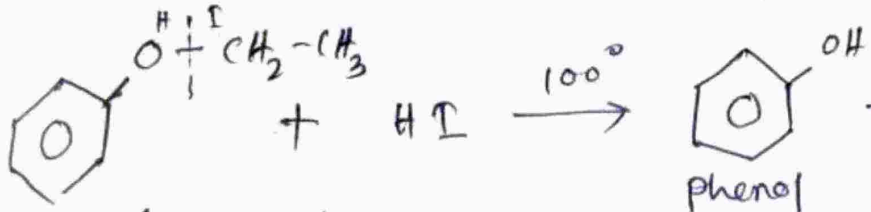
- ~~phyn~~ phenyl ether (one of the groups bonded to oxygen is a benzene ring) react with HI to give alkyl halides and phenols. Phenols phenol does react further to give halides because the sp^2-hybridised carbon atom of the phenol can not undergo the SN_2 or $SN1$ reaction needed for conversion to the halide.

Ex



methyl phenyl ether

phenol + CH_3-I methyl Iodide



Ethyl phenyl ether.

phenol + CH_3-CH_2-I Ethyl Iodide

— o —

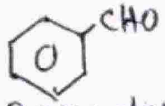
:((part-4)) :- :((Aldehyde & Ketone)) :-

- Both aldehyde and ketone are collectively called as carbonyl compound because both contain carbonyl $-\overset{O}{\overset{\|}{C}}-$
- Aldehyde :- The organic compound which contain CHO group is called as aldehyde.

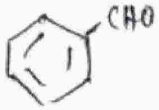
General Formula	→	$R-\overset{O}{\overset{\|}{C}}-H$ or $R-CHO$
Functional Group	→	$-CHO$
Prifix	→	Formyl
Suffix	→	al
IUPAC Name	→	Alkanal

Ex	IUPAC	C.N
$H-CHO$	methanal	Formaldehyde
CH_3-CHO	Ethanal	acetaldehyde
$C_6H_5-\overset{O}{\overset{\|}{C}}-H$	-	Benzaldehyde

Benzaldehyde :-



Benzaldehyde

or 

or $C_6H_5-\overset{O}{\overset{\|}{C}}-H$ or C_6H_5-CHO

- Ketone :- In ketone, the carbon atom of the carbonyl group is linked with both alkyl group or alkyl and aryl or both the aryl groups.

The General formula	→	$R-\overset{O}{\overset{\|}{C}}-R$ or $R-CO-R$
Functional Group	→	$-\overset{O}{\overset{\|}{C}}-$
Suffix	→	one
Prifix	→	oxo
IUPAC	→	Alkanone
C.N	→	Alkyl alkyl ketone

Ex	IUPAC	CN
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	Propanone	dimethy ketone (acetone)
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$	butanone	Ethyl methyl ketone

(A) Method of preparation :-

(i) From acid chloride

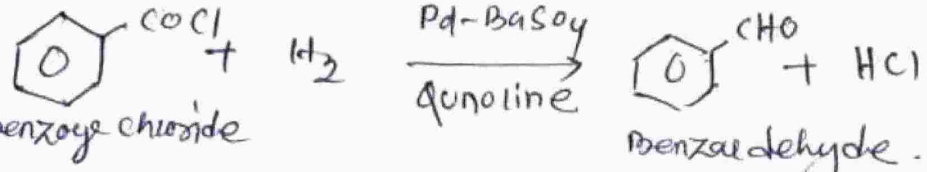
(ii) From nitriles

① From ~~alkyl nitriles~~ acid chloride :-

(a) in case aldehyde :- when acid chloride (R-CO-Cl) undergoes reduction in the presence of palladium catalyst and barium sulphate, poisoned by (To check further reduction of aldehydes to alcohol) adding a small amount of sulphur or quinoline, then aldehydes is formed. This reaction is called Rosenmund's reduction.

$$\underset{\text{Acid chloride}}{R-CO-Cl} + H_2 \xrightarrow[\text{Quinoline}]{Pd\ BaSO_4} \underset{\text{aldehyde}}{R-CHO} + HCl$$

$$\underset{\text{Acetyl chloride}}{CH_3-CO-Cl} + H_2 \xrightarrow[\text{Quinoline}]{Pd\ BaSO_4} \underset{\text{acetaldehyde}}{CH_3-CHO} + HCl$$



* Formaldehyde cannot be prepared by this method, since its corresponding acid chloride i.e formyl chloride is unstable at room temperature. Ketone also can't be prepared by rosenmund reduction.

(b) in case ketone :- when acid chloride reacts with dialkyl cadmium in the presence of dry ether then ketone is formed.

$$\underset{\text{acid chloride}}{2R-CO-Cl} + 2R_2Cd \xrightarrow{\text{dry ether}} \underset{\text{Ketone}}{2\ R-\overset{O}{\overset{\|}{C}}-R} + CdCl_2$$

$$\underset{\text{acetyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + (CH_3)_2-Cd \xrightarrow{\text{dry ether}} \underset{\text{acetone}}{2\ CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CdCl_2$$

② From nitriles :-

(a) in case aldehyde :- when alkyl nitrile on reduction with stannous chloride and hydrochloric acid in absolute ether followed by hydrolysis. This reaction is called as stephen's reduction

$$SnCl_2 + 2HCl \rightarrow SnCl_4 + 2H$$

$$\underset{\text{Ethane nitrile}}{CH_3-C\equiv N} + 2H \xrightarrow[HCl]{SnCl_2} \underset{\text{acetal diamine}}{CH_3-CH=NH} \xrightarrow{H_2O} \underset{\text{acetaldehyde}}{CH_3-CHO} + NH_3\uparrow$$

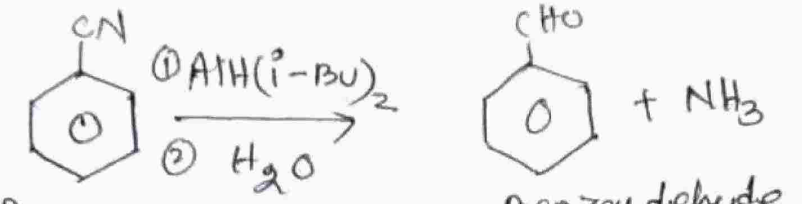
* Also nitriles are selectively reduced by di-isobutyl aluminum hydride (DIBAL-H) to imines which on hydrolysis yields corresponding aldehyde.

$$\underset{\text{alkyl nitrile}}{R-C\equiv N} \xrightarrow[(2)\ H_2O]{(1)\ AlH(\text{isobutyl})_2} \underset{\text{aldehyde}}{RCHO}$$

$CH_3-C\equiv N \xrightarrow{AlH(i\text{-}Bu)_2} CH_3-CH=NH \xrightarrow{H_2O} CH_3-CHO + NH_3$

methyl cyanide — acetaldehyde

Ethane nitrile



Benzene cyanide — benzaldehyde

benzonitrile

(b) incase ketone:- when alkyne nitriles react with Grignard's reagent to form an addition compound which on hydrolysis yields a ketone.

$R-C\equiv N + R-Mg\,X \xrightarrow[H_2O]{Ether} R-\overset{O}{\overset{\|}{C}}-R + Mg(OH)X + NH_3$

alkyl cyanide — Ketone

alkyne nitrile

$CH_3-C\equiv N + CH_3-Mg\,Br \xrightarrow{Ether} CH_3-CH_2-Mg\,Br$

Ethane nitrile

$\longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=N\,Mg\,Br \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + Mg(OH)Br + NH_3$

acetone

Reaction:- ① Reaction with HCN :-

when aldhyde and Keton reacts with hydrogen cyanide (HCN) in the presence of base (OH^-) to form corresponding cyanohydrin.

$H-\overset{H}{\overset{|}{C}}=O + HCN \xrightarrow{OH^-} H-CH(OH)-CN$

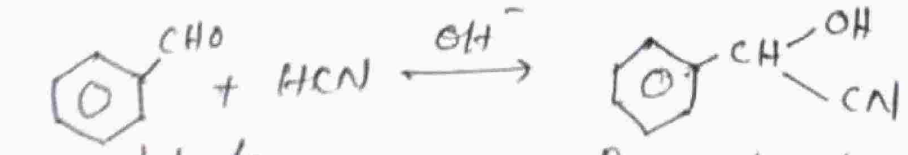
Formaldehyde — Formaldehyde cyanohydrin

$CH_3-\overset{H}{\overset{|}{C}}=O + HCN \xrightarrow{OH^-} CH_3-CH(OH)-CN$

Acetaldehyde — acetaldehyde cyanohydrin

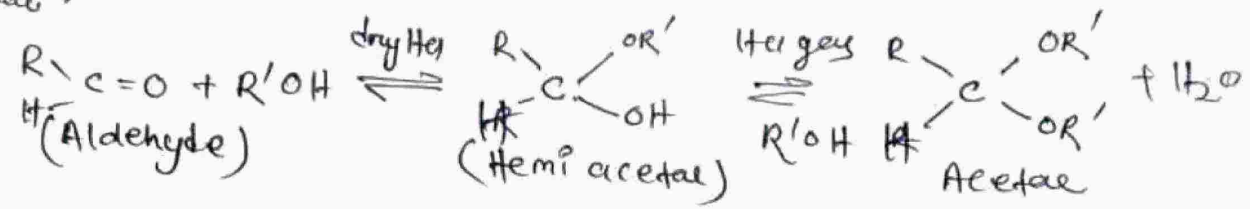
$CH_3-\overset{CH_3}{\overset{|}{C}}=O + HCN \xrightarrow{OH^-} CH_3-C(CH_3)(OH)-CN$

Acetone — Acetone cyanohydrin

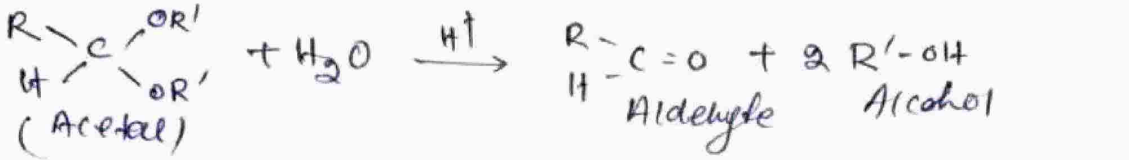


Benzaldehyde — Benzaldehyde Cyanohydrin

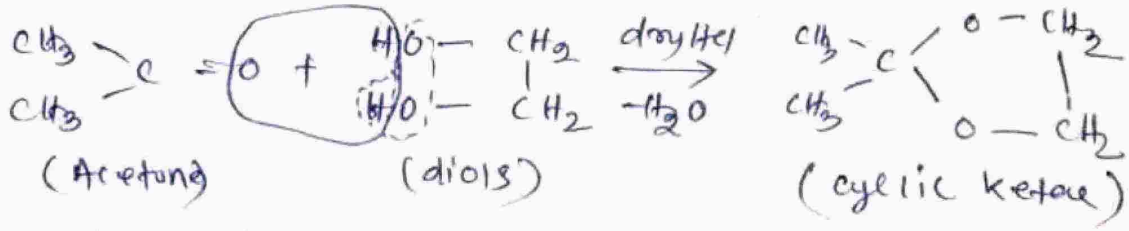
② Reaction with alcohol :- Aldehydes react with alcohol in presence of dry HCl gas to give acetals. Addition of one molecule of alcohol to an aldehyde yield a hemi acetal. It contains both an alcohol and ether group and it is unstable. It reacts with second molecule to form acetal.



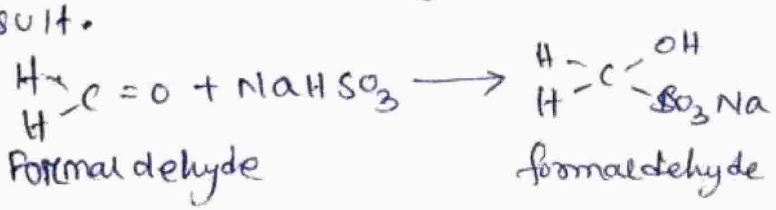
- Acetals are geminal ethers. They are quite stable but can be cleaved by acids to regenerate aldehyde. Acetal formation is useful in protecting an aldehyde group against alkaline oxidising agents.

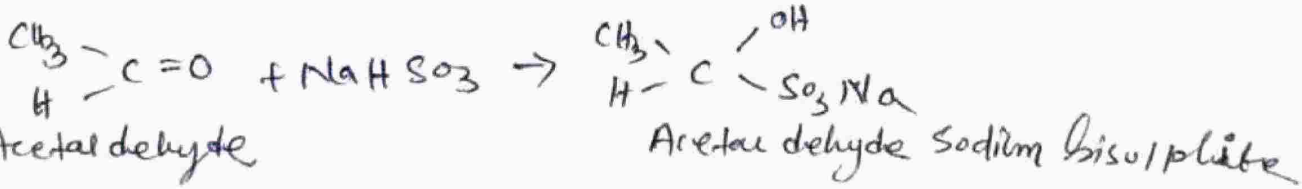


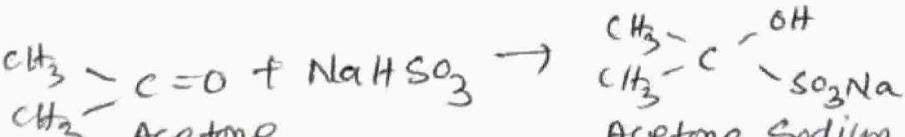
- Ketone donot reacts with a monohydric alcohol but reacts with diols to form cyclic ketals.

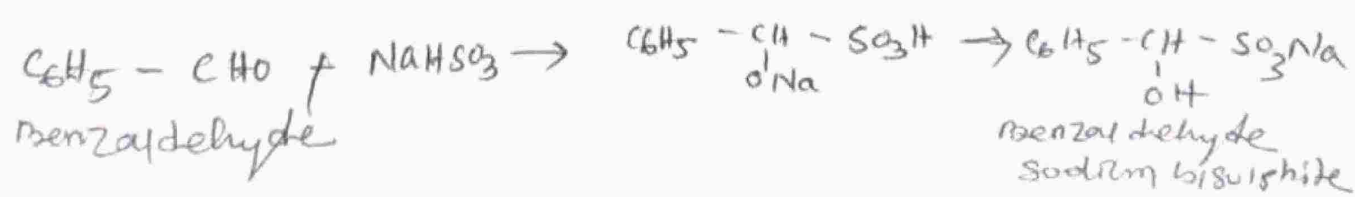


③ Reaction with Sodium bisulphate ($NaHSO_3$) :-
When aldehyde and ketone treated with a saturated solution of Sodium bisulphate, a crystalline white ppt. of the addition product result.







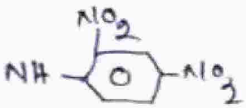


(4) Reaction with ammonia derivatives (NH_2-G) :- most aldehyde and ketone react with derivatives of ammonia to form compounds having carbon - nitrogen double bond with elimination of water. Such compound are crystalline with a sharp melting points. These are generally formed for the characterisation of aldehydes and ketones.

$$>C=O + H_2\ddot{N}-G \xrightarrow{H^+} C=N-G + H_2O$$

carbonyl compound

In the attacking reagent, $G-\ddot{N}H_2$, G may be;

G	Formula & name	Name of the product
(1) $-OH$	$H_2\ddot{N}-OH$ Hydroxylamine	oxime
(2) $-NH_2$	$H_2\ddot{N}-\ddot{N}H_2$ Hydrazine	Hydrazone
(3) $-NHC_6H_5$	$H_2N-NHC_6H_5$ phenyl hydrazine	phenyl hydrazone
(4) $-NHCONH_2$	$H_2N-NHCONH_2$ Semicarbazide	Semicarbazone
(5) 	$H_2N-NH-C_6H_3(NO_2)_2$ 2,4 Dinitro phenyl hydrazine	2,4, dinitro phenyl hydrazone.

(1) Reaction with H_2N-OH :-

$$H_2C=O + H_2N-OH \xrightarrow{HCl} H_2C=NOH + H_2O$$

Formaldehyde — Formaldehyde oxime

$$(CH_3)_2C=O + H_2N-OH \xrightarrow{HCl} (CH_3)_2C=NOH + H_2O$$

acetone — acetone oxime

(2) Reaction with H_2N-NH_2 :-

$$H_2C=O + H_2N-NH_2 \xrightarrow{H^+} H_2C=NNH_2 + H_2O$$

formaldehyde — formaldehyde hydrazone

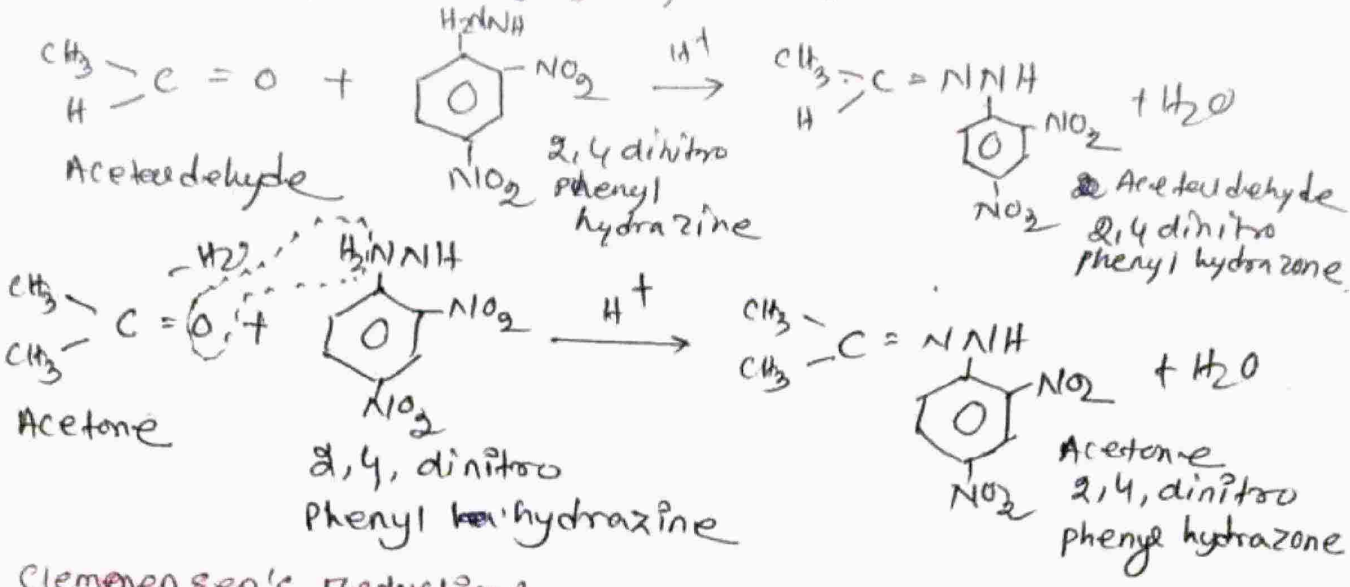
(3) $$(CH_3)_2C=O + H_2N-NHC_6H_5 \xrightarrow{H^+} (CH_3)_2C=NNHC_6H_5 + H_2O$$

acetone — phenyl hydrazine — acetone phenyl hydrazone

(4) $$(CH_3)(H)C=O + H_2N-NHCONH_2 \xrightarrow{H^+} (CH_3)(H)C=NNHCONH_2 + H_2O$$

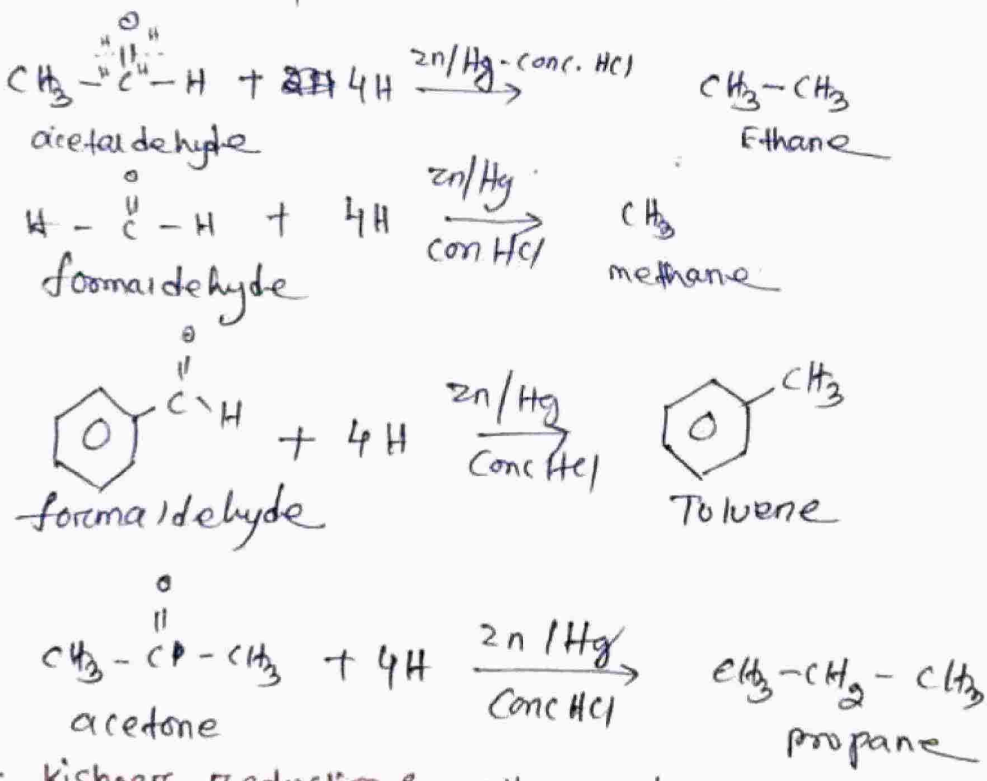
acetaldehyde — semicarbazide — acetaldehyde semicarbazone

(5) Reaction with 2,4 dinitrophenyl hydrazine :-



(6) Clemenensen's reduction :-

When aldehyde and ketone undergoes reduction in the presence of zinc(Zn) or Hg amalgam and conc. hydrochloric acid then alkanes is formed. This reaction is called as clemensen's reduction reaction.



(7) Wolf Kishner reduction :- ~~when aldehyde and ketone undergoes reduction in the presence of with hydrazine and KOH in boiling~~

When aldehyde and ketone undergoes reduction with hydrazine in the presence of KOH or gly(o) then alkane is formed, this reaction is called wolf kishner reduction.

$$R-CHO + H_2NNH_2 \xrightarrow[-H_2O]{KOH/Gly(o)} R-CH=NNH_2 \xrightarrow[Gly(o)]{KOH} R-CH_3 + N_2$$

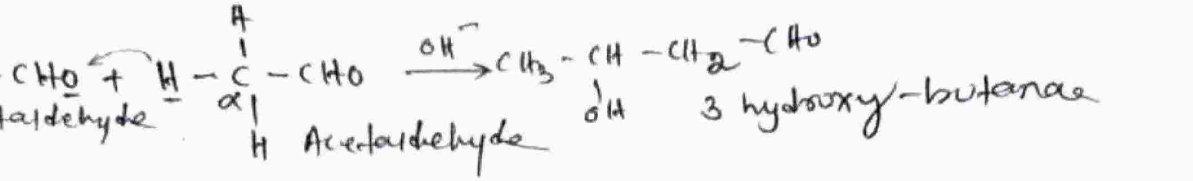
Aldehyde — alkane

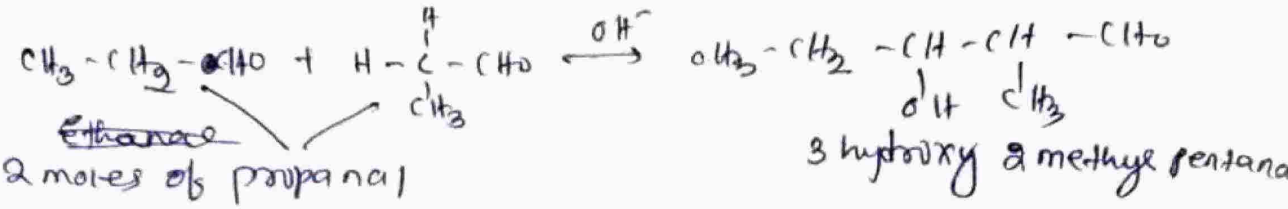
$$CH_3-CHO + H_2NNH_2 \xrightarrow[-H_2O]{KOH/Gly(o)} CH_3-CH=NNH_2 \xrightarrow[Gly(o)]{KOH} CH_3-CH_3 + N_2\uparrow$$

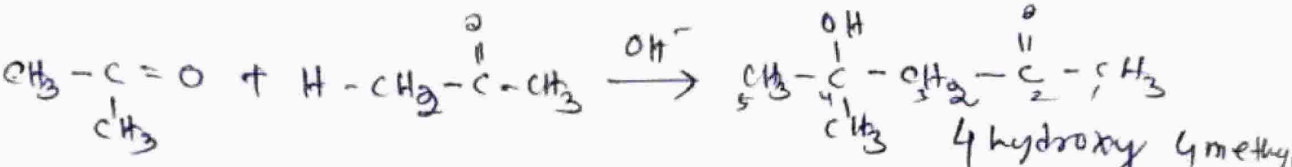
Acetaldehyde — Ethane

(8) **Aldol condensation :-** In this reaction, two molecule of a carbonyl compounds having atleast one α-H atom undergoes condensation in presence of dilute alkali. The product is formed is β-hydroxy aldehyde or β-hydroxy ketone. The reaction is called as aldol condensation. α-H atom of one carbonyl molecule join the oxygen atom of the other molecule of carbonyl compound.

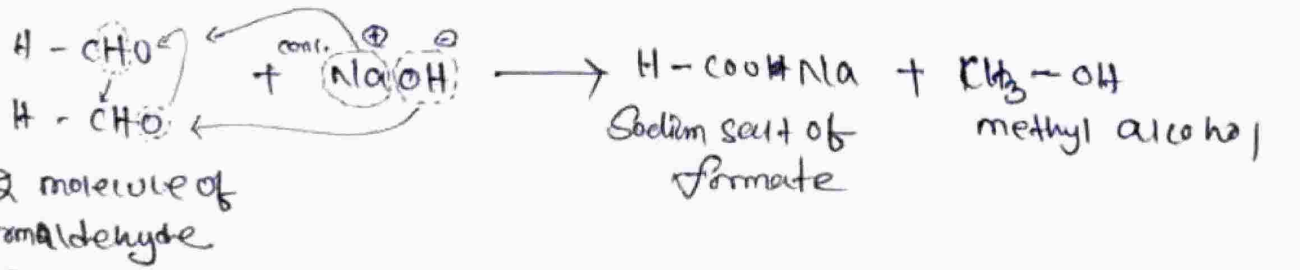
Ex:



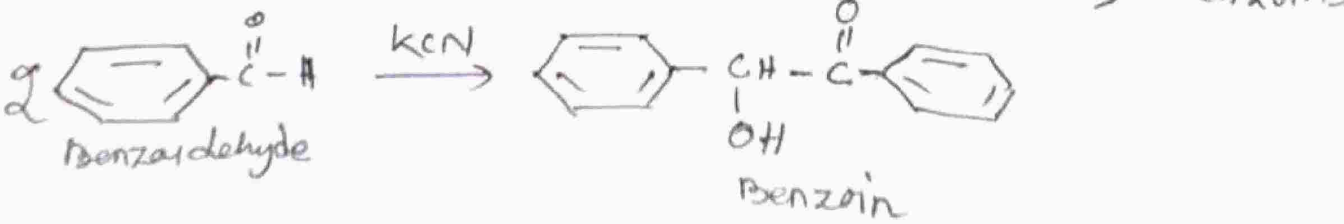




(9) **Cannizzaro's reaction :-** When aldehyde with no α-H atom such as formaldehyde react with concentrated alkali (NaOH / KOH) at room temperature, then aldehyde (Formaldehyde) undergoes self oxidation & reduction. Thus an alcohol and sodium or potassium salt of acid is formed. This reaction is called as Cannizzaro's reaction. In this reaction hydride shift occurs.



(10) **Benzoin Condensation :-** Aromatic aldehydes which donot contain α-hydrogen atom cannot undergo aldol condensation. However in the presence of potassium cyanide, they undergo self condensation in a different manner to form products known as benzoins.



(11) Iodoform Test :- A solution of I_2 in an alkaline medium such as NaOH or KOH is a oxidising agent.

- when ethanal react with this solution, then tri iodoethanal will be formed as the intermediate product. Tri iodoethanal then reacts with the base to form a yellow precipitate of triiodomethane (iodoform). This reaction is called as "Iodoform Test".

$$CH_3 - CHO + 3I_2 \longrightarrow CI_3CHO + 3HI$$

Tri iodoethanal

$$CI_3 - CHO + OH \longrightarrow CH - I_3 + CH\,COOH$$

iodoform

* Iodoform test is useful for the methyl ketone group ($CH_3-\overset{O}{\overset{\|}{C}}$) in ethanal & methyl ketones.