

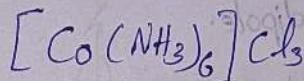
Unit-1

Co-ordination Complexes

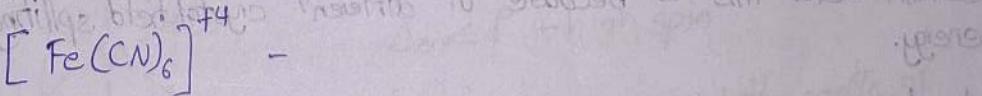
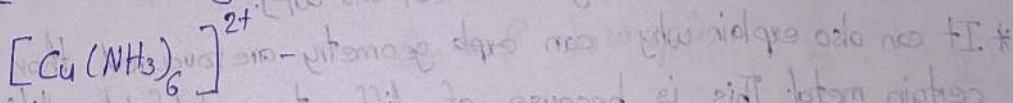
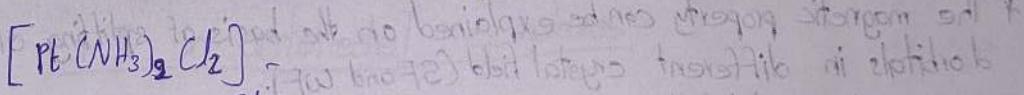
Co-ordination chemistry study of co-eff compounds that have a central metal atom surrounded by molecules or ions known as Ligands. These ligands are attached to the central metal atom by co-ordinate bonds.

Metal - Lewis acid (electron acceptor)
Ligand - Lewis base (electron donor)

An example of co-ordination compound



which has $[\text{Co}(\text{NH}_3)_6]^{+3}$ in co-ordination sphere with 6 (NH_3) molecules as Ligands and 3 chloride ions are outside of sphere acting as anion.



Secondary valency - covalent

- * Metal make available a no of empty orbitals to accept the electron from ligand.
- * This orbitals should undergo hybridisation to give the new orbital of equivalent energy.

Limitations:

not explained magnetic property.

not explained spectra or colour substance.

not consider 3 orbitals

Crystal Field Theory

<u>Strong field ligand</u>	<u>weak field ligand</u>
Diamagnetic low spin	Paramagnetic high spin

This theory is based on the different assumption that VBT.
The central metal ion is surrounded by ligand which contain lone pair of electron.

All types of ligands either they are ionic or molecular in nature are regarded as point charges. In case of neutral ligand the -ve end of dipole it's oriented towards central metal atom.
Ionic ligand - point charge.
Neutral ligand - point dipole.

- * The off b/w metal and ligand purely electrostatic (100% ionic)
- * The spectra of transition metal complex can be explained in terms of electronic transition b/w various energy levels of the orbital.
- * The magnetic property can be explained on the basis of splitting of d orbitals in different crystal field (SF and WF).
- * It can also explain why can ~~explore~~ geometry are favoured than certain metal. This is because of different crystal field splitting energy.

Advantages of crystal field theory:

- * The stability of complexes can be discussed by this approach. The more is the CF splitting energy, The more stable the system will be.
- * The colour and spectra of complexes can be explained by using this approach due to d-d transition.
- * The magnetic property of complexes can be understood by this theory.

Limitation:

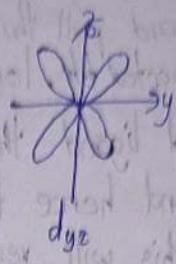
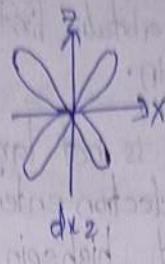
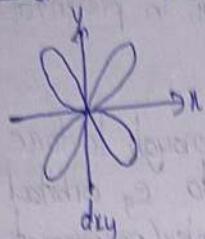
- * The idea that the interaction b/w metal and ligand is exclusively electrostatic is far from reality.
- * The hypothesis exclusively consider the d-orbital of metal atom. The s and p orbitals are not studied.
- * free bonding in ~~most~~ many complexes. This theory fails to explain how it is possible free bonding.

* The orbitals of the ligand has no significance on the view.
As a result it is unable to explain interaction b/w metal and ligand.

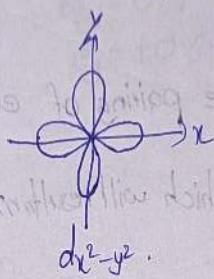
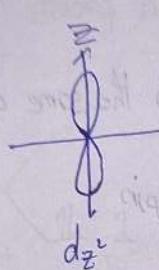
2.8.2 Grouping of d-orbitals into two sets :-

two types $\Rightarrow t_{2g}, e_g$

t_{2g} - simply degenerate - d_{xy}, d_{yz}, d_{zx} (non-axial orbitals).



e_g - doubly degenerate - $d_{x^2-y^2}, d_{z^2}$ (axial orbitals)



CFT in octahedral complexes :-

$\Delta_o > P$ - low spin

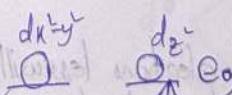


$\Delta_o < P$ - high spin

In an octahedral complex the metal ion, the ligand occupied six corners of the octahedron.

In case of octahedral complexes as the two ligands approach along the axis, the two axial orbitals, $d_{x^2-y^2}, d_{z^2}$ are repelled more than t_{2g} orbitals that is the energy of e_g orbital increases much more than t_{2g} orbitals.

hypothetical degeneracy while all the ligands opposite from equatorial orbitals



5 degenerate d-orbitals of some energy in

absent of ligand

splitting of d-orbitals in field in octahedral complex.

Δ_o is the difference b/w t_{2g} and e_g .

In a octahedral complex, the energy in t_{2g} orbital for one electron -0.4 eV .
energy of e_g orbital of each orbital $> 0.6 \text{ eV}$.

→ filling up of electrons in d-orbitals.

Filling up of electron depends on nature of ligand.
In case of strong ligand field Δ_o is large enough to force the electrons in pair up and pull the t_{2g} orbitals first. Thus, in presence of strong ligand the complex will be low spin.

In weak field ligand the Δ_o is not large enough to force the electron to pair up and hence the electron enter into e_g orbital before pairing. This will result in high spin complex (paramagnetic).

Pairing energy: (P)

The energy required to cause pairing of electrons in the same orbital $\Delta_o > P$

Pairing energy will be less which will result in low spin.

$\Delta_o < P$

Pairing energy is high that is electron remain unpaired which will result in high spin.

Crystal field splitting Energy: $\Delta_o < P$

The gain in energy achieved by preferential willing up of electron in t_{2g} and e_g orbitals is called CFSE.

Magnitude of Δ_o

The value of Δ_o depends on the following factors

1) oxidation state of metal ion

higher the ox. state of metal ion, higher will be attraction for ligand which result in more CFSE.

2) No. of d-electrons

higher the no. of d-electrons less will be the value of Δ_o for the electron occupying both t_{2g} and e_g level.

No. of d-electrons $\propto \frac{1}{\Delta_o}$

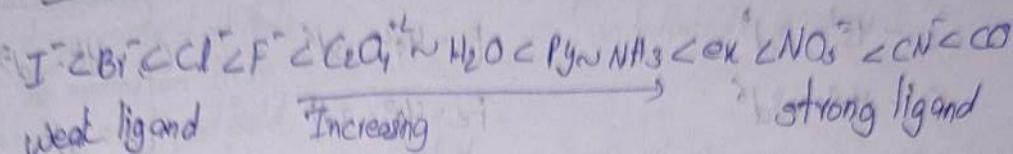
3) Stronger and weaker ligand:

stronger ligand splitting energy more therefore, the value of Δ_o is high. For weaker ligand pairing will be less therefore, the value of Δ_o is less.

a. Spectrochemical series

The common ligands arranged in the order of increasing splitting power because of orbital splitting. This series is called spectrochemical series.

- ligand in which donor atom can halogens, oxygen, sulphato - weak ligands
Ex: F^- , Cl^- , Br^- , I^- , H_2O , OH^- , SCN^- , $C_6O_4^{4-}$
- C/N/P, Ex: CN^- , NC^- , CO , NH_3 , PPh_3 . - strong ligand.



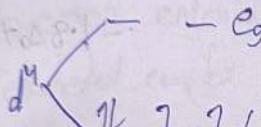
Calculation of CFSE for octahedral complex:

strong field

$$\Delta_{eg} = 0.4$$

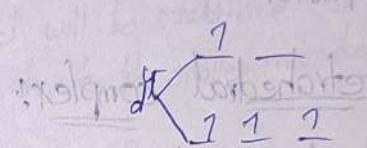
weak field

$$\Delta_{eg} = +0.6$$



$$1L \quad 1L \quad 1L$$

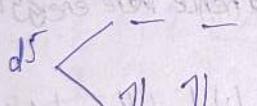
$$4 \times -0.4 = -1.6 \Delta_o + 1P$$



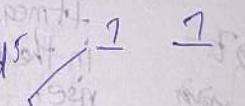
$$1 \quad 1 \quad 1$$

$$3 \times -0.4 = -1.2$$

$$-1.2 + 0.6 \Delta_o = -0.6 \Delta_o$$



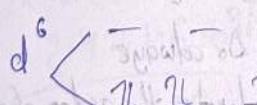
$$5 \times -0.4 = -2.0 \Delta_o + 2P$$



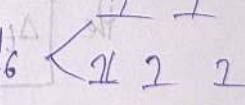
$$1 \quad 1 \quad 1$$

$$3 \times -0.4 + 2 \times 0.6 = 0.4$$

$$= -1.2 + 1.2 = 0.4$$



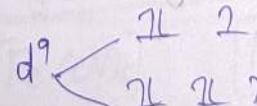
$$6 \times -0.4 = -2.4 \Delta_o + 3P$$



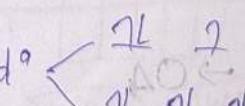
$$1 \quad 1 \quad 1$$

$$4 \times -0.4 + 2 \times 0.6 = 0.4$$

$$= -1.6 + 1.2 = -0.4 \Delta_o + 1P$$

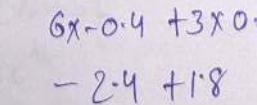


$$6 \times -0.4 + 3 \times 0.6 = -2.4 + 1.8 = -0.6 \Delta_o + 4P$$

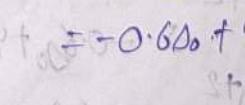


$$1 \quad 1 \quad 1$$

$$-0.6 \Delta_o + 4P = -0.6 \Delta_o + 4P$$

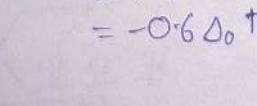


$$6 \times -0.4 + 2 \times 0.6 = -2.4 + 1.2 = -0.6 \Delta_o + 2P$$



$$1 \quad 1 \quad 1$$

$$-0.6 \Delta_o + 2P = -0.6 \Delta_o + 2P$$



$$6 \times -0.4 + 1 \times 0.6 = -2.4 + 0.6 = -1.8 \Delta_o + 1P$$



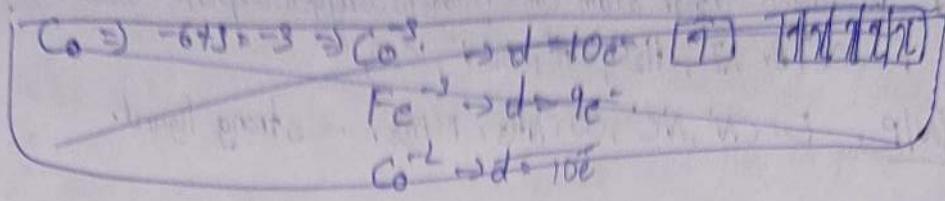
$$1 \quad 1 \quad 1$$

$$-1.8 \Delta_o + 1P = -1.8 \Delta_o + 1P$$

calculate the CFSC of octahedral complex

$$\begin{array}{l} \kappa = -4 \\ \kappa = +2 \end{array}$$

calculate the CFSC $[\text{Co}(\text{CN})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{+3}$ $[\text{Cr}(\text{Cl})_6]^{+2}$



$$\text{Co} = 4s^2 + 3d^1$$

$$\text{Co}^{+3} = 4s^0 + 3d^6$$

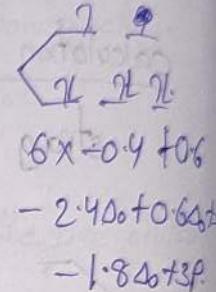
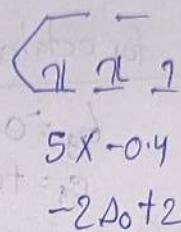
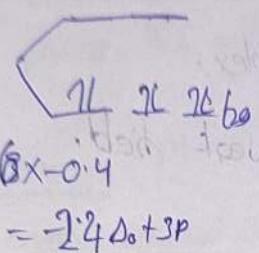
$$\text{Fe} = 4s^2 + 3d^6$$

$$\text{Fe} = 4s^0 + 3d^5$$

$$\text{Co} = 4s^2 + 3d^9$$

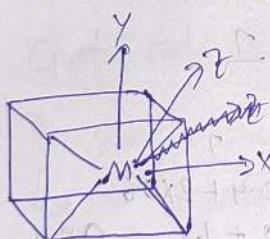
$$\text{Co} = 3d^7$$

\rightarrow



CFT in tetrahedral complex:

The co-ordination number of tetrahedral complex is 4. and 4 ligands are arranged the around central metal atom has a bisection of corners of cube. These 4 ligands lie in b/w the 3-axis, x, y, z-axis.



If means the $3d_{tz}$ orbital of the metal ion will be in the direction of ligand and hence there energy will be rise.

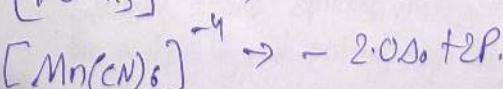
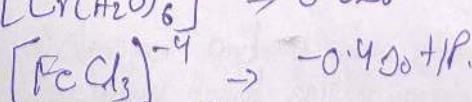
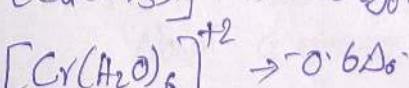
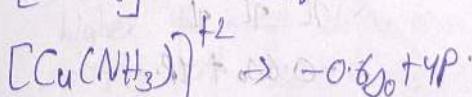
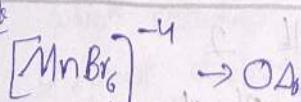
on the other hand the easy orbital of the metal will be pointing away from ligand that p there energy will be lower.

CFS in this case is denoted by Δ_t and it is estimated the $\Delta_t = -\frac{4}{9}\Delta_o$ $\Delta_t < \Delta_o$ always

sign denotes the order of splitting
is just reverse to octahedral complex.

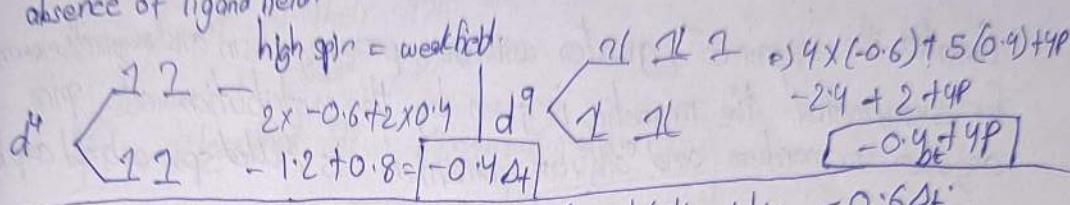
The reason for smaller value of Δ_t due to less no of ligands.

work

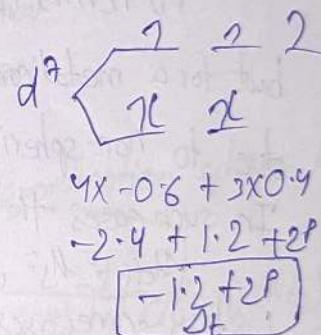
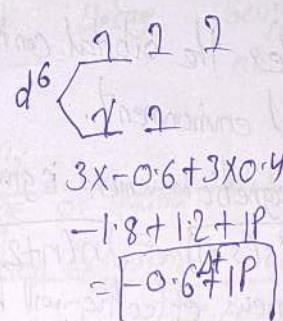
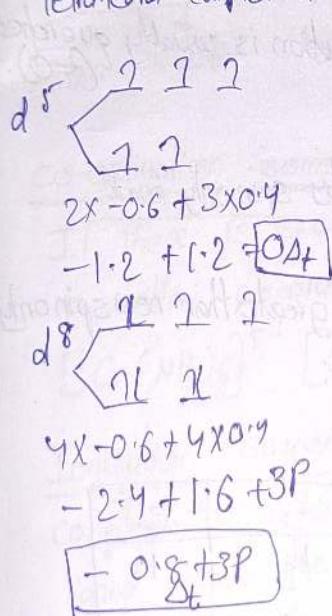


hypothetical degeneracy when all the ligand approach to metal ion in hcp

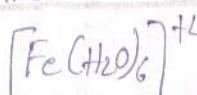
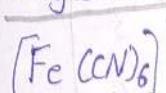
o o o o
5 degenerate d orbitals
of the metal ion in the
absence of ligand field.



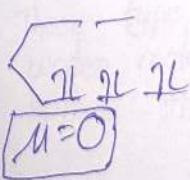
An electron entering in t_{2g} level will be stabilised by $-0.6\Delta t$.
 An electron entering in e_g level will be stabilised by $+0.4\Delta t$.
 Tetrahedral complex has high spin due to the smaller magnitude of $\Delta_t < \Delta$.



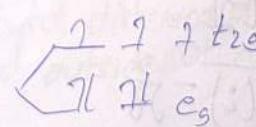
Magnetic Properties of transition elements:



C.N.-S.L



low spin Fe²⁺
 high spin Co²⁺
 high spin d⁶.



11 n=3

$$n = \sqrt{3(5)} = \sqrt{15} \approx 4$$

The E.C for 3D Transition elements : $4s^2 3d^{1-10}$

In transition metal, the e⁻ are filled in d-orbitals, hence these e⁻ decide the geometry and magnetic property of transition metal. These magnetic property greatly change when it's present in free state and in the ionic state.

Let us consider the 3D transition series:
 Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc.

Greater the unpaired e⁻, greater will be paramagnetism and magnetic moment for every metal. The magnetic is given by the contribution of spin angular momentum and orbital angular momentum is called spin-orbital coupling.

$$M_{eff} = \mu_s + \mu_l$$

$$= \sqrt{4s(s+1)} + \sqrt{l(l+1)}$$

$$= \sqrt{n(n+2)} + \sqrt{l(l+2)}$$

s = spin quantum.

l = orbital quantum.

n = no. of unpaired e⁻.

but for a metal complex, the orbital contribution is usually quenched (≈ 0). due to non-spherical environment.

In such cases the magnetic moment is given by spin only formula

$$M_{eff} = \mu_s = \sqrt{4s(s+1)} = \sqrt{n(n+2)}$$

but in some cases new effective will be greater than new spin only value this is due to orbital contribution.

Ex: low spin Fe⁺³, high spin Fe⁺², Co⁺²

high spin Fe ⁺²	high spin Co ⁺²	high spin Ni ⁺²
$\begin{array}{c} 7 \\ \\ 1 \\ \\ 0 \\ \\ 2 \end{array}$	$\begin{array}{c} 7 \\ \\ 1 \\ \\ 2 \\ \\ 0 \end{array}$	$\begin{array}{c} 7 \\ \\ 1 \\ \\ 2 \\ \\ 0 \end{array}$

Find magnetic moment for Ni⁺² comp.

$$\begin{array}{c} 7 \\ | \\ 1 \\ | \\ 2 \\ | \\ 2 \end{array}$$

$$\approx \sqrt{4(2)} = 5.8$$

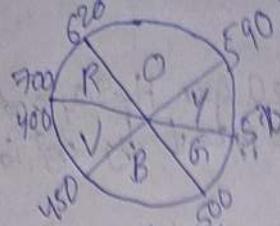
$5s$	$4p$
$\frac{1}{2}$	10
1	2
$\frac{3}{2}$	-3
2	4

↑ 57 sigma bond
 ↑ 60 sigma bond
 ↓ 60 sigma bond

JF JF JF
 O=N

optical properties of transition elements

Colour wheel



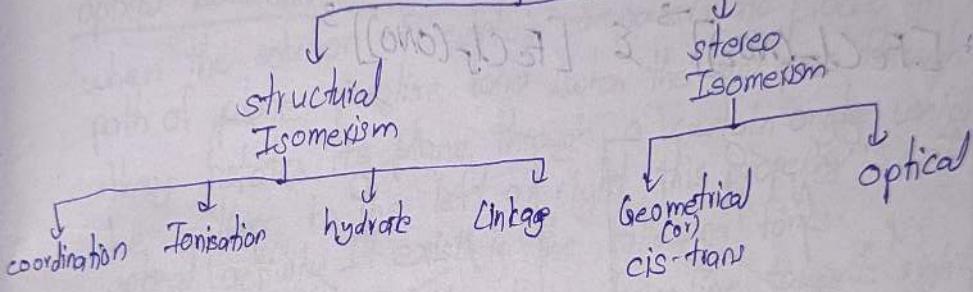
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Explaining the diagram

Isomerism

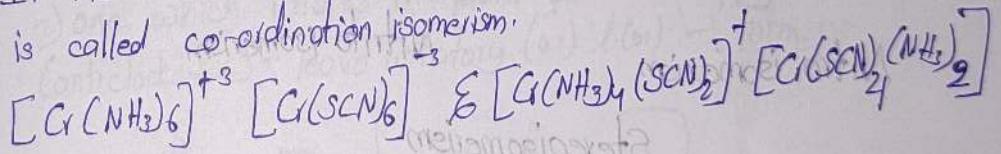
The compound having same molecular formula but with diff structural arrangement of their atom are known as Isomers and the phenomena is called Isomerism.

If it is classified as Isomerism



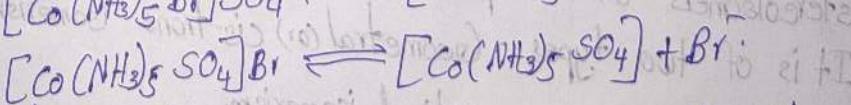
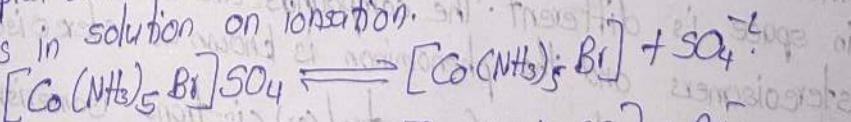
co-ordination isomerism:

If there is exchange of ligand b/w co-ordination sphere is called co-ordination isomerism.



Ionisation isomerism:-

Complexes in which there is an interchange the position of ligand inside the co-ord. sphere and the anion outside the complex zone are called Ionisation isomers. They give different ions in solution on ionisation.



Hydrate isomerism:-

These type of isomerism arises out of different disposition of water molecule on inside and outside of co-ordination sphere. $[\text{Cr}(\text{H}_2\text{O})_6]^{\text{Cl}_6}$ - violet

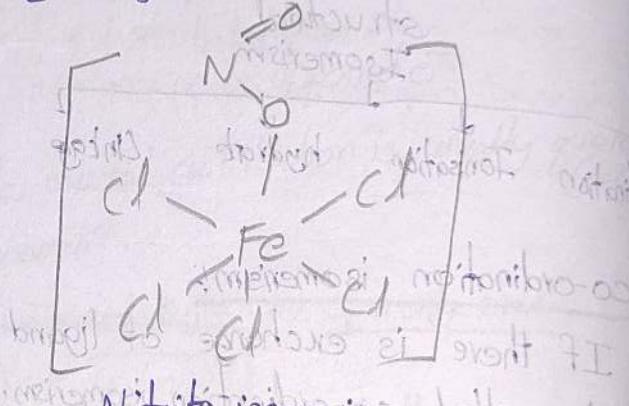
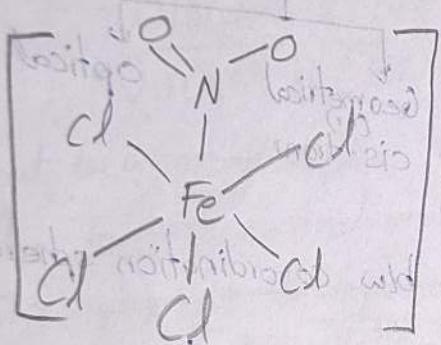
Ex: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ - violet - does not lose water molecules on H_2SO_4 , Ag^+ ions will be pptd by Ag^+

$[\text{Cr}(\text{H}_2\text{O})_5]\text{Cl}\cdot\text{H}_2\text{O}$ - light green - loses H_2O over H_2SO_4 , and ions are pptd by Ag^+ ions.

Linkage isomerism

These are the co-ord. comp. that have the same composition but differ the connectivity of the ligand to the metal.

Ex: $[\text{FeCl}_5(\text{NO}_2)]^{-3} \not\equiv [\text{FeCl}_5(\text{ONO})]^{-3}$.



Stereoisomerism

Geometrical isomerism:

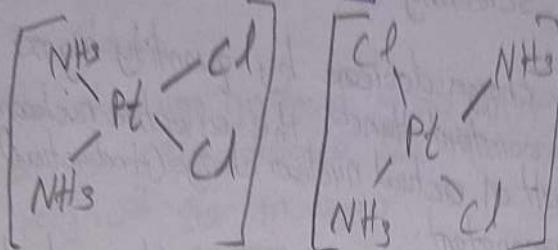
The two comp. contains the same ligand coordinate to the same central ion but the arrangement of ligand in space is different. The compounds are said to be stereoisomers and the phenomenon is known as stereoisomerism. It is of two types: Geometrical (or) cis-trans isomerism.

optical isomerism:

Geometrical isomerism :-

In the isomerism the ligand occupied diff position around the central metal ion if the two identical ligands occupied adjacent position isomer is cis, and if the two identical ligands occupied opposite position, isomer is trans.

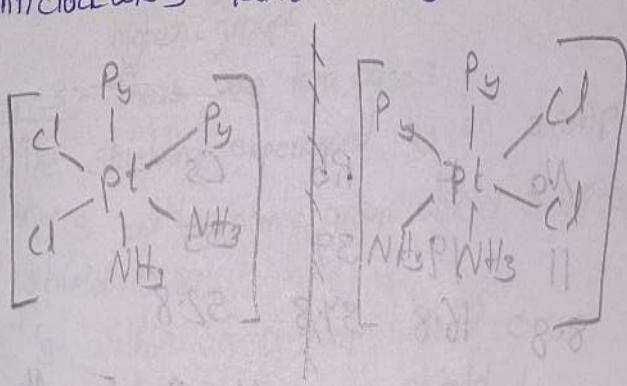
Ex: $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ - sq. planar complex.



optical isomerism:-

when the solution of certain compounds are placed in the path of plane polarise land (when the light pass through prism) they rotates its plane through a certain angle which may be either to the left or right this property is called optical activity. It exists in the following forms.

- 1) one which rotates the plane polarise line towards right (Clock wise) - dextro rotatory (or) d (or) + form.
- 2) one which rotates the plane polarise light towards left. (Anticlock wise) - leavo rotatory (or) l (or) - form.



In electrons residing in the shell b/w the nucleus and the valence shell are called Intervening electrons. These e^- reduce the force of attraction b/w the nucleus and outermost e^- shell. The reduction in the force of attraction b/w to the presence of intervening e^- is called screening effect.

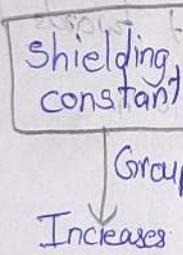
Hence the actual nuclear charge decrease by quantity sigma which is called screening constant. Hence the effective nuclear charge (Z_{eff}) is the result of actual nuclear charge (it is actual) minus sigma the screening constant.

σ = screening (or) shielding constant.

$Z_{\text{eff}} = Z_{\text{actual}} - \sigma$

Variation of σ in periodic table:

since sigma goes from top to bottom to in a group and also proceeding from left to right in a periodic table. The magnitude of screening effect also increases.



Group	Li	Na	F	Rb	Cs
Z	3	11	19	37	55
σ	1.7	8.8	16.8	34.8	52.8

Period	Li	Be	B	C	N	O	F	Ne
2	3	4	5	6	7	8	9	10
σ	1.7	2.05	2.4	2.75	3.1	3.45	3.8	4.15

Variation of Z_{eff} in Periodic table.

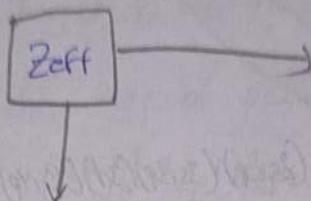
In period,

The value of Z_{eff} increases when we proceeds from left to right in period.

Reason: The e⁻ are added one by one in period and those e⁻ enters into the same shell which cause the inward pull by the nucleus which has the strong force of attraction.

In Group,

When we go down in the group the value of Z_{eff} almost same because the distance b/w the nucleus and the outermost e⁻ increases along with ρ_{σ} in sigma.

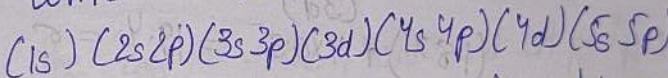


Slater's Rule:

The value of σ and is that Z_{eff} can be calculated by using slater's rule.

It is as follows

Step-1: write the EC of the atom in the following form.



Step-2: identify other e⁻ of interest and ignore all e⁻ in higher groups

Step-3: There are two cases

1) The shielding experienced by an s or p e⁻.

* e⁻s within name group shield 0.35 except the is which shield 0.30.

* e⁻s within (n-1) group shield 0.85

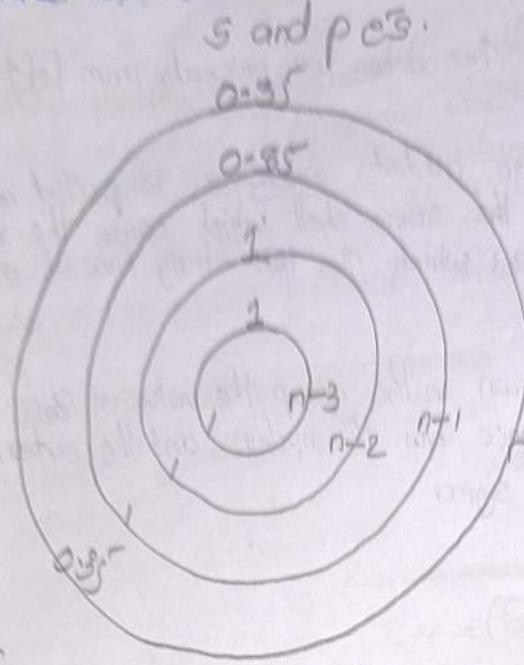
* e⁻s within (n-2) group shield 1.

The shielding experienced by nd (or) nf e⁻s

* e⁻s within same group shield 0.35.

* e⁻s within the lower group shield 1.

These rules are summarized in the figure.



d and f cs.

order: (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f)

→ calculate the Z_{eff}

Cr - At-24.

$$E:C = (1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^5)(4s^1)$$

(3d¹)

$$(18 \times 1) + 4 \times 0.35 = 19.4 = 6$$

$$Z_{\text{eff}} = 2 - 6$$

$$= 24 - 19.4 = 4.6$$

$$\boxed{Z_{\text{eff}} = 4.6}$$

Problems

1) what is the eff nuclear charge held by 1s of helium.

He - At-2

$$E:C = 1s^2$$

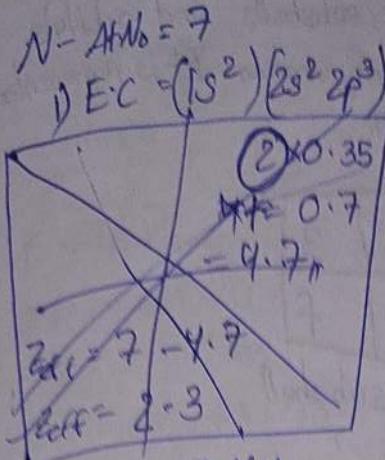
$$1s^1$$

$$Z_{\text{eff}} = Z - 6$$

$$= 2 - 1 \times 0.30 = 1.7$$



2) what is the Z_{eff} by $2p^5$ of N atom? what is Z_{eff} held by its $1s$ electron?



$$= (1s^2) (2s^2 2p^3)$$

$$(1s^2) (2s^2 2p^2)$$

$$2 \times 0.85 + 4 \times 0.35$$

$$\sigma = 3.1$$

$$Z_{\text{eff}} = 7 - 3.1 = 3.9$$

peri-peri means add $1e^-$
no change in At. No.
Add in last orbital.

$$2) N - 7 \text{ At. No}$$

$$Z_{\text{eff}} = 7 - 0.30 = 6.7;$$

3) calculate the Z_{eff} of peri-peri of Cr atom?

$$Cr = 24 \cdot \text{At. No} = (1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^5) (4s^2)$$

$$= (1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^5) (4s^1)$$

$$= (10 \times 1) (8 \times 0.85) (5 \times 0.85) (1 \times 0.35)$$

$$= 21.4$$

$$Z_{\text{eff}} = 24 - 21.4 = 2.6$$

$$\begin{array}{r} 8 \cdot 0.85 \\ 21 \cdot 15 \\ \hline 7 \cdot 85 \end{array}$$

$$\begin{array}{r} 10 \\ 19 \\ \hline 3.15 \end{array}$$

* 4) Calculate the Z_{eff} for $3dc^5$, $4se^-$ and at peri-peri of copper atom

29

$$) E.C = (1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^{10}) (4s^1)$$

$$(1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^9)$$

$$(18 \times 1) (9 \times 0.35) = 18 + 3.15 = 21.15$$

$$Z_{\text{eff}} = 29 - 21.15 = 7.85$$

$$2) E.C = (1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^{10}) (4s^1)$$

$$10 \times 1 + (18 \times 0.85) = 10 + 15.3 = 25.3$$

$$Z_{\text{eff}} = 29 - 25.3 = 3.7$$

$$3) E.C = (1s^2) (2s^2 2p^6) (3s^2 3p^6) (3d^{10}) (4s^2)$$

$$10 + 18 \times 0.85 + (2 \times 0.35) = 25.3 + 0.35 = 25.65$$

$$Z_{\text{eff}} = 29 - 25.65 = 3.35$$

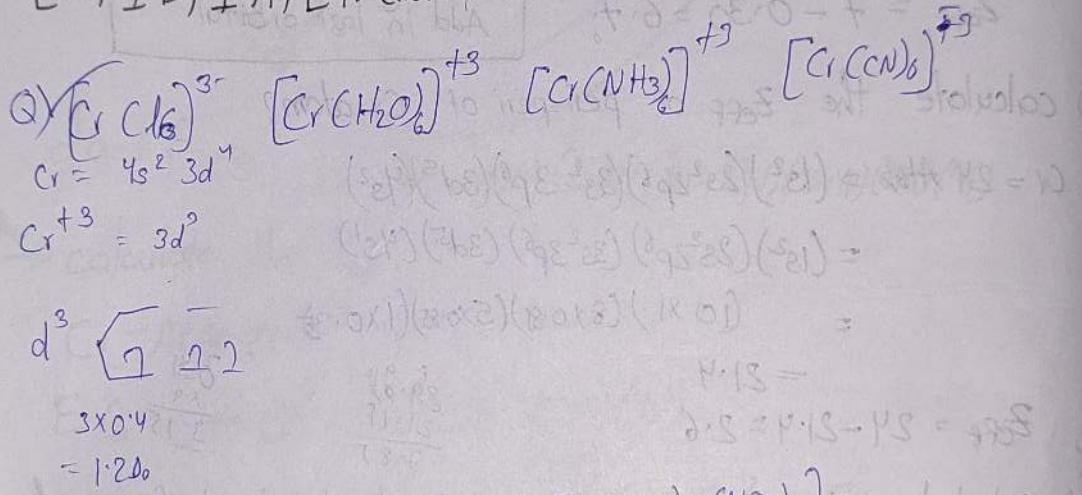
Electronic Configuration:-

The distribution of e^- in various shells, subshells and orbitals of an atom is called electronic configuration. It is represented as n^l^k . l indicates the subshell.

Value of l	0	1	2	3
subshell ℓ	s	p	d	f

x represent no. of e^- present in subshell.

E.C., I.E., F.A., E.N. (Note refer the copy).



How many geometrical isomers formed for $[Co(NH_3)_3(NO_2)_3]$.

②

$$d^5 \begin{pmatrix} 1 & 1 & - \\ 1 & 1 & e_g \end{pmatrix} \quad d^3 \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & e_g \end{pmatrix}$$

$$2 \times -0.6 + 2 \times 0.4$$

$$-1.2 + 0.8$$

$$= -0.4 \Delta_f$$

$$4 \times -0.6 + 3 \times 0.4 + 2P.$$

$$-2.4 + 1.2 + 2P$$

$$-1.2 \Delta_f + 2P$$

$$\Delta_O = 3.6$$

$$d^5 \begin{pmatrix} 1 & - \\ 1 & 2 & 1 \end{pmatrix}$$

$$3 \times -0.4 + 0.6$$

$$-1.2 + 0.6$$

$$= -0.6 \quad \Delta_f = \frac{-4}{9} \times -0.6 = \frac{2.4}{9} - 0.28$$

$$[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$$

$\frac{1}{\nu} = 20000 \text{ cm}^{-1}$

$$E = h\nu = \frac{hc}{\lambda}$$

$$\lambda \propto \frac{1}{\nu}$$

$$\frac{3p^6}{(1s^2)(2s^2 2p^6)(3s^2 3p^6)} = 10 + 2 \times 0.85 = 11.7$$

$$13 - 11.7 = 1.3$$

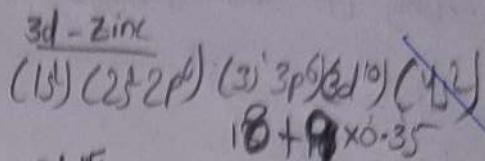
$$E = hc\nu$$

$$h = 6.634 \times 10^{-34}$$

$$c = 3 \times 10^{10} \text{ cm/s}$$

$$= 6 \times 6.634 \times 10^{-20}$$

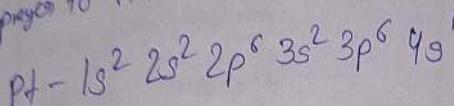
$$= 3.98 \times 10^{-19} \text{ J.}$$



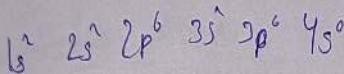
$$30 - 21.5 = 8.85$$

$$= 21.5$$

using slater's rule explain the filling of $4s$ orbital
prior to filling of $3d$ orbital in case of Potassium (1)

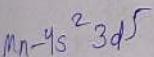


$$Z_{\text{eff}} = 19 - 16.8 = 2.2$$



$$10 \times 1 + 8 \times 0.85 = 10 + 6.8 = 16.8$$

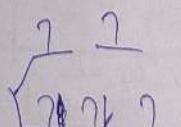
$$1s^2 (2s^2 2p^6) (3s^2 3p^6) 3d^10 Z_{\text{eff}} = 19 - 18 = 1$$



$$S.F. = \langle \overline{\ell} \overline{\ell} \overline{\ell} \overline{\ell} \overline{\ell} \rangle$$

$\Rightarrow 1$ unpaired e^-
determined CFSC and magnetic moment. of d^7 octahedral complex
having $\Delta_0 = 1300 \text{ cm}^{-1}$ & $P = 21000 \text{ cm}^{-1}$.

$\Delta_0 \subset P$ weak field.



$$= 5 \times -0.4 + 2 \times 0.6$$

$$\frac{4 \times 2000}{-1040}$$

$$= -2 + 1.2$$

$$\frac{-}{40960}$$

$$= -0.840 + 2P$$

$$= (-0.8)(1300) + 2(21000)$$

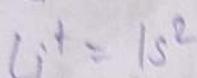
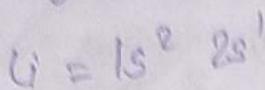
$$= -1040.0 + 42000$$

$$= 40960.0 - 40960$$

Calculate the wavelength of light observed by oct complex with wave number
 17830 cm^{-1} . (in nm).

$$\lambda = \frac{1}{17830 \times 10^8} = 5609 \text{ Å} \\ = 560.9 \text{ nm.}$$

→ why Li^+ atom is bigger in Li^+ .



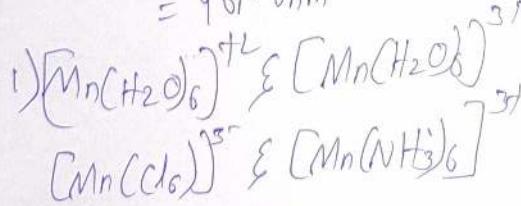
$Li \rightarrow Li^+$ because it has more orbital.

$$\begin{array}{ll} 1s^2 2s^0 & 1s^2 \\ 2 \times 0.85 & 1s^1 \\ = 1.9 & = 0.3 \\ 3 - 1.9 = 1.1 & 3 - 0.3 = 2.7 \end{array}$$

→ Energy gap b/w t_{2g} and e_g of an octahedral complex 259 kJ/mol , find the wavelength observed complex ($1 \text{ kJ/mol} = 83.6 \text{ cm}^{-1}$). find the colour of sample based on for d-d transition and predict the colour of sample based on its complimentary colour.

$$\Delta E = 259 \text{ kJ} = 259 \times 83.6 \text{ cm}^{-1} \\ = 21652.4 \text{ cm}^{-1} \text{ (wave number)}$$

$$\underbrace{\text{wavelength}}_{\lambda} = \frac{1}{21652} \times 10^8 = 4618 \text{ Å} \\ = 461.8 \text{ nm.}$$



Fe¹² ma large CFSC.
SE (low spin)

$$\begin{cases} 1L & 1L & 1L \\ 6 \times 0.4 \Rightarrow -2.4 & 3P \end{cases}$$

$$M = \sqrt{4(6)} = \sqrt{24} \text{ a.u.}$$

$$-1.6 + 1.2 \\ -0.4 \Delta_0 + IP$$

HSAB Concept

It is a qualitative concept introduced by Pearson to explain the stability of metal complex and mechanism of their reactions.

According to this theory Lewis A or B divided into Hard or soft acid and bases.

Hard acid	Soft Acid.
small size. highly (+) charge, low polarizability low electronegativity low electron affinity Ex: H^+ , Li^+ , K^+ , Ca^{+2} , Al^{+3} BF_3 , $AlCl_3$, CO_2 , SO_3 etc.	large ionic radii; low (+) charge high polarizability, filled atomic orbitals Ex: Cu^+ , Ag^+ , Hg^+ , Pt^{+2} , BH_3 , Br_2 , I_2

Hard base	Soft base
small ionic radii high electronegativity low polarizability no easily oxidised Ex: F^- , OH^- , NH_3 , H_2O , $SO_4^{=2-}$, $PO_4^{=3-}$.	large ionic radii; high polarizability low electronegativity easily oxidised Ex: H^- , R^- , Cl^- , SCN^- , $C_6H_5^-$, RNC^- .

Principle:

According to this concept hard acids prefer binding to hard bases to give ionic complexes. soft acids prefer binding to soft bases to give covalent complexes.

The large EN⁻ differences b/w hard acid and base to strong ionic interaction.

The EN⁻ difference of SA and SB are almost same
and hence have less ionic interaction.
The interaction b/w them more covalent.
The interaction b/w HA-SB, SA-HB are less stable.

Wt% H₂O
fiber sinol g/mol
sgdts (H) w/o

Wt% sinol b/w sinol w/o
E.C. 0.8, 0.8, 0.9, 0.9, 0.9, 0.9

b/w b/w
wt% wt%
sgdts (H) efft

Wt% sinol w/o
Wt% sinol w/o
Wt% sinol w/o
efft. 0.8, 0.9, 0.9, 0.9
0.8, 0.9, 0.9, 0.9

seed H₂O

fiber sinol g/mol
Wt% sinol w/o
Wt% sinol w/o
Wt% sinol w/o
efft. 0.8, 0.9, 0.9, 0.9
0.8, 0.9

seed b/w

fiber sinol wt%
Wt% sinol w/o
Wt% sinol w/o
Wt% sinol w/o
efft. 0.8, 0.9, 0.9, 0.9
0.8, 0.9, 0.9, 0.9

sgdts

Wt% of protein + Wt% of seed b/w + Wt% of protein
Wt% of protein + Wt% of seed b/w + Wt% of protein
.
seed b/w b/w b/w w/o
efft. 0.8, 0.9, 0.9, 0.9
0.8, 0.9, 0.9, 0.9

Unit-2

Thermodynamics:

It simply means the flow of heat. It deals with relation b/w heat and work.

System:

It is a part of universe under study
surrounding:

The remaining part of universe which is separated from the system by definite boundary

Types of system:

based on the boundary system divided into 3 types,

Isolated - there is no exchange of energy and matter with surrounding. [thermos flask]

Closed system - exchange of energy not matter [softdrinks]

Open system - there is exchange of both energy and matter with surrounding. [coffee].

Properties of a system:

Intensive property - which depend the amount of substance but nature of the substance.

Ex: temp, pressure, concentration, viscosity, density

Extensive property - which depend the amount of substance present in the system.

Ex: mass, entropy, enthalpy, internal energy etc.

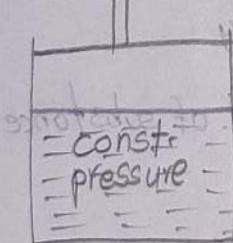
Internal Energy (E) or (U) :

- It is the total energy content of the system. It is the PE of molecules due to their mutual attraction and KE of molecules due to their motion.
- It is the Extensive property and state function.
Extensive - depends on amount of substance
- State - if it is defined only initial and final only.

Internal energy is characteristic property of system. absolute value cannot be determined. The change in IE is used.

Expression of I.E.

consider the expansion of a gas in closed system at constant pressure. Suppose the heat supplied to system is q . A part of this q may be used by the system itself to increase internal energy and rest of heat used for doing external work. $q = \Delta E + w$ — (1)



Since the expansion of gas carried at const pressure the workdone by the system $w = P\Delta V$

Substituting value of w in (1)

$$= q = \Delta E + P\Delta V$$

$$\Delta E = q - P\Delta V$$

Enthalpy (H):

It is the heat content of system. It is of different type.

Enthalpy of Combustion:

The change in heat content when one mole of the substance is completely burned in excess of oxygen.

Enthalpy of formation:

The change in heat content when one mole of product is formed from its reactant. Mathematically defined as

$$H = E + PV$$

It is also state function or extensive property.

Like IE, the absolute value of 'H' cannot be determined hence change in enthalpy ΔH is used.

From 1st law of thermodynamics

$$\Delta H = q$$

$$q = \Delta E + PV$$

$$= (E_2 - E_1) + P(V_2 - V_1)$$

$$q = H_2 - H_1 = \Delta H$$

The change in enthalpy ΔH is equal to quantity of heat change (q accompanying the process at const. pressure).

Entropy:

→ It is the quantity that tells whether a chemical reaction or a physical change can occur spontaneously in an isolated system or not.

→ It is defined as the thermal property of the substance which remains constant during an adiabatic cycle change. It is expressed in J/kelvin. Usually the change in entropy of the system is huge. for determining the change of state

$$\left(\frac{sT - sT}{sT}\right) \Delta T = (s_{\text{tot}}) \Delta T$$

$$s_{\text{tot}} = sT - T \text{ const. b/w } sT < T \text{ and } s_{\text{tot}} > 0 \text{ i.e. } s_{\text{tot}} = s_{\text{tot}}^2 \Delta T$$

Change in entropy of a system is defined as the integral of all the terms involving heat absorbed (q) divided by the 'Kelvin' temperature (T).

During each small change of the process carried out reversible,

$$\Delta S_{(\text{total})} + \Delta S_{(\text{sys})} + \Delta S_{(\text{surr})} = 0 \text{ for a reversible process}$$

$$\Delta S_{(\text{total})} + \Delta S_{(\text{sys})} + \Delta S_{(\text{surr})} > 0 \text{ for a irreversible process.}$$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

It is a state function, it is determined by initial and final states and not on the path taken by the system.

It is an extensive because the value depends on amount of substance involved.

Entropy change in reversible process:

Consider an isothermal reversible expansion of an ideal gas at temp 'T' during the expansion let q be the amount of heat absorbed by the system from the surroundings.

\therefore The change in entropy of the system $\Delta S = \frac{+q}{T}$

at the same time also loss the same amount of heat ' q ' at same 'T'.

This results in decrease in surr entropy, $\Delta S = -\frac{q}{T}$.

$$\Delta S_{\text{Total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{+q}{T} - \frac{-q}{T} = 0.$$

$\Delta S = 0$ (for a reversible process).

Entropy change in irreversible.

Let the system be at high Temp T_1 and its surr at low Temp T_2 .

q is the quantity of heat passes irreversible from the system to surr.

Decrease in entropy of the system $\Delta S_{\text{sys}} = -\frac{q}{T_1}$

Increase in entropy of the surr $\Delta S_{\text{surr}} = \frac{+q}{T_2}$.

$$\Delta S_{(\text{tot})} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -\frac{q}{T_1} + \frac{q}{T_2} = q \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta S_{(\text{total})} = q \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

but $T_1 > T_2$ and Hence $T_1 - T_2 = +ve$

$\therefore \Delta S_{\text{total}} = +ve \text{ or } > 0 \text{ for an irreversible process}$

Gibb's Free Energy:-

free energy of a system is thermodynamic state function which is related to enthalpy and entropy. $G = H - TS$

free energy change (ΔG) of a system or a reaction is "The measure of energy available for doing useful work".

Energy available for useful work = Total energy - Non-available form of energy.

$$G = H - TS \Rightarrow \Delta G = \Delta G_2 - G_1 = (H_2 - T_2 S_2) - (H_1 - T_1 S_1)$$

$$\Delta G = \Delta H - (T_2 S_2 - T_1 S_1)$$

at const temp, $\boxed{\Delta G = \Delta H - T \Delta S}$

$$\Delta H = \Delta E + P\Delta V.$$

$$\therefore \boxed{\Delta G = \Delta E + P\Delta V - T\Delta S}$$

Helmholtz free Energy (A):

It is also known as "A part of internal energy of a system to do some useful work at const temp. This part of internal energy (E) which is isothermally available is called work function (A) of the system. It is mathematically defined as

$$A = E - TS$$

for a small change in a reversible sys at const temp

$$\Delta A = \Delta E - T\Delta S \quad \text{--- (1)}$$

$$W \cdot K^{-1} \Delta S = \frac{q_{rev}}{T} \quad \text{--- (2)} \quad T\Delta S = q_{rev} \quad \text{--- (3)}$$

from (1) & (2)

$$\Delta A = \Delta E - q_{rev} \quad \text{--- (3)}$$

According to 1st law of thermodynamics,

$$\Delta E = q - w \quad \text{--- (4)} \quad \Delta E - q = w \quad \text{--- (5)}$$

from (3) & (5) $\Rightarrow \boxed{\Delta A = -w_{max}}$

$$\left(\frac{\partial \Delta}{\partial T} \right)_S + H = -w_{max}$$

using this we can calculate standard free energy of formation.

Gibbs - Helmholtz Equation:

W.R.T

$$G = H - TS$$

$$H = E + PV$$

$$G = E + PV - TS$$

upon differentiation

$$dG = dE + PdV - TdS - SdT \quad \text{--- (1)}$$

$$dE = d\varrho - PdV \quad (\text{1st law})$$

$$d\varrho = TdS \quad (\text{2nd law})$$

$$dE = TdS - PdV \quad \text{--- (2)}$$

From (1) & (2)

$$dG = TdS - PdV - TdS - SdT + PdV + TdP$$

$$dG = VdP - SdT \quad \text{--- (3)}$$

at const pressure, $dG = SdT$

for any two states of system $dG_2 = S_2 dT$

$$dG_1 = S_1 dT$$

$$dG_2 - dG_1 = (S_2 - S_1) dT$$

$$\Delta G = -(S_2 - S_1) dT = -(DS) dT$$

$$\frac{\Delta G}{dT} = -DS$$

definition of

According to free energy, $\Delta G = \Delta H - T\Delta S$

$$\frac{\Delta G - \Delta H}{T} = -DS$$

$$\frac{\Delta G - \Delta H}{T} = \frac{d\Delta G}{dT}$$

or

$$\Delta G = \Delta H + T \left(\frac{d\Delta G}{dT} \right)$$

It is called Gibbs - Helmholtz equation
in terms of free energy and enthalpy changes at const pressure

Application

1) Calculation of enthalpy change of the reaction is Galvanic cell?
If a cell is nF col of electricity in a reversible manner,
it must be equal to decrease in free energy.

$$-\Delta G = nFE^\circ \quad \text{--- (1)}$$

Hence Gibbs-Helmholtz equation written as

$$-nFE^\circ = \Delta H + T \left(\frac{d(-nFE^\circ)}{dT} \right)_P$$

$$-nFE^\circ = \Delta H - nFT \left(\frac{dE^\circ}{dT} \right)_P$$

$$\Delta H = -nFE^\circ + nFT \left(\frac{dE^\circ}{dT} \right)_P$$

$$\Delta H = -nF \left[E^\circ - T \left(\frac{dE^\circ}{dT} \right)_P \right]$$

know the value of E° and Temp coeff of cell reaction, it is
possible to evaluate the enthalpy change of the reaction.

2) Calculation of entropy change,
 ΔH and ΔS are related by the equation, $\Delta G = \Delta H - T\Delta S$.

$$\text{w.r.t } \Delta G = -nFE$$

$$\& \Delta H = -nF \left[E^\circ - T \left(\frac{dE^\circ}{dT} \right)_P \right]$$

Hence, ΔS can be easily calculated.

3) calculation of emf of the cell

$$\Delta H = -nF \left[E^\circ - T \left(\frac{dE^\circ}{dT} \right)_P \right]$$

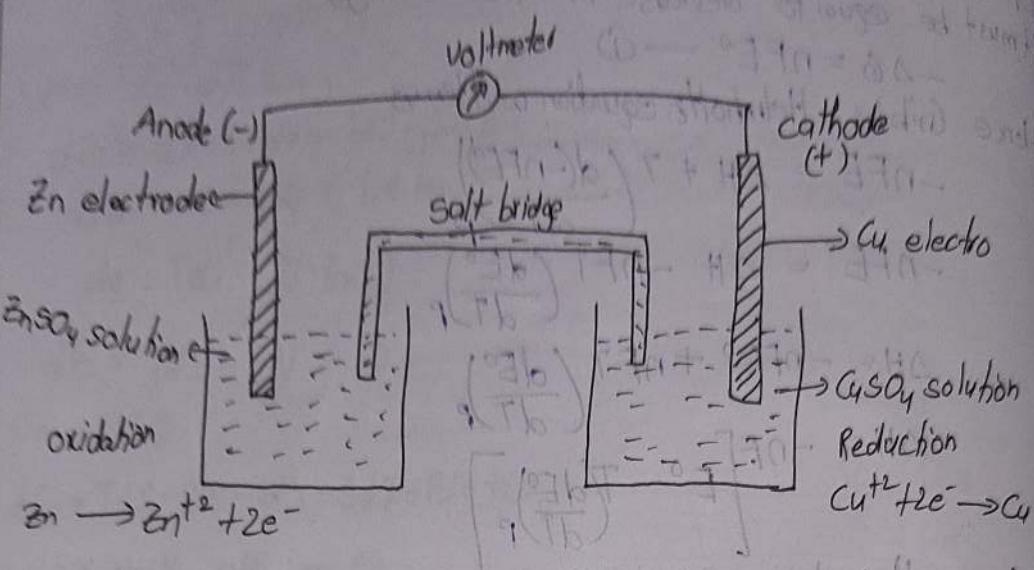
divide above eq by nF

$$\frac{\Delta H}{nF} = - \left[E^\circ - T \left(\frac{dE^\circ}{dT} \right)_P \right]$$

$$E^\circ = -\frac{\Delta H}{nF} + T \left(\frac{dE^\circ}{dT} \right)_P$$

27-9-23

Electrochemical cells



An electrochemical cell is a devise used to convert chemical energy into electrical energy.

It consists of 2 electrodes [Anode, cathode] and an electrolyte.
 In this cell the e^- transferred in the reaction if you thus has
 the force of producing electrical energy.

Galvanic cell:

Galvanic cell:
In a galvanic cell, a zinc rod is partially immersed in 1 molar Zinc sulphate solution and a copper rod is partially immersed 1 molar copper sulphate solution.

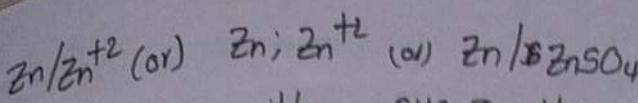
The two solution interconnected by salt bridge
 The saltbridge is an U-Tube containing saturated $KCl(a)$
 NH_4NO_3
 in agar agar jell it provides the electrical contact b/w two compartments each e^- is regarded as a half cell.
 anode 'oxidation occurs'. cathode 'Reduction occurs'.

Cell representation:

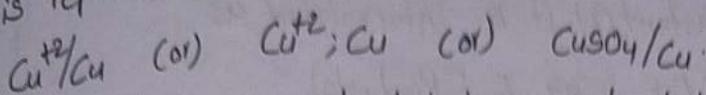
- Cell representation:

 - anode written on LHS while cathode written on RHS.
 - anode is written by writing the metal first and then electrolyte
the two are separated by vertical line

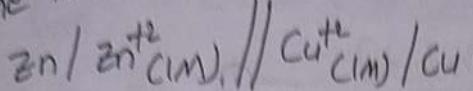
The electrolyte may be represented either as an ion or whole compound including concentration.



3) Cathode is written on RHS. In this case the electrolyte is represented first and then metal.



4) A salt bridge is indicated by 2 vertical lines separating the two half cells.



The practical application of Galvanic cell is called Daniel cell.

Relation b/w cell potential and free energy:

consider the electrochemical cell in which n equivalent of reactions converted into products. The quantity of electricity all flow through the cell is nF , F = Faraday constant

$$F = 96500 \text{ coul/eq}$$

when this amount of electricity transported through the cell of emf E volts then the amount of electrical work done by the cell is nFE . This is at the expense of loss of free energy resulting from the cell reaction.

Decrease in Gibbs free energy \downarrow = electrical work obtainable from the cell

$$-\Delta G = nFE$$

Single electrode potential (SEP)

An electrochemical cell consists of 2 half cells with an open circuit the metal electrode transfers its ion into solution. Thus the individual electrode develops the potential wrt to the solution. The potential of single electrode in a half cell is called SEP.

Volts 2.1
no longer term
Volts single red
potentiometer

$$\textcircled{1} - [M]_{\text{red}} \frac{1820.0}{1820.0 + 1} + E = 3$$

$$\textcircled{2} - [M]_{\text{red}} \frac{1820.0}{1820.0 - 6.7} + E = 3$$

Nernst Equation:-

Consider the following redox reactions. For such a redox reversible reaction, the free energy change and its equilibrium constant (K) it is interrelated as

$$\Delta G = -RT \ln K + RT \ln \frac{[\text{Products}]}{[\text{Reactants}]}$$

(i)

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Products}]}{[\text{Reactants}]} \quad \dots \quad (1)$$

ΔG° is standard free energy change. The above equation is known as one half isotherm.

In the cell if a reaction involves transfer of n e⁻s then F faraday of electricity will flow.

If E is emf of the cell, then the total electrical energy produced in the cell is equal to

$$-nFE$$

$$-nG^\circ = nFE^\circ \quad \dots \quad (2)$$

Substituting eq (2) in (1)

$$-nFE = -nFE^\circ + RT \ln \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^+]} \quad \dots \quad (3)$$

Divide eq (3) by $-nF$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^+]} \quad [\text{If } [M] = 1]$$

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]$$

$$R = 8.314 \text{ J/K/mol} \quad F = 96500 \text{ C/e⁻}$$

$$T = 25^\circ\text{C} (298\text{K})$$

$$E = E_{\text{red}}^\circ + \frac{0.0591}{n} \log [M^{n+}] \quad \dots \quad (4)$$

$$E = E_{\text{ord}}^\circ - \frac{0.0591}{n} \log [M^{n+}] \quad \dots \quad (5)$$

4, 5 are called
nernst equation
for single electric
potential.

Application:

1) The emf of the acid-base reaction is calculated with the help of Nernst Equation

$$E_{\text{cell}} = E_R - E_L$$

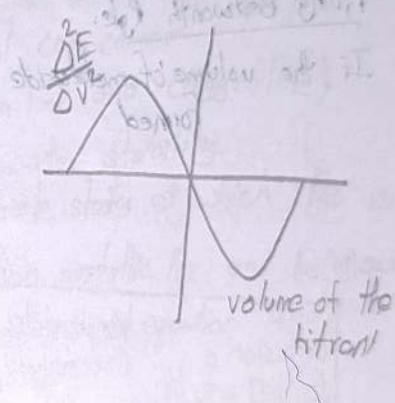
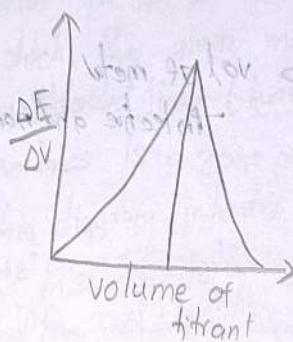
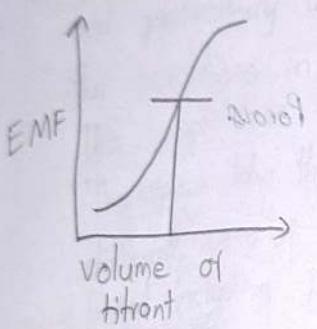
$$\approx 0.2422 - \frac{0.0591}{n} \log [M^{\text{II}}^{+}]$$

$$E_{\text{cell}} \approx 0.2422 + \frac{0.0591}{n} p^{\text{II}}$$

2) Predicting the spontaneity or feasibility of redox reaction
spontaneity of redox reaction can be predict from the emf value of complete cell reaction ($-\Delta G = nFE$)

- 1) If E is positive, ΔG is negative then reaction is feasible.
- 2) If E is negative, ΔG is positive then reaction is not possible.

$$\text{EMF of the cell for redox reaction} = \frac{E_1 + E_2}{2}$$

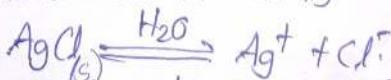


Solubility product (K_{sp}):

It is a type of dynamic equilibrium that exists when a chemical compound in the solid state is in equilibrium with the solution of that compound. It is the point back no more solid can dissolve and the solution becomes saturated. It is expressed by the solubility product constant (K_{sp}). This constant identify the degree of which the compound can disiasiante in water.

for example, The higher the K_{sp} , the more soluble the compound is.

Let us consider the solubility of AgCl



If 1g of AgCl is dissolved in 1lit of water only point 0.001 of AgCl will be disiasiante into ions then K_{sp} .

$$K_{\text{sp}} = \frac{[\text{Ag}^+] [\text{Cl}^-]}{[\text{H}_2\text{O}]}$$

conc of AgCl is not written in as it is a solid.

K equivalent written only for ions. The amount of water is also constant as it is not taking part in the reaction.

$$K_{sp} [H_2O] = [Ag^+][Cl^-]$$

(or)

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

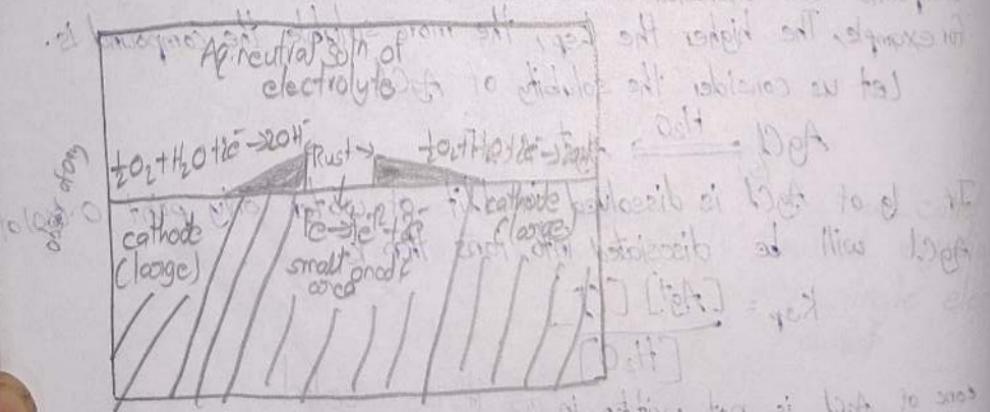
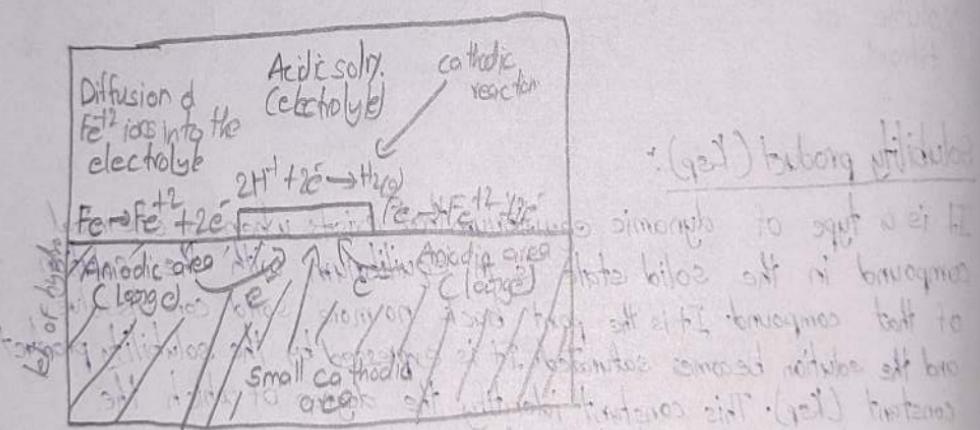
corrosion:

Ques

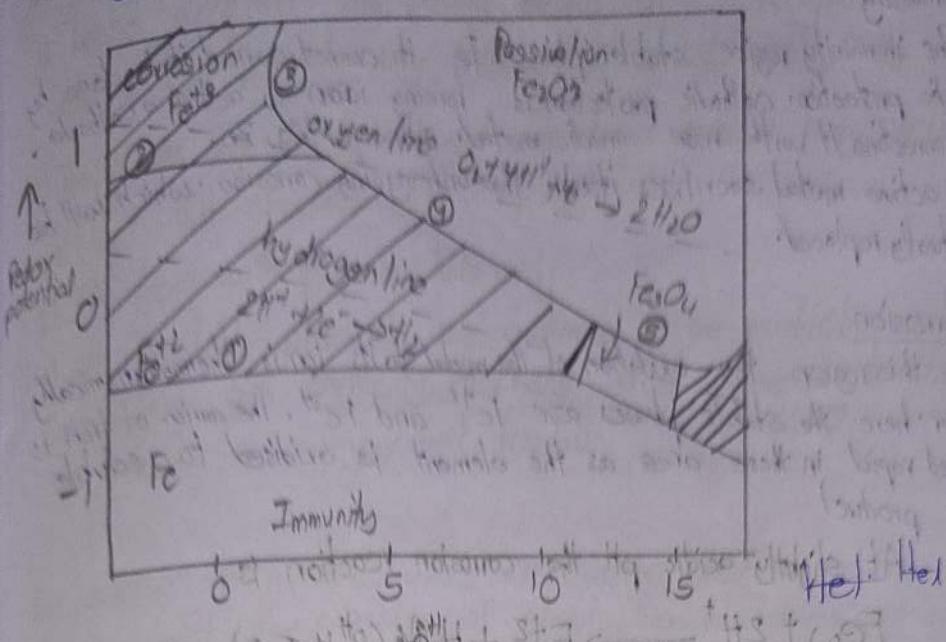
- i) corrosion by oxygen
 - ii) corrosion by other gases
 - iii) liquid metal corrosion
 - iv) Nature of layer
- Stable, unstable Volatile
not stable no control severe corrosion
Porous (having hole)
corrosion will continue.

Pilling Bedworth Rule:

If the volume of metal oxide $>$ vol of metal formed
- protective and non Porous



Pearson Diagram (stability diagram)

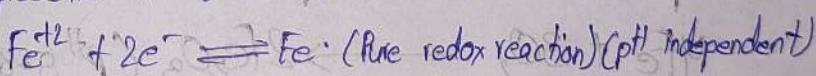


These are the plots of potential vs. pH and particularly useful in corrosion sign as they provide the conditions in which the given metal can corrode.

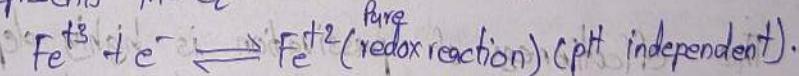
This graph has two dotted lines (Hydrogen line and Oxygen line).

The space b/w these lines is a zone of water stability different area of this diagram indicates stable states at which Fe is formed including Fe^{+2} in solution, Fe^{3+} in solution, metallic Fe and $\text{Fe}(III)$ oxide. This diagram is constructed from calculations based on Nernst equation and solubility data for the metal and its species.

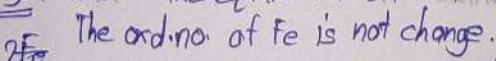
Line 1 : represents the equilibrium b/w Fe and Fe^{+2} .



Line 2 : represents the equilibrium Fe^{3+} and Fe^{+2}

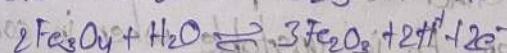
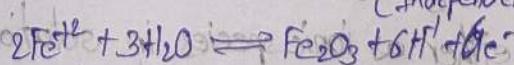


Line 3 : indicate the equilibrium between Fe^{+3} and Fe_2O_3 .



(Independent of potential) (pH is same) (for all potential)

Line 4



are Pure redox reactions in which both protons and e^- are transferred and the corresponding potential is changing with pH.

There are 3 regions in this diagram:

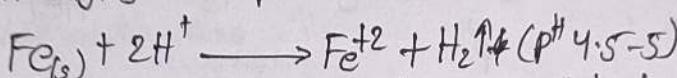
1) Immunity

In the immunity region stable phase in Fe. It cannot corrode, it is done by cathodic protection. Cathodic protection is forcing iron to act as a cathode by connecting it with more anodic metal, such as Mg, Zn. This active metal sacrifices itself that undergoing corrosion which will be eventually replaced.

2) Corrosion

In this region the oxidation of the metal to its ion is thermodynamically favourable here the stable phases are Fe^{+2} and Fe^{3+} . The corrosion of iron is indeed rapid in these areas as the element is oxidised to a soluble ionic product.

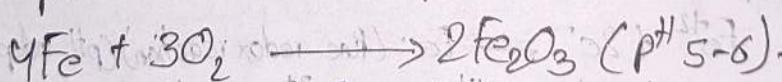
At slightly acidic pH the corrosion reaction is



This is possible for water containing relatively little oxygen that is in solution where the potential is near to hydrogen line.

Passivation:

Saturating water with air or oxygen moves the system closer to oxygen line where the most stable species Fe_2O_3 is formed. This acts as the protective coating on the metal surface that greatly reduces the corrosion reaction. This phenomenon is called passivation.



The effectiveness of passivation is highly dependent on the porosity of the metal oxide film and how it appears on the metal surface.

Hence in the region of water stability (space below dotted line) Fe is present either as ionic species in solution or as an outside. This means Fe is unstable when in contact with water regardless of pH or potential.

Limitations:

- 1) These diagrams are purely based on thermodynamic data and do not provide any information on the rate of the reaction.
 - 2) Temperature and velocity are not considered which may seriously effect the corrosion rate.
 - 3) It deals with pure metals only.
 - 4) All insoluble products are assumed to be protective which is not true as corrosivity, thickness and ^{adherence} to the substance or a important factor. ^{adherence}
- Ex: contact of liquid sodium with stainless steel can result in caustic embrittlement and cracking of steel. These phenomenon is observed in certain types of Na, cold nuclear reactors.
Liquid metal corrosion.

Dry corrosion

- 1) corrosion occur in absence of moisture
- 2) It involves the direct attack of chemicals on the metal surface.
- 3) process is slow
- 4) corrosion products are produced at the site of corrosion
- 5) The process of corrosion is uniform

wet corrosion

- 1) corrosion occurs in presence of conducting medium.
- 2) It involves the formation of electrochemical cells
- 3) process is rapid
- 4) corrosion occurs at anode but the rust is deposited at cathode.
- 5) It depends on the size of the anodic part of the metal.

Unit-3

Isomerism of organic compound.

The compound which possess same mol. formula but diff physical and chemical properties are called isomers. This phenomenon is called Isomerism.

It is 2 types:

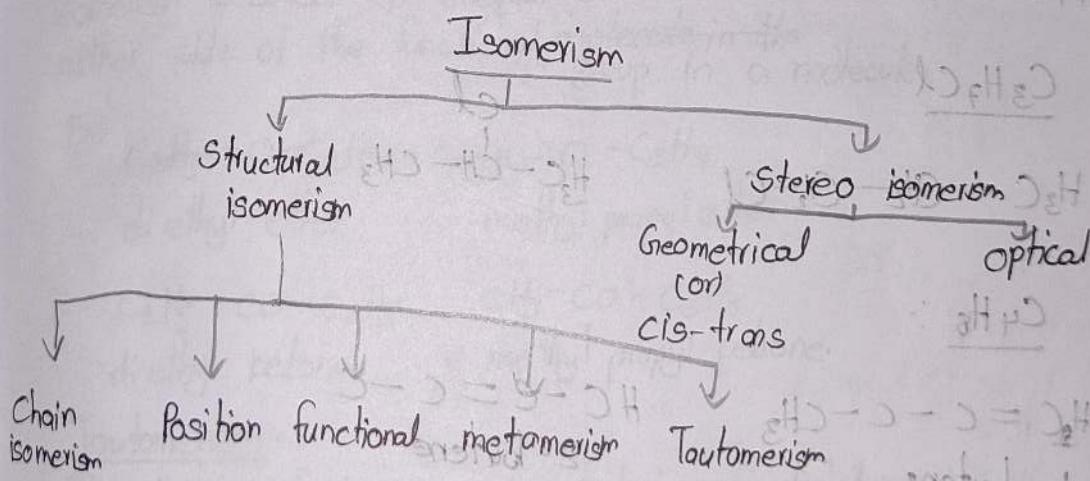
Structural isomerism:

The compound which possess same mol. formula but different structural arrangement structural isomer. This phenomenon is called structural isomerism

Stereo isomerism:

Compound possess same mol. formula but they differ in the atoms or groups in space are known as stereo isomers. This is also referred to as configuration of molecule.

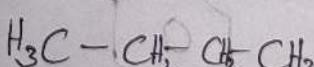
Classification:



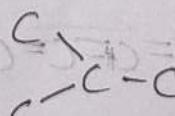
Chain (or) skeletal isomerism:

Isomers differ in the structure of carbon chain core known as chain isomers. The phenomenon is called chain isomerism.

Ex: C_4H_{10} - MF



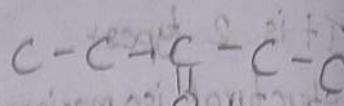
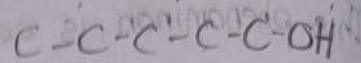
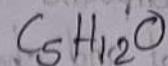
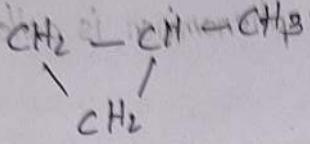
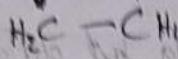
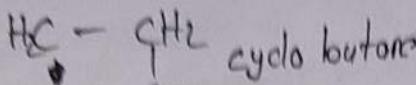
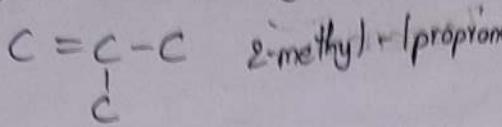
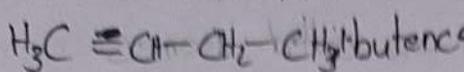
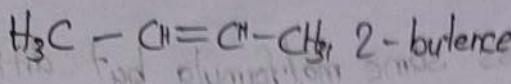
n-butane



Iso butane

2-methyl propane

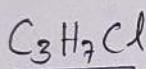
MF: C_4H_8



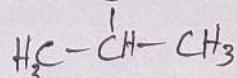
cyclo alkyl isomers will had elimination since 222209 bromine

position isomers:

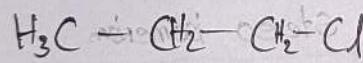
compound contains same carbon chain, the difference in the position occupied by a particular atom or functional group in the carbon chain is to give rise to position isomerism.



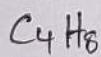
isomers I



isomer II

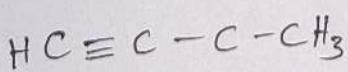
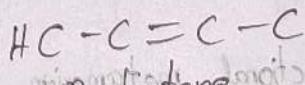
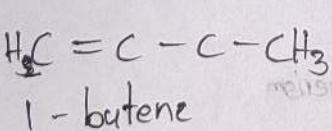


isomer III

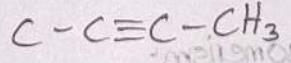


isomer IV

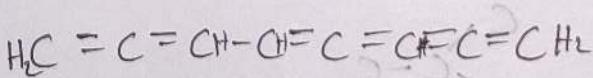
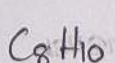
isomer V



1-butyne

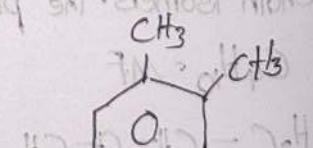


2-butyne



isomer VI

isomer VII



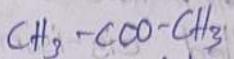
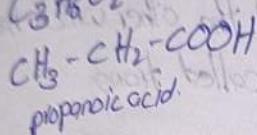
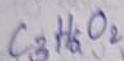
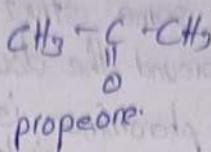
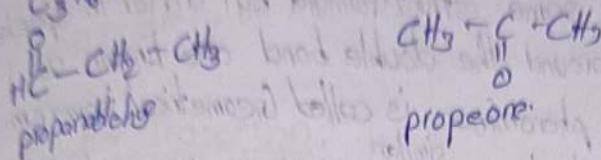
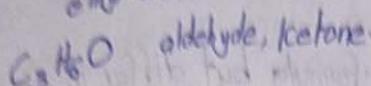
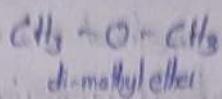
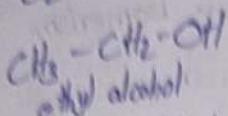
$CH_3 - C_6H_4 - CH_3$

O-xylene

Functional isomerism:

Isomers which possess some MF but diff functional group are known as functional isomers. This phenomenon is called functional isomerism. As the functional group diff from isomers they possess diff physical and chemical properties.

Ex: $\text{C}_2\text{H}_5\text{O}$ - alcohol + ether



methyl acetate

Metamerism:

Compounds of some Homologous series show this type of isomerism because of unequal distribution carbon atoms on either side of the functional group in a molecule.

Ex: $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$

diethyl ether

$\text{CH}_3-\text{O}-\text{C}_3\text{H}_7$

methyl propyl ether

$\text{C}_2\text{H}_5-\text{CO}-\text{C}_2\text{H}_5$

diethyl ketone

$\text{CH}_3-\text{CO}-\text{C}_3\text{H}_7$

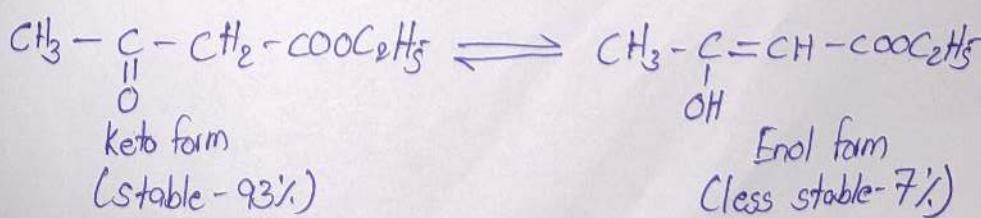
methyl propyl ketone

Tautomerism:

It is a type of isomerism in which two functional isomers exists together in equilibrium. The two forms existing in equilibrium are called tautomers.

Ex: aceto acetic ester exists in two forms

one has(keto)group and another has(enol)group.



Stereoisomerism:

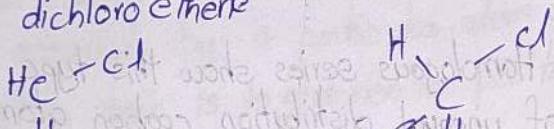
when isomerism is caused by the diff arrangement of atoms or groups in space, the phenomenon is called Stereoisomerism. These isomers have same structural formula but different spatial arrangements of atoms or groups in the molecule. It is of two types: Geometrical or cis-trans isomerism, optical isomerism.

Geometrical isomerism:

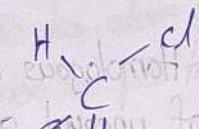
isomers which possess same struct. formula but differ in spatial arrangement of groups around the double bond are known as Geometrical isomers. This phenomenon is called Geometrical isomerism.

The isomer which have ^{similar} group on same side of double bond is called cis-isomer and the other which has ^{similar} group opp side of double bond is called trans.

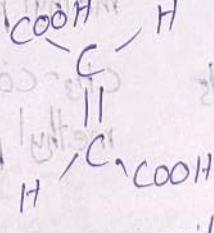
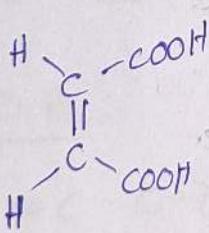
Ex: 1,2 dichloroethene



(cis)



(trans)



Maleic acid. Fumaric acid.

in which amide part remains in straight chain
carboxyl part lies in cis position

and amide part lies in trans position



acid form
(Keto form)

acid form
(Keto form)

optical isomerism:
 ↳ isomers

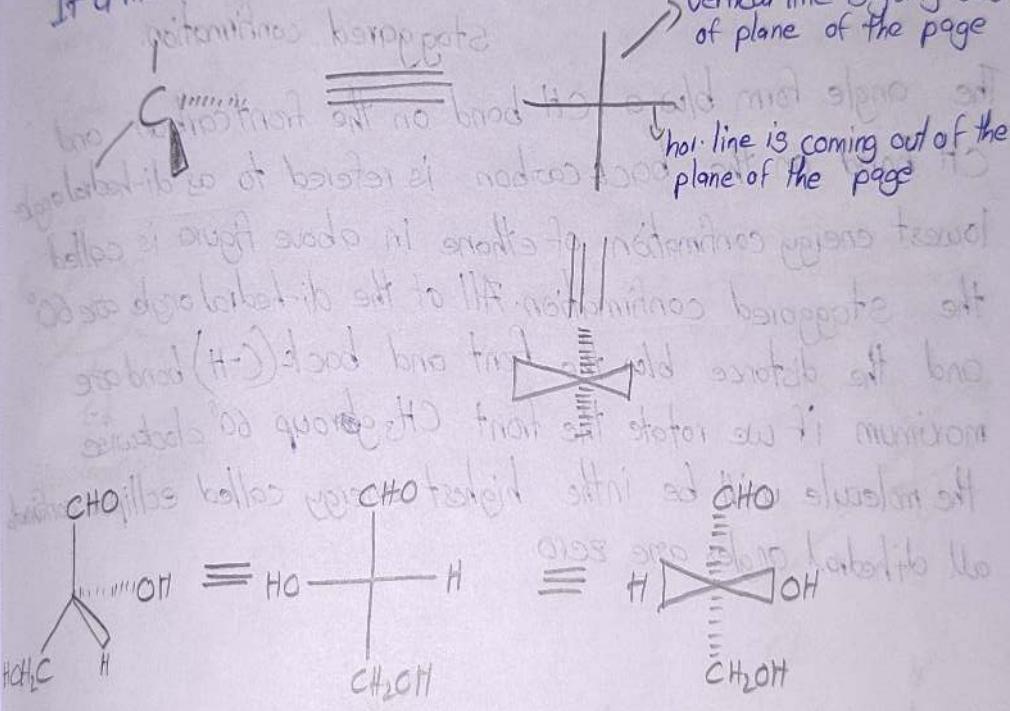
optical isomers have some physical and chemical properties except that they show a pronounced difference in the rotation of plane polarised light.

The isomer which rotates the plane of plane polarized light towards right or clockwise is called dextro rotatory (d) form
 (l) form.

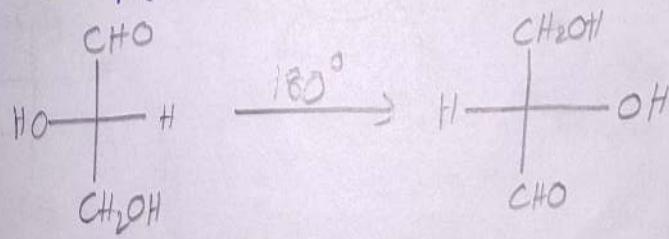
on the other hand the isomer which rotates the plain of plane polarise light to the left or anticlockwise is called (laevo rotatory or L-form or (-) form)

Fischer Projection:

Fischer projection:
It's a method of representing 3-D organic molecule in 2D structures.
vertical line is going back
of plane of the page



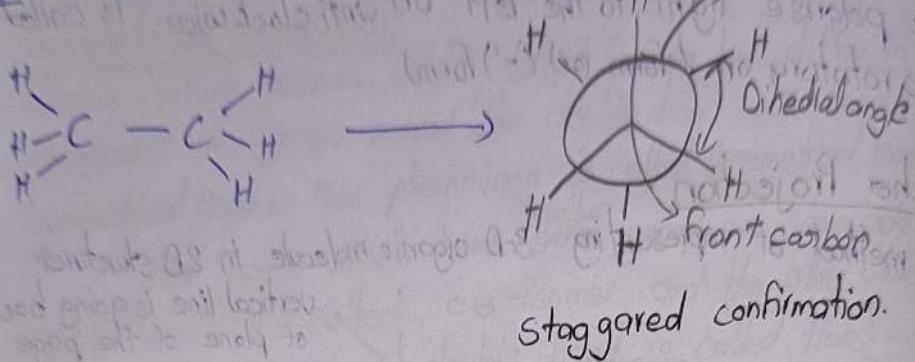
Fischer projection can be rotated to 180° only.



Newmann Projection:

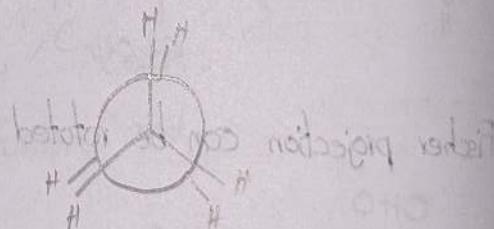
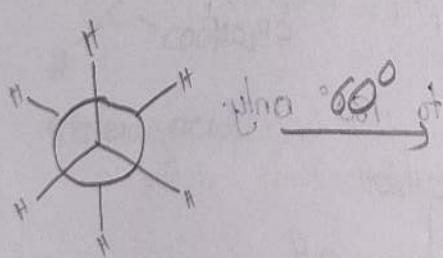
To visualise different confirmation of a molecule in a better way, it is convenient to use a drawing convention called the Newmann projection. In this projection we look lengthwise down a specific bond of interest. We depict the front carbon atom as a circle and back carbon atom as a dot.

Ex: Ethane.



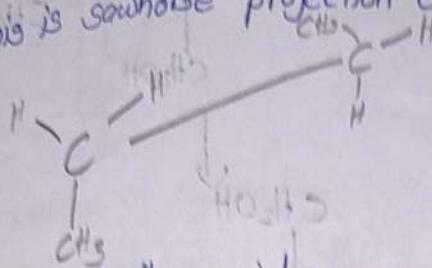
staggered confirmation.

The angle formed b/w a C-H bond on the front carbon and C-H bond on the back carbon is referred to as dihedral angle. Lowest energy confirmation of ethane in above figure is called the staggered confirmation. All of the dihedral angles are 60° and the distance b/w the front and back (C-H) bond are maximum if we rotate the front CH_3 group 60° clockwise. The molecule will be in the highest energy called eclipse confirmation. All dihedral angles are zero.



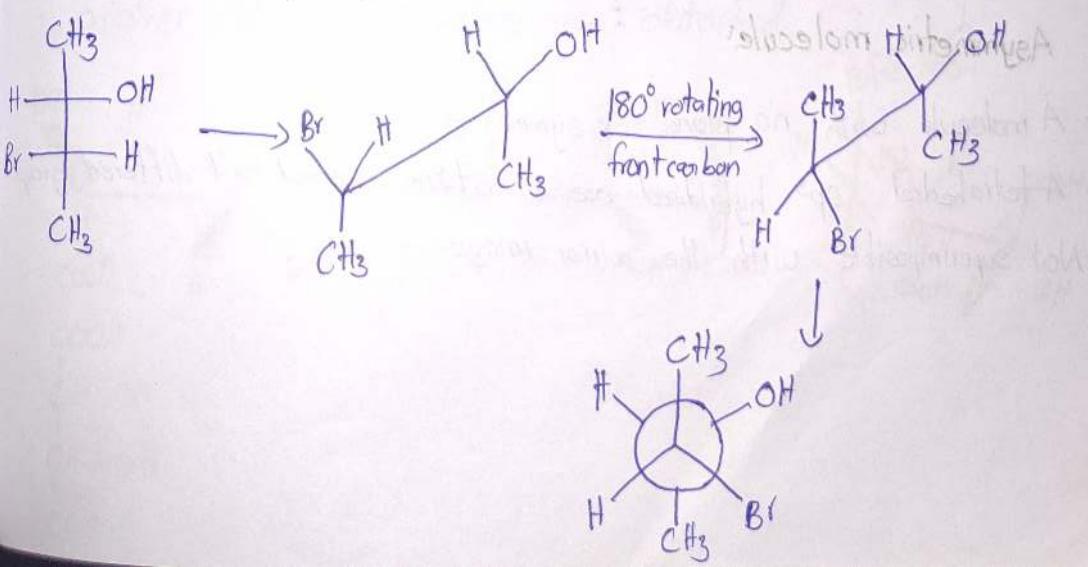
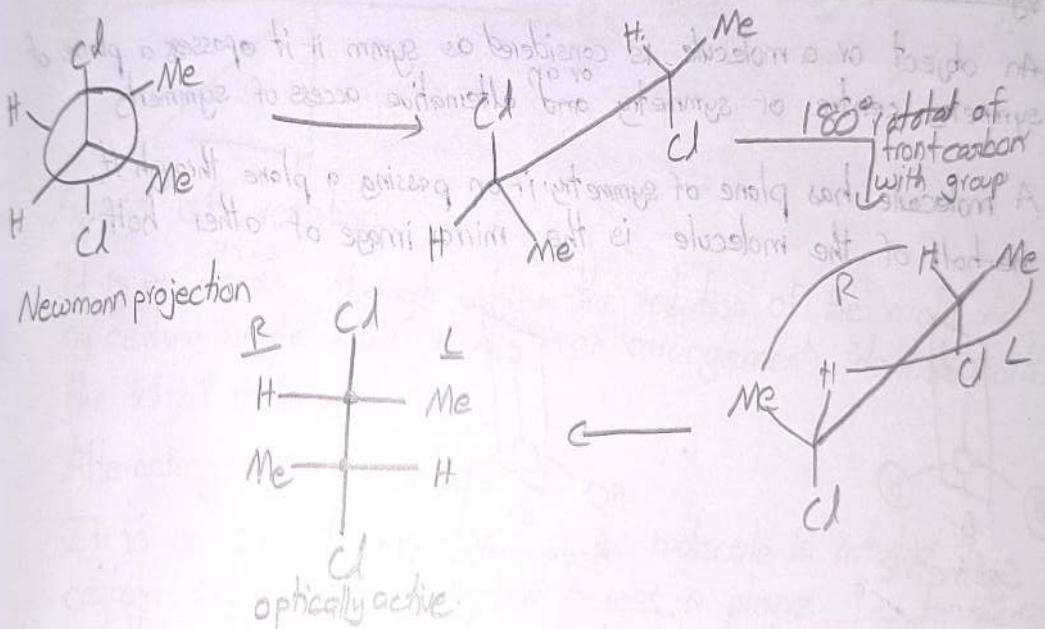
Sawhorse projection:-

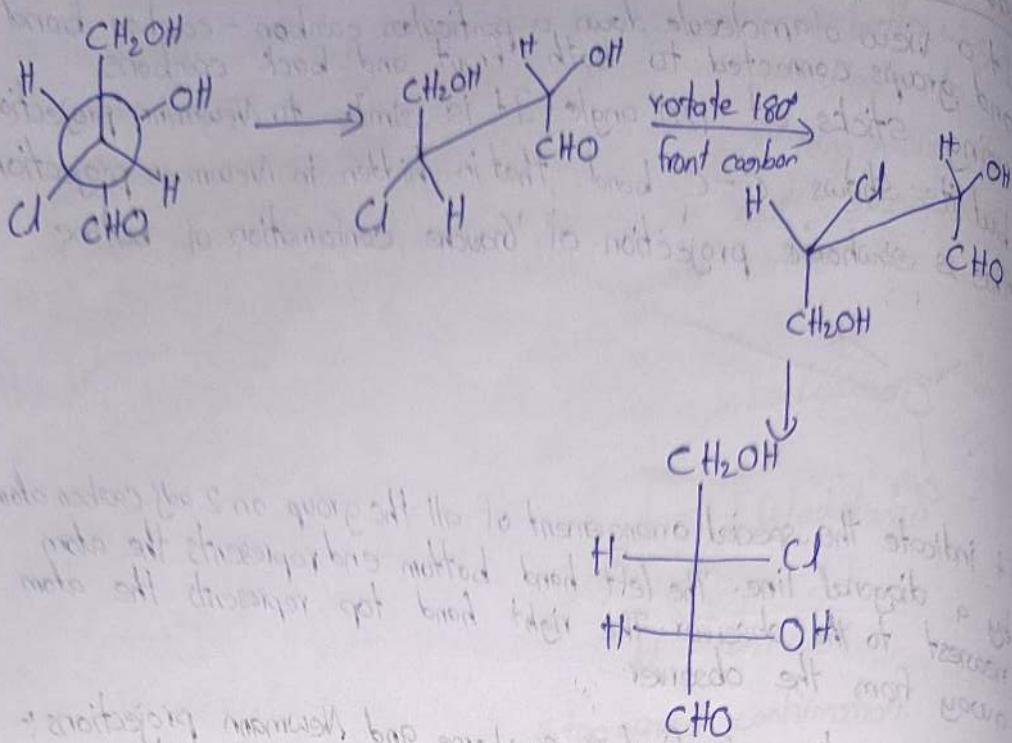
It's a view of a molecule down a particular carbon-carbon bond and groups connected to both front and back carbons using sticks at 120° angle. It is similar to Newmann projection but it shows C-C bond that is hidden in Newmann projection. This is sawhorse projection of gauche conformation of butane.



It indicates the special arrangement of all the groups on 2 adjacent carbon atoms by a diagonal line. The left hand bottom end represents the atom nearest to the observer. The right hand top represents the atom away from the observer.

Interconversion of Fischer, Sawhorse and Newmann projections:-

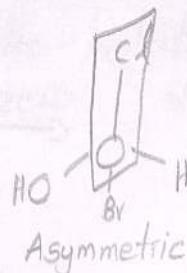
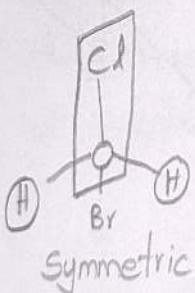




Symmetric Molecules: (Achiral)

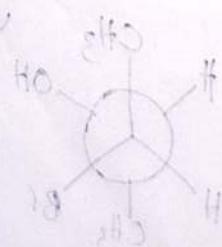
An object or a molecule is considered as symm if it ~~possess~~ possesses a plane of symmetry, centre of symmetry ^{or} ~~and~~ alternative access of symmetry

A molecule has plane of symmetry if on passing a plane through it, one-half of the molecule is the mirror image of other half.



Asymmetric molecule:

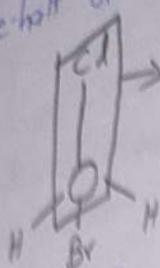
- A molecule with no plane of symmetry.
- A tetrahedral sp^3 hybridised carbon atom attached to 4 different groups.
- Not superimposable with the mirror image.



Symmetry elements:

Plane of symmetry:

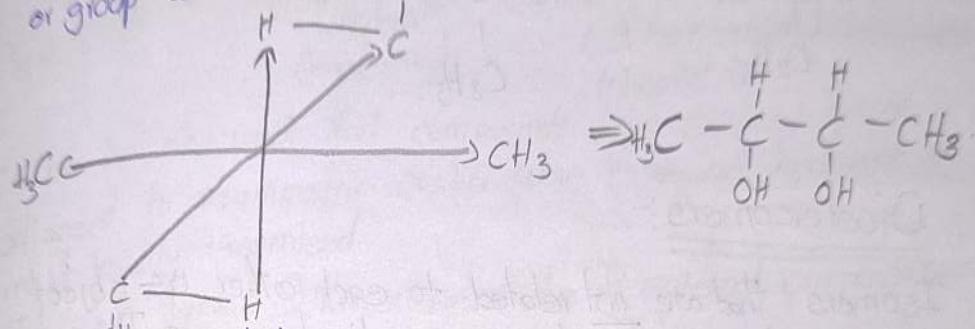
A molecule has a plane of symm. if on passing a plane through it one-half of the molecule is the mirror image of other half.



→ plane of symmetry

Centre of symmetry:

It is a point in the molecule, passing through which, if a line is drawn from any atom or group and then extended to equal distance in opp direction means an identical atom or group at that end. OH .

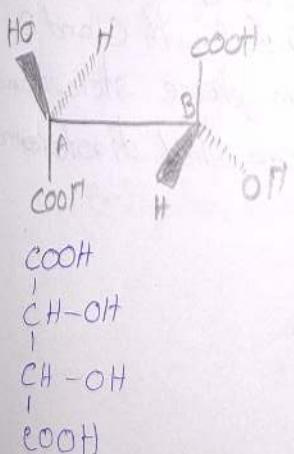


Access of rotation:

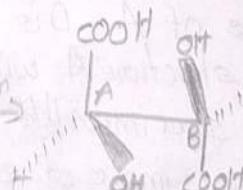
It is an access through which the rotation of the molecule by certain angle will result in an arrangement identical with the initial molecule.

Alternating axis of rotation:

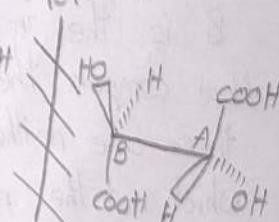
It is an axis through which if the molecule is rotated by certain angle and reflected across a plane perp to the axis, another identical structure is obtained.



180° rotation

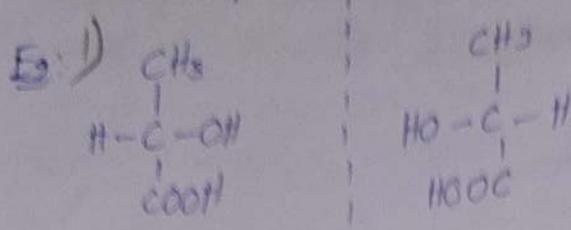


Reflection:

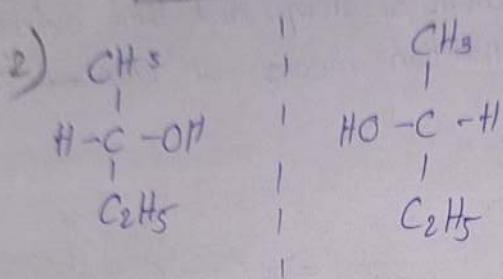


Enantiomers:-

A pair of molecules which are related to each other as an object and its mirror image are known as enantiomers
(or) enantiomorphs. (not superimposable)

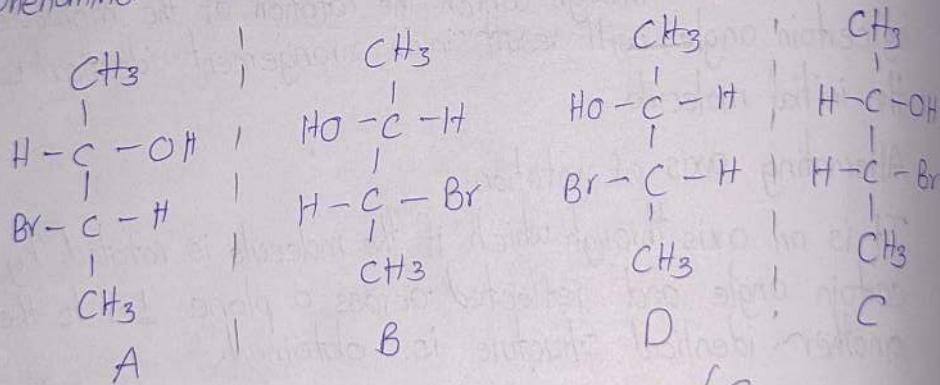


Lactic acid:-



Diastereomers:-

Isomers that are not related to each other as object and mirror image are known as diastereomers. This phenomenon is called diastereomerism.



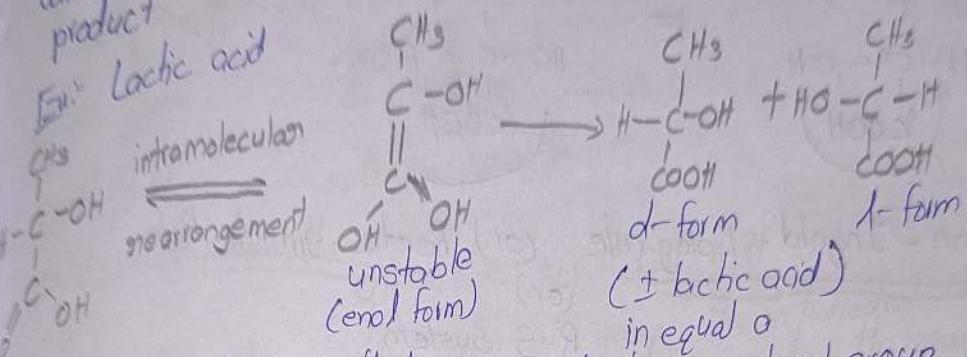
B is the image of A. D is mirror image of C.
Now compare the structure A with C and D & B with C and D.
These are neither superimposable nor mirror image hence stereoisomers which are not the mirror image of each other are called diastereomers.

b/w Diastereomers and Enantiomers

Q) Difference

Racemisation:-

When the optically active substance are kept for a long time or it is subjected to the application heat, light etc. may result in the loss of their optical activity. This conversion of dextro(d) or levo(l) compounds to their racemic forms (d-l) is called Racemisation. It occurs through some intra molecule rearrangement which exists temporarily in equilibrium with their rearranged product.

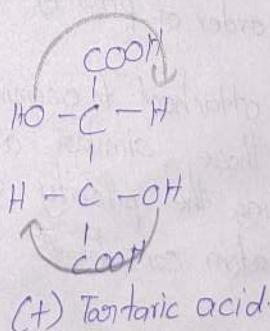
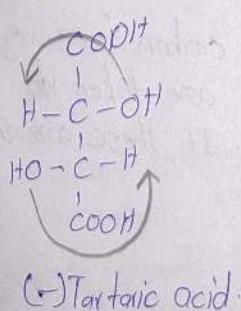


It has been observed that compounds have carbonyl group adjacent to asymmetric carbon atom carrying hydrogen or most easily racemised.

It is 2 types:- 1) Racemisation due to external compensation.
2)

Racemisation due to external compensation:-

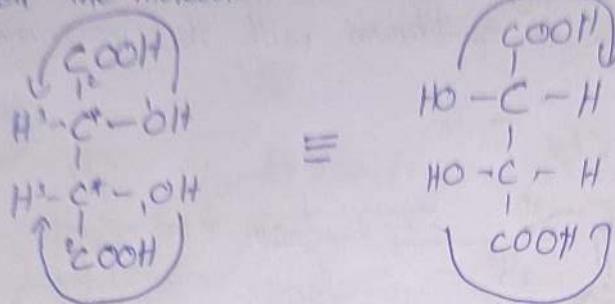
The optical inactivity consisting due to the presence of equal amount of d-l forms by equal and opposite optical activity of each isomer which arises due to external compensation is regarded as, racemisation due to external compensation.



Racemisation due to internal compensation

Ex: Meso form of tartaric acid.

This optical inactivity arises in the molecule because of equal and opposite rotation by 2 similar asymmetric carbon atom of the same molecule. d-rotation of one half of molecule is compensated by l-rotation of other half hence this compensation comes from within the molecule itself. The molecule is said to inactive due to internal compensation.

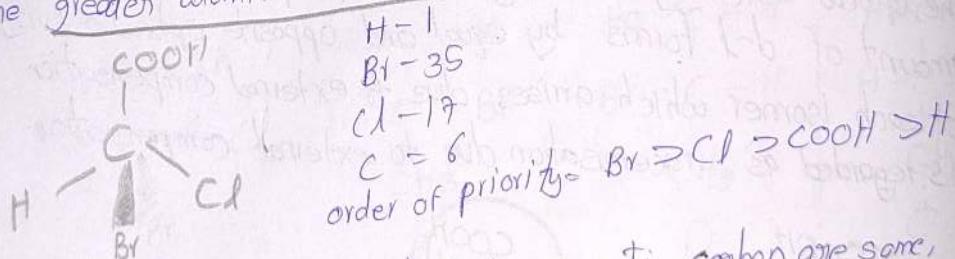


Cahn - Ingold - Prelog rule (or) Rectus - Similis Rule
 (or)
R-S system.

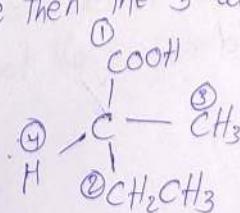
Sequence Rule:

These are used to name the isomers of chiral compound. In R-S system the atoms joined to the asymmetric carbon directly are assigned in a sequence.

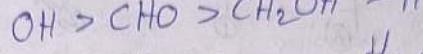
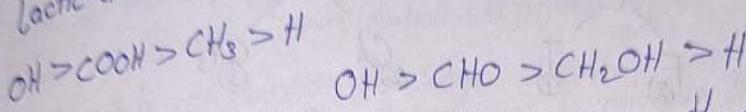
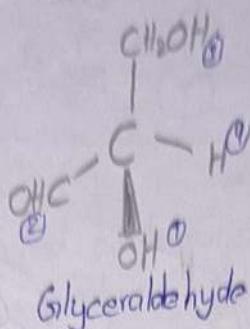
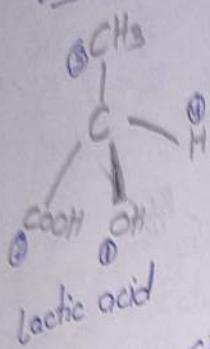
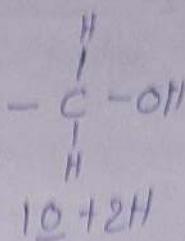
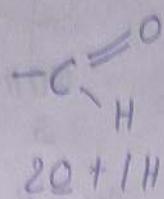
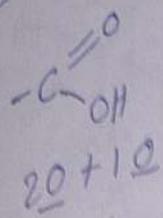
- The order of priority is determined on the basis of atomic number of the atom joined directly to asymmetric carbon. The greater atomic number, the higher the order.



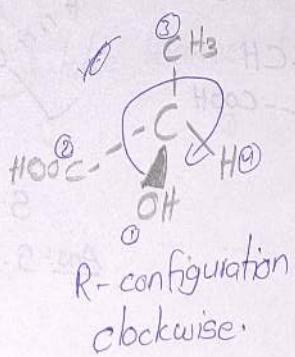
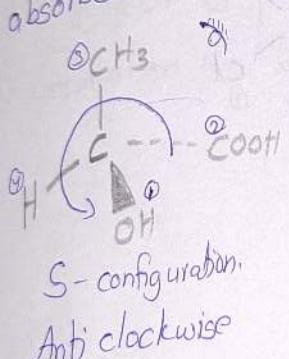
- If 2 or more atoms attached to asymmetric carbon are same, the atoms next to those similar atoms are taken into consideration for determining the priority order. If these are also same then the 3 atom considered.



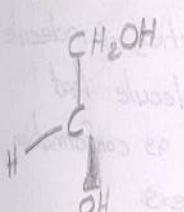
for determining the priority, the multiple bonds are treated as separate single bond thus $\text{H}-\text{C}\equiv\text{O}$ is regarded as carbon linked to 2 oxygen and 1 hydrogen.



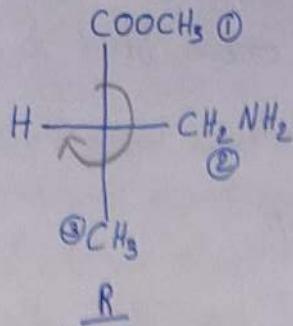
v) After fixing the priority order of groups, the tetrahedral structure of the isomer is viewed from the side opp. to the group of lowest priority, and the arrangement of rest of the group is absorbed



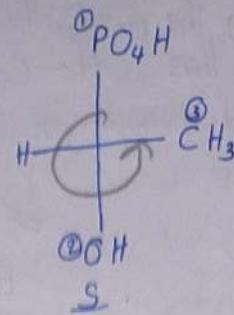
- Clayton's nomenclature



The racemic modification is turn as R-S. This system is very convenient for writing the absolute configuration of the compound. Usually the optical isomer must be represented by tetrahedral projection as the planar representation will not give the correct idea of molecule.

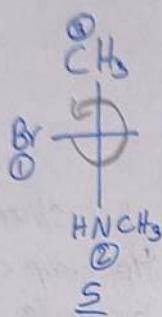


Ans : S ✓

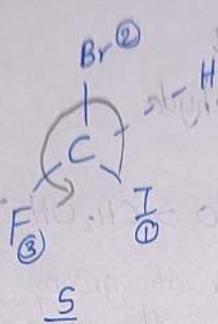


Ans : R

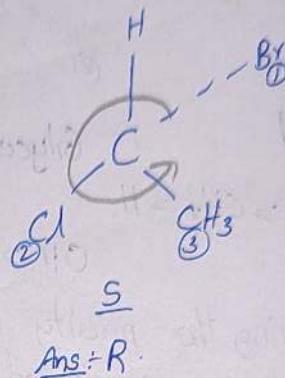
(because least priority is in down position otherwise answer will change)



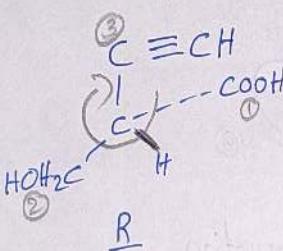
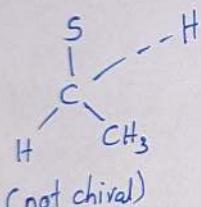
Ans : R



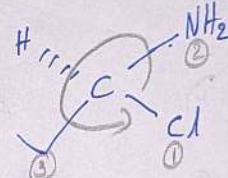
Ans : S
(hydrogen is in correct position)



Ans : R



Ans : S.



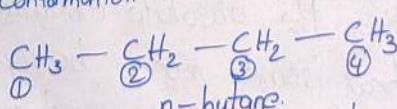
S.

Ans : S.

Conformational Analysis :-

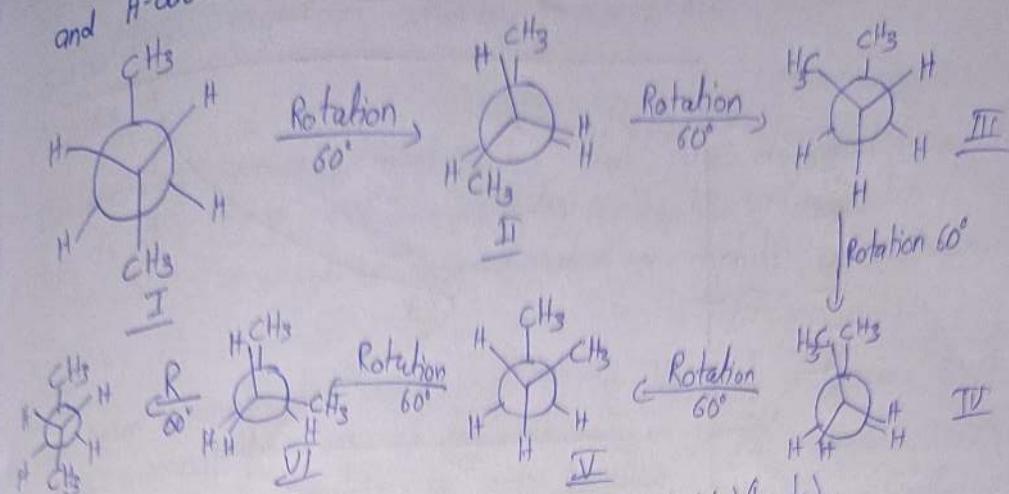
It is the study of effect of rotation on the properties of molecule.

Different special arrangement of atoms in a molecule that leads to free rotation around a single bond is known as conformation and these conformation are called conformers or Rotamers.



butane can be treated as derivative of ethane, where 1-H on each carbon of ethane is replaced by a methyl group. The sigma bond connecting the 2 middle carbons (C_2, C_3) is symmetrical about the nucleophilic and these symmetry of bond permits free rotation of C_2/C_3 w.r.t each other without breaking the bond.

These free rotation will lead to various arrangements of M.O and H-atoms attached to C₂ and C₃.



I - Anti (or) staggered conformation. (stable) (high).

II, IV, VI - Eclipsed conformation (highly unstable).

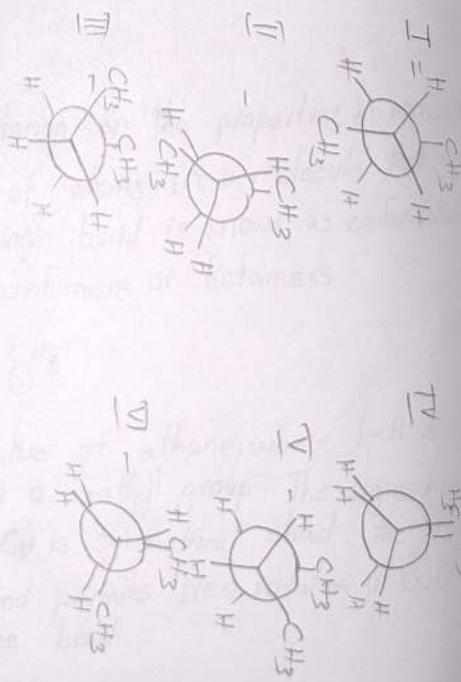
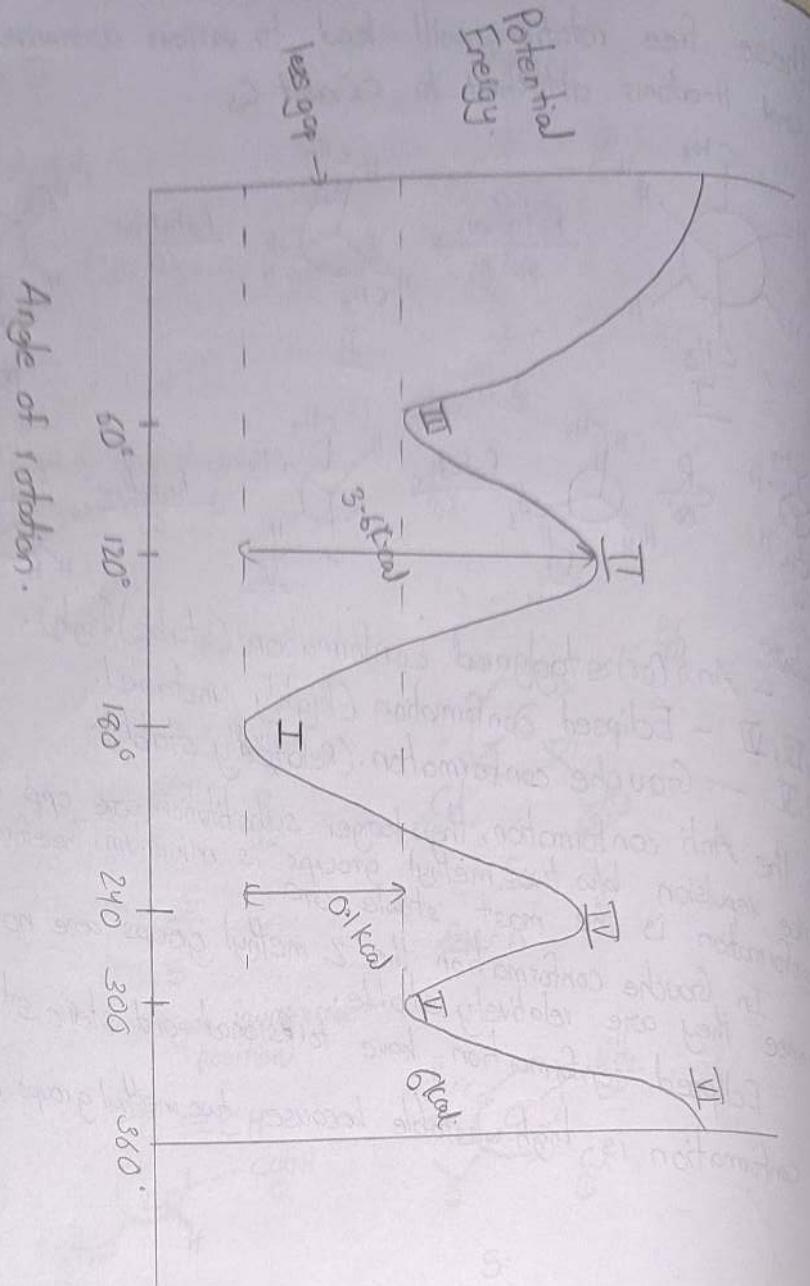
III, V - Gouche conformation. (Relatively stable).

In the Anti conformation, the longer substitution are opp to each other hence repulsion b/w two methyl groups is minimum. Therefore these conformation is the most stable OR

In Gouche conformation the 2 methyl groups are not as far and hence they are relatively stable.

Eclipsed conformation have torsional and steric strain

IV conformation is highly unstable because two methyl groups close to each other



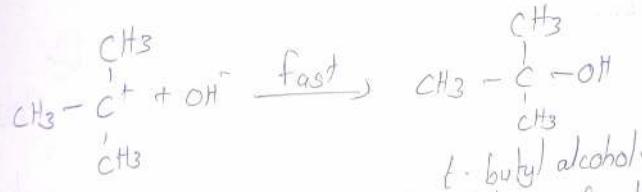
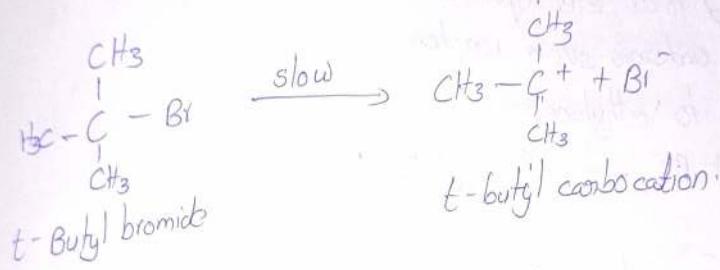
Nucleophilic substitution Reaction -
Nucleo

Nucleophiles generally react at sites that are deficient in electrons
it is of two types. S_N^1 - substitution Nucleophilic unimolecular.
 S_N^2 - substitution Nucleophilic bimolecular.

S_N^1 :
The term unimolecular used here is for the rate determine step
which involves the conc. of one molecule. In general

S_N^1 reaction follows first order kinetics.
Ex: hydrolysis of alkyl halide, acyl halide, Decomposition of ether with
 $R-X \rightarrow R-CO +$ hydrogen iodide.

S_N^1 mechanism is more preferable for tertiary alkyl halide because
the backside attack of hydroxyl group to the tertiary carbon will
be difficult because of the presence of 3 bulky methyl groups



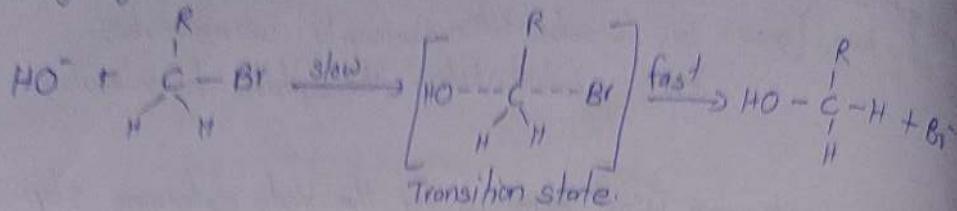
The 1st step is the slow dissociation of alkyl halide to give a Br^- ion
to and t-butyl carbocation which is stabilise due to hyperconjugation.
t-butyl carbocation combines with hydroxyl ion to give t-butyl alcohol.
t-alkyl halide have 3 alkyl groups attached to the central
carbon atom. The ($+I$) effect of the 3 alkyl groups increases the
electron density of the central carbon which increases the repulsion
towards the halogen thereby increase the chance of formation of
carbocation thus in t-alkyl halides, the tendency to follow the path of
 S_N^1 mechanism increases.

SN^F mechanism

primary alkyl halide follow S_N^2 mechanism.

This involves the attack by a nucleophile from the side opp to the leaving group

for hydrolysis of allyl halide (1° , 2°)

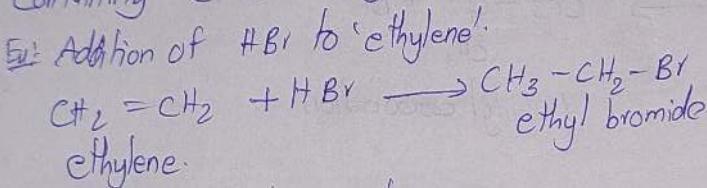


Addition reaction:

These are the reaction in which the atoms or groups are simple added to the double or triple bond without the elimination of any atom or other molecules. These reactions may be initiated by electrophiles, nucleophiles or free radicals.

Electrophilic Addition Reaction:

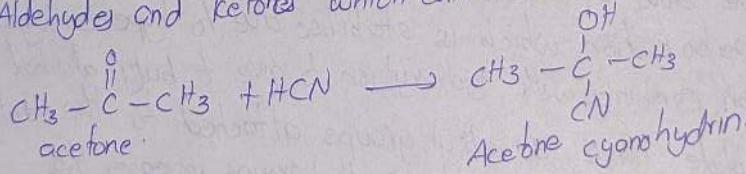
Electrophilic Addition Reaction: When an addition reaction involves the initial attack of an electrophile, the reaction is referred to as electrophilic addition reaction. Compounds containing $C=C$ undergo such reaction.



Nucleophilic addition reactions

Nucleophilic addition reaction:
When an addition reaction involves the initial attack of a nucleophile, the reaction is referred to as Nucleophilic addition reaction.

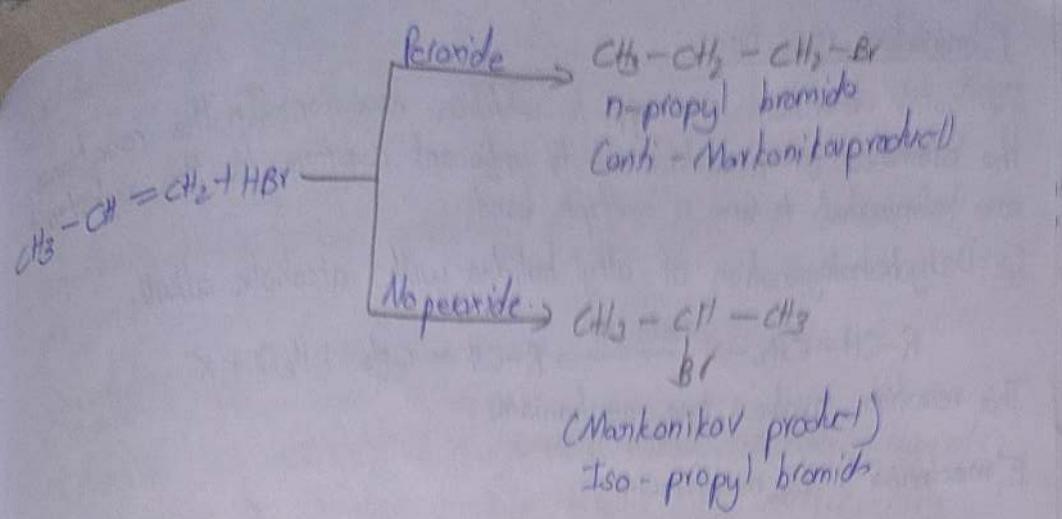
Aldehydes and ketones which contain 'C-O' double bond undergo such reaction



free radical mechanism :

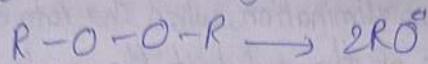
free radical mechanism:
 Acc-to Markovnikov's rule hydrogen is added to carbon with more hydrogens and halogen attached to carbon with less hydrogen is case of unsymmetrical alkenes during the addition of HBr but in presence of peroxide the reaction will proceed opp. to that subjected by Markovnikov this phenomenon of anti-Markovnikov addition of HBr caused by the presence of peroxide is known as peroxide effect.

phenomenon of anti-Markovnikov presence of peroxide is known as peroxide effect. For ex: when propylene reaction with HBr in presence of peroxide the major product is n-propyl bromide. In the absence of peroxide the major is iso-propyl bromide

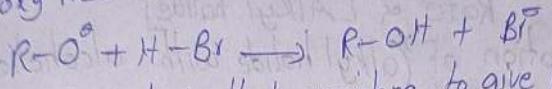


Mechanism:

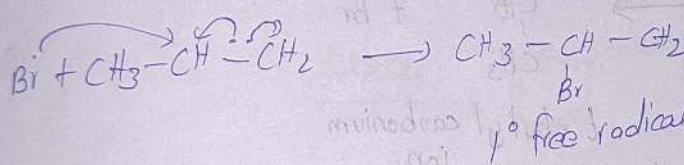
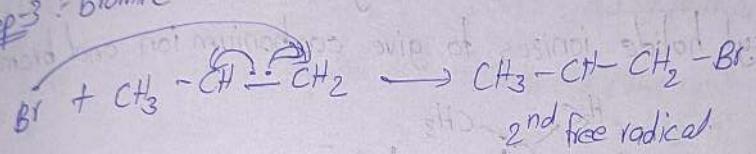
Step 1: peroxide dissociates to give alkoy free radical



Step 2: alkoy free radical attack HBr to form bromine free radical

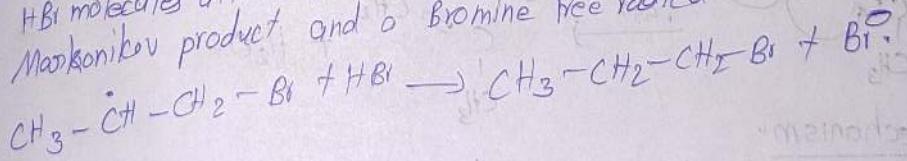


Step 3: bromine free radical attack propylene to give (1,2) free radical.

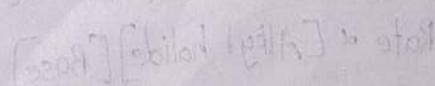
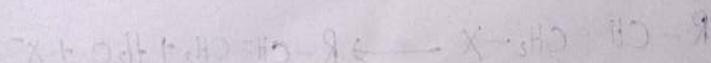


order of stability of free radical $\rightarrow 3^\circ > 2^\circ > 1^\circ$

Step 4: The most stable 2° free radical is formed. HBr molecules attacks the more stable 2° free radical to form anti-Markonikov product and a bromine free radical.



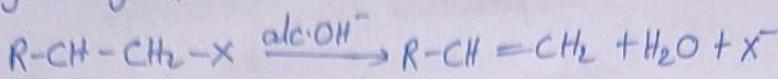
notations: no is shown in red, notations colored in blue
 not all blue simplification started by 2° not all red
 starting point of 2° not all blue simplification started by 1° not all red
 not all blue 2° not all red 1° not all blue 2° not all red 1° not all red
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 not all blue 2° not all red 1° not all blue 2° not all red 1° not all red
 not all blue 2° not all red 1° not all blue 2° not all red 1° not all red



Elimination reaction:

Elimination reactions are opp. to addition reaction. In the reactions, the atoms (or) groups attached to adjacent C-atoms in the substrate are eliminated to form a multiple bond.

Ex: Dehydrohalogenation of alkyl halides with alcoholic alkali.



This reaction involves two mechanisms:

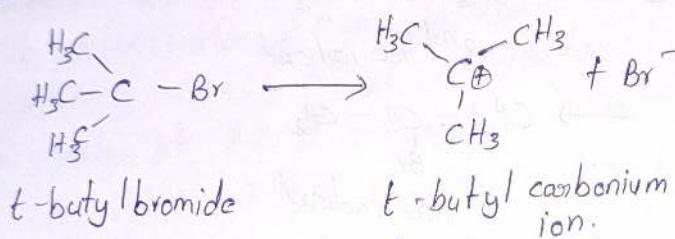
$$E_1 \text{ mechanism} > E_2 \text{ mechanism}$$

E_i mechanism:

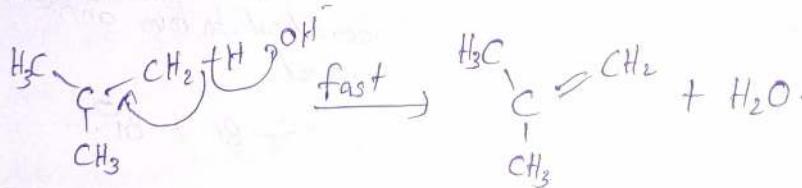
E_1 stands for uni-molecular elimination, when the rate of an elimination reaction depends on a conc. of the substrate, the reaction is first order and represented as E_1^+ . Rate $\propto [Alkyl\ halide]$

E: Dehydrohalogenation of (alkyl halide with alcoholic alkali)
 3° - Butyl Bromide

Step 1: The alkyl halide ionizes to give carbonium ion and bromide.



Step-2: A proton is absorbed by the base by the adjacent beta carbon to give alkene.



E₂ mechanism

E_2 mechanism: E_2 stands for bimolecular elimination when the rate of an elimination rxn depends on the conc. of substrate and nucleophile and the rxn of the 2nd order and it is represented as E_2 . This is a one step process in which the abstraction of proton from B "C" and the expression of halide ion from C carbon occur simultaneously.



$$\text{Rate} \propto [\text{Alkyl halide}] [\text{Base}]$$

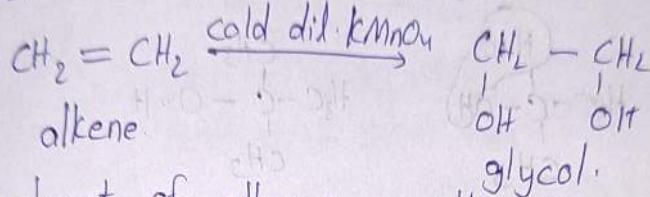
Oxidation & Reduction Reaction's:

oxidation of the organic compound is considered to be the rxn in which oxygen is added (or) hydrogen is removed similarly reduction is addition of hydrogen (or) removal of oxygen.

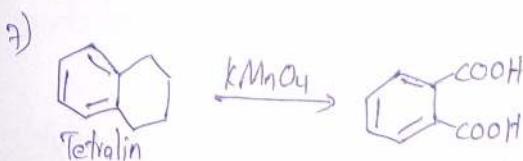
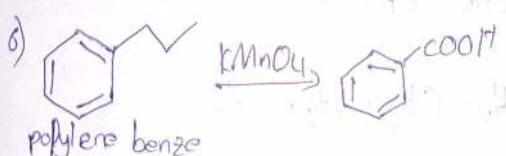
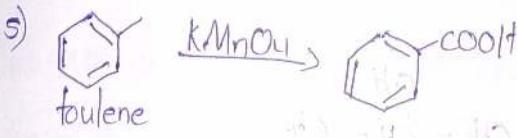
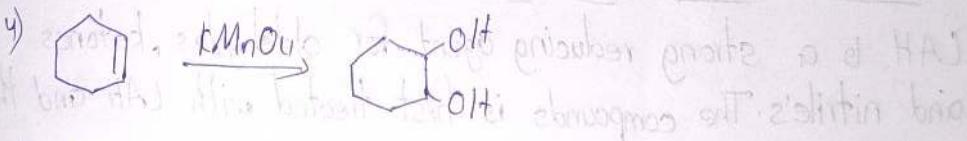
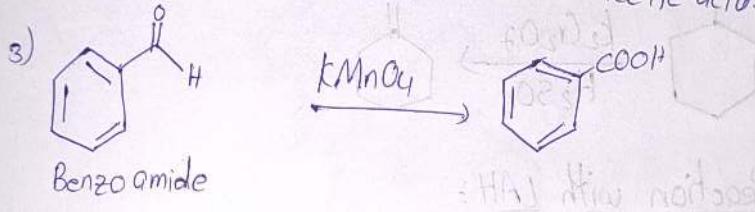
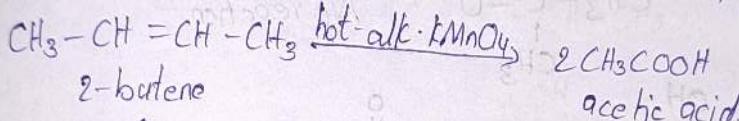
Oxidation with $KMnO_4$:

$KMnO_4$ is strong and commonly used oxidising agent. It is able to oxidise carbon atoms with sufficiently unbreak bond's (Pi-bonds, alcohols, aldehydes, ketones, etc.)

Diene oxidised with glycol.



2) treatment of alkene's with alk. $KMnO_4$ gives acetic acid.

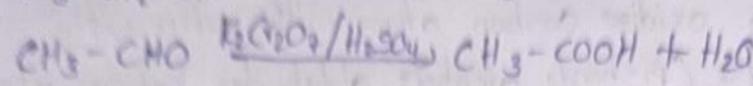
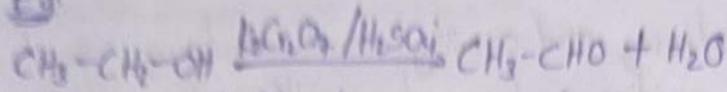


The rxn occurs if the carbon has atleast one hydrogen.

K₂Cr₂O₇

- 1) K₂Cr₂O₇ is a mild oxidising agent than KMnO₄
 2) It oxidises alcohol's into aldehydes under strong conditions to acids But KMnO₄ tends to provide carboxylic acid as product

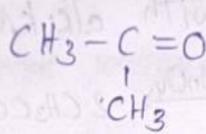
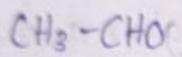
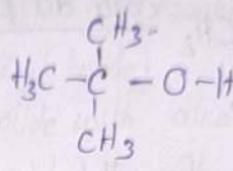
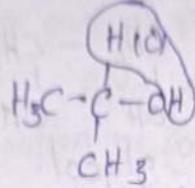
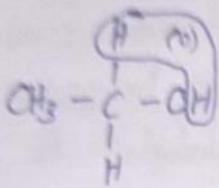
Ex:



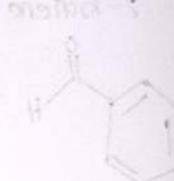
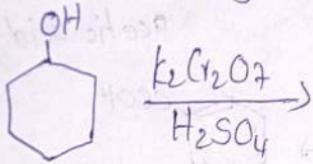
primary

secondary

tertiary

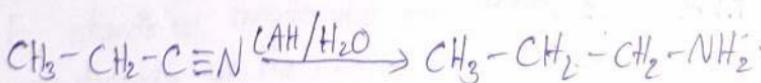
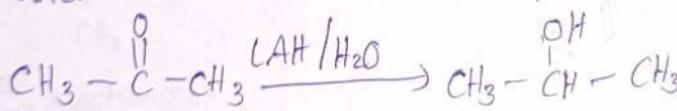


No reaction.

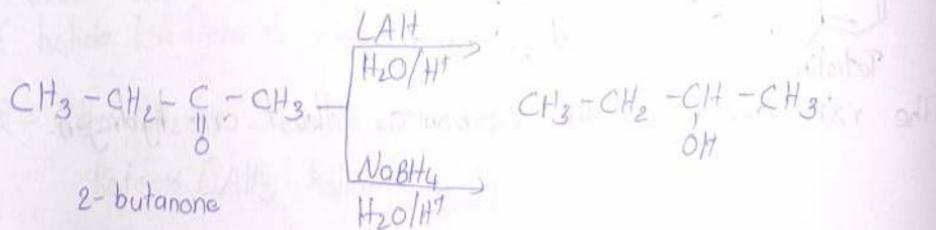


Reduction Reaction with LAH:

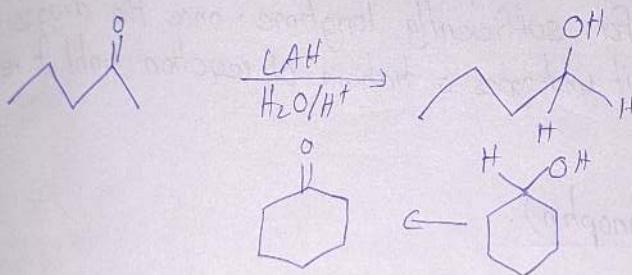
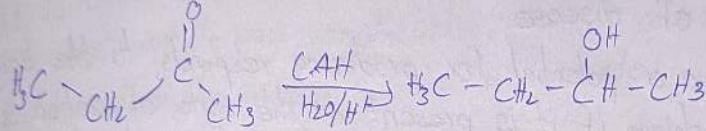
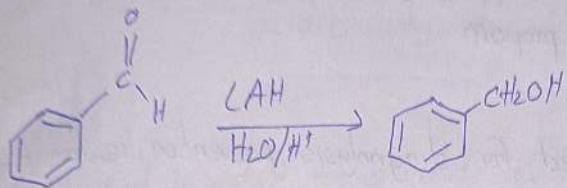
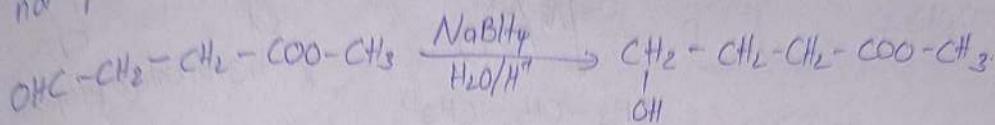
LAH is a strong reducing agent for aldehydes, ketones and nitrile's. The compounds is first treated with LAH and then water.



with NaBH₄:



The two metal hydrides are quite different in their reactivities. LAH is a powerful reducing agent that reduces not only aldehydes and ketones but also carboxylic acids, ester, amides and nitrile. LAH undergoes violent reaction with water. NaBH₄ is a mild reducing agent. It is less reactive towards water therefore aldehydes and ketones can be reduced without the simultaneous reduction of an ester group in the same molecule but this is not possible with LAH.

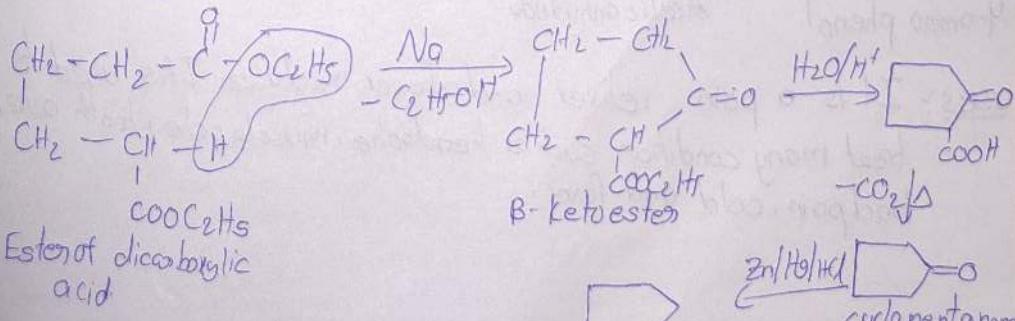


Dieckmann Condensation :-

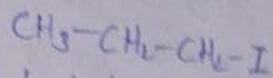
This reaction is useful for preparing cyclic alkenes.

Ester of dicarboxylic acid when treated with sodium, undergo intramolecular condensation and β -ketester is formed.

The β -ketester on hydrolysis gives cyclic ketones. This on reduction is the corresponding cyclic alkene.

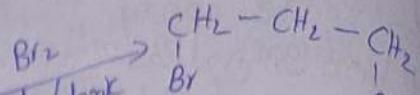


Ring opening reactions of cyclopropane:-

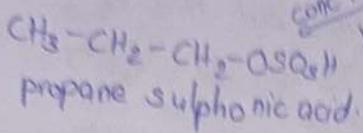


I- iodo propane.

(conc H₂O₂)



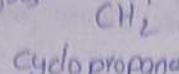
1,3 dibromo propane



propane sulphonic acid.

(conc H₂O₂)

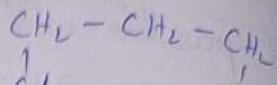
H⁺/OSO₃⁻



cyclopropane

~~Cl~~ CCl₄/dark

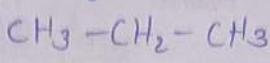
~~Cl~~ CCl₄/dark



1,3 dichloro propane

~~Ni/H₂~~

(80°C)



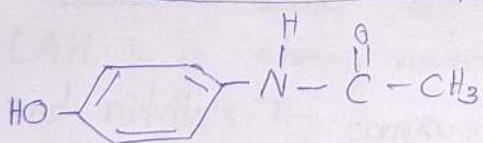
n-propam.

Drugs:-

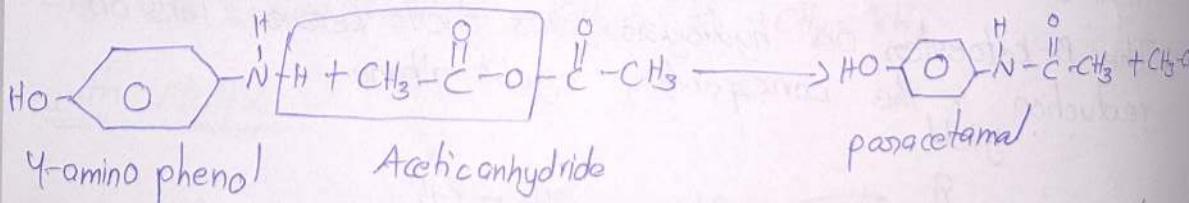
It is a medical agent used for diagnosis, prevention, treatment of symptoms and cure of disease.

The drugs have a potential for producing responds to the body but this can be achieve if it is present at the site of action is appropriate concentration for sufficiently longtime once the drug is administrated in the body it undergoes a chain of reaction until it reaches a target site.

Paracetamol (Acetaminophen):



It is synthesis by the reaction of 4 amino phenol with acetic anhydride this reaction forms an amide bond and acetic acid as a by product when the reaction is complete paracetamol is isolated and purified.



4-amino phenol

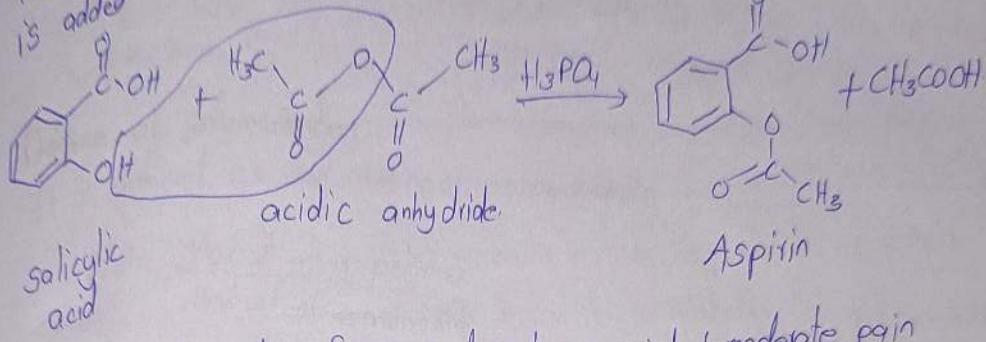
Acetic anhydride

paracetamol

uses:- It is a pain reliver and a fever reduces. It's used to treat many condition such as headache, muscle ache, tooth ache, back pain, cold and fever.

Aspirin:

The synthesis of Aspirin
 salicylic acid reacts with excess acetic anhydride in presence of SA
 (H_3PO_4) which acts as a catalyst to speed up the reaction.
 The excess of acetic acid is removed with the addition of water.
 The aspirin is not soluble in water and hence it will ppt. when water
 is added.

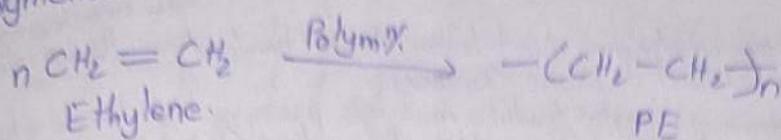


It is used to reduce fever and release mind to moderate pain such as muscle pain, tooth ache, common cold and headache. It may also be used to swelling in case of sprain.

Unit - IV

Polymers

Polymer is a macromolecule which is built by linking together of small particles is called polymer. This reaction is called polymerisation.



Degree of polymerisation:

It is defined as the avg. no. of monomer units

$$\text{D.P.} = \frac{\text{Molwt of a polymer}}{\text{Molwt of a monomer}}$$

Eg: D.P. of Ethylene, Molwt = 28.00

$$\text{D.P.} = \frac{28.00}{28} = 100.$$

D.P. effect: the size, and strength longer is the chain of polymer molecular weight.

of the polymer. The greater D.P. and greater will be strength and

Classification:

Based on source (or) origin:

1) Natural - cotton, wood

2) Polymer/synthetic - nylon 6, Nylon 6-6

Based on nature of the polymer

1) organic - Polymer whose backbone is made by carbon atoms and side chain will be H₂O, N etc.

2) inorganic - Polymer whose backbone is not made by carbon, it consists, B, Si, Na etc.

Silicon rubber.

Borosilicate

Glass.

Based on structures:

Linear - st. chain (long) simple, soft and flexible.

Branched - contains branches in chain these are weak and possess low density due to loose packing.

Crosslinked - if the monomer in the branches are connected by covalent bond with each other, crosslinked polymers will form. They are hard, rigid and

They donot melt, but burn on strong heating.

Based on the method of synthesis:

Addition - It is obtained by the polymerisation of identical monomer units without elimination of any molecule (P, PVC)

Condensation - obtained by the condensation by some or different type of monomer unit with elimination of molecules (H_2O , HCl , NH_3 , ...)

CO - obtained by the polymerisation of different type of monomer unit without elimination (Buna-S, Buna-N, ...)

Based on molecular forces:

Thermoplastic - These are linear/long chain polymers which can be melted on heat and hardened on cooling. They cannot be solvent (PVC)

Thermosetting plastic - These are cross-linked polymers due to heating. They get hardened once they are solidified.

Elastomers - If the ability to flex and twist its chains. (Rubber)

Fibre - These materials can be drawn into long thin threadlike materials possessing high tensile strength. These are held by strong intermolecular forces like H-bonding. (Nylon, Polyester etc.).

Nomenclature:

Homopoly - Made up of identical monomer units

Hetero (co) poly - Made up of different monomer units.

Linear Homo-Polymer = $-M_1-M_1-M_1-M_1-$

Branch H.P = $-M_1-M_1-M_1-M_1-$
 M_1

Cross linked H.P = $-M_1-M_1-M_1-M_1-M_1-$
 M_1 M_1
 $-M_1-M_1-M_1-M_1-M_1-$
 M_1 M_1

Hetero

Linear $\Rightarrow -M_1-M_2-M_1-M_2-M_1-$

Branch $\Rightarrow -M_1-M_2-M_1-M_2-M_1-$
 M_1 M_1

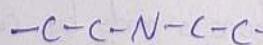
(cross linked)

Homo-chain polymer:

In the backbone contains only one type of atom [C or Si].

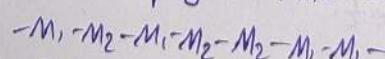
Hetero chain polymer:

In the backbone contains more than one type of atom in addition with carbon.

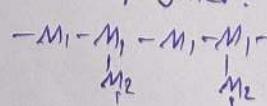


Types of co-polymers:

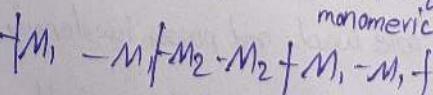
1. Random co-polymer : There is no definite sequence of monomer.



2. Graft co-polymer : The monomer segment in the backbone and in the branch differs.

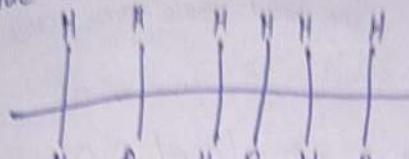


3. Block co-polymer : linear sequence of one monomeric unit followed by sequence of other monomeric unit.



Tacticity: special arrangement of functional group.
The orientation of monomeric unit or functional groups can take place in an orderly or disorderly manner w.r.t. to main chain.
This is known as Tacticity. This will give rise to 3 types of stereo regular polymers

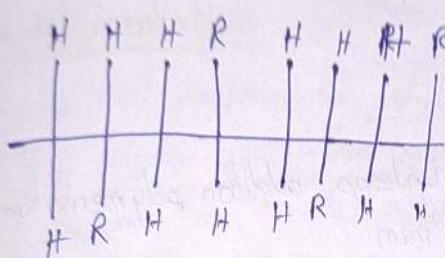
i) Isotactic - The functional groups are arranged on the same side w.r.t. to main chain.



Ex:- cis-poly isoprene.

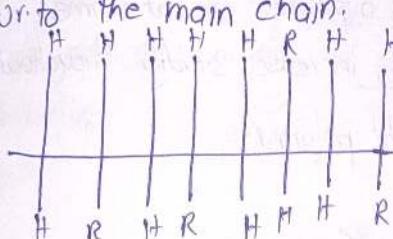
skelto = 109.100 Poly

Syndiotactic - The functional groups are arranged in alternative sequence w.r.t. to the main chain.



Ex:- Trans-polyisoprene

Atactic : The functional groups are arranged in randomly w.r.t. the main chain.

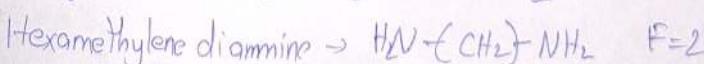
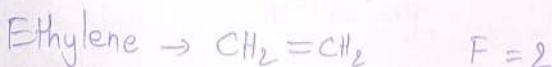
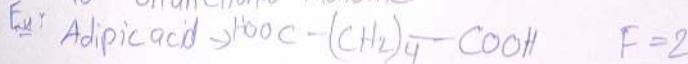


Ex:- Poly propylene.

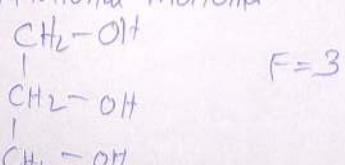
Functionality :-

The number of active side or bonding site in a monomer is referred as functionality.

For a substance to act as a monomer it must have 2 reactive sites.
for bifunctional monomer



glycol trifunctional monomer

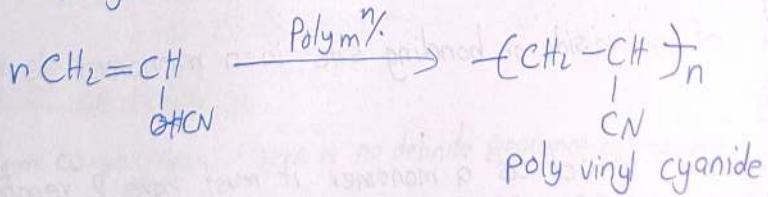
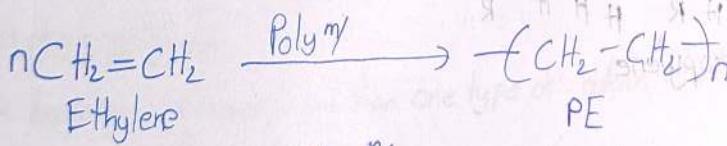


If the functionality of monomer is 2, only linear (or) straight chain polymeric can be produced each monomer unit in linear chain is held by strong covalent bond whereas different chain held together by weak van der waals force of attraction therefore there is no restriction to the moment of one over other such polymer possess less strength low heat resistance and they are soft and flexible.

If the functionality of monomer is 3 or cross-linked 3-D network polymers are produced All the monomers in the polymer are connected by strong covalent bonds therefore the moment of chain is totally restricted such polymers have high strength, hardness, toughness, heat resistance etc.

Addition Polymerisation:

- Monomers having multiple bonds undergo addition polymerisation.
- No other by product will be formed.
- formed from identical monomer unit.
- The mol. weight of the polymer will be the integral multiple of the mol. weight of monomer.
- During polymerisation monomer add to a polymer one at a time.
- Hence the number of monomeric units increase steadily throughout the reaction.
- longer reaction time give high mol. weight polymers.



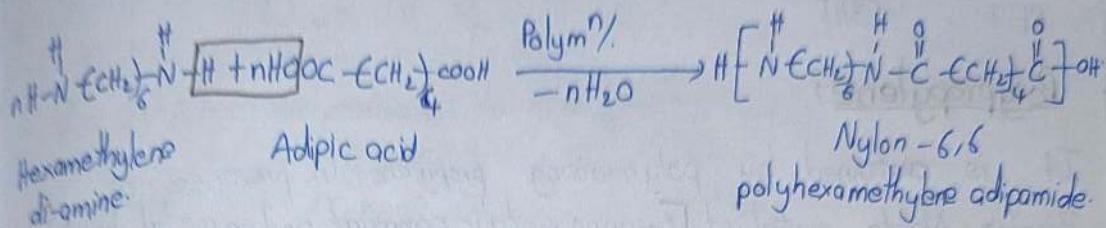
Condensation Polymerisation: formed by condensation

- Condensation

 - It is formed by condensation reaction between the functional group in a monomer with the elimination of simple molecule like H_2O , HCl , NH_3 , etc.
 - The mol weight of polymer need not be the integral multiple of mol. weight of monomer.
 - longer reaction times are essential to obtain high mol weight polymer.

Formation of Nylon-6,6

Formation of Nylon-6,6

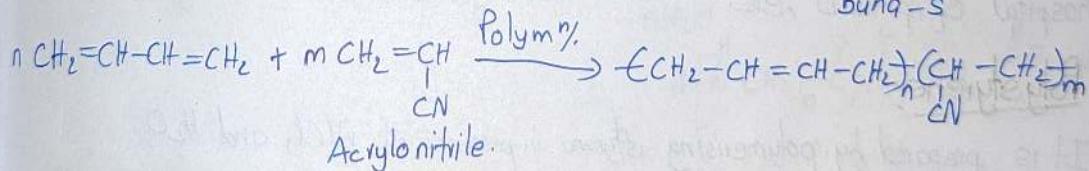
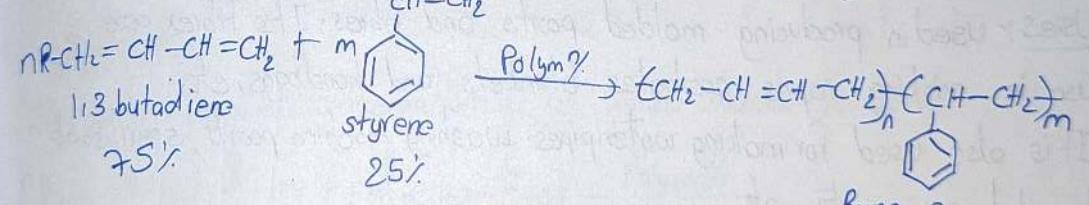


Co-polymerisation:

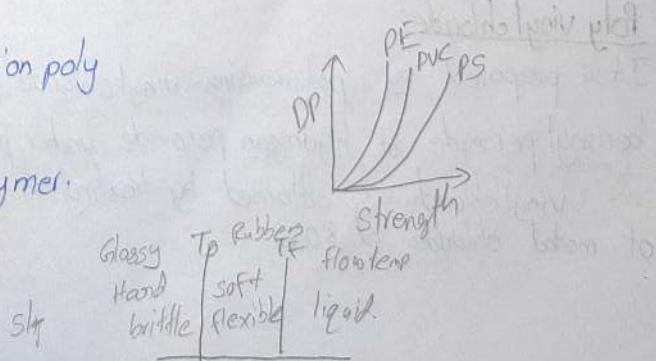
It is the joint polymerisation different type of monomers. The resulting polymer will contain more than one repeating unit.

It is superior than the other polymerisation reaction because the reaction controls various polymer property like strength, hardness, rigidity, heat resistance etc....

Formation of Buna-S Rubber (GR-S, SBR)



- Difference b/w thermoplastic and thermosetting plastics.
 - The properties and uses of polymers.
 - Maximum ^{c/o} molecules
 - Addition and Condensation poly
 - Elastomers
 - General property of polymer.



Synthesis of Polymers

1) Polypropylene $\xrightarrow{\text{Nylon}}$

2) Poly styrene

3) Poly vinyl chloride

4) Teflon

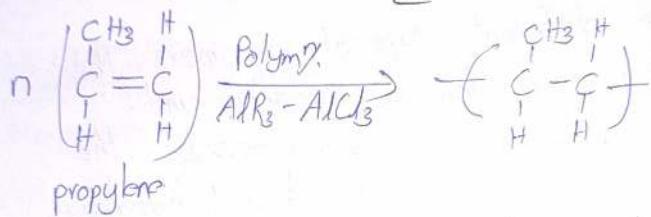
Condensation

Nylon Polyacrylate

PET PSHT

Polypropylene:

It is obtained by polymerising propylene in presence of Ziegler-Natta catalyst. [Organometallic compound and an metal halide] $[(\text{AlR}_3 - \text{AlCl}_3)]$.

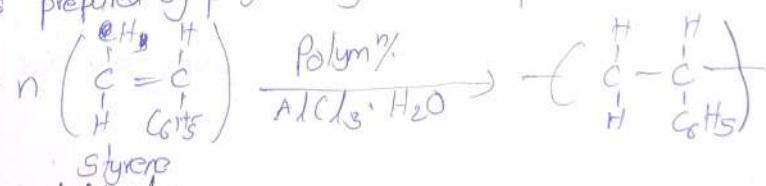


It is stereo regular and highly crystalline. It possess better hardness, strength, stiffness than polyethylene. It is more resistant than PE.

Uses:- used in producing molded parts and fibres. Its fibres are used in making ropes, combs, blankets and handbags, etc. It is also used for making water pipes, washing machine parts, sterilisable hospital equipments, etc.

Polystyrene:

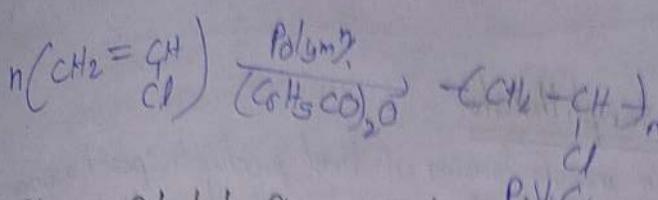
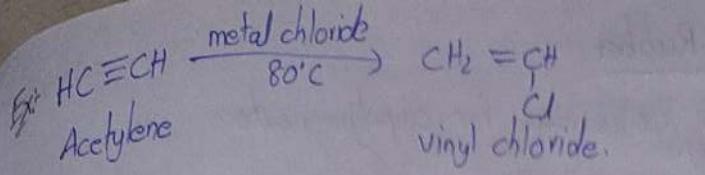
It is prepared by polymerising styrene in presence of AlCl_3 and H_2O .



Poly vinyl chloride:

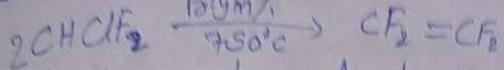
It is prepared by polymerising vinyl chloride in presence of small amount of benzoyl peroxide or hydrogen peroxide under pressure.

Vinyl chloride is obtained by treating acetylene with HCl in presence of metal chloride at 80°C .

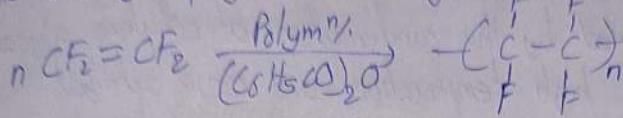


Teflon: Poly tetra fluoro ethylene (PTFE) P.V.C.

It is obtained by pyrolysis of chlorodifluoromethane.



This undergoes polymerisation to give Teflon.

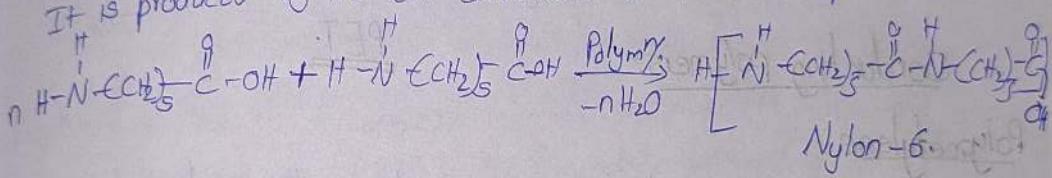


Teflon

Nylon 6/6: For preparation example of condensation polymerisation

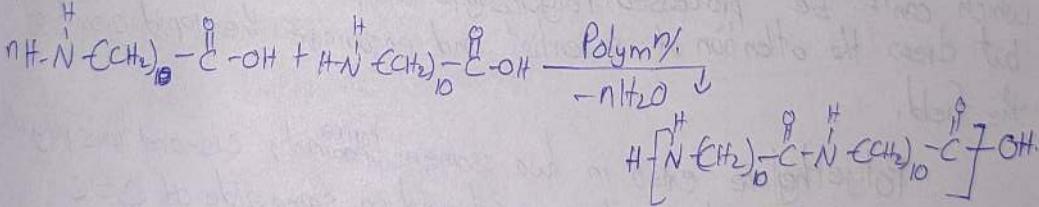
Synthesis of Nylon-6:

Synthesis of Nylon-6:
It is produced by the cell condensation of ϵ -amino caproic acid



Nylon-11

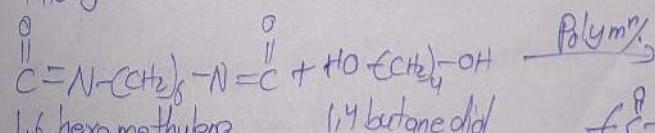
It is made by self condensation of ω -amino undecanoic acid.



Polyurethane:-

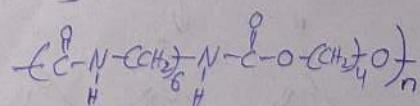
Nylon 11

Polyurethane: These are obtained commercially by linking di-isothiocyanate and di-ol. For example Perlon-U (crystalline polymer) is obtained by the reaction of 1,4 butane di-ol and 1,6 hexamethylenedioisothiocyanide.



1,6 hexamethylene diisothiocyanate

1,4 butone diol



Perlon-U.

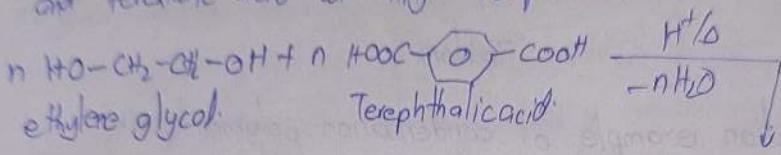
Synthesis of Synthetic Rubber

Buna-S γ -ray for example for copolymerisation.
Buna-N

PET: Polyethylene terephthalate

PET is mainly used in manufacturing of food products, packaging materials such as fruit and drink container. It is light weight transparent and also available in various colours. It belongs to poly-ester family.

It is a condensation polymer also known as Terylene, dacron or Terene. It is obtained by the condensation of ethylene glycol and terephthalic acid at high temperature and acid catalyst.

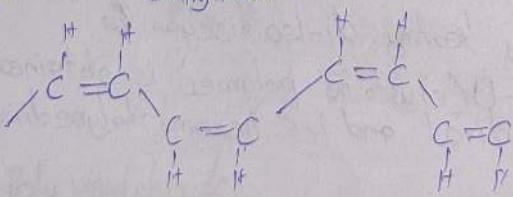


Conducting Polymers:

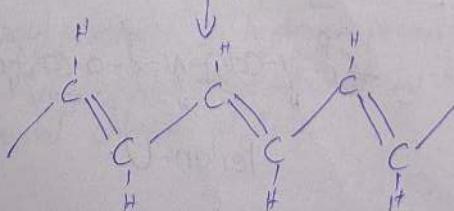
Polyacetylene:

It is the first conducting polymer to be synthesised. In its linear form, it ppt as a black insisive and infusible powder which can't be processed. Polyacetylene did not mind practical application but drew the attention of scientist and encourage the rapid growth of the field.

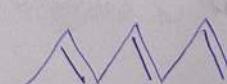
Polyacetylene exists in two isomeric forms namely cis- and trans polyeth



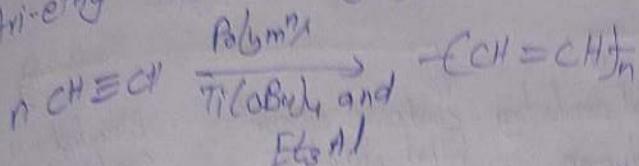
150°C



10°C



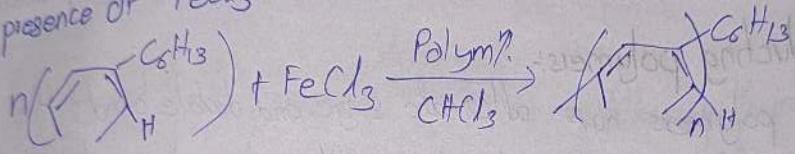
In trans configuration, H-atom are bound on the alternative side of $C=C$.
Synthesis:
 It is synthesised by passing acetylene gas over Ziegler Natta catalyst.
 It is tetrabutoxy Titanium (it is an organo metallic compound) and triethyl aluminium (Et_3Al)



The reaction forms copper coloured cis-polyacetylene at low temperature (78°C).
 At high temp, more stable silver coloured transpolyacetylene is formed (50°C)

Poly-3-hexyl thiophene (P3HT)

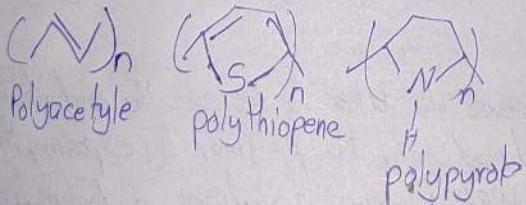
It is prepared by oxidative coupling 3-hexyl thiophene monomer in presence of FeCl_3



Polythiophene and its derivatives are insoluble and infusible. These are semi-conducting polymers. P3HT is most widely employed p-type donor material. They are also used in photo voltaic applications.

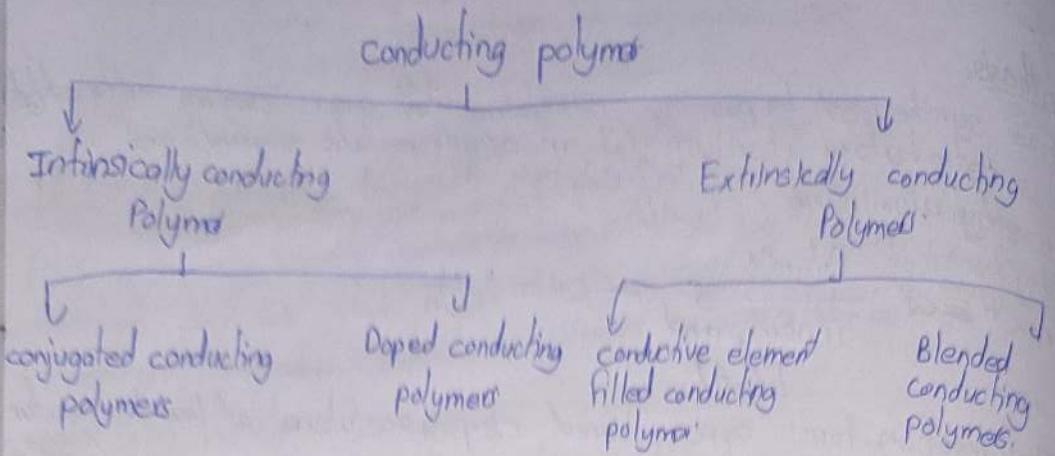
Conducting polymers:

The polymer that conduct electricity.



The presence of conjugation in polymers will make them conductive. The S^\bullet in these polymers have high mobility when the polymer is doped by oxidising or reducing agent which remove or donates sum of the delocalised electrons.

Types of conducting polymers



Intrinsically conducting polymers:-

In these type of polymer, conductivity is due to organic polymer itself. The factor responsible for conductance in these polymers are conjugated electrons. Some example are polyaniline, polythiophene.

Conjugated conducting polymers:-

The conducting polymers have alternate single and double bonds. The p-orbitals in these bonds are delocalised over the entire polymer chain which results in the formation of valence bond and conduction band. When the energy gap b/w the two band is low, the e^- undergo excitation from the lower energy valence band to the higher energy conduction band and show increased conductivity.

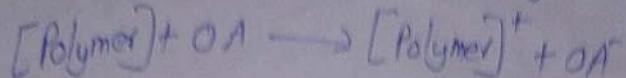
Doped conducting polymers:-

The conductivity of pure conjugated polymer can be increased by a process called doping.

Dopes are chemical species or agents used to increase the conductivity of the polymers. These are introduced into the polymer by exposing the polymer to the dopant. There are two types of dopes by electrochemical or electrochemical oxidation or reduction. They are 2 types of dopes p-type and n-type.

P-type dopants:

These are oxidising agent capable of removing e^- from the valence band to create a positive charge on the polymer backbone.



where OA = $\text{I}_2, \text{Cl}_2, \text{AsF}_5, \text{BF}_3, \text{FeCl}_3$, etc.

n-type dopants:

These are reducing agents which donate e^- to conduction band and make the polymer negatively charged.



where RA = Li, Na, K, etc.

Addition of small amount of dopants to the conjugated product produce a drastic change in the electrical, magnetic and structural property of the polymers.

Extrinsically conducting polymers:

These are prepared by mixing conducting fillers with insulating polymers. The insulating polymer forms the continuous phase and added fillers form the conducting network. A minimum conc. of conducting filler is sufficient to make the polymer conducting, hence, the conductivity of these type of polymers is not due to the polymer matrix but due to the conducting elements which are added.

Conductive element filled polymer:

These polymers are obtained by blending an insulating type of polymer with suitable conducting elements such as carbon black, metallic fibres, metallic oxides, etc. in less amount to make the polymer conducting. The minimum amount of conducting elements required is called percolation threshold.

Blended conducting polymer:

It is obtained by blending a semiconducting polymer with a suitable conducting polymer. Polymers obtained by this method possess better physical, chemical, electrical and mechanical properties which can be easily processed.

Unit-5

XPS : (ESCA)

XPS also known as ESCA is used for analysing the structure of atom and also gives us information about the surface phenomena. It uses electromagnetic radiation in the form of X-ray. X-ray attacks the surface of the atoms thereby ejecting electrons. This is also called as photoelectric effect.

Principle:

XPS is a surface sensitive quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical and electronic state of the element.

It is obtained by irradiating the material with a beam of X-rays and simultaneously measuring the kinetic energy and the no. of electrons that escapes from top 0 to 10nm of the material being analysed. The penetration top of these photons in solids is limited to few micromes. Thus interaction takes place b/w the incident photon and the atoms in the surface leading to photoelectric emission of electrons.

From the KE of the emitted electrons, the binding energy is calculated as follows.

$$E_{\text{Binding}} = E_{\text{photon}} - (E_{\text{KE}} + \phi)$$

E_{Binding} - binding energy of electron.

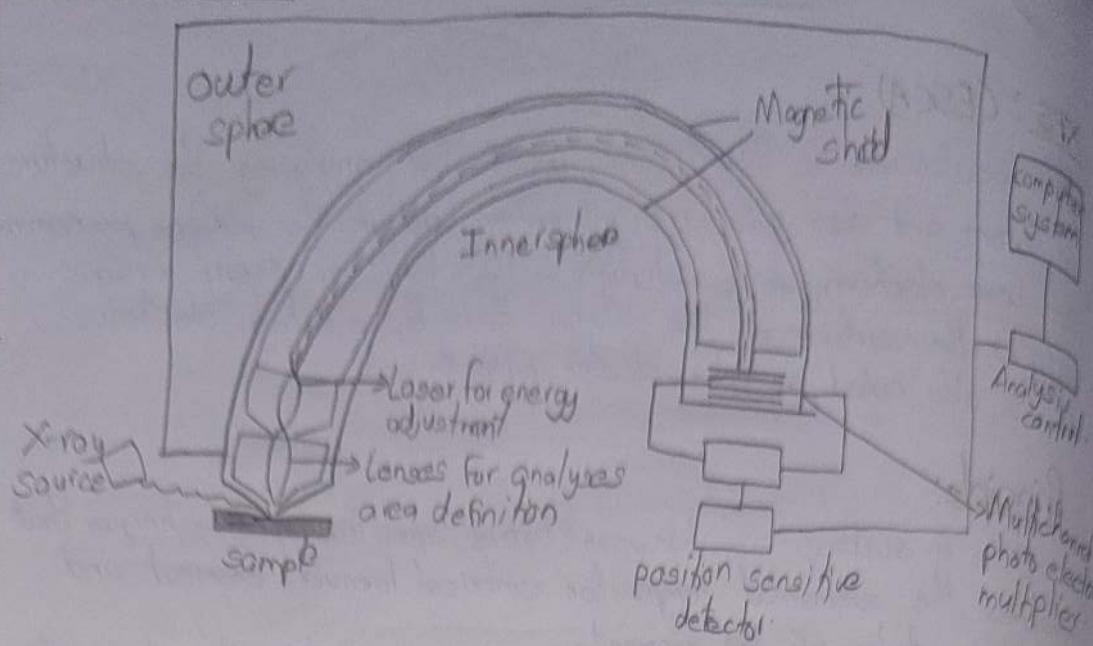
E_{photon} - the energy of incident photon.

E_{KE} = energy of emitted e measured by the instrument.

ϕ = work function depend on spectrometer and the material.

Instrumentation:-

Instrumentation:

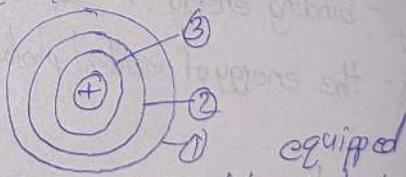


XPS contains the following components

- 1) Source
- 2) sample holder
- 3) Energy analyser
- 4) Electron detection
- 5) Ultra high Vacuum system

Source:

- ① He(I) and He(II) \rightarrow singly and doubly ionised helium for removing valence e^- to produce ions.
- ② Ytrium - M - Zeta - X-rays can cause ejection of outer core e^- .
- ③ AlK_α and CrK_α - Most energetic radiations to reach the inner shells causing ionisation



The simplest X-rays for XPS spectrometers are X-ray tube, circled with Mg or Al targets and suitable filter (monochromators). Al and Mg targeted tubes are generally used without a monochromator because of high intensity and narrow wavelength of bands.

Sample holder:

Solid samples are mounted in a fixed position as close to photon or e^- source and the entrance slit of the spectrometer as possible.

3) Energy analyser:
The energy analyser is placed b/w the sample and the detector. It should be very sensitive to identify the e^- being that is coming out of the sample. Most of the e^- spectrometers are of hemispherical type in which the e^- beam is reflected by an electrostatic magnetic field in such a manner that the e^- travel in a curved path.

Energy analyser has two conc. metal cylinder at different voltages. One of the metal cylinders will have +ve voltage and the other will have zero voltage. This will create an electrical field the two cylinders. When the e^- pass through the metal cylinders they will collide with one of the cylinders or they will just pass through. If the e^- velocity is too high it will collide with outer cylinder. If the e^- are going too slow then it will collide with inner cylinder. Only the e^- of right velocity will go through the cylinders and reach the detector.

Detectors:
The e^- multiplier is usually employed as a detector due to its sensitivity and convenience.

high vacuum system:-
The ultra high vacuum environment will prevent the contamination of the surface and provide an accurate analysis of sample. It will allow the photoelectrons to travel from the surface of the sample to the detector without striking a gas atom.

Working:-
In XPS, when the sample kept in ultrahigh vacuum is eliminated by the photons of energy, the surface of the sample emits e^- s called photo electrons. While leaving the atom some energy of the e^- is consumed in overcoming the coulombic attraction of nucleus their by decreasing its kinetic energy at this time the outer orbitals readjust and deliver the extra energy to the outgoing electrons. Then these e^- s travel through the analyser and reach the detector. The signal is amplified and the spectrum is obtained by determining the KE and the no. of e^- s escaping from top 0 to 10 nm of the sample under investigation.

Applications:

- 1) XPS is useful in the qualitative determination of chemical state, surface absorption, chemical structures, chemical bonding, etc.
- 2) It is useful in the quantitative determination of elemental composition of various organic and inorganic materials
- 3) It is useful in the identification of elements in the periodic table
- 4) It is also used in the determination of oxidation state of an element as well as the type of species to which it is bonded.
- 5) It is also used for analysing metal alloys, semiconductor, biomaterials, medical implants, etc.

X-ray diffraction:

$$n\lambda = 2ds \sin\theta$$

Bragg's Equation:

Bragg pointed out that scattering of X-ray by crystal is considered as reflection from successive plane of atoms in the crystals. These reflection will take place only at certain angles which are determined by the wavelength of X-ray and the distance b/w the planes in the crystal.

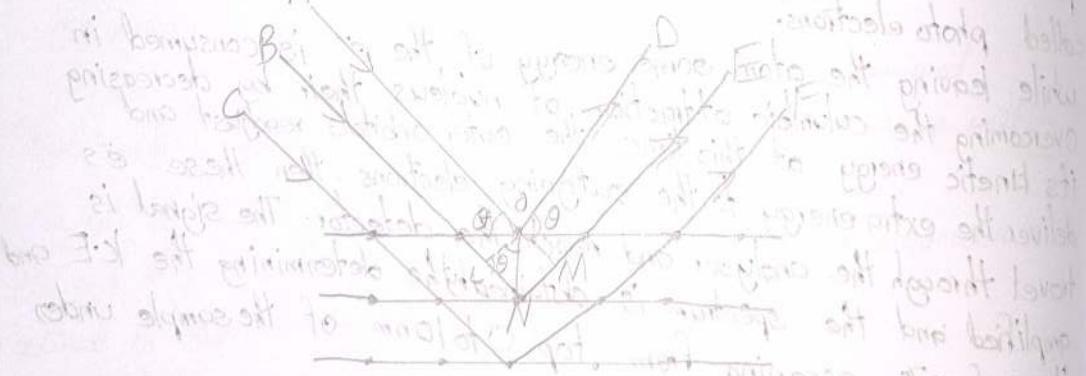
Definition:

The equation which gives a simple relation b/w the wavelength of X-rays, the interplanar distance in the crystals and the angle of reflection is known as Bragg's equation.

$$n\lambda = 2ds \sin\theta$$

A

D



X-ray reflection from the crystal.

In the above diagram Horizontal line represents parallel plane in crystal structure separate from one another with distance d . A beam of X-ray falls on the crystal at an angle θ some of these X-rays will be reflected from the upper plane at the same angle θ , while some others get reflected from the successive layers as shown.

Let the planes A, B, C are incident rays and D, E, F are reflected rays. OL and OM are the lines drawn for the incident and reflected beams. The waves reflected from the 1st two planes related to wavelength is as follows.

$$LN + NM = n\lambda$$

Since the triangles OLN and ONM are congruent.

$$LN = NM$$

$$\text{Hence } 2LN = n\lambda \quad (\text{or}) \quad 2ds\sin\theta = n\lambda.$$

Miller Indices:

Unit cell:

If it is the most basic repeating structure of any solid.

Lattice:

If the unit cell repeats that network is called lattice.

Crystal plane:

some imaginary planes inside a crystal in which large conc. of atoms exists in certain directions. These directions are called crystal direction.

$(h k l)$ - represents family of planes.

$[h k l]$ - represents a direction

$<h k l>$ - represents family of direction

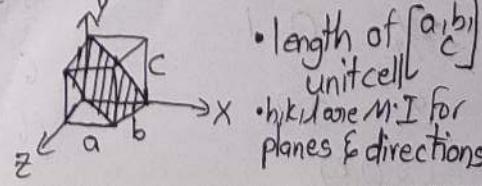
Definition of M.I.: $(h k l)$ - represents a plane

M.I. of the plane indicated by $(h k l)$ are given by reciprocal of the intercept of the plane on the 3-axis. It is usually refers to the plane nearest to the origin.

(Miller introduced a system to designate a plane in the crystal. he introduced a set of 3 numbers to specify a plane in a crystal. These set of 3 numbers are known as M.I. of consened plane.

X, Y and Z are the axis.

a, b, c are the lattice parameters.



Determination of MI:

Step-1 write the intercepts on the Z-axis

Step-2 write the reciprocal of intercept

Step-3 find the least common denominator and multiply the reciprocal by L.C.M.

Step-4 MI

find MI, for the parameters $a=2$, $b=3$, $c=2$

x	y	z	a	b	c
2	3	2	1/2	1/3	1/2
1/2	1/3	1/2	1/2	1/3	1/2

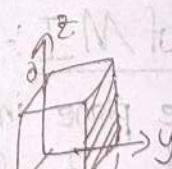
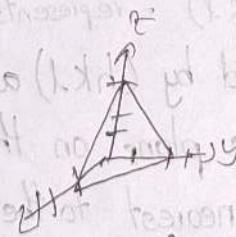
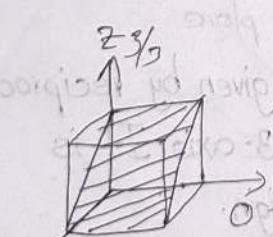
$$\frac{1}{2} \times 6 \quad \frac{1}{3} \times 6 \quad \frac{1}{2} \times 6 \quad (2) \quad (0) \quad (1)$$

(3 2 3)

x	y	z	a	b	c
1/4	1/4	1/2	3	1	2
1/4	1/2	1/2	1/3	1/3	1/2
4	1	2			

(4 1 2)

(2 6 3)



$\frac{2}{3}, 0, \frac{3}{3}$
 $\frac{3}{2}, 0, 1$
 $3, 0, 2$
 $(3, 0, 2)$

$\frac{1}{3}, \frac{2}{3}, \frac{3}{3}$

$\frac{3}{2}, 1, 1$

$(6, 3, 2)$

The spacing b/w planes in a crystal is known as inter-planar spacing.
It is denoted as d_{hkl}
for cubic $\frac{1}{d_{hkl}^2} = \frac{1}{a^2}(h^2+k^2+l^2)$

for tetragonal $\frac{1}{d_{hkl}^2} = \frac{1}{a^2}(h^2+k^2) + \frac{1}{c^2}(l^2)$

Applications of M.I.:

M.I influences optical properties, reactivity, surface tension and dislocation.

Problem based on inter-planar spacing:-

Find the value of inter-planar spacing for (2 3 1) plane of a fcc sta. whose atomic radius is 0.125 nm.

formula. $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$

$$a = 2\sqrt{2}r$$

$$a = 2\sqrt{2} \times 0.125$$

Given. $r = 0.125 \text{ nm}$

$$(h k l) = (2 3 1)$$

$$= 0.25 \times \sqrt{2}$$

$$= \frac{1}{4} \times \sqrt{2} = \frac{1}{2\sqrt{2}}$$

$$= \frac{1}{2\sqrt{2}(\sqrt{4+9+1})} = \frac{1}{2\sqrt{2}(\sqrt{14})} = 0.0944.$$

Calculate the inter-planar spacing b/w (2 2 1) plane of cubic lattice of edge length 450 pm.

$$\frac{1}{d_{hkl}^2} = \frac{1}{450} (4+4+1) = \frac{9}{450} = 0.02 \quad \therefore d_{hkl} = \sqrt{450}$$

Find the inter- (1 1 0) plane lattice par. 4.242 \AA

Bragg equation problems:-

A beam of X-ray of wavelength $\lambda = 0.07\text{nm}$ is diffracted by (110) plane of rock salt (FCC) with lattice constant a_0 of 0.28nm . Find the glancing angle for second order diffraction.

$$\lambda = 0.07\text{nm}$$

(110)

$$a = 0.28\text{nm}$$

$$n = 2$$

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

$$\frac{2(0.28)}{\sqrt{2}} \sin\theta = 2(0.071)$$

$$\sin\theta = \frac{(0.071)\sqrt{2}}{0.28} = 0.358$$

$$\theta = 20.97^\circ$$

→ The angle at which the first order Bragg reflection is observed from (110) plane in a simple cubic unit cell of side length 3.238A . The wavelength of radiation passed is 2.29A° . Find the glancing angle.

$$\lambda = 2.29 \quad (110) \quad \frac{1}{d^2} = \frac{1}{a^2} (h^2 + k^2 + l^2)$$

$$a = 3.238 \quad n = 1$$

$$\frac{1}{d^2} = \frac{1}{(3.238)^2} (52)$$

$$\frac{2(3.238)}{\sqrt{2}} \sin\theta = 2.29$$

$$\sin\theta = \frac{1}{2}$$

$$d = \frac{3.238}{\sqrt{2}}$$

$$\theta = 30^\circ$$

Mechanical properties of solids:-

Rigid body:

It is an idealisation of a solid body in which deformation is neglected. In other words the distance between any two given points of a rigid body remains constant regardless of the external forces exerted on it.

Elasticity:

The property in which the body opposes the deforming forces and regains its original shape and size when the applied force is removed is called elasticity.

Ex: rubber band, spring, etc.

These property is different for different materials.

Plasticity:

The property possessed by a body due to which it does not regain its original shape and size and remains in the deformed state even after the removal of external forces is called plasticity.

Ex: wax, etc.

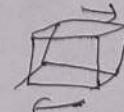
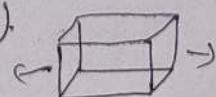
Stress:

It is the restoring force acting per unit area inside the body. This restoring force is equal and opposite to the applied force. Therefore $\text{Stress} = \frac{\text{deforming force}(F)}{\text{area}(A)} = \frac{F}{A}$ N/m² (or) Pa

Types of stress:

1) Normal stress: This leads to either decrease or increase in dimension. They are 2 types: 1) tensile stress (Yes in length) 2) compressive stress (Yes in length)

2) Tangential stress: when deforming force acts tangential to the surface of the body (no change in length or cross-sectional area, but only shape changes).



Strain:

The change in dimension or shape of a body due to the deforming force results in strain. It is measured by the ratio of change in dimension to the original dimension.

$$\text{Strain} = \frac{\text{change in dimension}}{\text{original dimension}} \quad (\text{No units})$$

Types of Strains:

They are 3 types

Linear strain :- change in length per unit length

$$\text{Linear strain} = \frac{\Delta l}{l}, \text{ shearing} = \frac{\Delta \theta}{A}$$

Shearing strain: It is change in area per unit area

Bulk strain :- change in volume per unit volume

$$\text{Bulk} = \frac{\Delta V}{V}$$

Elastic limit:

The max stress upto which a body exhibits the property of elasticity is called elastic limit.

Hooke's law:

It states that "within the elastic limit, stress in a body is directly proportional to strain produced on it".

Stress & strain

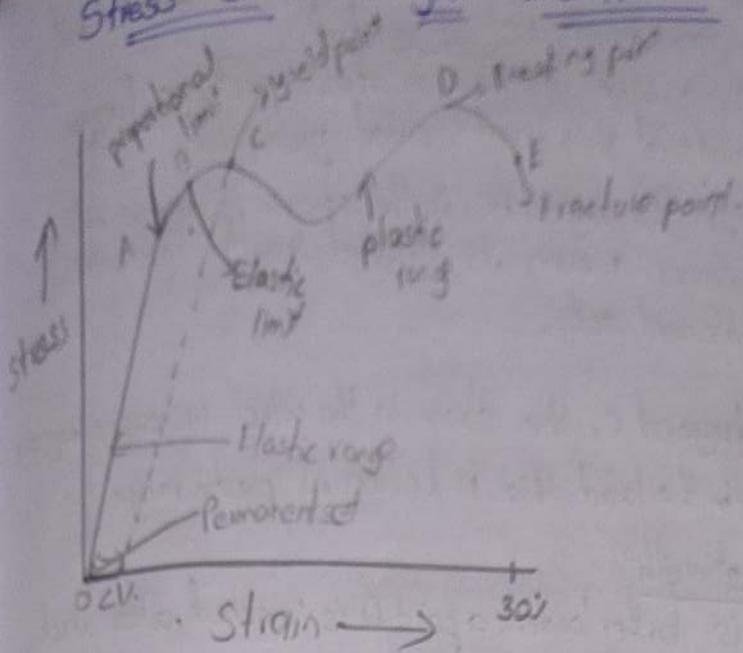
$$\text{stress} = \text{const} \times \text{strain}$$

$$= E \times \text{strain} \quad (E = \frac{\text{stress}}{\text{strain}})$$

E = coeff of elasticity (modulus of elasticity)



Stress-Strain Diagram and its uses:-



Consider a wire which is rigidly fixed at one end it is loaded at the other end. The strain produced for the different loads are noted until the wire breakdown.

A graph is drawn b/w strain along x-axis and stress along y-axis. This is known as stress-strain graph. From this diagram we get useful informations about the behaviour of solid materials.

Point ①: Hooke's law, the portion OA of the curve is a straight line in this region [stress & strain] this means that upto OA the material obeys Hooke's law. The wire is perfectly elastic. The point A is called limit of proportionality.

②) Elastic limit: The stress is further less till point B. The point B lying near to A denotes the elastic limit. Upto this point a wire regains its original length if the stress is removed. If the wire is loaded beyond this limit then it will not restore its original length.

yield point: on further increasing the stress beyond the elastic limit the curve bends and points 'c' is reached. In this region, a slight increase in stress produces large strain in the material this point is called yield point.

Permanent set: In the region BC, if the stress is removed the wire will never regain its original length. The wire will take a permanent set.

plastic range: beyond c, the strain in the wire increases rapidly without increase in the load this is known as plastic range.

Ultimate tensile strength:

If the wire is further loaded, a point D is reached, after which the wire begins to neckdown. Hence its cross-sectional area will no longer remain uniform. At this point the wire begins to thin down at some point and finally breaks, at this point the stress developed is maximum and is called breaking point.

Fracture point:

The point E, is known as fracture point here the wire breaks down completely.

Uses:

- It is used to measure the elastic strength, yield str, and tensile strength of metals.
- It is used to estimate the working stress and safety factor of an engineering material.
- The area under the curve in the elastic region gives the energy required to deform it elastically and the area under the curve in the plastic region gives the energy required to deform plastically.
- This diagram is also used to identify the ductile and brittle materials.

Tensile strength:

It is defined as the max value of stress which stand by the material before fracture under a steady load.
usually the tensile strength of metal and alloys increases on cooling and decreases on heating.

Tensile strength = $\frac{\text{Maximum tensile load}}{\text{original cross-sectional area}}$

It is the ratio b/w ultimate tensile stress and the working stress

$$\text{Safety factor} = \frac{\text{Ultimate tensile stress}}{\text{Working stress}}$$

Types of Modulus of elasticity:

1) Young's modulus of elasticity (γ)

2) Bulk modulus of elasticity

3) Modulus of Rigidity.

Young's modulus of elasticity (γ):

It is the ratio of tensile or compressive stress to longitudinal strain within the limits of elasticity.

$$\gamma = \frac{\text{Tensile stress}}{\text{Longitudinal strain}} = \frac{\sigma}{\epsilon} = \frac{F}{A} \times \frac{L}{\Delta L} \text{ N/m}^2 \text{ (or) Pa}$$

$$\sigma = FA \quad \epsilon = \frac{\Delta L}{L}$$

Bulk modulus of elasticity (K):

It is the ratio of normal stress to volumetric strain within the elastic limit.

$$K = \frac{F_A}{A} \times \frac{\Delta V}{\Delta V} = \frac{F_A}{A} \times \frac{-V}{V}$$

$$K = \Delta P \times \frac{\Delta V}{\Delta V} \text{ N/m}^2 (\Delta P = FA)$$

Modulus of Rigidity (η):

It is the ratio of tangential stress to shearing strain within the elastic limit.

$$\eta = \frac{\text{Tangential stress}}{\text{Shearing strain}} = \frac{T_{xy}}{\gamma_{xy}} \quad T_{xy} = F/A \quad \gamma_{xy} = \Delta y/y$$

$$\eta = \frac{F \cdot A}{A \cdot \Delta x}$$

Compressibility

This is the property of material reciprocal of its bulk modulus elasticity ($N^{-1} m^2$ units)

$$C = \frac{1}{K} N m^{-2}$$

Generally solids are more elastic than gases for liquids, the modulus of elasticity is zero.

Poisson's Ratio:

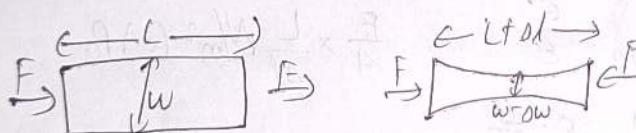
When we apply force on a body, the length changes in the direction of applied force but compresses in the direction opp. to that of applied force. This is called Poisson's effect. This is expressed as

$$\gamma = -\frac{\text{Lateral strain}}{\text{Longitudinal strain}}$$

-ve sign indicates compressive deformation.

If the sign tensile deformation it can also be written as

$$\gamma = -\frac{\text{change in length}}{\text{change in width}}$$



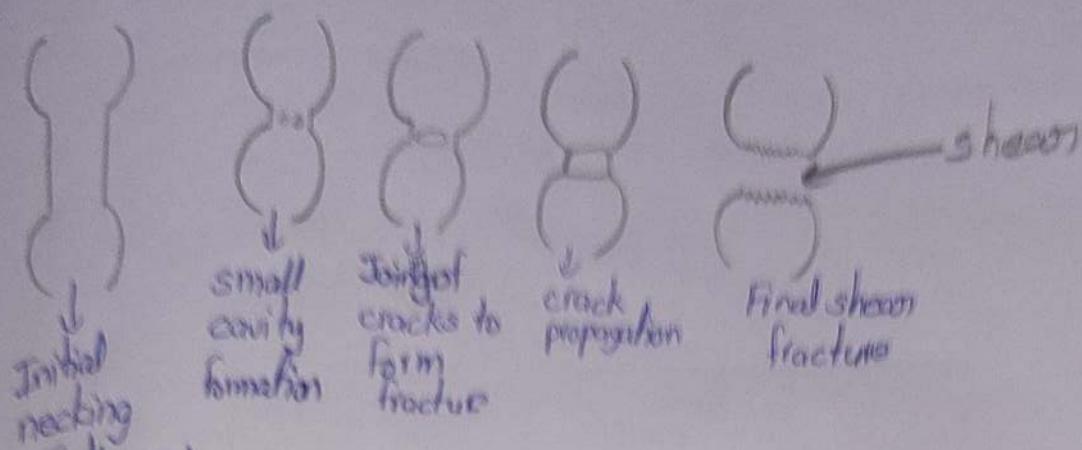
Fatigue & creep:

To understand Fatigue and creep we should know about fracture. It is the separation of a body into 2 or more pieces in responds to the stress. we have 2 types of fractures.

(Ductile fracture & Brittle fracture)

Ductile fracture occurs with plastic deformation and the crack is a stable one. It grows and propagate by absorbing energy.

Brittle fracture occurs with no plastic deformation is an unstable crack and absorbs low energy.



Fatigue:

Fatigue is the initiation and propagation of cracks in the material due to cyclic loading. Once the fatigue crack is initiated, it grows with each loading cycle, producing strains in some part of the fracture surface. The crack will continue to grow until it reaches a critical size producing rapid propagation and typically complete fracture of the structure.

Creep:

It is defined as the property of a material by which it deforms continuously under a steady load. progressive and slow plastic deformation takes place. Usually creep occurs at high temperature. This property is very much useful in designing internal combustion engine, jet engine, boilers and turbines.

Ni, Fe, Cu and their alloys exhibits this property at elevated temperatures whereas Zn, Sn, Pb and their alloys show this property at room temperature.