

21	Titanium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
22	Vanadium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
23	<del>Titanium</del> Chromium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
24	Chromium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
25	Manganese	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
26	Iron	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
27	Nickel	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
28	Cobalt	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
29	Copper	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
30	Zinc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

- The group of elements lying in the middle of the periodic table from group 3 to 12 are called Transitional Elements.
- They have intermediate characteristics properties between the most Electropositive s-block elements & least electropositive p-block elements.
- Here, the last electron enters into the penultimate shell. Ex:- Iron(Fe), Copper(Cu), Chromium(Cr), etc.
- The outermost electronic configuration of the Transition elements can be written as:  

$$\boxed{(n-1)d^{1-10} n s^{\frac{1}{2} or \frac{2}{2}}}$$
- Transitional Elements are classified into 4 series  
 They are:-  
 $\Rightarrow$

1) 1<sup>st</sup> Transition series (3d series)  
— includes 10 elements from Sc (21) to Zn (30)

2) 2<sup>nd</sup> Transition series (4d series)  
— includes 10 elements from Yttrium (39) to Cd (48)

3) 3<sup>rd</sup> Transition series (5d series)  
— includes 10 elements they are:  
Lanthanum (La (57)) &  
from Hafnium (Hf (72)) to Mercury (Hg (80))

4) 4<sup>th</sup> Transition series

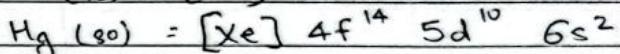
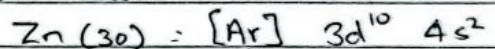
The group of elements in which the last electrons enter into anyone of the d subshell i.e. (n-1)d are collectively called d-block elements

4) 4<sup>th</sup> Transition series:

— includes all the Lanthanides & Actinides having incompletely filled f-orbital. They are also known as inner Transition elements

Q1) Which of the 3d-series elements is not true / non typical transitional element & why  
→ Zn (30)

Q2) which of the Transition elements are non typical or not true transitional elements  
→ The electronic configuration of Zinc, Cadmium & Mercury are shown below..



As we know that, to be a true Transition element, it should have incompletely or partially filled (n-1)d orbitals. The given elements have completely filled (n-1)d orbitals (i.e. - n-1 d<sup>10</sup>) So, they do not show the properties shown by true Transition elements like variable oxidation states, color formation, paramagnetic properties, etc.

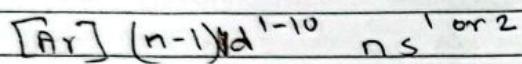
However, they show some of the properties like that of true Transition elements like: complex formation, alloy formation, catalytic behaviour, etc. So, they are studied together.

## (2 Questions Sure)

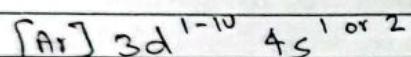
Date \_\_\_\_\_  
Page \_\_\_\_\_

### \* Electronic Configuration of 3d series elements :

General electronic configuration of 3d series :-



i.e.



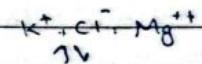
Elements	Symbol (At. No.)	Electronic configuration
Scandium	Sc (21)	$[\text{Ar}] 3\text{d}^1 4\text{s}^2$
Titanium	Ti (22)	$[\text{Ar}] 3\text{d}^2 4\text{s}^2$
Vanadium	V (23)	$[\text{Ar}] 3\text{d}^3 4\text{s}^2$
Chromium	Cr (24)	$[\text{Ar}] 3\text{d}^5 4\text{s}^1$ Half filled
Manganese	Mn (25)	$[\text{Ar}] 3\text{d}^5 4\text{s}^2$
Iron	Fe (26)	$[\text{Ar}] 3\text{d}^6 4\text{s}^2$
Cobalt	Co (27)	$[\text{Ar}] 3\text{d}^7 4\text{s}^2$
Nickel	Ni (28)	$[\text{Ar}] 3\text{d}^8 4\text{s}^2$
Copper	Cu (29)	$[\text{Ar}] 3\text{d}^{10} 4\text{s}^1$ Full filled
Zinc	Zn (30)	$[\text{Ar}] 3\text{d}^{10} 4\text{s}^2$

**NOTE:** Half-filled & full-filled orbitals are more stable & hence such configurations are acquired wherever possible. For eg:- Chromium, Copper

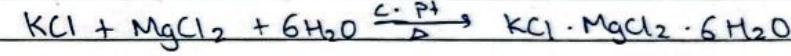
### # Complex, Rare <sup>Earth</sup> Elements and Metal Alloys.

When two normal salt solutions are mixed in an equimolar ratio (molar concn same (N or M)) & then heated upto the crystallization point then the crystals of new compound will be obtained known as Additional Compound. Based on ionization behaviour of these additional compounds, they are classified into two types:-

- 1) Double Salt (Lattice Compound)
- 2) Complex Salt (Coordination Compound)



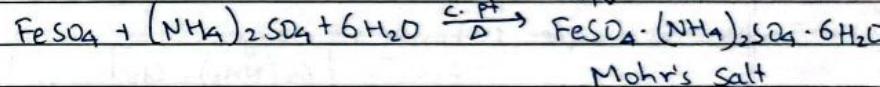
IV



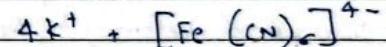
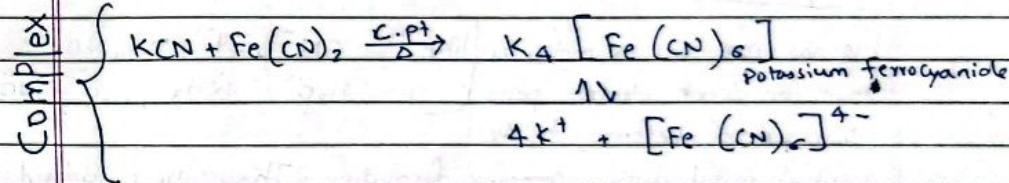
Carnallite



IV



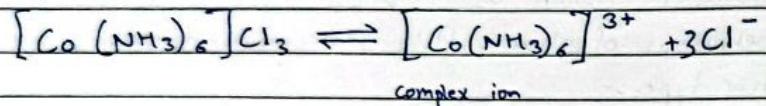
Mohr's salt



Not for Exam

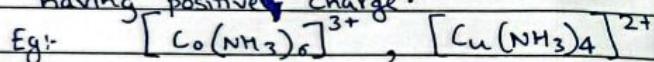
Complex compounds are the compounds that can give complex ions in aqueous sol<sup>n</sup>. Metals (usually Transition Metals) have the strong tendency to get attached with definite number of ions or molecules forming closely associated charged spheres known as cation or anion. These ions are called complex ions.

Eg:

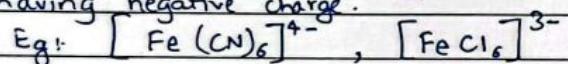


Complexes are of 3 types:

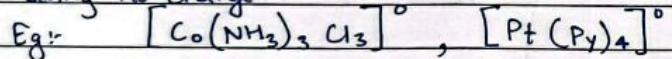
1) Cationic Complex : having positive charge.



2) Anionic Complex : having negative charge.



3) Neutral Complex : having no charge



### \* Ligands.

Ligands are ions or molecules like:  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$   
that can donate electron pairs ( $\text{H}_2\ddot{\text{O}}$ ,  $\ddot{\text{N}}\text{H}_3$ ,  $\text{C}\ddot{\text{O}}$ ,  $\ddot{\text{N}}\text{O}$ ) (one pair of electrons) to the central metal during complex formation. They are considered to be Lewis bases (electron pair donor).

### 1) Werner's Theory : [Not for Exam]

In 1893, Alfred Werner gave a theory to describe the structure and properties of complexes. This theory is known as Werner's Theory. It is mainly dependent on the following postulates:-

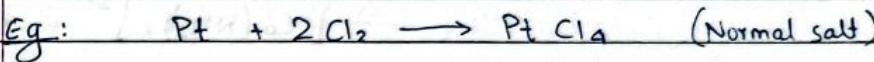
#### • Postulates of Werner's Theory:

a) Metals possess two different types of valencies:-

↳ Primary valency / Principal valency / Ionizable valency

↳ Secondary Valency / Auxiliary Valency / Non-ionizable valency

By using primary valency only, metal forms a normal salt whereas by using both the valencies (Primary & secondary) metal forms a complex salt.



$$\text{Pt} = \text{P.V.} - \text{O.S.} = +4$$



(complex salt)

$$\text{Pt} = \text{P.V.} - \text{O.S.} = +4$$

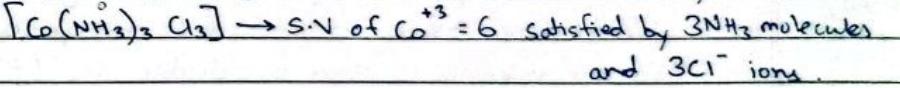
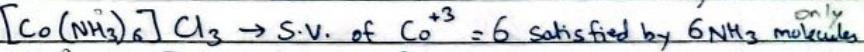
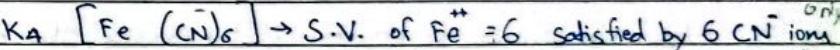
$$\text{S.V.} = \text{C.N.} = 6$$

#### b) Characteristics of secondary valencies :-

↳ Secondary valency is the coordination number (number of ligands attached) of the Central Metal Atom or Ion.

↳ The species satisfying secondary valency can be ions only, molecule only, or can be both.

Eg:



↳ The species satisfying secondary valency are always written inside big brackets, they do not ionize in aqueous sol<sup>n</sup> and hence, they never occur in free form.

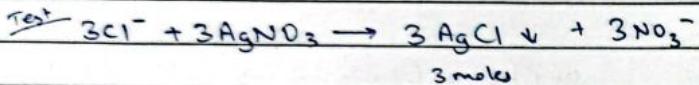
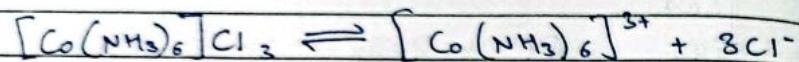
↳ They are directional in nature i.e. They get oriented at fixed position around the metal giving certain geometry to the complex.

↳ While writing the structure of complexes, the attachment between

### c) Characteristics of Primary Valency :-

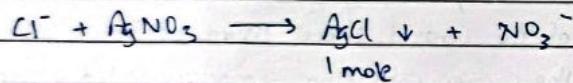
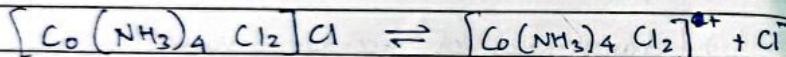
- Primary Valency is the oxidation number of central metal ion.
- It is always satisfied by anions.
- The species satisfying primary valency only are written outside big bracket, ionize in aqueous sol<sup>+</sup> & hence they give specific test with suitable reagent.

Eg:



- If the species satisfying P.V also satisfies S.V then, it is written inside big bracket, do not ionize in sol<sup>+</sup> & Hence do not give specific test with suitable reagent.

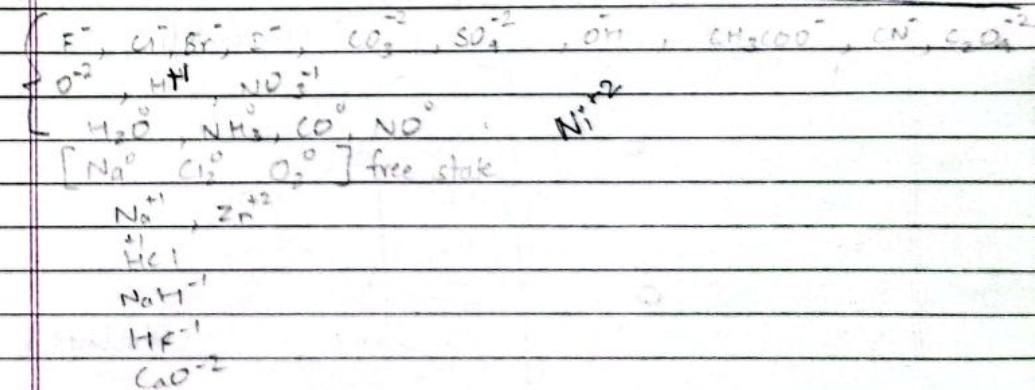
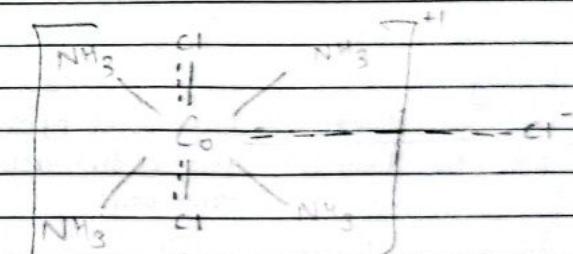
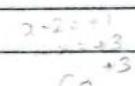
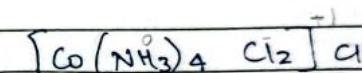
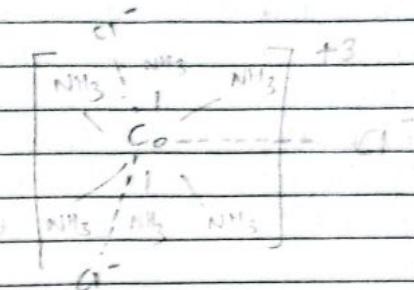
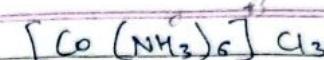
Eg:



- They may or may not occur in free form.

- They are non-directional in nature.

- While writing the structure of the complex, the attachment between the metal & the species satisfying P.V. only is given by dotted/broken line (.....) & with the species satisfying both the valencies is given by double line (----).



## \* Types of Ligands

Depending on the nature of ligands to donate electron pairs to the central metal, they can be classified as:

### 1) Monodentate Ligand:

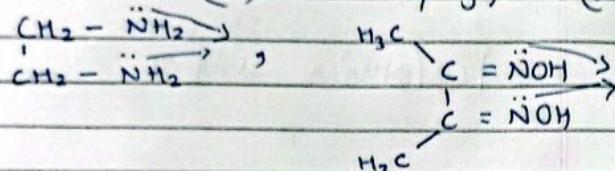
If ligand donates electron pairs from only one side site.

Eg:-  $X^-$  (Cl, Br, I, F),  $CN^-$ ,  $NO_3^-$   $\rightarrow$  -ve ligand  
 $H_2O$ ,  $NH_3$ , CO, NO, etc.  $\rightarrow$  neutral "

### 2) Bidentate Ligand:

If the single ligand can donate electron pairs from two sites.

Eg:- Ethylene diamine (en) Dimethyl glyoxime (DMG)

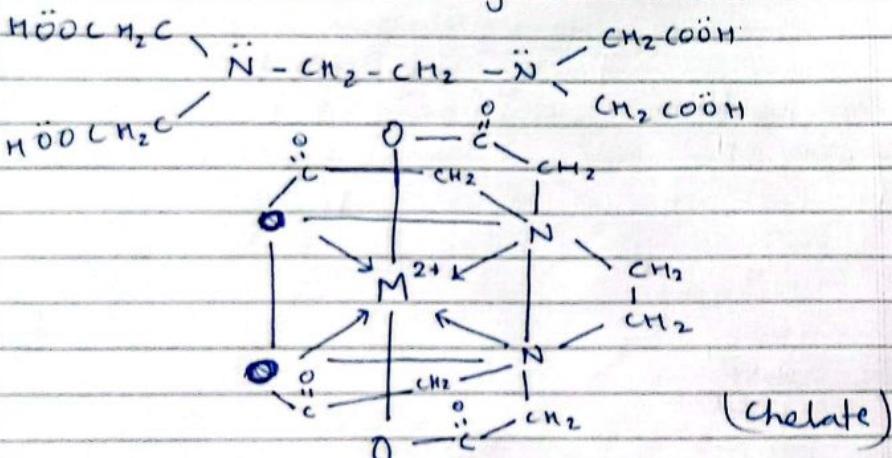


### 3) Polydentate Ligand:

If the ligand can donate electron pairs from more than two sites.

Eg:- Ethylene diamine tetra acetic acid (EDTA)  
tetraacetate

is a hexadentate Ligand.

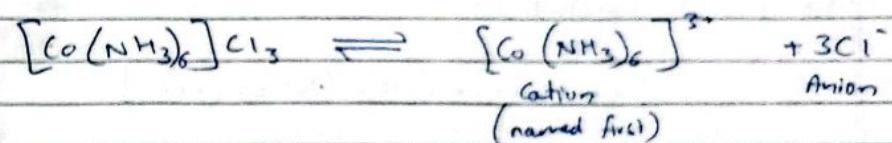
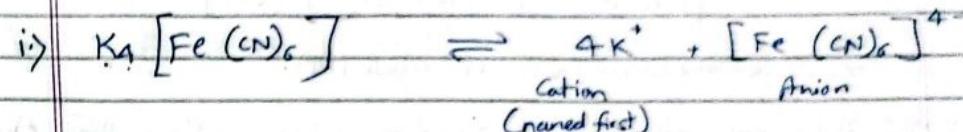


if, the complexes are formed by using polydentate ligands then such ligands are said to be Chelating Ligands and thus formed complexes are chelates. They are more stable than the complexes formed with monodentate ligand.

=||

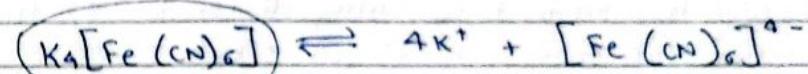
## Nomenclature of Complex Compound

Complex compounds are named on the basis of IUPAC rule as given below:



Rule:

1) If the complex compound shows ionization behaviour, then cation should always be named first



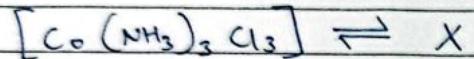
$\rightarrow$  Tetrapotassium hexacyanoferrato ion  $\rightarrow$  Potassium hexacyanoferrate (I)



$\rightarrow$  Hexammine  
 Hexammine Cobalt (III) chloride

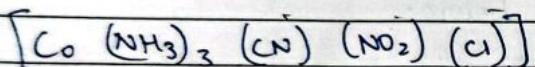
## Point (x)

2) If the complex does not show ionization behaviour then cation should be name they should be written in a single word without using any commas, space, —, etc.



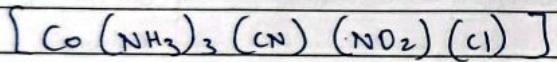
→ Triaminetrichloro cobalt (III)

3) Inside coordination sphere, ligands are named first followed by the name of metal.



→ Triammine chlorocyanonitrito cobalt (III)

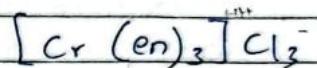
4) If there are more than one type of ligand then they should be named alphabetically



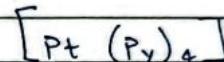
→ Triamminechlorocyanonitritocobalt (III)

5) If the simple ligand repeats more than one time then they should be prefixed by using "di" for two, "tri" for three, "tetra" for four, "hexa" for six.

6) In case of neutral organic ligands or complex ligands having already di, tri, tetra terms in their names are prefixed by using bis (for 2), tris (for 3), tetrakis (for 4), pentakis (for 5). Name of the Ligand is then written by its usual name enclosed inside small brackets ( ).



→ Tris(ethylene diamine)chromium (II) chloride



→ Tetrakis(pyridine) platinum (0)

7) If the name of negative ligand end with 'ide' then 'ide' should be converted into 'o'.

Eg:-

Cyanide ( $\text{CN}^-$ ) → Cyano

Chloride ( $\text{Cl}^-$ ) → chloro

Hydroide ( $\text{H}^-$ ) → Hydro

If the negative ligand end with 'ite' or 'ate' then, only 'e' is converted into 'o'

oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) → oxabto

nitrate ( $\text{NO}_3^-$ ) → nitrato

nitrite ( $\text{NO}_2^-$ ) → nitrito

salt sulphate ( $\text{SO}_4^{2-}$ ) → sulphato

- 8) In case of neutral ligands, ammonia ( $\text{NH}_3$ ) is converted to "ammine", water ( $\text{H}_2\text{O}$ ) is converted to "aqua" & other neutral ligands are written by their original names.

Eg:-  
 $\text{CO} \rightarrow$  carbonyl  
 $\text{NO} \rightarrow$  Nitrosyl / Nitroso  
 $\text{PH}_3 \rightarrow$  Phosphine



$\rightarrow$  Tetra carbonyl <sup>nickel</sup> (0)

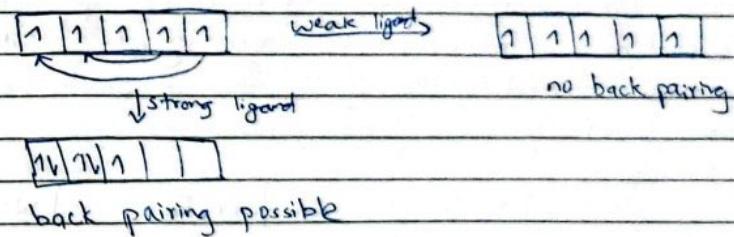
- 9) After naming ligands, the name of the central metal is given followed by its oxidation number in roman inside small brackets ( ).

- 10) If the complex is cationic or neutral then its name is represented by its usual name but in case of anionic complex, the name of the metal should be made to end with "ate".

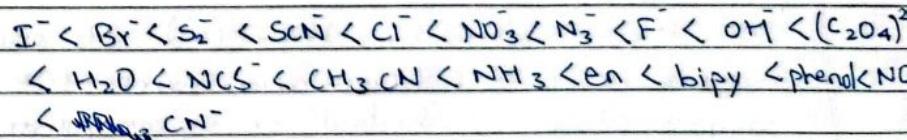
## Qualitative Valence Bond Theory (VBT)

This theory was given by Pauling and is based on the following postulates:-

- 1) The central metal atom or ion provides definite number of empty or vacant atomic orbitals which is equal to the co-ordination number of that metal.
- 2) These atomic orbitals then undergo hybridization to form hybrid orbitals which are also vacant.
- 3) The geometry of hybrid orbital is the geometry of complex.
- 4) Ligands are ions or molecules which can donate electron pairs to the central metal.
- 5) The lobe of orbital of the metal overlaps with Ligand's lobe axially forming Sigma ( $\sigma$ ) bond.
- 6) In presence of weak field ligands like  $\text{H}_2\text{O}$ ,  $\text{X}^-$ , etc. back pairing of unpaired electrons is not possible. However, in presence of strong field ligands like  $\text{CN}^-$ ,  $\text{NH}_3$  or organic ligands, back pairing occurs.



### Spectrochemical Series:



7) If the electronic configuration of the central metal contains one or more number of unpaired electrons ( $n \neq 0$ ) then it is paramagnetic, but if it contains no any unpaired electrons ( $n = 0$ ) are diamagnetic.

Thus, VBT is used to predict the geometry & magnetic property of complexes.

Some of the important complexes are:-

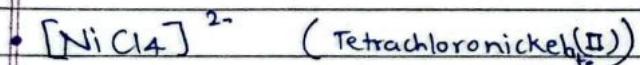
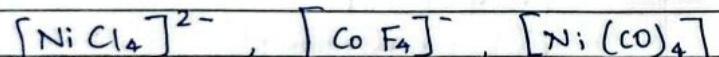
- Tetrahedral complexes ( $sp^3$ ) (C.N=4)
  - Square planar " ( $dsp^2$ ) (C.N=4)
  - Octahedral " ( $d^2sp^3$  or  $sp^3d^2$ ) (C.N=6)
- inner orbital complex                              outer orbital complex

### 1) Tetrahedral Complexes:

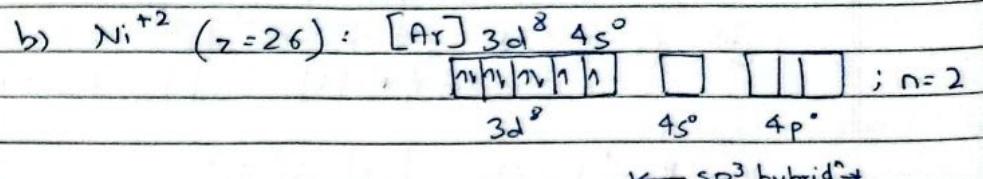
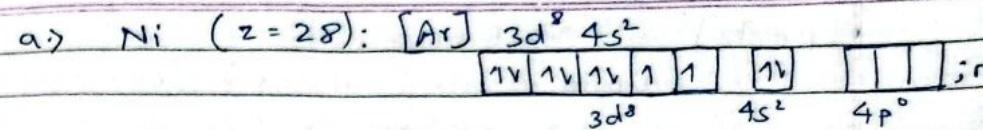
These complexes are formed as a result of  $sp^3$  hybridization.

Generally, they are formed by weak ligands. But sometimes they are also formed by strong ligands in which the central metal has  $(n-1)d^9 / (n-1)d^{10}$  configurations.

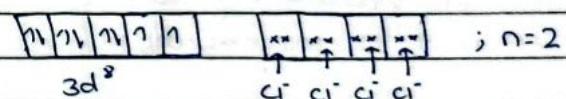
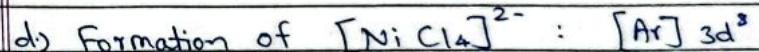
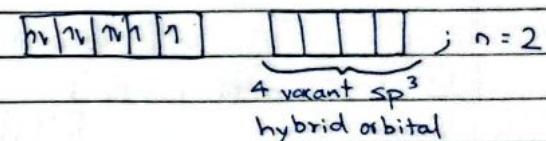
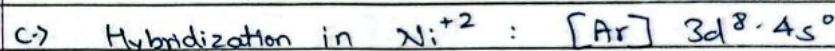
Example:



Here, the central metal is Nickel (Ni). Its oxidation number is +2. Its coordination number (C.N.) = 4. So, it has either tetrahedral or square planar geometry. Now, using VBT to decide its magnetic property & geometry:-



Since, chloride is a weak ligand, back pairing of unpaired electron in  $3d$  orbital is not possible. So, it undergoes  $sp^3$  hybridization.



Conclusion: Since, the given complex ion undergoes  $sp^3$  hybridization, it has tetrahedral geometry, the electronic configuration of  $Ni^{+2}$  contains two unpaired electrons so it is paramagnetic in nature.

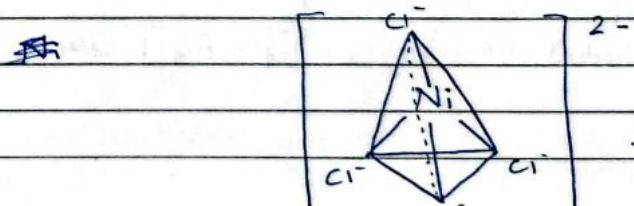
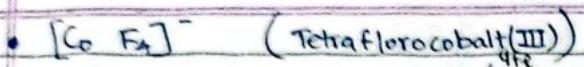


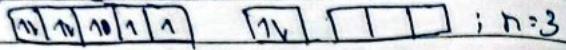
Fig: Tetrahedral geometry  $[NiCl_4]^{2-}$



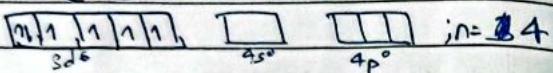
Central metal  $\rightarrow$  Co ( $O.N.=+3$ ) ( $C.N.=4$ )

Either tetrahedral or square planar

(a) Co ( $z=27$ ) :  $[\text{Ar}] 3d^7 4s^2$

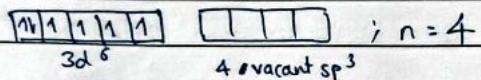


(b)  $\text{Co}^{+3}$  ( $z=24$ ) :  $[\text{Ar}] 3d^6 4s^0$

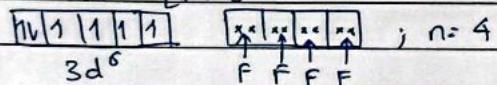


F is weak ligand, no back pairing

(c) Hybridization in  $\text{Co}^{3+}$  :  $[\text{Ar}] 3d^6 4s^0$



(d) Formation of  $[\text{Co F}_4]^-$  :  $[\text{Ar}] 3d^6$



Conclusion:-

$sp^3$   $\rightarrow$  tetrahedral geometry

$n=4$   $\rightarrow$  paramagnetic

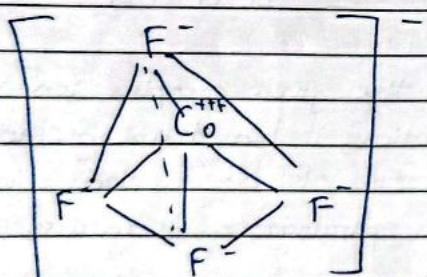
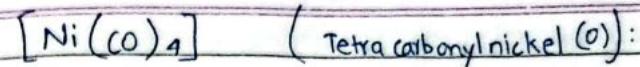
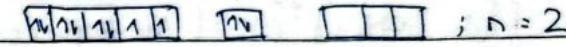


fig: Tetrahedral geometry of  $[\text{Co F}_4]^-$



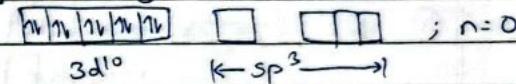
Here central metal is nickel. Ifs O:N=O, its C.N.=4 so it has either tetrahedral or square planar geometry. Now using VBT to decide its geometry & magnetic property

(a) Ni ( $z=28$ ) :  $[\text{Ar}] 3d^8 4s^2$



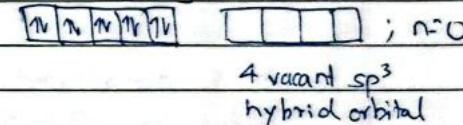
Since, CO is strong ligand, it releases large amount of energy. So, back pairing of unpaired electrons occurs.

(b) Ni in  $[\text{Ni (CO)}_4]$  :  $[\text{Ar}] 3d^{10} 4s^0$

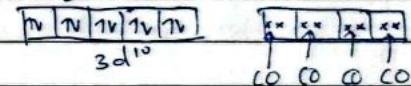


So, it undergoes  $sp^3$  hybridization.

(c) Hybridization in  $[\text{Ni (CO)}_4]$  :  $[\text{Ar}] 3d^{10} 4s^0$



(d) Formation of  $[\text{Ni (CO)}_4]$  :  $[\text{Ar}] 3d^{10} 4s^0$



Conclusion:  $sp^3$  - tetrahedral geometry  
 $n=0$  - diamagnetic

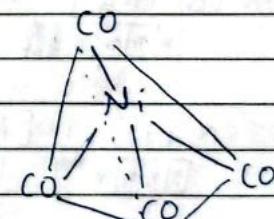
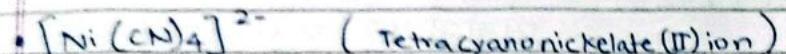


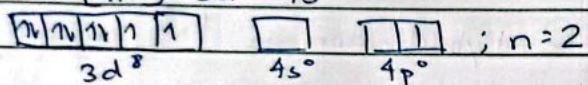
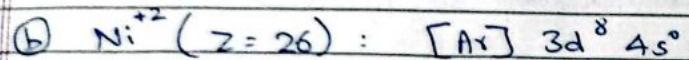
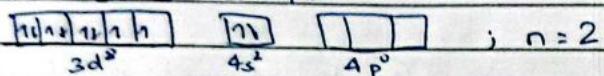
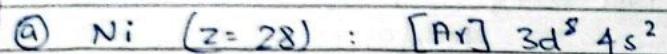
fig: Tetrahedral geometry of  $[\text{Ni (CO)}_4]$

## 2) Square Planar complexes:

These complexes are formed as a result of  $dsp^2$  hybridization. They are always formed by strong ligands. For example,  $[Ni(CN)_4]^{2-}$ ,  $[Co(NH_3)_6]^{3+}$ , etc.

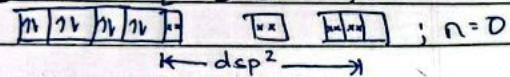
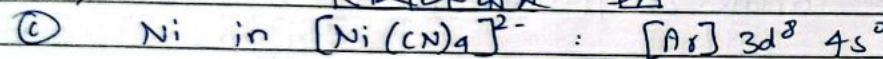


Here the central metal is nickel, its O.N. is 2, C.N. = 4, so it has either tetrahedral or square planar geometry. Now applying VBT to decide its magnetic property & geometry.

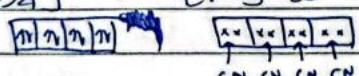
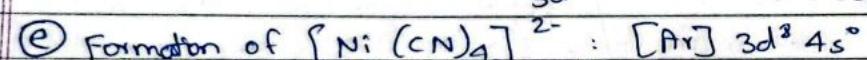
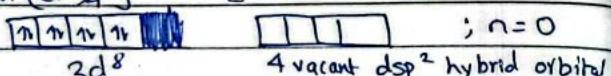
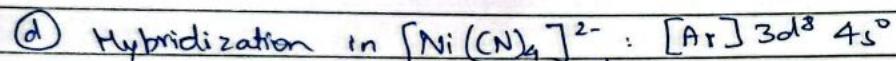


$CN^-$  is strong ligand, so, back pairing of unpaired electron occurs in  $3d$  orbital.

Now,



So, it undergoes  $dsp^2$  hybridization.



Conclusion: As the given complex ion undergoes  $dsp^2$  hybridization, it has square planar geometry. It contains no any unpaired electrons ( $n=0$ ) so it is diamagnetic in nature.

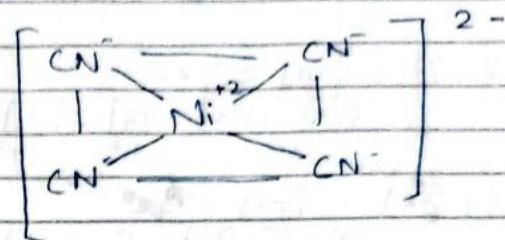


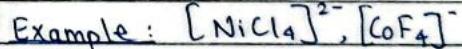
fig : square planar geometry of  $[Ni(CN)_4]^{2-}$

(Q) Differentiate between tetrahedral & square planar complexes

### Tetrahedral complexes

Geometry: The central metal ion is surrounded by four ligands forming a tetrahedron.

Hybridization: It involves  $sp^3$  hybridization.

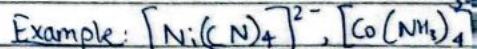


They are formed by weak ligands  
Mostly paramagnetic

### Square planar complexes

Geometry: The central metal ion is surrounded by four ligands in a flat, square arrangement.

Hybridization: It involves  $dsp^2$  hybridization.



They are formed by strong ligands  
Mostly diamagnetic

•  $[\text{Co}(\text{NH}_3)_4]^{3+}$  (Tetraamminecobalt(III) ion)

$\text{Co}^-$ ; O.N = 3, C.N = 4

either tetrahedral or square planar

a)  $\text{Co}^-$  ( $z=27$ ):  $[\text{Ar}] 3d^7 4s^2$

$n$	$n$	$1$	$1$	$1$	$\boxed{1V}$	$\boxed{I}$	$\boxed{II}$
		$3d^7$		$4s^2$		$4p^0$	

b)  $\text{Co}^{3+}$  ( $z=24$ ):  $[\text{Ar}] 3d^6$

$n$	$n$	$1$	$2$	$1$	$1$	$\boxed{2}$	$\square$	$\boxed{III}$
		$3d^6$		$4s^0$		$4p^0$		

c) Since,  $\text{NH}_3$  is a strong ligand, they undergo back pairing

c)  $\text{Co}^{3+}$  in  $[\text{Co}(\text{NH}_3)_6]^{3+}$ :  $[\text{Ar}] 3d^6 4s^0$

$n$	$n$	$n$	$n$	$\square$						
-----	-----	-----	-----	-----------	-----------	-----------	-----------	-----------	-----------	-----------

$SP^3$

3) Octahedral Complexes: These complexes are formed as a result of  $d^2sp^3$  hybridization /  $sp^3d^2$  hybridization. They are further classified into 2 types:-

- $d^2sp^3$  → Inner Orbital Complex / Low spin / Spin paired complex
- $sp^3d^2$  → Outer Orbital Complex / High spin / Spin free complex

#### A) Inner Orbital Complexes:

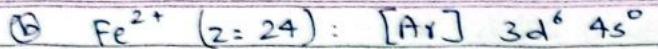
These complexes are formed by strong ligands and have  $d^2sp^3$  hybridization. Here,  $(n-1)d$ ,  $ns$  &  $np$  orbitals are involved. Examples:  $[\text{Fe}(\text{CN})_6]^{4-/-3-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$

#### • $[\text{Fe}(\text{CN})_6]^{4-}$ (Hexacyanoferrate(II) ion)

Here, the central metal is Fe. Its O.N = 2, C.N = 6, so it has octahedral geometry. Now, applying VBT to decide it is inner or outer orbital complex and also its mag properties

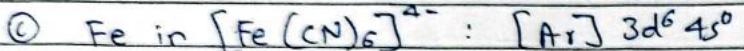
a)  $\text{Fe}^-$  ( $z=26$ ):  $[\text{Ar}] 3d^6 4s^2$

$n$	$n$	$n$	$n$	$n$	$n$	$\boxed{I}$	$\boxed{II}$	$\boxed{III}$
		$3d^6$		$4s^2$		$4p^0$		



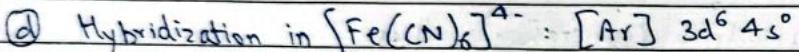
$n_1   n_1   n_1   n_1$	$\square$	$\square \quad \square$
$3d^6$	$4s^0$	$4p^0$

Since CN is strong ligand, back pairing occurs

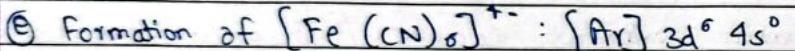


$n_1   n_1   n_1$	$\square$	$\square \quad \square$
$3d^6$	$d^2 \text{sp}^3$	$4s^0$

So, it undergoes  $d^2 \text{sp}^3$  hybridization



$n_1   n_1   n_1$	$\square \quad \square \quad \square$
$3d^6$	6 vacant $d^2 \text{sp}^3$ hybrid orbital



$n_1   n_1   n_1$	$\square \quad \square \quad \square \quad \square \quad \square \quad \square$
$3d^6$	CN CN CN CN CN CN

Conclusion: Since the given complex ion undergoes  $d^2 \text{sp}^3$  hybridization, it has octahedral geometry. Here,  $3d$ ,  $4s$  &  $4p$  orbitals are involved in hybridization so it is inner orbital complex. It contains no any unpaired electrons ( $n=0$ ) so it is diamagnetic in nature.

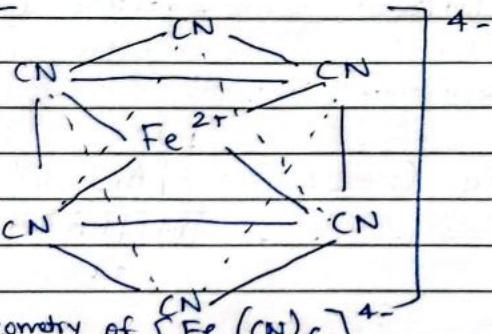


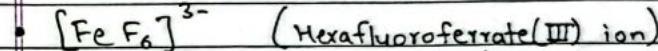
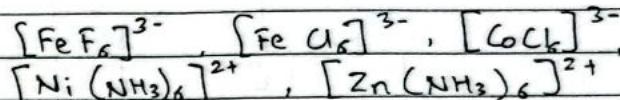
fig.: Octahedral geometry of  $[\text{Fe}(\text{CN})_6]^{4-}$

### B) Outer Orbital Complexes:

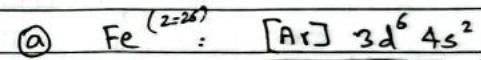
These complexes are formed as a result of  $\text{sp}^3\text{d}^2$  Hybridization.

Here  $ns$ ,  $np$  &  $nd$  orbitals are involved so they are also said to be outer orbital or spin free or high spin complexes. Generally, they are formed by weak ligands but sometimes they can also be formed by strong ligands in which the central metal has  $(n-1)d^7/d^3/d^9/d^0$  configurations.

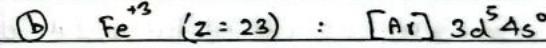
Examples:



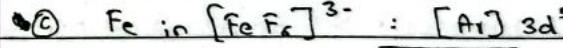
Here the central metal is iron(Fe), its oxidation no. is +3, its coordination no. = 6 - So, it has octahedral geometry. Now applying VBT to decide if it is inner or outer orbital complex its magnetic property.



$n_1   n_1   n_1   n_1$	$n_1$	$\square \quad \square$
$3d^6$	$4s^2$	$4p^0$

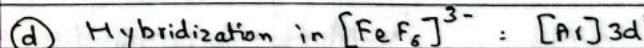


$n_1   n_1   n_1   n_1$	$\square$	$\square \quad \square$	$\square \quad \square$
$3d^5$	$4s^0$	$4p^0$	$4d^0$

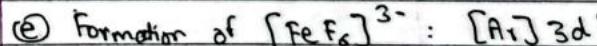


(No back pairing)

$n_1   n_1   n_1   n_1$	$\square$	$\square \quad \square$	$\square \quad \square$
$3d^5$	$4p^0$	$4d^0$	$5s^0$



$n_1   n_1   n_1   n_1$	$\square \quad \square \quad \square$
$3d^5$	$4p^0$



$n_1   n_1   n_1   n_1$	$\square \quad \square \quad \square$
$3d^5$	$4p^0$

### Conclusion :

Since the given complex ion undergoes  $sp^3d^2$  hybridization, it undergoes octahedral geometry. Here, 1s, 3p, 4d orbitals are involved in hybridization so it is outer orbital complex. It contains 5 unpaired electrons ( $n=5$ ) so it is <sup>highly</sup> paramagnetic in nature.

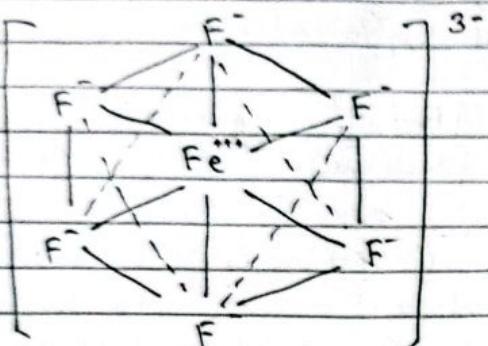


Fig: Octahedral geometry of  $[FeF_6]^{3-}$

Q.) Differentiate between low spin & high spin complexes

Low spin complexes	High spin complexes
• It is also called spin paired or inner orbital	• also called spin free or outer orbital complex
• as a result of $d^2sp^3$ hybridization	• as a result $sp^3d^2$ hybridization
• Generally formed by strong ligands	• Generally formed by weak ligands
• Back pairing of unpaired electron occurs	• Not possible back pairing
• $(n-1)d$ , ns, & np orbitals are involved in hybridization	• ns, np & nd orbitals are involved in hybridization
• Mostly diamagnetic, sometimes paramagnetic.	• Mostly paramagnetic, sometimes diamagnetic.
• Example: $[Fe(CN)_6]^{4-}$ , $[Co(NH_3)_6]^{3+}$	• Example: $[FeCl_6]^{3-}$ , $[Zn(NH_3)_6]^{2+}$

### # Limitations of VBT:

Although VBT describes about the geometry & magnetic property of complexes, it cannot explain the following facts:-

- Color formation in complexes.
- Magnetic property in detail.
- Real existence of inner orbital or outer orbital complexes.
- Nature of the ligands like strong or weak, etc.

### # Crystal Field Theory (CFT):

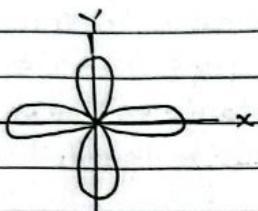
This theory <sup>was</sup> given by Hans Bethe & Van Vleck from about 1929 to 1935. This theory is dependent on the following postulates :-

- A complex is considered to be the combination of central metal atoms (CMA) and the ligands surrounding it, containing one or more lone pairs of electrons.
- Ligands are considered as point charges (-ve ligands such as  $X^-$ ,  $CN^-$ ,  $NO_3^-$ , etc. are negative point charges whereas the neutral ligands like  $H_2O$ ,  $NH_3$ , etc are dipoles).
- The attraction between the metal ion & the ligand (ionic or dipolar) is purely electrostatic (100% ionic).
- There is no overlap between the central metal & the ligand but the interaction between the electrons of central atom & those of ligands is repulsive. Because of this repulsion, the energy of d orbitals raises.
- As the d orbitals have different orientation in space they experience different repulsion. This repulsion causes splitting of d orbitals known as crystal field splitting.

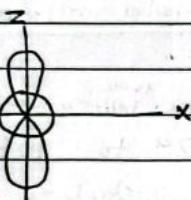
### \* Shapes of d-orbitals:

- Axial shape ( $e_g$  set)

$\rightarrow d_{z^2-y^2}$

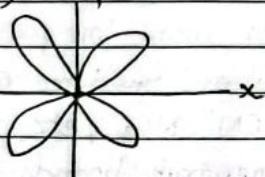


$\rightarrow d_{z^2}$

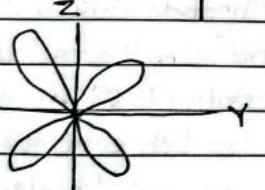


- Non-axial shape ( $t_{2g}$  set)

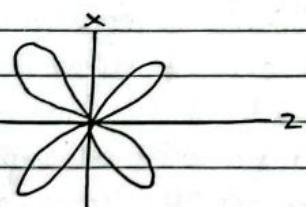
$\rightarrow d_{xy}$



$\rightarrow d_{yz}$



$\rightarrow d_{zx}$



Note:-

The crystal field splitting will be different in different structures with different co-ordination number.

In an isolated state, all the 5 d orbitals are said to be degenerate (having equal energy). When the ligands approach them with electrons, their energy rises and get splitted into two different sets. One set consists of 2d orbitals (i.e.  $d_{x^2-y^2}$  &  $d_{z^2}$ ) and known as  $e_g$  set whereas the other set consists of 3d orbitals (i.e.  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) known as  $t_{2g}$  set.

This process of splitting of 5 d orbitals into two sets is known as  $\Delta$  crystal field splitting and their difference in energy is crystal field energy ( $\Delta_{CFSE}$  or  $\Delta_{CFE}$ ).

In case of octahedral complexes, 6 ligands approach the central metal axially. So,  $e_g$  set experiences better repulsion than  $t_{2g}$  set so, its splitting process can be shown as:

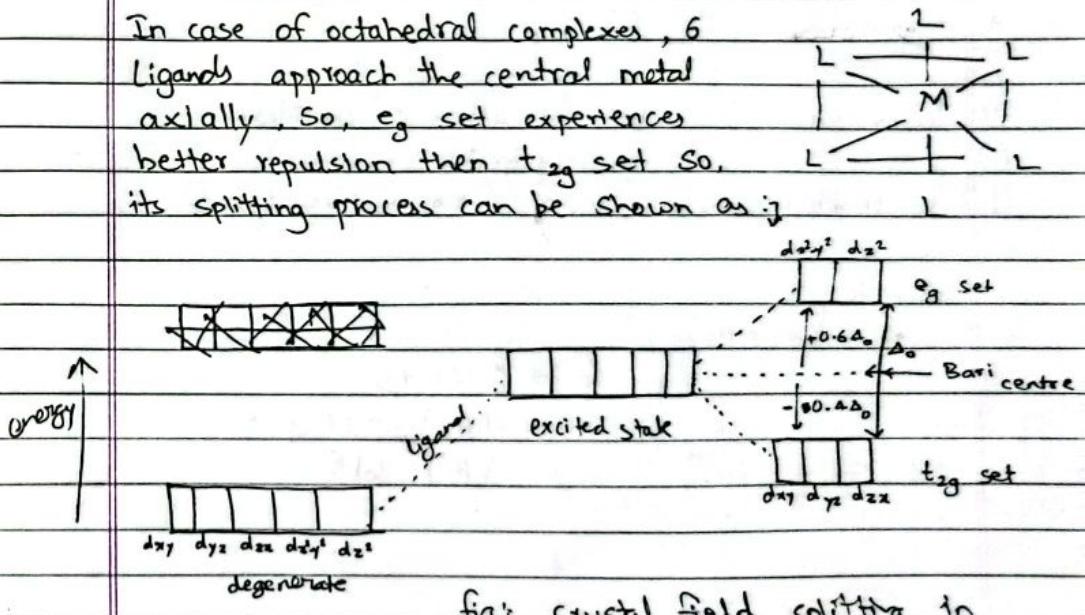


fig: crystal field splitting in octahedral complexes

Central complexes, If a complex compound has C.N = 4 it has 2 possibilities i.e. tetrahedral or square planar. In case of tetrahedral complexes, four ligands approach the central metal non-axially i.e.  $t_{\text{tg}}$  set experiences greater repulsion than  $e_g$  set & its splitting can be shown as:-

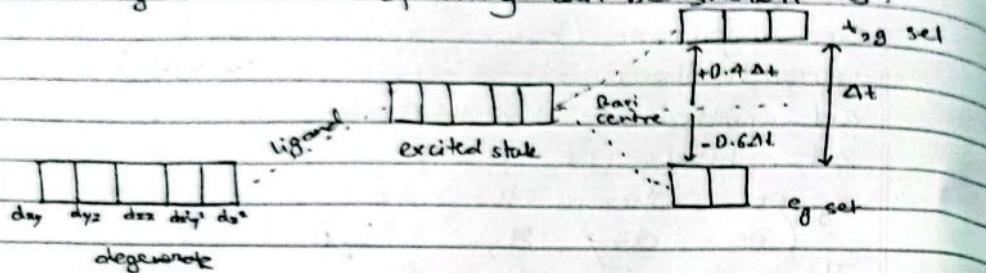
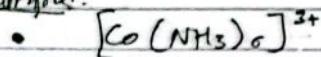


Fig.: Crystal field splitting in octahedral complexes

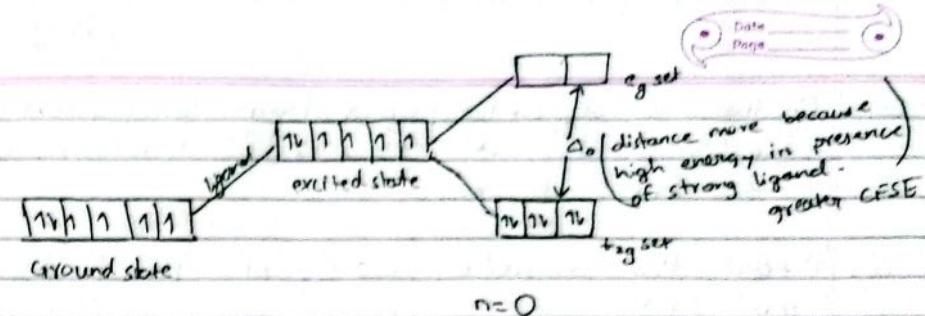
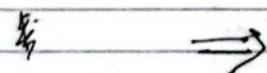
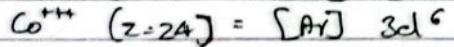
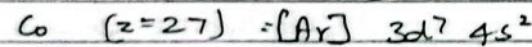
#### Applications of CFT:

- ① To determine the color formation of complexes.
- ② " " " magnetic properties " " .
- ③ Give information about spectra (weak vs strong ligand)

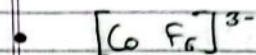
Example:



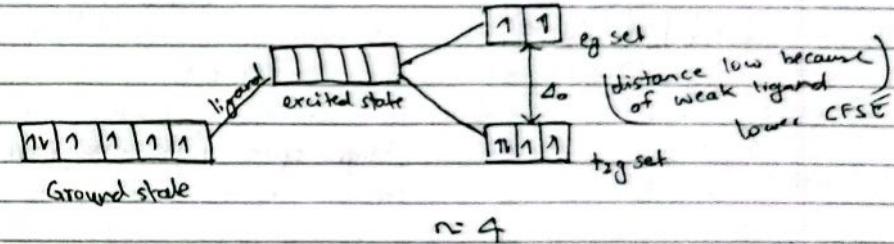
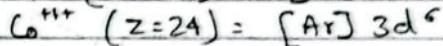
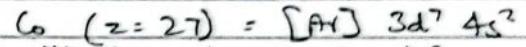
$$\text{Co} \rightarrow \text{O.N.} = +3$$



Low spin (diamagnetic)



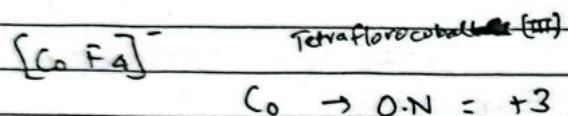
$$\text{Co} \rightarrow \text{O.N.} = +3$$



High spin (Paramagnetic)

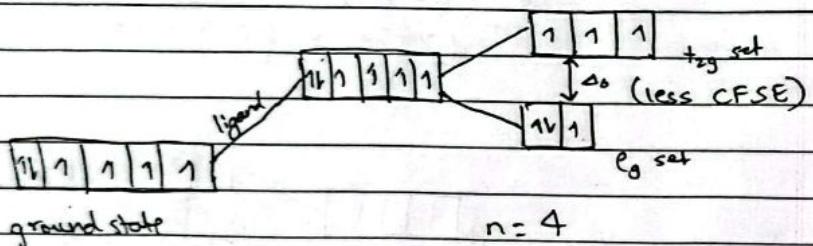
Q) On the basis of CFT, predict the magnetic property of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  &  $[\text{CoF}_6]^{3-}$  based on CFT  
 → Done before

Q) Predict the magnetic property of  $[\text{CoF}_6]^{-}$  based on CFT

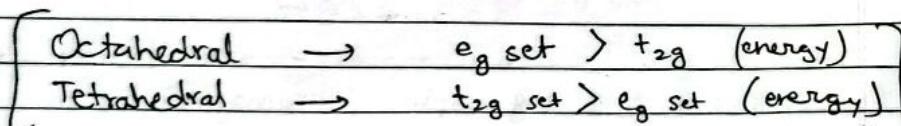


$$\text{Co (z=27)} = 3d^7 4s^2$$

$$\text{Co}^{+++} (\text{z}=24) = 3d^6 1$$



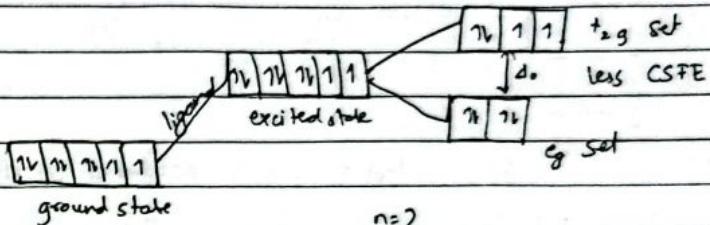
High spin (paramagnetic)



$$\text{Ni} \rightarrow \text{O.N.} = +2$$

$$\text{Ni (z=28)} = [\text{Ar}] 3d^8 4s^2$$

$$\text{Ni}^{++} (\text{z}=26) = [\text{Ar}] 3d^8$$



High spin (paramagnetic)

#### \* Color Formation:

Transition metals form colorful compounds in the solid state as well as in the sol<sup>n</sup> form. This is bcz of the presence of 1 to 9 electrons in n-1 d orbital.

Eg:-  $\text{Cu}^{2+}$  = blue color  
 $\text{Ni}^{+2}$  = dark green  
 $\text{Fe}^{+2}$  = light green.

Even the metals with different oxidation states can give different colors.

$$(n-1) \text{d}^{1-9} \rightarrow \text{colorful}$$

$$(n-1) \text{d}^{10} \rightarrow \text{colourless}$$

The reason for the formation of colorful compounds is d-d transition. For d-d transition to occur certain wavelength of light from visible region ( $\lambda = 400-750\text{ nm}$ ) is absorbed and unabsorbed <sup>color</sup> is reflected back. This reflected color is complementary color of the absorbed color & is the color of the substance.

For this color absorption there should be presence of 1-9 electrons in  $(n-1)d$  orbitals.

Fig:-

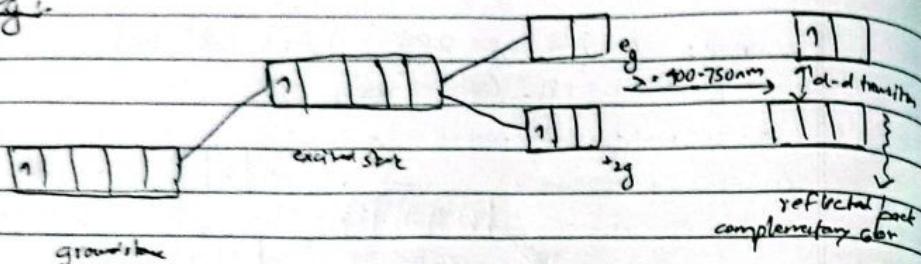


Fig:- d-d transition in octahedral complex

i.e. color of substance = white light - absorbed color  
ordinary light

Sunlight

= reflected (complementary color)

Q.) Predict the magnetic property & color formation of  $[\text{Cu}(\text{NH}_3)_6]^{2+}$

Tetraamminecopper(II) ion

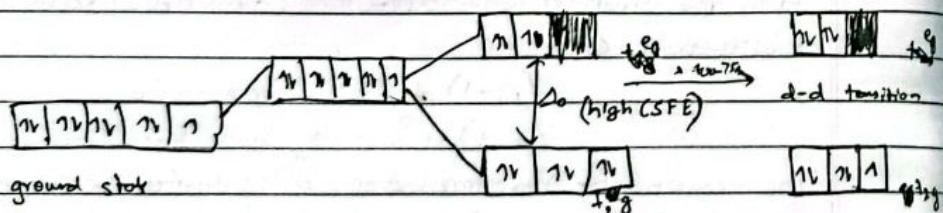
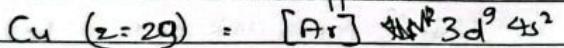


Fig:- d-d transition in tetrahedral complex  
(high spin)  $\text{S}_{\text{tot}} = 1$   
reflected back complementary color

Q.) Differentiate between CFT & VBT

### Crystal Field Theory

→ CFT predicts gradual change in the magnetic properties of the complexes.

→ According to CFT, the bond between metal and ligand is purely ionic in nature.

→ CFT explains the spectral properties of complexes

→ CFT explain certain thermodynamic and kinetic properties

→ CFT explain distortion in the regular geometries like octahedron. For e.g. - tetragonally distorted octahedron.

→ CFT provides a theoretical basis for understanding and predicting the variation of magnetic moment with temperature as well as detailed magnetic properties of complexes

### Valence Bond Theory

→ VBT predicts abrupt change in the magnetic properties of complexes.

→ According to VBT, the bond between metal and ligand is purely covalent in nature.

→ VBT does not explain the spectral properties of complexes

→ VBT does not explain certain thermodynamic and kinetic properties

→ VBT does not explain distortion in the regular geometries like octahedron.

→ VBT does not do this but, it explain magnetic property only on the basis of number of unpaired electron.

## \* Rare Earth Elements (REE):

21	Sc	The group of 17 elements in the modern periodic table including 15 Lanthanides & Scandium (21), Yttrium (39) are collectively called Rare Earth Elements. (REE).
39	Y	
57	La	
58	Ce	
59	Pr	
60	Nd	
:	:	
70	Yb	
71	Lu	availability is low. :- For eg:- Lanthanum (La), Cerium (Ce), Neodimium (Nd) are available in great extent than lead (Pb). Even today, modern technologies are used to extract them and is costly. However, they've wide applications from industries, T.Vs, smartphones, electric vehicles to many other fields.

- ① Neodimium (Nd) is mostly used REE to make permanent magnet.  
Eg:- NdFeB is permanent magnet mostly used in electric vehicles or in turbines which convert wind energy to electricity.
- ② Cerium (Ce) & Neodimium (Nd) both are used to make alloys, fuel cells, nickel-metal hydride batteries.
- ③ They are also important in electronics and are used in making LCDs.
- ④ Nd also has luminescent property, so they are used in Smart phones, televisions, laptop screens, etc.
- ⑤ They also show catalytic behaviour.
- ⑥ Cerium (Ce) is used in polished glass products.

Thus, REE are used in our daily life in any means having the following applications / uses:-

- i) Permanent Magnet
- ii) Catalyst
- iii) Polishing glasses
- iv) Alloy formation
- v) Metallurgical activities
- vi) Agricultural activities

## \* Metallic Alloys:

An alloy is the mixture of two or more elements in which one must be a metal. Alloys have high M.P., B.P., hard, stronger than parent elements from which they are made. So, alloys are prepared. Usually transition metals are used to prepare alloys. This is because they are similar in size, miscible in their molten form and can get easily substituted over one another. Examples:- stainless steel ( $Fe + Ni + Cr + C$ )

Brass ( $Zn + Cu$ ), Bronze ( $Cu + Sn$ )

Depending on the composition from which alloys are prepared, they are classified as ferrous alloys (one of the elements is Fe).  
Eg:- Steel ( $Fe + C$ ), Nickel steel ( $Fe + Ni + C$ )

Non ferrous alloys: having no iron. Eg.: Brass ( $Zn + Cu$ ), Aluminium alloys, etc.

### A) Iron Alloys / Ferrous Alloys / Steel Alloys:

These alloys are formed by the mixture of two or more metals including C, on which one of the elements is Fe. Eg:-

- Steel ( $Fe + C$ ), Stainless Steel ( $Fe + Ni + Cr + C$ ), Nichrome steel ( $Fe + Ni + C + Mn$ )
- (Construction usage) Household utensils, Medical devices
- (Machineries) Manganese Steel ( $Fe + Mn + C$ )
- Has high strength to bear temp. in boilers, etc.

### B.) Aluminium Alloys (Light Weight Alloys):

Although the name aluminium alloy is given, magnesium is also used in these alloys. Depending on the composition of aluminium and magnesium, aluminium alloys are classified as:-

- i) Duralumin ( $\text{Al} \rightarrow 95\%$ ,  $\text{Cu} \rightarrow 4\%$ ,  $\text{Mn} \rightarrow 0.5\%$ ,  $\text{Mg} \rightarrow 0.5\%$ )
- ii) Magnalumin ( $\text{Al} \rightarrow 70\% - 90\%$ ,  $\text{Mg} \rightarrow 10\% - 30\%$ )
- iii) Elecon ( $\text{Al} \rightarrow 7\% - 11\%$ , other metals  $\rightarrow 4\%$ , Magnesium  $\rightarrow$  remaining)

Because of their low density, good strength, cheap in nature they are used in aircraft industries, automobiles, cheap balances, scientific instruments, making pans, oil tanks (petrol tanks), etc.

## Electro chemistry & Buffer

2 x 5 = 10

(1 OR question)

### Buffer:

The solution which can resist the change in pH with the addition of small amt. of acid or base is buffer sol<sup>n</sup>. They are of two types:-

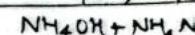
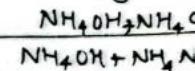
i) Acidic Buffer: Mixture of weak acid & its salt having common ion derived from strong base. Eg:-



They have  $\text{pH} < 7$

ii) Basic Buffer: It is the mixture of weak base & strong salt having common ion, derived from strong acid. Eg:-

Its  $\text{pH} > 7$



iii) Natural Buffer: Blood ( $\text{pH}: 7.36$ ), Sea water ( $\text{pH}: 8.1$ )

Buffer Capacity: It is the capacity of buffer sol<sup>n</sup> which can resist the change in pH with the addition of small amt. of strong acid or base. It can be defined as the number of moles of acid or base added in 1 ltr sol<sup>n</sup> to create a unit change in pH.

Buffer capacity =  $\frac{\text{No. of moles of acid/base added in 1 ltr sol}^n}{\text{change in pH}}$

pH Range: The range of the buffer sol<sup>n</sup> over which pH is effective. For acidic buffer  $\text{pH} = \text{PK}_a \pm 1$  where

$$\text{PK}_a = -\log K_a$$

For basic buffer  $\text{pOH} = \text{PK}_b \pm 1$  where

$$\text{PK}_b = -\log K_b$$

$K_a$  is ionization constant for acidic buffer.

$K_b$  is ionization constant for basic buffer.

$$\text{pH} = 14 - \text{pOH}$$

### \* Mechanism of Buffer:

In the mechanism of Buffer sol<sup>7</sup>, two principles are involved:-

#### (1) Common ion effect :-

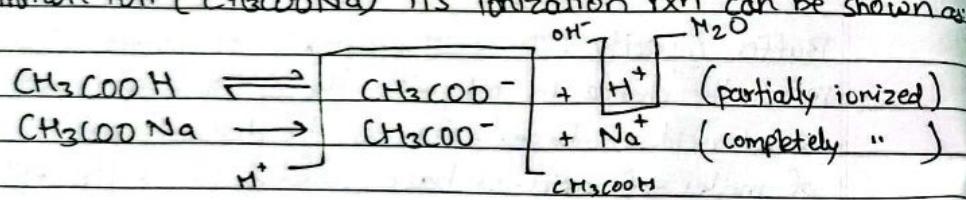
The suppression of ionization of weak electrolyte in presence of strong electrolyte having common ion is common ion effect.

#### (2) Le-Chatelier's Principle:-

It describes about the effect of temperature, pressure and concentration on chemical equilibria.

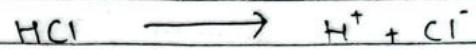
### \* Mechanism of acidic buffer

To explain the mechanism of acidic buffer, let us take an example of weak acid ( $\text{CH}_3\text{COOH}$ ) and its ionizable salt having common ion ( $\text{CH}_3\text{COONa}$ ) its ionization rxn can be shown as

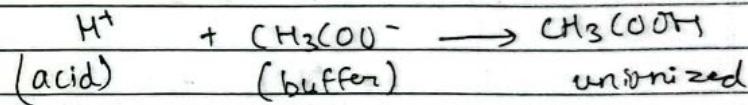
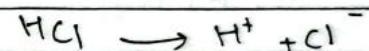


#### i) On addition of acid :

When small amount of acid like  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  is added to this buffer system, it gets completely ionized as

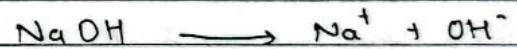


Addition of  $\text{H}^+$  ions in this solution should have altered pH, however they get consumed by acetate ion ( $\text{CH}_3\text{COO}^-$ ) and formed unionized  $\text{CH}_3\text{COOH}$  according to Le-Chatelier's principle, the equilibrium shifts towards left and maintains the pH of the sol<sup>7</sup>.

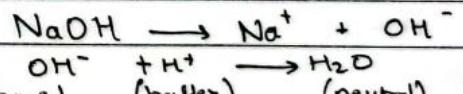


#### ii) On addition of base:

When small amount of strong base like  $\text{NaOH}$ ,  $\text{KOH}$ , is added to this buffer sol<sup>7</sup>, they get completely ionized as:

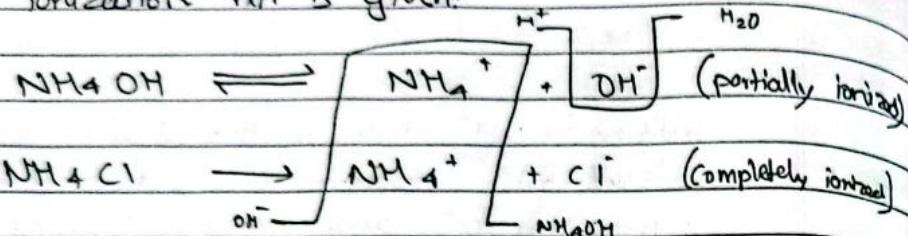


Addition of  $\text{OH}^-$  ions in this solution again should have altered pH. But these  $\text{OH}^-$  ions react with  $\text{H}^+$  ions in the sol<sup>7</sup> forming neutral  $\text{H}_2\text{O}$  molecule. According to Le-Chatelier's principle, chemical equilibrium shifts towards right generating more amount of  $\text{H}^+$  ions as required & maintains the pH of the sol<sup>7</sup>.



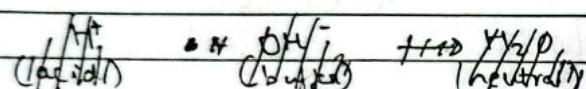
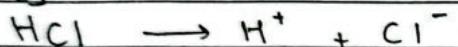
### Mechanism of basic buffer

To explain the mechanism of basic buffer, let us take the mixture of weak base ( $\text{NH}_4\text{OH}$ ) & its ionizable salt ( $\text{NH}_4\text{Cl}$ ). Their ionization is given:

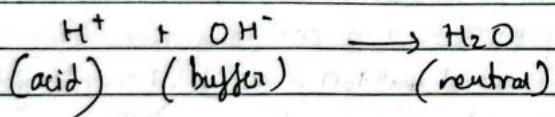


#### i) On addition of acid:

When small amount of strong acid like  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  is added to this buffer soln, it gets completely ionized as:



Addition of  $\text{H}^+$  ion should have altered pH, but these  $\text{H}^+$  ions get consumed by  $\text{OH}^-$  ion in the soln, forming neutral water. According to Le-chatelier's principle, chemical equilibrium shifts towards right generating more amount of  $\text{OH}^-$  ions, thus maintaining the pH of the solution.

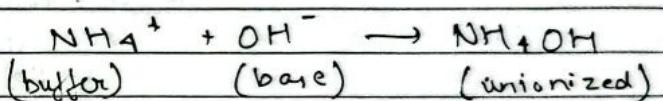


#### ii) On addition of base:

When small amount of strong base like  $\text{NaOH}$ ,  $\text{KOH}$  is added to this buffer soln, they get completely ionized as:



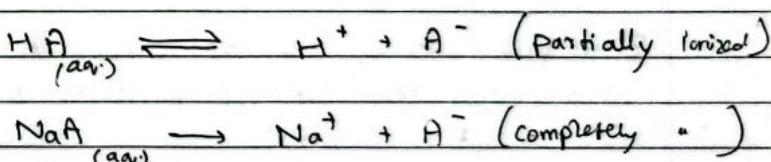
Addition of  $\text{OH}^-$  ions should in this soln, again should have altered pH. However these  $\text{OH}^-$  ions react with common ion ( $\text{NH}_4^+$ ) forming unionized ( $\text{NH}_4\text{OH}$ ). According to Le-chatelier's principle, chemical equilibrium shifts towards left forming unionized  $\text{NH}_4\text{OH}$  maintaining the pH of soln.



### # Henderson - Hasselbalch Equation:

#### \* For acidic Buffer:

let us take the mixture of weak acid  $\text{HA}$  & its ionizable salt  $\text{NaA}$ . They get ionized as:



From Law of mass action, ionization constant for given weak acid can be written as:

$$K_a = \frac{[H^+] [A^-]}{[HA]} \quad \dots \textcircled{i}$$

ionization constant  
for acidic buffer

$$\text{or } [H^+] = \frac{K_a \cdot [HA]}{[A^-]}$$

Taking -ve log on both sides

$$\text{or } -\log [H^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \dots \textcircled{ii}$$

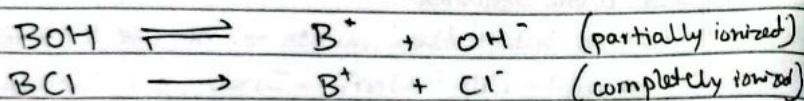
$pH = -\log K_a$   
&  $K_a$  is ionization  
constant of acidic  
buffer

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Due to common ion effect,  
the ionization of weak acid  
is highly suppressed.  
So, the common ion can be  
considered as the conc' of salt.

#### \* For basic buffer:

Let us take the mixture of weak base  $BOH$  and its  
ionizable salt  $BCl$ . They gets ionized as:-



From law of mass action, ionization constant for  
given weak base can be written as:-

$$K_b = \frac{[B^+] [OH^-]}{[BOH]}$$

ionization constant  
for basic buffer

$$\text{or, } [OH^-] = \frac{K_b \cdot [BOH]}{[B^+]}$$

Taking -ve log on both sides.

$$\text{or, } -\log [OH^-] = -\log K_b - \log \frac{[BOH]}{[B^+]}$$

$$pOH = pK_b + \log \frac{[B^+]}{[BOH]}$$

Due to common ion effect the ionization of weak  
base  $BOH$  is highly suppressed. So the conc' of common  
ion can be considered as the conc' of salt.

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$pH = 14 - pOH$$

#### # Auto ionization of Water:

Water is a weak electrolyte & it gets ionized as



Applying Law of mass action, we get:

$$K_w = \frac{[H_3O^+] [OH^-]}{[H_2O]^2}$$

$$K_w \cdot [H_2O]^2 = [H_3O^+] [OH^-] \quad \dots \textcircled{i}$$

↳ ionization constant of water & at  $25^\circ C$  it  
 $\bullet$  value =  $10^{-14}$  mol/ltr.

Now,

$$10^{-14} = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

Taking -ve log on both sides:-

$$\begin{aligned}-\log(10^{-14}) &= -\log [\text{H}_3\text{O}^+] - \log [\text{OH}^-] \\ 14 &= \text{pH} + \text{pOH} \\ \text{pH} + \text{pOH} &= 14 \\ \text{pH} &= 14 - \text{pOH}\end{aligned}$$

Formulae required in Buffer numericals:

$$\text{pH} = -\log [\text{H}^+]$$

Required

$$\text{pH} = \text{pka} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

■ ■ ■ ■ ■

$$\text{pOH} = -\log [\text{OH}^-]$$

~~Required~~

$$\text{pOH} = \text{pkb} + \log \frac{[\text{salt}]}{[\text{base}]}$$

~~Required~~

$$g/\text{litr} = N \times \text{Eq. wt}$$

$$M = \frac{\text{No. of moles}}{\text{vol. in ltr}}$$

$$M = \frac{\text{wt. in gm}}{\text{mol. mass}} \times \frac{1000}{\text{vol. in ml}}$$

1 Q) The pH of the sol<sup>n</sup> is 2. Find the amount of HCl present in 1 ltr sol<sup>n</sup>.

Soln:-

$$\text{pH} = 2$$

$$g/l = ?$$

$$1 \text{ ltr.}$$

$$\begin{array}{ll} 1 \text{ H: } 1 \\ 2 \text{ He: } 4 \end{array}$$

$$3 \text{ Li: } 7$$

$$4 \text{ Be: } 9$$

$$5 \text{ B: } 10$$

-

Now,

$$\text{g/litr} \quad \text{pH} = -\log [\text{H}^+] \quad 6 \text{ C: } 12$$

$$2 = -\log [\text{H}^+] \quad 7 \text{ N: } 14 \quad -$$

$$[\text{H}^+] = 10^{-2} \text{ M} \quad 8 \text{ O: } 16$$

$$= 10^{-2} \text{ N} \quad 9 \text{ F: } 19$$

$$10 \text{ Ne: } 20$$

$$11 \text{ Na: } 23$$

$$12 \text{ Mg: } 24$$

$$13 \text{ Al: } 27$$

$$14 \text{ Si: } 28$$

$$g/l = N \times \text{Eq. wt}$$

$$= 10^{-2} \times 36.5$$

$$= 0.365 \text{ gm}$$

2 Q) Calculate the pH of 0.0001 M HCl. 15 Ph: 3.0 -  
Soln.

$$\text{pH} = ?$$

$$M = 0.0001$$

$$16 \text{ S: } 32$$

$$17 \text{ Cl: } 35.5$$

$$18 \text{ Ar: } 34.0 \quad -$$

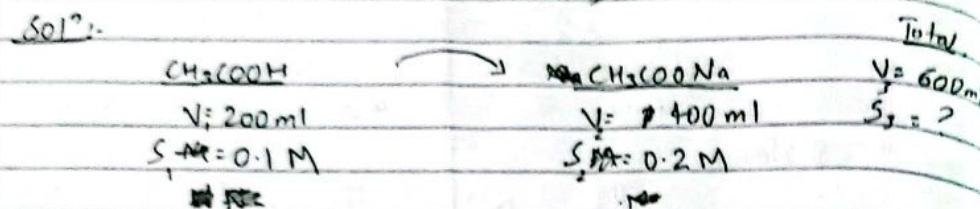
$$19 \text{ K: } 39$$

$$20 \text{ Ca: } 40$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ &= -\log 0.0001 \\ &= 4\end{aligned}$$

Buffer related Numericals

3 Q) 200 ml of 0.1 M Acetic acid ( $\text{CH}_3\text{COOH}$ ) is mixed with 400 ml of 0.2 M sodium acetate sol<sup>1</sup>. Calculate the pH of resulting sol<sup>1</sup>.  
 (Given :  $K_a$  for acetic acid =  $1.8 \times 10^{-5}$ )



$$\frac{V_1 S_1 + V_2 S_2}{V_1 + V_2} = S_3$$

$$200 \times 0.1 + 400 \times 0.2 = 600 S_3$$

$$\therefore S_3 = 0.167$$

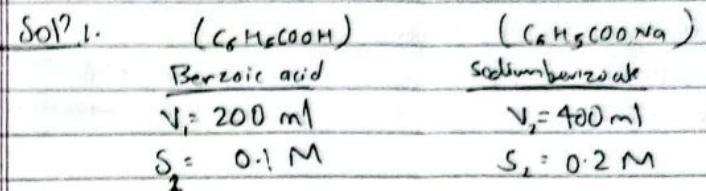
$$\text{New strength of } \text{CH}_3\text{COOH} = \frac{0.1 \times 200}{600} = 0.03 \text{ M}$$

$$\text{New strength of } \text{CH}_3\text{COO}^- = \frac{0.2 \times 400}{600} = 0.13 \text{ M}$$

Now,

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= -\log K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= -\log (1.8 \times 10^{-5}) + \log \frac{0.13}{0.03} \\ &= 5.38 \end{aligned}$$

4 Q) 200 ml of 0.1 M benzoic acid is mixed with 400 ml of 0.2 M sodium benzoate at 30°C dilute sol<sup>1</sup>. Calculate the pH of the sol<sup>1</sup>.



$$\text{New strength of } \text{C}_6\text{H}_5\text{COOH} = \frac{0.1 \times 200}{600} = 0.03 \text{ M}$$

$$\text{New strength of } \text{C}_6\text{H}_5\text{COO}^- = \frac{0.2 \times 400}{600} = 0.13 \text{ M}$$

Now,

$$\text{pH} = \text{p}K_a + \log [\text{salt}]$$

← same

5 Q.) 1.64 gm of anhydrous sodium acetate is added to 100 ml of 0.02 M acetic acid. What is pH of buffer.

Sol:-

$$\text{wt. of } \text{CH}_3\text{COONa} \text{ in gm} = 1.64 \text{ gm}$$

$$\text{CH}_3\text{COO}^- - \text{Vol} = 100 \text{ ml}$$

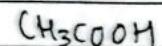
$$\text{CH}_3\text{COOH} - S = 0.02 \text{ M}$$



~~wt. in gm~~

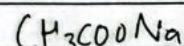
pKa =

$$S = \frac{1.64}{82} \times \frac{1000}{\text{Vol in ml}}$$



$$S_1 = 0.02 \text{ M}$$

$$V_1 = 100 \text{ ml}$$



$$\text{wt.} = 1.64 \text{ gm}$$

$$[\text{CH}_3\text{COONa}] = \frac{\text{wt. in gm}}{\text{mol. mass}} \times \frac{1000}{\text{vol in ml}}$$

$$= \frac{1.64}{82} \times \frac{1000}{100}$$

$$= 0.2 \text{ M}$$

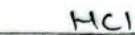
$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$= 4.74 + 1$$

$$= 5.74 //$$

6 Q.) What is the pH of resulting mixture obtained by mixing 100 ml of 0.2 M HCl & 50 ml of 0.5 M NH<sub>4</sub>OH soln (K<sub>b</sub> for ammonia =  $1.8 \times 10^{-5}$ )

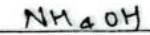
Sol:-



$$V_1 = 100 \text{ ml}$$

$$S_1 = 0.2 \text{ M}$$

$$K_b = 1.8 \times 10^{-5}$$



$$V_2 = 50 \text{ ml}$$

$$S_2 = 0.5 \text{ M}$$

$$\text{New strength of HCl} = \frac{0.2 \times 100}{150}$$

$$= 0.133 \text{ M}$$

$$\text{.. .. .. NH}_4\text{OH} = \frac{0.5 \times 50}{150}$$

$$= 0.167 \text{ M}$$

Now,

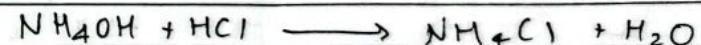
$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log(1.8 \times 10^{-5}) + \log \frac{0.167}{0.133}$$

$$= 4.84$$

$$\text{pH} = 14 - 4.84$$

$$= 9.156$$



Initial (y) (x)

Final:

$$= 0.034$$

$$= 0.133$$

Now,

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

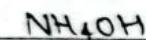
$$= -\log(1.8 \times 10^{-5}) + \log \frac{0.133}{0.034}$$

$$= \frac{5.337}{2} = 5.337$$

$$\text{pH} = 14 - 5.337 \\ = 8.663$$

7 Q.) Calculate the pH of 100 ml of 0.4 M ammonia solution in which 20 ml of 0.5 M HCl is added. ( $\text{P}K_b = 4.74$ )

Sol?..



$$S_1 = 0.4 \text{ M} \\ V_1 = 100 \text{ ml}$$



$$S_2 = 0.5 \text{ M} \\ V_2 = 20 \text{ ml}$$

$$\text{P}K_b = 4.74$$

$$\text{New strength of NH}_4\text{OH} = \frac{0.4 \times 100}{120} \\ = 0.33$$

$$\text{HCl} \quad \frac{0.5 \times 20}{120} \\ (y) \quad 120 \\ = 0.083$$

Now,



Init	x	y	0
Final	x-y	0+y	0.083

$$= 0.247$$

$$\text{pOH} = \text{P}K_b + \log \frac{[\text{salt}]}{[\text{acid}]} \\ = 4.74 + \log \frac{0.083}{0.247} \\ = 4.266$$

$$\text{pH} = 14 - 4.266 \\ = 9.73 //$$

8 Q.) Calculate the pH of the mixture when 2 ml of 0.01 M HCl is added into a system having 400 ml of 0.2 M  $\text{NH}_4\text{OH}$  & 200 ml of 0.05 M  $\text{NH}_4\text{Cl}$  soln. Sol?..

$$\begin{array}{lll} \text{HCl} & \text{NH}_4\text{OH} & \text{NH}_4\text{Cl} \\ V_1 = 2 \text{ ml} & V_2 = 400 & V_3 = 200 \\ S_1 = 0.01 \text{ M} & S_2 = 0.2 & S_3 = 0.5 \end{array}$$

$$\text{Total volume} = 602 \text{ ml}$$

$$\text{New strength of HCl} = \frac{0.01 \times 2}{602}$$

$$= 3.32 \times 10^{-5}$$

$$\text{New strength of NH}_4\text{OH} = \frac{0.2 \times 400}{602} \\ (a) = 0.13$$

$$\text{New strength of NH}_4\text{Cl} = \frac{0.5 \times 200}{602} \\ (c) = 0.166$$

Now,

$$\begin{array}{ccccccc} \text{NH}_4\text{OH} & + & \text{HCl} & = & \text{NH}_4\text{Cl} & + & \text{H}_2\text{O} \\ a & & b & & c & & \\ a-b & & & & c+b & & \\ 0.129 & & & & 0.166 & & \end{array}$$

$$\text{pOH} = \text{P}K_b + \log \frac{[\text{salt}]}{[\text{acid}]} \\ = 4.74 + \log \frac{0.166}{0.129} \\ = 4.849$$

$$\text{pH} = 14 - 4.849 \\ = 9.15$$

Q.1 0.005 mole of KOH is added to 400 ml of 0.1 M  $\text{CH}_3\text{COOH}$ . Calculate the pH of given mixture ( $\text{pK}_a = 4.74$ )

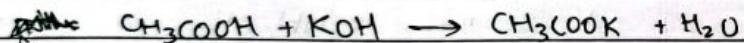
Sol:-

$$\text{KOH mole} = 0.005, S_2 = ?$$

$$\text{CH}_3\text{COOH} \rightarrow V_1 = 400 \text{ ml}, S_1 = 0.1 \text{ M}$$

$$S_2 = \frac{0.005}{0.4} \\ = 0.0125 \text{ M}$$

Now,



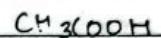
a	b	c
<del>a-b</del>		<del>0+b</del>
<del>0.1 - 0.0125</del>		<del>0.0125</del>
$= 0.0875$		$= 0.0125$

$$\text{pH} = \text{pK}_a + \log \frac{0.0125}{0.0875} \\ = 3.894 //$$

$$\text{pH} = 14 - 3.894 \\ = 10.105$$

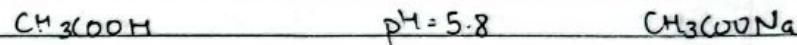
Q.2 Determine the amount of sodiumacetate required in 100 ml 0.2 M acetic acid sol to prepare a buffer soln of pH = 5.8 ( $\text{pK}_a = 4.74$ )

Sol:-

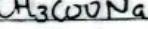


$$S = 0.2 \text{ M}$$

$$V = 100 \text{ ml}$$



$$\text{pK}_a = 4.74$$



$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$\text{or}, 5.8 = 4.74 + \log \left( \frac{x}{0.2} \right)$$

$$\text{or}, 5.8 - 4.74 = \log \left( \frac{x}{0.2} \right)$$

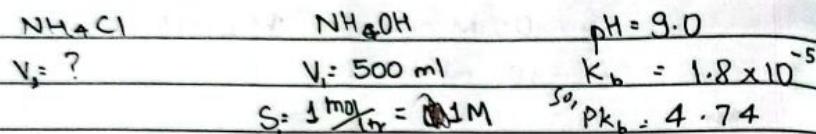
$$\text{or}, x = \sqrt{5.8 - 4.74} \times 0.2 = 2.29$$

Now,

$$\text{wt. to be taken} = \frac{m \times V}{1000} = \frac{x \times 82 \times 100}{1000} \\ = \frac{2.29 \times 82 \times 100}{1000} \\ = 18.778 \text{ gm}$$

18 Q.) What mass of  $\text{NH}_4\text{Cl}$  must be added to 0.5 L of 1 mol/litr  $\text{NH}_3$  sol<sup>n</sup> to yield a sol<sup>n</sup> with a pH of 9.0? Assume no change in volume ( $K_b$  for  $\text{NH}_3 = 1.8 \times 10^{-5}$ ) ( $\text{pK}_b = 4.74$ )

Sol<sup>n</sup>:



Now,

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3\text{OH}]}$$

$$\begin{aligned} & 4.74 + \log [\text{NH}_4\text{Cl}] - \log S_1 \\ & \log [\text{NH}_4\text{Cl}] = 0.26 \\ & [\text{NH}_4\text{Cl}] = 1.81 \end{aligned}$$

Amt of  $\text{NH}_4\text{Cl}$  to be added to 0.5 L  $\text{NH}_3\text{OH}$  sol<sup>n</sup>:

$$2 = 4.74 + \log \frac{[\text{NH}_4\text{Cl}]}{0.1}$$

$$1.819 \times 10^{-4} \text{ on } 5 - 4.74 = \log [\text{NH}_4\text{Cl}]$$

$$\text{on } \log^{-1}(0.26) = [\text{NH}_4\text{Cl}]$$

$$\therefore [\text{NH}_4\text{Cl}] = 1.819 \times 10^{-4}$$

~~W.~~ to be taken ~~mM~~

$$V_1 S_1 = V_2 S_2$$

$$0.5 \times 0.1 = V_2 \times 1.819 \times 10^{-4}$$

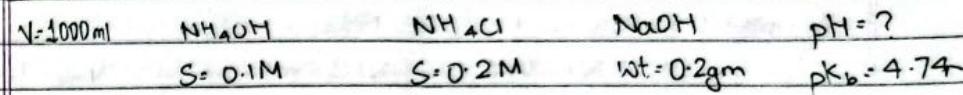
~~$\therefore V_2 = 274.87 \text{ ml}$~~

$$\therefore V_2 = 274.87 \text{ ml}$$

$$\begin{aligned} & 1.819 \times 10^{-4} \times 53.5 \times 10^3 \\ & = 97.3 \text{ gm} \\ & = 1.86 \times 10^{-3} \\ & - 0.0048 \end{aligned}$$

16 Q.) To 1 ltr of buffer sol<sup>n</sup> containing 0.1 M  $\text{NH}_3\text{OH}$  & 0.2 M  $\text{NH}_4\text{Cl}$ , if 0.2 gm of NaOH is added what will be the pH of resulting sol<sup>n</sup>? ( $\text{pK}_b = 4.74$ )

Sol<sup>n</sup>:



Now,

$$\text{pH} = \text{pK}_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3\text{OH}]}$$

$$= 4.74 + \log \frac{0.2}{0.1}$$

$$= 5.041$$

$$\begin{aligned} \text{pH} &= 14 - 5.041 \\ &= 8.959 \end{aligned}$$

if not added  
 $\text{NaOH}$

Now,

$$N = \frac{N \times S}{1000}$$

$$0.2 = N \times 39.40$$

$$\therefore N = 5 \times 10^{-3}$$



$$\begin{array}{cccc} 0.2 & 5 \times 10^{-3} & 0.1 & 0 \\ (0.2 - 5 \times 10^{-3}) & 0 & (0.1 - 5 \times 10^{-3}) & 5 \times 10^{-3} \\ & & 0.195 & 0 \end{array}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3\text{OH}]}$$

$$= 4.74 + \log \frac{0.195 - 5 \times 10^{-3}}{0.105} \quad 0.195$$

$$\begin{aligned} & = 5 \\ \text{pH} &= 14 - 5 \\ &= 9 // \end{aligned}$$

17 Q) Calculate the pH of buffer sol<sup>n</sup> prepared by mixing 100 ml of 0.2M NH<sub>4</sub>Cl & 200 ml of 0.3M ammonia sol<sup>n</sup> which is 3.1% ionized in dilute sol<sup>n</sup>.

Sol<sup>n</sup>:

pH = ?	NH <sub>4</sub> Cl	NH <sub>4</sub> OH
V = 100 ml	V = 200 ml	V <sub>mix</sub> = 300 ml
S = 0.2 M	S = 0.3 M	

~~NH<sub>4</sub>Cl + H<sub>2</sub>O → NH<sub>4</sub>OH + HCl~~

$$\text{New strength of NH}_4\text{Cl} = \frac{0.2 \times 100}{300} = 0.06 \text{ M}$$

$$\text{.. .. .. NH}_4\text{OH} = \frac{0.3 \times 200}{300} = 0.2 \text{ M}$$

Now,

$$K_b = \frac{C \alpha^2}{(1-\alpha)} = \frac{0.2 \times (0.03)^2}{1 - 0.03} = 1.98 \times 10^{-4}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]}$$

$$= 9.8 \times 10^{-4} + \log \frac{0.06}{0.2}$$

$$= -\log 1.98 \times 10^{-4} + \log \frac{0.06}{0.2}$$

$$= 3.703 + 0.522$$

$$= 3.1813$$

$$\text{pH} = 14 - 3.1813$$

$$= 10.8187$$

10 Q)

Calculate the change in pH of buffer system having 200 cc of 0.1M CH<sub>3</sub>COOH and 0.1M CH<sub>3</sub>COONa when 1 millimole NaOH is added into it. ( $K_a = 1.8 \times 10^{-5}$ )

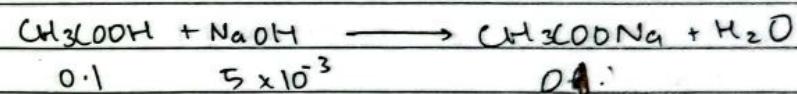
Sol<sup>n</sup>:

Total volume of mixture = 200 cc = 200 mL

Strength of CH<sub>3</sub>COOH = 0.1 M

" " CH<sub>3</sub>COONa = 0.1 M

" " NaOH =  $\frac{1 \times 10^{-3}}{200} \text{ Mole} = 5 \times 10^{-3} \text{ M}$



0.1  $5 \times 10^{-3}$

$(0.1 - 5 \times 10^{-3})$

0.095

$(0.1 + 5 \times 10^{-3})$

~~= 0.105~~  $0.105$

$= 5 \times 10^{-3}$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{0.095}{0.105}$$

$$= 3.46 // 4.78 - 3.46$$

Change in pH = pH' - pH

$$= 4.74 - 3.46 + 4.78 - 3.46$$

$$= +2.8 // = 0.04 = 1.28 //$$

11Q.) A litre of solution contains 0.1 mole of acetic acid and 0.1 mole of sodium acetate. What is the change in pH of the solution after adding 0.02 mole of NaOH? ( $K_a = 1.8 \times 10^{-5}$ )

Sol:-

$$\text{Total volume of solution} = 1 \text{ ltr}$$

$$\text{Strength of } \text{CH}_3\text{COOH} = \frac{0.1 \text{ mole}}{1 \text{ ltr}} = 0.1 \text{ M}$$

$$" " \text{CH}_3\text{COONa} = \frac{0.1 \text{ mole}}{1 \text{ ltr}} = 0.1 \text{ M}$$

pH of sol<sup>n</sup> :-

$$\text{we know, } pK_a \text{ of } \text{CH}_3\text{COOH} = 4.74$$

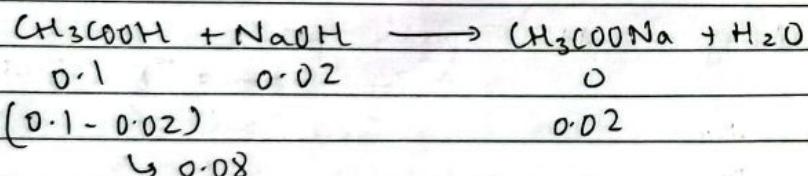
Now,

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log \frac{0.1}{0.1} \end{aligned}$$

$$\therefore \text{pH} = 4.74$$

After adding 0.02 mole of NaOH.

$$\text{Strength of NaOH} = \frac{0.02 \text{ mole}}{1 \text{ ltr}} = 0.02 \text{ M}$$



$$\begin{aligned} \text{pH}' &= pK_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ &= -\log (1.8 \times 10^{-5}) + \log \frac{0.02}{0.08} \\ &= 4.14 \end{aligned}$$

$$\begin{aligned} \text{change in pH} &= 4.74 - 4.14 \\ &= 0.61 \end{aligned}$$

12.Q.) Calculate pH of a buffer sol<sup>n</sup> that has a concn of 0.25M with respect to sodium formate and 0.03M with respect to formic acid. ( $K_a$  for formic acid =  $1.8 \times 10^{-4}$ )

Sol:-

$$\text{Strength of } \text{HCOONa} = 0.25 \text{ M}$$

$$" " \text{HCOOH} = 0.03 \text{ M}$$

$$K_a \text{ of } \text{HCOOH} = 1.8 \times 10^{-4}$$

Then,

$$\text{pH} = pK_a + \log \frac{[\text{HCOONa}]}{[\text{HCOOH}]}$$

$$= -\log (1.8 \times 10^{-4}) + \log \frac{0.25}{0.03}$$

$$= 4.66 //$$

13Q.) The pH of a buffer sol<sup>n</sup> containing 0.1M CH<sub>3</sub>COOH and 0.1M CH<sub>3</sub>COONa is 4.74. If 0.05 mole of HCl is added to 1 ltr of this buffer sol<sup>n</sup>. What will be the pH? ( $K_a$  for CH<sub>3</sub>COOH =  $1.8 \times 10^{-5}$ )

Sol:-

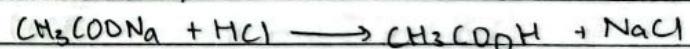
$$\text{Total volume of buffer sol}^n = 1 \text{ ltr}$$

$$\text{Strength of } \text{CH}_3\text{COOH} = 0.1 \text{ M}$$

$$" " \text{CH}_3\text{COONa} = 0.1 \text{ M}$$

$$" " \text{HCl} = \frac{0.05 \text{ mole}}{1 \text{ ltr}} = 0.05 \text{ M}$$

After adding HCl,



$$\begin{array}{ccccccc} 0.1 & 0.05 & 0.1 & 0 & & & \\ 0.1 - 0.05 & & 0.1 + 0.05 & 0.05 & & & \\ \therefore 0.05 & & = 0.15 & & & & \end{array}$$

$$\text{pH} = pK_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$= -\log (1.8 \times 10^{-5}) + \log \frac{0.05}{0.15}$$

$$= 4.267 //$$

(Q) Differentiate between electrolytic cell & galvanic (voltaic) cell

(4Q) A acidic buffer solution of pH 4.8 has to be prepared from acetic acid of 2N and sodium acetate. What amount of sodium acetate should be added to 1 ltr of acetic acid? (pKa for acetic acid : 4.74)

Sol:

Total volume of buffer sol = 1 ltr

Strength of  $\text{CH}_3\text{COOH}$  = 2 N : 2 M

pH = 4.8

pKa = 4.74

Now,

$$\text{pH} = \text{pKa} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{or}, 4.8 = 4.74 + \log [\text{salt}] - \log [\text{acid}]$$

$$\text{or}, 0.06 + \log [\text{CH}_3\text{COO}^-] = \log [\text{CH}_3\text{COONa}]$$

$$\text{or}, \log [\text{CH}_3\text{COONa}] = 0.06 + \log(2)$$

$$\text{or}, \log [\text{CH}_3\text{COONa}] = 0.06 + 0.3$$

$$\text{or}, \log [\text{CH}_3\text{COONa}] = 0.36$$

$$\therefore [\text{CH}_3\text{COONa}] = 2.29 \text{ gm mol L}^{-1}$$

Then,

The molecular mass of  $\text{CH}_3\text{COONa} = 82 \text{ gm}$

Amt. of  $\text{CH}_3\text{COONa}$  to be added in 1 ltr of acetic acid.

$$= 2.29 \times 82$$

$$= 187.85 \text{ gm } //$$

$$\frac{\text{mM}}{1000}$$

$$= 2.29 \times 82$$

$$= 187.85 \text{ gm}$$

Q.) Differentiate between electrolytic cell & galvanic (voltaic) cell

Electrolytic cell	Galvanic (voltaic) cell
A cell that drives a chemical rxn.	A cell that produces electrical energy
It converts electrical to chemical energy	It converts chemical energy to electrical energy
Electron flows from cathode to anode	Electron flows from anode to cathode
A non-spontaneous reaction occurs	A spontaneous reaction occurs
The anode is +vely charged & the cathode is -vely charged	The anode is -vely charged, and the cathode is +vely charged.
Eg:- Electroplating	Eg:- Battery

## # Electrochemistry:

The branch of physical chemistry that studies about interconversion of electrical energy to chemical energy and vice versa is electrochemistry.

Those compounds which ionize in aqueous solution are electrolytes. They are classified into two types:-

(a) Strong Electrolyte: ionizes completely into respective ions in aqueous solution. Examples: NaOH, NaCl, HCl, CH<sub>3</sub>COONa, NH<sub>4</sub>Cl, etc.

(b) Weak Electrolyte: ionizes partially or incompletely in aqueous sol' into their respective ions. Eg:- CH<sub>3</sub>COOH, NH<sub>4</sub>OH, (COO)<sub>2</sub>, etc.

A cell that converts electrical energy into chemical energy is electrolytic cell. For example: extraction of Na from NaCl by down's process is carried out by electrolytic process.

The cell that converts chemical energy into electrical energy is voltaic/galvanic cell. For example: daniel cell is an example of galvanic cell

In a daniel cell, Zinc is made anode (oxidation occurs) and copper is made cathode (where reduction occurs). Both of these electrodes are dipped in their respective salt sol<sup>n</sup>. These two solutions are separated from each other by using a salt bridge. Zn is connected to the -ve terminal of battery whereas Cu is connected to the +ve terminal of battery.

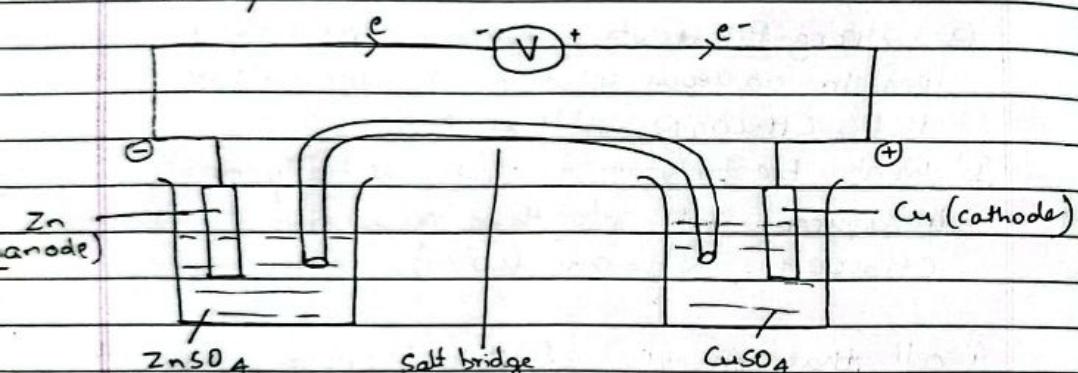
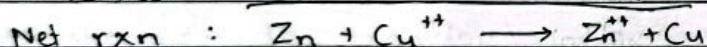
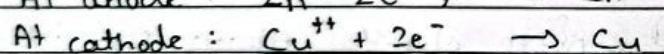
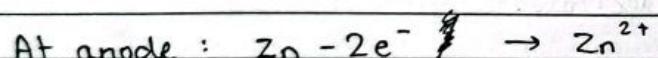
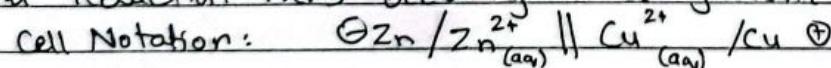


Fig: Daniel Cell



### Cell Notation

It is a short hand notation representation of oxidation and reduction rxns occurring in a galvanic cell.



### Electrochemical Series:

Series in which the elements are arranged on the basis of their rxn potential. On moving from top to bottom their rxn potential is also increasing. At stand. condition (25°C, 1M concn sol<sup>n</sup> & at 1 atm pressure) rxn potential of Hydrogen is 0.00 Volt. Thus NHE (Normal Hydrogen Electrode, SHE) is used as a reference electrode to measure the electrode potential of other electrode.

$E^\circ_{\text{Th}}$

$$E^\circ_{Zn^{2+}/Zn} = -0.75 V$$

$$E^\circ_{H^+/H_2} = 0.00 V$$

$$E^\circ_{Cu^{2+}/Cu} = 0.34 V$$

$$E^\circ_{Ag^+/Ag} = 0.80 V$$

R.P

Electromotive force of the cell is the maximum potential difference between two electrodes of a cell. It can also be defined as the sum of voltage between oxidation & reduction half rxn. It is used to determine if the cell is galvanic or not.

$$E^\circ = E^\circ_{\text{anode}} + E^\circ_{\text{cathode}}$$

$$= E^\circ_{\text{oxid. potential}} + E^\circ_{\text{reduc. potential}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$(R.P) \quad (R.P)$$

### Nernst Equation:

$E^\circ$  is an equation that relates the reduction potential of a rxn (full cell or half cell rxn) to the standard electrode potential, absolute temp (K), concn of the chemical species undergoing redox and oxid.

Free energy change in redox rxn at standard condition:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \dots \text{①}$$

where,  $\Delta G$  = Free energy change (Gibbs & free energy change)

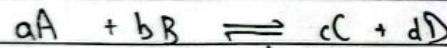
$\Delta G^\circ$  = standard Gibbs free energy change

R = Universal Gas constant (8.314)

T = absolute temp (298 K)

Q = Quotient

For a rxn,



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

Using common log, eqn ① can be written as

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q \quad \dots \text{②}$$

We know that the potential is developed at the electrode on exposure of decrease in free energy of the electrode which can be represented as:

$$\Delta G = -nFE_{cell}$$

$$\Delta G^\circ = -nFE_{cell}^\circ$$

where, n = no. of electrons involved

F = Faraday's constant

E = Emf of the cell

$E^\circ$  = Standard Emf of cell

Substituting those values in eqn ②

$$-nFE = -nFE^\circ + 2.303 RT \log Q \quad \dots \text{③}$$

Dividing ③ on both sides by  $-nF$

$$\frac{-nFE}{-nF} = \frac{-nFE^\circ}{-nF} + \frac{2.303 RT}{-nF} \log Q$$

$$E_{cell} = E_{cell}^\circ - \frac{2.303 RT}{nF} \log Q \quad \dots \text{④}$$

At standard condition; R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>  
T = 298 K

$$1F = 96500 \text{ coulomb mol}^{-1}$$

From ④

$$E_{cell} = E_{cell}^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log Q$$

Standardized to 25°C

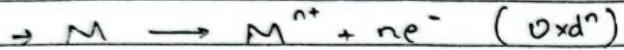
$$E_{cell} = E_{cell}^\circ - \frac{0.0591 \log Q}{n}$$

$$E_{cell}^\circ - E_{cell} = \frac{0.0591 \log Q}{n}$$

$$\log Q = \log \frac{E_{cell}}{E_{cell}^\circ}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303 RT}{nF} \log Q$$

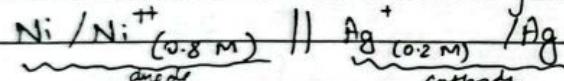


$$E_{halfcell} = E^\circ_{(R.P)} - \frac{0.0591}{n} \log [M^{n+}]$$



$$E_{halfcell} = E^\circ_{(R.P)} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

1 Q.) Calculate the emf of the following cell at 25°C



$$\text{Given: } E^\circ_{\text{Ni}/\text{Ni}^{2+}} = 0.25 \text{ V} \quad (R.P) \quad E^\circ_{\text{Ag}^+/\text{Ag}} = -0.80 \text{ V} \quad (R.P)$$

~~Sol:~~

$$\begin{aligned} \text{emf} &= E^\circ_{\text{cathode}} + E^\circ_{\text{anode}} \\ &= 0.25 \text{ V} - 0.80 \text{ V} \\ &= -0.55 \text{ V} \end{aligned}$$

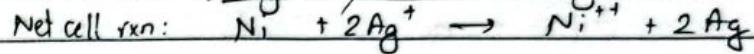
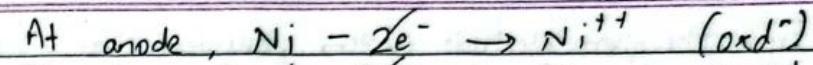
$$\begin{aligned} \text{emf} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= -0.80 \text{ V} - 0.25 \text{ V} \\ &= -1.05 \text{ V} \end{aligned}$$

~~Sol:~~

$$E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \quad (R.P) \quad E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \quad (R.P)$$



cathode value of cathode > anode no



$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

$$= \left( E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \right) - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]}$$

$$= 0.80 - (-0.25) - \frac{0.0591}{2} \log \frac{0.8}{0.2^2}$$

$$= 1.0115 \text{ V} //$$

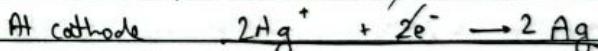
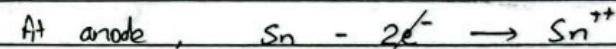
2 Q.) Calculate the emf of the following cell at 25°C.



Where,  $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$  (anode) (R.P)

$$E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V} \quad (\text{cathode}) \quad (R.P)$$

~~Sol:~~



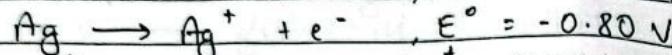
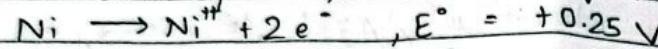
$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

$$= \left( E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \right) - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 0.80 + 0.14 - \frac{0.0591}{2} \log \frac{0.15}{0.03^2}$$

$$= 0.8743 \text{ V} //$$

3Q) From the given electrode system, answer these questions.



$$Ni^{++} = 0.8 M, Ag^{+} = 0.2 M$$

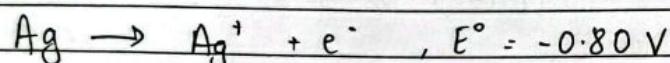
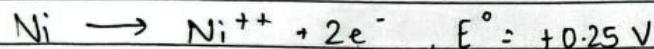
$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

a) Which of the given electrode acts as anode & why?

b) Construct a galvanic cell using proper cell notation when the electrodes are coupled.

c) Calculate the emf of the cell at 27°C

Sol:-



$$Ni^{++} = 0.8 M$$

$$Ag^{+} = 0.2 M$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

~~Ag~~ acts as anode because  $\text{Ag} < \text{Ni}$  hence we can conclude that Ni is cathode & ~~Ag~~ acts as anode.

a)

$$E^{\circ}_{Ni^{++}/Ni} = -0.25 V$$

(R.P)

$$E^{\circ}_{Ag^{+}/Ag} = +0.80 V$$

(R.P)

Since reduction potential of  $Ag > Ni$ , so,  $Ag$  acts as cathode and  $Ni$  acts as anode.

b)

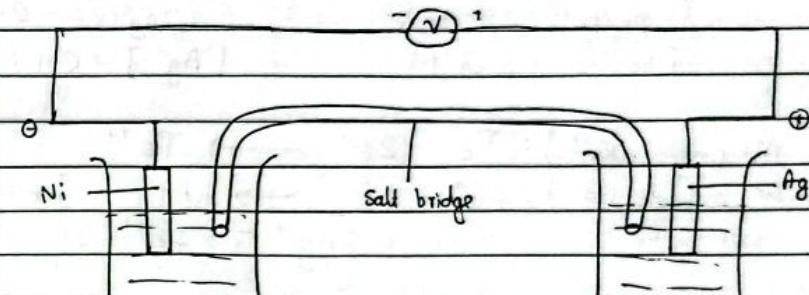
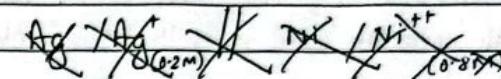
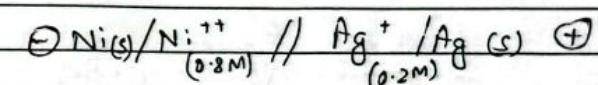


Fig: Daniell cell

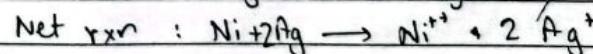


$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{n F} \log G$$

$$= \left( \frac{E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}}{(R.P)} \right) - \frac{2.303 \times 8.314 \times (27 + 273)}{2 \times 96500} \log \frac{G}{G_0}$$

$$(0.80 + 0.25)$$

$$= 1.0112$$



emf : +ve : spontaneous  
-ve : non-spontaneous

Date \_\_\_\_\_  
Page \_\_\_\_\_

Date \_\_\_\_\_  
Page \_\_\_\_\_

4Q) Write electrode reaction, net cell rxn, emf of cell at 25°C & cell notation of the following electrode couple and predict spontaneity of the cell rxn.

SQRT.

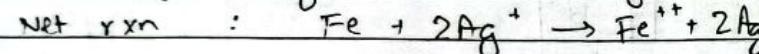
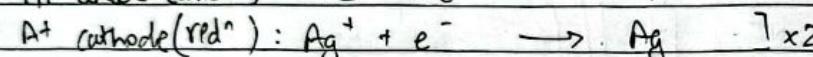
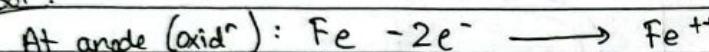
$$E^\circ_{Fe/Fe^{++}} = 0.44V$$

$$[Fe^{++}] = 0.01M$$

$$E^\circ_{Ag^+/Ag} = -0.80V$$

$$[Ag^+] = 0.1M$$

Sol<sup>n</sup>:



$$E^\circ_{Fe^{++}/Fe} = -0.44V \text{ (R.P.)}$$

$$E^\circ_{Ag^+/Ag} = 0.80V \text{ (R.P.)}$$

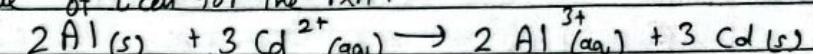
$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= -0.44 - 0.80 + 0.44 \\ &= +1.24 \text{ (not spontaneous)} \end{aligned}$$

Cell notation:  $\ominus Fe(s) / Fe^{++}(aq) \parallel Ag^+/Ag \oplus$

$$E_{cell} = +1.24 - 0.0591 \times \log \frac{[0.01]}{[0.1]^2}$$

$$= -1.24 \parallel$$

5Q) The value of  $E^\circ_{cell}$  for the rxn:



is 1.26 V, calculate the emf of the cell ( $E_{cell}$ ) at 30°C.

$$\begin{aligned} \text{Given: } [Al^{3+}] &= 0.5M \\ [Cd^{2+}] &= 0.2M \end{aligned}$$

Sol<sup>n</sup>:

$$E^\circ_{cell} = 1.26V$$

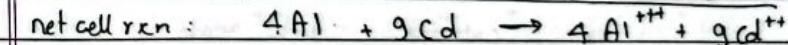
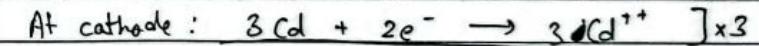
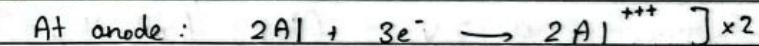
$$E_{cell} = ?$$

$$T = 30^\circ C = 303K$$

$$\begin{aligned} [Al^{3+}] &= 0.5M \\ [Cd^{2+}] &= 0.2M \end{aligned}$$

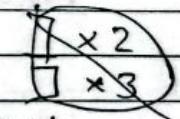
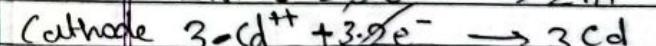
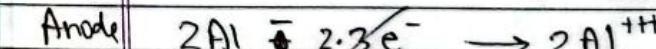
$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

$$= 1.26 - \frac{0.0591}{n} \log \frac{[Al^{3+}]}{[Cd^{2+}]}$$

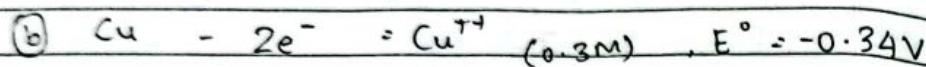
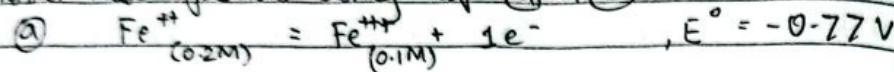


$$= 1.26 - \frac{0.0591}{6} \log \frac{0.5^2}{0.2^3}$$

$$= 1.245V \parallel$$



6Q.) Answer these questions using eqn (a) & (b)



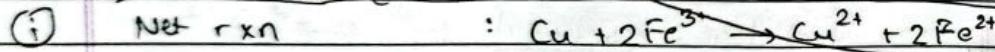
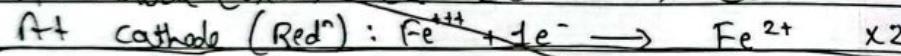
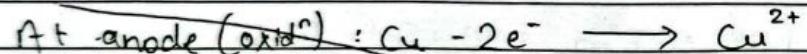
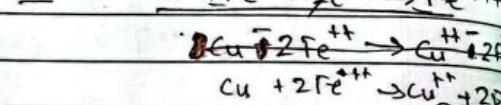
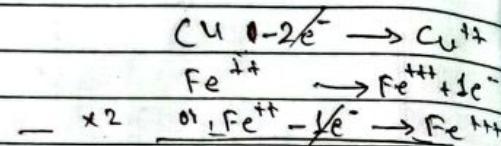
i) Net cell rxn.

ii) Spontaneity of redox rxn.

iii) Cell notation

iv) Emf of cell

~~Net rxn~~



(ii)  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$  (R.P) (anode)

$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{V}$  (R.P) (cathode)

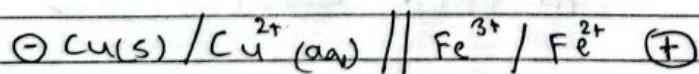
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 0.34 - 0.77 = -0.43$$

$$= -0.43\text{V} \leftarrow + 1.11 = 0.43$$

∴ Spontaneity of redox rxn is ~~this~~ spontaneous.

(iii) Cell notation

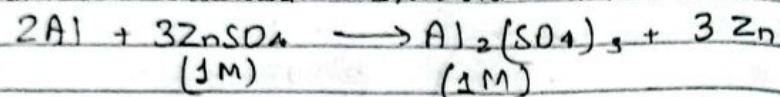


(iv)

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log Q$$

$$\begin{aligned} 0.43 &= -0.43 - \frac{2.303 \times 8.314 \times 303 \times \log [0.3]}{2 \times 96500} \\ &= -0.43 - \frac{2.303 \times 8.314 \times 303 \times 0.875}{2 \times 96500} \\ &= -0.43 - 0.026 \\ &= -0.456\text{V} \\ &\leftarrow 1.084\text{V} \end{aligned}$$

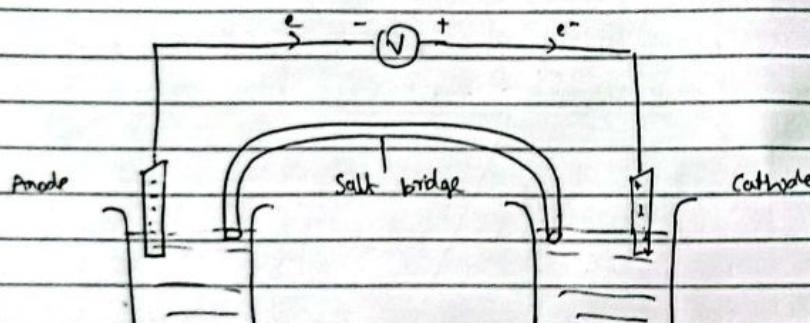
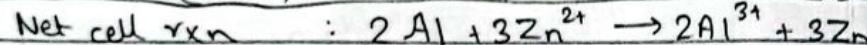
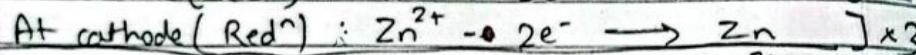
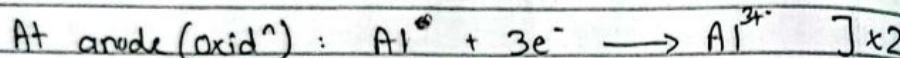
7Q) Construct a cell with the following rxn, write its notation & calculate standard emf of cell:



at 298 K.

Given: Standard redx" potential of Al & Zn are -1.66V and 0.76 V respectively.

Sol:-



Al-Zn cell

$$E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \quad < \quad E^\circ_{\text{Zn}^{2+}/\text{Zn}} = 0.76$$

anode                                                                                                          cathode

$$\begin{aligned} \text{Electr } E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= 0.76 + 1.66 \\ &= 2.42 \end{aligned}$$

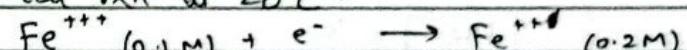
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 \times 8.314 \times 298}{6 \times 96500} \times \log \frac{1}{1}$$

$$= 2.42 - 0$$

$$= 2.42$$

//

8Q) Calculate the oxidation electrode potential of given half cell rxn at 20°C :



$$E^\circ = +0.77\text{ V}$$

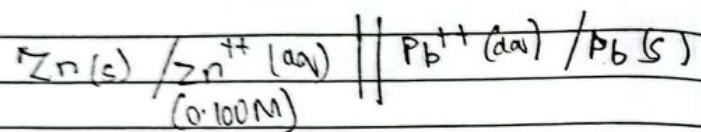
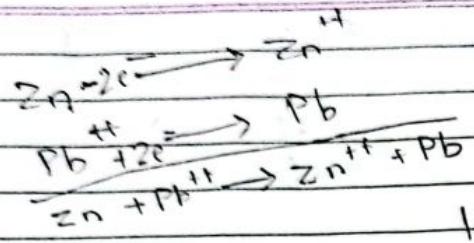
Sol:-

~~$$E_{\text{half cell}} = E^\circ_{\text{Fe}} + 0.0591 \log \frac{0.2}{0.1}$$~~

$$E_{\text{half cell}} = E^\circ_{\text{Fe}} - \frac{2.303 \times 8.314 \times 293}{6 \times 96500} \log \frac{0.2}{0.1}$$

$$\begin{aligned} &= 0.77 - 0.0581 \times 0.3 \\ &= 0.752 \end{aligned}$$

//



$$E = 0.45 \text{ V} \quad \text{at } 25^\circ\text{C}$$

$$[\text{Pb}^{++}] = ?$$

$$E^\circ = 0.64$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2 \text{ F}} \times \log \frac{0.100}{[\text{Pb}^{++}]}$$

$$0.45 = 0.64 - 0.0591 \times \log \frac{0.1}{[\text{Pb}^{++}]}$$

$$-0.3215 = -\log \frac{0.1}{[\text{Pb}^{++}]}$$

$$0.3215 = \log \frac{0.1}{[\text{Pb}^{++}]}$$

$$\frac{0.1}{[\text{Pb}^{++}]} = 10^{0.3215}$$

$$[\text{Pb}^{++}] = 0.1$$

$2.0^{\circ}$

$$[\text{Pb}^{++}] = (0.047 \text{ M})$$

$$0.45 = 0.64 - 0.0591 \times \log \frac{0.1}{[\text{Pb}^{++}]}$$

$$0.15 = -\log \frac{0.1}{[\text{Pb}^{++}]}$$

$$0.15 = 0.643 \times \log \frac{0.1}{[\text{Pb}^{++}]}$$

$$0.15 = 0.022 \text{ M}$$

The phenomenon or redistribution resulting in creation of electric field of

Date \_\_\_\_\_  
Page \_\_\_\_\_

Date \_\_\_\_\_  
Page \_\_\_\_\_

## # Polarization:

It is a process in which there is a variation of electrode potential due to insufficient supply of metal ions from the bulk of the solution to the surface of electrode. (concn' polarization) or an opposing emf/back emf generated as electrolytic cell behaves as voltaic cell after product formation (electrode polarization)

The electrode potential given by Nernst eq<sup>n</sup> can be written as:

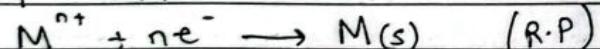
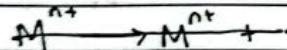
$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

where,

$E^\circ$  is standard emf of half cell

$[M^{n+}]$  is molar ion concn' surrounding the electrode surface at equilibrium.

When an electric current is passed, the metal ion concn' surrounding the electrode gets decreased due to reduction.



Thus there is a shift in equilibrium and a change in electrode potential occurs. Although due to concn' gradient (movement of ions from the sol<sup>1</sup> towards electrode), equilibrium is re-established. But the rate of diffusion is slow and there appears variation in electrode potential. Under such condition, the electrode is said to be polarized. In case of Galvanic cell, less emf is generated due to polarization & in electrolytic cell more emf is required to carry out electrolysis.

\* Decomposition Potential: The minimum amount of potential required to carry out the process of electrolysis is called decomposition potential. It is required to supply potential with higher value than decomposition potential to carry out electrolysis process continuously.

\* Over Potential /Over Voltage: To carry out electrolysis continuous applied voltage should overcome opposing or back emf. Thus a potential higher than the theoretical decomposition potential is applied. Thus, the difference between the potential of the electrodes at which electrolysis actually proceeds continuously & the theoretical decomposition of the same electrolyte is called over voltage /over potential. This value varies from metal to metal. For eg:- theoretical decomposition potential value for electrolysis of dilute  $H_2SO_4$  with Pt electrode at  $25^\circ C$  is  $1.229 V$ . However, it requires  $1.70 V$  potential to carry out the process practically. ~~It is~~ Over voltage is observed in gases. For eg:- in case of evolution of  $H_2$ , the different potential value (theoretical & practical) is called Hydrogen over voltage.

## # Industrial & Applied Electrochemistry:

\* Batteries: A battery is an electrochemical cell or several electrochemical cells connected in series that can be used as a source of direct electric current at a constant v.d.b. They can be classified as follows:- (They store chemical energy for later use as electrical energy)



- Primary (1<sup>o</sup>) cells:** These are the types of cells in which the cell rxn is not reversible. When the majority of reactants gel convert to products, it cannot function & is termed as dead cell. Eg:- Dry cell (Leclanche cell). Used in remotes, digital watches, hearing aids, etc.
- Secondary (2<sup>o</sup>) cells:** These are the types of cells in which the cell rxn is reversible by passing direct electric current in opposite direction. It functions through many cycles of discharging and charging. Eg:- Pb acid storage cell, Li ion battery, Ni-(d) (Nicad) batteries. Used in electric vehicle, mobile, laptop, etc.
- Fuel cells:** It is the cell that does not store energy but converts chemical energy into electrical energy continuously, as long as fuel is supplied. It is used in space vehicles. The most common example of fuel cell is: H<sub>2</sub>-O<sub>2</sub> fuel cell.

### 1) Pb acid battery:

Pb acid battery is a storage cell that can function both as voltaic cell and electrolytic cell. When operating as a voltaic cell, it converts chemical energy into electrical energy and becomes run-down. At this point, electricity is passed through generator where electrical energy is utilized to get decomposition rxn and the chemicals are again set in original pos<sup>n</sup> to give back electricity.

In this Pb acid Battery, one of the electrodes is made of lead and the other electrode is made of lead dioxide (PbO<sub>2</sub>). (paste of PbO<sub>2</sub> is pressed into the grid of Lead metal). Both of these electrodes are placed in the dilute soln of H<sub>2</sub>SO<sub>4</sub> which is around 20 to 21.5%. Here, Lead (Pb)

acts as -ve plate whereas PbO<sub>2</sub> acts as +ve plate. Usually a series of plates are arranged in this order used in automobile. Both of these electrodes are separated from each other by insulators like strips of wood, rubber, glass, etc. These cells functions as both voltaic cell (discharging) and as electrolytic cell (Charging) as shown in the diagram below:-

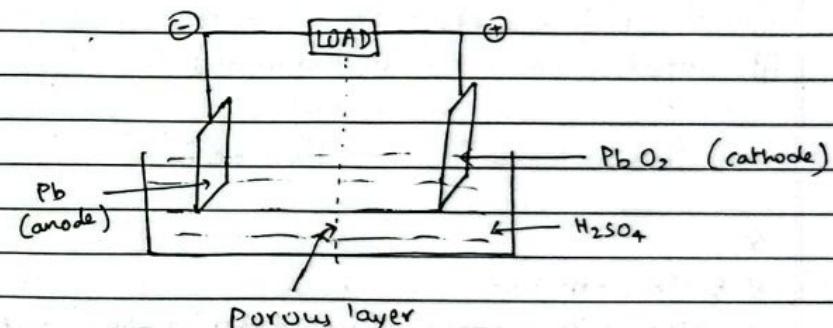
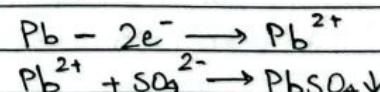
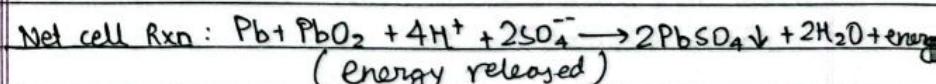
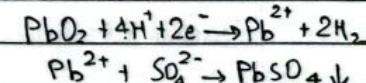


Fig: Discharging (Voltaic cell)

At anode, (oxid<sup>n</sup>)



At cathode, (Red<sup>n</sup>)



After discharging both the compartments get filled with PbSO<sub>4</sub> and it stops to function. Now electric current having greater emf value than its generation value should be supplied from the generator to carry out reversible rxn. At around 21.4% dilution of H<sub>2</sub>SO<sub>4</sub> at 25°C, each  $\frac{1}{2}$ -sheet generates emf of around 2V. So, emf greater than 2V should be supplied for backward rxn process.

Now in charging process it behaves as electrolytic cell. Here, anode is connected to the +ve terminal whereas cathode is connected to the -ve terminal of generator. The following rxn takes place:

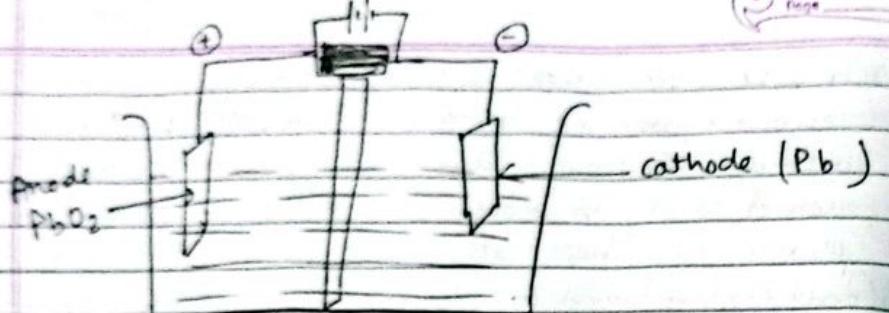
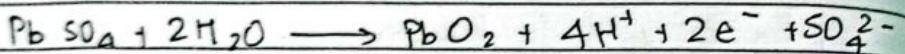


Fig: Charging (Electrolytic cell)

At anode (oxid<sup>n</sup>) (+ve terminal)

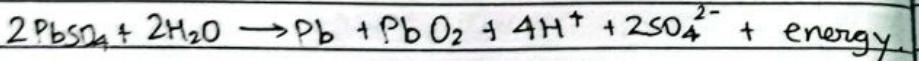


At cathode (Red<sup>n</sup>) (-ve terminal)



So,

Net Cell rxn:



(energy utilized)

During the process of discharging, the concen<sup>n</sup> of H<sup>+</sup> & SO<sub>4</sub><sup>2-</sup> ions get decreased but again on charging, their concen<sup>n</sup> rises.

Used to supply power in electric vehicles, wrist watches, automobiles, powerstations, etc.

## 2.) Li ion battery:

It is also a secondary cell that functions both as Voltaic & Electrolytic cell. It provides power to most of the latest technologies like cell phones, laptops, aircraft engines, watch, etc.

Lithium is extremely reactive metal. So, Lithium Metal Oxides and Lithium carbons (Graphite) are used to supply lithium ions. Lithium metal oxides are used as cathode whereas lithium carbon is used as anode in discharging process. They allow for intercalation, i.e. these electrodes are able to have lithium ions move easily in and out of their structures as per requirement. These electrodes are then separated from each other by a porous separating layer that allows the movement of Li ions as shown in the diagram below:-

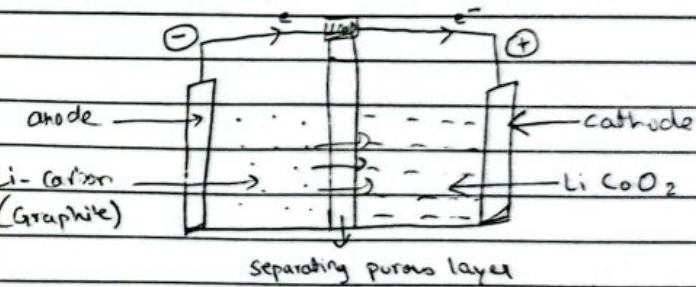
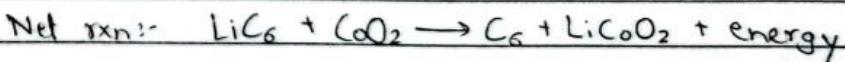
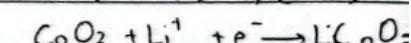


Fig.: Discharging (Li-ion Battery)

At anode (oxid<sup>n</sup>)



At cathode (Red<sup>n</sup>)



The redox (redn & oxdn) rxn takes place inside Li<sup>+</sup> ion battery.

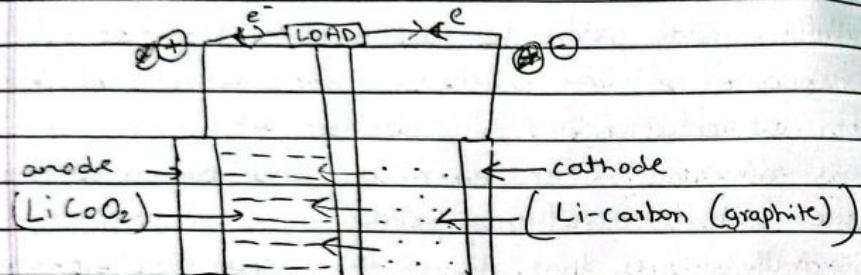
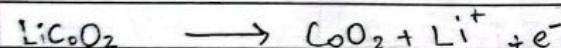
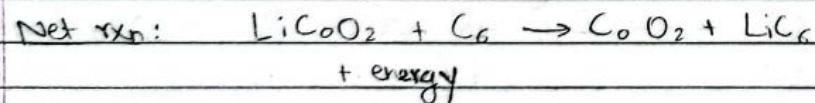
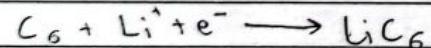


Fig: Discharging ~~battery~~ (Li-ion battery)

At anode: (ox<sup>n</sup>)

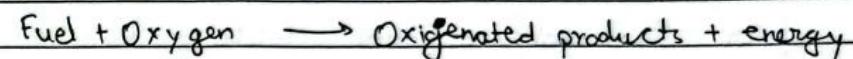


At cathode: (red<sup>n</sup>)



## # Fuel Cells:

It is the type of cell in which the chemical energy of fuels is directly converted to electrical energy. Electricity is generated continuously as long as the fuel is supplied.



The most common fuel cell is H<sub>2</sub>-O<sub>2</sub> fuel cell. It consists of 2 inert porous electrodes in the electrolytic soln of hot (at around 25°) KOH or NaOH. Here H<sub>2</sub> gas is passed through left electrode, that behaves as anode and oxygen gas is passed through other electrode that behaves as cathode. Generation of electrons occur at anode that travel through external circuit and reaches to cathode generating electrical energy as shown below.

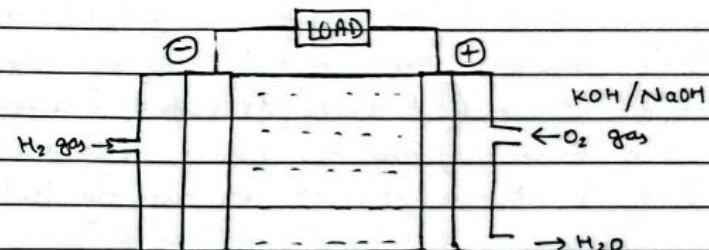
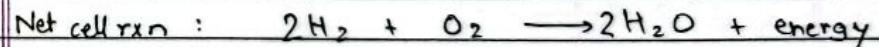
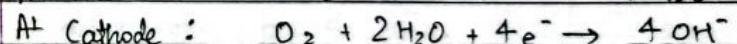
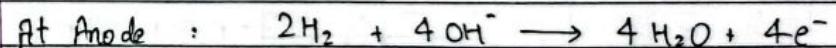


Fig: H<sub>2</sub>-O<sub>2</sub> fuel cell



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{oxid}}^\circ + E_{\text{red}}^\circ \\ &= 0.83 + 0.4 \\ &= 1.23 \text{ V} \end{aligned}$$

Although theoretically 1.23V is expected, only 0.8 to 1.0V energy is released practically. Such cells are connected in series to make it effective. The only product obtained during this process is water. It is used in space vehicles, submarines or many other military vehicles.

### # Photovoltaic (Solar) Cells:

A photovoltaic cell (PV-cell) commonly known as solar cell is an electronic device that converts sunlight directly into electricity. Some of the PV cells can also convert artificial light into electrical energy. Such cells are used to generate electricity for houses, temporary traffic signs, roadway lighting, etc.

A solar cell is made up of two semiconductors like silicon that has been converted into a PN junction. These junctions are made by doping one side of the silicon (~~P type~~) (trivalent elements like Boron, Arsenic) and the other N type (pentavalent like phosphorus as shown in the fig. below:-

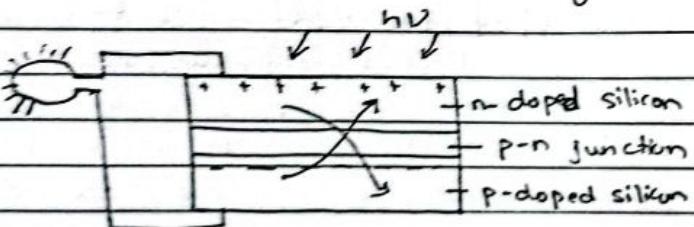


Fig: PV-cell

0.5 to 0.6 V  
15 V to 18 V

After ~~P-N~~ junction is formed, the electrons from 'n-type' try to reach 'p' region creating a negatively charged layer. Similarly, holes of 'p-type' materials try to reach 'n' region creating positively charged layer. The region between these two layers is called depletion region of semiconductor.

Due to the charge deficiency in depletion region, it contains neutral atoms. Sunlight can easily penetrate the top thin layer and reaches depletion region. When the photons from the sunlight strike this region, electron is removed from the neutral atom leaving behind hole. i.e. the electrons in the valence band get promoted to conduction band by absorbing photons from sunlight and now it behaves as intrinsic semi-conductor. When external electronic device is connected or the circuit is completed then electricity is generated by the flow of electrons collected in 'n' region towards the holes formed in 'p' region.

A single solar cell generates about 0.5 to 0.6 V energy, when such 36 cells are connected in series (~~solar panel~~) (solar panel), it generates 15 V energy.

\* **Corrosion (Electrochemical Mechanism & Prevention)**  
 The process of destruction/deterioration and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment, starting at its surface is called corrosion.  
 Eg: Rusting of iron on exposure to moist air where  $\text{Fe}_2\text{O}_3$  is formed making iron weak.

Formation of green film on the surface of copper on exposure to moist air containing  $\text{CO}_2$  due to the formation of basic carbonate  $[\text{Cu}(\text{CO}_3) + \text{Cu}(\text{OH})_2]$

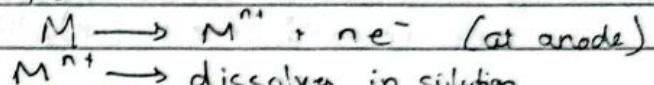
Main types:  
 1. Dry or chemical corrosion  
 2. Wet or Electrochemical corrosion

Differences:-

Chemical corrosion	Electrochemical corrosion
Occurs in dry condition.	Occurs in wet condition, i.e. presence of moisture or electrolyte
Due to the direct attack of metal by the environment.	Due to the formation of large no. of anodic & cathodic areas
It is a self-controlled process.	It is continuous process.
Corrosion products accumulate at the place of corrosion.	Corrosion occurs at anode but the products are accumulated somewhere else.
Eg: formation of mild scale on iron surface. $\text{M} + \text{O}_2 \rightarrow \text{Metal oxide}$	Eg: Rusting of iron in moist air. $2\text{Fe} + \text{O}_2 + n\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3$

- **Electrochemical or wet corrosion Mechanism:**  
 This type of corrosion is seen when a conducting liquid is in contact with metal or when two dissimilar metals or alloys are either immersed or dipped partially in a solution.

Here, anodic and cathodic part exists between which current flows through the conducting soln. At anode,  $\text{oxid}^-$  (loss of  $e^-$ ) takes place resulting corrosion i.e.



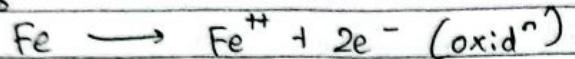
↳ Metal ion forms compounds such as oxides.

At cathode,  $\text{redox rxn}$  (gain of  $e^-$ ) takes place which usually doesn't affect the metal. Thus, an electrochemical corrosion involves,

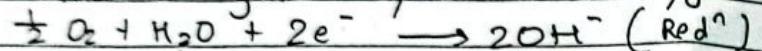
- Formation of anodic & cathodic parts in contact with each other.
- Presence of a conducting medium
- Corrosion of anodic areas only
- Formation of corrosion product somewhere between anodic and cathodic areas resulting in presence of moist air is an example of electrochemical corrosion.



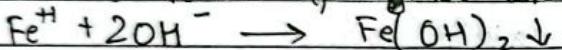
At anodic areas of iron, electrons are liberated forming ferrous ions



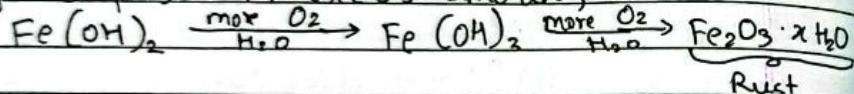
These liberated electrons flow from anode to cathode through metal which are gained by dissolved oxygen.



$\text{Fe}^{+2}$  ions (anode) and  $\text{OH}^-$  ions (cathode) diffuse and get precipitated as ferrous hydroxide when they meet.



If oxygen is present in excess amount,



Passivity is the result of the formation of a highly protective but very thin and quite invisible film on the surface of the metal or an alloy which makes it more inert and stable. The film is insoluble and non-porous. The action of conc.  $\text{HNO}_3$  on active metals like Fe, Al, produce a thin protective oxide film and make them passive.

#### • Procedure of Corrosion:

Some of the methods applied to control / prevent corrosion are:

→ Proper designing of the material should be done, so, even if corrosion occurs, if it is uniform and doesn't harm the material much.

→ Pure metal should be used as we know that impure metals are more prone to corrosion.

→ Protective coatings can be applied like enamel, paint which protect the material from coming in direct contact to the environment causing corrosion.

- Coating can also be done by using more active metal such as galvanization of iron with zinc.
- When the metal surface we want to protect is not possible to galvanize, we can connect it to the sacrificial anode. For eg:- to protect ships, storage tanks, bridges, we can connect them with strip of Zn or Mg, a more active metal which gets oxidized easily preserving ion. Hence they're known as sacrificial anodes.

#### # Butler - Volmer Equation

This equation was first published by John Alfred Butler in 1919 and later on extended by Max Volmer in 1923. The equation was developed to describe the relationship between the current passing through an electrode and potential difference across it in an electrochemical rxn. This equation is derived from the laws of thermodynamics. Considering, both a cathodic & anodic rxn occurring in the same electrode, its eqn can be written as:

$$j = j_0 \left[ \exp \frac{\alpha_a n F}{RT} (E - E_{\text{eq}}) \right] - \exp \left[ -\alpha_c n F (E - E_{\text{eq}}) \right]$$

$$j = j_0 \left[ \exp (\alpha_a n F) \frac{n}{RT} \right] - \left[ \exp \left( -\alpha_c n F \right) \frac{n}{RT} \right]$$

where,  $j$  = electrode current density ( $\text{A/m}^2$ )

$j_0$  = exchange current density (current density at 0 overpotential) ( $\text{A/m}^2$ )

$\alpha_a$  = anodic charge transfer coefficient, dimensionless [ $\alpha_a \alpha_c = 1$ ]

$\alpha_c$  = cathodic charge transfer coefficient

$n$  = no. of electrons involved

$F$  = Faraday's constant ( $96500 \text{ C/mol}$ )

$R$  = Universal Gas constant ( $8.314 \text{ J/mol.K}$ )

$T$  = Absolute Temperature (Kelvin)

$\eta$  = overpotential =  $E - E_{\text{eq}}$

The value of  $\eta$  may be +ve or -ve depending on the direction of half cell rxn.

According to Butler-Volmer Equation, current has an exponential dependency on potential. A Graph representing the relation of Current density with over potential is given :-

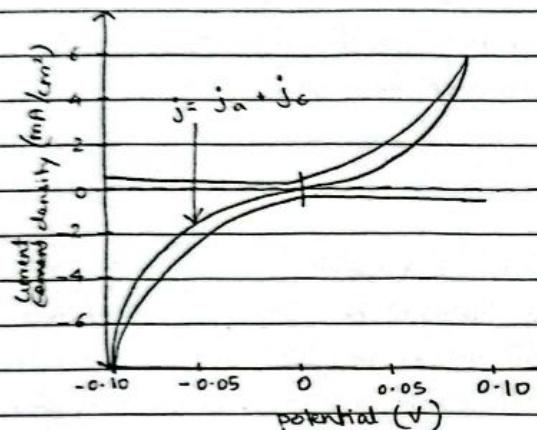


Fig: Current density vs overpotential

### Uses:

- Used in the study of corrosion process.
- Used for the modeling of the behaviour of an electrode or Batteries or to optimize their performances.
- It is used to understand the process occurring on the surface of electrode.
- In many other electrochemical processes.

### \* Tafel Equation:

It is an equation in electrochemical kinetics that relates the rate of an electrochemical rxn to the overpotential. The eq<sup>n</sup> is named after the name of chemist Julius Tafel.

Where an electrochemical rxn occurs in two half rxns on separate electrodes, the Tafel eq<sup>n</sup> is applied to each electrode separately. On a single electrode, the Tafel eq<sup>n</sup> can be written as:-

$$\eta = \pm A \log_{10} \left( \frac{i}{i_0} \right)$$

where,  $\eta$  = over potential / over voltage

+ = anodic process

- = cathodic "

A = Tafel's slope

i = Current density (A/m<sup>2</sup>)

$i_0$  = exchange current density (A/m<sup>2</sup>)

Tafel plot is a specific type of Polarization curve graph in which the potential is plotted against the log of current.

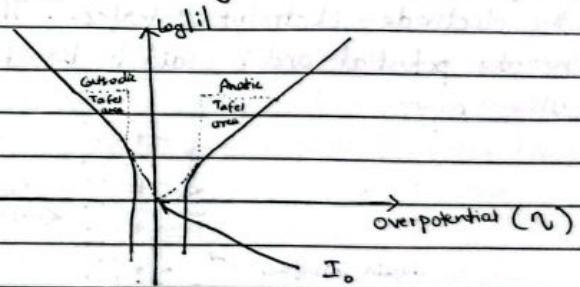


Fig:  $\eta \propto \log(i/i_0)$

### Uses:

It is useful for understanding and analyzing the kinetics of electrochemical rxns. (Butler-Volmer Eq<sup>n</sup> is more preferred as it covers wide area)

To study the corrosion process in electrodes.

It is used for the calculation of activation energy which ultimately helps to find the rate of rxns.

## Electrode Process & Mechanism

In an electrochemical cell, red<sup>o</sup> & oxid<sup>o</sup> rxns take place at electrodes. These rxns involve the electron transfer from electrode to ion or vice versa. The chemical rxn occurring at the electrode - electrolyte surface during electrochemical rxn is Electrode Process. It involves either loss of electron (oxid<sup>o</sup>) or the gain of e<sup>-</sup> (red<sup>o</sup>). Here, oxid<sup>o</sup> occurs at anode and red<sup>o</sup> occurs at cathode. Electrode process is influenced by many factors such as temperature, applied voltage, electron transfer between the electrode and electrolyte, mass transfer, nature of the electrode, etc.

Electrode Process is applied in many electrochemical processes such as: electrolysis, electroplating, electroorganic synthesis, etc.

### \* Electrode-Electrolyte Double Layer:-

In an electrode is dipped in its respective salt sol<sup>o</sup>, then it either loses e<sup>-</sup> to the sol<sup>o</sup> or gains e<sup>-</sup> from the sol<sup>o</sup>.

During this process, Double layers of opposite charges are formed in the electrode-electrolyte interface. This double layer generates potential and is said to be Helmholtz Electrical Double Layer:

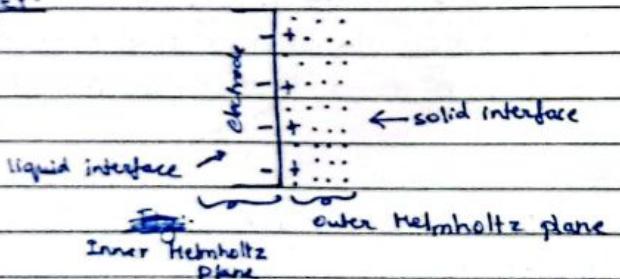


Fig:- Helmholtz Electrical Double Layer

Electrode Process takes part in series of process. They are:

### 1) Electrode Rxns:

This involves oxid<sup>o</sup> and red<sup>o</sup>. Electrode having higher electrode potential acts as cathode and the other electrode having less reduction potential acts as anode. Greater their potential difference, greater will be generated electrode potential.

### 2) Movement of ions:

Charge neutrality is maintained by the movement of ions. Cations move towards cathode & anions move towards anode.

### 3) Electron Transfer:

Movement of electrons between the electrode and the species in the electrolyte. This changes in oxidation states and formation of new substances.

### 4) Electrolyte Interaction:

They provide the movement of electrons and ions in electrode process.

### 5.) Electrode Kinetics: (Electrodics)

It is the rate of electrode rxns.

### \* Charge Transfer process at Electrode:

Charge transfer reaction is very important in many electrode processes. It involves the transfer of electrons from one chemical species to another between the electrode and first layer of electrolyte. The chemical species involved in the electron transfer may be a neutral molecule like water, methanol or ions like Cu<sup>++</sup>, Ag<sup>+</sup>, etc.

Suppose the chemical species is placed in the outer Helmholtz plane, it can accept electron from electrode or donate electron to the electrode accompanied by change in oxid<sup>o</sup> state.

If there is loss of electron, the process is said to be de-electronation (oxid<sup>o</sup>) but if there is acceptance of electron, the process is referred as electron atom (red<sup>o</sup>)

For eg:-

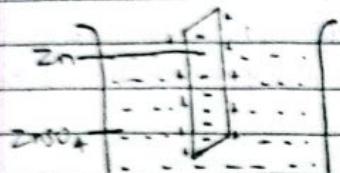
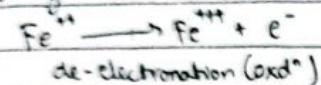


Fig: De-electronation

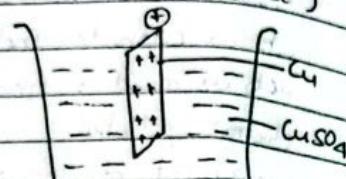
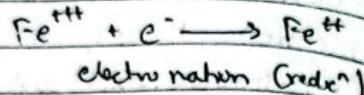


Fig: Electronation

Charge transfer occurs at electrified interface implies a chemical transformation from one oxidation state to another. The electron transfer at interface is heterogenous charge trans.  
The unidirectional flow of electrons results into current.

[ Electron transfer in the bulk of the sol<sup>n</sup> is homogenous or random type and there is no net current. ]

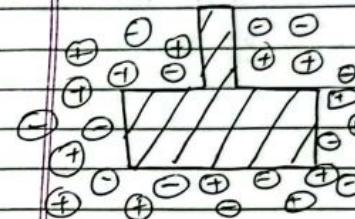
The important application of charge transfer process is observed in supercapacitor. The charge transfer model across electrode - electrolyte interface could be electric double layer charging [EDLC] type or Faradic type or pseudocapacitive type.

#### \* Mass Transfer & Diffusion in electrochemical series :

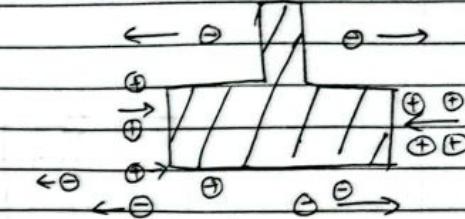
In electrochemical rxns, mass transfer means the state at which materials get transferred from the electrode to the bulk of the sol<sup>n</sup> & vice-versa. It takes place by migration, convection & diffusion.

#### a) Migration :

Mass transfer by migration is driven by applied electric field such that ions get discharged at the corresponding electrode. The amount of substance liberated or deposited at the corresponding electrode is governed by faraday's law of electrolysis.



a) Mass transfer in absence of electric field

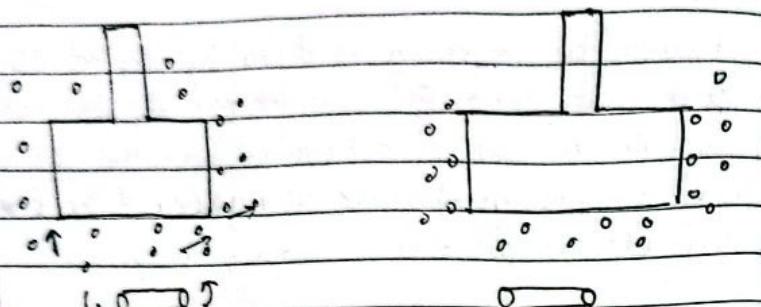


b) Mass transfer in presence of electric field

#### c) Convection :

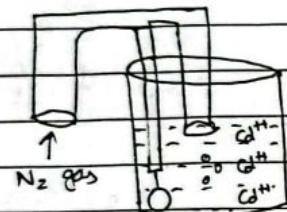
Mass transfer can also be caused by natural or forced movement of sol<sup>n</sup> known as convection. It can be brought about by mechanical stirring or agitation of the sol<sup>n</sup> by passing some inert gas as shown below:

→ limiting current is the max. current that can be achieved during the redx<sup>n</sup> or oxid<sup>n</sup> of an electroactive species at an electrode



a) Mechanical stirring

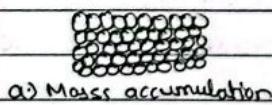
b) without mechanical stirring



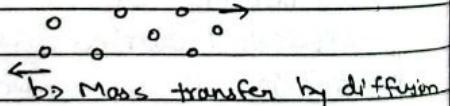
c) Mass transfer by purging gas

## c) Diffusion:

Mass transfer in electrochemical process is governed by concentration gradient, known as diffusion. Here, random movement of ions from higher concentration to lower concentration takes place. The transfer of materials under the influence of concentration gradient is given by Fick's law.



a) Mass accumulation



b) Mass transfer by diffusion

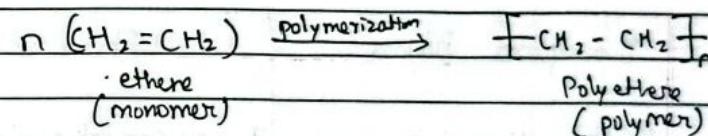
Each type of method of mass transport contributes in the current production. Thus,  
Limiting Current ( $I_{lim}$ ) =  $I_d + I_c + I_m$

Engineering Materials:

Polymers are very large macromolecules or giant molecules obtained by the polymerization of small monomeric units. The word polymer is derived from Greek work;

Poly → many & merous → parts / unit  
polymer = many parts.

The process of conversion of monomeric units to their polymer is called polymerization. For eg: Polyethene (PE) is the polymer obtained by the polymerization of ethane as a monomer.

~~x Classification of Polymers:~~~~a) On the basis of origin or sources.~~

## Natural Polymer

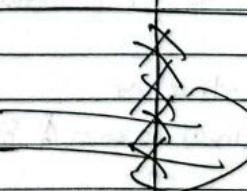
The polymers that occur in nature are .... They are found in plants & animals in different forms & can be isolated from them.

Eg: Starch, Cellulose, Natural Rubber, Protein, Acid, etc

## Man Made (Synthetic) Polymer

These are man made polymers / artificial polymers which are obtained by the synthesis of different compounds.

Eg: Nylon 6,6, Bakelite, PVC, PE, Silicon, etc



b) On the basis of Monomers:

Homopolymer	Co-polymer
If the polymer is made by the repetition of single type of monomeric unit then it is said to be homopolymer.	If the polymer is prepared by the use of more than one type of monomer then they are said to be co-polymer.
Eg:- PE, PVC, Polystyrene, etc.	Eg:- Nylon 6,6, Bakelite

c) On the basis of action of heat:

Thermoplastic Polymer	Thermosetting Polymer
They are linear type of polymers in which temp. shows temporary effect i.e. they can be softened on heating and get hardened on cooling. They can be reused and reused.	These are cross linked polymers having 3D structures in which temp. has permanent effect. Once they acquire certain shape, they cannot be reused and reused - reshaped.
Eg:- PE, Nylon 6,6, polyurethane, etc.	Eg:- Bakelite, Urea formaldehyde resin

d) On the basis of molecular forces:

→ Fibers & Elastomers

e) On the basis of synthesis:

→ Addition polymer & condensation polymer

f) On the basis of structure:

→ Cross linked polymer, linear polymer & Branched chain polymer

g) On the basis of elements present on the backbone of polymer:

Organic Polymer	Inorganic
If the main chain or the skeleton or backbone of the polymer contains covalently bonded carbon atoms. They have greater tensile strength than inorganic and they get softened even at lower temp. Eg:- Polythene, Bakelite, poly urethane, etc.	If the main chain or skeleton or backbone of the polymer is made of other elements than Carbon like P, Si, N, S, etc. then they are. They melt only at high temp. & their tensile strength is lower than that of organic polymers. Eg:- Polyphosphazene, Silicones, Poly thiazyl, etc.

h) On the basis of their conducting nature:

Conducting polymers	Non-conducting polymers
The polymers that can conduct electricity or are made to conduct electricity either by doping or ICP process are. Eg:- Polyacetylene, Polyaniline, Polypyrrole, etc.	These are the polymers that cannot conduct electricity and hence are used as insulators. Eg:- Polystyrene, Nylon 6,6, Teflon, PE, PVC, etc.

\* Types of polymerization:

a) Addition or Chain polymerization

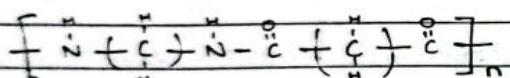
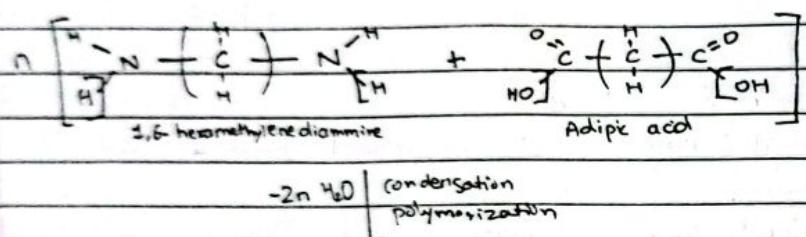
b) Condensation or Step-Growth Polymerization

## • Condensation or Step-Growth Polymerization:-

→ is a reaction occurring between simple polar group containing monomers with the formation of polymers and elimination of small molecules like  $H_2O$ ,  $NH_3$ ,  $HCl$ , etc occurs.

For e.g.: Nylon 6.6 is a condensation polymer obtained by the polymerization of 1,6-Hexamethylenediamine and

### • Adipic acid.

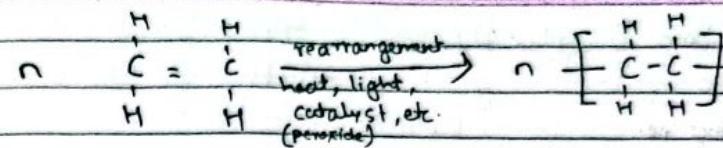


Nylon 6.6

## • Addition / Chain Growth Polymerization:

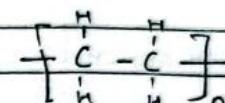
It is a rxn that forms the product which is an exact multiple of original monomeric unit. Such monomeric units contain 1 or more multiple bonds which by rearrangement behaves as bi-functional molecule. This process is carried out in presence of heat, light or catalysts (usually peroxides). This bi-functional molecule undergoes addition polymerization to form addition polymer. For e.g.: Polyethene (PE) is obtained by the addition polymerization of ethene in presence of catalyst.

=)



Ethene

Bi functional molecule



Polyethene

Addition  
polymerization

In addition polymerization, a reactive species such as free radical, cation or anion is generated. It is a chain rxn that involve chain initiation step, chain propagation step & chain termination step.

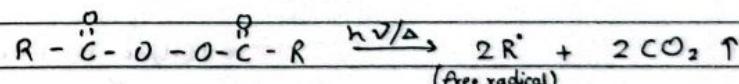
## \* Mechanism of Polymerization

### i) Free Radical Mechanism of Polymerization:-

→ Free radical mechanism of polymerization occurs in 3 steps :-

#### 1) Chain Initiation Step:

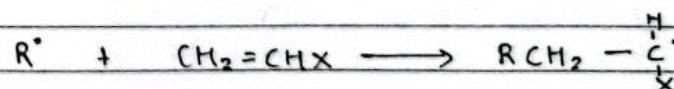
In this step, free radicals are generated by the homolytic bond fission of an initiator or catalyst which are usually peroxides.



These free radicals then attack monomers generating free radicals of monomers.

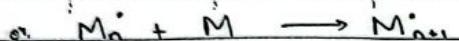


Eg:-

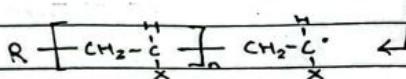
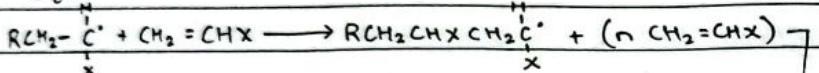


### 2. Chain Propagation Step:-

This step consists of growth of  $M_i^{\cdot}$  free radical by successive add<sup>n</sup> of large no. of monomer molecules

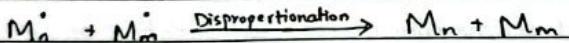
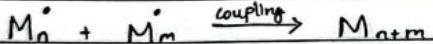


Eg:-

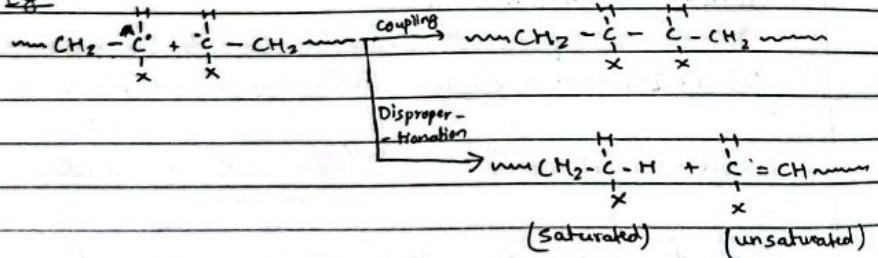


### 3. Chain Termination Step:-

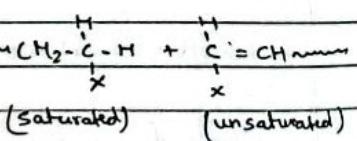
At some point, the propagating polymer chain stops growing and terminates, either by coupling or by disproportionation rxn in which Hydrogen or Proton from 1 monomer gets added to the other forming products, one being unsaturated and the other being saturated as shown below:-



Eg:-



Disproper-  
-termination

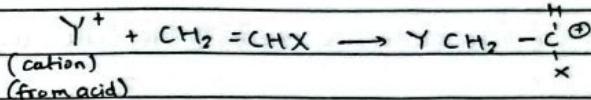


### iii) Cationic Mechanism of Polymerization :-

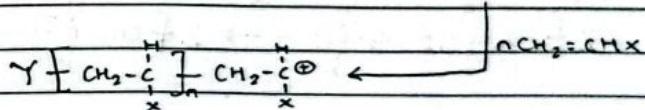
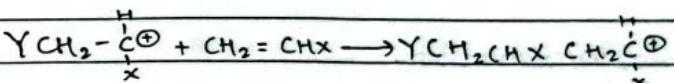
In this method of polymerization, cation usually generated from an acid initiates the rxn. It attacks monomer resulting in the formation of cationic monomer. It then reacts with other monomeric units propagating the rxn forming macro molecule in a continuous pattern. At some point, these cations react with the anions present in the sol<sup>-</sup> itself terminating the chain rxn. as shown below:-

STEP 1 →

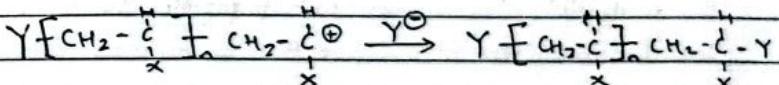
#### 1. Chain Initiation Step:-



#### 2. Chain Propagation Step:-

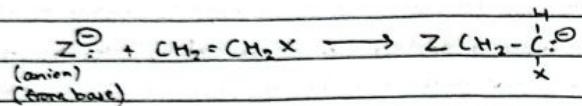


#### 3. Chain Termination Step:-

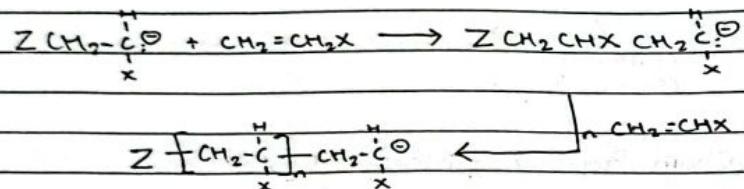


### iii) Anionic Mechanism of Polymerization:

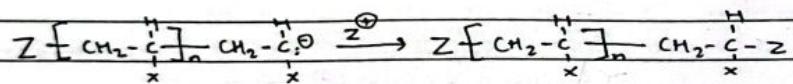
#### 1 > Chain Initiation Step:



#### 2 > Chain Propagation Step:



#### 3 > Chain Termination Step:



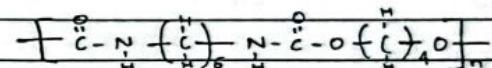
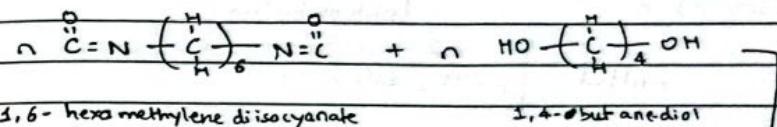
→ In this method of polymerization, anion usually generated from base initiates the rxn. It attacks monomer resulting in the formation of anionic monomer. It then reacts with other monomeric units propagating the rxn forming macro molecule in a continuous pattern. At some point, these anions react with the cations present in the sol<sup>+</sup> itself terminating the rxn chain rxn. as shown above.

### \* Preparation and uses of Polymers

#### 1. Polyurethane:

It is prepared by the polymerization of diisocyanates and diols.

For ex: Perlon 'U' is a polyurethane prepared by polymerization of  
1,6 hexamethylene diisocyanate & 1,4-butanediol



Perlon 'U'  
Polyurethane

Note: Since, No molecules are lost during the process but the functional grp. rearrange themselves, it is considered to be an Additional Polymer.

Uses:- It is used as gaskets or sit seals.

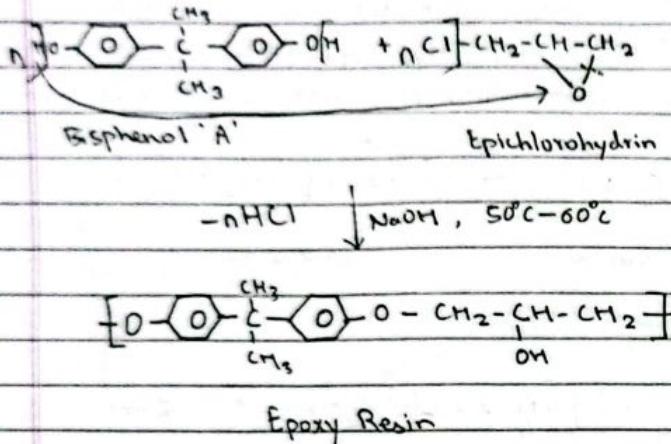
- It can be used as leather substitute.

- Used in making water repellent fabrics like swim suits.

- Bio-medical applications like medicinal devices, artificial skin, tissue engineering.

## 2) Epoxy Resin:

It is a condensation polymer obtained by heating bisphenol 'A' with Epichlorohydrin in presence of alkali like NaOH at around  $50^{\circ}\text{C}$ - $60^{\circ}\text{C}$ .

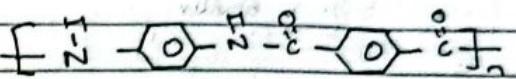
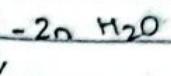
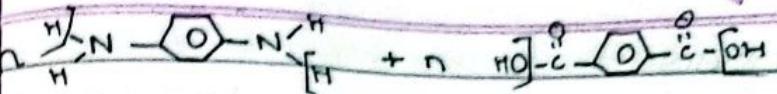


Uses:- They are used as binding materials and as coating materials.

- Composite of Epoxy Resin is used in highways to make road resistant to moisture damage.
- Epoxy Resin are also mixed with cotton fabrics to impart proper crease.
- Moulds from Epoxy Resins are used in prep of parts of automobiles, aircrafts, etc.

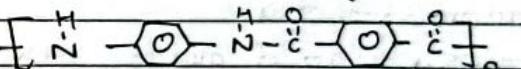
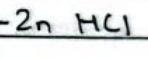
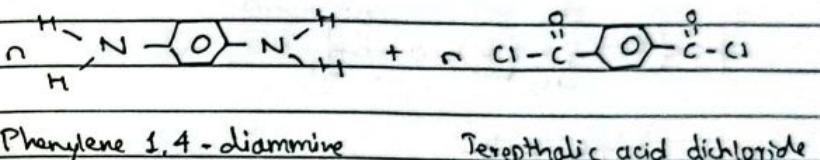
## 3) Kevlar:

It is an aromatic polyamide similar to Nylons but with benzene rings rather than aliphatic change linked to amide group. It is prepared by the polymerization of phenylene 1,4-diamine with Terephthalic acid or Terephthalic acid Dichloride.



Kevlar

OR.

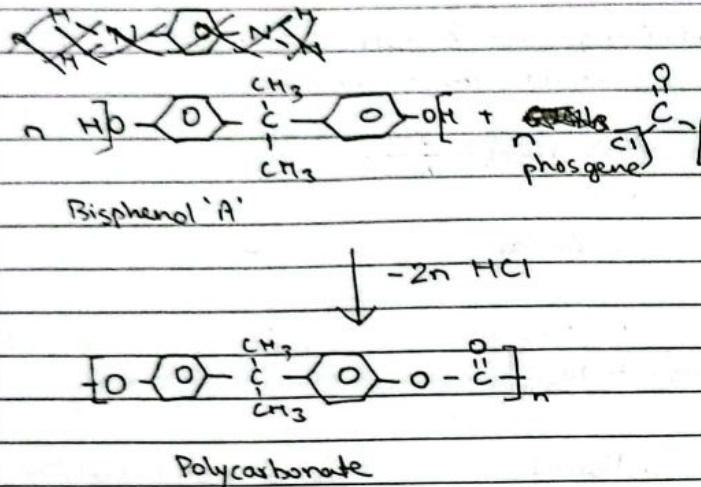


Kevlar

Uses:- In the aerospace and aircraft industries (light weight), car parts, ropes, cables, helmets, bullet proof vests, etc.

#### 4) Polycarbonate:

It is the type of synthetic polymer having carbonate linkage. It is prepared by the polymerization of bisphenol 'A' with phosgene ( $\text{COCl}_2$ )

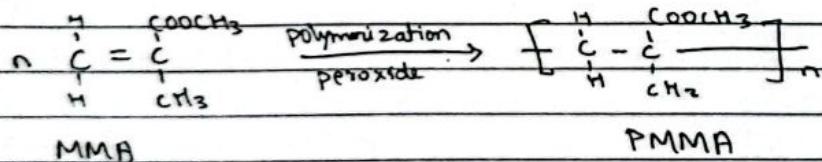


Uses:- Housing for apparatus, electrical insulator in electrical as well as electronic industries.

- Security windows, bullet proof glasses, safety helmets, bottles, roofing, etc.

#### 5) Polymethyl methacrylate (PMMA)

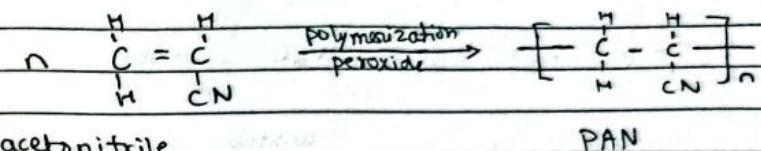
PMMA is obtained by the polymerization of methyl methacrylate (MMA) (ester of aceto methyl acrylic acid) in presence of acetyl peroxide or hydrogen peroxide as a catalyst. It is an acrylic polymer.



Uses:- It is used for making lenses, artificial eyes, adhesives, paints, enamels, TV screens, safety glasses, etc.

#### 6.) Polyacetonitrile (PAN):

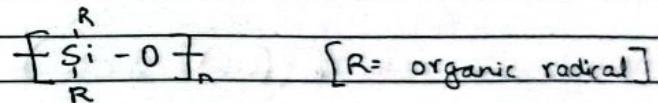
It is an addition polymer obtained by the polymerization of acetonitrile in presence of peroxides as a catalysts.



Uses:- As a substitute for wool, used for making warm clothes, carpets, blankets, etc.

#### 7) Silicones:-

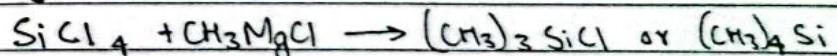
Silicones contain alternate silicon-oxygen structure having organic radicals attached to silicon as shown below:-



Silicones

#### Prep?:-

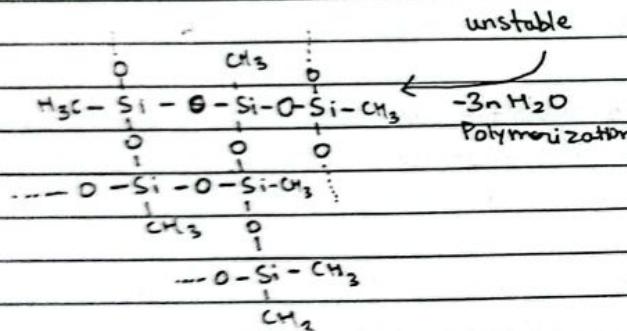
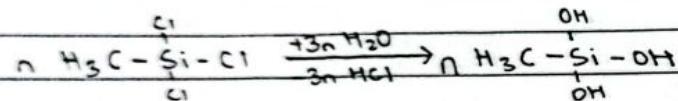
At first, organosilicon halides can be prepared by reacting Silicon with methyl chloride or by reacting silicontetrachloride with Grignard's reagent ( $\text{RMgX}$ )



These organosilicon chlorides are separated from their mixture by fractional distillation. Upon careful hydrolysis, different silicones with their varying structures can be obtained as shown below:-

### ( $\text{CH}_3\text{SiCl}_2$ ) (Monomethyl Silicon trichloride) :-

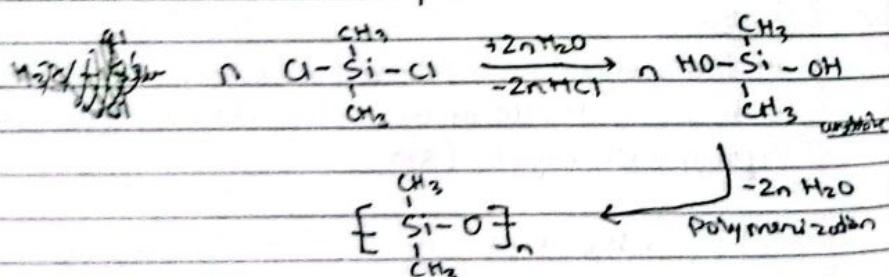
- It is a trifunctional molecule and upon hydrolysis, it forms silicones with cross linked structures.



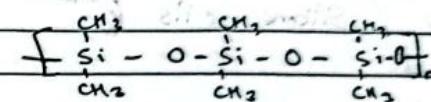
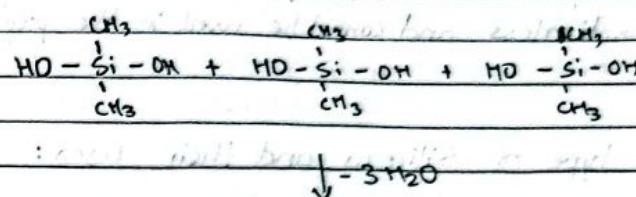
Cross linked silicones.

### ( $\text{CH}_3)_2\text{SiCl}_2$ ) (Dimethyl Silicon dichloride) :-

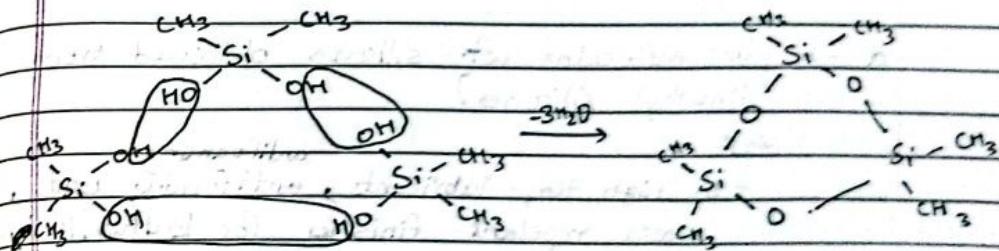
- It is a bifunctional molecule; on hydrolysis, it results in the formation of linear & cyclic silicones.



### i> Linear Silicone

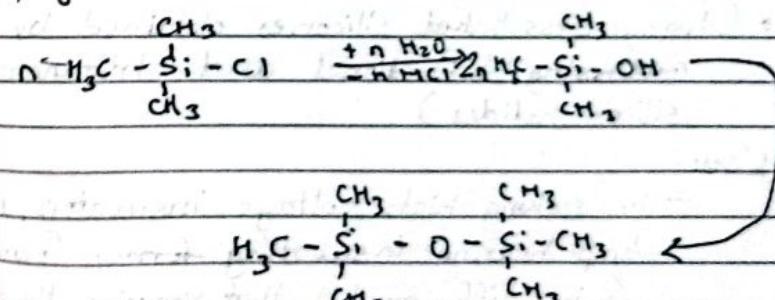


### ii> Cyclic Silicone:



### (c) TriMethyl Silicon chloride ( $(\text{CH}_3)_2\text{SiCl}$ )

- It is a monofunctional and hence is a chain stopper. It is used to stop or control the chain length in bifunctional and trifunctional organo-silicon halides.



(d) Tetramethyl Silicon  $((\text{CH}_3)_2\text{Si})$

→ It is functionless and cannot be used in the prep of Silicones.

### Different types of Silicones and their uses:

- (a) Liquid Silicone / Silicone Oils
- (b) Silicone Grease
- (c) Solid Silicones
- (d) Silicone ~~Rubber~~ Rubber

a → (low molecular wt. silicones obtained from dimethyl silicones)

Uses:

- as high temp. lubricants, antifoaming agents, water repellant finishes for leather, textile, etc.
- in cosmetics, polishes, etc.

b → (modified Silicones oils by adding fillers like carbon black, silica, etc.)

Uses:

- as lubricants where very high and very low temp is encountered.

c → (highly cross linked silicones obtained by condensing bifunctional and trifunctional silicon halides)

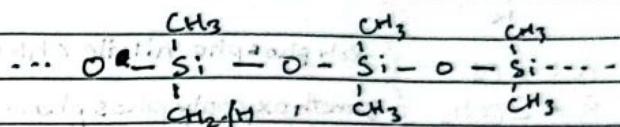
Uses:

- in making high voltage insulators, high temp bearing insulating former foams & in diff. moulds that require thermal stability.

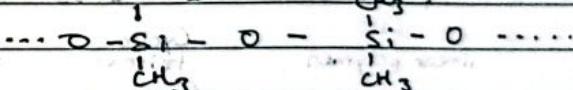
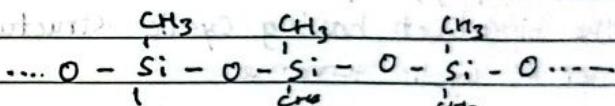
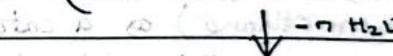
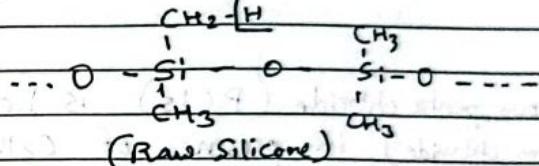
d → (obtained by mixing high molecular wt. linear silicones with fillers like finely divided silica in presence of peroxide & also ~~or~~ curing agents that help to harden the surface.)

Uses:

- Structure:



peroxide  $\rightarrow$   $\text{O}_2$



(Vulcanized Silicone)

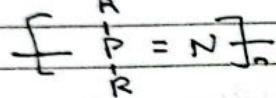
Uses:

- insulating electrical wiring in ships.
- making lubricants, protective coatings in fabrics, water proofing materials.
- as insulators for iron board covers, refrigerators, washing machines, etc.
- for making boots that function properly even at low temp.

### 8) Phosphorous Based Polymers:

(Polyphosphazene):

→ These are the inorganic polymers containing phosphorous atoms having the general formula



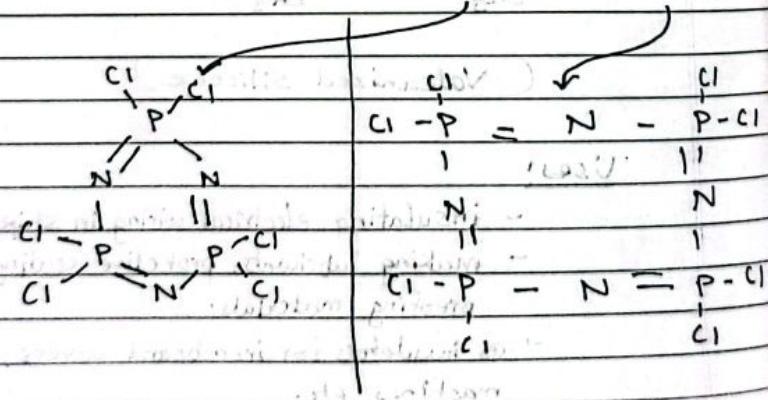
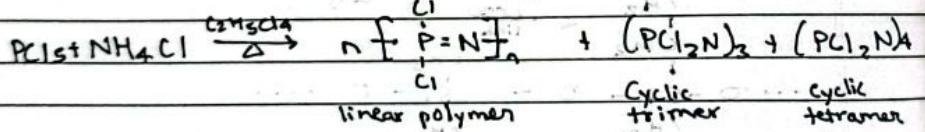
Where  $R = -Cl$  (Polyphospho nitrile chloride)

$R = -OCH_3$  (Dimethoxy polyphosphazene)

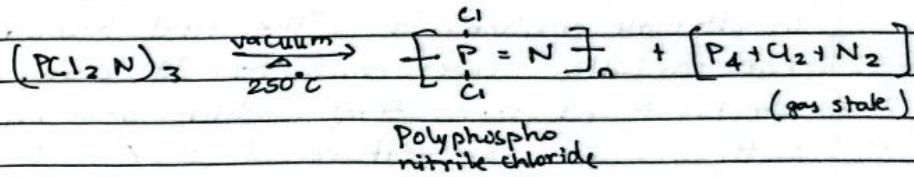
$R = -OC_2H_5$  (Diethoxy polyphosphazene)

Prep.:

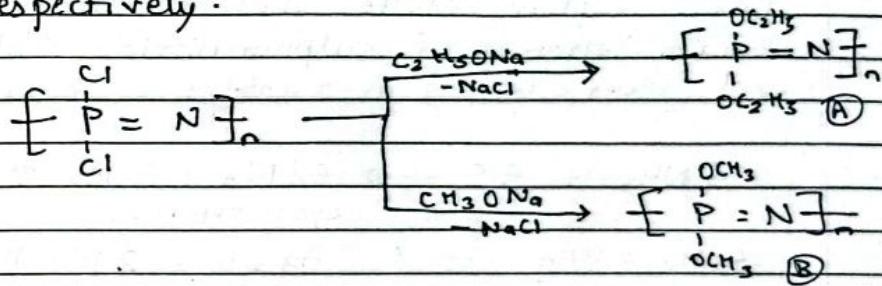
At first phosphorous penta chloride ( $PCl_5$ ) is heated with  $NH_4Cl$  (ammonium chloride) in presence of  $C_2H_2Cl_4$  (1,1,2,2-tetrachloro ethane) as a catalyst where linear polymer of polyphosphonitrile chloride is obtained along with the biproducts having cyclic structures i.e. cyclic trimer & cyclic tetramer.



When this cyclic trimer is heated in vacuum at around  $250^\circ C$  then polyphospho nitrile chloride is obtained.



Thus obtained polyphosphonitrile chloride is then heated with sodium ethoxide & Sodium methoxide to get Diethoxy polyphosphazene & Dimethoxy polyphosphazene respectively.



A → Diethoxy polyphosphazene

B → Dimethoxy polyphosphazene

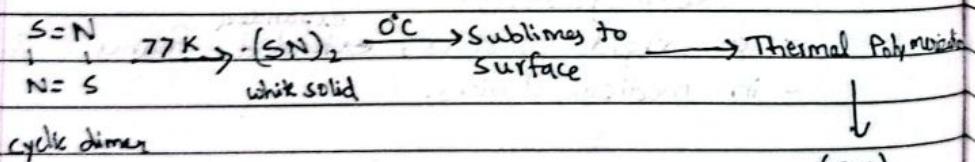
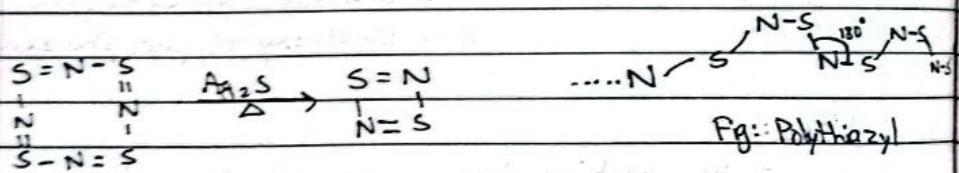
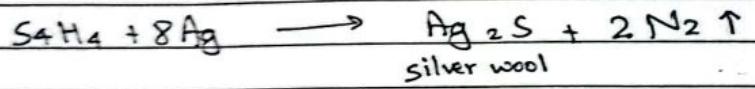
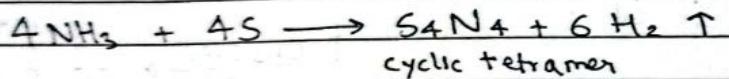
Uses:

- In making transparent, colorless film forming thermoplastics.
- as rigid plastics, expanded foams & fabrics.
- in medical devices.

### 9) Sulphur Containing Polymer: (Polythiazyl)

→ It is a linear polymer having Nitrogen and Sulphur in alternate position. It is the first known non-metallic super conductor. It can conduct electricity at room temp. which goes on increasing with decreasing temperature at 0.26 K, it behaves as a superconductor.

Polythiazyl (Polymeric Sulphur nitride) is prepared by the thermal polymerization of dimeric sulphur nitride which is obtained by reacting Tetramer of Sulphur nitride with silver wool (silver sulphid) as a catalyst as shown below:



#### Uses:

Because of its electricity conducting power it is used in LED's, transistors, battery cathode, solar cell, etc.

### \* Composite

FRP = (Fiber Reinforced Polymer / Plastic)

A composite material is made up of two or more material with different physical and chemical property that remain distinct and separate in the finished structure. A composite material is prepared to improve rigidity, hardness, insulating property, thermal stability, mechanical strength, external appearance, etc.

FRP is a composite material in which the polymers of low strength, lesser anticorrosive property, low degree of elasticity are combined with fibers or fillers.

In this combined products, Fibre acts as reinforcing material whereas the polymer acts as binder. Some of the commonly used fillers are carbon Black, Glass, Metallic Oxides or can even be Sandbut. For example, addition of China Clay to PVC can increase its insulating property. Similarly addition of carbon Black to natural rubber can increase its tensile strength. These day's nano fiber's or carbon nano-tubes are also used in silicon rubbers to increase their insulating and thermal stability.

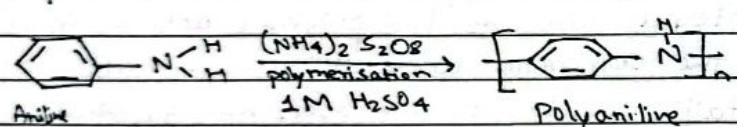
## \* Conducting Polymers:

The polymers that can conduct the electricity or are made redimade to conduct electricity are conducting polymers. Eg: Polyacetylene, Polyaniline, Poly pyrrole.

### \* Polyaniline (PANI):

→ PANI is one of the most studied conducting polymer that is important in rapidly developing technology. Because of its low cost precursor and can easily prepared.

It is synthesized by the oxidation of aniline with oxidized agent such as ammonium per sulphate in presence of 1 molar concentration  $H_2SO_4$



→ Polyaniline exist in 3 diff. forms:

- i) Leucoemeraldine Base (white)
- ii) Pernigraniline Base (Blue/Violet)
- iii) Emeraldine Base (Blue)

Among them Emeraldine Base is the most useful form because of its high stability at room temp. Thus, polyaniline is one of these forms or the mixture of all.

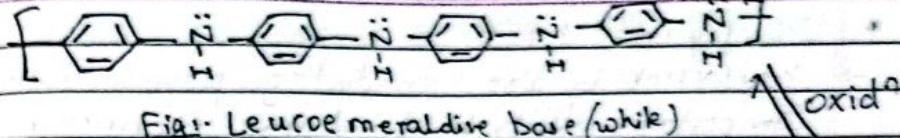


Fig: Leucoemeraldine base (white)

Insulator

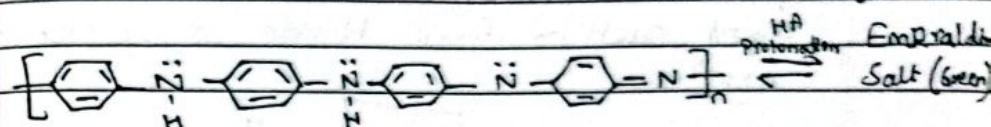


Fig: Pernigraniline base (Blue/Violet)

Insulator

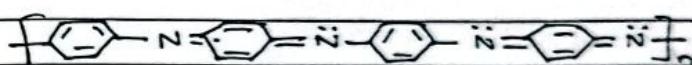
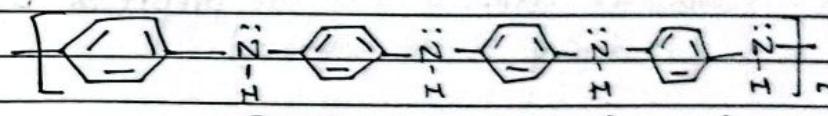


Fig: Emeraldine Base (Blue)



Emeraldine Salt (Green)

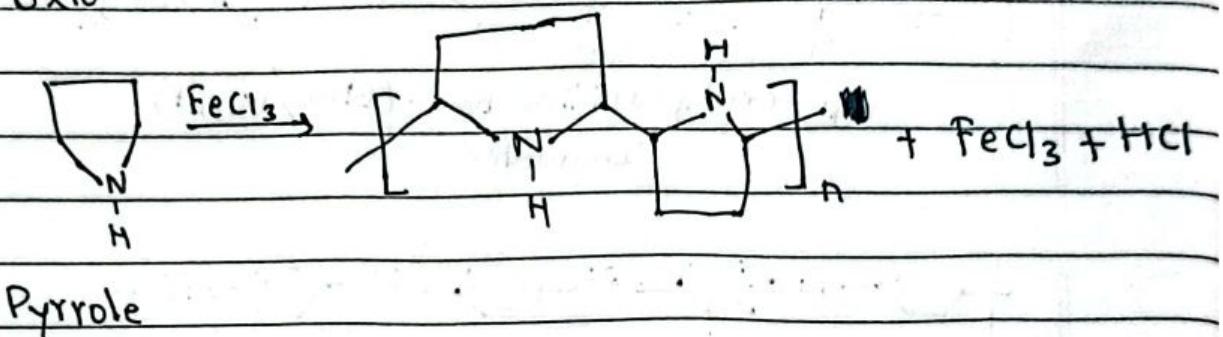
Only conjugated bond in organic polymer is not sufficient electrical conductivity, there must be space for the movement of electrode. The space is created by doping (oxid<sup>+</sup>, red<sup>-</sup>). Emeraldine base when protonated gets converted to emeraldine salt which is the conducting form of polyaniline.

### Uses:

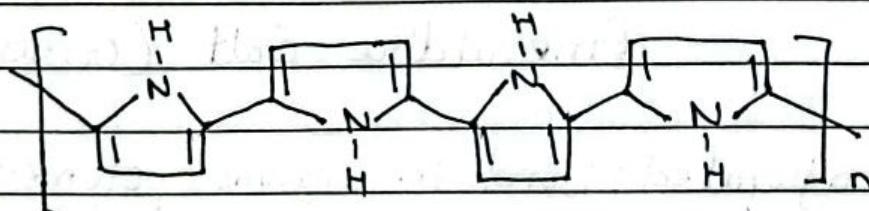
- It is greatly used in Photovoltaics, Energy storage devices, corrosion resistant application, sensors, biomedical engineerings and in different forms of nanofiber and nanotubes.

- Poly pyrrole (PPY) :

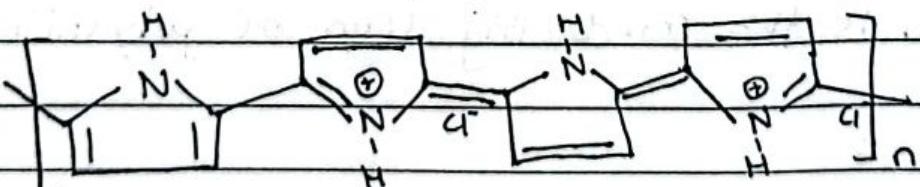
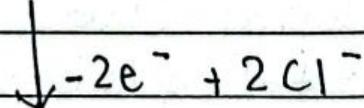
→ Poly Pyrrole is also a conducting polymer having important utility in developing technology. It is prepared by the oxid<sup>n</sup> of Pyrrole with oxidizing agent such as ferric chloride or by electrochemical oxid<sup>n</sup>.



Conductive forms of PPy are prepared by oxid<sup>n</sup>  
(P-doping of the polymer).



Polypyrrole (Non-conducting)



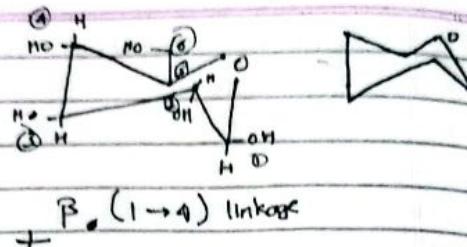
Conducting

Uses:

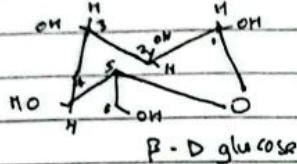
- PPy acts as intrinsically conducting polymer that can be used in electronics, biological or medical field, photovoltaic

### Natural Polymer

- i) Cellulose
- ii) Chitin
- iii) Chitosan
- iv) Collagen



Note in pdf



### Cement:

Cement is one of the most commonly used construction materials having both adhesive & cohesive property i.e. capable of bonding materials like bricks stones building blocks, etc. The chemical composition of Portland Cement is:-

Name	Abbreviated form	Formula	Composition	Setting time
Tri calcium Silicate	C <sub>3</sub> S	3CaO · SiO <sub>2</sub>	45%	7 days
Dicalcium Silicate	C <sub>2</sub> S	2CaO · SiO <sub>2</sub>	25%	28 days
Tricalcium Aluminate	C <sub>3</sub> A	3CaO · Al <sub>2</sub> O <sub>3</sub>	1%	1 day
Tetra calcium Aluminoferrite	C <sub>4</sub> AF	4CaO · Al <sub>2</sub> O <sub>3</sub> · Fe <sub>2</sub> O <sub>3</sub>	9%	1 day

~~880 KJ~~

### Hydration, setting and Hardening of Cement

Application of cement in construction begins with mixing of water where various chemical changes occur such as hydration, hydrolysis, gelation, crystallization, etc. Some heat is released during this process.

C<sub>3</sub>A : 880 KJ / Kg

C<sub>4</sub>AF : 420 KJ / Kg

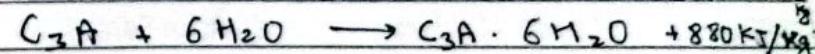
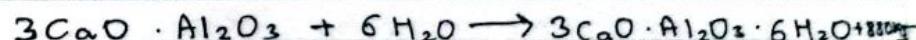
C<sub>3</sub>S : 500 KJ / Kg

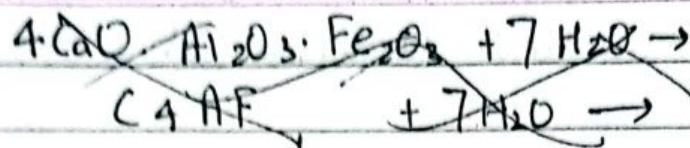
C<sub>2</sub>S : 250 KJ / Kg

In order to avoid shrinkage and cracks during hardening & setting, it is necessary to pour concrete in position in such amounts that the heat generated during hydration is dissipated (distributed) as quickly as possible.

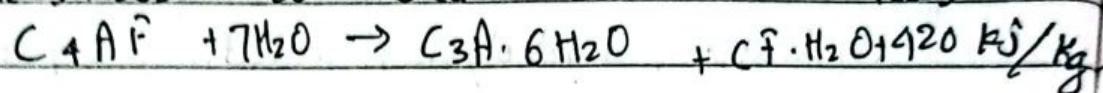
The process of solidification consists of setting and then hardening. Setting is stiffening of the original plastic mass due to initial gel formation & Hardening is the development of strength due to Crystallization. The strength of cement at any situation depends on the formation of gelation and crystallization.

Initial setting of cement paste is mainly due to the hydration of Tricalcium Aluminate and tetra calcium alumino ferrite.

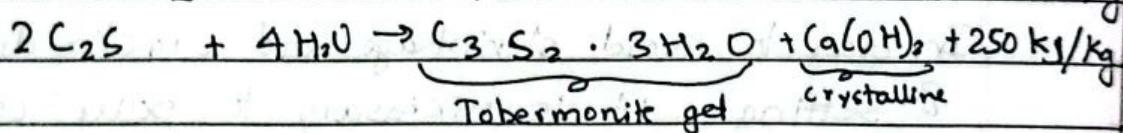
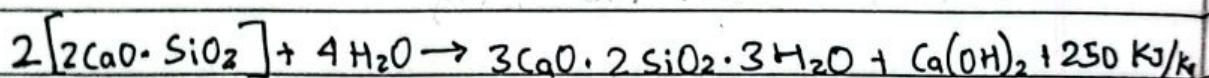




+ 420 kJ/kg

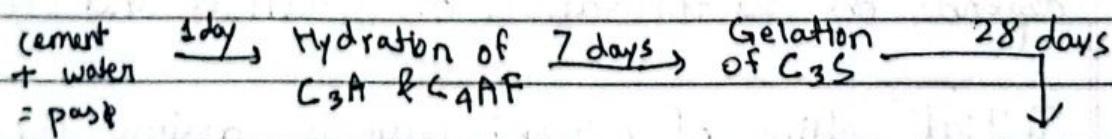
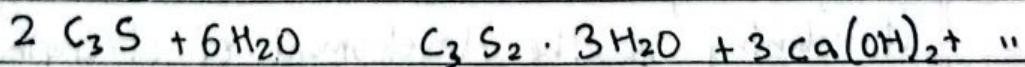
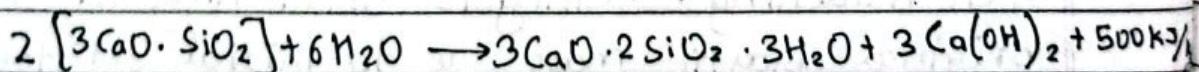


Also, dicalcium silicate starts hydrolysing to Tobermorite gel and calcium hydroxide as crystalline products which has great contribution in initial setting.



crystalline

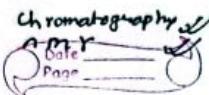
Final setting and hardening of cement paste is due to the formation of Tobermorite gel + crystallization of calcium hydroxide & hydrated Tricalcium silicate as well as aluminato.



Gelation & crystallization  
of  $\text{C}_2\text{S}$  &  $\text{C}_3\text{S}$

{ Principle  
use  
Application }

OR question



Date \_\_\_\_\_  
Page \_\_\_\_\_

## # Analytical chemistry: ( $1 \times 5 = 5$ marks)

### \* Analytical Techniques and their applications:

Analytical Technique is a method used to determine a chemical or physical property of a chemical substance. There are a lot of techniques used in chemical analysis from simple weighing method to advanced analytical techniques. Some of them are-

Chromatography, X-ray diffraction (XRD), mass spectrometry, IR, UV-visible or NMR techniques

## ④ Chromatography:

Chromatography is the technique used in identification, separation and purification of chemicals from their mixtures. They have different affinities towards different phases and can be separated. The term Chromatography was given by a Russian Scientist Michael Tswett in 1903. It was derived from Greek word (Chroma → color & graphy → writing) i.e. "written in color"

### Principle:

Chromatography is based on the principle of selective distribution of different components of a mixture between two phases i.e. stationary phase and mobile phase.

The stationary phase can be solid or liquid whereas the mobile or moving phase can be liquid or gas. When the stationary phase is solid its selective distribution is by adsorption process but if it is liquid, then the selective distribution is partition.

Types	Stationary	Mobile
Column / Adsorption	Solid	liquid
Paper	liquid	liquid
Thin layer chromatography (TLC)	solid/liquid	liquid
Gas Chromatography (GC) (GLC / GSC)	solid liquid	gas

### Advantages:

- Can be used for a mixture containing any type of components.
- Very small quantity of substance is sufficient to be detected effectively.
- Can be used for purification of substances.
- Method is simple to use.

## \* Paper Chromatography:

It is a very simple and most widely used separation technique. A small quantity of sample is sufficient for analysis in this method. It was discovered by A. Martin and R. Synge in 1943.

### Principle:

It is a liquid-liquid chromatography (i.e. both the stationary phase and mobile phase are in liquid state). The mobile phase is an organic solvent whereas the stationary phase is mostly water. Both of them are immiscible to each other (do not mix). Here the mixture of different components are applied on the one end of filter paper which is inserted into solvent saturated chamber with proper solvent system. The paper is held properly in the chamber and its end having mixture to be analysed is dipped in the solvent. The solvent moves upward in the filter paper by capillary action. The components of the analyte (Mixture) are separated by differential migration of components due to their diff. partition coefficient.

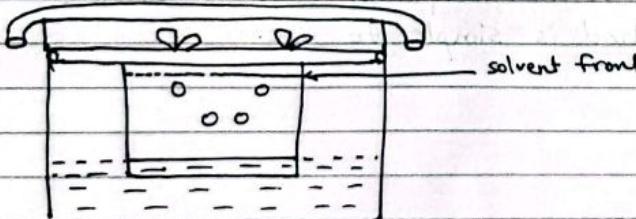


fig : paper chromatography

The ratio of distance travelled by solute to the distance travelled by solvent is expressed in terms of Retention (Retardation) factor ( $R_f$ ): Which is given as:

( $R_f$ )

$$R_f = \frac{\text{Distance travelled by Solute}}{\text{Distance travelled by Solvent}}$$

Its value is always less than 1. So,  $R_f$  value can be the basis for identifying components as it does not change for same sample (same chemical) under given conditions.

### Applications:

- To identify and separate diff. components from analyte.
- To check pharmaceutical compounds.
- To separate amino acids.
- In foreign-seek studies.

\*

## Thin layer chromatography (TLC):

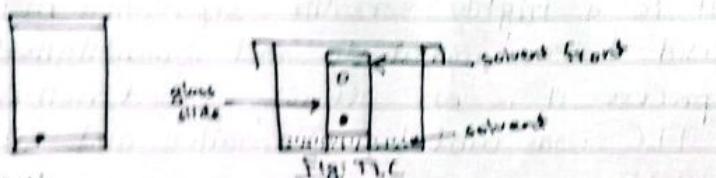
It is a highly versatile separation method that is used both qualitatively and quantitatively analytical process. It is an affinity based method. At first TLC was used by Izmair and Schreiber in 1938.

=)

## Principle:

TLC is performed in a glass slide or sheet of glass or aluminium foil coated with thin layer of Silica ( $\text{SiO}_2$ ) or Alumina ( $\text{Al}_2\text{O}_3$ ). The separation technique depends on the relative affinity of compounds towards both phases. In TLC, stationary phase can be solid or liquid whereas mobile phase is a liquid. The sample to be studied is spotted onto the surface of adjacent layers adsorbent layer which is placed in the beaker having suitable solvent. The compounds then move over the surface of adsorbent layer along with mobile phase (solvent). The compounds having higher affinity towards stationary phase travels slowly whereas those having lesser affinity travel faster. At last, the individual components are spotted as certain spots at different position on the plates later on, their nature and characteristics properties are studied by using other advanced techniques. The retention factor can be calculated as:

$$R_f = \frac{\text{Distance travelled by component (sub)}}{\text{Distance travelled by solvent}}$$



## Applications:

- To check the purity of the substance.
- Identify " " compounds.
- Separate " " components from their mixture.
- Purify " " compounds.
- Check or monitor the progress of reaction.

## (Q) X-Ray Diffraction (XRD)

XRD is a non-destructive technique used for analysing the structure of materials i.e. at atomic or molecular level. It works for materials that are crystalline or partially crystalline but sometimes it can also be used to study the properties of amorphous compounds.

Most of the compounds or the structures of the crystals we know today are because of the study or use of XRD. When light falls on an object which is of the same size range as the wavelength of light, it is diffracted. This property of diffraction is utilized to study or investigate the structure of solids.

## Principle:

XRD is based on a constructive interference of monochromatic X-Rays and a crystalline sample. These X-rays are produced by a cathode ray tube which is filtered to generate monochromatic X-ray radiation, aligned & parallelly and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg's law.

At first, Bragg's Diffraction was proposed by W.H. Bragg and W.L. Bragg in 1913. Bragg's Diffraction occurs when a subatomic particle or electromagnetic wave radiation waves have wavelength  $\lambda$  that are comparable to atomic spacing in a crystal lattice, given by the following eqn:

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

Where  $n$  = numeric constant (known as the order of diffracted beam)

$\lambda$  = X-ray wavelength

$d$  = interplanar spacing

$\theta$  = angle of diffracted wave.

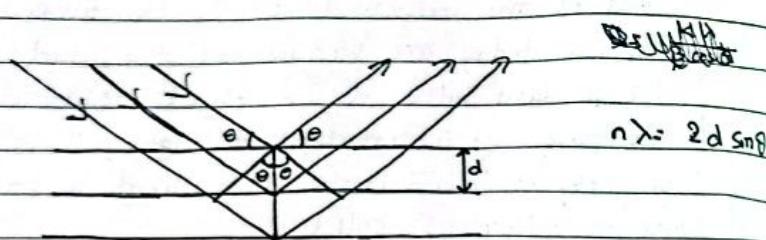


fig: X-Ray Diffraction

Crystalline solids has a well defined edges and faces, diffract X-rays properly and has sharp melting points. In contrast, amorphous compounds has irregular or curved surfaces, do not give well result X-ray diffraction and their melting points do ~~not~~ vary.

where,  $D$  = avg. size of crystal

$K$  = constant

$\beta$  = line broadening in radian

$\lambda$  = wavelength of X-Ray

$\theta$  = Braggs angle.

#### Applications:

- To study about the size, dimensions, melting points of solids.
- To characterize polymers.
- To identify the size of particles.
- To study / characterize nano materials.

#### Spectroscopy

The interaction of electromagnetic radiations with the matter i.e. atoms or molecules is called Spectroscopy.

#### Mass Spectrometry (MS):

#### \* Particle Size / Grain Size XRD :

Paul Scherrer used X-Rays to determine the size of crystals in nano phase materials in 1918. Thus, size of particles can be determined by using the following Debye-Scherrer formula / eqn:

$$D = \frac{k\lambda}{\beta \cos\theta}$$