

# Inorganic Chemistry

## Semester I

### M.Sc. Chemistry Notes

Also useful for **NET**

The image features a woman in a red t-shirt with the text "chemistry ABC.com" printed on it. She is standing in front of a background that includes several logos and chemical glassware. On the left, there are logos for "CSIR-NET", "GATE", and "IIT-JAM". Below these is a green square logo for "IIT JAM Joint Admission Test for M.Sc.". On the right, there is a blue rounded square logo for "GATE" and a black rounded rectangle with an information icon and the text "VIEW Details". At the bottom left, there are four pieces of laboratory glassware containing colored liquids (red, green, yellow, and blue). At the bottom right, there is a large pink Erlenmeyer flask with the text "chemistry ABC.com" on it. A vertical watermark "www.ChemistryABC.com" is visible on the right side of the image.

ChemistryABC.com  
quizzes | posts | downloads | study materials more

## Metal Carbonyl Cluster $\rightarrow$

Such clusters contain metal atom in low oxidation state and have carbonyl groups to stabilize low oxidation state.

They have long M-M bond. These clusters are formed by transition metals which are placed on the right hand side of periodic table such as Fe, Co etc.

It is grouped into 2 categories

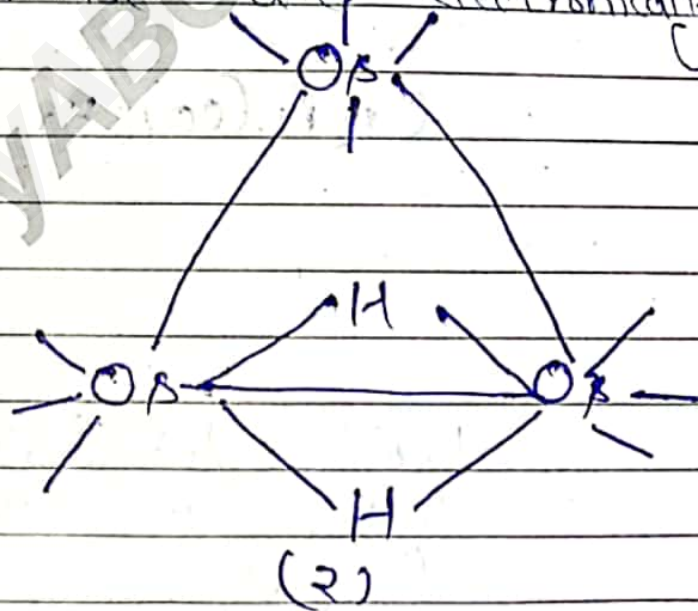
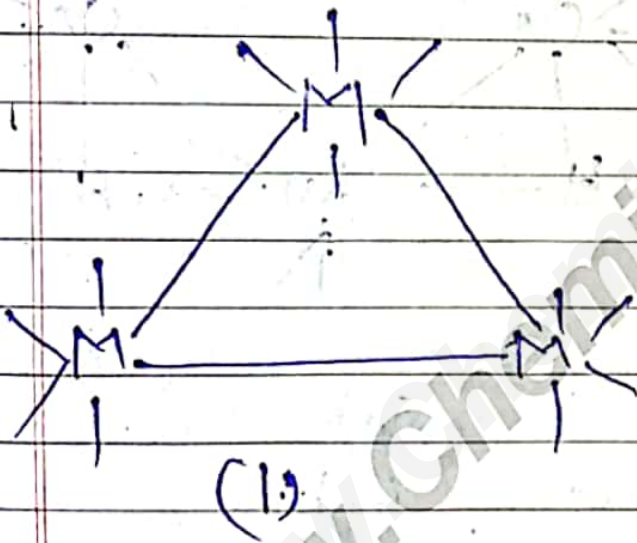
- 1- low nuclearity carbonyl cluster.  
(LNCC) - It contains 2 to 4 metal atoms.
- 2- High nuclearity carbonyl cluster.  
which contains 5 or more metal atoms.



# 1- low nuclearity $M_3$ and $M_4$ cluster

(i) Triatomic cluster - The metal of triangular  $M_3$  cluster and are  $M_3(CO)_12$  and have general formula  $M_3(CO)_12$  where  $M = Os, Ru$  etc

These cluster may be represented as shown in fig. where "Co" (group) are denoted by lines and those are electronically saturated



In such system there must be  $48 e^-$

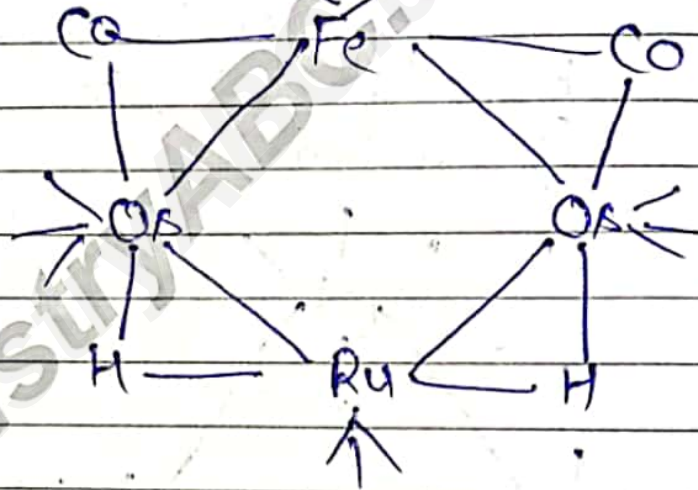
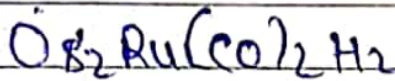
On other hand  $H_2Os_3(CO)_10$  cluster is an unsaturated system having 46 total  $e^-$  as shown in fig. (2)

(ii) 4 atom cluster

A large no. of 4 atom clusters are known.

These are represented by general formula  $M_4(CO)_x$  where  $M = Rh, Co, Ir$

Some heteronuclear carbonyl cluster are also known as shown in fig.



Beside tetrahedral geometry 4 atom cluster are known which have butterfly (fig a) and planar (fig b)



(a)

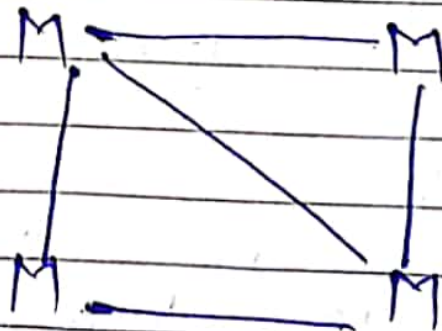


fig (b)



## High nuclearity carbonyl cluster

These contain 5 or more metal atoms, each forming at least one M-M bond.

The first HNC is  $Rh_6(CO)_{16}$  was structurally studied by Coray Dahl, Beck in 1963.

Now a day number of such cluster have be prepared and studied.

Synthesis  $\rightarrow$  The HNC are synthesis by generation of reactive fragments, which combine to form HNC.

These fragments may be prepared thermally or by reduction process.

Osmium HNC was prepared by vacuum pyrolysis of  $Os_3(CO)_{12}$ .

# METAL CARBONYL CLUSTER

# ORGEL DIAGRAMS

Orgel diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes, much like Tanabe-Sugano diagrams.

Name of Orgel belongs to the creator of this Orgel.

Orgel diagrams are restricted to only show weak field (i.e. high spin) cases, and offer no information about strong field (low spin) cases.

Because Orgel diagrams are qualitative, no energy calculation can be performed from these diagrams.

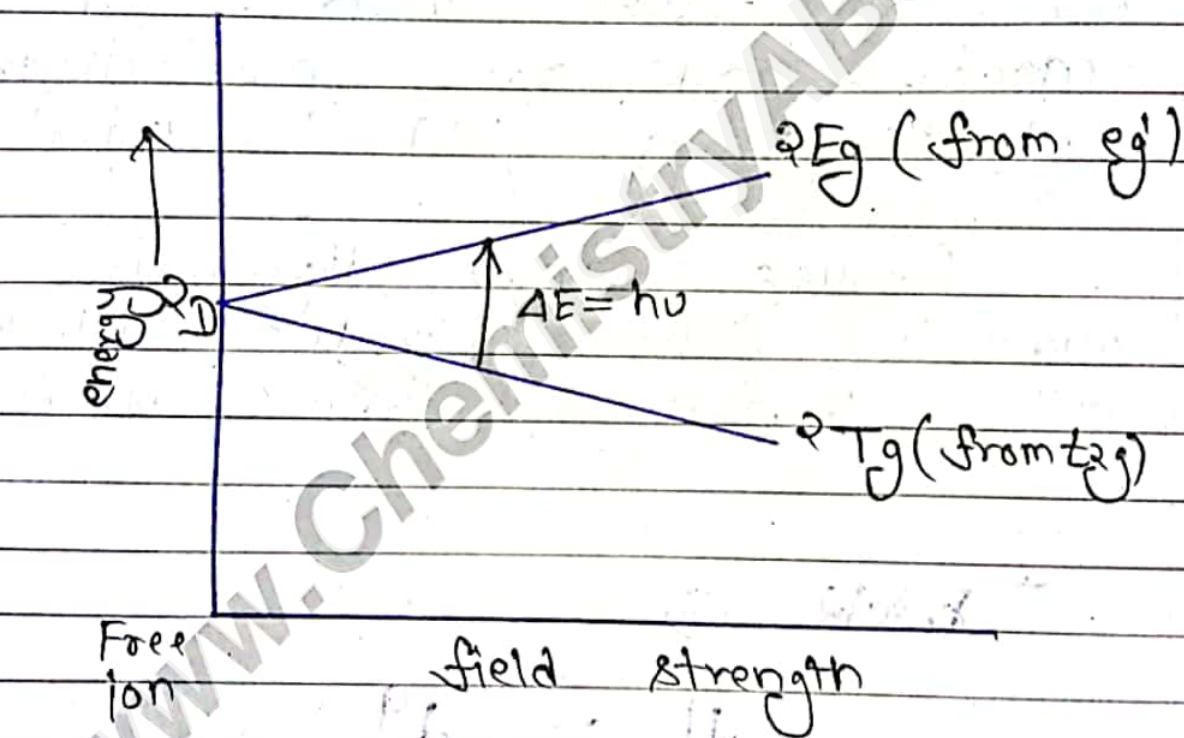
Trick  $\Rightarrow$

$$\begin{aligned}d^1 &= d^9 \\d^2 &= d^8 \\d^3 &= d^7 \\d^4 &= d^6\end{aligned}$$



# Applications of Orgel diagrams to electronic spectra of transition metal complexes.

**d<sup>1</sup> Metal ions** → The splitting of energy levels for d<sup>1</sup> ion is shown in fig

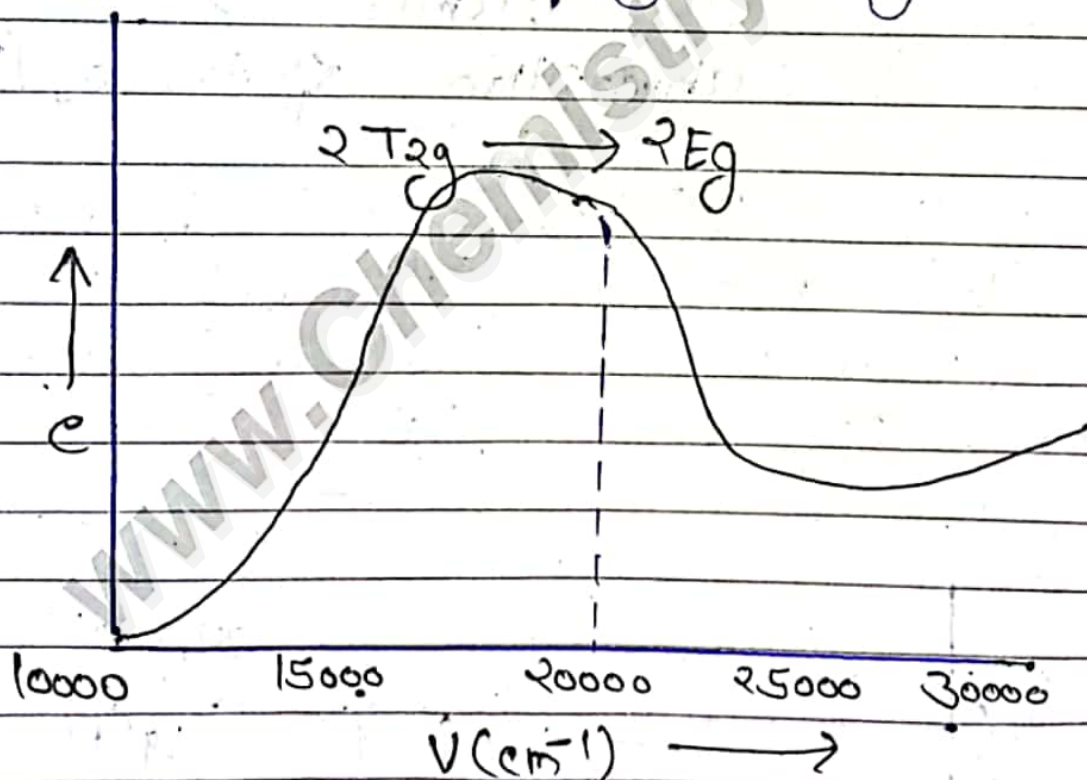


Free  $Ti^{3+}$  ion contains only one electron in d-orbital hence it has only one energy term denoted as  $2D$

When 6  $\text{H}_2\text{O}$  molecules approach  $\text{Ti}^{3+}$  ion, this electron enters  $t_{2g}$  set ( $d_{xy}, d_{yz}$  and  $d_{zx}$  called  ${}^2T_g$  energy levels) of orbitals.

On absorption of radiation of frequency  $\nu$ , the electron gets excited to one of  $e_g$  orbitals.

The absorption band at  $20400\text{ cm}^{-1}$  can be assigned to  ${}^2T_g \rightarrow {}^2E_g$

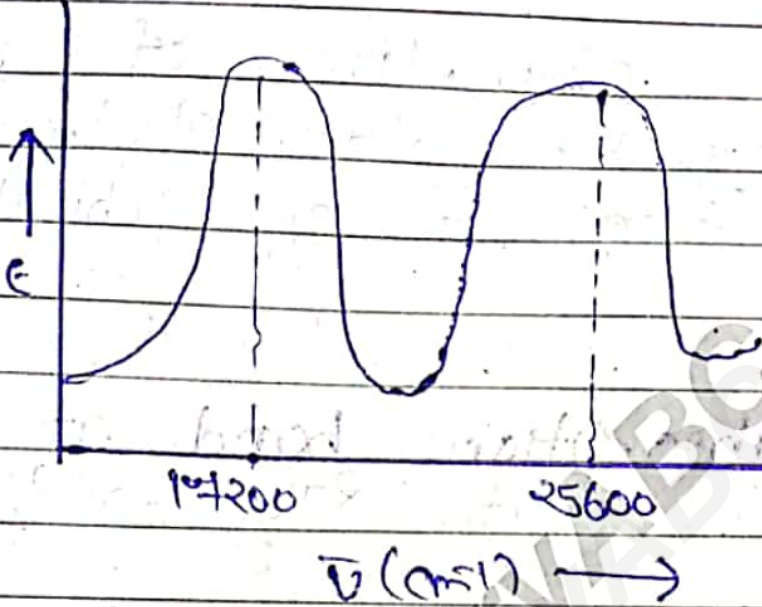


(absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ )



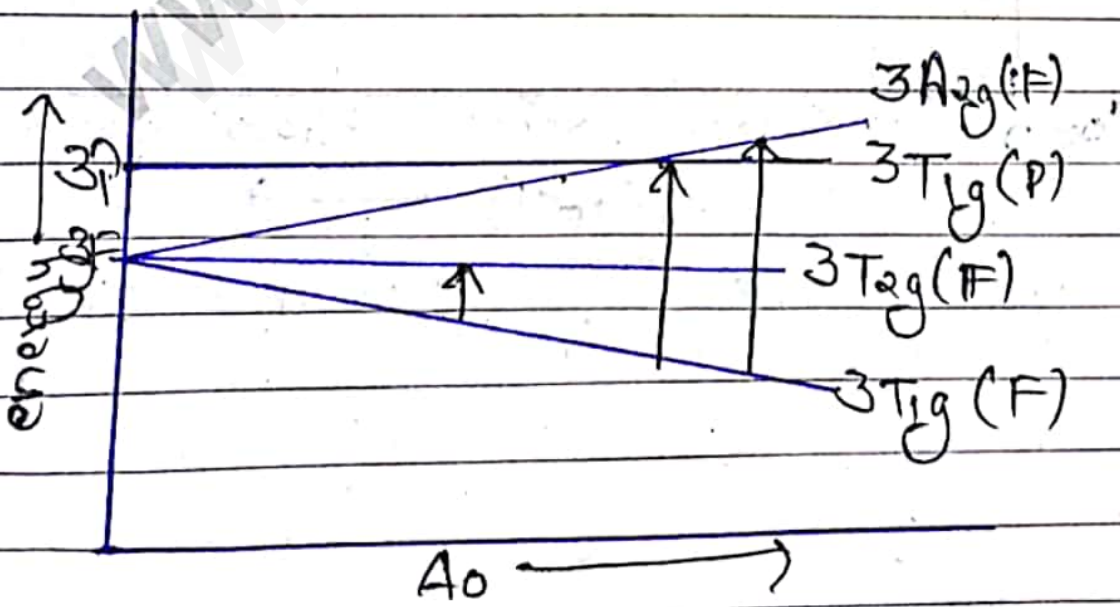
# $d^2$ Metal ions

The complex ion  $[V(H_2O)_6]^{3+}$  absorbs at  $17200\text{ cm}^{-1}$  and  $25600\text{ cm}^{-1}$  as in fig.



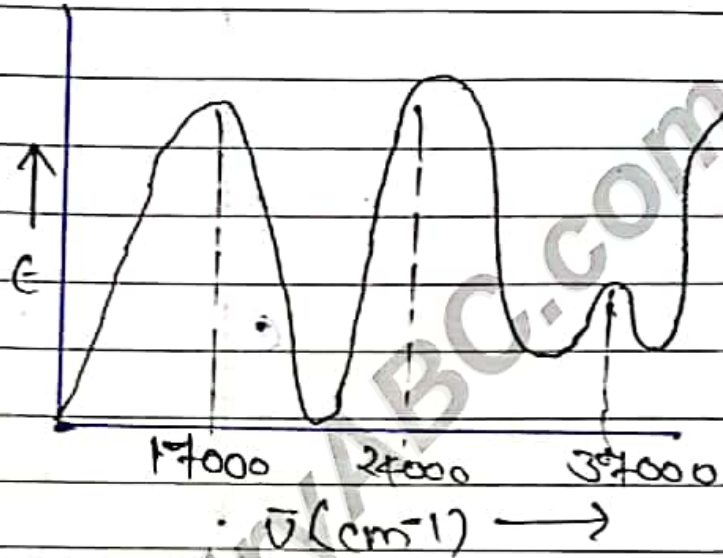
(Absorption spectra of  $[V(H_2O)_6]^{3+}$ )

The free  $V^{3+}$  ion has  $d^2$  configuration which can be  $dx^2y^2$ ,  $dyz^2$ ,  $dyz^2 dz^2$  or  $dx^2y^2 dx^2y^2$  in ground state represented as  $3F$  state.

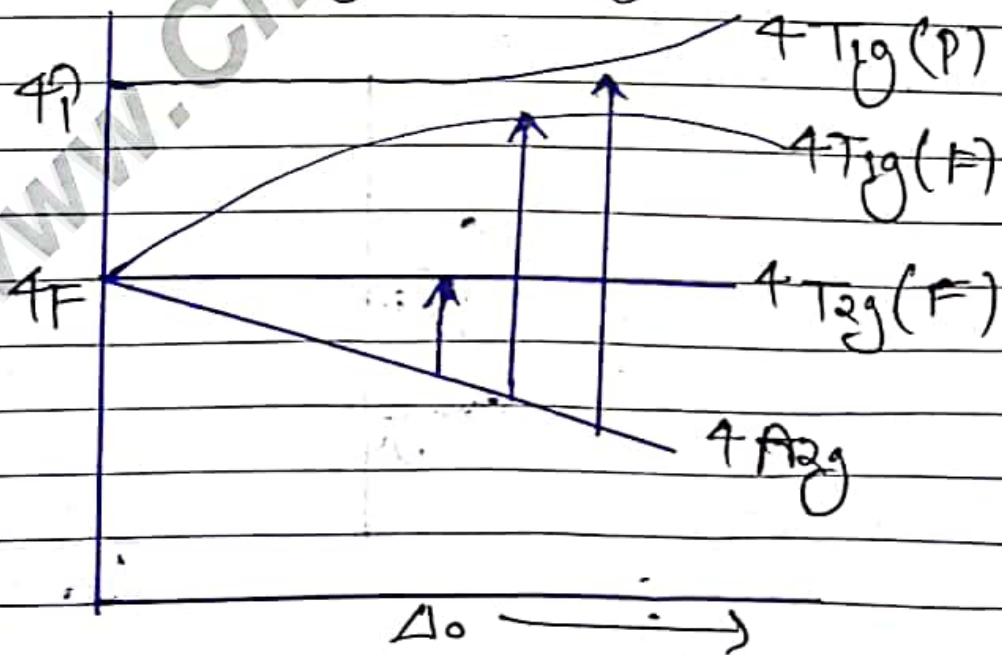


# $d^3$ Metal ions

The complex ion  $[Cr(H_2O)_6]^{3+}$  shows absorption bands at  $17000\text{ cm}^{-1}$ ,  $24000\text{ cm}^{-1}$  and  $37000\text{ cm}^{-1}$  (weak absorption band)



In this case three electronic transitions viz  ${}^4A_{2g} \rightarrow {}^4T_{2g}$ ,  ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$  and  ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$  are possible.



for  $d^3$  ion in octahedral ligand field.



# Metal Ligand Equilibria

DATE: / / 201

V. Imp.  
Q1 → What do you understand by stability of what metal complex? Discuss step wise and over all formation constants of complex.

Ans

Stability of metal complex → The term of stability mean that a compound exist under suitable conditions and it can be stored for a long time. The use of this term in general way is not possible in case of co-ordination comp. or complex, because these complexes may be stable in one reagent but may decompose in other reagent.

In study of formation of complexes in solution two kinds of stability of complex are generally considered as discussed below.

(2) Thermodynamic stability → It depends upon the strength of bond bet metal and ligand in complex. Stronger the metal ligand bond higher will be thermodynamic stability of the complex.



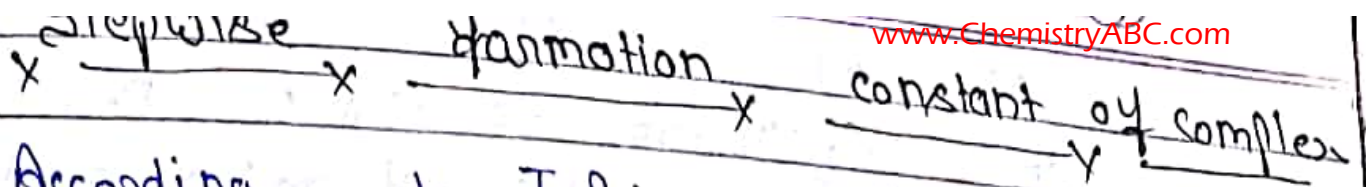
Thermodynamic stability  
metal ligand bond energies stability  
and several thermodynamic variables.  
In thermodynamic sense complexes  
are called stable and unstable.

Thermodynamic stability of a  
species is a measure of extent.  
The strength of metal ligand bond  
varies widely. In case of  $[\text{Co}(\text{SCN})_4]^{2-}$   
the bond is very weak on  
dilution this bond breaks and forms  
another complex. On the other  
hand  $[\text{Fe}(\text{CN})_6]^{3-}$  is very stable.  
In aqueous solution it does  
not give test of  $\text{Fe}^{3+}$  ions.

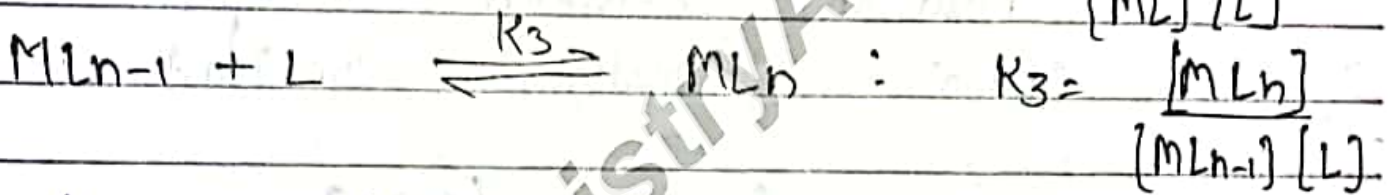
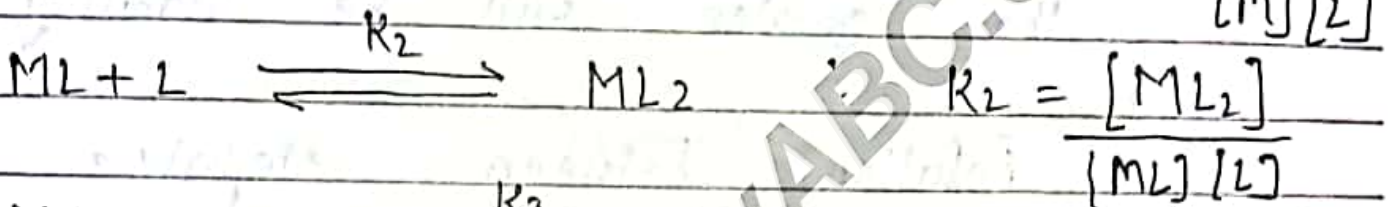
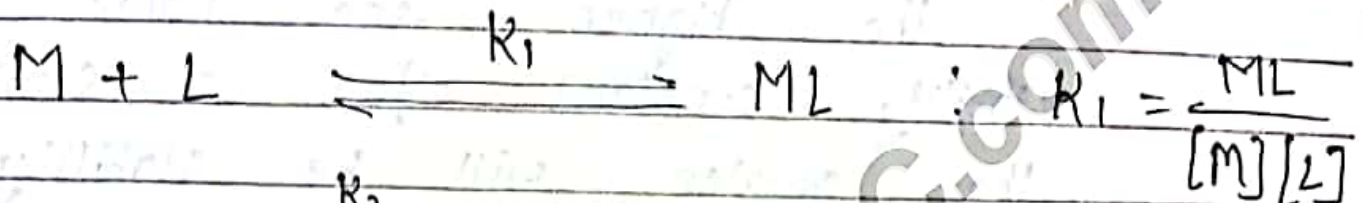
2 - Kinetic Stability  $\Rightarrow$  It refers the  
rate at which the  
complex formation or transformation  
reaction proceeds to equilibrium. Time  
factor plays an important role in  
deciding the kinetic stability of  
a complex.

Kinetic stability deals with rate  
and mechanism of chemical reaction.  
In kinetic sense the complexes  
are referred to as inert and labile.



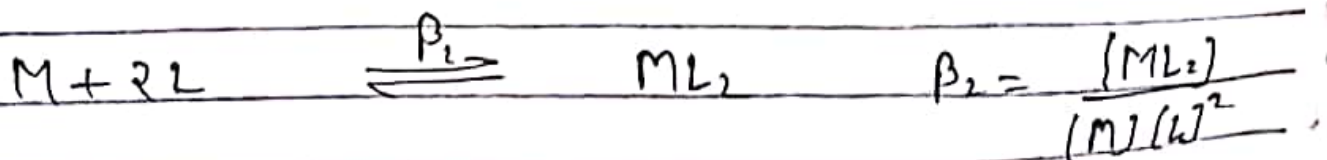
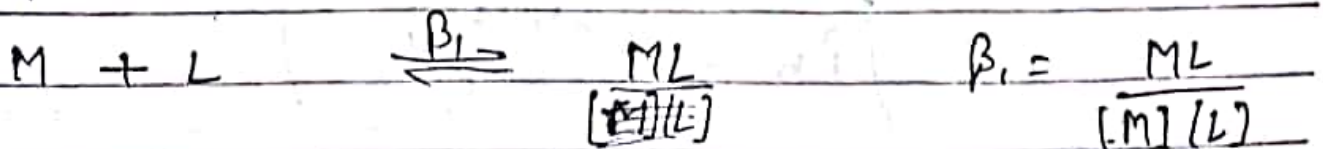


According to I. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligand to the metal ion.



The equilibrium constants  $K_1, K_2, \dots, K_n$  are called stepwise formation or stepwise stability constants. These constants are also expressed as  $\log_{10} K_1, \log_{10} K_2, \dots, \log_{10} K_n$  respectively.

Overall formation constant  $\Rightarrow$  The formation of  $ML_n$  also expressed as below,



$M + nL \xrightleftharpoons{\beta_n} ML_n$        $\beta_n = \frac{[ML_n]}{[M][L]^n}$   
 the equilibrium constants  $\beta_1, \beta_2, \beta_n$  are called formation constant.

With a few exception the value of stepwise formation constants decrease gradually from  $K_1$  to  $K_n$ .  $K_1 > K_2 > K_3 \dots > K_n$ .  
 The higher the value of stability constant for a complex ion the greater will be stability.

Relation between stepwise and overall formation constant.

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$\beta_3 = \frac{ML_3}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]}$$

$$\beta_3 = K_1 \cdot K_2 \cdot K_3$$

$$\beta_n = K_1 \cdot K_2 \cdot \dots \cdot K_n$$

$$\beta_n = \sum_{h=1}^{n=h} K_h$$



Q-2) What is meant by stability of complex ion? Discuss the factors which affect the stability of complexes.

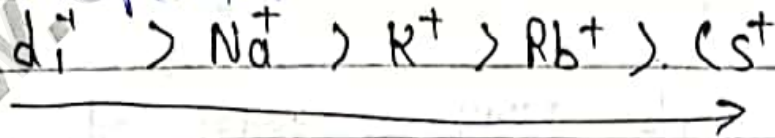
Ans - Q.1.  
 Factors affecting the stability of complexes. The stability is depend largely on.

- (A) - The nature of the central metal ion.
- (B) - The nature of the ligand.

★ (A) The nature of central metal ion.

The following properties of central metal ion affect the stability of a complex.

(1) Ionic size → In general the metal ion smaller size will form more stable complexes.



Ionic size increases, stability decreases.  
 exception of this  $Mg^{2+}$  (0.72) less stable than  $Ca^{2+}$  (0.99)

(2) Ionic charge → In general the greater the charge the greater is stability of complex.  
 ex  $[Fe(CN)_6]^{3-}$  is more stable than  $[Fe(CN)_6]^{4-}$ .

Similarity  $\text{Co}^{III}$  is more stable than  $\text{Co}^{II}$ .

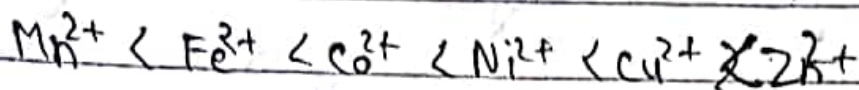
The ratio of charge and size of central metal ion called ionic potential or Polarising power of that ion.

$$\text{Ionic potential } (\phi) = \frac{\text{charge}}{\text{Radius}}$$

Higher value of  $\phi$  form <sup>more</sup> stable complexes

(3) Electronegativity of the central metal ion the bonding bet central metal ion and ligand is due to the donation of  $e^-$  by ligand to central metal ion. the central metal ion having higher  $e^-$  negative will attract  $e^-$  strongly from the ligand and hence most stable complex will be formed.

(4) Irving - William order of stability :  
Stability of complexes of the ions between  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  with a given ligand vary in the order.



this order is called natural order or Irving - William order.



\* B The nature of the ligands  $\rightarrow$  The following properties of the ligands affect the stability of a complex.

(1) Size and charge of the ligands  $\rightarrow$  It is observed that the higher the charge and smaller the size of ligand, then more stable complexes are formed.

2 Basic nature of ligands  $\rightarrow$  A strong base is a good  $e^-$  donor and can donate  $e^-$  pair easily to central metal ion to form more stable complex.  
 $\cdot$   $\text{NH}_3$  better ligand than  $\text{H}_2\text{O}$ ,  $\text{HF}$   $\text{NH}_3 > \text{H}_2\text{O} > \text{HF}$

3. Chelate effect  $\rightarrow$  The ligand which form chelate is more stable than which ligand don't form chelate.

ex-  $[\text{Ni}(\text{en})_3]^{2+}$  is more stable than  $[\text{Ni}(\text{NH}_3)_6]^{2+}$

(4) Chelate No and rings  $\rightarrow$  Greater No of chelate ring greater the stability.

(5) Steric effect  $\rightarrow$  Small type of ligand form more stable the larger ligand. It is due to the atom are present near the donor atom of a ligand mutual repulsion among the ligand occurs. This weak metal ligand bond. than larger bulky ligand form less stable complex.

(6) Back bonding  $\rightarrow$  Ligand which have back bonding ability form stable complexes.  
 ex  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{R}_3\text{P}$ ,  $\text{R}_3\text{As}$ , etc.



Q → Bent rule → According to this rule <sup>66</sup> more  $e^-$  negative substituents prefer hybrid orbital having less s character and more  $e^-$  positive substituents prefer hybrid orbitals having more s character.

It is shown in ethane provide example of its rule.  $CH_2F_2$  the  $F-C-F$  bond angle is less than  $109.5^\circ$  and less than 25% s character, but in  $H-C-H$  bond angle is larger and has more s character. The bond angle in the other ethane gives similar result.

The tendency of more  $e^-$  negative seek out the low  $e^-$  negative  $p_{d^2}$  orbital in trigonal bipyramidal etc. is called apicophilicity.

It is well illustrated in a series of oxysulfurane of the margin type which were prepared by Martin & Cowan.

Bent rule provides alternate rationalization for VSEPR model.

Thus bent rule prediction  $e^-$  rich will attract s character and reduce bond angle. Strong s rich covalent bond require a larger volume. Thus double bonded oxygen s rich orbital

Q →  
Ans =

(1)

2-



# Chapter - 5

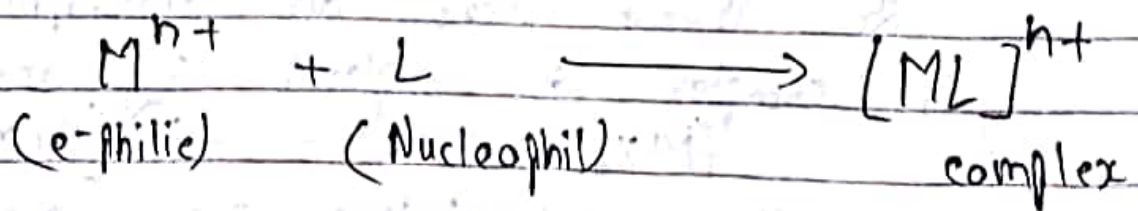
## [Reaction mechanism of Transition metal]

Q → Attacking reagents ?

Ans = This reaction proceed when a reagent attack on a substrate. these reagents are called attacking reagent and its two types.

Q1) Electrophilic reagents → These are also known as  $e^-$  philides. (electrophilic - [ $e^-$  loving]). It is  $e^-$  loving and accepts these are lewis acids. these may be positively charged, ex  $Bn^+$ , nitronium ion ( $NO_2^+$ ),  $-C^+$

Q2- Nucleophilic reagents → The nucleophilic reagents are nucleus loving. It negatively charged ion  $-C^-$ . ex  $Cl^-$ ,  $OH^-$ ,  $CN^-$ ,  $H^-$ . These have unshaned pair of  $e^-$ .



Q2-

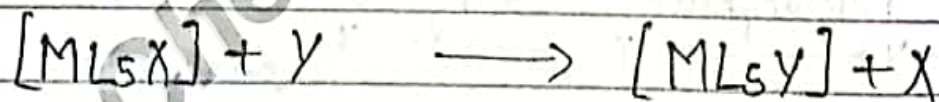
What are substitution reaction?  
Discuss  $SN^1$  or  $SN^2$  mechanism for octahedral complexes.

Ans: Substitution reaction → Those reactions in which there is a change in the composition of the co-ordinate sphere of the complex without any change in oxidation state of metal are called substitution reactions.

These reac. are two types.

(1) Nucleophilic or ligand subst ( $SN$ )

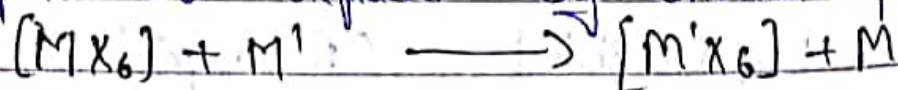
In these reaction a nucleophile from co-ordination sphere of a complex is replaced by other ligand.



these represent by  $SN$  where 's' is substituents & N - nucleophile.

2 Electrophilic or metal substituents reaction

In these reac an electrophile present in complex is replaced by another e-philic.



e-philic substitution reac are less common than nucleophile. and represent

by SE S - stand for substitut

E - " " " " " " " "



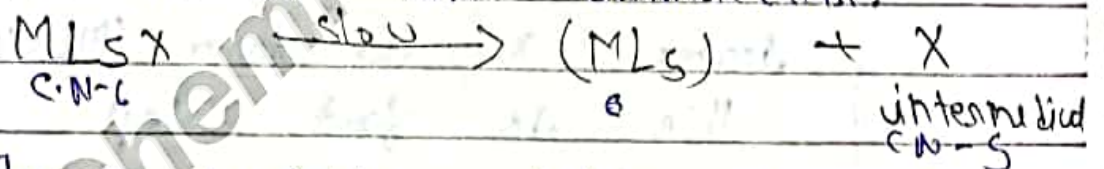
## SN reactions in octahedral

- 
- 1) Unimolecular nucleophilic substitution  $SN^1$  on dissociative mechanism
  - 2) Bimolecular nucleophilic on displacement.

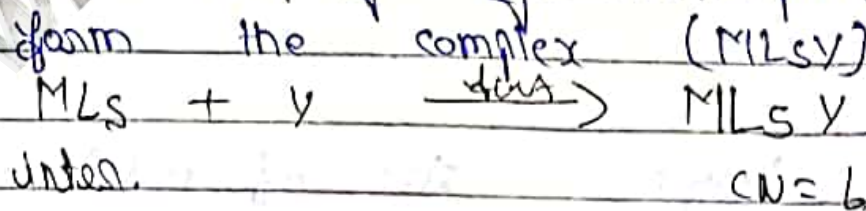
⇒  $SN^1$  reactions → gts complete 2 steps

(i) → the octahedral complex first dissociate losing the ligand to be replaced and form a five co-ordinated (square pyramidal (SP) or trigonal bipyramidal), intermediate.

This is slow and rate determining step and reaction is unimolecular.



(ii) → The unstable intermediate is attacked rapidly by nucleophilic Y to form the complex  $(ML_5Y)$

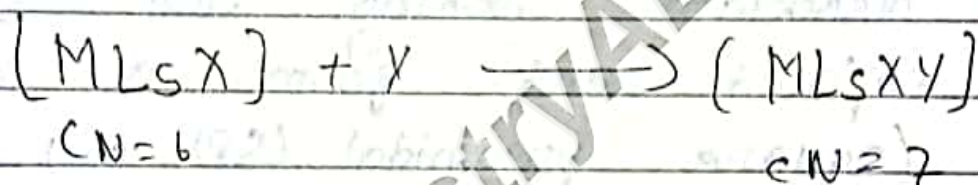


Factor favouring  $SN^1$  Mechanism.

- 1 - larger size of metal atom/ion
- 2 - lower charge on metal
- 3 - larger size of leaving group.
4. Presence of more basic ligands in complex.

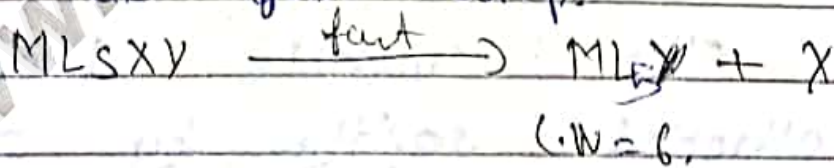
$SN^2$  on Displacement mechanism,  
there are 2 types.

(1) → The ligand  $Y$  directly attacks through one of the edges of the complex  $(ML_5X)$  to form a 7-co-ordinated unstable intermediate which is pentagonal bipyramidal in shape.



this reaction is bimolecular.

(2) → The unstable intermediate  $ML_5XY$  leaves  $X$  to form  $(ML_5Y)$ .  
this is fast step.



Factors favouring  $SN^2$  mechanism

- 1- larger size of metal.
- 2- Higher charge on metal
- 3- Small size of leaving group.



Ans

Q → What do you understand by labile and inert complexes.

Ans Inert complexes → The complexes in which the ligand substitution does not take place or take place very slowly are called inert complexes.

labile complexes → The complexes in which the ligand rapidly replaced by other one called labile complexes.

Stability or inertness of octahedral complexes according to VBT

We know it in 2 types

(1) Outer Orbital octahedral complex → These complexes are formed by  $ns\ n^3\ d^2$  hybridisation, and are called high spin complexes. Such complexes are generally labile ex  $Cr^{3+}(3d^3)$ ,  $Mn^{2+}(3d^5)$ , etc exchange ligand and hence are labile. In terms of VBT it is due to the weakness of  $sp^3d^2$  type bond as compared to  $d^2sp^3$  bond. And orbital have high energy than  $(n-1)d$  orbital.

(ii) Inner orbital octahedral complexes. These complexes are formed by  $(n-1)d^2 ns np^3$  hybridisation and called low spin complexes.

The formation of labile or inert in octahedral shown below.

| Vacant $(n-1)d$ orbitals | 3   | 2      | 1      | No    | No    | No    | No    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
|--------------------------|---|--------|--------|-------|-------|-------|-------|---|----|----|----|----|----|----|---|----|----|----|----|----|----|---|----|----|----|----|----|----|--|----|----|----|----|----|----|---|----|----|--|----|----|----|---|----|----|----|----|----|----|---|---|--|----|----|----|---|---|---|---|---|---|---|---|---|---|---|---|
| Reactivity               | labile  | labile | labile | inert | inert | inert | inert |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| Configuration            | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>xx</td><td>xx</td><td>xx</td></tr> </table> | xx     | xx     | xx    | xx    | xx    | xx    | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>xx</td><td>xx</td><td>xx</td></tr> </table> | xx | xx | xx | xx | xx | xx | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>xx</td><td>xx</td><td>xx</td></tr> </table> | xx | xx | xx | xx | xx | xx | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>xx</td><td>xx</td><td>xx</td></tr> </table> | xx | xx | xx | xx | xx | xx | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>xx</td><td>xx</td><td>xx</td></tr> </table>                                      | xx | xx | xx | xx | xx | xx | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>xx</td><td>xx</td><td>xx</td></tr> </table> | xx | xx | xx   | xx | xx | xx | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>xx</td><td>xx</td><td>xx</td></tr> </table> | xx | xx | xx | xx | xx | xx |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| Metal Ionic              | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td></td><td></td><td></td></tr> </table>       | xx     | xx     | xx    |       |       |       | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>↑</td><td></td><td></td></tr> </table>      | xx | xx | xx | ↑  |    |    | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>↑</td><td>↑</td><td></td></tr> </table>     | xx | xx | xx | ↑  | ↑  |    | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> </table>    | xx | xx | xx | ↑  | ↑  | ↑  | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> </table> | xx | xx | xx | ↑  | ↑  | ↑  | ↑   | ↑  | ↑  | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> </table> | xx | xx | xx | ↑   | ↑  | ↑  | ↑  | ↑  | ↑  | ↑  | ↑ | ↑ | <table border="1"> <tr><td>xx</td><td>xx</td><td>xx</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td></tr> </table> | xx | xx | xx | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
|                          |   |        |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        |   |        |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   |        |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| xx                       | xx  | xx     |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
| ↑                        | ↑   | ↑      |        |       |       |       |       |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |
|                          | $d^0$   | $d^1$  | $d^2$  | $d^3$ | $d^4$ | $d^5$ | $d^6$ |   |    |    |    |    |    |    |   |    |    |    |    |    |    |   |    |    |    |    |    |    |  |    |    |    |    |    |    |   |    |    |  |    |    |    |   |    |    |    |    |    |    |   |   |  |    |    |    |   |   |   |   |   |   |   |   |   |   |   |   |



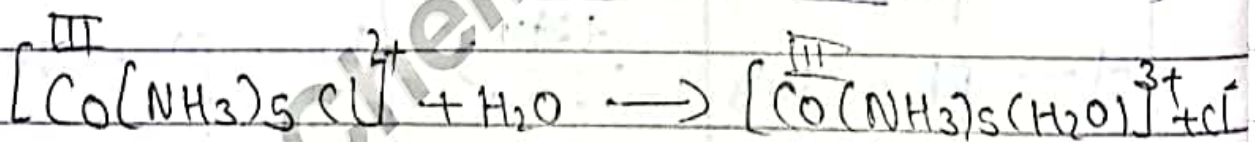
→ \* What are <sup>acid</sup> hydrolysis reactions.

Hydrolysis reaction → These are the substitution reaction in which a ligand is replaced by H<sub>2</sub>O molecule or by OH<sup>-</sup> groups.

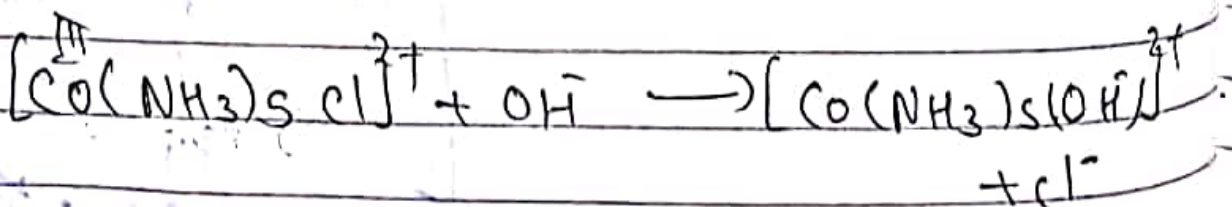
These reactions are two types.

1. Aquation or Acid Hydrolysis reaction.

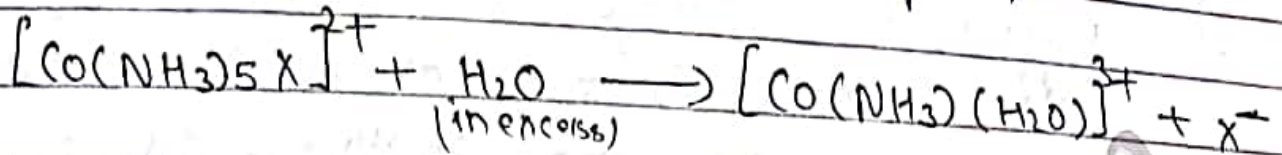
In such reactions an aqua complex is formed by the replacement of a ligand by H<sub>2</sub>O molecules. These reactions occur in neutral and acid solution. (pH < 3)



2. Base hydrolysis reaction → In such reaction an hydroxo complex is formed by the replacement of a ligand by OH<sup>-</sup> molecule. These reactions occur in basic solution (pH > 10)



⇒ Acid Hydrolysis on aquation reaction of six co-ordinated  $\text{Co(III)}$  ammine complexes. Let us consider hydrolysis of  $\text{Co(III)}$  ammine complexes.



This reaction is found to be of first order as the rate is dependent on the concentration of the complex only.

Since in aqueous solution the concentration of water is always constant, the effect of changes in water concentration on the rate of the reaction can be determined.

The rate laws may be written as below

$$\text{rate} = k [\text{Co(NH}_3)_5\text{X}]^{2+} [\text{H}_2\text{O}]$$

$$\text{or } \text{rate} = k' [\text{Co(NH}_3)_5\text{X}]^{2+}$$

$k' = k [\text{H}_2\text{O}]$  as concentration of water is constant.

The rate law given above does not indicate whether these reactions proceed by  $\text{S}_\text{N}1$  or by  $\text{S}_\text{N}2$  mechanism.



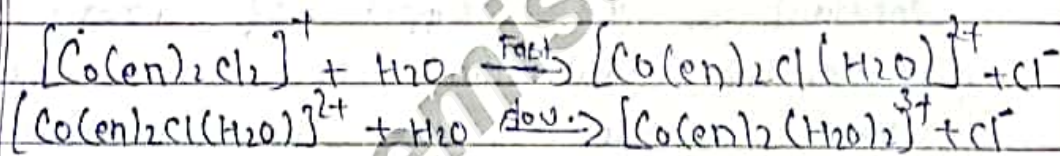
last  
day

It is evident from above discussion that SN1 mechanism is much more important than SN2 mechanism during acid hydrolysis of octahedral complex.

However the following factors give us an information about the mechanism of the reaction

(i) Effect of charge on the complex  
It has been observed that an increase in the positive charge on the complex decreases its rate of aquation e.g.

e.g. the rate of aquation of  $[\text{Co}(\text{en})_2\text{Cl}]^{2+}$  is 100 times faster than the rate of aquation of  $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$



(ii) effect of strength of metal leaving group bond  
It has been observed that rate of aquation decrease with increase in the basicity of leaving group.

(iii) Inductive effect of inert ligands  
the ligand which remain attached to metal ion during the substitution reaction are called inert ligand.

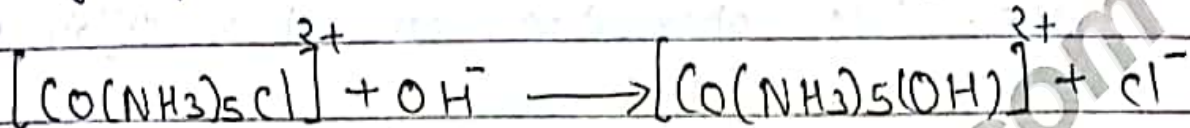
(iv) Stability constant  
(v) effect of chelation  
steric effect

Q → Base hydrolysis. discuss in details mechanism

Ans  $S_N2$

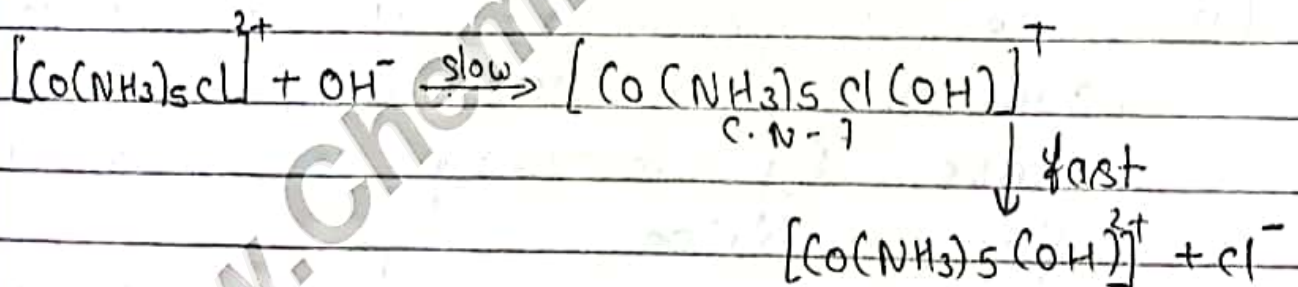
Mechanism of base hydrolysis

most of the kinetic work has been done on six co-ordinated  $Co(III)$  ammine complex let us consider the base hydrolysis of the following reaction.



The following two mechanism have been suggested.

1  $S_N2$  Displacement mechanism → According to this mechanism the reaction proceeds as below



The rate of hydrolysis is determined by slow step which is second order reaction.

First order with respect to the complex and first order with respect to the base Thus

$$\text{Rate of reaction} = k [\text{Complex}] [\text{Base}]$$

$$k [Co(NH_3)_5Cl]^{3+} [OH^-]$$



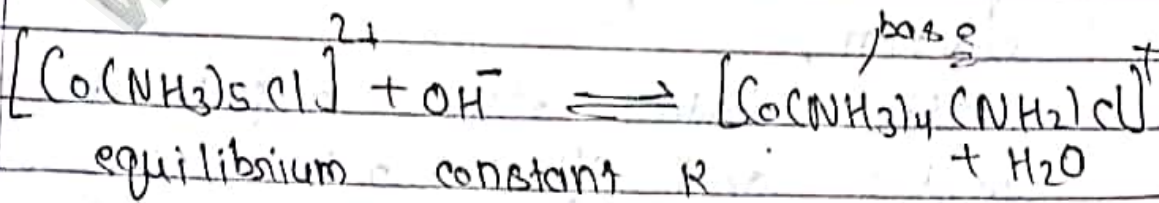
3-1  
Q. A  
Ans. →

limitation → The above mechanism fails to explain some of the experimental observation.

(1) At high concentration of OH<sup>-</sup> ions, the rate of this reaction does not depend on the OH<sup>-</sup> concentration and its first order reaction with complex ion. this observation can not be explained by SN<sup>1</sup> mechanism.

(2) SN<sup>1</sup>CB mechanism → This mechanism was proposed by Gemick. SN<sup>1</sup> stands for substituted nucleophilic unimolecular, conjugate base.

(a) The complex act as a Bronsted acid and converted into its conjugate base by removing a proton H<sup>+</sup> from amine group. the hydroxyl group which is a base is converted into its conjugate acid as below



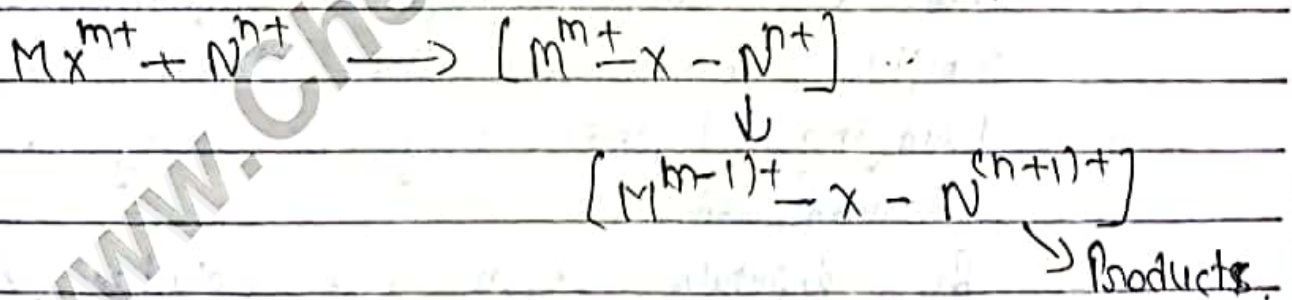
for the above reaction

$$K = \frac{[CB][H_2O]}{[Co(NH_3)_5Cl]^{2+}[OH^-]}$$

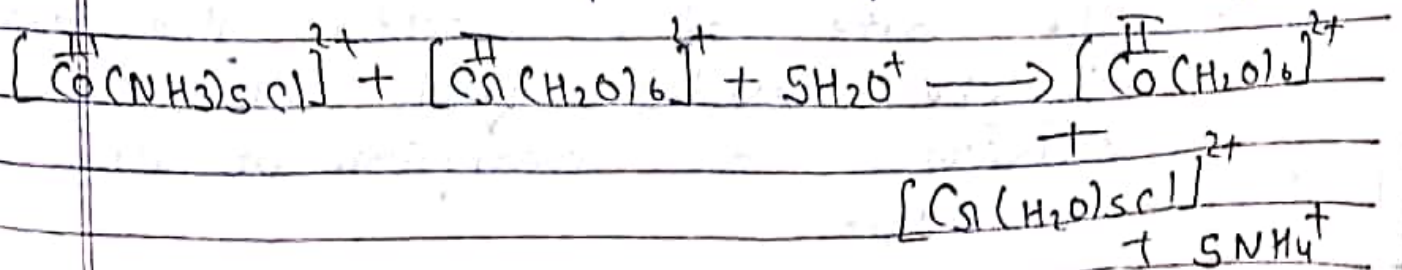


Q. #  $e^-$  transfer in inner-sphere or outer-sphere reaction  $\rightarrow$  such reaction occur by the following 2 mechanism.

1- Bridge or atom transfer of inner-sphere mechanism. These are  $e^-$  transfer reaction in which  $e^-$  and ligand transfer occur. This reaction proceeding through inner sphere mechanism have one inert complex and other labile complex. The inert complex has a co-ordinated ligand which forms a bridged activated intermediate with labile complex. The inner sphere mechanism may be represented as



example Traube and his co-workers have shown that oxidation of  $[Cr(H_2O)_6]^{2+}$  by  $[Co(NH_3)_5Cl]^{2+}$  in acidic medium is represented by the following equation





1- The essential features of mechanism are  
 In the activated intermediate (AI) an  $e^-$  is transferred from  $Co^{II}$  to  $Co^{III}$  through the bridging of ion to convert  $Co^{II}$  to  $Co^{III}$  and  $Co^{III}$  to  $Co^{II}$ .

2- Now  $Co^{III}$  attracts  $e^-$  ion more strongly than that of  $Co^{2+}$  and hence  $e^-$  ion become a part of complex of  $Co^{III}$ .

characteristics of inner sphere mechanism  $e^-$  transfer reaction.

(1) One complex should be inert and the other should be labile.

(2) The inert complex ion should have a ligand capable of forming bridge between both the complex ion.

(3) One  $e^-$  is transferred from one complex ion to the other but the bridging ligand may or may not be transferred.

It depends upon the relative stability of the products.

4- These reaction are faster than the similar reaction occurring through outer sphere mechanism.

5. The rate of  $e^-$  transfer also increases if the bridging ligand has unsaturation or conjugation in its structure.

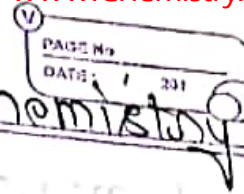


- ★
- 1- If both the oxidant and reductant complex ions are inert and their inner co-ordination shells are saturated the rate of exchange of ligand would be very slow and the formation of a ligand bridge is not possible.
  - 2- However the rate of  $e^-$  transfer bet such pairs of complex ions is quite fast. Such  $e^-$  transfer reaction occur through outer sphere mechanism.
  - 3 In this mechanism direct transfer of an  $e^-$  occurs. This process may occur when a critical requirement is reached which is given by Frank-Condon Principle.
  - 4- According to this principle there can be no appreciable change of atomic arrangement during the time of an  $e^-$  transition i.e. very light  $e^-$  move more rapidly than the heavier atoms. We shall now consider some example of  $e^-$  transfer reactions occurring through this mechanism.

Some examples here.



# chapter - 1 - Stereochemistry in comp



Q1- Walsh diagram on MO correlation?

Ans

1- Many years ago Walsh first applied MO correlation diagram simple cases. This approach led to certain rules called Walsh rule.

2- Which related the shape of diatomic molecules to their electronic structure.

3- The basic approach is calculate the energies of molecular orbitals for 2 limited structures say linear and bent to  $90^\circ$  for  $AB_2$  type molecule.

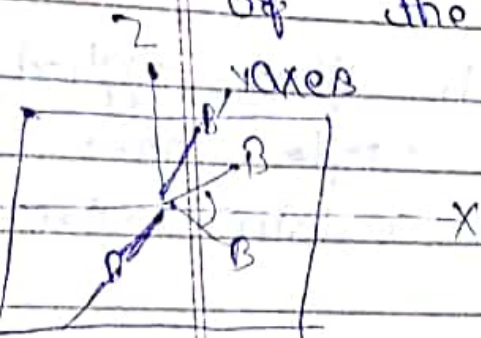
4- And draw a diagram showing how the orbitals of one configuration correlate with those of other.

5- Then depending on which orbitals are occupied, one or the other structure can be seen to be preferred.

6- By means of approximate MO theory, implemented by digital computers, this approach has been extended and generalised in recent years.



Triatomic molecule → let us consider a triatomic molecule of the type  $AB_2$  whose coordinate axes are shown in fig

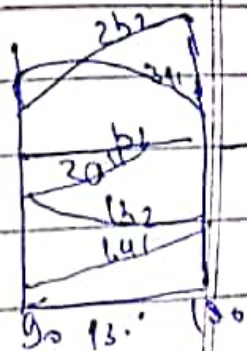


the  $AB_2$  molecule has  $C_{2v}$  symmetry when it is bent and  $D_{\infty h}$  symmetry when the molecule is linear. To simplify notation, the linear configuration is considered to be simply an extremum of the  $C_{2v}$  symmetry.

The atom A of the molecule  $AB_2$  will be supposed to have only  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  orbitals in its valence shell and each B atom has only a single orbital which forms a bond with A.

In linear configuration  $p_x^A$  and  $p_z^A$  are equivalent non-bonding orbitals labeled  $2a_1$  and  $b_1$  respectively.

The orbitals  $s^A$  and  $p_y^A$  interact with  $1s^B$  and  $1p_y^B$  to form one strongly bonding.



From the diagram it is seen that an  $AB_2$  molecule is more stable when linear than when bent.



$\text{H}_2\text{O}$  molecule  $\rightarrow$  This molecule has been studied in details. The Walsh diagram calculated for  $\text{H}_2\text{O}$  is shown in the fig. (1). Although it is different from the general  $\text{AB}_2\text{E}_2$  diagram, it is seen that the important features are same.

The general diagram (space filling) pertains to a situation in which there is only a small energy difference between ns and np orbitals of the central atom. It is not clear whether  $\text{AB}_2\text{E}_2$  molecule should necessarily be bent.

In the diagram calculated expressly for  $\text{H}_2\text{O}$  it can be determined from this diagram that the energy is minimised at an angle of  $106^\circ$ .

For  $\text{H}_2\text{O}$  the lowest level is practically pure  $2s$  and its energy is essentially constant for all angles. It can be  $\sim 106^\circ$ .

In this diagram show that Walsh's diagram approach can give reliable result for specific molecules.

It can be seen that the assumption made in the VSEPR theory, that all valence shell electron pairs can be treated as having similar requirements for space of the surface.



Q →

## $d\pi - p\pi$ Bonding

Ans

There are several structures which have been explained by the formation of  $d\pi - p\pi$  bond but recently it has been shown that this type of bonding explanation is not true in all the cases recent work has raised more doubts

ex

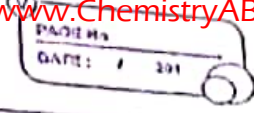
- 1- The amines such as  $(R_3Si)_2NHR$ ,  $(R_3Si)_3N$ ,  $(H_3C)_3N$  the central  $NSi_2C$ ,  $NSi_3$ ,  $NGe_3$  skeleton are planar.
- 2- Many tetrahedral species  $SiO_4$ ,  $PO_4$ ,  $ClO_4$ ,  $SO_4$  have bond length shorter than those predicted for single bond.  
In silicate  $Si-O-Si$  units show that  $Si-O$  distances are very short than expected for single bond.

Recently theoretical and experimental methods have suggested that the  $d\pi - p\pi$  contribution to these effects are <sup>at</sup> best small.

Thus the literature written prior to 1985 where much instructions are often accorded great importance has been ignored.



## Chapter - 2



Q → How will you determine the stability constant of a complex.

Ans Although there are many methods for determination of stability constant, here only two methods are given.

- 1 Spectrophotometric method
- 2 pH metric method

1- Spectrophotometric method <sup>①</sup> → The light absorbed by metal ion is different from that absorbed by complex.

The relationship bet absorbance or optical density at a particular wave length and concentration is given by the following

Bern's law.

$$A = \epsilon \cdot L \cdot C \quad \text{--- ①}$$

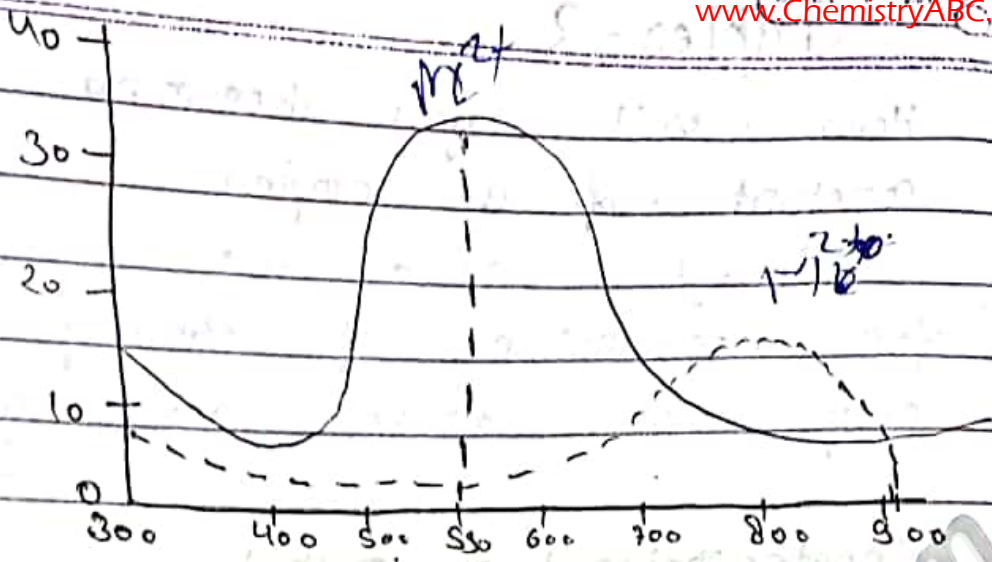
A = Absorbance

L = length of absorption cell

C = Concentration of complex

$\epsilon$  = Molar extinction coeff.

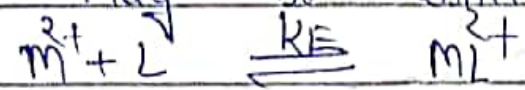
② Absorbance (A) is a measured with a spectrophotometer. If the value of  $\epsilon$  and L are known, the concentration can be calculated by eq - ①



③ The changes in spectrum of metal ion show on coordination with ligand (L) has been shown in fig. The spectra of metal ion shown by dotted line (curve) and its complex (ML<sup>2+</sup>) is shown by solid curve.

4- It is seen that the absorption by complex ion take place over the entire region of metal ion absorption, while at 550 nm only the complex absorbs.

The reaction for the complex formation may be written as



thus the formation constant  $K_F$  will be given

$$K_F = \frac{[ML^{2+}]}{[M^{2+}][L]} \quad \text{--- (1)}$$



① In order to obtain the value of  $K_F$  the solution of known amount of total  $M^{2+}$  and total  $L^-$  are prepared and their absorption at 550 nm is measured. Now the value of  $K_F$  is calculated.

$$C_M = [M^{2+}] + [ML^{2+}] \quad \text{--- 3}$$

$$C_L = [L^-] + [ML^{2+}] \quad \text{--- 4}$$

$$A = \epsilon (C_M L^{2+}) \cdot d \cdot [ML^{2+}]$$

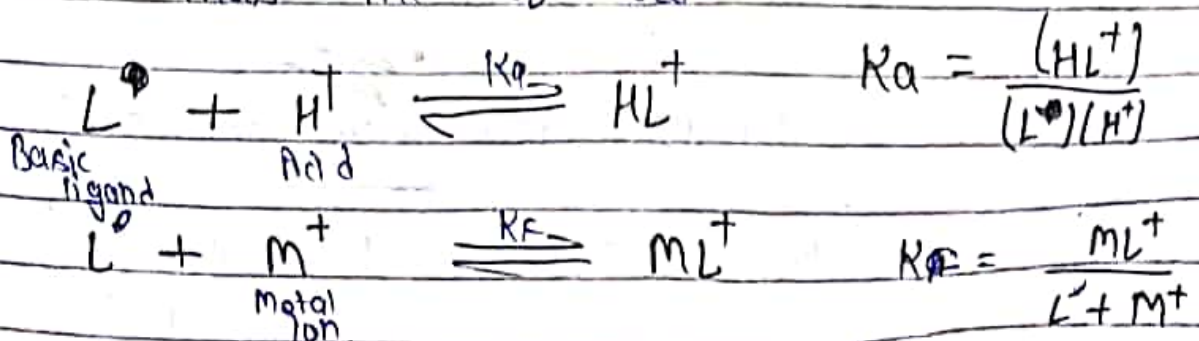
$$[ML^{2+}] = \frac{A}{\epsilon (C_M L^{2+}) \cdot d}$$

$C_M =$  total concn of metal  
 $C_L =$  " " of ligand.

(2) **pH metric method or Potentiometric method (Benjennum method)**. If a ligand weak base  $L^-$  acid  $HL$ , competition  $\exists$  bet  $H^+$  ion and metal ions for ligand use for  $G_{11}$   $\exists$  for determination of the formation constant.

Let us consider the equilibria in which an acid and metal ions are added to a basic ligand  $L^-$  in solution.

thus the eq are.



$K_a =$  Acid dissociation constant

Suppose  $C_H$ ,  $C_M$  and  $C_L$  are total amounts are equal of acid  $H^+$  metal ion ( $M^+$ ) and basic ligand  $L$  respectively we have

$$C_H = [H^+] + [HL^+] \quad \text{--- 1}$$

$$C_L = [L] + [HL^+] + [ML^+] \quad \text{--- 2}$$

$$C_M = [M^+] + [ML^+] \quad \text{--- 3}$$

from eq 2

$$ML^+ = C_L - [L] - [HL^+] \quad \text{--- 4}$$

Now substituting the value of  $[HL^+]$  from eq 1 in eq 4

$$ML^+ = C_L - [L] - C_H + [H^+] \quad \text{--- 5}$$

but  $K_a = \frac{[HL^+]}{[L][H^+]}$

on  $L = \frac{[HL^+]}{K_a[H^+]}$

$HL^+ = C_H - H^+$  putting this

to  $L = \frac{C_H - H^+}{K_a[H^+]}$

Putting this value in eq's

$$ML^+ = C_L - C_H + H^+ - \frac{C_H - H^+}{K_a[H^+]}$$

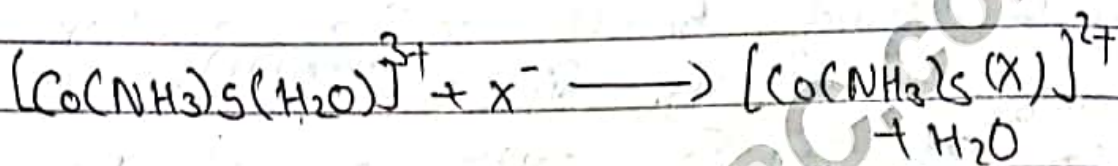


## Chapter - 3

Q → Anation Reaction ?

Ans  
2

Anation reactions → वे reaction जिन्हें H<sub>2</sub>O molecule from aqua complex are replaced from the coordination sphere, कुछ anion के द्वारा कहना है, anation reaction



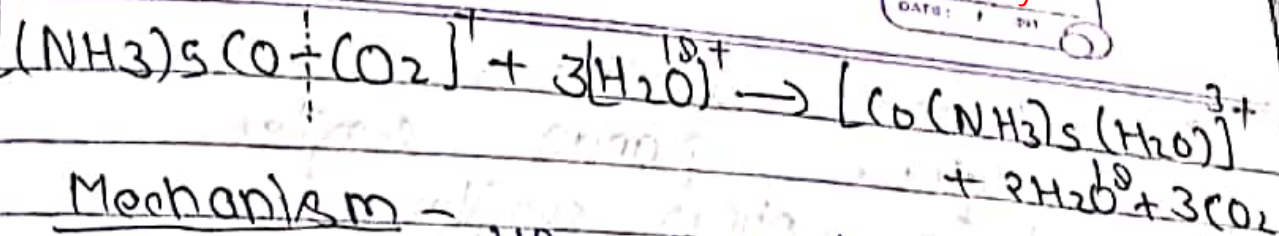
इस प्रकार anation reaction, reverse है, acid hydrolysis का।

Substitution reaction जिसे metal-ligand bond के हटने और reaction ऐसी जाती जाती है, जिसे ligand बदलती, take place जिसे metal-ligand bond हटता है

e.g → कभी aqua complex  $[Co(NH_3)_5(H_2O)]^{3+}$  from its carbonate complex  $[Co(NH_3)_5(CO_3)]^{2+}$  साथ में production of CO<sub>2</sub> गल reaction carried out होता है।

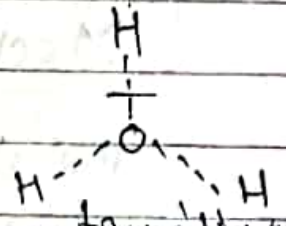
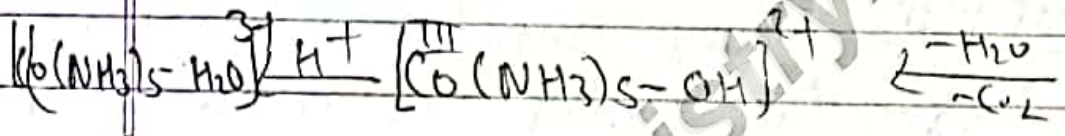
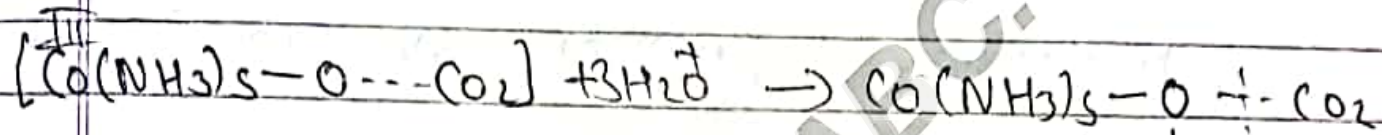
$(H_2O)^{3+}$  में none of the aqua complex को CO<sub>2</sub> मुक्त किया जाता है, यह इसलिए कहा है, कि CO<sub>2</sub> बनती है, C-O bond के cleavage से बिना Co-O के bond हटने से during the aquation reaction



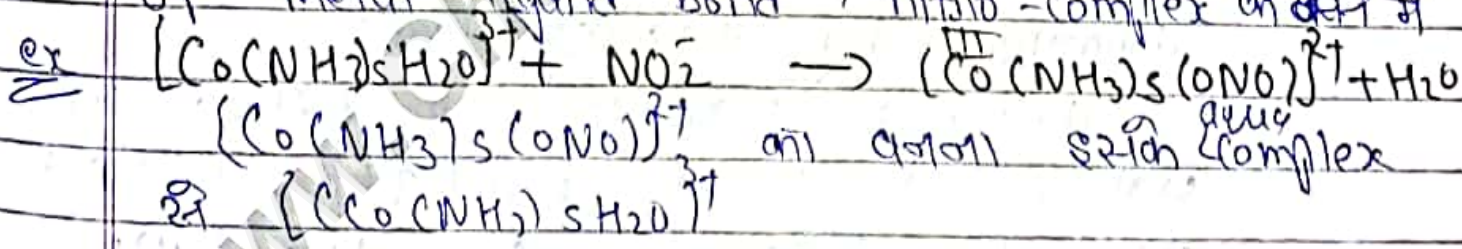


Mechanism -

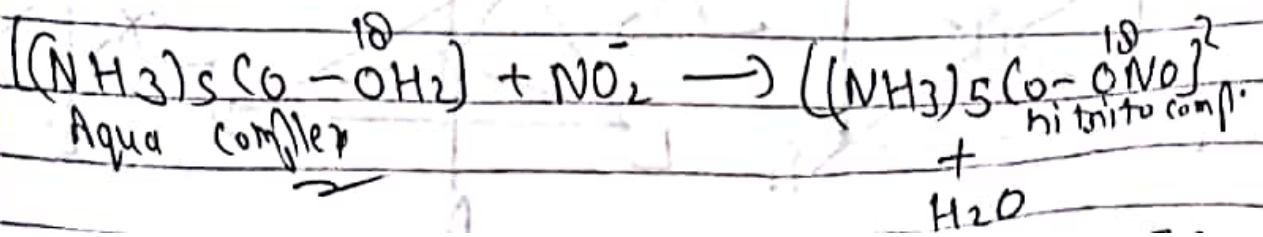
ये suggest करता है, कि reaction proceed होती है, proton के attack के द्वारा on O atom bonded जो Co follow  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  के formation के द्वारा and then protonation होता है Hydroxo complex का!



Anation reaction take place बिना cleavage of metal ligand bond, nitro-complex के रूप में



ये reaction fastest होती है, और suggest करता है कि Co-O bond नहीं टूटता. ये confirm होता है O/O की study से





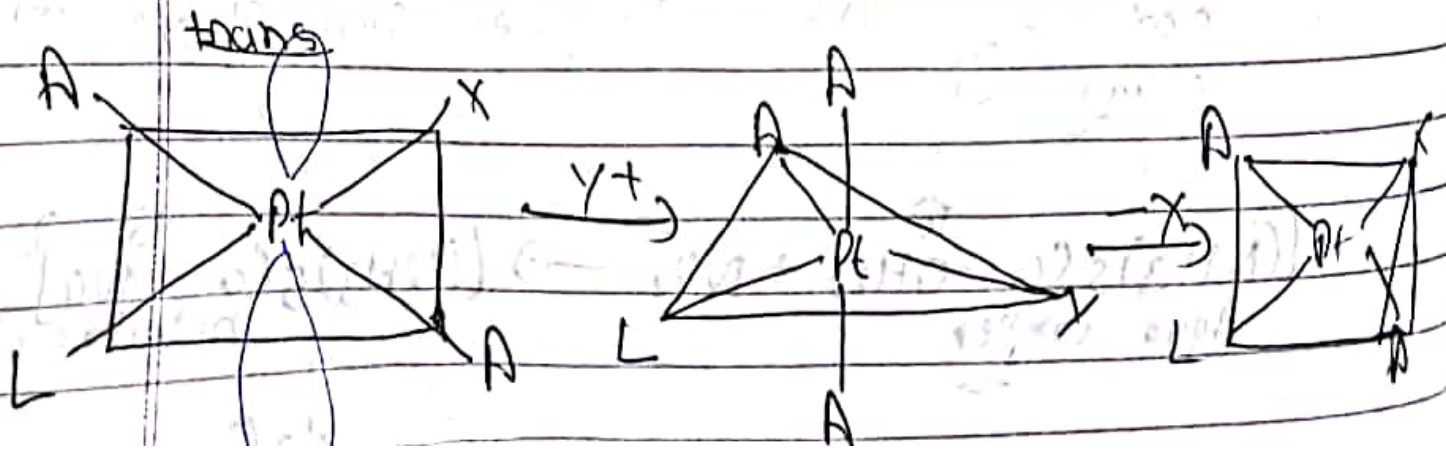
Ans

Square planar complex.  
digan → planar complex →

digan substitution reaction square planar is Pt II complex the study of it shows that details of reaction in this complex slow due to slow towards substitution. This reaction proceed through bimolecular displacement  $S_N2$  mech. के द्वारा

Mechanism → experiments से ये देखा गया है कि C.N of metal बढ़ती है, ligand के enter करने पर. Further Pt(II) रखता है, vacant  $Pz$  orbital जो  $e^-$  pairs को accept करता है donating by entering ligand.

Substitution reaction of cis/trans  $(PtA_2LX)$  with Y to form  $(PtA_2LY)$  explained की गई है, on the basis of nucleophilic attacks of Y, trigonal bipyramidal str. के द्वारा





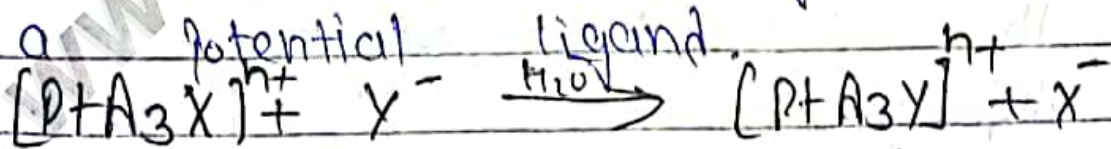
Martin ने दिखाया कि rate of hydrolysis reaction of  $(PtCl_4)^-$ ,  $[Pt(NH_3)Cl_3]^-$ ,  $[Pt(NH_3)_2Cl_2]^-$  and  $[Pt(NH_3)_3Cl]^-$  vary होती है। इन 2 factors में आर change on complex change होता है, -2 से +1 this variation in rate में बहुत कम है।

Pt-Cl bond बहुत difficult ही जाती है। जैसे change आये positive होता है।  
However new bond को बनाना increase होता है in same order

संभवतः Pt-Cl bond टूटता है, और Pt-OH<sub>2</sub> bond making one of comparable importance.

This is a strong evidence in favour of S<sub>N</sub><sup>2</sup> mechanism.

The substitution reaction of  $[PtA_3X]^{n+}$  with  $Y^-$  to form  $[PtA_3Y]^{n+}$  in water involves a complicated because water always also act as a potential ligand.



For this we a two term rate law is given by the reactant

$$\text{Rate} = k_1 [PtA_3X]^{n+} + k_2 [PtA_3X]^{n+} [Y^-] \quad \text{--- (1)}$$

$k_1 = 1$  order rate constant

$k_2 = 2$  order rate constant



# (Metal ligand bonding)

## CFT

Q → ~~Q~~ Describe CFT

1- CFT → This theory was proposed by Bethe and Van Vleck and was initially proposed for ionic crystal and therefore was given the name CFT.

2- In 1952 Orgel applied this theory to coordination compound.

In crystal field theory a complex compound consist of a metal ion surrounded by anionic or negative ends of polar ligand.

3- which creates an electrostatic field and the bonding bet metal and ligand is consider to be purely static in nature.

4- The nature of splitting decides the distribution of  $e^-$  among different sets of d orbital and hence provides an explanation for magnetic and spectral properties.

And is often very useful in the explanation of distorted structure, thermodynamic properties and kinetics.



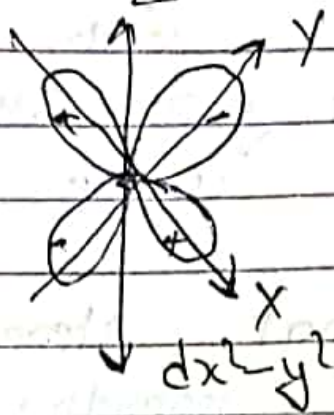
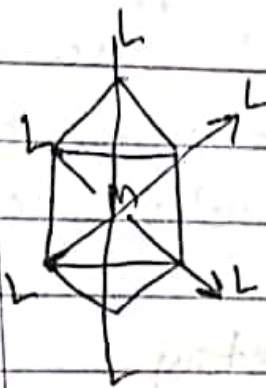
5 The five d-orbitals are degenerate in a free ion. i.e. all the five d-orbitals have same energy, although they have different orientation with respect to Cartesian axes,  $x, y, z$  the origin of which is the centre of metal ion.

### Octahedral Stereochemistry

- 1- In this geometry six ligands are brought near the positively charged central metal ion along the three Cartesian axes,  $x, y, z$ .
- 2- There will be net electrostatic attraction between positively charged metal ion and negatively charged ligands, but due to repulsion between the ligand  $e^-$  and d-orbitals  $e^-$  of the metal.
- 3- There will be a general increase in the energy of these d-orbitals.
- 4- Not all d- $e^-$  will be affected equally those in  $dx^2-y^2$  and  $dz^2$  orbital will be repelled more than the  $dxy, dyz, dxz$  orbitals.



5- The repulsion between the ligands and the orbitals ( $x^2-y^2$ ,  $d_{z^2}$ ) are greater than the repulsion between the ligands and  $d_{xy}$ ,  $d_{yz}$ ,  $d_{yz}$ .



Tetragonal elongation and square planar (ii)

(i) If the 2 trans ligands placed along the z axis of an octahedron are taken away from the metal ion

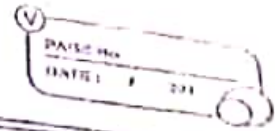
(ii) So that their distance from metal cation is slightly more than that for other, 4 ligands lying in xy plane, we find a tetragonal structure.

(iii) During the tetragonal elongation the  $d_{z^2}$  orbital as long as two other orbitals with z components. e.g.  $d_{xz}$ ,  $d_{yz}$  become more stable.

to The average value of complex the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals become less stable.

The orbitals  $d_{xy}$  and  $d_{yz}$  are degenerate and thus have equal





(v) Thus under the influence of the ligand in tetragonal complex the order of energy of various d orbital can be written as

$$d_{yz} = dxz < d_{xy} < d_{z^2}, (d_{x^2-y^2})$$

Square planar: If the 2 trans ligand on z axis are completely removed we find a square planar geometry for complex compound.

(ii) As consequence of which a further rise in the energy of  $d_{x^2-y^2}$  &  $d_{xy}$  orbital take place and orbital all which have z component become more stable  $d_{z^2}, dxz, dyz$ .

(iii) As the lobes of  $d_{x^2-y^2}$  orbitals lie along the axes. This orbital has highest energy in square planar geometry. The lobes of  $d_{z^2}$  point out of plane. Hence  $d_{z^2}$  orbital is next highest energy. The orbital  $d_{xy}, dyz$  are lowest in energy.

order of energy of d orbitals

$$d_{xy} = dyz < d_{z^2} < dxz < d_{x^2-y^2}$$



## Tetrahedral Stereochemistry

(i) Both the octahedron and tetrahedron can be inscribed in a cube.

The splitting pattern of a tetrahedral complex is just opposite of the splitting pattern of octahedron.

(ii) In order to find the d orbital splitting in tetrahedral crystal field, we place the metal ion at the center of cube.

(iv) While the four ligands occupy the 4 alternate corners of the cube.

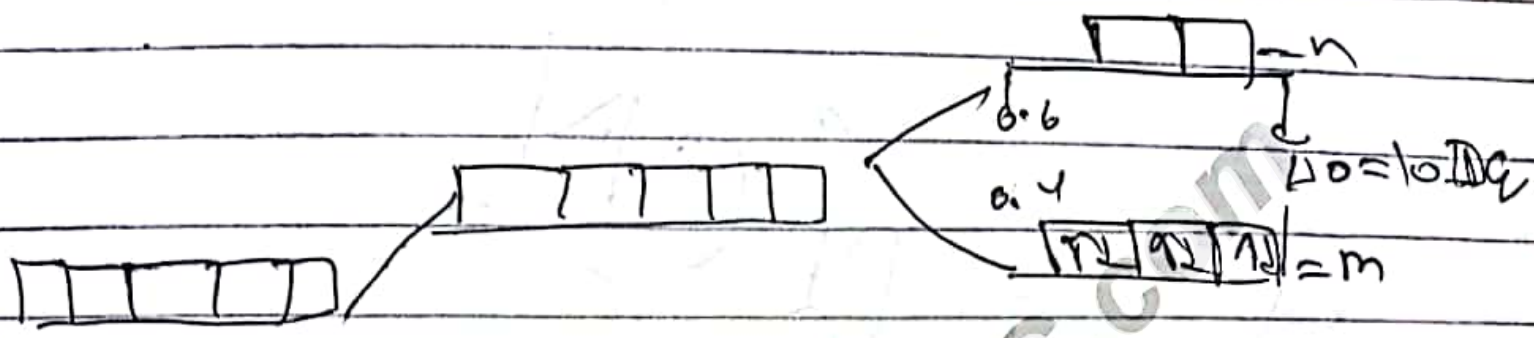
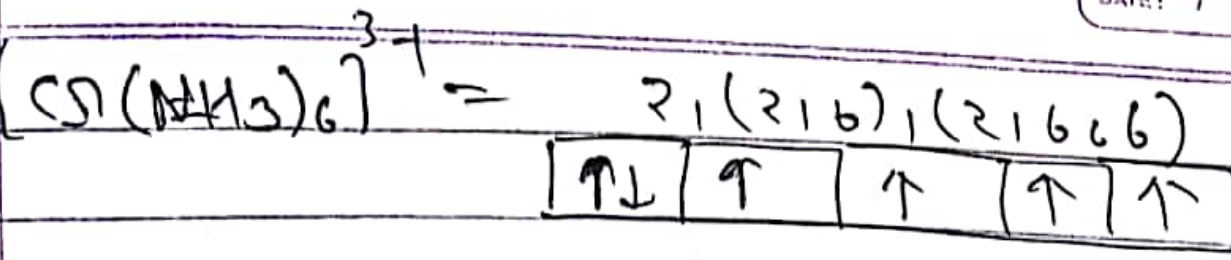
Crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex  $\Delta t = 4/9 \Delta_o$ .

This energy is so small that it is not able to force the  $e^-$  to pair up in tetrahedral geometry.

Hence tetrahedral complexes are generally high spin complexes.

Factor affecting it

- 1- Nature of metal cation
- 2 " " Ligand
- 3 " " Complex



$$= (-0.4 \times m + 0.6 \times n) \Delta_0 + 2 P P,$$

$$R = 216721$$