Simplified Study Material

Slow learners are those students' whose learning pace is slower than their peers. The respective4 class teachers provide simplified study notes to enhance the confidence in the subject and augment their learning peace.

B.Sc CHEMISTRY

IV-SEMESTERPAPER –V

UNIT-II

Inorganic Reaction Mechanism Stability of metal complexes Bio-inorganic Chemistry:

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LECTURER

INORGANIC REACTION MECHANISM

Introduction :

Inorganic reaction mechanism means studying the reactions occurs in complex compounds, it give complete information about reaction, intermediate / Transition state involved, and the product formed in the reactions.

Types of reactions in complexes :

Complexes mainly undergoes

1. Substitution reaction
2. Redox reactions / Electron transfer reactions.

1. Substitution reactions : The complex compounds in which one of the atom / group substituted by another atom / group are called substitution reactions.

These are again classified into two types.

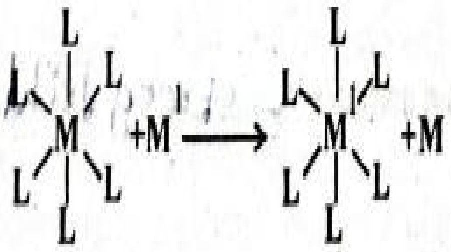
1. Electrophilic / metal ion substitution reactions :

The reactions in which metal ion in the complex is replaced by other metal ion. These are highly difficult reactions, need more energy, less common in complexes.

$$ML_6 + M^I \longrightarrow M^IL_6 + M$$

M – metal ion

L – ligand



C.N=6 oh-complex

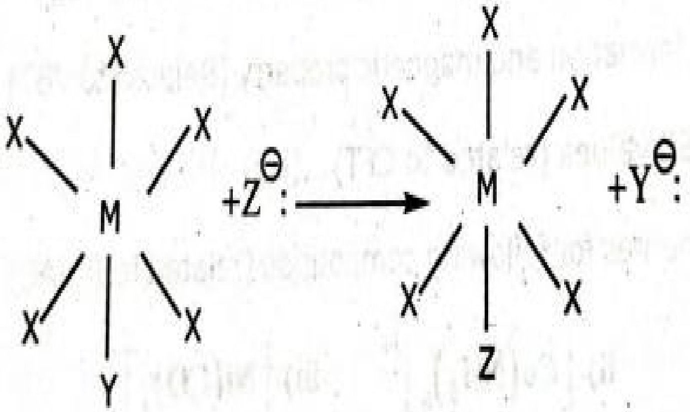
C.N=6 / oh-complex

2. Nucleophilic / Ligand substitution reactions

The reactions in which one of the ligand in a complex is replaced by another ligand are called ligand substitution reactions.

$$MX_5Y + Z^{\ominus}: \longrightarrow MX_5Z + Y^{\ominus}:$$

$$CN = 6$$



These are again two types

1. SN^1 – mechanism 2. SN^2 –mechanism

Ex : $[CO(NH_3)_5X]^{2+} + H_2O \longrightarrow [CO(NH_3)_5(H_2O)]^{3+} + X^{\ominus}$

2) Nucleophilic substitution reactions:- These are also known as ligand substitution reactions. These are of two types.

(i) Unimolecular nucleophilic substitution reactions

(ii) Bimolecular nucleophilic substitution reactions

(i) SN^1 reaction:-

It is also known as unimolecular nucleophilic substitution reaction. The rate of reaction depends only on the conc of metal complex. Hence, these are also known as **"First order reaction"**.

$$\underset{(Oh)}{ML_5X} + Y \longrightarrow \underset{(Oh)}{ML_5Y} + X$$

$$\text{Rate of reaction} \propto [ML_5X]$$

Mechanism:- SN^1 reaction takes place in two steps. In the first step six-coordinated 'oh' complex looses ligand 'X' and converted to five coordinated TBP (or) square pyramidal complex. Because, It is a slow step, It is called as the rate determing step (RDS).

In the second step, a new ligand (Y) is adding to five coordinated complex and converted to 'oh' complex. It is a $6 \rightarrow 5 \rightarrow 6$ mechanism.

Step-I:-

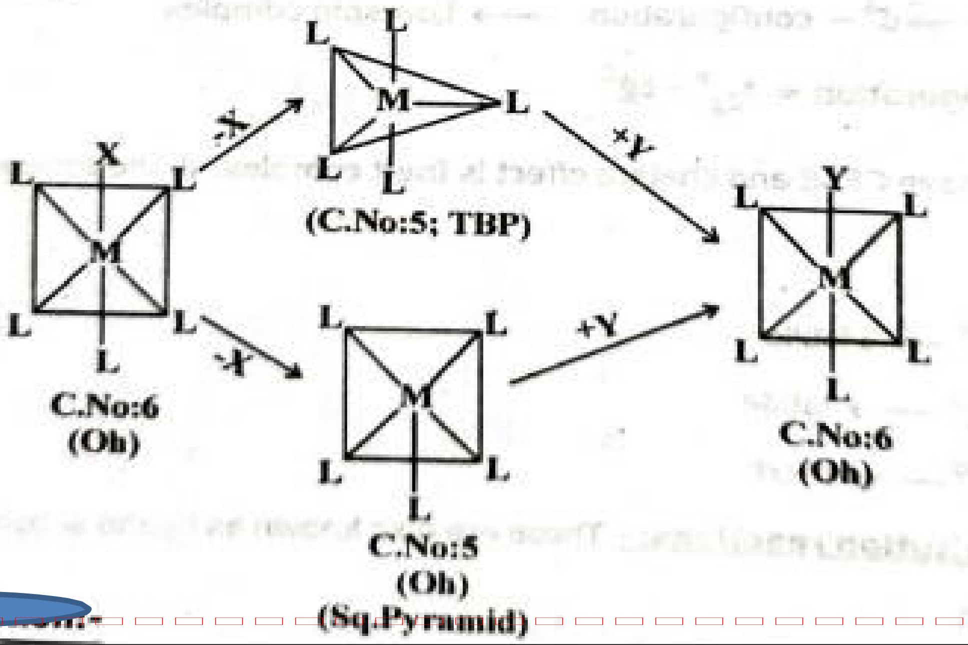
$$\underset{\substack{\text{C.No : 6} \\ \text{(Oh)}}}{ML_5X} \xrightarrow[\text{R.D.S}]{\text{Slow step}} \underset{\substack{\text{C.No : 5} \\ \text{(TBP / Sq.pyramid)}}}{ML_5} + X$$

Step-II:-

$$\underset{\substack{\text{C.No : 5} \\ \text{(TBP / Sq.pyramid)}}}{ML_5 + Y} \xrightarrow{\text{Fast}} \underset{\substack{\text{C.No : 6} \\ \text{(Oh)}}}{ML_5Y}$$

3) **Diagramatically :-**

Step-I:-



[redacted]on:-

(ii) SN^2 Reaction:- [redacted]

It is also known as **"Bi molecular nucleophilic substitution reaction"**. The rate of reaction depends on the concentration of metal complex and newly coming ligand.

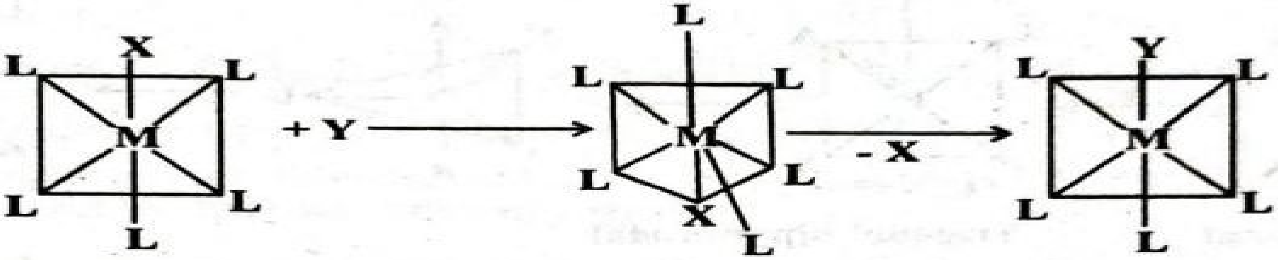
$$ML_5X + Y \longrightarrow ML_5Y + X$$

$$\boxed{\text{Rate of reaction} \propto \left[ML_5X\right]\left[Y\right]}$$

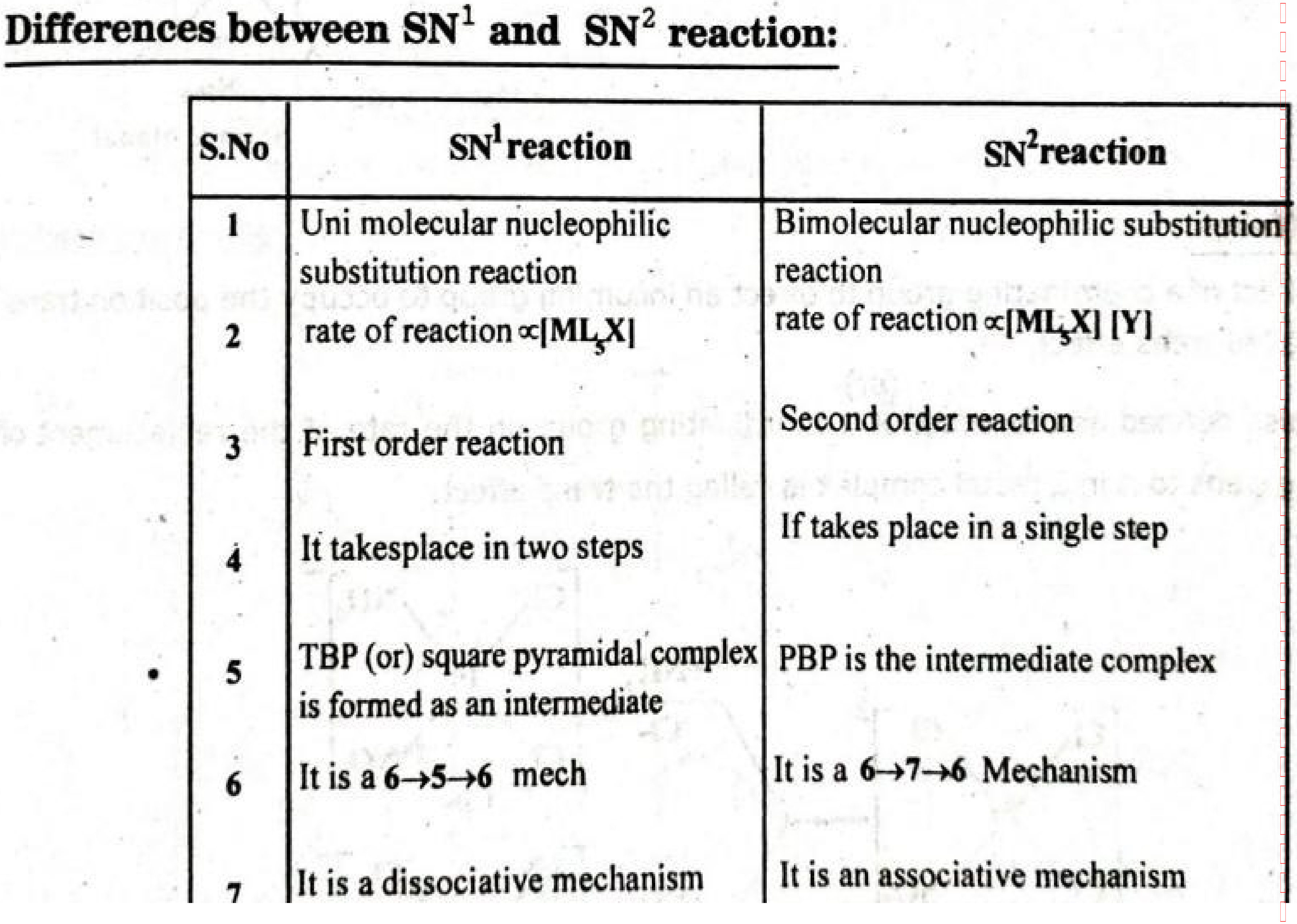
Mechanism:- SN^2 reaction takes place in a single step. A six coordinated 'oh' complex reacts with a newly coming ligand 'Y' to form a seven - coordinated PBP-complex which looses 'X' and form an 'oh' complex.

$$\underset{\substack{\text{C.No}:6\\(\text{Oh})}}{ML_5X + Y} \longrightarrow \underset{\substack{\text{C.No}:7\\(\text{PBP})}}{ML_5XY} \longrightarrow \underset{\substack{\text{C.No}:6\\(\text{Oh})}}{ML_5Y + X}$$

Diagramatically :



C.No:6 (Oh) C.No:7 (PBP) C.No:6 (Oh)



Differences between SN^1 and SN^2 reaction:

S.No	SN^1 reaction	SN^2 reaction
1	Uni molecular nucleophilic substitution reaction	Bimolecular nucleophilic substitution reaction
2	rate of reaction $\propto[ML_5X]$	rate of reaction $\propto[ML_5X]\ [Y]$
3	First order reaction	Second order reaction
4	It takesplace in two steps	If takes place in a single step
5	TBP (or) square pyramidal complex is formed as an intermediate	PBP is the intermediate complex
6	It is a 6→5→6 mech	It is a 6→7→6 Mechanism
7	It is a dissociative mechanism	It is an associative mechanism

Intermediate :

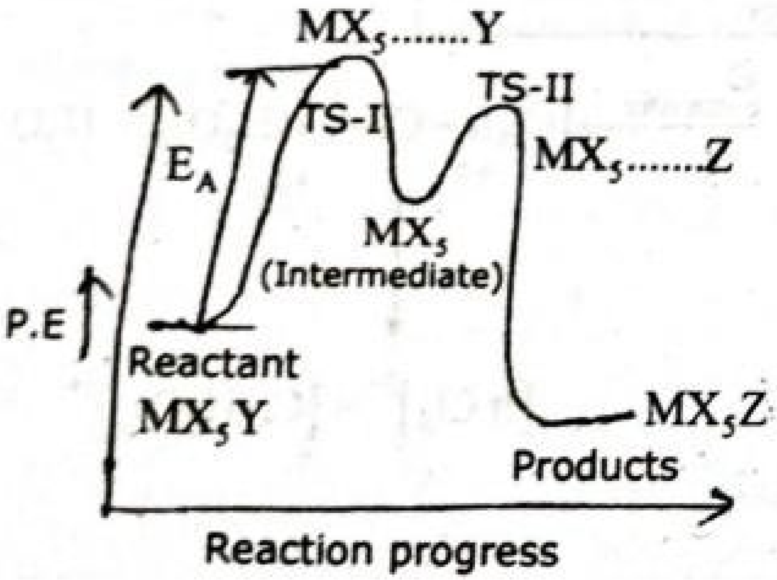
It is a molecular entity which has comparatively long lived that can be experimentally detected and characterized.

Ex : SN^1 –Reactions

$$MX_5Y + Z: \longrightarrow MX_5Z + Y:$$

$$\underset{C.N = 6}{MX_5Y} \xrightarrow[RDS]{Slow} \underset{C.N = 5}{MX_5}$$

$$MX_5 \xrightarrow[Z:]{Fast} \underset{C.N = 6}{MX_5Z}$$



E_A – Activation energy

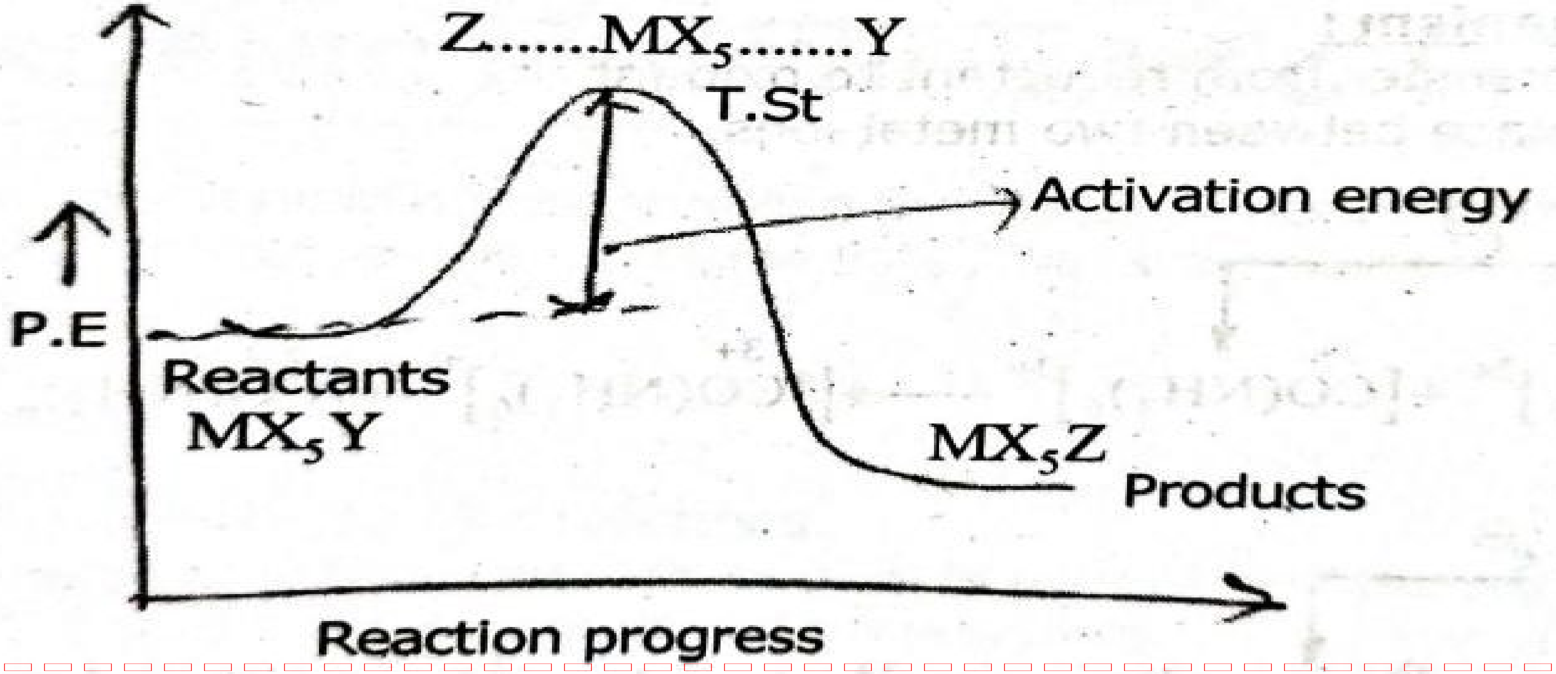
Transition state / Activated complex :

Transition state is a molecular entity that has very short life time that exhibits some structural characteristics of both the reactants and products.

Ex : SN^2 –Reactions

$$\underset{\text{C.N=6}}{MX_5y+Z:}\xrightarrow{\text{Slow/RDS}}\underset{\substack{\text{T.St}\\\text{C.N=7}}}{[MX_5YZ]}\xrightarrow[-Y^{\ominus}]{\text{fast}}\underset{\text{C.N=6}}{[MX_5Z]}$$

$$\underset{\text{C.N=6}}{MX_5-Y+Z:}\xrightarrow{\text{Slow/RDS}}\underset{\substack{\text{T.St / Activated complex}\\\text{C.N=7}}}{[Z\ldots\ldots\ldots MX_5\ldots\ldots\ldots Y]}\xrightarrow{-Y^{\ominus}}\underset{\text{C.N=6}}{[MX_5Z]}$$



Substitution reactions in square planar complexes :

Usually transition metals with d^8 configuration show square planar geometry.

Ex : $Ni^{+2}, Pt^{+2}, Rh^{+}, Ir^{+}, Au^{3+}$ ....

All Pt (II) complexes are square planar.

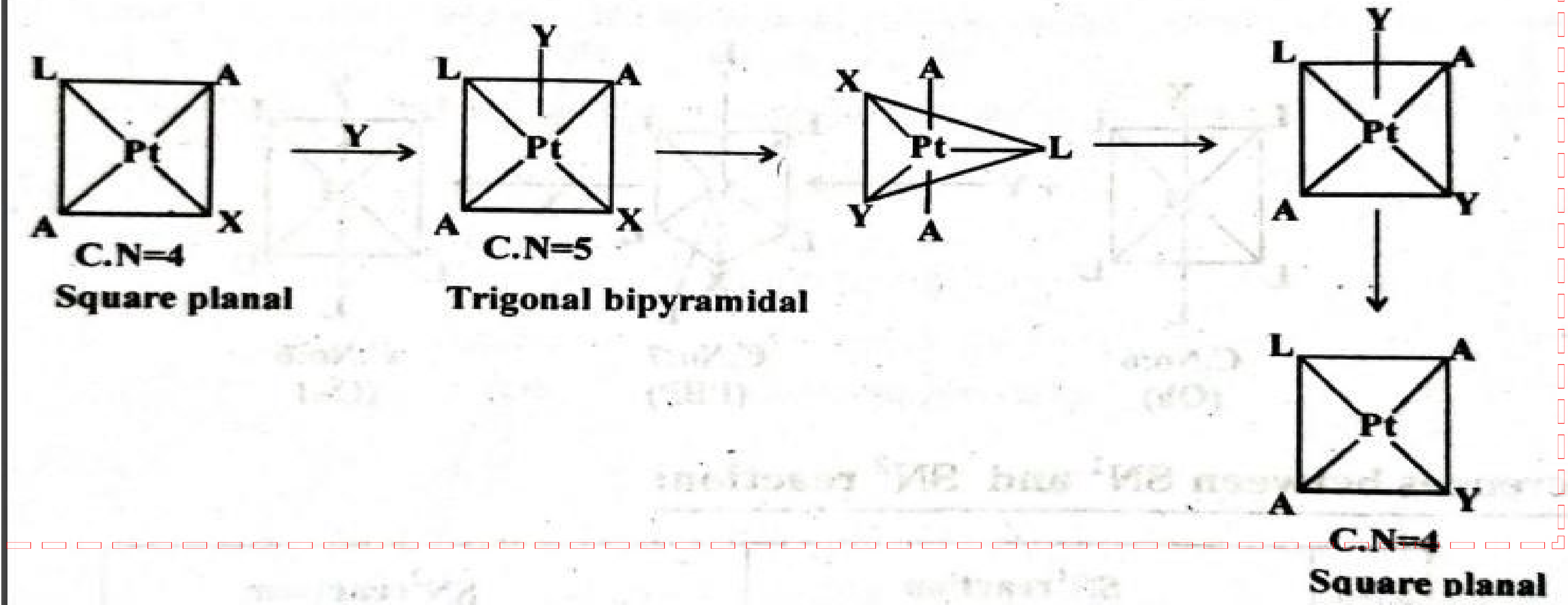
Ni (II) complexes are square planar in presence of strong field ligands and tetrahedral in weak field ligands.

- It follow associative (SN^2) mechanism.
- Pt (II) square planar substitution reactions follows retention in configuration.

$$[PtA_2LX] \xrightarrow{Y} [Pt\,A_2LY]$$

C.N=4 C.N=4

Square planar Square planar



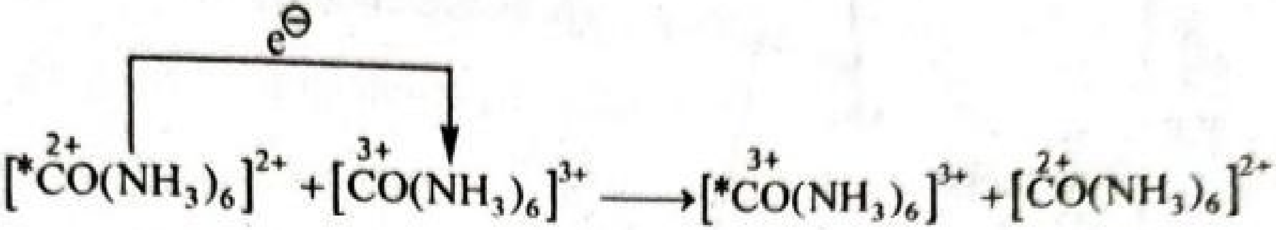
2. Redox reactions / Electron transfer reactions :

The reactions which are taking place by the transfer of electrons between complexes are called redox reactions. In these reactions the complex which undergo oxidation is called reductant, and which undergo reduction is called oxidant.

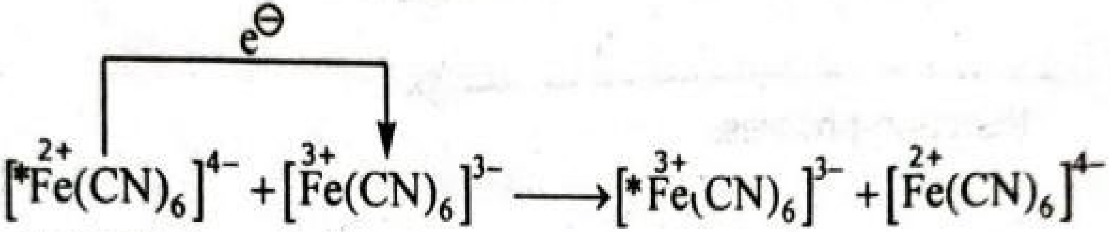
One or more electrons transfer from reductant to oxidant electron transfer reactions are again two types.

Outer sphere mechanism :

- Direct electron transfer from reductant to oxidant
- Transfer takes place between two metal ions.



Ex : 1. $[^*\overset{2+}{\text{CO}}(NH_3)_6]^{2+} + [\overset{3+}{\text{CO}}(NH_3)_6]^{3+} \longrightarrow [^*\overset{3+}{\text{CO}}(NH_3)_6]^{3+} + [\overset{2+}{\text{CO}}(NH_3)_6]^{2+}$



2. $[^*\overset{2+}{\text{Fe}}(CN)_6]^{4-} + [\overset{3+}{\text{Fe}}(CN)_6]^{3-} \longrightarrow [^*\overset{3+}{\text{Fe}}(CN)_6]^{3-} + [\overset{2+}{\text{Fe}}(CN)_6]^{4-}$

Reductant Oxidant

2. Inner sphere mechanism :

○ Transfer of ligand between oxidant and reductant.

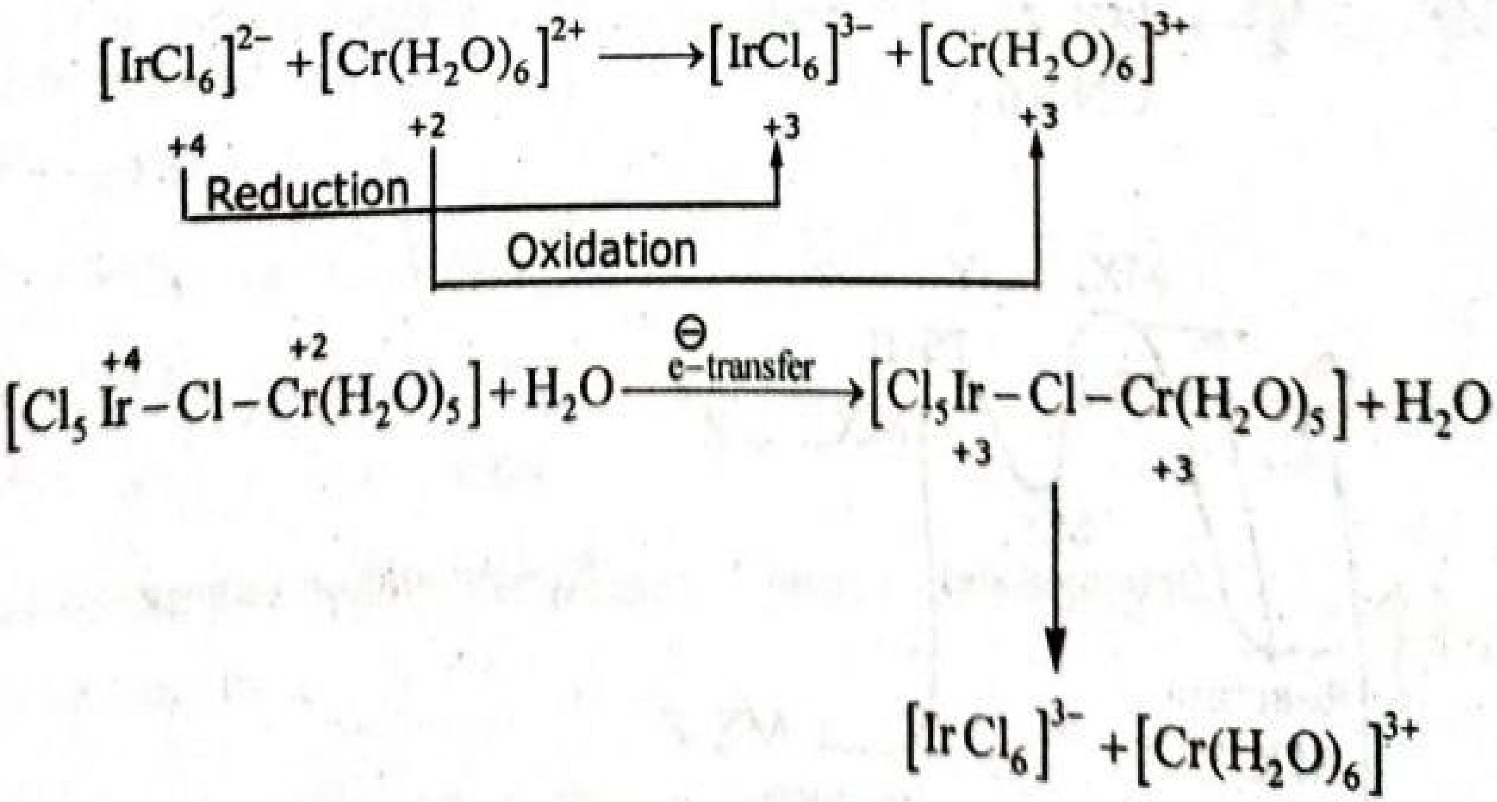
○ Form a bridged complex, the electron is then transferred through bridging ligand.

Conditions :

One complex ⟶ labile (more reactive)

One complex ⟶ Inert (less reactive)

Ex :



$$[\overset{+4}{Ir}Cl_6]^{2-} + [\overset{+2}{Cr}(H_2O)_6]^{2+} \longrightarrow [\overset{+3}{Ir}Cl_6]^{3-} + [\overset{+3}{Cr}(H_2O)_6]^{3+}$$

$$[Cl_5\overset{+4}{Ir}-Cl-\overset{+2}{Cr}(H_2O)_5] + H_2O \xrightarrow{\overset{\ominus}{e}\text{-transfer}} [Cl_5\underset{+3}{Ir}-Cl-\underset{+3}{Cr}(H_2O)_5] + H_2O$$

$$\downarrow$$

$$[IrCl_6]^{3-} + [Cr(H_2O)_6]^{3+}$$

Labile and Inert complexes :

Based on difference in rate of replacement of one ligand by the other, complexes are of two types.

1. Labile complexes 2. Inert complexes.

1. **Labile complexes :** The complexes in which substitution of ligand takes places rapidly are called Labile complexes.

$$ML_5X + Y \xrightarrow{\text{Fast}} ML_5Y + X$$

2. **Inert complexes :** The complexes in which ligands are slowly replaced by the others are called inert complexes.

$$ML_5X + Y \xrightarrow{\text{Slow}} ML_5Y + X$$

Acc. To VBT

- Square planar complexes are always labile.

  Ex : $[Cu(H_2O)_4]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + 4H_2O$

- Octahedral complexes nature depends on electron configurations.
- Outer d-orbital complexes (sp^3d^2) are labile.
- Inner d-orbital complexes (d^2sp^3) are inert

  Ex : $d^0.d^1.d^2 \longrightarrow$ Labile, $d^3 \longrightarrow$ Inert

  $d^4.d^5.d^6 \longrightarrow$ any electron in eg orbital are labile.

  $d^7.d^8.d^9 \longrightarrow$ are labile

  Ex : $[PtCl_4]^{2-} \longrightarrow$ square planar complex $\longrightarrow$ labile.

  $[FeF_6]^{4-} \longrightarrow d^6 -$ configuration. $\longrightarrow$ High spin complex

  electron configuration = $t_{2g}{}^4 - eg^2$

  $\therefore$ Labile.

  $[Fe(CN)_6]^{4-} \longrightarrow d^6 -$ configuration. $\longrightarrow$ Low spin complex

  electron configuration = $t_{2g}{}^6 - eg^2$

According to CFT

Any complex will have CFSE and chelate effect is Inert complex. While the complex with CFSE zero is labile complex.

$d^0 \longrightarrow$ labile

$d^1 \longrightarrow t_{2g}{}^1.eg^0 \longrightarrow$ labile

$d^2 \longrightarrow t_{2g}{}^2.eg^0 \longrightarrow$ labile

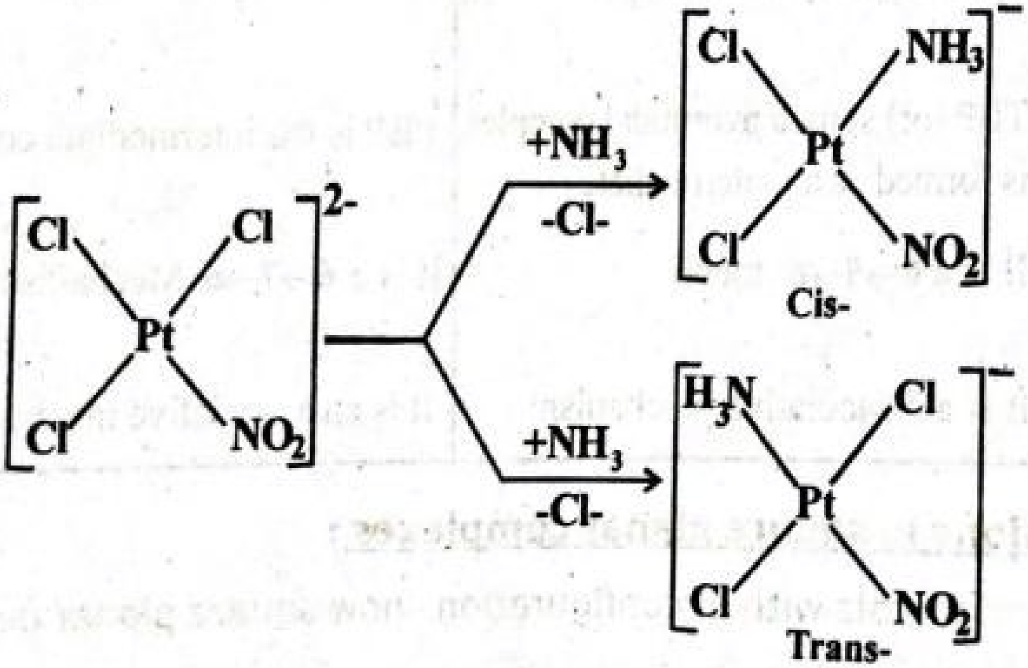
$d^3 \longrightarrow t_{2g}{}^3.eg^0 \longrightarrow$ Inert

Trans effect:-

The effect of a coordinating group to direct an incoming group to occupy the position trans to it self is called trans effect.

(or)

It is also defined as the effect of a coordinating group on the rate of the replacement of a group lying trans to it in a metal complex is called the trans effect.



Theories of transeffect:- There are two theories have been proposed to explain the trans effect.

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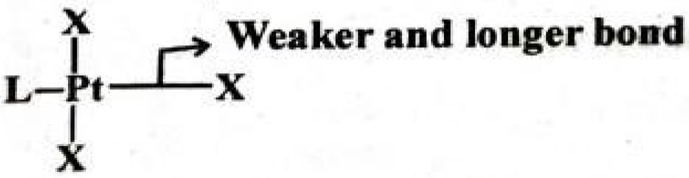
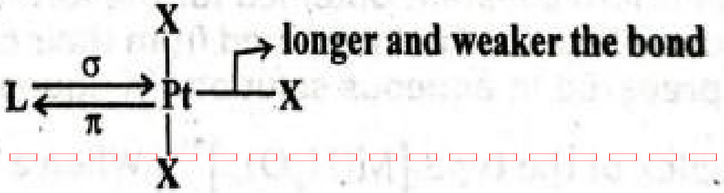
(1) Polarisation theory:- It was proposed by **'Grienberg'**. In $PtLX_3$ complex the primary positive charge on Pt(II) induces a dipole in all the four ligands.

Since 'L' is larger and has greater polarizability than 'X', the bond trans to 'L' is weakend and consequently lengthed. Then, the newly coming ligand substitutes the ligand 'X' which is trans to 'L'.



(2) π-bonding theory:- According to this theory, the vacant $\pi\,(or)\,\pi^*$ orbitals of the π-bonding ligands accept a pair of electrons from the filled d-orbitals of the metal to form a metal- ligand π-bond.

In case of $Pt\,X_3\,L$ ('L' is the π-bonding ligand), the d_{yz} orbital of Pt(II) accepts a pair of electron from the π-bonding ligand, L to form the $d^{\pi}-p^{\pi}$ bond between Pt(II) and L. Stronger this double bond results weaker the opposite bond which is trans to 'L'. Then, X is replaced by another incoming ligand.

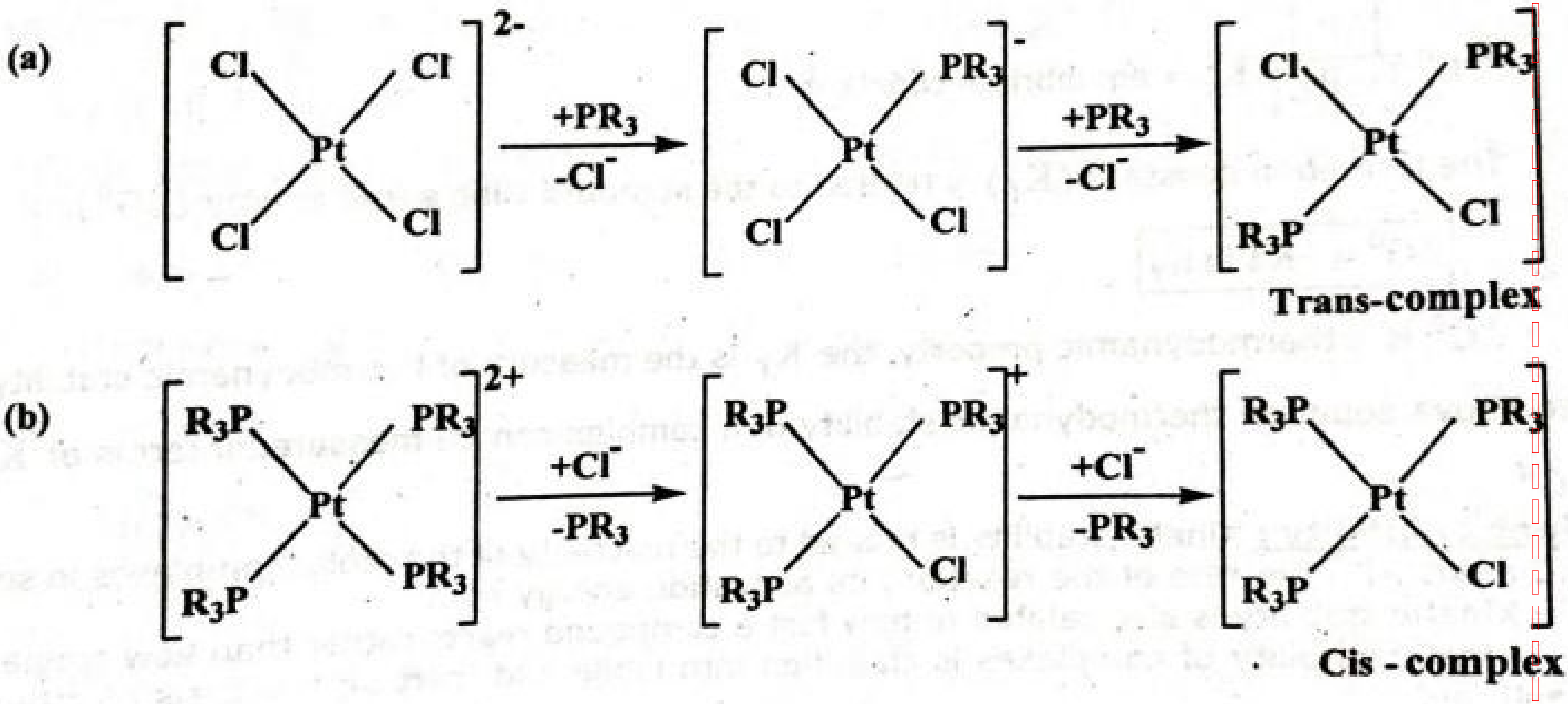


Applications of trans effect:-

1) Synthesis of Pt (II) complexes:-

Trans effect is used to synthesisc *Cis* – complex and trans- complex.

Synthetic process:-



Trans-complex

Cis - complex

2. STABILITY OF METAL COMPLEXES

The stability of metal complex generally means that it exists under favourable conditions without undergoing decomposition. The stability of metal complex is governed by two different aspects

1. Thermodynamic stability 2. Kinetic stability

1. Thermodynamic stability : It refers to it's tendency to exist under equilibrium conditions. It determines the extent to which the complex will be formed or be converted into another complex at the point of equilibrium.

The thermodynamic stability of complexes is represented by formation constant / stability constant, which is the equilibrium constant obtained for the formation of metal complex.

In general, the metal complexes are not prepared from their corresponding starting materials in gaseous phase but are prepared in aqueous solution. In aqueous solution a metal cation gets hydrated to give aqua complex of the type $[M(H_2O)_x]^{n+}$. When a ligand replaces water molecule from aqua complex ion, a new metal complex is formed and equilibrium is established as shown.

$$[M(H_2O)_X]^{n+} + L \xrightleftharpoons{k_f} [M(H_2O)_{X-1}L]^{n+} + H_2O$$

x = no. of water molecules

n = oxidation number

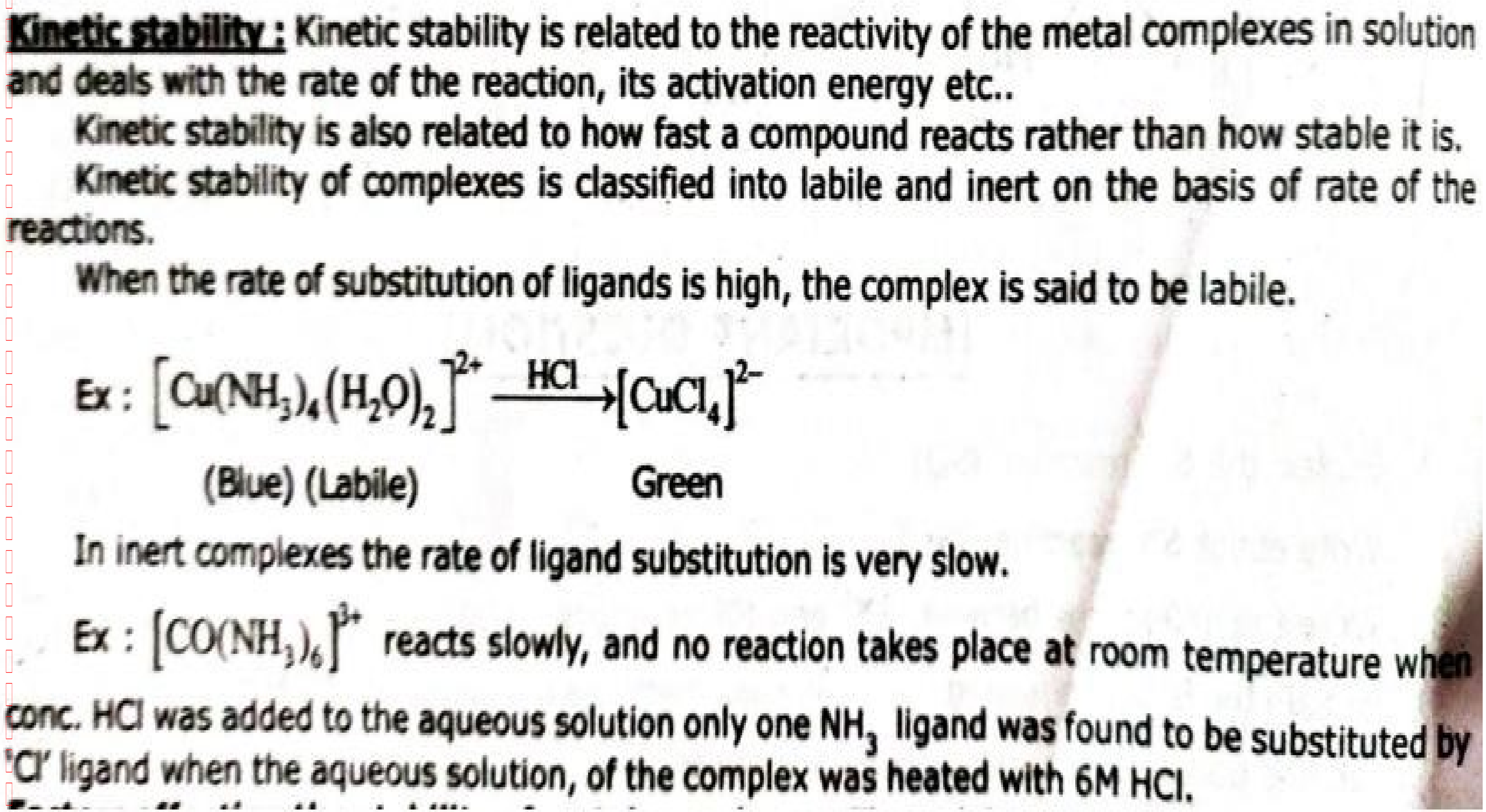
$$M + L \xrightleftharpoons{K_f} ML$$

$$K_f = \frac{[ML]}{[M][L]}$$ K_f = equilibrium constant

The formation constant (K_f) is related to the standard Gibb's free energy (ΔG^0).

$$\boxed{\Delta G^0 = -RT \ln K_f}$$

ΔG^0 is a thermodynamic property, the K_f is the measure of thermodynamic stability form the above equation thermodynamic stability of a complex can be measured interms of K_f and ΔG^0.



Kinetic stability : Kinetic stability is related to the reactivity of the metal complexes in solution and deals with the rate of the reaction, its activation energy etc..

Kinetic stability is also related to how fast a compound reacts rather than how stable it is.

Kinetic stability of complexes is classified into labile and inert on the basis of rate of the reactions.

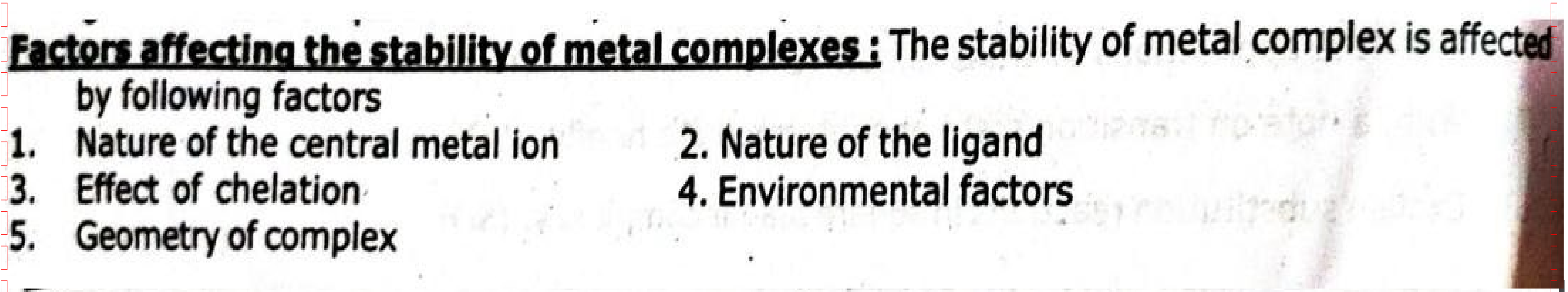
When the rate of substitution of ligands is high, the complex is said to be labile.

Ex : $[Cu(NH_3)_4(H_2O)_2]^{2+} \xrightarrow{HCl} [CuCl_4]^{2-}$

(Blue) (Labile) Green

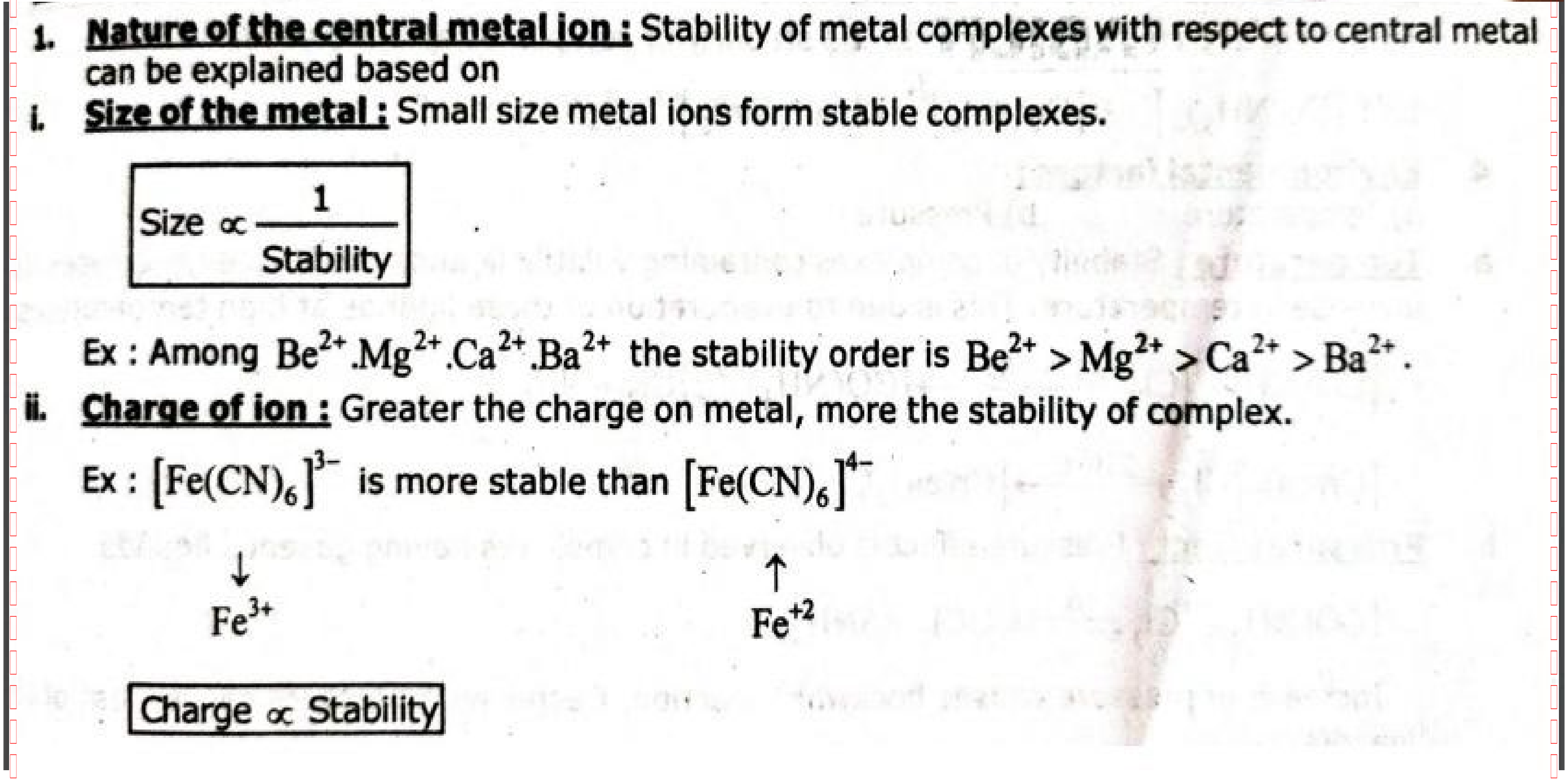
In inert complexes the rate of ligand substitution is very slow.

Ex : $[CO(NH_3)_6]^{3+}$ reacts slowly, and no reaction takes place at room temperature when conc. HCl was added to the aqueous solution only one NH_3 ligand was found to be substituted by 'Cl' ligand when the aqueous solution, of the complex was heated with 6M HCl.



Factors affecting the stability of metal complexes : The stability of metal complex is affected by following factors

1. Nature of the central metal ion
2. Nature of the ligand
3. Effect of chelation
4. Environmental factors
5. Geometry of complex



1. **Nature of the central metal ion :** Stability of metal complexes with respect to central metal can be explained based on

i. **Size of the metal :** Small size metal ions form stable complexes.

$$\boxed{\text{Size} \propto \frac{1}{\text{Stability}}}$$

Ex : Among $Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}$ the stability order is $Be^{2+} > Mg^{2+} > Ca^{2+} > Ba^{2+}$.

ii. **Charge of ion :** Greater the charge on metal, more the stability of complex.

Ex : $\underset{Fe^{3+}}{\underset{\downarrow}{[Fe(CN)_6]^{3-}}}$ is more stable than $\underset{Fe^{+2}}{\underset{\uparrow}{[Fe(CN)_6]^{4-}}}$

$$\boxed{\text{Charge} \propto \text{Stability}}$$

2. **Nature of the ligand :** In complexes ligand act as a electron pair donor nature of the ligand also paly an important role in the stability of complexes.

i. **Size & charge of ligand :** Ligands with small size and greater charge can form stable complexes.

Ex : $F^- > Cl^- > Br^- > I^-$

Among halogens F^- with small size form stable complex than $I^{\ominus}$ with greater size ligand.

Ex : $[COF_6]^{3-} > [COI_6]^{3-}$

ii. **Basic nature of ligand :** Ligand which can donate lone pair of electrons easily (strong ligands) can form stable complexes.

Ex : Strong bases like F^- & NH_3 form stable complexes

Than weak ligands I^- & H_2O.

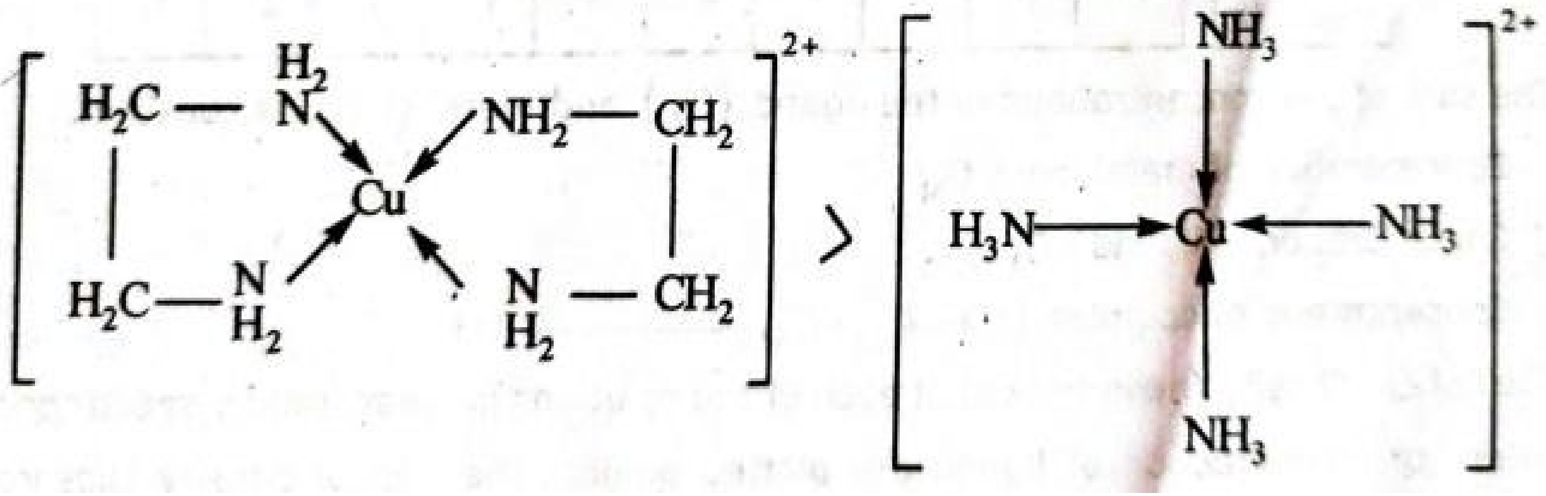
Ex : $[COF_6]^{3-} > [COI_6]^{3-}$

$[CO(NH_3)_6]^{3+} > [CO(H_2O)]^{3+}$

If ligand is strong, it can donate electron easily and form a strong bond with central metal to form stable complexes.

3. **Effect of chelation / chelating effect :** formation of cyclic ring by a polydentate ligand is called chelation complexes with chelating ligands are more stable than the complexes with monodentate ligands. This is called chelating effect.

Ex : $[Cu(en)_2]^{2+} > \left[\underset{(Cu)}{Cu}(NH_3)_4\right]^{2+}$ en → ethylene diamine



As the chelate ring size increases the stability of complexes also increases.

Ex : $[Cu(NH_3)_4]^{2+} < [Cu(en)_2]^{2+} < [Cu(dien)_2]^{2+} < [Cu(trien)_2]^{2+}$

4. Environmental factors :

a) Temperature b) Pressure

a. Temperature : Stability of complexes containing volatile ligands like NH_3, en decreases with increase in temperature. This is due to evaporation of these ligands at high temperatures.

$$[CO(NH_3)_6]Cl_3 \xrightarrow{175\text{–}180^0C} [CO(NH_3)_5Cl]Cl_2 + NH_3$$

$$[Cr(en)_3]Cl_3 \xrightarrow{210^0C} [Cr(en)_2Cl_2]Cl + en$$

b. Pressure effect : Pressure effect is observed in complexes having gaseous ligands.

$$[CO(NH_3)_6]Cl_3 \overset{\Delta}{\rightleftharpoons} COCl_2 + 6NH_3$$

Increase in pressure causes backward reaction, Decrease in pressure causes loss of NH_3 ligand(s).

5. Geometry of complex : Generally four co-ordinated complexes are less stable than six co-ordinated complexes due to bond energy criteria.

$$[Cu(NH_3)_4]^{2+} < [Cu(NH_3)_6]^{3+}$$

$[Cu(NH_3)_4]^{2+}$ ↓ More reactive less stable

$[Cu(NH_3)_6]^{3+}$ ↓ Less reactive more stable

Determination of the composition of a complex:-

JOB's Method:-

Job's method is used to determine the composition of a complex. Different experiment steps are involved in this process are

(i) Prepare ten solutions in ten different test tubes of a fixed volume of the complex.

(ii) In each test tube different amounts of metal and ligands are to be taken.

(iii) Let the total volume of the complex prepared in each of the ten solutions is 10ml.

S.No	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
Volume of metal ion(ml)	0	1	2	3	4	5	6	7	8	9
Volume of ligand (ml)	10	9	8	7	6	5	4	3	2	1

The sum of the concentrations of the ligand (C_L) and metal (C_M) is constant.

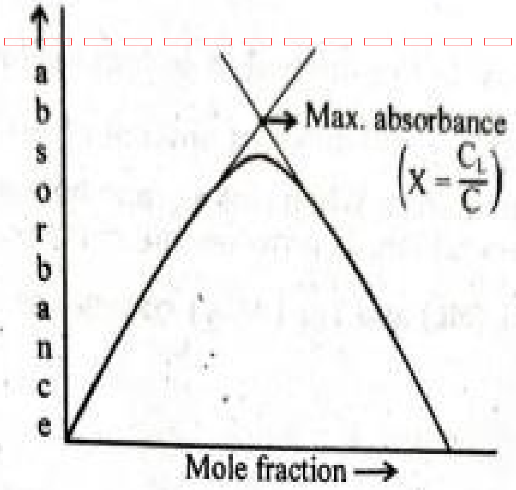
Concentration of metal ion $= C_M$

Concentration of ligand $= C_L$

Concentration of complex $(C) = C_L + C_M$ ———— (1)

(iv) The optical density (absorbance) of each of the solutions is measured by spectrophotometer.

(v) Values of mole fraction of ligand are plotted against the optical density (absorbance) of solution



Now, if the formula of the complex is ML_n, then,

$$n=\frac{C_L}{C_M} \text{———————} (2)$$

divide the equation (1) by 'C'

$$\frac{C_L}{C}+\frac{C_M}{C}=\frac{\cancel{C}}{\cancel{C}}$$

$$\frac{C_L}{C}+\frac{C_M}{C}=1 \text{------->} (3)$$

But, $\frac{C_L}{C}=X$ (mole fraction) ------> (4)

Substitute (4) in (3)

$$x+\frac{C_M}{C}=1$$

$$\frac{C_M}{C}=1-X \text{------->} (5)$$

$$\frac{C_M}{C}=1-X \text{------->} (5)$$

doing $\frac{④}{⑤}$

$$\frac{\frac{C_L}{\cancel{C}}}{\frac{C_M}{\cancel{C}}}=\frac{X}{1-X}$$

$$\frac{C_L}{C_M}=\frac{X}{1-X} \text{------>} (6)$$

Acc. to equation -(2) $\frac{C_L}{C_M}=n$; When written in equation-(6)

$$\boxed{n=\frac{x}{1-x}}$$

based on 'n' value, it can be possible to determine the composition of complex.

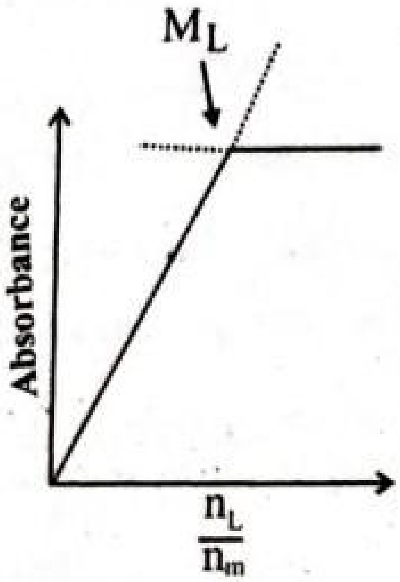
Limitations:-

(i) It gives un reliable results when more than one complex is formed in the system.

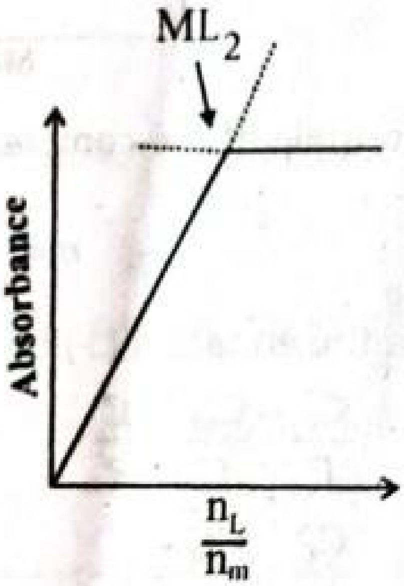
(ii) It is applicable when there is no change in volume on mixing the solution of the metal ion and the ligand.

2. Mole- Ratio method:-

It was introduced by Yoe and Jones. In this method. A series of solutions prepared containing a constant amount of the metal ions (C_M) and different amount of the ligand (C_L) Keeping the total volume constant under similar conditions. When plot a graph between absorption against the ratio of moles of Ligand to moles of metal ion, It provides the composition of the complex. This method is also useful to determine 1:1 (ML) and 1:2 (ML_2) complexes.



ML - complex
(1:1)



ML_2 - complex
(1:2)