UNIT-I

1. REACTIVITY OF METAL COMPLEXES

LONG ANSWER TYPE QUESTIONS

1. Explain labile and inert complexes with examples?

[AdNU 18; AU 17; SKU 18; VSU 17; YVU 18, 17]

A. In metal complexes based on the rate of substitution of one ligand by another ligand, the metal complexes are classified into two types. They are

i) Labile complexes ii) Inert complexes

i) Labile complexes : In a metal complex one ligand is rapidly replaced by another ligand the complex is known as labile complex.

Example : $[Cu\,(H_2O)_4]^{2+} + 4NH_3 \rightarrow [Cu\,(NH_3)_4]^{2+} + 4H_2O$

In above equation Cu^{2+} complex exhibits co-ordination number-4, are labile complexes.

At $25^{\circ}C$, in 0·1M solution of complexes the substitution takes place in less than one minute the complexes are called labile complexes.

The complexes are designated as stable and unstable on the based on equilibrium constant K.

$$ML_n \overset{K}{\rightleftharpoons} M^{n+} + nL^-$$

If the value of K is large the complex is unstable.

If the value of K is small the complex is stable.

ii) Inert complexes : In a complex, one ligand substitution on another ligand is slow the complex is known as inert complex.

Example : $[RhCl_6]^{3-} + 4NH_3 \rightarrow Cu(NH_3)_4 + 4H_2O$

Inert complexes are exhibited co-ordination number -6.

In solvent complexes at $25^{\circ}C$ in 0·1M solution of complex, the substitution takes place more than one minute the complex is said to be inert complex.

The nature of both labile, inert complexes depends on the following factors.

i) The electronic configuration of the central metal ion of the complex.
ii) The three dimensional geometry of the complex.
iii) The co-ordination number exhibited by the metal ion
iv) The values of CFSE of the reactant complex and the activated state complex.

2. Discuss SN^1 and SN^2 reactions in ligand substitution reactions?

[AdNU 18, 17; ANU 18; AU 18, 17; BRAU 18, 17; RU 18, 17; SKU 17; SVU 18; VSU 17]

A. Ligand substitution reactions are classified into two types. They are

i) SN^1 reactions ii) SN^2 reactions

1) Nuclephilic unimolecular substitution reaction- SN^1 :

Generally SN^1 reaction can be written as $[ML_n X] + Y \rightarrow [ML_n Y] + X$

Reaction mechanism :

$$[ML_n X] \xrightarrow[K_1]{\text{slow}} [ML_n] + X$$

rate determing step

$$[ML_n] + Y \xrightarrow{\text{fast}} [ML_n Y]$$

In this reaction the slow step is called as rate determining step. In this step the rate is dependent on the concentration of the reactant molecule(complex).

rate = $K_1[ML_n X]^1$

Hence this is called unimolecular or first order reaction.

2) Nuclephilic bimolecular substitution reaction- SN^2 :

These reaction can be written as follows.

$[ML_n X] + Y \rightarrow [ML_n Y] + X$

Reaction mechanism :

$$[ML_n X] + Y \xrightarrow[K_2]{\text{slow}} [ML_n XY]$$

rate determining step

$$[ML_n XY] \xrightarrow{\text{fast}} [ML_n Y] + X$$

In this reaction the rate depends on the concentrations of $[ML_n X]$ and Y.

Hence the rate equation is

Rate = $K_2\,[ML_n X][Y]$

The rate depend on the concentrations of both $[ML_n X]$ and $[Y]$. Hence it is called second order reaction.

Some important aspects regarding Nucleophilic substitution reactions :

i) Labile complexes exhibit SN^2 reactions and the co-ordination number of intermediate is increases.

ii) Inert complexes exhibit SN^1 reactions and the co-ordination number of intermediate is decreases.

3. What is trans effect? Explain trans effect and given their applications? **[ANU 18; AdNU 17; BRAU 18; KU 18; RU 18; SKU 18, 17; VSU 18; YVU 17]**

A. In 1893 Werner recognised a theory for a better understanding of the kinetic behaviour of planar complexes, this is called "Trans effect". This theory was latter elabrated by different scientists.

Trans effect : Trans effect was defined in different ways by different sciensists.

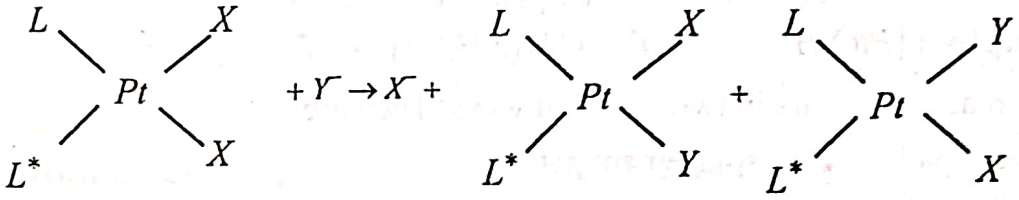
1) In a complex the trans effect of a group co-ordinated to metal ion is defined as the tendency of group to direct the incoming group to occupy the position trans to that group is called trans effect.

2) In a complex labilization of the ligand trans to other trans directing group is called trans effect.

3) In a square planar complex the stability of the bond between the central metal atom and the substituent in the trans position on the diagonal is effected more than the bonds formed by the neighbouring atoms in neighbouring positions is called trans effect.

Explanation : Langford and Gray were explanied the trans capacity of different groups.

Trans position directing series.



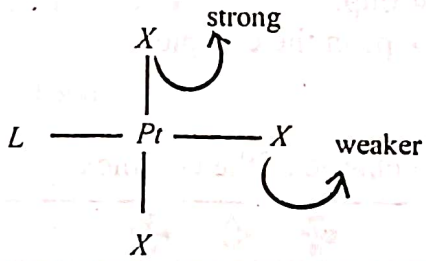
Trans position directing series are

High end $CN^-, CO, C_2H_4, NO > PR_3, H^- > CN^- > Sc(NH_2)_2 > C_6H_5^-, NO_2^-, I^-, SCN^- > Br^-, Cl^- > Py$ low end.

Trans effect is explained by

i) Electro static polarisation theory
ii) π - bonding theory.

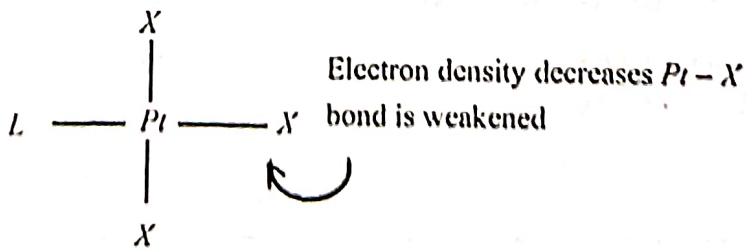
i) Electrostatic polarisation theory : In a metal complex due to electro-static polarisation the trans bands are weakness and provides the substitution in this trans position.



In this complex $Pt - X$ bond in cis position is strong and shorter. $Pt - X$ bond in transposition is weak and longer due to this reason the substitution is takes place in trans position.

ii) π **- bonding theory :** π - bonding theory was introduced by chatt and orgel. According to this theory to explain the high trans effect of ligands of $PR_3, NO, CO, C_2H_4, CN^-$ etc.

As per the theory the vacant π or π^* orbitals of the π - bonding ligands acept a pair of electrons from the filled d - orbitals of the metal (d_{xz} or d_{yz}) to form metal ligand π - bond ($d\pi - d\pi$ or $d\pi - P\pi$).



Applications :

i) It was used for synthesis of cis and trans $[PtA_2X_2]$ complexes.
ii) To distinuish between cis and trans isomers of $[pt\,A_2X_2]$ type complexes.

4. Explain substitution reactions in square planar complexes with examples?

[VSU 18; YVU 18]

A. $Pt(II)$, $Pd(II)$, $Ni(II)$, $Au(II)$, $Rh(I)$, $Ir(I)$ etc metal ion having d^8 configuration. Generally these type of ions from square planar complexes.

Example : $[Pt(NH_3)_3Cl]^+ + Y^- \rightarrow [Pt(NH_3)_3Y]^+ + Cl^-$

above reaction occurs in two different ways. They are

i) solvent path ii) displacement path

i. Solvent path :

$$[Pt(NH_3)_3Cl]^+ + H_2O \overset{\text{slow}}{\rightleftharpoons} [Pt(NH_3)_3H_2O]^{2+} + Cl^-$$

$$[Pt(NH_3)_3H_2O]^{2+} + Y^- \xrightarrow{\text{Fast}} [Pt(NH_3)_3Y]^+ + H_2O$$

Displacement path :

$$[Pt(NH_3)_3Cl]^+ Y^- \xrightarrow{\text{slow}} \left[(NH_3)_3Pt\begin{matrix}Y\\Cl\end{matrix}\right] \rightarrow [Pt(NH_3)_3Y]^+ + Cl^-$$

The factors that influence the rate of these reactions :

i) The effect of leaving group.
ii) The effect of other groups in the complex.
iii) Entering group effect.
iv) Effect of solvent.
v) The effect of electrical charge of the complex.

Applications of Trans Effect in Synthesis of Pt (II) Complexes

a. Synthesis of cis- and trans – $[PtA_2X_2]$
where A= Ammine, X= halide, NO_2^-, SCN^-

b. Synthesis of cis- and trans – $[PtABX_2]$
where A= Ammine, Py etc. B= NO_2^-, CO etc. X= halide

c. Synthesis of [PtABCD] where A, B, C, D are four different ligands

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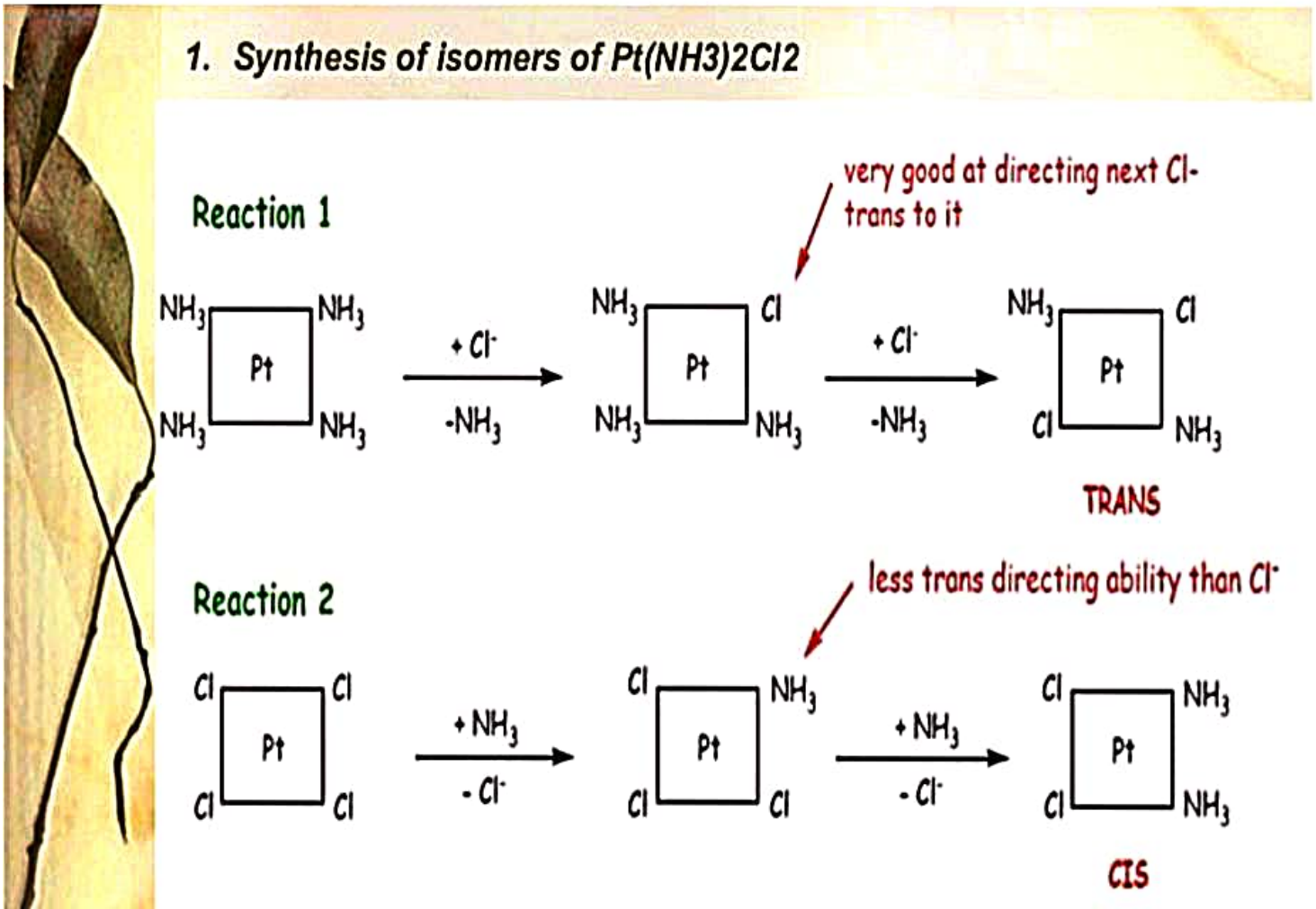
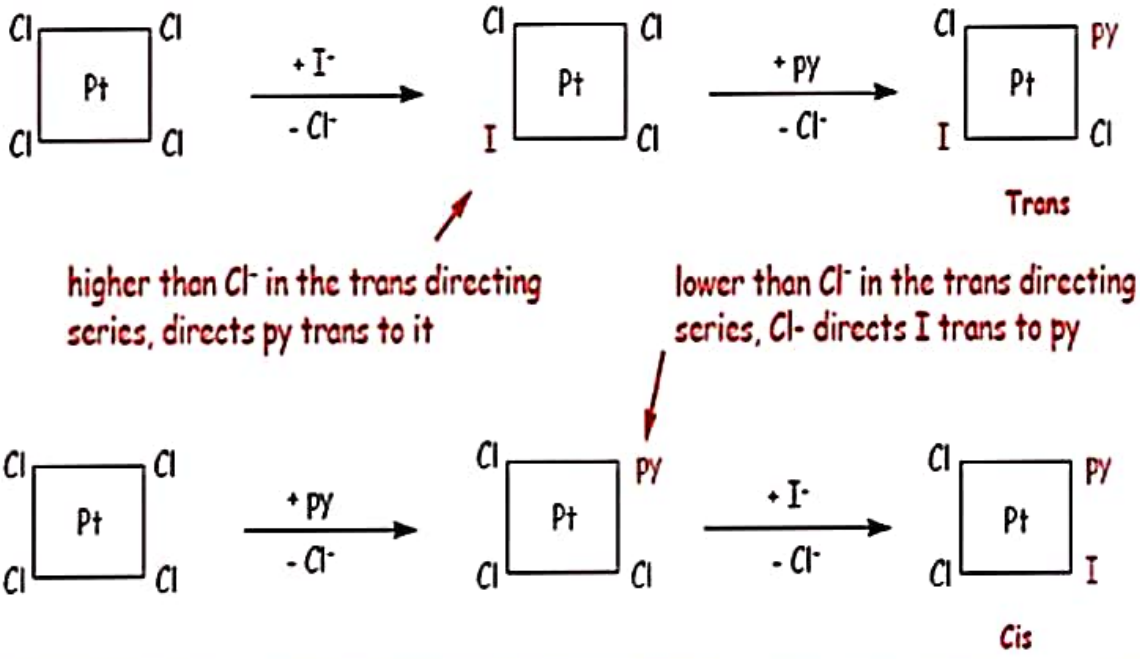
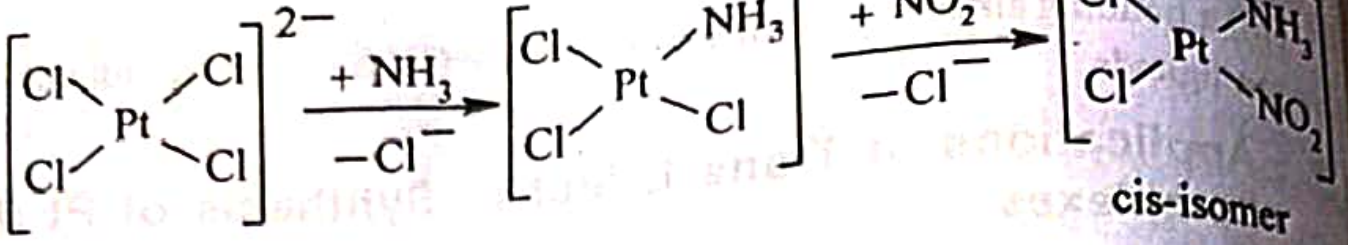


2. Preparation of cis and trans $PtCl_2I(py)$ from $PtCl_4^{2-}$, I^- and py.



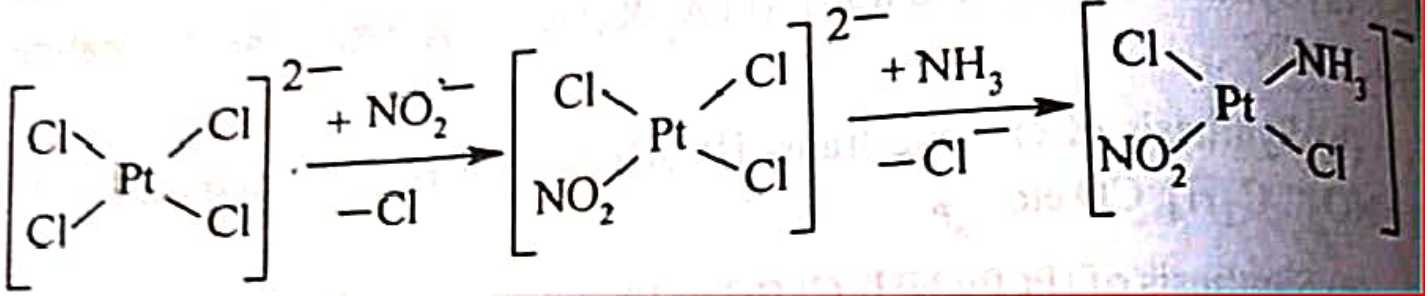
(b) Synthesis of cis- and trans- isomers of [Pt AB X_2]

e.g. (i) In order to get cis- $[Pt\,Cl_2\,(NO_2)\,(NH_3)]^-$, $[Pt\,Cl_4]^{2-}$ is reacted with NH_3 first and then with NO_2^-.

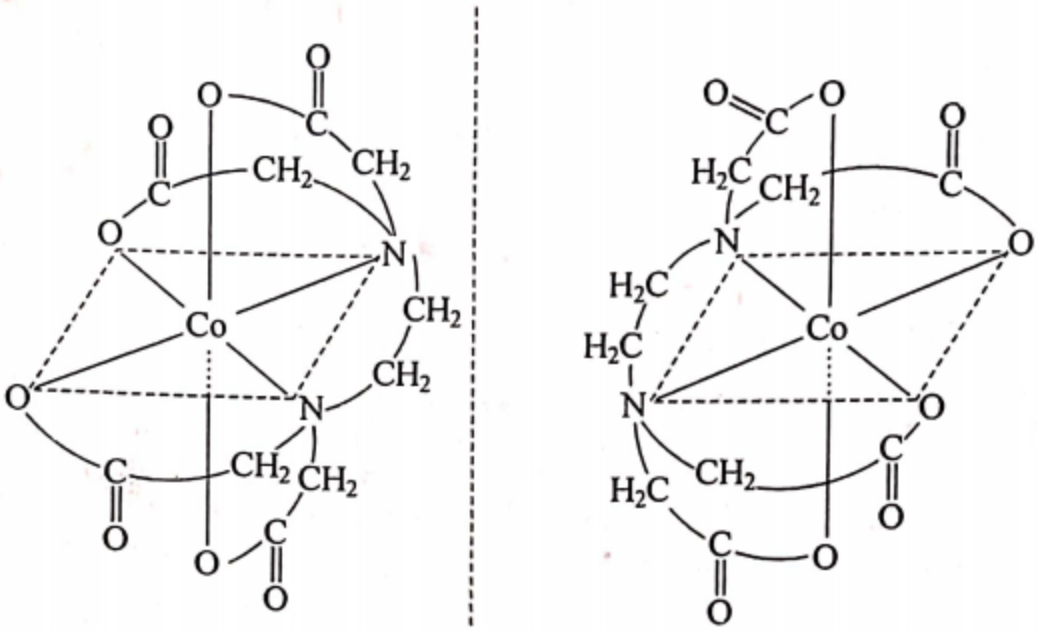


cis-isomer

(ii) In order to get trans isomer of $[Pt\,Cl_2\,(NO_2)\,(NH_3)]^-$ $[Pt\,Cl_4]^{2-}$ is reacted with NO_2^- first and then with NH_3.



(*v*) **Complexes containing hexadentate ligand** have also been resolved into *d*-. and *l*-forms. The typical example is $[Co(EDTA)]^-$, where EDTA = ethylenediamine tetra-acetic acid.



Enantiomeric pair of $[Co(EDTA)]^-$

Summery : Thus, we can conclude that the optical isomerism frequently occurs in octahedral complexes (CN 6), although examples are known in planar and tetrahedral complexes having CN 4, while geometrical isomerism occurs in octahedral complexes (CN 6) as well as in square planar complexes (CN 4).

1.9. DETERMINATION OF THE COMPOSITION OF A COMPLEX (JOB'S METHOD)

Different experiment steps involved in the process are as follows.

(*i*) A series of solutions (say ten solutions) of a fixed volume of the complex in each case but containing different amounts of the metal ion and the ligands is prepared.

(*ii*) Let the total volume of the complex prepared in each of the ten solutions is 10 mL and the proportions of the metal ion and the ligand in these solutions is varied as below :

Metal ion (vol)	0	1	2	3	4	5	6	7	8	9
Ligand (vol)	10	9	8	7	6	5	4	3	2	1

Thus, it is obvious that the sum of the concentrations of the ligand (C_L) and metal ion (C_M) is constant (10) in each case and only their ratios are changed.

i.e.,
$$C_L + C_M = C \qquad \ldots(1)$$

(*iii*) The optical density (absorbance) of each of the solutions is measured by spectrophotometer. In this process, such a wavelength of light is chosen which is absorbed strongly by the complex only, and not by the metal ion and the ligand.

(*iv*) Values of mole fraction of the ligand ($x = C_L/C$) are plotted against the optical density (absorbance) of the corresponding solution.

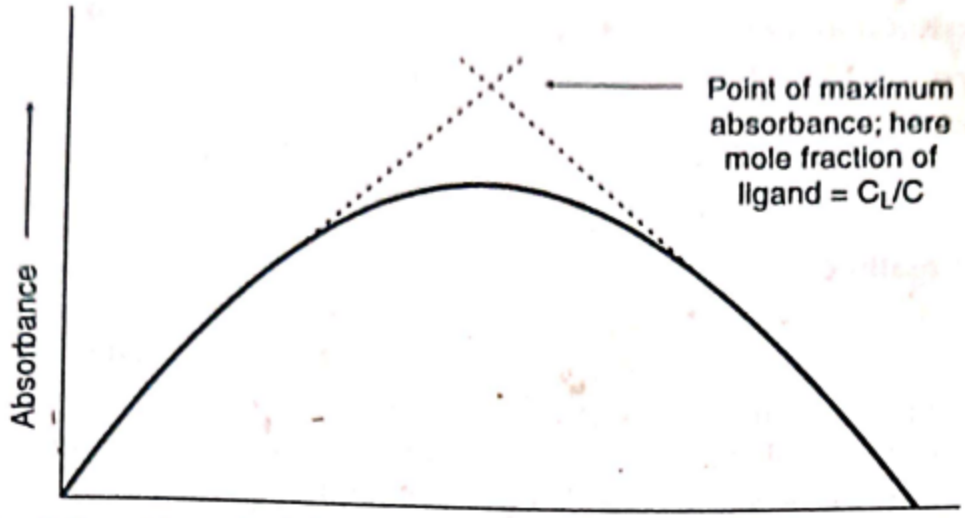


Fig. 1.7. Job's method for the determination of composition of a complex.

When the legs of the curve are extrapolated, they cross each other at a point at which absorbance is maximum.

Now if the formula of the complex is ML_n, then

$$n = \frac{C_L}{C_M} \qquad \ldots(2)$$

Dividing equation (1) throughout by C,

$$\frac{C_L}{C} + \frac{C_M}{C} = \frac{C}{C} = 1 \qquad \ldots(3)$$

We also know that

$$x = \frac{C_L}{C} \qquad \ldots(4)$$

From eqs. (3) and (4)

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

$$\therefore \qquad \frac{C_M}{C} = 1 - x \qquad \ldots(5)$$

Dividing equation (4) by (5), we get

$$\frac{C_L}{C} \times \frac{C}{C_M} = \frac{x}{1-x}$$

or

$$\frac{C_L}{C_M} = \frac{x}{1-x} \qquad \ldots(6)$$

From equations (2) and (6),

$$n = \frac{x}{1-x} \qquad \ldots(7)$$

Thus, by knowing the value of n from equation (7), the composition of the complex ML_n can be determined.

Limitations of Job's method

1. In case more than one species is formed in the system, the method gives unreliable results.
2. The method is applicable only when there is no change in volume on mixing the solution of the metal ion and the ligand.

Mole-ratio method

This method was introduced by Yoe and Jones. In this method a series of solutions are prepared containing a constant amount of the metal ions (C_m) and varying amount of the ligand (C_l) keeping the total volume constant under identical conditions. The absorbance of these solutions is measured and plotted against the ratio of moles of ligands to moles of metal ion ($R = C_l / C_m$). The break in the curve will provide the composition of the complex.

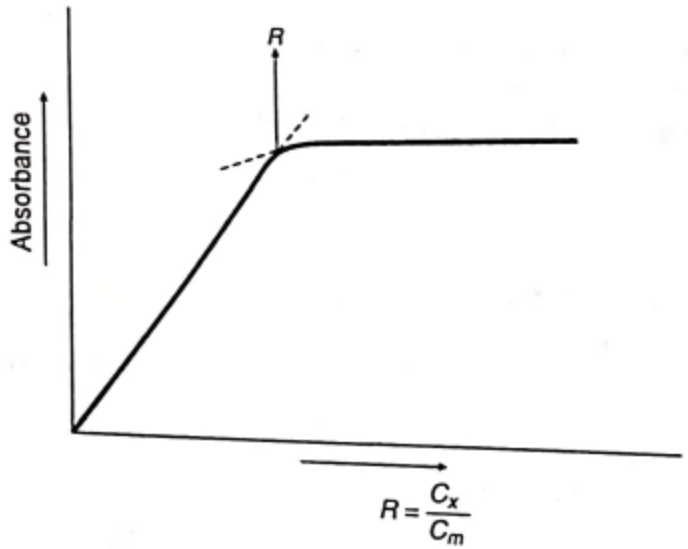


Fig. 1.8 Curve of mole-ratio method

1.10. STABILITY (STABILITY CONSTANT) OF COMPLEX IONS

Most of the complex ions are highly stable. However, in aqueous solution most of them dissociate although to a slight extent to establish an equilirbium between the central ion and the ligands, *e.g.*,

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

The equilibrium constant, K is given by the following expression.

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+}$$

The value of constant K is found to be very low (6×10^{-8}) indicating that the degree of dissociation of the complex ion is extremely small, *i.e.*, the complex ion is highly stable. The equilibrium constant, K is known as the *dissociation constant or instability constant* of the complex ion. The smaller the value of the dissociation constant (instability constant), the greater will be the stability of the complex.

However in complex ions especially in chelate complex ions, the term dissociation constant is replaced by the **stability constant** which is reciprocal of the dissociation constant, *i.e.*,

$$\text{Stability constant} = \frac{1}{\text{Dissociation constant}}$$

Thus, *greater the stability constant of a complex ion, lesser is its dissociation (i.e., more will be its stability).* The instability constants and stability constants of some of the common ions are tabulated below.

Stability Constants of Some Complex Ions

Complex ions	Instability constant	Stability constant
$[Cu(NH_3)_4]^{2+}$	1.0×10^{-12}	1.0×10^{12}
$[Co(NH_3)_6]^{3+}$	6.2×10^{-36}	1.6×10^{35}
$[Ag(CN)_2]^-$	1.8×10^{-19}	5.4×10^{18}
$[Hg(CN)_4]^{2-}$	4.0×10^{-42}	2.5×10^{41}
$[Fe(SCN)]^{2+}$	1.0×10^{-3}	1.0×10^{3}

Thus, among the above complexes, $[Hg(CN)_4]^{2-}$ is the most stable while $[Fe(SCN)]^{2+}$ is the least stable.

1.11. FACTORS AFFECTING THE STABILITY OF COMPLEX

The stability and hence, formation of complex ions depends on the following factors.

1. Nature of the central ion

(ionic potential of the central metal ion). In general, greater the ionic potential (charge/radius ratio) of a metal ion higher will be its tendency to attract electrons of the ligand and hence, more stable will be the complex. Thus, in other words, *the greater the charge and smaller the size of the central metal ion, greater will be the stability of the complex.* For example, complexes of the Fe^{3+} ion (having greater ionic potential) are more stable (stability constant 10^{31}) than that of Fe^{2+} ion (stability constant 10^6).

$$\phi_{Fe^{3+}} = \frac{3}{0.67} \quad \phi_{Fe^{2+}} = \frac{2}{0.76}$$

where ϕ stands for ionic potential.

The above view is supported by the following facts.

(*i*) The stability of complexes of somes of the cations having same charge but different ionic radii decreases with the increase in ionic radii

(*a*)	*Ion*	Cu^{2+}	>	Ni^{2+}	>	Co^{2+}	>	Fe^{2+}	>	Mn^{2+}
	Ionic radii (Å)	0.69		0.78		0.82		0.83		0.91
(*b*)	*Ion*	Be^{2+}	>	Mg^{2+}	>	Ca^{2+}	>	Sr^{2+}	>	Ba^{2+}
	Ionic radii (Å)	0.31		0.65		0.99		1.13		1.15

(*ii*) Stability of complexes formed by cations having almost constant ionic radii decreases with decrease of the cationic charge, *e.g.*, the stability of complexes of La^{3+}, Sr^{2+} and K^+ having nearly similar ionic radii decreases in the order.

$$La^{3+} > Sr^{2+} > K^+$$

2. Electronegativity of the central ion

The higher the electronegativity of the central ion, the greater is the stability of its complexes. This is because the bonding between a central ion and a ligand is due to donation of electron pairs by ligands, hence, naturally a strongly electronegative central ion will form stable complexes.

3. Electronic configuration of the central ion

In general, the most stable complexes are obtained from ions of transition elements because they have vacant $(n-1)$ *d* orbitals which can accommodate electrons donated by ligands.

4. Effective atomic number of the metal (*EAN rule*)

According to this rule a metal having effective atomic number equal to the atomic number of the next noble gas will form the more stable complex than the other of which EAN is different from the atomic number of the noble gas. The **effective atomic number** *of a metal in a complex is obtained by deducting the number of electrons lost in ion formation from the atomic number of the metal and then adding the number of electrons gained by coordination.* In short,

EAN = At. No. of metal – No. of electrons lost in ion formation
+ Electrons gained by coordination

However, there are number of exceptions to the EAN generalisation.

5. Nature of the ligand

The ligand which can donate its lone pair of electrons more easily to the central metal ion is said to be more basic and hence, it will form more stable complex. Thus, strong bases like CN^-, F^- and NH_3 are good ligands and form stable complexes with more electropositive metals like Na, Ca, Al, Ln, Ti and Fe.

In case of negative ligands, *the higher the charge and smaller the size, the more stable is the complex formed.* Thus, the stability of the complexes involving halide ions as ligands follows the order.

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

In case of neutral ligands, *the larger the permanent dipole moment, the greater is the stability of the complex formed, e.g.,* the order of stability of the complexes formed by some neutral ligands is as follows :

Ammonia > Ethylamine > Diethylamine > Triethylamine

6. Environmental factors

Temperature and Pressure. The effect of temperature can be two fold. Firstly, the compounds containing volatile coordinating groups or ligands (*e.g.*, water, ammonia and ethylenediamine) are less stable at elevated temperature and commonly undergo decomposition on heating, *e.g.*, the hydrates loose water, the $[Co(NH_3)_6]Cl_3$ loses ammonia and the $[Cr(en)_3]Cl_3$ loses ethylenediamine (*en*) molecule on heating.

$$[Co(NH_3)_6]Cl_3 \xrightarrow{175-180^\circ} [Co(NH_3)_5Cl]Cl_2 + NH_3$$

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

Secondly, certain coordination compounds are changed from one form to other, *e.g.*,

$$\underset{\text{Red}}{AgHg[AgI_4]} \overset{45^\circ}{\rightleftharpoons} \underset{\text{Yellow}}{Ag_2[HgI_4]}$$

Similarly, reduction in pressure above a compound usually results in loss of volatile components.

7. Concentration factors

Certain complexes may exist in water solution only in presence of a high concentration of the coordinating particles, since, in such cases the water molecules apparently have greater coordinating tendencies than the molecules or ions originally present. For example, the yellow species of $[CuCl_4]^{2-}$ complex exists in the solid state but when dissolved in water, a pale blue hydrate of copper(II) ion is formed which on addition of excess of chloride ions (in the form of HCl, LiCl or other very soluble chloride) regenerates the yellow complex.

$$\underset{\text{Yellow}}{[CuCl_4]^{2-}} \underset{4Cl^-}{\overset{xH_2O}{\rightleftharpoons}} \underset{\text{Yellow}}{[Cu(H_2O)_x]^{2+}}$$

Similarly, the blue complexes of cobaltous ion of the type $[Co(CNS)_4]^{2-}$ undergoes the changes as represented below.

$$\underset{\text{Blue}}{[Co(CNS)_2]^{2-}} \underset{4CNS^-}{\overset{6H_2O}{\rightleftharpoons}} \underset{\text{Pink}}{[Co(H_2O)_6]^{2+}}$$

Another analogous competition between coordinating particles involves the CNS^- ion and the F^- ion (in place of water) for the Fe^{3+} ion. The things will be clear in the following equation; in the presence of excess of thiocyanate ions the complex is dark-reddish brown, while in presence of excess of fluoride ions the complex is colourless.

$$\underset{\text{Dark-reddish brown}}{[Fe(CNS)_6]^{3-}} \underset{6CNS^-}{\overset{6F^-}{\rightleftharpoons}} \underset{\text{Colourless}}{[FeF_6]^{3-}}$$

8. Nature of the ion outside the coordination sphere

Whenever the ionisation sphere of a coordination compound has ions like CN^-, SCN^-, Cl^-, Br^-, $C_2O_4^{2-}$ and NO_2^- there is a great tendency of above types of ions to shift from ionisation to coordination sphere on thermal heating. On the other hand, the ions like NO_3^- and ClO_4^- show little or no such tendency and hence, complete absence of coordination reactions is usually assured in presence of perchlorate ions.

9. Ring formation (cyclization)

Ring formation is the most important factor in the formation of a coordinate compound, *a compound capable of cyclization will be relatively more stable* (owing to the reduced strain especially in case of five and six membered, including the ion metal)