STABILITY OF METAL COMPLEXES

A **metal complex** is formed when a central metal ion is bonded to one or more ligands through coordinate covalent bonds.

The **stability** of such a complex refers to its **resistance to dissociation** into the metal ion and free ligands.

There are **two types of stability**:

1. **Thermodynamic Stability**
2. **Kinetic Stability**

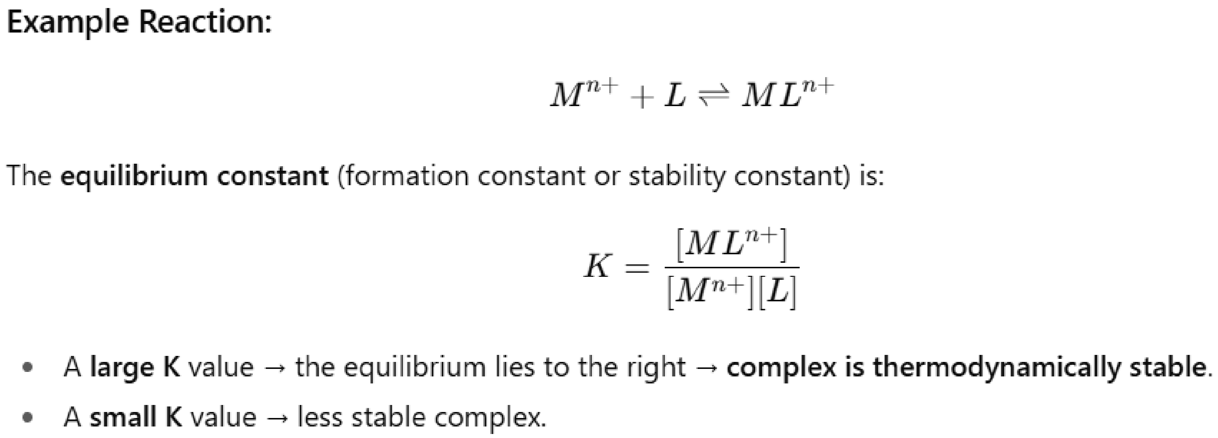
These two are **independent concepts** — a complex can be **thermodynamically unstable** but **kinetically inert**, or vice versa.

1. Thermodynamic Stability

Definition:

When the stability of the complexes formed in the solution is defined by the thermodynamic parameters like bond energy, stability constant or formation constant then such type of the stability concept is called as thermodynamic stability concept of the complexes.

Thermodynamic stability refers to the **extent to which a complex resists dissociation** into its components under equilibrium conditions.
It depends on the **energy change** (ΔG, ΔH, ΔS) when the complex is formed or dissociated.



Example Reaction:

$$M^{n+} + L \rightleftharpoons ML^{n+}$$

The **equilibrium constant** (formation constant or stability constant) is:

$$K = \frac{[ML^{n+}]}{[M^{n+}][L]}$$

- A **large K** value → the equilibrium lies to the right → **complex is thermodynamically stable**.
- A **small K** value → less stable complex.

According to the thermodynamic stability concept, complex compound can be deluded into 2 different types

1. **Stable complexes :** Those complexes which exhibit very high formation constant in the solution are known as stable complexes.

2. **Unstable complexes :** Those complexes which exhibit low formation constant in the solution are known as unstable complexes.

2. Kinetic Stability

Definition:

When the stability of the complexes formed in the solution is defined by the kinetic parameter then the stability concept is called the kinetic stability concept of the complexes.

Kinetic stability refers to the **rate** at which a complex undergoes **ligand substitution** or **decomposition reactions**.
It depends on **activation energy (Ea)** and not on equilibrium position.

According to the kinetic stability concept, complex compounds in the solution can be divided into two types.

1. **Inert Complex:** Those complexes which exhibit very low or negligible rate of replacement reaction in the solution are known as inert complexes.
2. **Labile Complex:** Those complexes which exhibit a very high rate of replacement reaction in the solution are known as labile complexes.

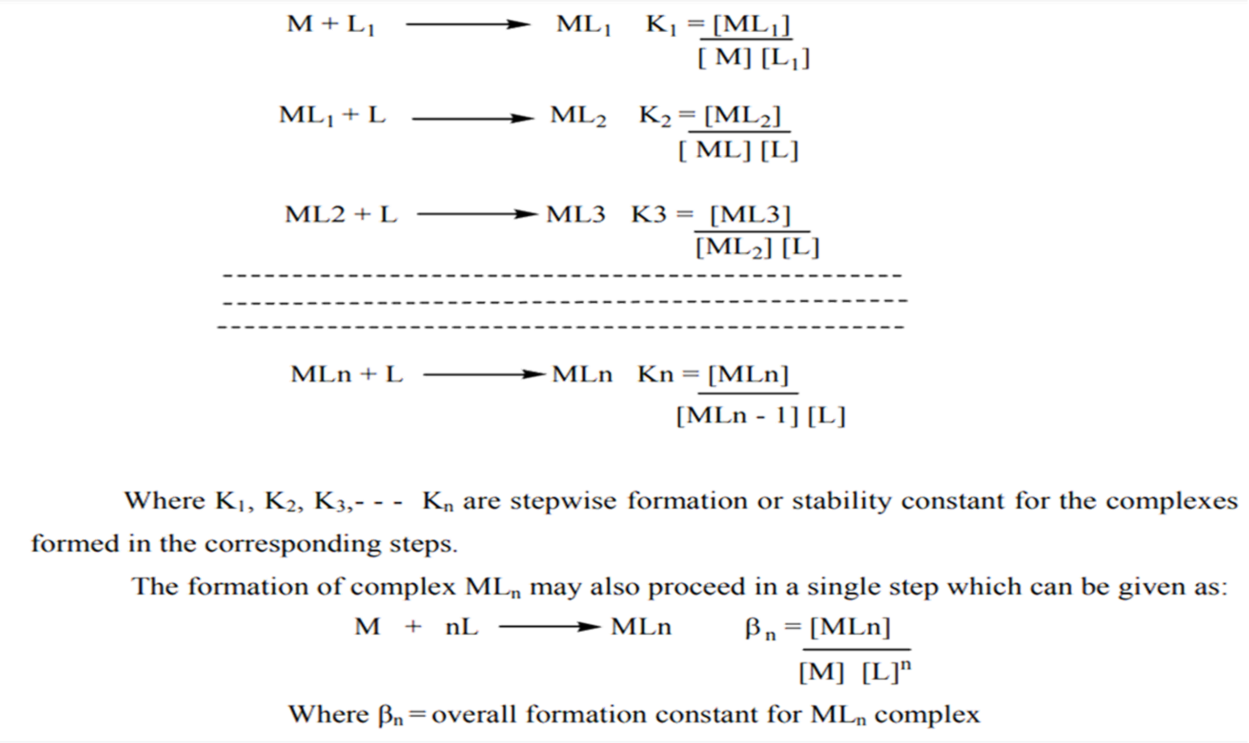
Examples:

1. **Kinetically Labile Complexes:**
   - Undergo ligand exchange rapidly (within seconds).
   - Example: $[Ni(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$
2. **Kinetically Inert Complexes:**
   - Undergo substitution very slowly (minutes, hours, or even days).
   - Example: $[Co(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$

Stepwise formation of the complexes and stepwise formation constant:

For a complex MLn:

Stepwise formation of the complexes is given below



$$M + L_1 \longrightarrow ML_1 \quad K_1 = \frac{[ML_1]}{[M][L_1]}$$

$$ML_1 + L \longrightarrow ML_2 \quad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML2 + L \longrightarrow ML3 \quad K3 = \frac{[ML3]}{[ML_2][L]}$$

$$MLn + L \longrightarrow MLn \quad Kn = \frac{[MLn]}{[MLn - 1][L]}$$

Where K_1, K_2, K_3,- - - K_n are stepwise formation or stability constant for the complexes formed in the corresponding steps.

The formation of complex ML_n may also proceed in a single step which can be given as:

$$M + nL \longrightarrow MLn \qquad \beta_n = \frac{[MLn]}{[M]\ [L]^n}$$

Where β_n = overall formation constant for ML_n complex

Cumulative stability constant:

$$\beta_n = K_1 \times K_2 \times K_3 \times ... \times K_n$$

Usually,

$$K_1 > K_2 > K_3 > K_4$$

because the addition of each successive ligand becomes more difficult due to **electrostatic repulsion** and **steric hindrance**.

FACTORS AFFECTING THE STABILITY OF METAL COMPLEXES:

There are two different factors which can affect the stability of complexes formed in the solution given as below:

1. Nature of the central metal ion (CMI)
2. Nature of the ligands

1. Nature of Central Metal Ion

The stability of a complex depends strongly on the **properties of the central metal ion** — mainly its **charge, size, oxidation state, and electronic configuration**.

(a) Charge on the Metal Ion

- A metal ion with **higher positive charge** attracts the negatively charged ligand more strongly.
- Hence, **higher oxidation states** usually form **more stable complexes**.

✤ **Example:**

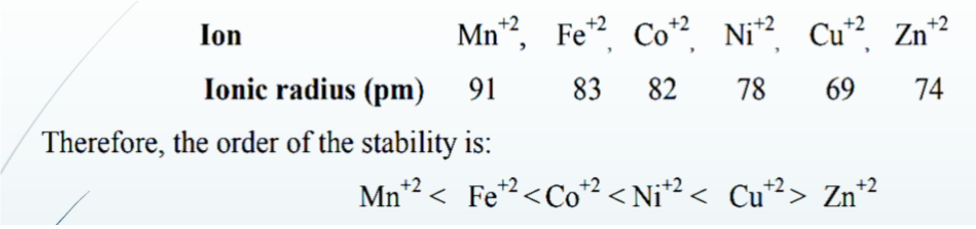
$$[Fe(CN)_6]^{4-} \quad \text{(Fe}^{2+}\text{ complex, less stable)}$$

$$[Fe(CN)_6]^{3-} \quad \text{(Fe}^{3+}\text{ complex, more stable)}$$

Here, Fe^{3+} has a higher charge density than Fe^{2+}, so it binds CN^- more strongly.

(b) Ionic Size of Metal Ion

- Smaller cations have **greater charge density** (charge per unit area).This increases electrostatic attraction between metal ions and ligands gives higher stability.
- As the size of metal ions decreases, the stability of the complex increases. If we consider the divalent metal ions, then the stability of their complexes increases with decrease in the ionic radius of the central metal as given below.



Ion	Mn^{+2},	Fe^{+2},	Co^{+2},	Ni^{+2},	Cu^{+2},	Zn^{+2}
Ionic radius (pm)	91	83	82	78	69	74

Therefore, the order of the stability is:

$$Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$$

Irving–Williams Series

For divalent first-row transition metal ions (M^{2+}), the stability of complexes follows the general order:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This trend is known as the Irving–Williams series, valid for many ligands such as NH_3, en, or H_2O.

Reason: gradual increase in charge density and crystal field stabilization energy (CFSE) up to Cu^{2+}.

(c) Electronic Configuration

- Transition metal ions with partially filled *d* orbitals form stronger coordinate bonds due to **better orbital overlap**.
- d^{10} ions (Zn^{2+}, Cd^{2+}, Hg^{2+}) form comparatively **less stable** complexes.

(d) Polarizing power:

With the increases in the polarizing power of CMA, stability of complexes also increases.

Stability α Polarizing power of CMA

2. Nature of the Ligand

The ligand plays an equally crucial role in determining the complex's stability.

(a) Size and charge of the ligands:

In general Ligands with less charge and more size are less stable and form less stable coordination compounds. Ligands with higher charge have small size and form more stable compounds. With the increase in the – ve charge value of the ligand stability of complexes is increased i.e.

Stability α –ve charge at the ligand

(b) Basic Strength of Ligand

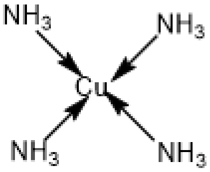
- Stronger bases (those donating electron pairs easily) form more stable complexes.

Stability α Basic character of ligand

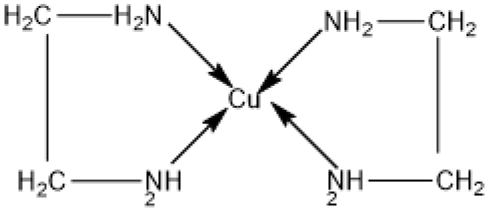
For example: Aromatic diamines form unstable coordination compounds while aliphatic diamines form stable coordination compounds. Ligands like NH_3, CN- etc. have more basic character and thus, they form more stable compounds.

(b) Chelate Effect

- The term chelate effect is used to describe special stability associated with complexes containing chelate rings when compared to the stability of related complexes with monodentate ligands. The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands.
- We observed that complexes formed by chelating ligands such as ethylene diamine (en), ethylene diamine tetra acetic acid (EDTA), etc. are more stable than those formed by monodentate ligands such as H_2O or NH_3. This enhanced stability of complexes containing chelating ligands is called the chelate effect.



Less stable



More stable

because “en” (ethylenediamine) is **bidentate**, forming two five-membered rings with Cu^{2+}.

Reasons for chelate effect:

1. **Entropy increases** – fewer particles after chelation → higher disorder → favorable.
2. **Ring formation** – reduces strain and strengthens bonding.

Crystal field stabilization energy (CFSE)

The crystal field stabilization energy (CFSE) is one of the most important factors that decides the stability of the metal complexes.

CFSE is the stability that arises when a metal ion coordinates to a set of ligands, which is due to the generation of a crystal field by the ligands. Thus, a higher value of CFSE means that the complex is thermodynamically stable and kinetically inert.

Configuration	**Distribution**	**CFSE (in Δ_0)**	**Example**
d^1	t_{2g}^1	$-0.4\Delta_0$	$[Ti(H_2O)_6]^{3+}$
d^2	t_{2g}^2	$-0.8\Delta_0$	$[V(H_2O)_6]^{3+}$
d^3	t_{2g}^3	$-1.2\Delta_0$	$[Cr(H_2O)_6]^{3+}$
d^4 (high-spin)	$t_{2g}^3\ e_g^1$	$-0.6\Delta_0$	$[Mn(H_2O)_6]^{3+}$

Configuration	**Distribution**	**CFSE (in Δ_0)**	**Example**
d^4 (low-spin)	$t_{2g}^4\ e_g^0$	$-1.6\Delta_0 + P$	$[Mn(CN)_6]^{3-}$
d^5 (high-spin)	$t_{2g}^3\ e_g^2$	0	$[Fe(H_2O)_6]^{3+}$
d^5 (low-spin)	$t_{2g}^5\ e_g^0$	$-2.0\Delta_0 + 2P$	$[Fe(CN)_6]^{3-}$
d^6 (high-spin)	$t_{2g}^4\ e_g^2$	$-0.4\Delta_0$	$[Fe(H_2O)_6]^{2+}$
d^6 (low-spin)	$t_{2g}^6\ e_g^0$	$-2.4\Delta_0 + 2P$	$[Co(NH_3)_6]^{3+}$
d^7 (high-spin)	$t_{2g}^5\ e_g^2$	$-0.8\Delta_0$	$[Co(H_2O)_6]^{2+}$
d^8	$t_{2g}^6\ e_g^2$	$-1.2\Delta_0$	$[Ni(H_2O)_6]^{2+}$
d^9	$t_{2g}^6\ e_g^3$	$-0.6\Delta_0$	$[Cu(H_2O)_6]^{2+}$
d^{10}	$t_{2g}^6\ e_g^4$	0	$[Zn(H_2O)_6]^{2+}$

3. Nature of the Solvent

The solvent can influence complex stability by **competing with ligands** for coordination.

- **Aqueous medium:** water can coordinate with metal ions, sometimes replacing weaker ligands.
- **Non-aqueous medium:** less competition → more stable complexes.

Example:

- $[Cu(NH_3)_4]^{2+}$ is **more stable** in **liquid ammonia** than in **water**, because in water, H_2O molecules compete for coordination.

4. pH of the Solution

The protonation or deprotonation of ligands changes their donor ability.

- In **acidic medium**, ligands with basic donor atoms (like NH_2, $COOH^-$, etc.) get **protonated**, reducing their ability to coordinate.

- Therefore, complexes are **less stable at low pH**.

Example:
EDTA is less effective at low pH because its carboxylate groups are protonated.

Summary Table

Factor	Effect on Stability	Example
Charge on metal ion	↑ charge → ↑ stability	$[Fe(CN)_6]^{3-}$ > $[Fe(CN)_6]^{4-}$
Ionic radius	↓ size → ↑ charge density → ↑ stability	Cu^{2+} > Ni^{2+} > Co^{2+}
Basicity of ligand	↑ basicity → ↑ stability	CN^- > NH_3 > H_2O
Chelation	Multidentate > Monodentate	$[Cu(en)_2]^{2+}$ > $[Cu(NH_3)_4]^{2+}$
Solvent	Polar solvents may reduce stability	$[Cu(NH_3)_4]^{2+}$ less stable in water
pH	↓ pH → protonation → ↓ stability	EDTA less effective at low pH
CFSE	↑ CFSE → ↑ stability	Ni^{2+} complex > Fe^{2+} complex

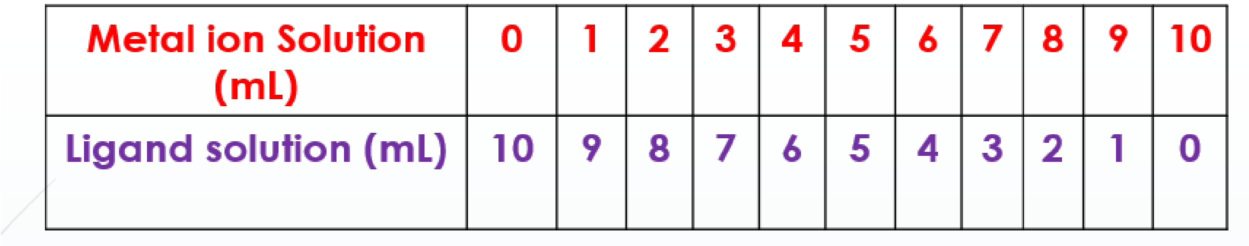
DETERMINATION OF COMPOSITION OF METAL COMPLEXES (JOB’S METHOD)

The Job’s method is based on the principle of **continuous variation**, which states that:
“If two reactants (metal ion and ligand) form a single complex in solution, and the total molar concentration of both is kept constant, the maximum property (such as absorbance, conductance, or color intensity) occurs at the mole fraction corresponding to the composition of the complex formed.”

Let a metal M react with ligand 'L' to form a complex as shown below.

$$M + nL \longrightarrow ML_n$$

Here 'n' denotes the number of moles of ligand that binds with one mole of metal ion. The value of this is to be determined experimentally.
In this method of Job, equimolar solutions of the metal ion and the ligand solution are prepared separately. These solutions are mixed as shown below and the mixed solutions are prepared. The total volume is constant (10mL). The necessary buffer solution of required pH must also be added in constant volume.



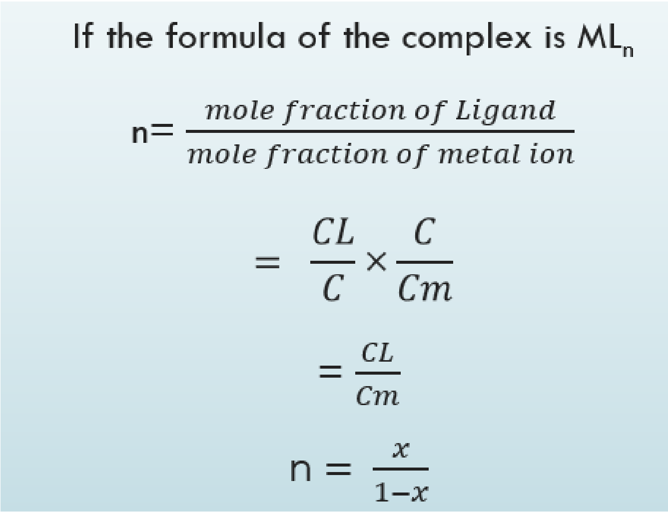
Metal ion Solution (mL)	0	1	2	3	4	5	6	7	8	9	10
Ligand solution (mL)	10	9	8	7	6	5	4	3	2	1	0

In all the above mixed solutions the total number of moles is the same. If the concentration of the mixed solution is 'C'.

$$C_M + C_L = C \quad \rightarrow (1)$$

C_M =concentration of metal ion solution
C_L =concentration of ligand solution
The mole fraction of ligand= CL /C = x

The mole fraction of metal ion = CM /C = 1-x



If the formula of the complex is ML_n

$$n = \frac{mole\ fraction\ of\ Ligand}{mole\ fraction\ of\ metal\ ion}$$

$$= \frac{CL}{C} \times \frac{C}{Cm}$$

$$= \frac{CL}{Cm}$$

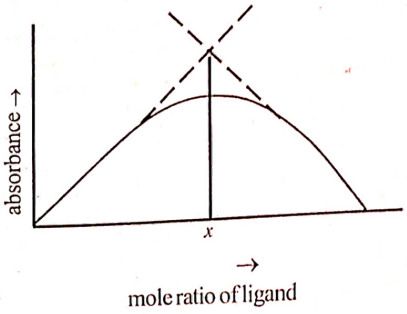
$$n = \frac{x}{1-x}$$

The wavelength at which the metal complex formed exhibits maximum absorbance must be first experimentally established. At this wavelength (λmax) the absorbance (A) of each of the mixed solutions is measured with a spectrophotometer.

A graph is drawn between the absorbance (A) and the mole fraction of the ligand.

A curve shown in the figure is obtained. The mole fraction of the ligand corresponding to the point of maximum absorbance is obtained from the graph by extrapolation method.

The mole fraction of ligand corresponding to this maximum point is identified and it denotes x.



$x/(1-x)$ *gives 'n' Value*

If more than one complex is formed under the experimental conditions, this method may not be suitable.